The Geochronology And Geochemistry Of Plagiogranites And Metamorphic Sole Rocks From The Forearc Bay Of Islands Complex And Coastal Complex Ophiolites And Arc Twillingate Granite, Newfoundland

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ABSTRACT

LA-ICP-MS U-Pb zircon analyses for five cogenetic plagiogranites from the Northern Appalachian Bay of Islands Ophiolite Complex (BOIC) yield comparable ages from two nearby plutons allowing a new composite age of 488.3 ± 1.5 Ma. This age is highly correlated with similar ages of the peri-Laurentian Notre Dame arc-proximal Betts Cove and Point Rousse ophiolites indicating they formed along a contiguous set of supra-subduction zone spreading centers at high angles to the westward (present-day reference frame) verging trench. The spreading centers were offset by left-lateral offset transform faults that rifted an older Coastal Complex (CC)-Lushs Bight forearc basement. Five plagiogranite plutons in the CC yield a set of older composite ages ranging from 514.3-502.7 Ma indicating prolonged forearc magmatism. A new composite age of $504.3 \pm$ 1.8 Ma from three co-genetic samples from the Twillingate arc batholith overlaps youngest CC forearc plagiogranite magmatism and establishes the oldest age of voluminous silicic magmatism in the juvenile Notre Dame arc. It also provides a minimum age for the intruded arc tholeiitic and boninitic ophiolitic basement of Sleepy Cove volcanics, a correlative of undated Lushs Bight volcanics and sheeted dikes terrane to the west.

Metamorphic sole subcreted to the base of BOIC ophiolite upon subduction initiation was examined to establish a high-temperature metamorphism age. A prior 40 Ar- 39 Ar amphibole age of 469 Ma is thought to be incorrect, based on ~20 Ma of cooling of the 488.3 Ma BOIC, which would be incapable of producing sole granulites and amphibolites. A new LA-ICP-MS zircon rim metamorphic age of 491.8 ± 6.0 Ma from a sample immediately below the ophiolite-sole contact indicates the sole formed near-simultaneously with overlying BOIC ophiolite.

Petrogenetic modeling of the BOIC plagiogranites indicates they are part of the tholeiitic magma series and derived by fractionation of primitive MORB-like BOIC forearc basalts within a SSZ forearc. They result from, in part, deep-crustal fractional crystallization of primitive magmas, followed by post-cumulate equilibrium crystallization, migration, and reaction with mid-crustal gabbroic crystal-rich mushes, and final segregation to shallow plutons just below the sheeted dike that accounts for significant variability in Al₂O₃ and their trace element enrichments.

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Chapter 1 Introduction

1.1 Reginal geologic framework

1.1.1 The Humber Zone and Notre Dame Subzone in Newfoundland

Newfoundland is located at the northernmost extremity of the Northern Appalachian and can be divided into four tectonostratigraphic zones including, from west to east, Humber Zone, Dunnage Zone, Gander Zone and Avalon Zone (Fig. 1.1) (Williams et al., 1988). The Humber Zone is the westernmost zone recognized in Newfoundland area underlain by the oldest continental Grenville basement of ca. 1250-950 Ma (Williams, 1988; Hodgin et al., 2021). This basement is unconformably overlain by Cambro-Ordovician autochthonous siliciclastic rocks and locally early rift volcanics and succeeded by an eastward thickening carbonate succession (Stevens, 1970; Williams, 1975; Malpas, 1976; Williams, 1979; Waldron and Stockmal, 1994) forming the foundations of stable margin shelf of Laurentia. The Taconic Humber Arm and Hare Bay Allochthons deformed the shelf margin in the Middle Ordovician as these ophiolites were being obducted and emplaced onto the continental margin. The allochthons include Ediacaran to Ordovician slope-rise sedimentary rocks, early rift volcanics, flysch, mélanges and ophiolitic complexes that include the Bay of Islands Ophiolite Complex, the Coastal Complex and the St. Anthony Complex.

In this dissertation, I primarily focus on the Bay of Islands Ophiolite Complex and Coastal Complex ophiolites that comprise the uppermost allochthonous ophiolitic assemblages of the Humber Arm Allochthon in Western Newfoundland. These two ophiolites preserve a direct igneous contact in the Lewis Hills massif but are in structural contact and dismembered elsewhere to the north (Fig. 1.1 and 1.2). The Notre Dame Subzone within the western Dunnage Zone is separated from Humber Zone by Baie Verte Line ophiolitic zone to the west and bounded by a tectonic Red Indian Line to the east (Fig. 1.1). The Notre Dame Subzone is thought to consist of Middle Cambrian to Middle Ordovician island arc volcanics, ophiolites and marine epiclastic, tuffaceous and siliciclastic rocks (Williams, 1988). Late Ordovician to Silurian felsic plutons stitching Humber Zone and Notre Dame arc terrane are also exposed. Ophiolitic assemblages in Humber Zone and Notre Dame Subzone were part of Cambrian peri-Laurentian arc that are interpreted to have once formed a contiguous composite forearc-arc basement above a westerly vergent subduction zone (Nelson and Casey, 1979; Dewey and Casey, 2013, 2015, 2021).

The final collision of the Notre Dame arc terrane with eastern Laurentia continental margin is now represented by the Baie Verte Line with the Fleur de Lys metamorphic siliciclastic margin rocks to the west and the Notre Dame arc volcanic and plutonic rocks to the east. The Taconic Allochthon forearc crystalline ophiolite sheets remain isolated by erosion to the west of the Baie Verte Line as Taconic klippes that were transported across the margin over the older Laurentian continental basement (e.g., the Grenville basement) and stable margin cover sequences (Fig. 1.1).



Fig. 1.1 Tectonostratigraphic zones and subzones of the Newfoundland Island area in Northern Appalachians (modified from Williams et al., 1988; Whalen, 2012). The focus of this study is on the Humber Zone representing the former Ediacaran to Early Ordovician Laurentian stable continental margin and Notre Dame Subzone of the western Dunnage Zone representing Cambro-Ordovician arc sequences.

1.1.2 Humber Arm Allochthon ophiolites

Igneous assemblages of the Taconic Humber Arm Allochthon of Western Newfoundland (e.g., Stevens, 1970; Dewey and Bird, 1971; Williams, 1973, 1975; Karson and Dewey, 1978; Casey et al., 1981, 1983; Karson, 1984; Karson et al., 1984) tend to comprise the highest structural slices including the Bay of Islands Ophiolite Complex and the Coastal Complex that we widely sampled and investigated in this dissertation (Fig. 1.2). The Bay of Islands Ophiolite Complex (BOIC) (Dewey, 1969; Stevens, 1970; Dewey and Bird, 1971; Williams, 1973), from north to south, includes the Table Mountain (TM) massif, the North Arm Mountain (NA) massif, the Blow Me Down Mountain (BMD) massif, and the eastern half of Lewis Hills (ELH) massif (Karson and Dewey, 1978; Casey et al., 1983, 1985; Casey and Dewey, 1984; Kurth et al., 1998) (Fig. 1.2). The BMD and NA massif expose relatively intact and complete ophiolitic stratigraphies, whereas the TM and ELH massif preserve only basal crustal and ultramafic portions that are largely devoid of plagiogranite (Williams, 1973; Karson and Dewey, 1978; Casey and Karson, 1981; Casey et al., 1983; Williams and Cawood, 1989).

The Coastal Complex discontinuously crops out as a highly deformed, NW-SE trending, narrow belt along the western leading edge of the Humber Arm Allochthon (Fig. 1.2). It includes the northern dismembered ophiolite exposures (also known as "Little Port Complex", after Williams, 1973, 1975; Jenner et al., 1991) adjacent to the west of the three BOIC massifs including the Table Mountain massif, North Arm Mountain massif and Blow Me Down Mountain massif. It also involves the western part of the Lewis Hills massif that is in direct igneous contact with the Eastern Lewis Hills of BOIC (Fig. 1.2) (Karson and Dewey, 1978; Casey and Karson, 1981; Casey et al., 1983, 1985; Casey and Dewey, 1984; Karson et al., 1984; Idleman, 1991; Cawood and Suhr, 1992; Kurth et al., 1998; Kurth-Velz et al., 2004; Dewey and Casey, 2013, 2015, 2021; Yan and Casey, 2020). The original direct igneous contact preserved in the Lewis Hills massif and stitching plutons and dikes derived from the BOIC indicate that the CC and BOIC once formed a contiguous forearc basement and juxtaposed along a ridge-transform intersection. The CC was deformed along a ridge-ridge transform domain and then carried past the offset of ridgeaxis termination, during which it was injected by newly formed basaltic magmas in response to the BOIC formation (Karson and Dewey, 1978; Casey and Karson, 1981; Casey et al., 1981, 1983, 1985; Casey and Dewey, 1984, Karson, 1984; Karson et al., 1984; Suhr and Cawood, 2001).

Sub-ophiolitic allochthonous volcanic assemblages documented throughout the Bay of Islands region such as Skinner Cove and Older Man Cove were previously thought to be part of the CC formed as an integrate assemblage in early Paleozoic time (e.g., Stevens, 1970; Williams, 1971, 1975; Comeau, 1972; Williams and Malpas, 1972; Malpas et al., 1973; Malpas, 1976, 1979; Karson and Dewey, 1978). However, more recent age data show that they should be excluded from the Coastal Complex as originally defined (Comeau, 1972; Karson and Dewey, 1978). These rocks include the Skinner Cove Volcanic Assemblage (Baker, 1979; Strong, 1974) and other correlated and informally named sub-ophiolitic volcanic rocks (e.g., Chimney Cove, Beverly Cove, Couchers, Fox River Island) (Williams and Cawood, 1989), as well as numerous undifferentiated sub-ophiolitic volcanic rocks mapped in this region (see Fig. 1.2). They are now generally regarded based on U-Pb zircon ages from the Skinner Cove type locality as allochthonous rift-related Ediacaran (ca. 550 Ma) volcanic rocks derived from the nearby Laurentian ocean-continental crust transition (Williams, 1975; Cawood et al., 2001; Hodych et al., 2004). These volcanic rocks were tectonically accreted to the allochthon and emplaced from the distal parts of the ancient passive margin as the lowest igneous slices below the upper ophiolitic massifs and welded metamorphic sole rocks. This age represents a probable near upper limit for the completion of Laurentian margin rifting and Iapetus Ocean formation.

The dynamothermal metamorphic sole widely occurs at the base of the four main BOIC massifs with variable thicknesses of ~300-1000 m. They show typical inverted metamorphic gradients and facies, as well as polyphase deformation intensity decreasing structurally downward (Williams and Smyth, 1973; Malpas, 1979; McCaig, 1983; Savci, 1988; Cawood and Suhr, 1992; Fergusson and Cawood, 1995; Dewey and Casey, 2011, 2013, 2015). The peak metamorphism within the sole consistently occurs near the ophiolite basal porphyroclastic to mylonitic residual lherzolitic mantle-sole contact with estimated temperature of > 800 °C and pressure of ~8.5-11 kb (McCaig, 1983; Savci, 1988). To simultaneously accommodate the high temperature (> 800 °C) and pressure (~8.5-11 kb) estimated near the ophiolite-sole contact and the lower P-T gradient downsection (from two-pyroxene garnet granulites and garnet amphibolites to amphibolites and greenschists), as well as other geochemistry and structure features observed in sole rocks, the upper mafic dynamothermal metamorphic sole was proposed to be produced near-simultaneously with the overlying BOIC ophiolite by the metamorphism of MORB- and OIB-like rocks and sediments originating from the subducting plate. These metamorphic rocks then subcreted to an overlying supra-subduction ophiolite forearc basement during exhumation of flattening of the overlying plate (Savci, 1988; Dewey and Casey, 2013, 2015). The forearc basement with the sole would then be transported in an oceanic setting for ~20 Ma before obduction and emplacement (ca. 470 Ma). The final stages of transport resulted in the generation of more pelitic matrix lower greenschist facies and anchimetamorphic mélanges marking the base of the sole between ca. 470-460 Ma.

Fig. 1.2 Generalized regional geologic map of allochthonous ophiolitic rocks of the Bay of Islands region of Western Newfoundland, Canada (modified from Casey et al., 1985), showing four main discrete BOIC ophiolitic massifs, which, from north to south, are the Table Mountain massif, the North Arm Mountain massif, the Blow Me Down Mountain massif and the Eastern Lewis Hills massif, and the highly deformed adjacent to sub-adjacent Coastal Complex (Karson and Dewey, 1978), which is inclusive of the Little Port Complex in the north (Williams, 1975) and the Western Lewis Hills in the south. The Coastal Complex (CC) includes more highly deformed and older ophiolitic assemblages than the BOIC. Other allochthonous rift-related volcanics include the Skinner Cove Volcanics and various sub-ophiolitic basalts of Ediacaran age. The CC was demonstrated to have an autochthonous relationship with the BOIC in the Lewis Hills massif (Karson and Dewey, 1978) but is now in thrust or in fault contact to the north with the overlying BOIC massifs. Note that the red, yellow and blue stars respectively indicate sampling locations from Blow Me Down Mountain massif (of BOIC), Coastal Complex and metamorphic sole assemblage at the base of North Arm Mountain massif in this dissertation (for detailed GPS sample locations see Chapters 2, 3, 4 and 5.



1.1.3 Twillingate Granite pluton in Notre Dame Subzone

The Notre Dame Subzone represents the western portion of the Dunnage Zone. It is bounded by the Baie Verte Line that largely separates volcanic and plutonic ophiolitic and arc rocks from the Humber Zone margin rocks to the west. To the east it is bounded tectonically by the Red Indian Line where it is juxtaposed to the Exploits Subzone along a shear zone (Fig. 1.1 and 1.3). The Baie Verte Line and Red Indian Line are associated with mélanges and highly deformed rock assemblages (e.g., Williams and St-Julien, 1982; Williams et al., 1988) consistent with the interpretation as representatives of the approximate locations of tectonic sutures or fault bounded terrane boundaries with strike-slip components. The Notre Dame arc is considered to be once outboard adjacent arc terrane to ophiolitic BOIC and CC forearc outlier klippe atop the Humber Arm and Hare Bay Taconic Allochthons (Dean, 1978; Nelson and Casey, 1979, Williams et al., 1988, Colman-Sadd et al., 1992; Kean et al., 1995, O'Brien, 2003, van Staal et al., 2007, Dewey and Casey, 2021) prior to collision and subsequent complex convergent tectonics, as well as dismemberment and exhumation between the Baie Verte Line and outlier allochthons. The Twillingate Granite is the oldest large intrusion recognized in the Notre Dame Subzone of the Dunnage Zone (Williams and St-Julien, 1982; Williams et al., 1988; Williams and Curries, 1995) that we have sampled for age determinations (Fig. 1.3). It is of batholitic dimension cropping out the northernmost area in the Appalachian orogen and consists dominantly of felsic rocks including soda granite (trondhjemite), granodiorite and felsite that show a gradation of deformation from northern massive or mildly foliated to intensively foliated and mylonitic in the south. The Sleepy Cove and Lushs Bight arc tholeiites and boninites are the only groups thought to be older in the Notre Dame Subzone because the Sleepy Cove volcanics are intruded by Twillingate Granite (e.g., Payne, 1974; Williams and Payne, 1975; Williams et al., 1976). They collectively were interpreted

to be the products of island arc activities within a subduction zone based on their intimate association and similar structural fabric and deformation patterns (Williams and Payne, 1975; Williams et al., 1976).



Fig. 1.3 Generalized geologic map of the distribution of major rock units in Western Newfoundland including Humber Zone in the west and Notre Dame Subzone in the east, which are separated by the Baie Verte Line suture (modified from Dewey and Casey, 2021). Ages reported in this dissertation are marked in red and include new LA-ICP-MS U-Pb zircons ages for the BOIC (Chapter 2), CC (Chapter 3), Twillingate arc batholith (Chapter 3) and the BOIC metamorphic sole (Chapter 5). Bay of Islands Ophiolite Complex (BOIC) including Blow Me Down Mountain (BMD) massif, North Arm Mountain (NAM) massif, Table Mountain (TM) massif and eastern part of Lewis Hills (LH) massif.CC: Coastal Complex; FP: Fortune Peninsular; MH: Moretons Harbour volcanics.

1.2 Research objective and significance

U-Pb TIMS geochronological investigations of the BOIC and CC ophiolites in Humber Arm Allochthon, as well as the Twillingate Granite in Notre Dame Subzone, were mostly conducted over 30 years ago when modern U-Pb dating techniques and data-treatment standards were just developing or not available. Age results reported in earlier studies were based on limited numbers (< 2-5) of mineral fraction analyses dominantly of zircon and some other minerals including apatite and baddeleyite by using ID-TIMS techniques (e.g., Mattinson, 1975, 1976; William et al., 1976; Dunning and Krogh, 1985; Elliott et al., 1991; Jenner et al., 1991; Kurth et al., 1998). Although relatively precise, some of these reported ages are likely of limited geological significance based on our reviews because 1) the multi-grain (i.e., mineral fraction) dissolution techniques used in prior ID-TIMS analysis is more likely to yield mixed ages of different domains including rim, core, alteration and unknown inclusions of a single or multiple grains (e.g., Schaltegger et al., 2015; Tichomirowa et al., 2019; Widmann et al., 2019), 2) modern developed chemical abrasion technique that could more efficiently remove altered and damaged parts were not applied in early studies (e.g., Mattinson, 2005; Crowley et al., 2014; Huyskens et al., 2016; Widmann et al., 2019), 3) some arbitrary data processing techniques such as fixing lower intercepts may have yielded more precise upper intercept ages than warranted when applied in final age calculations minimizing reported age errors (e.g., Mattinson, 1976; Dunning and Krogh, 1985), 4) uranium decay constant errors were not applied in uncertainty calculations (e.g., Mattinson, 1987; Ludwig, 1998, 2000; Schoene et al., 2006), and 5) more advanced modern community-based data reduction software and reporting recommendations were not utilized (e.g., Mattinson, 1987, 2005; Ludwig, 2008; Solari and Tanner, 2011; Schoene et al., 2013; Condon et al., 2015; Horstwood et al., 2016; Vermeesch, 2018; Zhang et al., 2020).

Although the evolution mechanism has been well established for the BOIC dynamothermal metamorphic sole (see Dewey and Casey, 2013, 2015 for a summary), the precise metamorphic ages of these sole rocks are still somewhat ambiguous. This is because detailed U-Pb geochronological study on BOIC metamorphic sole is still absent. The thermochronological history of the BOIC sole assemblage so far appears to be poorly constrained by a few K-Ar and/or ⁴⁰Ar-³⁹Ar amphibole analyses conducted over 40 years ago (e.g., Dallmeyer and Williams, 1975; Archibald and Farrar, 1976). These analyses yielded an unrealistically young ⁴⁰Ar-³⁹Ar sole age of ca. 469 Ma (see Nelson and Casey, 1979 for recalculation based on new K decay constant) compared to the ca. 488.3 Ma crystallization age of the directly overlying BOIC ophiolite (Yan and Casey, 2020). The age difference of ~20 Ma is thought to be incorrect as cooling of the young BOIC lithosphere over 20 Ma in a subduction setting with old Iapetus near-margin lithosphere subducting would suggest significant cooling (within 5 Ma long) of the BOIC forearc lithosphere prior to obduction onto the continental margin. Therefore, it would be incapable of producing sole metabasic two-pyroxene-garnet granulites (estimated temperature of > 800 °C from McCaig, 1983; Savci, 1988). In addition, the correlatable Taconic St. Anothony ophiolitic sole directly along strike (~190 km north of the BOIC) in Newfoundland Taconic Allochthon yielded a much older 40 Ar- 39 Ar age of 489 ± 5 Ma (see recalculation in Dunning and Krogh, 1985), raising some question about the significantly younger age of ca. 469Ma suggested for the BOIC sole. It is also notable that such young metamorphic sole age (i.e., ~20 Ma younger than the directly overlying ophiolite) is contrasting with other sole assemblages such as the one beneath Semail Ophiolite where metamorphic sole is only slightly younger than or near-simultaneous with the overlying ophiolite (e.g., Rioux et al., 2013, 2016, 2021).

In early studies, the BOIC plagiogranites were suggested to be dominantly formed by low-pressure fractional crystallization based on petrogenetic modeling studies and structural and textural observations. In fact, plagiogranitic melts could be produced by a variety of mechanisms including 1) low-pressure (i.e., upper crust level) extreme differentiation of a primitive basaltic magma (e.g., Spulber and Rutherford, 1983; Berndt et al., 2004; Koepke et al., 2018), 2) partial melting of hydrothermally altered or metamorphosed gabbroic or diabasic oceanic/ophiolitic crustal rocks within the conductive lid or magma chamber roof zone (e.g., Beard and Lofgren, 1991; Koepke et al., 2004; France et al., 2010, 2014), 3) immiscible segregations of silicic liquid from high Fe-Ti gabbroic rocks in shallow oceanic or ophiolitic crust (e.g., Rutherford et al., 1974; Dixon and Rutherford, 1979; Charlier and Grove, 2012; Charlier et al., 2013), and 4) mixing of (replenished) primitive basaltic magmas with felsic melts (e.g., Whalen and Curries, 1984; Tatsumi et al., 2008; Tatsumi and Suzuki, 2009), although recent studies suggest that partial melting is the dominant process within the oceanic crust producing most of the large and small felsic intrusions around the world (see Furnes and Dilek, 2017 for a summary). Furthermore, latest developed dynamic magma chamber model within the oceanic crust suggests that deep-crustal primitive to evolved melt may migrate upwards as reactive porous flow through crystal-dominated gabbroic mush zone(s) where pervasive reactions of intercumulus melt and surrounding crystals exist (e.g., Lissenberg et al., 2013, 2019; Lissenberg and MacLeod, 2016). All these processes may produce unique major and trace element features that are finally being frozen and recorded in latestage melt-like compositions such as plutonic plagiogranites and fine-grained silicic dikes, veins and intrusions, which allow us to re-examine the petrogenetic processes of these silicic samples.

To mitigate the problems mentioned and upgrade our understanding of the formation and evolution of the Humber Arm Allochthon ophiolites and their tectonic correlation with the Twillingate arc pluton of Notre Dame Subzone, we conducted new major and trace element analyses and LA-ICP-MS U-Pb zircon studies on a variety of plagiogranite plutons from 1) the Bay of Islands Ophiolite Complex (Chapter 2 and 4), 2) the Coastal Complex (Chapter 3), 3) the Twillingate Granite batholith (Chapter 3), and 4) the metamorphic sole rocks collected from the base of the Blow Me Down Mountain and North Arm Mountain massifs in Bay of Islands Ophiolite Complex (Chapter 5) (Fig. 1.2 and 1.3). These analyses were based on state-of-the-art techniques and methods including solution work with ICP-OES for major element and triple-quad ICP-MS for trace element, a new novel Milestone ultraWAVE Microwave for rock digestion and LA-ICP-MS (depth-profiling) technique for zircon U-Pb geochronology.

In Chapter 2, we presented our new LA-ICP-MS U-Pb zircon age results yielded by pooling a large population of cogenetic zircons from two nearby plagiogranite plutons in the BOIC ophiolite (red stars in Fig. 1.2). We also recalculated prior BOIC legacy age results based on modern recommended data treatment techniques by using the same isotopic ratios and uncertainties reported in prior studies. By comparing these legacy ages reported with our recalculated ages and new LA-ICP-MS ages, we attempted to better confine the igneous crystallization age of the BOIC ophiolite, by which we could better understand its formation and evolution. Chapter 2 has been published in Gondwana Research (Yan and Casey, 2020).

Chapter 3 included LA-ICP-MS U-Pb zircon dating on a series of plagiogranite plutons from the Coastal Complex ophiolite and Twillingate Granite batholith (yellow stars in Fig. 1.2). Likewise, we reviewed and recalculated prior legacy age results and compared them with our new LA-ICP-MS age results. In this chapter, we attempted to date the oldest magmatism in the juvenile early Cambrian peri-Laurentian Taconic forearc-arc terrane in Newfoundland, by which the subduction initiation process and juvenile composite forearc-arc basement establishment could be better characterized. Chapter 3 has been submitted to peer-reviewed journal and is now under review.

Chapter 4 systematically described the petrogenetic modeling results of Rayleigh and equilibrium fractionation of a primitive MORB-like diabase, partial melting of altered roof zone diabases and metagabbros and magma mixing of felsic and basaltic endmembers. By comparing major and trace elements modeled with earlier available datasets as well as our newly acquired data of basaltic to felsic compositions, we attempted to quantitatively investigate the petrogenesis of BOIC plutonic plagiogranites and silicic fine-grained dikes within a suprasubduction zone forearc region. Chapter 4 is now under our final review to finalize for submission.

Chapter 5 included a preliminary investigation of the BOIC ophiolitic metamorphic sole to understand protoliths and their evolution as they were subcreted to the base of the ophiolitic residual peridotites in a subduction zone while subduction initiated beneath the BOIC (blue star in Fig. 1.2). In this chapter, we provided new major and trace element analyses to investigate the protolith of these sole rocks. We also attempted to look for high temperature (> 800 °C) metamorphic ages of the subcreted sole rocks using LA-ICP-MS U-Pb depth-profiling technique on unpolished zircon.

Finally in Chapter 6, we summarized our conclusions and significance of the four studies presented for the overall evolution of the Northern Appalachian Orogen. We provided a more precise temporal tectonic evolutionary model for development of the Early Cambrian island arc and forearc, as well as emplacement of the Taconic Humber Arm Allochthon ophiolites and Notre Dame arc onto the Laurentian rifted margin during the Middle Ordovician.

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Chapter 2 A new concordia age for the 'forearc' Bay of Islands Ophiolite Complex utilizing spatially-resolved LA-ICP-MS U-Pb analyses of zircon

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2.1 Introduction

There are three distinct U-Pb dating techniques including the high precision single grain or multigrain bulk techniques of ID-TIMS (isotope dilution-thermal ionization mass spectrometry) and the two high spatial resolution, but less precise, in-situ techniques of SIMS (secondary ion mass spectrometry) and LA-ICP-MS (laser ablation-inductively coupled plasmamass spectrometry) dominantly applied to zircon, among other minerals (e.g., Gehrels, 2011; Corfu, 2013; Schoene, 2014). U-Pb dating by LA-ICP-MS to determine the crystallization age of magmatic zircon is becoming a more widely used technique to obtain reliable and spatiallyresolved concordant dates that are statistically pooled to determine commonly precise resultant ages. Because zircon is both enriched in U and radiogenic Pb and relatively chemically robust to subsequent thermal disturbances and regional metamorphism, it is the best geochronometer to establish magmatic crystallization ages (Gulson and Krogh, 1973; Black, 1987; Hölzl et al., 1994; Mezger and Krogstad, 1997). Modern precise analyses of zircon crystals selected for ID-TIMS are typically treated before full dissolution by the CA (chemical abrasion) technique, originally developed by Mattinson (2005) to selectively and more completely remove zircon domains with high degrees of accumulated α -recoil radiation damage that did not behave as isotopically closed systems. A modified and improved CA technique for application to single-zircon crystals is now

standard practice in high-resolution zircon U-Pb geochronology for determining the most precise dates possible (e.g., Schoene et al., 2013). The key advantage of the CA routine is that by selectively removing zircon domains that may have behaved as "open systems" due to the enhanced element mobility enabled by radiation damage, solid residues representing pristine zircon domains can then be dissolved and analyzed subsequently, especially for single zircon grains. In the case of the earlier ID-TIMS age studies of the Bay of Islands Ophiolite Complex (BOIC) in the Ordovician Humber Arm Taconic Allochthon of Western Newfoundland, Canada (Fig. 2.1), the ID-TIMS analyses conducted more than 30 years ago were not based on single minerals, but mineral fractions and were treated with less reliable physical abrasion, a technique developed nearly 40 years ago by Krogh (1973, 1982).

These studies collectively produced three sets of heterogeneous, although often individually precise, 207 Pb/ 206 Pb dates between ca. 476 and 494 Ma, two different precisely reported upper intercept ages that were guided by somewhat arbitrarily constraining or fixing two different lower intercepts likely to prevent larger age error dispersion (e.g., Mattinson, 1976; Dunning and Krogh, 1989) and finally presented as a consensus age of 484 ± 5 Ma or 485 ± 5 Ma (Jenner et al., 1991; Cawood and Suhr, 1992). The consensus ages appear akin to a simple average of a set of heterogeneous dates of single sample fractions with uncertainties that are not clearly defined and that were set to bracket a certain range of 207 Pb/ 206 Pb individual dates (e.g., Jenner et al., 1991). These consensus ca. 484 or 485 Ma ages are clearly not calculated weighted means and are without defined methods of error propagation when assigning age uncertainties. If Pb loss was unremedied by the physical abrasion techniques used, zircon fractions could have yielded mixed dates that may tend to be too young by different amounts, both large or small, producing a systematic bias towards somewhat younger dates. In these pioneering TIMS studies, there are

observed differences between less variable and utilized ²⁰⁷Pb/²⁰⁶Pb dates and more precise, but younger, ²⁰⁶Pb/²³⁸U dates (see below). Samples used in three of the four prior studies were collected from the Blow Me Down Mountain massif of the Bay of Islands Ophiolite Complex (Fig. 2.1), the massif that we have selected here to reinvestigate using the spatial capabilities of LA-ICP-MS U-Pb dating technique coupled with abundant single zircon analyses of five samples (Fig.

2.2).

Fig. 2.1 Generalized regional geologic map of allochthonous ophiolitic rocks of the Bay of Islands region of Western Newfoundland, Canada, showing four main discrete BOIC ophiolitic massifs (modified from Casey et al., 1985), which, from north to south, are the Table Mountain massif, the North Arm Mountain massif, the Blow Me Down Mountain massif and the Eastern Lewis Hills massif, and the highly deformed adjacent to sub-adjacent Coastal Complex (Karson and Dewey, 1978), which is inclusive of the Little Port Complex in the north (Williams, 1975) and the Western Lewis Hills in the south. The Coastal Complex (CC) includes more highly deformed and older ophiolitic assemblages than the BOIC. Other allochthonous rift-related volcanics include the Skinner Cove Volcanics and various sub-ophiolitic basalts of Ediacaran age. The CC was demonstrated to have an autochthonous relationship with the BOIC in the Lewis Hills massif (Karson and Dewey, 1978), but is now in thrust or in fault contact to the north with the overlying BOIC massifs. Note that the two red stars within the Blow Me Down Mountain massif show approximate trondhjemite sample locations in this study (for detailed GPS sample locations see Table A2.1-2.5 in Appendix).



Fig. 2.2 Geologic map of the Blow Me Down Mountain massif. (a) Geological map and legend (right) of the Blow Me Down Mountain massif (generalized from detailed 1/15,000 unpublished maps of Casey and Karson, 1985), showing details of the main lithologies and tectonic features of the ophiolitic massif, (b) field photograph of close proximity of four sample locations within a single plagiogranite pluton, (c) Google Earth satellite image of four sample locations (yellow pins) and trondhjemitic outcrops, (d) enlarged view of a portion of the geologic map near four sample locations (yellow stars with sample labels) within the plagiogranite pluton and (e) photograph of hand specimen of BMD-08-17Y showing typical plagiogranite texture. Note that (c) and (d) have the same scale and are enlarged view of red box in (a). Detailed GPS locations of each sample are provided in Appendix Table A2.1-2.5.



2.2 LA-ICP-MS and legacy multigrain ID-TIMS U-Pb dating approaches

LA-ICP-MS analyses, in general, can yield concordant dates within the limits of uncertainty and can result in relatively high sample precision generally within \pm 1-2% (Shaulis et al., 2010). LA-ICP-MS U-Pb ages of zircon reference materials commonly achieve an accuracy of ~1-2%. This, of course, is relative to U-Pb ages determined by ID-TIMS, which have better internal precision (measurement repeatability) for ²⁰⁶Pb/²³⁸U and/or ²⁰⁷Pb/²⁰⁶Pb ages of ~1% absolute (e.g., Košler et al., 2013; Horstwood et al., 2016; Mukherjee et al., 2019). For our purposes, LA-ICP-MS techniques were more accessible, efficient and cost effective in attempting to resolve the geological interpretation of prior precise but heterogeneous sets of ID-TIMS dates reported from single samples from the Bay of Islands Ophiolite Complex. The techniques used also allow a more rapid analysis and throughput rate of approximately one analysis per minute enabling acquisition of more abundant dates (data points = N) per sample and per single pluton with respect to single zircon ID-TIMS analysis (e.g., Mattinson, 2005) and other types of spatially resolved analyses involving SIMS (e.g., Košler et al., 2013). Prior age interpretations or estimations were based on 1) multigrain mineral fractions that may have been influenced somewhat by the analytical techniques used, data reduction, limited discordance resulting in lower intercept assumptions in computing upper intercept ages and uncertainties, 2) minerals that may have been subject to interior domainal Pb-loss, or 3) homogenization of mixed dates from mineral fractions within the same samples. Our goal was to mitigate some of these issues by selective domain analyses of single zircon grains and by using modern data reduction, analysis and more abundant pooled concordant dates collected by LA-ICP-MS for statistical robustness in our final age determination.

Here we show that the ability to conduct selective analyses at a scale of ≤ 25 microns by LA-ICP-MS for U-Pb dating not only can result in relatively high precision individual dates, but can produce a more precise and geologically reasonable resultant age when large populations of concordant dates from multiple samples are utilized for pooling for a single pluton, similar to spatially selective analyses conducted by SIMS dating techniques (Simonetti et al., 2005; Gerdes and Zeh, 2006; Guillong et al., 2014; Schaltegger et al., 2015; Schoene et al., 2015). The larger populations of selected zircon grains that can be efficiently analyzed in single or multiple samples within the same pluton can yield carefully selected, spatially resolved concordant dates and ultimately precise and consistent igneous age results when compared to prior single sample TIMS dates from a limited number of mineral fractions that may suffer from certain age and interpretation uncertainties (e.g., Gehrels et al., 2008; Frei and Gerdes, 2009; Schoene, 2014). In comparison to prior age studies of the Bay of Islands Ophiolite Complex, an advantage of our spatial analysis approach is that it may resolve 1) interpretation problems associated with heterogeneous concordant and near-concordant dates, 2) the lack of more highly discordant data points that could have better constrained the upper or lower reported intercept ages of discordant lines (e.g., Mattinson, 1976; Dunning and Krogh, 1985), 3) the presence of inclusions, damage zones and mixtures within zircon fractions measured, and 4) the lower statistical robustness of low repeat numbers (N = 3-6) of heterogeneous near-concordant single sample fraction dates that are used to define ages.

It is well known that U-Pb zircon dating techniques can be compromised by mobilization of Pb that is inherently incompatible in the zircon lattice and may lead to variable degrees of Pb loss or more rarely Pb gain, producing discordant or reversely discordant U-Pb data and spread data along a discordant line (e.g., Williams et al., 1984; Corfu, 2013; Schoene et al., 2013; Spencer et al., 2016). The exact nature of Pb mobilization is difficult to recognize, especially 1) if it occurs shortly after zircon crystallization as the discordia is sub-parallel to the concordia curve and commonly within the analytical uncertainties, or 2) if multiple episodes or continuous Pb loss are responsible for slightly discordant dates in which upper intercept ages cannot be well constrained by more highly discordant data points (e.g., Jenner et al., 1991). Likewise, lattice damage zones, metamict regions and well-recognized mineral inclusions in BOIC zircon grains (see examples in Fig. 2.3) can result in ages significantly younger or older than the crystallization age (Kusiak et al., 2013; Schoene et al., 2013; Spencer et al., 2016; Ge et al., 2018). Age discordance in zircon is commonly interpreted to be due to discrete events of open-system mass transfer and usually recorded by chemical heterogeneity fluid-assisted recrystallization (e.g., Corfu, 2013; Villa and Hanchar, 2017).

Trondhjemites targeted for LA-ICP-MS U-Pb zircon dating in the Bay of Islands Ophiolite Complex (BOIC) typically are found as small plutons and veins in the upper gabbroic unit just below the sheeted diabase dike unit. Both units are within zones that have commonly suffered some extent of fluid-assisted hydrothermal or deuteric alteration, but at rather low waterrock ratios compared to shallower level upper ophiolite units, for example, pillow lavas. With LA-ICP-MS 25-micron laser spots and more simple magmatic zircon grains separated, it is possible to find original magmatic inclusion-free and metamict-free core domains that are relatively unaffected by Pb loss or gain and that yield high numbers of concordant dates. Because of the heterogeneity and wide range (~20 Ma) of more precise individual ID-TIMS dates reported for homogenized single mineral fractions in the prior studies of Mattinson (1976), Dunning and Krogh (1985) and Jenner et al. (1991), our goal in this study was to selectively avoid inclusions, microfractures, damaged domains and outer zircon rim zones (e.g., see rim-core dating test of Fig. 2.3i) with potentially high U and Th concentrations where zircon lattices suffer the highest radiation damage by natural alpha decay, alpha recoil and spontaneous fission processes. Our results indicate that there may be some advantages over previously published analyses conducted with physically abraded multiple mineral fractions of single samples by ID-TIMS that produced somewhat heterogeneous sets of dates, particularly manifest by more precise ²⁰⁶Pb/²³⁸U dates (or their ratios used for calculating U-Pb intercept ages) that are commonly significantly younger than reported ²⁰⁷Pb/²⁰⁶Pb dates. Weighted averaging of large numbers of even lower precision concordant analyses has repeatedly been demonstrated to produce rather precise age information. Furthermore, repeatable accuracy and consistency check on standards as well as internal age consistency of multiple samples from a single pluton can lead to confidence in a geologically reasonable age by LA-ICP-MS. In this chapter we report a large number of LA-ICP-MS analyses for five samples, of which four are from a single pluton, that results in a consistent set of sample ages and a more precise composite age for the BOIC. We also retrospectively review previous ID-TIMS dating of ophiolitic rocks in the Bay of Islands region and the assumptions that may have limited these more precisely reported dates and age determinations, and then assess the tectonic significance of this new age.

2.3 Regional geology and legacy of Humber Arm Allochthon ophiolitic age dating

Igneous assemblages of the Taconic Humber Arm Allochthon of Western Newfoundland (e.g., Stevens, 1970; Dewey and Bird, 1971; Williams, 1973, 1975; Karson and Dewey, 1978; Casey et al., 1981, 1983; Karson, 1984; Karson et al., 1984) tend to comprise the highest structural slices (Fig. 2.1). They can be divided into three distinct age groups based on structural and crosscutting relationships and prior radiometric dating outlined below. These include, from youngest to oldest, 1) the Bay of Islands Ophiolite Complex (BOIC), which is a 100

km-long and 25 km-wide belt of less deformed ophiolitic rocks including from north to south, the Table Mountain (TM) massif, the North Arm Mountain (NA) massif, the Blow Me Down Mountain (BMD) massif and the Eastern Lewis Hills (ELH) (Casey et al., 1981, 1983; Karson and Dewey, 1978; Kurth et al., 1998; Williams, 1973, 1975), 2) the Coastal Complex (CC), which is here reestablished to include a narrower, more westerly, overall parallel belt of more highly deformed and older ophiolitic rocks which includes the Little Port Complex and the Western Lewis Hills (WLH) (Comeau, 1972; Williams, 1973, 1975; Karson and Dewey, 1978; Casey et al., 1983, 1985; Casey and Dewey, 1984; Karson et al., 1984; Idleman, 1991; Cawood and Suhr, 1992; Kurth et al., 1998; Kurth-Velz et al., 2004; Dewey and Casey, 2013, 2015), and 3) the Skinner Cove Volcanic Assemblage and other sub-ophiolitic volcanic assemblages related to early rifting of the Laurentian margin in the uppermost Ediacaran (Williams, 1973, 1975; Strong, 1974; Karson, 1977; Baker, 1979; Casey, 1980; Rosencrantz, 1980; Williams et al., 1989; Cawood et al., 2001; Hodych et al., 2004).

Most prior investigations with the goal of determining the crystallization age of ophiolitic rocks from the Bay of Islands region, except for a single apatite date reported by Kurth et al. (1998) in the ELH, were generally carried out by high precision ID-TIMS U-Pb dating of a limited number (small N) of U-bearing mineral fractions (zircon or baddeleyite). These analyses were conducted approximately 30 years ago prior to many analytical improvements. These include changes from multigrain to single grain analyses, decreases in Pb blanks and jointly calibrated tracers and many technical improvements in mass spectrometry, chemical abrasion-annealing techniques, zircon selection, elimination of mixed grain domains, unresolved systematic errors, inter-laboratory bias, improvements in propagation of errors, weighted mean and uncertainty calculations and recent more comprehensive community-based data reduction software and recommendations (e.g., Mattinson, 1987, 2005; Ludwig, 2008; Schoene et al, 2013; Condon et al., 2015; Horstwood et al., 2016; McLean et al., 2016; Vermeesch, 2018). Utilized multigrain techniques themselves may have been susceptible to accidental mixing of materials with distinct ages from concordant, metamict, inclusion-bearing, and/or rim domains, which may produce points along a mixing line (Mezger and Krogstad, 1997) or multiple mixing lines. These issues are more likely for methods that involve many whole grains that are dissolved and homogenized (e.g., multigrain TIMS analysis). Alternatively, this issue may be remedied when high numbers (N) of dates of spatially resolved analyses such as LA-ICP-MS or SIMS are collected, which allow such heterogeneities to be better reconciled by selective domain analysis, post-analysis observation of grains, data reduction, and statistically robust pooling to a resultant age. The prior ID-TIMS measurements were all characterized by limited number of whole grain mineral fraction dates on single samples to produce ages. The individual dates generated are typically heterogeneous given precisions quoted, although concordant to slightly discordant. The small N and the lack of highly discordant dates for better evaluation and more precise calculation of discordant lines and upper intercept ages in these early studies tended to plague or limit robust statistical analysis of dates in determining or estimating ages and uncertainties. LA-ICP-MS dates of multiple samples presented below may, in contrast, allow more efficient acquisition of much larger number of concordant measurements for age computation.

2.3.1 The Bay of Islands Ophiolite Complex geochronology

Mattinson (1975, 1976) reported the first ID-TIMS age of trondhjemite collected from the Bay of Islands Ophiolite Complex (BOIC) (Williams, 1973), as well as the Coastal Complex (CC) (Karson and Dewey, 1978). From the BOIC, Mattinson (1976) obtained a trondhjemitic sample from the upper gabbroic section of the Blow Me Down Mountain (BMD)

massif and reported three 207 Pb/ 206 Pb dates of 480 ± 7 , 485 ± 7 , and 494 ± 5 Ma and U-Pb isotopic ratio data but without clearly defined uncertainties from three multi-grain zircon fractions of the same sample. Faced with these heterogeneous dates, Mattinson (1976) constructed a discordant line within a Wetherill concordia plot (although all dates were nearly concordant within uncertainty) in order to determine an upper intercept age of 504 ± 10 Ma. In fitting the discordia Mattinson interpreted and then constrained the lower intercept to an assumed 460 Ma obduction age. However, this lower intercept was based on an erroneous, but understandable, presumption of the obduction timing event using a dynamothermal sole ⁴⁰Ar-³⁹Ar age reported by Dallmeyer and Williams (1975). The amphibole separates from amphibolite of the BOIC dynamothermal metamorphic sole were dated by 40 Ar- 39 Ar method yielding an age of 460 ± 5 Ma, which was later revised to 469 ± 5 Ma by using the revised K decay constant (see Nelson and Casey, 1979). The recalculated age rendered Mattinson's choice of the lower intercept invalid (see discussion in Dunning and Krogh, 1985). Studies of the BOIC using K-Ar and ⁴⁰Ar-³⁹Ar techniques were reported by both Archibald and Farrar (1976) and Dallmeyer and Williams (1975) for ophiolitic rocks. Archibald and Farrar (1976) obtained a result from the metamorphic sole of 454 ± 9 Ma by K-Ar dating, which was approximately recalibrated to 464 ± 9 Ma using the revised K decay constant (see Dunning and Krogh, 1985 for details). Both the ca. 469 and 464 Ma recalibrated sole ages were comparable and were then used as indirect evidence to constrain the minimum BOIC crystallization age. Most of the ophiolitic igneous rock (recalculated) cooling dates by Archibald and Farrar (1976) for the BOIC or CC (Little Port Complex) (Fig. 2.1) were either similar in age or younger than that of the sole and derived from samples collected at or near major tectonic boundaries that were subjected to retrograde effects and could have been subject to argon loss. However, these cooling dates were unusually young (~50 to 15 Ma younger) with respect to later reported BOIC or CC ID-TIMS zircon ages (proposed crystallization ages for the ophiolitic rocks), even for quickly chilled diabases. Many of these Ar dates obtained, therefore, are close to or younger than final transport and allochthon emplacement ages of the igneous slices and the underlying sedimentary portions of the allochthon. As these rock units must have been exposed to surface weathering and substantially cooled before final emplacement (ca. 460-470 Ma) (Casey and Kidd, 1981; Dewey and Casey, 2013, 2015), the younger Ar-Ar or K-Ar dates in the allochthon have been conjectured to result from later thermal-tectonic events in the Mid-Paleozoic (e.g., Idleman, 1991; Cawood et al., 2001). Similarly, Whitehead et al. (2000) have outlined that in the Quebec ophiolitic terranes to the southwest younger sole post-kinematic, but pre-finalemplacement granitic intrusions with crystallization ages of ca. 469-470 Ma intrude both the ophiolitic peridotites and the sole (Ar-Ar cooling age of ca. 477 Ma). They also indicate that younger Silurian Ar ages have been measured in the Quebec Thetford ophiolites, although the igneous U-Pb zircon crystallization age is much older (ca. 480 ± 2 Ma). This may attest to probable local post-ophiolite and post-sole formation protracted tectonothermal late cooling or argon loss events associated with these Taconic ophiolite complexes cropping out along strike to the southwest of the BOIC. Likewise, the data show the closeness (~3 Ma) of the cooling age of the sole to the ophiolite formation age.

Jacobsen and Wasserburg (1979) also produced two Sm-Nd internal isochrons for gabbroic samples from the BMD massif and reported two similar ages to Mattinson (1976) based on a three-point isochron of plagioclase, clinopyroxene and bulk rock of 508 ± 6 Ma and a two-point isochron of plagioclase and clinopyroxene with large ratio errors yielding a less precise age of 501 ± 13 Ma. They then interpreted an average of ca. 505 Ma as BOIC formation age without specified uncertainties.

Dunning and Krogh (1985) then cast doubt on the older U-Pb ID-TIMS age (ca. 504 Ma) of Mattinson (1976) and the Sm-Nd age (ca. 505 Ma) of Jacobsen and Wasserburg (1979). They presented six ²⁰⁷Pb/²⁰⁶Pb dates clustered between ca. 480 and 487 Ma from a trondhjemite collected near Mattinson's (1976) sample location on the BMD massif without expressly reporting specified ²⁰⁷Pb/²⁰⁶Pb date uncertainties for zircon fractions. They computed an upper intercept age of $485.7^{+1.9}_{-1.2}$ Ma from this trondhjemite by, like Mattinson's age computation, constraining the lower intercept to a somewhat arbitrary 50 Ma age. The lower intercept constraint makes little difference to the upper intercept age calculated for the BOIC that they reported but may lead to the much smaller uncertainty (based on our recalculated ages and age uncertainties presented below). Their upper intercept age was based on a discordant line derived from five separate zircon fractions from a single trondhjemite sample and the interpreted 50 Ma lower intercept. The fractions showed only slightly discordant dates (reported as up to 2.8%). Like Mattinson's data, the discordant line of Dunning and Krogh (1985) lacked any significantly discordant data points to be more tightly constrained. Thus, they forced it to pass through an arbitrary lower intercept of 50 Ma \pm 90% to more precisely report the upper intercept age.

Jenner et al. (1991) recovered three baddeleyite and three zircon fractions from a gabbroic sample from the BMD massif and argued that because of the total of six 207 Pb/ 206 Pb heterogeneous dates that lay between 476 and 489 Ma (with unreported age uncertainties), a 207 Pb/ 206 Pb age of 484 Ma should be considered appropriate with an age uncertainty of ± 5 Ma that was designed to encompass most of the range of individual dates reported in their study. Although a Wetherill concordia diagram was plotted and presented, it was not discussed in their paper and no upper intercept age was presented. Their suggested age of ca. 484 Ma has been ubiquitously referenced as the BOIC formation or consensus age.

Kurth et al. (1998) added a single concordant TIMS 206 Pb/ 238 U date of 485.0 ± 1.0 Ma from one apatite fraction separated from an evolved gabbroic rock in the Eastern Lewis Hills (ELH). The ELH is considered part of the BOIC immediately adjacent to the Coastal Complex of the WLH (Karson and Dewey, 1978; Casey and Karson, 1981; Casey et al., 1983; Kurth et al., 1998). Although there is evidence that apatite dates from plutonic environments might be more appropriate for post-magmatic mid-temperature (~375-600 °C) thermochronology (e.g., Kirkland et al., 2018), Kurth et al. (1998) concluded that their single date was in agreement with the previous formation age results of Dunning and Krogh (1985) and Jenner et al. (1991); so that based on the collection of above referenced studies, the BOIC crystallization age has been considered to be 484 ± 5 Ma or 485 ± 5 Ma (Jenner et al. 1991; Cawood and Suhr, 1992).

2.3.2 The Coastal Complex geochronology

The first crystallization ages reported for ophiolitic rocks from the CC were again obtained by dating zircon fractions from trondhjemites, one of which was collected from what Mattinson termed the "Trout River ophiolite" (Mattinson, 1975). For the "Trout River" trondhjemite, two zircon fractions were separated and analyzed and yielded a poorly-constrained, two-point discordia with an upper intercept age of 508 ± 5 Ma, significantly older than the BOIC consensus age of ca. 484 Ma described above (e.g., Jenner et al., 1991). Mattinson (1976) recognized that he had mistakenly treated the "Trout River ophiolite" as part of the BOIC. In fact, the Trout River section was recognized to be distinct from the BOIC and to be part of the "Little Port Complex" (named by Williams, 1973, 1975). Williams (1973) documented that the Little Port Complex was a fault-bounded structural slice of deformed ophiolitic assemblages (including pillow lavas, sheeted dikes, trondhjemitic plutons, and gabbroic rocks with minor ultramafic rocks) and structurally below the BOIC (TM massif, NA massif and BMD massif). Subsequently, Karson and Dewey (1978) concluded that the Little Port Complex was part of a more broadly defined Coastal Complex, which they extended from coastal dismembered ophiolitic exposures west of the three northern BOIC massifs (mapped previously as the Little Port Complex) (Williams, 1973) to an intact western part of the Lewis Hills massif in the south that was not dismembered (i.e., not in thrust contact with the BOIC) and included correlative deeper lower crustal and upper mantle ophiolitic assemblage that showed strong crystal-plastic deformation (see Fig. 2.1). Karson and Dewey (1978), Casey and Karson (1981), Casey et al. (1981, 1983, 1985), Casey and Dewey (1984), Karson (1984) and Karson et al. (1984), in fact, documented an original autochthonous igneous contact relationship between ophiolitic basement of the BOIC that is exposed in the ELH with the older deformed ophiolitic basement of the CC in the WLH (Fig. 2.1). The deeper, older and previously deformed ophiolitic crustal and mantle rocks of the CC (WLH) are intruded by the younger BOIC dikes and plutons emanating from the ELH acting to weld the two types of basements. The CC in the WLH and northern coastal outcrops (also called the Little Port Complex) were together interpreted as an older group of deformed ophiolites that formed along a transform fault zone based on geological mapping and structural and crosscutting relationship in the Lewis Hills massif by Karson and Dewey (1978). They described shallowly plunging crystal-plastic linear kinematic indicators and fault slip directions suggestive of a strike-slip transform deformation zone in the CC indicating a major tectonic plate boundary domain welded to the BOIC at a ridge-transform intersection. The BOIC younging direction was interpreted based on kinematic indicators to be to the southwest, i.e., toward the younger Taconic ophiolites of Quebec (ca. 480 Ma).

These distinctions between the BOIC and CC and the correlation of the WLH (CC) in the south with the Little Port Complex (CC) in the north, as well as the distinct age of CC with

respect to the BOIC were later confirmed by additional U-Pb age dating in the WLH and ELH (Kurth et al., 1998) and by the petrogenetic differences with stronger arc or forearc affinities for assemblages in the CC versus a more subtle MORB- to FAB- (forearc basalt) like geochemical signatures recorded in rocks of the BOIC (e.g., Casey et al., 1985; Casey and Dewey, 1984, 2014; Jenner et al., 1991; Kurth et al., 1998; Kurth-Velz et al., 2004; Dewey and Casey, 2013, 2015). The clear autochthonous ophiolitic basement relationship established with the BOIC (ELH) intruding an older deformed ophiolitic assemblage of the CC (WLH) (Karson, 1977, 1984; Karson and Dewey, 1978; Casey et al., 1981, 1983; Casey and Dewey, 1984; Karson et al., 1984) indicates that the northern part of the CC (Little Port Complex) was likely originally part of the same structural ophiolitic basement slice within the Humber Arm Allochthon prior to final emplacement and partial dismemberment that took place in the northern CC during transport (Fig. 2.1). The CC appears to have formed along a transform fault (Karson and Dewey, 1978; Casey and Dewey, 1984; Karson, 1984) offsetting supra-subduction forearc spreading centers of the BOIC (Dewey and Casey, 2013, 2015) within the Baie Verte Oceanic Tract (e.g., Van Staal et al., 2007). The CC and BOIC relationships are thus interpreted as analogous to modern-day forearcs with contiguous, but distinct, older and younger generated supra-subduction forearc ophiolitic basements fronting arcs, i.e., in this case fronting the Cambro-Ordovician Notre Dame Island Arc of Central Newfoundland (Nelson and Casey, 1979; Casey and Dewey, 1984; Dewey and Casey, 2011). Jenner et al. (1991) had rejected the correlation of the Little Port Complex with the WLH and the idea of the broader CC designation, apparently on the basis of the different ophiolitic structural levels. Their interpretation was adopted in the map of the Humber Arm Allochthon by Williams et al. (1989), although, in fact, these different CC ophiolitic levels and contacts with the BOIC were clearly outlined by Karson and Dewey (1978), Casey and Karson (1981), Casey et al. (1983, 1985), Casey

and Dewey (1984), Karson (1984) and Karson et al. (1984) and subsequent studies referenced above. Although Jenner et al. (1991) stated that the WLH and the Little Port Complex could not be correlated and that the term Coastal Complex should be abandoned, we think that the correlation is well based and should be retained.

The apparent older igneous crystallization age of the Coastal Complex (CC) ophiolitic rocks in the Western Lewis Hills (WLH) with respect to the Bay of Islands Ophiolite Complex (BOIC) in the Eastern Lewis Hills (ELH) was subsequently clearly demonstrated by two samples with zircon ID-TIMS upper intercept ages of 503.7 ± 3.2 Ma and 500.6 ± 2.0 Ma in the WLH (Kurth et al., 1998). These two mineral fraction ages also confirm an age correlation of the WLH with the Northern CC as they are within error of each other and also similar to the original "Trout River ophiolite or Little Port Complex" upper intercept age of 508 ± 5 Ma reported by Mattinson (1975), as well as the trondhjemite upper intercept age of 505^{+3}_{-2} Ma that Jenner et al. (1991) reported from the nearby Little Port Complex in Blow Me Down Provincial Park. This narrow age range and age similarities are expected, of course, if both the WLH and Little Port Complex are appropriately interpreted to be part of the CC assemblage as originally described by Karson and Dewey (1978) and the older part of a forearc basement complex with a more protracted igneous history (Dewey and Casey, 2013, 2015). In addition, lower E_{Nd} values for plutonic rocks from both the Little Port Complex and the WLH, with respect to higher values of the later BOIC (including the ELH), further confirm this correlation and inclusion of both into the CC (Jacobsen and Wasserburg, 1979; Kurth et al., 1998; Jenner et al., 1991; Kurth-Velz et al., 2004). In contrast, the much higher E_{Nd} values from the BOIC (Jacobsen and Wasserburg, 1979) and the ELH (Kurth et al., 1998) show clear depleted mantle source signatures devoid of the crustal inputs recorded in the older CC. The definition of the CC is here clearly reestablished to include the western part of the Lewis Hills massif and coastal exposures previously termed as the Little Port Complex (see further discussion by Cawood and Suhr, 1992; Kurth-Velz et al., 2004; Dewey and Casey, 2013, 2015).

Idleman (1991) also conducted ⁴⁰Ar-³⁹Ar thermochronologic age dating on hornblendes from plutonic and metamorphosed rocks of the CC and obtained a cooling age in a hornblende gabbro of ca. 490 Ma (closure temperature of ~580 °C) and a gabbroic amphibolite facies mylonite age of ca. 475 Ma. Both rock types are cut by undeformed mafic dikes, indicating that the CC ophiolite at these times was likely still part of the active supra-subduction and seafloor magmatic zone. Therefore, the CC is unlikely to have been obducted by 475 Ma or earlier (e.g., see discussions in Cawood and Suhr, 1992; Swinden et al., 1997; van Staal et al., 2007; Skulski et al., 2010; Zagorevski and van Staal, 2015). Some ophiolitic rocks of the CC were, however, certainly cooled by 475 Ma adjacent to the younger and hotter BOIC. It is important to note that many other samples dated in the region by Dallmeyer and Williams (1975), Archibald and Farrar (1976) and Idleman (1991) using Ar-Ar and/or K-Ar method yielded cooling ages significantly younger than and are incompatible with much older zircon ages of both ophiolitic assemblages. Archibald and Farrar (1976) and Idleman (1991) interpreted these younger ages in the allochthon to be related to later mid-Paleozoic tectonothermal events (see Cawood et al., 2001 and personal communications within). These dates may indicate that there are regional to local disturbances that have to be addressed for the range of younger Ar-Ar or K-Ar dates reported in the Bay of Islands region.

2.3.3 Skinner Cove and other sub-ophiolitic volcanics geochronology

Sub-ophiolitic allochthonous volcanic assemblages documented throughout the Bay of Islands region that we do now exclude from the originally defined Coastal Complex (Comeau, 1972; Karson and Dewey, 1978) include the Skinner Cove Volcanic Assemblage (Baker, 1979; Strong, 1974), and other correlated and informally named sub-ophiolitic volcanic rocks (e.g., Chimney Cove, Beverly Cove, Couchers, Fox River Island) (Williams et al., 1989), as well as numerous undifferentiated sub-ophiolitic volcanic rocks mapped in this region (see Fig. 2.1). They are now generally regarded based on U-Pb zircon ages from the Skinner Cove type locality as allochthonous rift-related Ediacaran (ca. 550 Ma) volcanic rocks derived from the nearby Laurentian ocean-continental crust transition (Williams, 1975; Cawood et al., 2001; Hodych et al., 2004). These volcanic rocks were tectonically accreted to the allochthon and emplaced from the distal parts of the ancient passive margin as the lowest igneous slices below the upper ophiolitic massifs and welded metamorphic sole rocks. This age represents a probable upper limit for the completion of Laurentian margin rifting and ocean formation.

2.4 Sampling locations

The Bay of Islands Ophiolite Complex (BOIC), from north to south, includes the Table Mountain (TM) massif, the North Arm Mountain (NA) massif, the Blow Me Down Mountain (BMD) massif and the Eastern Lewis Hills (ELH) (Fig. 2.1) (Williams, 1973; Karson and Dewey, 1978; Casey et al., 1983, 1985; Kurth et al., 1998). The BMD massif as well as the NA massif expose relatively intact ophiolite stratigraphies that fit the typical ophiolite definition given by Penrose Ophiolite Conference (Anonymous, 1972), whereas the TM massif and the ELH only preserve basal crustal and ultramafic portions and are mostly made up of ultramafic rocks and largely devoid of trondhjemitic rocks (Williams, 1973; Casey and Karson, 1981; Casey et al., 1983; Williams et al., 1989). Plagiogranites within the BMD massif generally occur as meter- to kilometer-scale intrusive plutons, smaller pods and veins within the upper gabbroic unit and/or as fine-grained dikes within diabase dike unit, but mainly are located near the dike-gabbro transition

zone (Fig. 2.2a) as would be expected if cogenetic with and fractionation products of the ophiolite gabbroic assemblages.

Early studies suggested that the BOIC was a relatively undeformed ophiolitic assemblage when compared to the CC, representative of remnant oceanic lithosphere and upper mantle that was generated during ancient Iapetus spreading (Stevens, 1970; Church and Stevens, 1971; Karson and Dewey, 1978), which was subsequently emplaced onto the eastern margin of North America in the Middle Ordovician (Williams, 1971; Williams and Malpas, 1972; Malpas, 1979). However, later studies argued that the BOIC was more likely to be formed within an upper plate forearc, arc or back-arc primarily based on negative tantalum and niobium anomalies in some BOIC diabases and basalts (Casey and Dewey, 1984; Elthon, 1991; Jenner et al., 1991) and BOIC-CC structural and relative age relationships (Nelson and Casey, 1979; Casey et al., 1983, 1985; Casey and Dewey, 1984; Dewey and Casey, 2013, 2015). On these bases, Dewey and Casey (2013, 2015) further proposed a trench-trench-ridge (TTR) triple-junction model with forearc suprasubduction spreading centers offset by transform faults bounded by an older supra-subduction zone ophiolitic forearc lithosphere (the CC-Lushs Bight terrane) as the tectonic setting for the origin of the BOIC. They emphasized that these younger trench-orthogonal supra-subduction spreading centers within the upper plate would account for the BOIC and other ophiolite sheeted dike attitudes and sole lineations within the Baie Verte oceanic tract in Newfoundland.

To better constrain the formation age of the Bay of Islands Ophiolite Complex we analyzed four trondhjemites, labeled BMD-03-17Y, BMD-04-17Y, BMD-07-17Y and BMD-08-17Y, that were collected from a single plagiogranite pluton located ~200 m below the sheeted dike unit on the Blow Me Down Mountain massif (Fig. 2.1 and 2.2b-d) during summer of 2017. Each of the four samples was chosen spatially separated from one another to cover largest contiguous

portion of the exposed area of the pluton and to simultaneously assure they were cogenetic. We also report a result from an additional sample BMD-01-17Y derived from a nearby plagiogranite pluton (starred location in Fig. 2.1) in order to test consistency in age between different plutons on the BMD massif. Careful examination of these specimens presented shows that they all have undergone some degree of hydrothermal alteration (Fig. 2.2e), similar to trondhjemites reported by Elthon (1991) and Suen et al. (1979), although euhedral to subhedral prismatic igneous zircon is dominant (e.g., Fig. 2.3).

2.5 Analytical procedures

2.5.1 Zircon separation

Trondhjemite samples were first processed by conventional techniques (Chisholm et al., 2014) to concentrate denser (than methylene iodide) and nonmagnetic grains, among which zircon grains were then randomly handpicked under polarizing microscope regardless of their shape, color or size to avoid potential artificial bias (Sláma and Košler, 2012). These handpicked grains were mounted in epoxy resin and polished at 2500 grit to remove the outermost part of grains and expose an inner surface for each zircon crystal to reduce chances of common Pb contamination.



Fig. 2.3 Photomicrographs of representative zircon crystals under plane polarized light from this study. Individual dates given within each photomicrograph are high precision ²⁰⁶Pb/²³⁸U dates with 1 sigma uncertainty (red). (a-d) representative zircon crystals with prism-like, transparent, euhedral to subhedral appearance; (e) large zircon piece with breakage caused by sample preparation (e.g., mechanical crushing); (f-g) zircon crystals with murky brown domains and unknown mineral or fluid inclusions; (h-i) zircon grains with marginal oscillatory zoning. Note (i) is greyscale to enhance view of rim oscillatory zoning.

The appearance of zircon crystals was examined before and after ablation using a petrographic microscope under plane polarized light. Overall, the majority of grains are prism-like, transparent to semi-transparent, euhedral to subhedral and have an outermost altered (sponge-like) rim (see Fig. 2.3a-d). The single zircon grains analyzed by LA-ICP-MS include euhedral, subhedral and broken crystals with long axes of intact prismatic zircon varying from approximately 100 microns to 400 microns and aspect ratios ranging between 2 and 5 (Fig. 2.3). No petrographic

evidence of inherited cores in zircon crystals was observed as oscillatory rim zoning was concordant with prismatic cores. Microfractures are visible within nearly every crystal preferentially cutting through the entire grain. It is noteworthy, however, that these microfractures are more likely to have been induced by sample crushing since they are all randomly distributed and rarely occur with narrow murky-brown or dark bands (e.g., Nasdala et al., 1996; Geisler et al., 2002; Takehara et al., 2018). Large broken zircon pieces also exist (Fig. 2.3e), similarly indicating that mechanical-induced damage is ubiquitous. Inclusions are not rare and appear as red, black and brown pods or more common, elongated rods with their length varying from several to tens of microns (Fig. 2.3f and g). Pronounced marginal oscillatory zoning is common (Fig. 2.3h and i). In general, within larger intact euhedral grains the rims of grains are more likely damaged and yielded younger dates than the cores when they were tested by LA-ICP-MS (Fig. 2.3i), although the certain rim dates are likely mixed because the 25-micron laser spot may be larger than some of the rims or sample compositional zoning. Core ages are used as the crystallization ages because they are the first generated and least disturbed parts of the grains. In all cases, we attempted to isolate laser spots to the clear core domains of each grain away from rims, fractures, brownish domains and inclusions.

2.5.2 LA-ICP-MS analysis

In situ U-Pb zircon dating was carried out on a Varian 810 quadruple inductively coupled plasma-mass spectrometer (ICP-MS) equipped with a Photon Machines Excite 193 nm wavelength laser ablation system at the University of Houston (UH) ICP Lab. The laser was operated with a fluence of 3.95 J/cm^2 , repetition rate of 10 Hz and ablation spot diameter of 25 µm. The pulse counts were 300 shots enabling a 30-second static ablation. Detailed LA-ICP-MS instrumental operating conditions used in this study are provided in Appendix Table A2.6, and

more detailed descriptions of instrumental conditions, pulse counting detector linearity and dynamic range of the UH Varian 810 quadruple ICP-MS can be found in Shaulis et al. (2010). Derived dates were corrected for instrumental fractionation and time drift by standard bracketing techniques by alternating between standards and unknowns, correcting the standards to the known ages and applying the correction factors to the unknowns. Sample bracketing strategies included one of the reference materials treated as an unknown to independently assess the accuracy and precision of every analytical session and demonstrate repeatability. Specifically, a single analytical session starts with five analyses of standard Peixe followed by five analyses of standard FC5z and then another two analyses of Peixe, and the session ends with three analyses of FC5z followed by three analyses of Peixe. In between the starting and end standard suites, a small group of 7 analyses including 5 unknowns immediately followed by one Peixe and one FC5z was analyzed successively until all zircon grains from the same sample have been measured. Peixe with an accepted ID-TIMS value of 564 ± 4 Ma (Dickinson and Gehrels, 2003) was used as primary standard to calibrate instrument-related time drift and mass bias and laser-induced elemental fractionation (Jackson et al., 2004; Košler et al., 2005; Kuhn et al., 2010) because of its similar matrix to the BOIC zircon grains analyzed. FC5z has an accepted ID-TIMS value of 1099.0 ± 0.6 Ma (Paces and Miller, 1993) and was used as secondary standard to evaluate the accuracy and precision of each session. Every LA-ICP-MS acquisition lasted 60 s and consisted of a 15 s background measurement (blank) followed by a 30 s ablation on sample with measurements of ²⁰²Hg, ²⁰¹Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th and ²³⁸U and finally another 15 s wash-out delay before the next acquisition. We only conducted one shot per zircon crystal, and based on availability of individual zircon crystals separated, 35 shots were conducted for samples BMD-0317Y and BMD-04-17Y, 25 shots for BMD-07-17Y, 29 shots for BMD-08-17Y and 40 shots for BMD-01-17Y.

2.5.3 Data processing and screening

Raw data were reduced off-line by using GLITTER (Griffin, 2008) with Peixe being set as the "reference material". Each analytical session was performed separately, but with an identical protocol. GLITTER has an advantage of allowing instant updating of the results whenever any change of parameters is made during data reduction (van Actherbergh, 2001) so that the standard results could be monitored instantaneously. The blank and sample signal intensity integration intervals of each analytical session were first selected and similar signal integration intervals relative to the rise time were adopted for blank and sample to avoid any unintentional biasing of the data. GLITTER allows this to be fulfilled manually by dragging the vertical markers in a colored pixel map where the horizontal and vertical axis respectively display rise time and relevant isotopic ratios. After signal selection, ²⁰⁶Pb/²³⁸U, ²⁰⁷Pb/²³⁵U and ²⁰⁷Pb/²⁰⁶Pb ratios were inspected for possible inclusion and/or cracks that contain high common Pb and/or age zoning to modify the signal selection accordingly. In general, the initial 1 s after ablation starts and the final 1 s before the ablation ends were excluded purposely to ensure a relatively flat signal "plateau". A linear fit of background interpolation was applied. After blank correction, downhole fractionation factors for ${}^{207}\text{Pb}/{}^{206}\text{Pb}$, ${}^{206}\text{Pb}/{}^{238}\text{U}$ and ${}^{207}\text{Pb}/{}^{235}\text{U}$ ratios (with ${}^{235}\text{U} = {}^{238}\text{U}/{}137.88$ after Jaffey et al., 1971) were calculated for primary standard Peixe. A quadratic fit of calibration was used to correct other fractionations of unknowns. No common Pb correction was performed. As a check on data reduction by GLITTER, we also reduced data with a software package of Iolite (Paton et al., 2010) plus an in-house Excel spreadsheet program (see method described in Shaulis et al., 2010), by which identical weighted mean age results for each sample were produced and the computed

composite age was identical with GLITTER results. The GLITTER-reduced U-Pb isotopic ratios and dates are reported here with 2 sigma (2s) uncertainties in the data tables (Appendix Table A2.1-2.5).

After initial data reduction, we re-examined each ablation spot location in detail under microscope to assure result quality. As shown in Fig. 2.3f, g and i, some of the spots analyzed penetrated partly on metamict (murky brown) and/or rim domains or appeared to penetrate into inclusions not observed prior to ablation, all of which tend to produce mixed, ambiguous and less reliable dates. Thus, any results from such spots have been rejected and the remnant resultant data are all inspected to be from transparent core regions.

The advantage of zircon U-Pb geochronometer is based on simultaneous decay of two isotopes of the same radioactive parent to two stable Pb isotopes. This provides the geochronometer with a check of internal consistency between the two decay systems. Therefore, the discordance (%) of each remnant data point was calculated as $|(^{206}\text{Pb}/^{238}\text{U}_{date})/(^{207}\text{Pb}/^{235}\text{U}_{date}) - 1| * 100$, irrespective of whether the analytical points are normally or reversely discordant. The resulting percentage discordance provides a qualitative assessment of whether the isotopic ratios have experienced disturbance following zircon crystallization (e.g., Eglington and Harmer, 1993; Schoene et al., 2013; Gehrels, 2014).

Migration of Pb within the mineral lattice will generally produce the discordance in the U-Pb system (Mezger and Krogstad, 1997; Cherniak and Watson, 2001). In detrital zircon studies where relative proportions of different age populations are important and the discordance for each population may be different for old and young dates, generous discordance filters of 10-30% rather than tight filters are applied to avoid biasing the proportion and importantly the distributions of the age populations toward young ages (e.g., Spencer et al., 2016). In contrast, our goal was to obtain a precise age of crystallization. Thus, we tightened the discordance filter to 3%. This discordance filter was applied to the remnant data so that spot analyses on intact transparent cores with \leq 3% discordance were retained and then processed to obtain the igneous age. The final retained isotope ratios with uncertainties for all spots within each sample as well as a composite for pooled spots of all 4 samples within the pluton (i.e., accepted repeat analyses within each sample or pooled repeats from all 4 samples from the single pluton) or the second pluton added are then readied for final age calculations and plotting by input into Isoplot (version 4.15) (Ludwig, 2008).

Therefore, with the discordance filter and the characteristics mentioned above for data rejection, we determined an age from a final 21, 27, 25, 23 and 31 data points for each of the 5 samples analyzed including BMD-03-17Y, BMD-04-17Y, BMD-07-17Y, BMD-08-17Y and BMD-01-17Y, respectively, followed by a composite of the 4 sample data points (N = 96) for a single pluton age. Because the second pluton age is identical in age to the 4-sample composite, we then also computed a composite with all the 5 samples analyzed (N = 127). This 5-sample composite age result, we suggest, is the best-constrained age for formation for the Blow Me Down Mountain portion of the Bay of Islands Ophiolite Complex. It is important to recognize that the tight discordance filter is not an assurance of robustly coincident igneous dates if Pb loss occurred soon after crystallization as measurements may yield a range of analytically concordant dates (e.g., Mattinson, 1976). However, all dates are concordant within uncertainties, dominantly clustered overlapping within 2 sigma errors and are similar for all 5 samples. No filtering of highest and lowest concordant dates or outliers that cause dispersion relative to the weighted mean age or concordia age was involved in selecting remnant analyses for age determinations. All output

resultant age calculations and their graphical error ellipses/bars are presented with 2 sigma (2s) or 95% confidence level of uncertainty (e.g., Schoene et al., 2013; Horstwood et al., 2016).

The Wetherill concordia diagram (Wetherill, 1956; Ludwig, 1998), as well as the weighted means of ²⁰⁶Pb/²³⁸U dates, which are derived from the most precise ratios and ages calculated, were used to visualize internal consistency for each of the samples used to develop the final composite age of the pluton or massif intrusions. Although the calculated concordia and weighted mean ages for each sample are overall identical within one pluton and between plutons analyzed, the Wetherill concordia age from individual samples or the 4-sample pooled dates for the single pluton composite and the 5-sample composite for the massif was chosen for reporting age results. The concordia age weighs both ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U ratio and thus, provides a more precise and more objective result (e.g., Spencer et al., 2016). As noted, all uncertainties of individual analyses are reported at the 2s level and the age results calculated by Isoplot are presented at the 2s level for the concordia age (Horstwood et al., 2016). Likewise, all weighted mean ages extracted from pooled ²⁰⁶Pb/²³⁸U dates are reported at the 95% confidence interval (i.e., near 2s).

Sample points that plot further away the concordia line can be due to 1) the existence of inherited non-radiogenic components, 2) the partial loss of radiogenic Pb during alteration, 3) initial daughter disequilibrium, and/or 4) a mixture of different growth zones or domains of different ages during isotopic analysis. Based on petrographic examination, we regard partial loss of radiogenic Pb due to alteration as the dominant process because we observed simple igneous zoning of euhedral zircon grains without evidence of inherited cores. Primary igneous zoning variations are likely unresolvable in these older zircon grains, within the uncertainty, given the short cooling times likely at about 2 km depths in the oceanic crust relative to ages determined.

The likely cooling times do not exceed the temporal precision of individual dates. The resultant 4sample composite age for a single pluton or 5-sample composite age for the massif reported here include dates that are clustered and concordant within uncertainties of the analyses, for which there is a high level of confidence.

2.5.4 Secondary standard FC5z age results

FC5z served as secondary standard to access the quality of every analytical session as well as the integration of all the five sessions. The results are summarized in Table 2.1 and also plotted in Appendix Fig. A2.1. FC5z associated with BMD-03-17Y, BMD-04-17Y and BMD-07-17Y yielded similar and precise concordia age results of 1103.0 ± 8.3 Ma (N = 14), 1106.5 ± 7.8 Ma (N = 14) and 1107.5 \pm 8.4 Ma (N = 11), respectively, all of which are within 1% of the accepted value of 1099.0 ± 0.6 Ma (Paces and Miller, 1993). The MSWD (of concordance) of these three sessions are comparable and range between 7.8 and 8.4 (Table 2.1). The analytical session of BMD-08-17Y produces somewhat older standard result of 1112.0 ± 11 Ma (N = 13) within 1.2% of the accepted age but has the lowest MSWD (of concordance) of 0.79 and the highest uncertainty of 11 Ma. The last analytical session of sample BMD-01-17Y yielded the most accurate result of 1098.4 ± 6.4 Ma (N = 15) within 0.3% of the accepted age and low MSWD (of concordance) of 3.9. We also obtained an integration standard result of the five analytical sessions that yielded an extremely accurate concordia age of 1104.3 ± 3.7 Ma and a slightly older, but still accurate, weighted mean age of 1109.5 ± 4.4 Ma (N = 67) with a somewhat higher MSWD (of concordance) of 16. In general, ²⁰⁶Pb/²³⁸U weighted mean ages are less scattered, slightly older, and have slightly higher errors when compared with their corresponding concordia age results.

In summary, each analytical session as well as the integration of the five analytical sessions yielded reliable check standard results with the accuracy within 1-2% and uncertainty of

both concordia and weighted mean age within 1% (Table 2.1). It should be pointed out that scatter of the individual data points (e.g., error ellipses in concordia plots and error bars in weighted mean plots) and slightly older age results of FC5z can also partially be attributed to its internal heterogeneity (of a natural zircon), matrix effects and ablation related processes (Black, 2005; Chang et al., 2006; Klötzli et al., 2009), rather than solely instrumental problem or data reduction methods.

Table 2.1 Summarized U-Pb age results of secondary standard FC5z measured together with five samples for each analytical session and integration of all five analytical sessions. Uncertainties for concordia age and weighted mean age are quoted at 2s level and 95% confidence interval, respectively. Note N points analyzed are typical lower than sample N (see standard-sample bracketing technique in Section 2.5.2). The accepted age for secondary standard FC5z is 1099.0 \pm 0.6 Ma (Paces and Miller, 1993)Accuracy (%) = |Measured age/Accepted age -1|*100

Analytical session	N	Concordia age					Weighted mean age of ²⁰⁶ Pb/ ²³⁸ U				
		Age (Ma)	Error (Ma)	MSWD (of con.)	Probability	Accuracy (%)	Age (Ma)	Error (Ma)	MSWD	Probability	Accuracy (%)
BMD-01-	15	1098.4	6.4	3.9	0.049	0.26	1103.5	9.8	1.33	0.22	0.41
17Y											
BMD-03-	14	1103.0	8.3	3.3	0.070	0.36	1108.0	10.0	0.97	0.49	0.82
17Y											
BMD-04-	14	1106.5	7.8	4.0	0.046	0.68	1112.4	9.5	0.40	0.97	1.22
17Y											
BMD-07-	11	1107.5	8.4	4.8	0.029	0.77	1114.0	10.0	0.97	0.47	1.36
17Y											
BMD-08-	13	1112.0	11.0	0.79	0.38	1.18	1115.0	12.0	0.32	0.99	1.46
17Y											
Integration	67	1104.3	3.7	16	0.00	0.48	1109.5	4.4	0.80	0.88	0.96

2.6 Zircon LA-ICP-MS U-Pb age results of BMD trondhjemite

To obtain a precise crystallization age of the host trondhjemitic rocks, crystal domains devoid of microfracture (alteration- and metamict-related), visible zonation, inclusion and metamict region were primarily targeted. Dates that were in excess of 3% discordance were eliminated from the datasets for the purpose of final age calculations. Analyses for the four samples from the single plagiogranite intrusion yielded nearly identical and comparable concordia and weighted mean age results (Table 2.2), respectively, of 487.2 ± 4.0 Ma and 487.8 ± 4.2 Ma (N = 21) for BMD-03-17Y (Fig. 2.4a), 488.3 ± 3.2 Ma and 488.5 ± 3.4 Ma (N = 27) for BMD-04-17Y (Fig. 2.4b), 488.4 ± 2.9 Ma and 488.3 ± 4.4 Ma (N = 25) for BMD-07-17Y (Fig. 2.4c), and 488.9 \pm 4.8 Ma and 488.4 \pm 5.1 Ma (N = 23) for BMD-08-17Y (Fig. 2.4d). As these four samples are from the same pluton, we combined all 96 dates to produce a 4-sample composite concordia age of 488.2 ± 1.8 Ma and also weighted mean age of 488.3 ± 1.9 Ma (Fig. 2.4e). It is noteworthy that there are outliers that are apparently much older or younger than the weighted mean or concordia ages (e.g., Fig. 2.4c) that we have not rejected, but because there is a large number of concordant data points (N = 96), statistically, these outliers have negligible effects on final concordia age and weighted mean age reported. The additional single sample BMD-01-17Y from a nearby but separate plagiogranite pluton yielded almost identical results of a concordia age of 488.6 ± 2.6 Ma and a weighted mean age of 489.1 ± 3.6 Ma (N = 31) (Fig. 2.4f). Because all these five samples were collected from closely spaced plagiogranite intrusions within the same ophiolite massif and yielded very comparable age results of ca. 488 Ma, we combined them together producing a 5sample composite concordia age of 488.3 ± 1.5 Ma (N = 127) (Fig. 2.4g), which we propose as the most reliable determination of the crystallization age of the BOIC on the Blow Me Down Mountain massif.

The ²⁰⁶Pb/²³⁸U date histograms of zircon grains separated from the five trondhjemites including four within the same pluton (BMD-03-17Y, BMD-04-17Y, BMD-07-17Y and BMD-08-17Y) and one from a nearby pluton (BMD-01-17Y) have similar and relatively narrow ²⁰⁶Pb/²³⁸U date spectra with the majority of points ranging within 480 to 500 Ma, and the highest number of peaks at ca. 490 Ma (Fig. 2.5a-e). Their relative probability is generally symmetrical and normally distributed, especially displayed in the date histogram of the 5-sample composite (Fig. 2.5f).
Table 2.2 Summarized U-Pb sample age results of each of the five trondhjemite samples, composite age of four trondhjemites from the single pluton, and composite age of all the five trondhjemites including an additional trondhjemite from a nearby pluton. Uncertainties for concordia age and weighted mean age are quoted at 2s level and 95% confidence, respectively. Note N only includes results with discordance less than 3% and spots devoid of fractures, inclusions and rim and internal metamict regions. The 5-sample composite concordia age (black box) is the proposed age for the BOIC

		Concordia age				Weighted mean age of ²⁰⁶ Pb/ ²³⁸ U			
Sample Label	Ν	Age	Error	MSWD	Drobability	Age	Error	MSWD	Drobability
		(Ma)	(Ma)	(of con.)	Flobability	(Ma)	(Ma)		Flobability
BMD-03-17Y	21	487.2	4.0	0.46	0.50	487.8	4.2	0.43	0.99
BMD-04-17Y	27	488.3	3.2	0.039	0.84	488.5	3.4	0.63	0.92
BMD-07-17Y	25	488.4	2.9	0.018	0.89	488.3	4.4	1.7	0.015
BMD-08-17Y	23	488.9	4.8	0.21	0.64	488.4	5.1	0.22	1.00
4-sample	06	188 2	1.9	0.037	0.85	188.3	1.0	0.75	0.07
Composite	90	400.2	1.0	0.037	0.85	400.5	1.9	0.75	0.97
BMD-01-17Y	31	488.6	2.6	0.48	0.49	489.1	3.6	1.6	0.026
5-sample	127	188 3	15	0.31	0.58	188 5	16	0.04	0.67
Composite	127	400.3	1.J	0.31	0.38	400.3	1.0	0.94	0.07

Fig. 2.4 Concordia and ranked ²⁰⁶Pb/²³⁸U weighted mean age plots for samples (a) BMD-03-17Y, (b) BMD-04-17Y, (c) BMD-07-17Y and (d) BMD-08-17Y from the single plagiogranite pluton shown in Fig. 2.1 and 2.2, (e) composite of the four samples from the single pluton, (f) sample BMD-01-17Y from a nearby trondhjemite intrusion (Fig. 2.1), and (g) composite of all the five samples from the Blow Me Down Mountain massif interpreted as the age of crystallization of the plutons. Note the extremely comparable and similar concordia age results between the 4-sample composite of 488.2 \pm 1.8 Ma and the 5-sample composite of 488.3 \pm 1.5 Ma, which we propose as the BOIC crystallization age. Note black error ellipses for individual data points are given at 1s level, whereas concordia age (red ellipses) and weighted mean age (red dashed line with shaded area) of pooled dates are calculated by Isoplot shown with 2s uncertainty. See data tables in Appendix for individual isotopic ratios and individual dates for all 5 samples.







Fig. 2.5 206 Pb/ 238 U date histogram showing 206 Pb/ 238 U date distribution pattern of (a) single sample from a nearby trondhjemite intrusion, (b-e) four samples from the same plagiogranite pluton, and (f) 5-sample composite of (a-e) for all the BMD samples.

2.7 Discussion

The new age reported here warrants a re-examination of the previously published ID-TIMS-derived legacy dates and uncertainties for direct comparisons. We have recalculated (see Fig. 2.6 and 2.7 and Table 2.3) the ages previously reported for the Bay of Islands Ophiolite Complex in light of our newly obtained ca. 488.3 Ma age. Our reexamination of published legacy dates from the original U-Pb and Pb-Pb datasets highlights the difficulties in evaluating and comparing these ages due to 1) the extent of data reporting, 2) the lack of specific uncertainty reporting for some reported dates, 3) unknown extent of Pb loss, 4) three different minerals dated, 5) variation in preparation techniques, 6) different interpretative assumptions in fixing lower intercepts for discordant lines, 7) the potential of mixed dates from homogenized mineral

multigrain fractions and resultant error reporting, 8) emphasis on less precise ²⁰⁷Pb/²⁰⁶Pb vs. more precise ²⁰⁶Pb/²³⁸U dates/ages in some studies, and 9) some issues and contrasts with modern procedures, error propagation and data reporting. In particular, as discussed, modern and more precise single zircon CA-ID-TIMS techniques (e.g., Mattinson et al., 2005) that remove all parts of zircon grains affected by Pb mobility were not used in these prior analyses and likely resulted in some of the heterogeneity in single sample dates. ID-TIMS ²⁰⁷Pb/²⁰⁶Pb ages were widely adopted in early U-Pb studies because, although less precise, the ²⁰⁷Pb/²⁰⁶Pb age will not be as significantly affected by Pb loss effects as the more precise ²⁰⁶Pb/²³⁸U age (e.g., Hansen and Friderichsen, 1989; Gehrels, 2011). We show a comparison between the recalculated ID-TIMS ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁶Pb/²³⁸U dates and uncertainties for all previously published data in Fig. 2.7b. The ²⁰⁷Pb/²⁰⁶Pb individual dates are typically emphasized in the BOIC age studies of Mattinson (1976), Dunning and Krogh (1985) and Jenner et al. (1991) with or without Wetherill concordia ages. They are generally less precise dates and some of these dates were reported without date uncertainties (see Table 2.3). For the single apatite date of Kurth et al. (1998), the more precise 206 Pb/ 238 U date was adopted rather than the 207 Pb/ 206 Pb date.

In general, for weighted averaging of LA-ICP-MS dates, it is more common and practical to use the more precise ²⁰⁶Pb/²³⁸U age for zircon younger than ~1 Ga whereas the ²⁰⁷Pb/²⁰⁶Pb age is normally used for those older than ~1 Ga because the uncertainties vary typically as a function of age. For younger samples, the ²⁰⁶Pb/²³⁸U age is more precise than the ²⁰⁷Pb/²⁰⁶Pb age, whereas for older samples the uncertainties are reversed (Black et al., 2003; Gehrels, 2011, 2014). For the age range documented for the BOIC, the greater error is because of the larger imprecision introduced by measuring ²⁰⁷Pb/²⁰⁶Pb isotopic ratios, in which the ²⁰⁷Pb/²⁰⁶Pb is also

difficult to assess because even very small errors in decay constant propagate into highly magnified errors in calculated ²⁰⁷Pb/²⁰⁶Pb ages (e.g., Mattinson, 1987; Ludwig, 2000). Spencer et al. (2016) summarized ~38000 LA-ICP-MS zircon analyses from Voice et al. (2011) and ~5000 SIMS data from Wingate et al. (2015) and demonstrated that if dated material has an age of ca. 500 Ma, the 207 Pb/ 206 Pb age uncertainty is respectively ~7 and ~5 times higher than 206 Pb/ 238 U age. Although more imprecise, it is observed that upon our recalculation of the ²⁰⁷Pb/²⁰⁶Pb dates from all prior BOIC ID-TIMS studies, they are less heterogeneous and plot closer to our proposed age of ca. 488.3 Ma than many of the ²⁰⁶Pb/²³⁸U dates (see Fig. 2.7b). The more precise ²⁰⁶Pb/²³⁸U ID-TIMS dates collectively are more heterogeneous ranging from the most concordant 493 Ma date of Mattinson (1976) to the youngest 467.6 Ma date from Jenner et al. (1991), again suggesting a Pb loss effect. This result is consistent with samples being affected by Pb loss, as evidenced by TIMS data discordance on the Wetherill concordia plot (up to 5 % in prior TIMS studies), in which the calculated dates increase from ²⁰⁶Pb/²³⁸U to ²⁰⁷Pb/²⁰⁶Pb dates (Gehrels, 2011). Discordance analysis on the Wetherill plot shows that the BOIC ID-TIMS data lie along and slightly below the concordia (Fig. 2.6) suggesting Pb loss during younger thermal/hydrothermal disturbance activity.

Mattinson (1987) drew attention to the "unacceptable" practice of early ID-TIMS U-Pb zircon studies that lacked adequate error analysis and reported ages without full indications of the date or age uncertainty. Understandably, recent community-based recommendations for more complete error analysis and error propagation procedures (Horstwood et al., 2016) indicate uncertainties should include propagation of uranium decay constant errors for all U-Pb age data reported (see also Ludwig, 2000). Therefore, in order to re-evaluate prior ID-TIMS ages and uncertainties, we report recalculated intercept ages with uncertainties reported both without brackets for direct comparison to ages reported by Mattinson (1976), Dunning and Krogh (1985),

and Jenner et al. (1991) that appear not to have included decay constant errors (method of Davis, 1982) and within brackets where uranium decay constant errors are included, which allow direct comparison with our new LA-ICP-MS concordia ages and uncertainties. If only one age error is shown (e.g., Fig. 2.6d), this indicates that the intercept age errors with and without uranium decay constant errors included are almost equivalent (Ludwig, 2008), which only occurs when the uncertainty is exceptionally large (e.g., Fig. 2.6d, data from Jenner et al., 1991). Furthermore, recalculations in Isoplot show that the probability of discordia line fits for some prior datasets are very low (e.g., Fig. 2.6b, c and e), so Model-2 of Ludwig (2008) has been applied to construct more reliable discordant lines (see Ludwig, 2008 for more details). Below we review each prior ID-TIMS study, results of recalculating upper intercept ages and uncertainties without assumptions and fixing lower intercepts, and the recalculated age uncertainties with and without uranium decay constant errors included.

Fig. 2.6 Wetherill concordia diagrams with 2 sigma uncertainties using Isoplot showing the best-fit discordant lines recalculated without fixing the lower intercepts for analyses from the BOIC of (a) three zircon fractions from trondhjemite of Mattinson (1976) yielding an upper intercept age of 492 ± 11 [± 17] Ma, (b) five zircon fractions from trondhjemite (excluding gabbro) of Dunning and Krogh (1985) vielding an upper intercept age of $484.5 \pm 6.5 \pm 7.6$ Ma, (c) five zircon fractions from trondhjemite (red) and one from gabbro (green) of Dunning and Krogh (1985) yielding an upper intercept age of 487 ± 16 [± 18] Ma, (d) subset of three zircon fractions from trondhjemite of Jenner et al. (1991) yielding an upper intercept age of 502 ± 110 Ma and (e) summary plot of all prior ID-TIMS zircon data from the three studies pooled yielding an upper intercept age of $492.3 \pm 9.0 \pm 14$ Ma, and (f) analyses from the Betts Cove Ophiolite of four zircon fractions from gabbro of Dunning and Krogh (1985) yielding an upper intercept age of $488.5 \pm 3.2 \pm 8.0$ Ma. Note that age errors are shown both within brackets where uranium decay constant errors are included for direct comparison with our LA-ICP-MS zircon age calculations and without brackets where decay constant errors are not incorporated for direct comparison with the original ages reported by Mattinson (1976), Dunning and Krogh (1985) and Jenner et al. (1991). If shown as one single error, it indicates the intercept age errors with and without uranium decay constant errors are almost equivalent (Ludwig, 2008). For (a), the three individual ellipses are concordant within error (discordance < 0.2%) but spread along the concordia curve or essentially form a sub-parallel discordant line that is hardly distinguishable. Note that the U-Pb isotopic ratios and uncertainties were not provided for (a), so they are recalculated based on U-Pb dates and errors reported. The errors on the U-Pb dates are assumed to be $\pm 0.5\%$ (2s) (see notes included below Table 1 of Mattinson, 1976). In (b), (c) and (f), uncertainties of the U-Pb isotopic ratios are given as $\pm 0.5\%$ (2s) (see "Sample preparation and analytical techniques" section in Dunning and Krogh, 1985). Note much larger age uncertainties are typical when the lower intercept is not fixed for the recalculated ages of Dunning and Krogh (1985). Because of the low probability of line fit for dataset in (b) (4.23%), (c) (0.04%) and (e) (0.23%), Model-2 fit has been applied to them (see Ludwig, 2008). Recalculated ages are sometimes different than those reported and appear to consistently demonstrate underestimation of the age uncertainties. The recalculated ID-TIMS ages are within error of the new LA-ICP-MS ca. 488.3 Ma age reported here.



2.7.1 Discussion of reported legacy ID-TIMS ages of the Bay of Islands Ophiolite Complex

Mattinson (1976) ID-TIMS U-Pb age of the Bay of Islands Ophiolite Complex was based on three zircon fractions from a single trondhjemite from the BMD massif. Notably, he reported three heterogeneous 207 Pb/ 206 Pb dates of 480 ± 7, 485 ± 7 and 494 ± 5 Ma, and similar 206 Pb/ 238 U dates of 477, 486 and 493 Ma. Mattinson (1976) did not report U-Pb and Pb-Pb isotope ratio errors nor the U-Pb age uncertainties, but only stated that errors on the U-Pb age are assumed to be 0.5% (see notes below Table 1 in his paper). The zircon crystals were physically abraded (Krogh, 1973) in order to minimize the effects of Pb loss. The physical abrasion technique is intended to preferentially remove the U-rich outer layers of the zircon crystals, because they are weaker due to the higher U contents, which results in accumulation of radiation damage and subsequent metamictization of the zircon crystals. As those regions are also more susceptible to cracking and thus, to ingress of 204 Pb carried by external fluids, the Krogh (1973, 1982) method was expected to have achieved a removal of as much as 80% of the 204 Pb present in the zircon crystals (see review of comparisons of chemical abrasion and physical abrasion methods by Schoene et al., 2013).

On the concordia plot presented by Mattinson (1976), each analysis was effectively concordant within error limits, but he interpreted the date range to suggest that Pb loss occurred a short time after ophiolite formation. So Mattinson (1976) chose to use an Ar-Ar age of 460 Ma from hornblende collected from amphibolite within the metamorphic sole reported by Dallmeyer and Williams (1975) as the age of Pb loss related to obduction. A best-fit chord through the data with the somewhat arbitrary age of 460 Ma as the lower intercept was utilized to derive an upper intercept age of 504 \pm 10 Ma. Mattinson (1976) also argued that although the lower intercepts could reasonably range between 410 and 470 Ma that led to upper intercept ages of 496 to 514 Ma,

these upper intercept ages still are covered within the error (\pm 10 Ma) stated before. Our recalculations and replotting in Isoplot for the isotope ratios and errors reported were accomplished without constraining the lower intercept. This yielded an upper intercept of 492 \pm 11 [\pm 17] Ma and lower intercept of 331 \pm 230 Ma (MSWD = 0.42) (Fig. 2.6a). The upper intercept age uncertainty without uranium decay constant errors included (\pm 11 Ma) is somewhat similar to the previously reported uncertainty (\pm 10 Ma) whereas the uncertainty with uranium decay constant errors included (\pm 17 Ma) is slightly larger. The previously reported higher age precision resulted from lack of the uranium decay constant errors typical of intercept age uncertainty reporting in the past (Mattinson, 1987). This recalculated ca. 492 Ma age without constraining the lower intercept is significantly younger but appears to be more geologically meaningful, likely indicating that this recalculated age is consistent within error with the more precise LA-ICP-MS age reported here of 488.3 \pm 1.5 Ma (Fig. 2.7a and c).

Dunning and Krogh (1985) analyzed six zircon fractions including five zircon fractions from a single trondhjemite sample was taken from a site less than 100 m of Mattinson's (1976) sample location on the BMD massif and one single zircon fraction from a hornblendebearing gabbro from the nearby Blow Me Down Brook. They presented more clustered ²⁰⁷Pb/²⁰⁶Pb dates with a 7 Ma spread including 484, 484, 487, 485 and 486 Ma for the five trondhjemitic fractions with moderate U content (~300 ppm), and ²⁰⁷Pb/²⁰⁶Pb date of 480 Ma from the gabbroic fraction with an extremely high U concentration (1058 ppm). The zircon fractions were described as yellow in color and contained unknown needle-like inclusions. All of their zircon grains were physically abraded to avoid Pb loss effects as well (Krogh, 1973, 1982). They presented a Wetherill concordia plot (see their Fig. 3) with the analyses closely clustered and nearly concordant within the uncertainty limits (discordance reported between 1.2 to 2.8%) for the 5 zircon fractions from the trondhjemite sample and did not include the gabbroic zircon fraction. They indicated that the limited data spread resulted from a small amount of Pb loss for the sample fractions and so the line fit method of Davis (1982) could not be directly used.

To reconcile this problem, an arbitrarily lower intercept was chosen so that the Davis (1982) method could then be applied (see Appendix in Dunning and Krogh, 1985) and a precise asymmetric age uncertainty was obtained. Their upper intercept age was reported as $485.7^{+1.9}_{-1.2}$ Ma, a high precision age that was somewhat enabled by choosing an arbitrarily constrained lower intercept in an unorthodox way to pass through 50 Ma \pm 90%. They lamented the fact that the lack of significantly discordant points inhibited a more accurate upper intercept age (see Krogh and Turek, 1982, Appendix 1; Dunning and Krogh, 1985). The Davis (1982) method does not include the uranium decay constant errors propagation. The asymmetric error is more widely reported for imprecise concordia intercept ages (Ludwig, 2008); i.e., the regression line is either imprecise or intersects the concordia curve at a shallow angle. When we replotted the data after entering them into Isoplot with the exact same assumption of the 50 Ma \pm 90% lower intercept (2s error assumed), we calculated an age of $486.2 \pm 2.4 [\pm 5.5]$ Ma. The uncertainty without uranium decay constant errors included (\pm 2.4 Ma) is comparable with their original reported uncertainty (+1.9/-1.2 Ma) whereas the uncertainty with uranium decay constant errors included (\pm 5.5 Ma) is apparently larger for the 5 trondhjemitic zircon fractions. Thus, using the Davis (1982) approach, it appears that asymmetrical age uncertainties previously reported could be somewhat underestimated, although the recalculated ca. 486.2 Ma age is within the uncertainty of our new LA-ICP-MS ca. 488 Ma age reported here. Our recalculation when using the same 5 zircon fractions but with a more orthodox approach without a constrained lower intercept age yields a best-fit discordant line with an upper intercept age of $484.5 \pm 6.5 \pm 7.6$ Ma and a lower

intercept of -70 ± 540 Ma (MSWD = 2.7) with larger dispersion in the uncertainty (Fig. 2.6b). This upper intercept age also has somewhat more significant uncertainty compared with the original age reported. All these recalculations together suggest that the uncertainties may have been generally underestimated with the lower intercept assumption being fixed at 50 Ma \pm 90% and without uranium decay constant errors included. Based on these recalculated ages and uncertainties, we view the less precise recalculated upper intercept ages both with uranium decay constant errors included. Based on these recalculated ages and uncertainties, we view the less precise recalculated upper intercept ages both with uranium decay constant errors included and without a constraining lower intercept are more rational and are consistent within uncertainty with the new precise LA-ICP-MS ca. 488 Ma age reported here. If the gabbroic zircon fraction from their study is added to the five trondhjemite zircon fractions, the best-fit discordia yields an even less precise upper intercept age of 487 \pm 16 [\pm 18] Ma (MSWD = 0.24) again with larger dispersion in the error for the lower intercept (143 \pm 540 Ma) (Fig. 2.6c). In summary, the various recalculated upper intercept ages of Dunning and Krogh (1985) presented here with uranium decay constant errors included are all consistent with the more precise new LA-ICP-MS ca. 488.3 Ma age we report here (Fig. 2.7 and c).

Jenner et al. (1991) similarly reported a single gabbro age of 484 ± 5 Ma based on a range of 6 slightly discordant (< 3%) and heterogeneous ²⁰⁷Pb/²⁰⁶Pb dates of 479, 479 and 476 Ma for three zircon fractions and older ²⁰⁷Pb/²⁰⁶Pb dates of 489, 489 and 484 Ma for three baddeleyite fractions. None of these dates were reported with uncertainties, although the uncertainties of ²⁰⁷Pb/²⁰⁶Pb and other isotopic ratios were provided. Based on this, ²⁰⁷Pb/²⁰⁶Pb date uncertainties were calculated here for zircon fractions as ± 4 , ± 2 and ± 3 Ma, respectively, and for baddeleyite fractions the uncertainties are all ± 3 Ma (Table 2.3). In Fig. 2.7b, we show our recalculated date uncertainties for both the ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁶Pb/²³⁸U dates. The ²⁰⁶Pb/²³⁸U dates display higher precisions compared to the ²⁰⁷Pb/²⁰⁶Pb dates, but notably the ²⁰⁶Pb/²³⁸U dates are considerably more heterogeneous and overall younger than the ²⁰⁷Pb/²⁰⁶Pb dates actually proposed for the sample by Jenner et al (1991). Based on our calculation of ²⁰⁷Pb/²³⁵U and ²⁰⁶Pb/²³⁸U dates for the six fractions reported by Jenner et al. (1991), the more precise ²⁰⁶Pb/²³⁸U dates cover a significantly younger range between 467 and 475 Ma (Fig. 2.7b and Table 2.3). The calculated ²⁰⁶Pb/²³⁸U dates with 2s error include 473.8 \pm 2.1 Ma for No.1 baddeleyite fraction, 473.0 \pm 1.4 Ma for No.2 baddeleyite fraction, 475.1 \pm 2.1 Ma for No.3 baddeleyite fraction, 472.9 \pm 1.6 Ma for No.4 zircon fraction, 470.6 \pm 1.6 Ma for No.5 zircon fraction, and 467.6 \pm 1.6 Ma for No.6 zircon fraction (Table 2.3). The younger dates are consistent with a range of Pb loss of different extents for these fractions yielding mixed ages in a single sample collected from the BMD massif. Of the six fractions, only the three zircon fractions were physically abraded.

Jenner et al. (1991) offered the interpretation that because of 207 Pb/²⁰⁶Pb dates recorded by the three baddeleyite fractions were older in comparison with the zircon dates, the baddeleyite dates could be indicative of radon gas loss and depletion of 206 Pb. These dates were, therefore, interpreted as too old when explaining their choice of a younger 207 Pb/²⁰⁶Pb ca. 484 Ma age for the formation age of the BOIC. While acknowledging the crystallization age of the gabbro could fall anywhere between the 476 and 489 Ma 207 Pb/²⁰⁶Pb dates, they chose a final age of 484 \pm 5 Ma with the uncertainty uncomputed and to encompass most of the range of all reported 207 Pb/²⁰⁶Pb dates. The exact method of choosing this age and arriving at uncertainty, however, was not fully presented. When we entered these pooled 207 Pb/²⁰⁶Pb dates into Isoplot, a calculated weighted mean age of 482.2 \pm 5.6 Ma (MSWD = 14) was obtained for the total of six mineral fractions including three zircon and three baddeleyite fractions, whereas a weighted mean age of 478.2 \pm 4.0 Ma (MSWD = 1.5) for three zircon fractions only, and age of 487.3 \pm 7.2 Ma (MSWD = 3.7) for three baddeleyite fractions only. Jenner et al. (1991) did present a Wetherill concordia diagram of the data (see Fig. 2 in their paper) in which an upper intercept of ca. 490 Ma can be approximately visualized, but the discordant chord seemingly passes through only two of the six data ellipses (No. 1 and No. 2 baddeleyite fraction). They did not provide any discussion of this discordant line. We plotted the two tightly clustered baddeleyite fractions and could compute a poorly constrained upper intercept of 487 \pm 60 Ma and a lower intercept of -52 \pm 2700 Ma of limited reliability (MSWD = 0). Recent studies of baddeleyite U-Pb dating have shown along with high U that baddeleyite has minor or no common Pb, is resistant to secondary Pb loss (metamorphism), has good reproducibility, shows consistency with the U-Pb zircon age, and is highly suitable as a U-Pb chronometer for magmatic events (e.g., Heaman and LeCheminant, 1993; Rubatto and Scambelluri, 2003; Heaman, 2009; Rodionov et al., 2012). If so, the calculated baddeleyite ²⁰⁷Pb/²⁰⁶Pb weighted mean age of 487.3 \pm 7.2 Ma may be the better constraint on the magmatic crystallization age of the sample and the zircon dates would appear too young, rather than the opposite as argued by Jenner et al. (1991).

Using the U-Pb isotopic ratios of six fractions reported by Jenner et al. (1991), a poorly constrained discordant line on the Wetherill concordia plot can be obtained with a lower intercept of 458 ± 38 Ma but with an unrealistic upper poorly constrained intercept age of 747 ± 670 Ma (MSWD = 3.1, Model-2 fit), which is geologically meaningless. We also recalculated the upper intercept age only for the three zircon separates and obtained a poorly constrained and unreliable upper intercept age of 502 ± 110 Ma and a lower intercept age of 368 ± 370 Ma (MSWD = 0.52) (Fig. 2.6d); again, it appears geologically meaningless, with much larger uncertainties. Thus, we suggest the heterogeneous dataset and age most commonly referenced for the formation of the BOIC does not lend itself to a precise concordia age calculation and that the Pb loss effects or inclusion effects of the sample appear unresolvable.

Kurth et al. (1998) reported one apatite date from an evolved gabbroic sample in the eastern part of the Lewis Hills massif, which is considered part of the Bay of Islands Ophiolite Complex sub-adjacent to the Coastal Complex (Karson and Dewey, 1978). They did not publish U-Pb and Pb-Pb isotopic ratios but reported a 207 Pb/ 206 Pb date (475 ± 12 Ma), 206 Pb/ 238 U date (485.0 ± 1.0 Ma) and 207 Pb/ 235 U date (483.3 ± 2.9 Ma). Because the smallest error among these was recorded by the 206 Pb/ 238 U date, they chose that date as the best age estimate for this single sample. Due to the lack of reported U-Pb and Pb-Pb isotopic ratios, we are unable to evaluate these results. There is also some question whether plutonic apatite may tend to record a younger age than the magmatic crystallization (e.g., Chamberlain and Bowring, 2001; Chew et al., 2011; Kirkland et al., 2018), whereas zircon or baddeleyite may be the more appropriate geochronometers if a closed system can be assumed.

Two of the datasets above were capable of producing single sample internal isochrons. It has been realized that there is a high possibility of inaccuracy when comparing interlaboratory analyses (Košler et al., 2013) and that there is a problem of data equivalence if using different calibration standards for data reduction (Klötzli et al., 2009). However, given that all previous zircon fractions were prepared with similar procedures (physical abrasion after Krogh, 1973, 1982) and all measured by ID-TIMS, we chose to plot all of the zircon data from the three prior ID-TIMS studies to produce a synthetic Wetherill concordia plot, which yields an upper intercept age of $492.3 \pm 9 [\pm 14]$ Ma and lower intercept of 293 ± 110 Ma (MSWD = 2.7) (Fig. 2.6e). This composite age of ID-TIMS zircon dates (492.3 ± 14 Ma) and our recalculated concordia ages for the data of Mattinson (1976) (492 ± 17 Ma) and for Dunning and Krogh (1985) (484.5 ± 7.6 and 487 ± 18 Ma) are now all within the larger computed uncertainties of each other. Furthermore, these less precise ID-TIMS ages recalculated with uranium decay constant errors propagated are now directly comparable within uncertainties to our proposed more precise composite LA-ICP-MS concordant age of 488.3 ± 1.5 Ma for the BOIC (Fig. 2.7).

It is important to note that to the extent possible all the ID-TIMS mineral age datasets reviewed or discussed in this paper are recalculated with dates, ages and uncertainties evaluated based on community-recommended U-Pb data treatment techniques. We included all legacy BOIC ages with presented details above, but also reviewed other Newfoundland and Quebec ophiolite ages for direct age comparisons mentioned in the discussion section. The latter are not comprehensively demonstrated here but will be considered in a regional study to follow. We do present a re-evaluation of the Betts Cove Ophiolite as an example of a directly correlated ophiolite (see Fig. 2.6f). In some cases, we found no significant difference between ages reported and those recalculated (e.g., Quebec and Betts Cove). Commonly, however, the age uncertainties did differ somewhat from those originally reported. We re-examined all ages, in part, because of age or date dispersions and poorly constrained (two-point isochron) ages that are in some cases outside the analytical uncertainty reported and because even small degrees of Pb loss may have biased the apparent individual ²⁰⁶Pb/²³⁸U dates to younger dates without necessarily resulting in recognizable or significant deviations from the concordia curve. We examine the effect of applying decay constant errors because when using two isotope ratios simultaneously for concordia age or ²⁰⁷Pb/²⁰⁶Pb dates, the errors can be magnified and can be the limiting factor on accuracy of the age (Ludwig, 2000).

Our goal was to understand the nature of the date or age heterogeneity observed and the way age uncertainties were calculated or reported in these earlier studies to allow more direct comparisons of dates, ages and associated uncertainties. This enabled us to critically evaluate and assess the new LA-ICP-MS ages and uncertainties reported directly with respect to legacy data. We also reviewed some of the early geologic and technical assumptions that influenced the computation of ages and uncertainties resulting from more limited understanding of the regional geology, decay constants, and certain limitations of the methods used. We certainly recognize, however, that the ID-TIMS U-Pb methods produced far superior individual date precisions when compared with our individual single-grain LA-ICP-MS dates (e.g., see review of Schoene and Baxter, 2017). Because of various differences between the ID-TIMS methods represented by these pioneering studies and modern sample preparation, data processing and statistical treatment techniques for calculating dates and ages, the heterogeneous legacy dates and ages and assumptions applied may not always have produced the most accurate "age" estimate for the BOIC.

We are confident in the age and uncertainty reported here because of standard monitoring, consistency of multiple samples from a single pluton and between two different plutons, and statistical robustness of 127 repeat analyses. We are also confident after reassessments of legacy datasets that many of the early datasets collected are of value in comparing our reported age and point to a somewhat older age than the previous consensus. We recognize that significant improvements in the current CA-ID-TIMS U-Pb single-zircon techniques have allowed precisions to increase even more from ~0.5% levels on large multigrain fractions to 0.02-0.05% for ²⁰⁶Pb/²³⁸U dates on single grains (Schoene, 2014; Schoene and Baxter, 2017). These improvements would undoubtedly improve on these earlier multigrain ID-TIMS studies and potentially improve on our reported age of the BOIC if conducted in the future. Even these improved techniques and exceptional precisions, however, have revealed in some cases complex date distributions within single samples that can make interpretation of age more complex (e.g., see Tichomirowa et al., 2019; Widmann et al., 2019). For this reason, less precise, but spatially resolved, statistically

robust, multi-sample in situ ICP-MS or SIMS U-Pb analyses may play a role in improving on some older multigrain results and even have a companion role to help to unravel certain complications in modern TIMS results. Table 2.3 Summarized and recalculated individual ²⁰⁷Pb/²³⁵U, ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb dates and uncertainties of the three prior ID-TIMS studies of Dunning and Krogh (1985), Jenner et al. (1991) and Mattinson (1976), together with reported ages and recalculated ages with and without uranium decay constant errors included for each study. Note that the italicized dates/ages and uncertainties indicate recalculated results in this study

 207 Pb/ 235 U 206 Ph/ 238 U 207 Pb/ 206 Pb Sample No. Mineral Discordance /Analysis Uncertainty Uncertainty Uncertainty Date Date Date Fractions/Rock (%) No. (Ma) (Ma) (Ma) (Ma) (Ma) (Ma) Mattinson, 1976 Reported age: 504 ± 10 Ma Recalculated upper intercept age: $492 \pm 11 [\pm 17 \text{ Ma}] (N = 3)$ **BMDnm** Zircon/Trondhjemite 486 486 2.4 485 0.00 2.4 7 **BMDmc** Zircon/Trondhjemite 478 2.4 477 480 0.21 2.4 7 **BMD**mf Zircon/Trondhjemite 493 2.5 493 2.5 494 5 0.00 **Dunning and Krogh, 1985** Reported age: $485.7^{+1.9}_{-1.2}$ Ma *Recalculated upper intercept age:* $487 \pm 16 \ \pm 18$ *Ma* (*N* = 6) Zircon/Trondhjemite 480.8 480.0 2.3 484 1 1.9 2 0.17 Zircon/Trondhjemite 480.7 2.3 2 1.9 480.0 3 0.15 484 Zircon/Trondhjemite 3 479.4 477.6 0.37 1.9 2.3 487 2 Zircon/Trondhjemite 4 477.2 1.9 475.8 2.3 3 0.30 485 5 Zircon/Trondhjemite 475.1 1.9 472.8 2.3 486 3 0.48 Zircon/Gabbro 474.6 1.9 473.4 2.3480 2 0.25 6 **Jenner et al., 1991** Reported age: 484 ± 5 Ma Recalculated ${}^{207}Pb/{}^{206}Pb$ weighted mean age: 482.2 ± 5.6 Ma (N = 6) Recalculated upper intercept age: $502 \pm 110 \text{ Ma}$ (N = 3) 1 Baddelevite/Gabbro 476.3 1.8 473.8 2.1 489 3 0.53 2 Baddeleyite/Gabbro 475.7 1.3 473.0 1.4 489 3 0.56 3 Baddeleyite/Gabbro 476.5 1.8 475.1 2.1 484 3 0.31 4 Zircon/Gabbro 473.9 1.3 472.9 1.6 479 4 0.21 5 Zircon/Gabbro 472.0 1.4 470.6 1.6 479 2 0.29 6 Zircon/Gabbro 469.0 1.4 467.6 1.6 476 3 0.28

Discordance (%) is recalculated by $|(^{206}Pb/^{238}U_{date})/(^{207}Pb/^{235}U_{date}) - 1| * 100$

Fig. 2.7 BOIC age results compilation of (a) Wetherill concordia ages at 2 sigma uncertainty for each of the five samples analyzed in this study and the derived 5-sample composite age (also represented by the dashed red line with 2 sigma shaded area) of 488.3 ± 1.5 Ma calculated from all the five sample dates pooled from the BMD massif plagiogranite intrusions, (b) all previously reported 207 Pb/ 206 Pb dates (dashed lines) from Dunning and Krogh (1985), Jenner et al. (1991), Kurth et al. (1998) and Mattinson (1976), and our recalculated individual ²⁰⁶Pb/²³⁸U dates (solid lines), showing heterogeneity and differences in precision between them, and (c) previously reported and suggested ID-TIMS ages for each of the three prior age studies (solid lines with dots) based on their stated assumption on lower intercepts compared to our recalculated upper intercept ages (dashed lines with dots) in which no lower intercept assumptions were made in plotting the discordant lines fitting the ID-TIMS data (see Fig. 2.6). The upper intercept age derived from pooling all prior BMD ID-TIMS zircon analyses is designated by the purple dashed line with dot (492.3 \pm 14 Ma). Without lower intercept assumptions, much larger age errors occur for each intercept ages as the consequence of the lack of highly discordant data points (e.g., Dunning and Krogh, 1985). Our composite age reported in this study has lower uncertainty and is essentially within error of ages from individual datasets or the pooled zircon ID-TIMS data. It is also within error of the oldest Mattinson's ²⁰⁷Pb/²⁰⁶Pb date or weighted mean of baddeleyite dates (487.3 ± 7.2 Ma) of Jenner et al. (1991). Physical air abrasion (Krogh 1973, 1982) was applied to all zircon fractions before dissolution in these prior studies, but the younging trends of individual ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb zircon dates are still evident even in fractions from the same samples. Note that error bars with dots in (c) indicate exclusively the upper intercept age results. The uncertainties presented with our recalculated upper intercept ages in (c) include the uranium decay constant errors (see Fig. 2.6). Uncertainty recalculated from Mattinson (1976) is 17 Ma, from Dunning and Krogh (1985) is slightly larger (18 Ma), and from Jenner et al. (1991) is exceedingly large (110 Ma). The latter is not geologically meaningful so that the age uncertainty could not be fully shown graphically.

¹ U-Pb date uncertainties are assumed to be 0.5% at 2s level (see notes below Table 1 in Mattinson, 1976).

² Uncertainties of ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb dates are not provided by the study, so we recalculated their uncertainties based on the assumption that the U-Pb and Pb-Pb isotopic ratio uncertainties are assigned to be 0.5% and 0.1% at 2s level, respectively (see "Sample preparation and analytical techniques" section in Dunning and Krogh, 1985).

³ Uncertainties of ²⁰⁷Pb/²⁰⁶Pb dates are not provided by the study, so we recalculated the errors based on ²⁰⁷Pb/²⁰⁶Pb isotopic ratio uncertainties reported.

⁴ Uncertainty level (i.e., 1s or 2s) of 206 Pb/ 238 U and 207 Pb/ 206 Pb date is not mentioned in the single apatite date study of Kurth et al. (1998), so here we have assumed they were reported at 2s level.



2.7.2 Tectonic implications of the new LA-ICP-MS age

The ca. 488.3 Ma crystallization age of BOIC is similar to the previously reported ID-TIMS ages of the nearby Notre Dame arc-proximal Betts Cove Ophiolite (488.6^{+3.1}_{-1.8} Ma) of Newfoundland determined by Dunning and Krogh (1985). Although the discordia for this age was somewhat arbitrarily constrained as well to pass through a lower intercept of 50 Ma \pm 90% similar to their BOIC age determination, a recalculated age without choosing a lower intercept is identical and appears well constrained, but with a notably greater uncertainty (488.5 ± 8.0 Ma with uranium decay constant errors included, Fig. 2.6f). Skulski et al. (2010) also reported an often-quoted preliminary U-Pb age of ca. 489 Ma for the nearby Point Rousse Ophiolite (see unpublished data from V. McNicoll, 2009 referenced within their study) likely using the same analytical techniques. We are unable to evaluate this age as there is no data as yet published. Nonetheless, both ages reported are comparable to the ca. 488.3 Ma age of the BOIC and may indicate that the three ophiolites have likely formed along a contiguous set of supra-subduction zone spreading centers at high angles to a westward-facing (present-day coordinates) trench and that they were offset by large and small left-lateral offset transform faults within the forearc of the Cambro-Ordovician Notre Dame Arc of Central Newfoundland (Fig. 2.8) (Dewey and Casey, 2013, 2015). The reconstructed attitudes of the sheeted dikes of the BOIC and the Betts Cove Ophiolite are nearly orthogonal to allochthon structural front assumed to mark the overall trend of the former westerly facing trench (e.g., Williams and Malpas, 1972; Karson and Dewey, 1978; Casey and Kidd, 1979; Upadhyay and Neale, 1979; Casey, 1980; Rosencrantz, 1980, 1983; Idleman, 1981; Casey et al., 1983; Casey and Dewey, 1984; Dewey and Casey, 2013, 2015). The spreading centers (Fig. 2.8b) within the forearc would be at high angles to the Notre Dame Arc west-facing frontal trench intersecting it at a trench-trench-ridge triple junction (Casey and Dewey, 1984; Dewey and Casey,

2013, 2015). The spreading centers are also likely to extend to the rear of the forearc, into the

Notre Dame arc and possibly to the back arc (e.g., Annieopsquatch ophiolite, ca. 478-481 Ma)

(Fig. 2.8).

Fig. 2.8 Generalized BOIC geologic map and tectonic model for its formation. (a) Generalized geologic and tectonic map modified after Dewey and Casey (2013) that includes the Humber Zone (former Laurentian stable margin and Taconic allochthons) and the Notre Dame Arc Subzone of the Dunnage Zone of the Western Newfoundland Appalachians (Williams, 1995). The Notre Dame Subzone is bounded by the Baie Verte Lineament to the west and the Red Indian Line Fault zone to the east. The map shows elements involved in the collision between the Laurentian stable margin and the Notre Dame forearc-arc-backarc with ages of ophiolites representing the forearc basement consisting of composite ophiolitic CC-Lushs Bight older terrane and the younger ophiolitic Baie Verte oceanic tract (e.g., BOIC-Betts Cove- Point Rouse-St. Anthony ophiolites) with similar ages shown, and a back arc ophiolite (Annieopsquatch ophiolite - potentially a younger part of the Baie Verte Oceanic Tract). (b) Schematic 3D cross-section of the trench-forearc-arc-backarc system with subduction of the oceanic lithosphere adjacent to the Laurentian margin with lithosphere of supra-subduction zone Bay of Islands of the Baie Verte oceanic tract (which includes forearc Betts Cove and Pointe Rousse ophiolites of same ages, and potentially the younger back arc Annieopsquatch ophiolite). The Baie Verte oceanic tract spreading centers are oriented approximately orthogonal to the trench and left stepping transforms were approximately parallel requiring a trench-ridge-ridge triple junction in the front of the forearc (Dewey and Casey, 2011, 2013, 2015). Instantaneous subduction initiation beneath the spreading centers and hot sole subcretion of the downgoing oceanic lithosphere is shown to form metamorphic soles (cooling starting at ca. 489 Ma) below the Baie Verte oceanic tract. The ophiolites of the Baie Verte oceanic tract start to form at ca. 490 Ma, which involved rifting of the older CC-Lushs Bight forearc (formed early at ca. 510-500 Ma). The arc encroachment on the Laurentian margin results in ophiolite obduction over Laurentian Humber margin starting at ca. 470 Ma during the Taconic orogeny.



The minimum igneous age of Notre Dame Arc inception is provided by the arcrelated rocks and the Twillingate granite U-Pb zircon ages of ca. 507-513 Ma (e.g., Dunning et al., 1987; Elliott et al., 1991) within the Notre Dame Arc terrane that ultimately collides with Laurentia. This age range is almost identical to the reported U-Pb ages of ca. 500-508 Ma of the older CC ophiolitic assemblage and the presumed infant Notre Dame arc volcanic terrane (ca. 501-510 Ma) (Van Staal et al., 1998, 2007). This includes the Lushs Bight mafic forearc-arc assemblage. We consider the CC as the comparable oldest part of the forearc lithosphere formed in the middle Cambrian (Fig. 2.8). This older forearc was eventually rifted by the inception of the late Cambrian supra-subduction zone (SSZ) BOIC-Betts Cove-Point Rousse spreading centers of the Baie Verte Oceanic Tract that were offset in a left lateral sense by transforms within the forearc (Fig. 2.8b). The exact former distances of these lateral offsets between ophiolite complexes are unknown because of later strike-slip faulting along the late Devonian Cabot Fault that now separates the BOIC from other ophiolites of the Baie Verte Oceanic Tract (e.g., Waldron et al., 2015). The spreading centers were at high angles to the Notre Dame Arc cutting across the arc to the front of the forearc as it intersected the west facing trench (present-day coordinates) at an upper plate ridgetrench-trench triple junction (Casey and Dewey, 1984; Dewey and Casey, 2013, 2015). The BOIC-CC boundary in the Lewis Hills massif represents a transform margin between the older CC (reported as ca. 500-508 Ma) forearc lithosphere and the newly formed BOIC (ca. 488.3 Ma) forearc lithosphere (Dewey and Casey, 2013, 2015). Thus, the age difference between the two forearc basements is at least approximately 12-20 Ma.

This composite aged trench-forearc-arc system and its older and younger ophiolitic forearc lithospheric basements with largely already subcreted subduction channel metamorphic soles and accretionary prisms encroached on the Laurentian continental margin for the next ~18

Ma after BOIC formation. The encroachment resulted in obduction of this composite intact CC-BOIC ophiolite basement onto the Laurentian stable margin at ca. 470 Ma. Final emplacement of the allochthon occurred during the middle Ordovician (Dapingian to Darwillian) Taconic Orogeny (ca. 460-470 Ma). During this obduction phase, the colliding Central Newfoundland Notre Dame Arc was magmatically active shedding ash and arc-related detrital zircon as young as 460 Ma (Darwillian) to allochthonous and autochthonous foreland flysch (Casey and Kidd, 1981; Macdonald et al., 2017; our unpublished flysch detrital zircon studies). The subducting slab adjacent to Laurentia underwent slab breakoff and Laurentian margin assemblages underwent eduction, i.e., inversion and partial exhumation of the buoyant partially-subducted stable margin rocks of the Fleur De Lys Super Group. These events closely correlate in time with the Notre Dame Arc subduction polarity reversal (e.g., De Wit, 1974; Williams, 1977; Hibbard, 1983; Castonguay et al., 2014).

A wide range of very young heterogeneous K-Ar and ⁴⁰Ar-³⁹Ar "cooling dates" with large errors (> 12 Ma) are common in Humber Arm igneous and sole rocks of the BOIC and the CC ophiolites (Archibald and Farrar, 1975; Dallmeyer and Williams, 1975; Idleman, 1991). The U-Pb ages of ophiolitic igneous zircon are significantly older (> 19 Ma), with respect to the long-accepted Ar-Ar sole age of ca. 469 Ma. Nevertheless, there are some Ar-Ar hornblende gabbroic cooling dates (ca. 490 Ma) closer to the zircon igneous ages and some mylonite dates (ca. 475 Ma) older than obduction ages within the CC (e.g., Idleman, 1991). These mylonites are cut by younger pre-final emplacement quickly-chilled mafic igneous dikes indicating active igneous activity post-475 Ma cooling. Also, in the Hare Bay allochthon in Northern Newfoundland thought to be a correlative with other Taconic ophiolitic allochthons that is ~190 km north of the Humber Arm Allochthon, the St. Anthony ophiolite subcreted sole rocks are dated by ⁴⁰Ar-³⁹Ar techniques

(Dallmeyer, 1977) at 489 \pm 5 Ma, recalculated with new decay constant. This age, although interpreted to indicate diachronous obduction from the Bay of Islands to St. Anthony Complexes by Dallmeyer (1977), may be more compatible with evolution within the Baie Verte oceanic tract with rapid intra-oceanic cooling of the subcreted amphibolites in a subduction channel. This age is almost identical with the ca. 488.3 Ma ophiolite generation age for the BOIC reported here. Similar rapid cooling of the sole has been suggested in many ophiolite complexes around the world (e.g., Hacker, 1996; Roberts et al., 2016) and appears similar in the Quebec Ophiolites (Whitehead et al., 2000). There is no ophiolite generation age as yet for St. Anthony ophiolite. We speculate, however, that if it is close in age or nearly coincident with the BOIC or Betts Cove ophiolite, this much older sole age (~20 Ma older than K-Ar and Ar-Ar ages of the BOIC sole) may suggest that the much younger date of ca. 469 Ma for the BOIC metamorphic sole could be suspect. We are now in the process of careful revaluation and collection of new data for the BOIC sole age. The BOIC-CC ophiolite assemblage was in a tectonically active subduction plate boundary regime and later obduction zone for a minimum of ~28 Ma after ophiolite formation until final emplacement. Even younger tectonothermal disturbances of Ar dates have been suggested in the Humber Arm igneous assemblages (Cawood et al., 2001). Thus, reevaluation of the sole age of the BOIC may be required as suggested by Dewey and Casey (2015).

In a broader context, the trench-orthogonal spreading center geometry of the BOIC within the forearc upper plate is not atypical of modern forearc environments. Both upper plate ridge-trench-trench or ridge-trench-transform triple junction geometries and rifting of older forearcs like the CC are not uncommon. Modern early juvenile forearcs like the BOIC-Betts Cove-Point Rousse ophiolitic lithosphere are characterized by MORB-like forearc basalts (FAB) nearer the trench (e.g., BOIC) and FAB, boninites and arc tholeiites somewhat more distal to the trench

(e.g., DeBari et al., 1999; Reagan et al., 2010; Pearce and Reagan, 2019); consistent with the progression of ophiolitic terranes from the Humber Arm allochthon structural front to the northeast within ophiolites of the Baie Verte Oceanic Tract (e.g., Casey et al., 1985; Coish, 1989; Jenner et al., 1991). In modern environments, spreading centers within the forearc may extend from the trench triple junction through the arc and into the back arc at high angles to the trench. These analogous forearc triple junctions include a myriad of examples, including the modern Southern Hebredes Arc, the Southernmost Mariana Arc and the Northern Tonga Arc, as well as former extinct forearc spreading centers (e.g., associated with the IBM and Tonga forearcs) and other ancient ophiolite examples (e.g., Troodos among others) (e.g., Casey and Dewey, 1984; Falloon et al., 2008; Dewey and Casey, 2011; Resing et al., 2011; Meffre et al., 2012; Patriat et al., 2015, 2019).

2.8 Conclusions

New LA-ICP-MS U-Pb dating of a large population (N = 127) of zircon grains from four trondhjemite samples from a single pluton and one additional sample from a nearby plagiogranite pluton on the Blow Me Down Mountain massif indicates that the BOIC formed at 488.3 ± 1.5 Ma. LA-ICP-MS analyses and the ages presented in this study show high precision, high degree of internal consistency among the five samples analyzed, and high accuracy governed by secondary standard FC5z for single analytical sessions as well as their integration. With the advantage of in situ U-Pb dating by LA-ICP-MS, metamict domain, inclusion, rim and crack were avoided, and only clear, intact cores have been targeted during ablation. Some reevaluated and less precise legacy ages of the BOIC appear consistent within recalculated errors with our more precise new LA-ICP-MS age, whereas previously interpreted and designated consensus ages may lack a high degree of precision and accuracy. The proposed 488.3 ± 1.5 Ma age of the BOIC is interpreted to show that spreading centers that formed the BOIC rifted an older CC-Lushs Bight (ca. 500-508 Ma) ophiolitic forearc terrane and formed a welded composite forearc terrane with disparate ages. The trench-proximal BOIC is virtually identical in age within errors to the trench-distal Betts Cove and Point Rousse ophiolites that lie close to the Baie Verte suture zone between the Notre Dame Arc and Fleur de Lys Supergroup metamorphosed rocks of the Laurentian margin. These ophiolitic terranes have typical forearc volcanic geochemistry (including FAB to boninite) and constitute the younger once-contiguous Baie Verte Oceanic Tract within the Notre Dame forearc region in Western and Central Newfoundland.

We interpret the age similarities of these ophiolites to indicate that they may have formed along a set of supra-subduction zone forearc spreading centers offset by trench-parallel transform faults. These spreading centers were linked to a trench-trench-spreading center triple junction to the northwest. The spreading centers were likely offset by many long trench-parallel transforms including the older CC transform deformation zone. As documented within the CC, the transforms were characterized by left-lateral offsets as they progressed from the trench to the northeast across the forearc to the Notre Dame Arc. Ophiolite formation and hot subcretion of sole rocks to the BOIC as spreading proceeded was simultaneous. The sole began to immediately cool in an oceanic realm. Spreading and sole formation takes place simultaneously and subduction initiates instantaneously beneath the lengthening forearc of the Baie Verte Oceanic Tract at the triple junction. As the trench and forearc lengthen, FAB and boninites erupt as part of the newly formed forearc seafloor above the dehydrating slab.

This westerly verging trench-ophiolitic forearc-arc system continued to subduct oceanic crust adjacent to the Laurentian stable margin and drew closer over the next ~18 Ma after

BOIC formation. The progression eventually resulted in ophiolite and a cooled sole obduction, the detachment and cold accretion of the rift-related Skinner Cove and other sub-ophiolitic basalts near the ocean-continent transition to complete the igneous portion of allochthon, and then complete assembly and final emplacement of the Humber Arm allochthon during the Taconic Orogeny (ca. 470-460 Ma). The ophiolitic welded forearc CC-BOIC basement composite was partially dismembered as the Humber Arm Allochthon was emplaced, except in the Lewis Hills where the contact is preserved in autochthonous relationship between the older and younger ophiolitic basements. The downgoing slab connected to Laurentia underwent slab breakoff followed by a subduction polarity reversal as westward subduction of the outboard Iapetus oceanic lithosphere initiated beneath the composite Laurentia-Notre Dame Arc collision zone forming an Andean-type margin.

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Chapter 3 New LA-ICP-MS zircon ages of plagiogranites from the Coastal Complex ophiolite and Twillingate Granite, Newfoundland: evidence for the oldest magmatism in the nascent Cambrian peri-Laurentian forearc-arc terranes

3.1 Introduction

The Coastal Complex (CC) (Comeau, 1972; Karson and Dewey, 1978) is the oldest and most complexly deformed and partially dismembered ophiolite assemblage recognized in the Northern Appalachian Taconic Humber Arm Allochthon of the Humber Zone (Williams, 1995). It crops out in a narrow NE-SW belt located along the west coast of Newfoundland that is most commonly in structural contact with the Bay of Islands Ophiolite Complex (BOIC) to the east, but is preserved on the west side of the Lewis Hills massif (WLH) where it is in direct igneous contact with the BOIC on the east side of the Lewis Hills (ELH) exists (Fig. 3.1) (Karson and Dewey, 1978; Casey and Karson, 1981; Casey and Dewey, 1984; Karson, 1984; Karson et al., 1984; Casey et al., 1983,1985, Kurth et al., 1998). Although the CC is dismembered in the North, the Lewis Hills preserves the original autochthonous igneous relationship with a younger and less deformed BOIC. Here, it can be demonstrated that the CC and BOIC formed part of the once contiguous forearc basement sheet juxtaposed along a forearc spreading center transform system (Karson and Dewey, 1978; Casey et al, 1983, 1985; Karson, 1984; Karson et al., 1984; Casey and Dewey, 1984; Dewey and Casey, 2013, 2015, Yan and Casey, 2020). At the time of obduction, it formed the uppermost obducted crystalline nappe at the leading edge of the Humber Arm Allochthon as it was emplaced onto the Humber margin of Laurentia. However, compared with the BOIC, the CC ophiolitic assemblage has undergone even more pronounced, pervasive and variable retrogradeprograde-retrograde sequences of dynamic, hydrothermal and contact metamorphism, as well as deep high temperature crystal-plastic deformation and shallow level faulting. The deformation and metamorphism occurred syn-accretion and syn-subduction as part of the Notre Dame forearc while magmatically active in the forearc and then during syn-BOIC rift-transform deformation with renewed magmatism and culminating in ductile to brittle syn-obduction and final emplacement dismemberment (e.g., Comeau, 1972; Williams, 1973, 1975b; Karson and Dewey, 1978; Casey et al., 1983, 1985; Casey and Dewey, 1984; Karson et al., 1984; Idleman, 1991; Cawood and Suhr, 1992; Kurth et al., 1998; Kurth-Velz et al., 2004; Dewey and Casey, 2013, 2015, 2021; Yan and Casey, 2020). Therefore, zircon grains collected from the CC samples have suffered even more extensive U-Th-Pb disturbances than the younger BOIC that we have analyzed.

Fig. 3.1 Generalized regional geologic map of the Bay of Islands region of Western Newfoundland, Canada, showing the Coastal Complex (CC) ophiolite and main ophiolitic assemblages of the Bay of Islands Ophiolite Complex (BOIC) (modified from Casey et al., 1985;). Note the highly deformed, northeasterly trending Coastal Complex (Karson and Dewey, 1978), which is inclusive of the Little Port Complex in the north (Williams, 1975) and the Western Lewis Hills massif in the south. The CC was demonstrated to have an autochthonous relationship with the BOIC in the Lewis Hills massif (Karson and Dewey, 1978), but is now in thrust or in fault contact to the north with the three adjacent discrete BOIC massifs. Other allochthonous rift-related volcanics including the Skinner Cove Volcanics and various sub-ophiolitic basalts of Ediacaran age have now been excluded from the CC. Note that the five vellow stars within the CC ophiolitic belt show approximate plagiogranite sample locations analyzed in this study (for detailed GPS sample locations see Table 3.1). The single and multiple cogenetic samples analyzed by LA-ICP-MS in this study were collected from Green Gardens Trail intrusion (GG), Trout River intrusion (TR), Southhead Lighthouse Trail intrusion (LHT), Murray Mountain intrusion (MM) and Tortoise Mountain intrusion (in Blow Me Down Provincial Park, BMDP) (see Fig. 3.2 for details). Note the TR and BMDP sample from this study are spatially close to trondhjemite reported by Mattinson (1975a, b) and Jenner et al. (1991), respectively.



In this study, we use our previously developed LA-ICP-MS techniques in age dating of the Bay of Islands Ophiolite Complex (BOIC), which, when possible, prescribes multiple samples for each pluton that result in repeatable and precise individual sample LA-ICP-MS U-Pb zircon ages and assemblage of all analyses to yield a more precise composite age for each pluton (Yan and Casey, 2020). To help constrain tectonic and timing models of juvenile to more mature ophiolitic forearc-arc systems and early arc massifs that developed in the Northern Appalachians, comparisons are made with the age ranges in the modern nascent trench proximal forearcs and more distal arc terranes. With the oldest forearc ages, we also examine the age of initiation of subduction in the Iapetus Ocean with vergence toward Laurentia, the progression of juvenile magmatism from the forearc to the arc massif, and the relationships to younger forearc spreading ophiolitic lithosphere in Western Newfoundland generated within the confines of the older CC-Lushs Bight forearc-arc basement terrane, such as the younger Bay of Islands Ophiolite Complex that is preserved in autochthonous relationship to the CC.

3.2 LA-ICP-MS U-Pb zircon dating technique and Tera-Wasserburg plot

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is our preferred U-Pb dating technique for the CC and Twillingate Granite because its high resolving power can commonly result in large populations of concordant dates (e.g., Yan and Casey, 2020). The LA-ICP-MS U-Pb dating technique is also one of the most popular rapid in-situ microanalytical tools for the U-Pb geochronological studies dominantly on zircon among many other minerals over the past several decades (e.g., Košler and Sylvester, 2003; Jackson et al., 2004; Solari et al., 2010; Chew et al., 2011, 2014; Harrison et al. 2015; Xie et al., 2018). Compared to the other two high-precision dating techniques of ID-TIMS (isotope dilution-thermal ionization mass spectrometry) and SIMS (secondary ion mass spectrometry), the LA-ICP-MS method has the highest ionization efficiency and analytical sample throughput ($\leq \sim 60$ s per analysis) and very high spatial resolution but with a significantly lower cost (e.g., Chang et al., 2006; Solari et al., 2010; Gehrels, 2011; Corfu, 2013; Pullen et al., 2014; Schoene, 2014; Yan and Casey, 2020). By pooling a large population of cogenetic analyses, high precision of generally within \pm 1-2% uncertainty can be achieved for LA-ICP-MS dating techniques (e.g., Shaulis et al., 2010), with accuracy within \pm 1% of ages obtained by ID-TIMS (e.g., Košler et al., 2013; Horstwood et al., 2016; Mukherjee et al., 2019; Yan and Casey, 2020). However, because the sources of uncertainty and the calibration methods employed for age/date calculation vary for different dating techniques, fully quantifying random and systematic uncertainty introduced during sample preparation, measurement, instrument operation and data reduction is fundamental for inter- and intralaboratory age result comparison particularly in the case where the analyses are from different decay schemes (e.g., U-Pb vs. Ar-Ar) (Schoene et al., 2013) and/or where the data are calibrated with different reference materials (Klötzli et al., 2009; Košler et al., 2013). Many efforts have been made to improve the equivalence and comparability of age results from different sources since early investigations (e.g., Mattinson, 1987; Ludwig, 2000; Horstwood, 2008; Schoene et al., 2013). Recently a community-derived data treatment routines have been advocated as a way to standardize uncertainty propagation, calculation procedures and reporting, after which different ages are believed to allow for direct comparison (see Horstwood et al., 2016 for details). Disturbance in U-Th-Pb system of zircon caused by mixing of different domains, Pb loss, intermediate daughter product disequilibrium and common Pb contamination, as well as their potential influence on subsequent age calculations have been investigated by many studies (e.g., Mezger and Krogstad, 1997; Corfu, 2013; Kusiak et al., 2013; Schoene et al., 2013; Schoene, 2014; Spencer et al., 2016; Ge et al., 2018; Yan and Casey, 2020), although U mobility may also play a

role under some circumstances (e.g., Sinha et al., 1992; Seydoux-Guillaume et al., 2015). Yan and Casey (2020) in a prior study in the Humber Arm Allochthon related to the CC reexamined the crystallization age of the adjacent BOIC ophiolite of Western Newfoundland and determined that LA-ICP-MS selective domain analysis with a 25-µm ablation spot and a discordance filter of $\leq 3\%$ on a large populations of primary magmatic zircon grains collected from demonstrably cogenetic multiple samples (i.e., samples from a single plagiogranite pluton) could effectively avoid most of the disturbances in U-Pb zircon system and yield simple, precise and repeatable concordia ages for each sample, and a more precise composite pluton age using multiple samples. However, the younger BOIC is generally regarded as less deformed and less dynamically, as well as hydrothermally, metamorphosed compared with the CC targeted for age determinations here (e.g., Karson and Dewey, 1978; Casey et al., 1983; Karson, 1984).

Tera-Wasserburg (T-W) diagram (Tera and Wasserburg, 1972a, b) is a popular alternative to the Wetherill concordia diagram (Wetherill, 1956) with x-axis of ²³⁸U/²⁰⁶Pb against y-axis of ²⁰⁷Pb/²⁰⁶Pb. In general, concordant and discordant datasets plotted within T-W diagram are interpreted identically to those within the Wetherill diagram. However, T-W diagram is more commonly utilized to graphically present U-Pb isotope data with variable common Pb components (e.g., Rubatto et al., 1999; Sun et al., 2002; Zheng et al., 2007), by which common Pb can be corrected without requiring an estimate of the initial Pb isotopic composition or applying an appropriate initial Pb isotopic composition to individual analyses (e.g., Davis et al., 2003; Batumike et al., 2008; Chew et al., 2011, 2014; Kirkland et al., 2018a, b; Xie et al., 2018; Andersen et al., 2019; Bonamici and Blum, 2020; Peverelli et al., 2020). These data points of variable proportions of common Pb will together determine a regression line intersecting with the concordia curve at a lower age point (i.e., lower intercept age) representing the true crystallization age of a

suite of cogenetic analyses, but with the ²⁰⁷Pb/²⁰⁶Pb axis (i.e., y-axis) at an initial ²⁰⁷Pb/²⁰⁶Pb ratio (i.e., no radiogenic Pb) recording common Pb composition (e.g., Ludwig, 1998; Li et al., 2012; Schoene, 2014; Mohammadi et al., 2019). Therefore, the individual U-Pb and Pb-Pb dates, particularly those highly discordant ones from single or cogenetic samples, likely have limited geological meaning but indicate variable extents of contamination by a single initial Pb composition (Schoene, 2014) or more complex, a combination result of elevated common Pb, Pb loss and/or some degree of inheritance (Crowley et al., 2014).

Common Pb detected during U-Pb isotope measurement could be derived from multiple sources primarily including 1) initial Pb incorporated into the mineral lattice during or shortly after mineral formation, 2) secondary structures (e.g., microfractures and radiation damaged zones) and accessory mineral/gas/liquid inclusions and 3) contamination introduced during sample preparation (e.g., surface contamination such as polishing and mounting for LA-ICP-MS analysis or gold coating for SIMS analysis) (Williams, 1998; Schoene, 2014; Liu et al., 2015; Pidgeon et al., 2017; Anderson et al., 2019), although ancient redistribution of radiogenic Pb that is unrelated to crystal morphology or damage may also lead to some meaningless old ages (> 4.0 Ga) (see Kusiak et al., 2013 for details). Zircon has been widely documented to have little or no initial Pb because the ionic radius of Pb²⁺ (1.43 Å; Shannon, 1976) is too large to fit into the 8-coordinated positions in the zircon structure occupied by Zr^{4+} (0.98 Å) and substituents such as Hf⁴⁺ (0.97 Å) or U⁴⁺ (1.14 Å). Therefore, in the LA-ICP-MS U-Pb dating technique on younger zircon, common Pb has been assumed to be primarily derived from secondary structures and surface contamination, which, in most cases, could be partially or fully remedied by surface cleaning, pre-ablation and/or rejecting the first few seconds of analysis followed by selective domain analysis with an optimal ablation spot size (e.g., Xie et al., 2018; Yan and Casey, 2020).

An average present-day crustal common Pb composition (Stacey and Kramers, 1975) is sometimes used for correcting common Pb introduced by surface contamination during sample preparation (e.g., Compston et al., 1992; Li et al., 2013; Liu et al., 2015). In fact, intercept age calculated by pooling a set of cogenetic samples with variable common Pb contamination within T-W plot has been demonstrated to be identical to the concordia age yielded from the same samples but after common Pb correction (Compston et al., 1992; Crowley et al., 2014). Crowley et al. (2014) further introduced chemical abrasion technique (Mattinson, 2005) on zircon before laser ablation, suggesting that age results yielded from non-treated and chemically abraded zircon population of the same sample are indistinguishable, although non-treated zircon analyses are more scattered and discordant whereas chemically abraded ones are essentially clustered and highly concordant.

It is notable that due to the specific zircon lattice structure commonly resistant to external Pb incorporation, common Pb correction in many cases is not necessary (e.g., Lana et al., 2017; Xie et al., 2017, 2018) and sometimes may even result in overcorrection yielding apparently young dates (e.g., Compston et al., 1992). Furthermore, whether common Pb or Pb loss is accounted for the discordant data spreading could be distinguished for young samples (i.e., younger than Mesoproterozoic) because in the T-W diagram, scattered data points from single or cogenetic suite of samples influenced by common Pb contamination are apparently aligned at a high angle to concordia curve and towards an unrealistic old age of > 4-4.5 Ga (e.g., Wendt, 1984; Williams et al., 1984; Ludwig, 1998; Kusiak et al., 2013; Schoene, 2014; Hosseini et al., 2017), whereas Pb loss effect tends to produce "outliers" displaced to the right hand side of the discordia determined by the majority of data points (Compston et al., 1992). It is notable, however, that analyses of zircon inherited cores would similarly drive the regression line to intersect with the concordia curve, both within Wetherill and Tera-Wasserburg diagram, at an older upper intercept

representing the source rock age inherited, and at a younger lower intercept representing the more recent metamorphism or magmatic age (e.g., Mezger and Krogstad, 1997; Heilbron et al., 2010; Shahbazi et al., 2010).

Here we provide a new set of 11 LA-ICP-MS U-Pb zircon age constraints for five plagiogranite plutons and reevaluate prior ID-TIMS results within the Coastal Complex (CC) ophiolitic assemblage (Comeau, 1972, Karson and Dewey, 1978) included in the Northern Appalachian Taconic Humber Arm Allochthon of Western Newfoundland (Stevens, 1970; Dewey and Bird, 1971; Williams, 1971, 1973). We also report a new precise LA-ICP-MS age and reinvestigate prior ID-TIMS ages for the Twillingate plagiogranite batholith in Central Newfoundland (Strong and Payne, 1973; Payne, 1974) that is interpreted to be one of the earliest major felsic plutons within the once-adjacent juvenile Notre Dame arc massif in Central Newfoundland to the east (e.g., see Williams et al., 1976; Nelson and Casey, 1979; Elliot et al., 1991, van Staal et al., 2007; Zagarovski et al., 2011). It places a minimum age constraint on the intruded Sleepy Cove arc tholeiites and boninitic pillow lavas (and by extension the correlated Lush Bight Oceanic Tract) which form the juvenile basement of the Notre Dame arc (Swinden, 1996, 1997, Kean et al., 1995; Szybinski, 1995).

3.3 Tectonic framework of the Coastal Complex and Twillingate Granite

3.3.1 The Coastal Complex

The Coastal Complex (Fig. 3.1 and 3.2) is a narrow, discontinuous, overall northeast-southwest trending belt of highly deformed and older ophiolitic rocks adjacent to the western edge of the Bay of Islands Ophiolite Complex (BOIC). It includes both the northern dismembered ophiolitic exposures west of the three northern BOIC massifs including the Table Mountain massif, North Arm Mountain massif and Blow Me Down Mountain massif (also known

as "Little Port Complex", after Williams, 1973, 1975b; Jenner et al., 1991) and the western part of the Lewis Hills (WLH) massif in the south that lies adjacent to the BOIC in the eastern Lewis Hills (ELH) with a preserved igneous contact and stitching dikes derived from a ridge-transform intersection (Karson and Dewey, 1978; Casey and Karson, 1981; Casey et al., 1983, 1985; Casey and Dewey, 1984; Karson et al., 1984; Idleman, 1991; Cawood and Suhr, 1992; Kurth et al., 1998; Kurth-Velz et al., 2004; Dewey and Casey, 2013, 2015, 2021; Yan and Casey, 2020) (Fig. 3.1). The contacts from the Little Port area north to Bonne Bay (Fig. 3.2) are structural with the underlying parts of allochthon and BOIC, whereas in the Lewis Hills the contact is igneous with younger BOIC intruding and stitching the older and deformed CC (Williams, 1973; Karson and Dewey, 1978; Casey and Karson, 1981, Karson, 1984; Casey and Dewey, 1984; Casey et al., 1983).

Early U-Pb TIMS zircon fraction ages from geochronologic studies of plagiogranites from the Coastal Complex (CC) ophiolite were reported as 508 ± 5 Ma for the Trout River region (Mattinson,1975a), 505^{+3}_{-2} Ma for the Little Port region (Jenner et al.,1991) and 502 Ma (without uncertainty) for the Western Lewis Hills (Kurth et al., 1998). Jenner et al. (1991) had proposed to abandon the term CC, but we retain it based on these correlatives ages (e.g., Kurth et al., 1998) as predicted by Karson and Dewey (1978). These studies confirm an older age for the CC with respect to the younger BOIC and a narrow age range from 508 ± 5 Ma to 502 Ma for both the WLH and Little Port Complex as part of the same CC ophiolite assemblage and with the same igneous and structural history (e.g., see discussions in Karson and Dewey, 1978; Kurth et al, 1998; Dewey and Casey, 2013, 2015; Yan and Casey, 2020).

The initial interpretations of age relations were based on structural fabrics and igneous intrusive crosscutting relationships relative to the BOIC. These interpretations appear to be correct on the basis of later isotopic ages in the WLH, as well as lower \mathcal{E}_{Nd} values for plutonic

rocks from both the Little Port Complex and the WLH with respect to higher values of the ELH in BOIC (e.g., Karson and Dewey, 1978; Jacobsen and Wasserburg, 1979; Casey et al., 1981, 1983; 1985; Karson, 1984; Kurth et al., 1998; Kurth-Velz et al., 2004; Dewey and Casey, 2013, 2015, 2021). However, these legacy ages at face value are within analytical errors for the two ages reported with age uncertainty by Mattinson (1975a) and Jenner et al. (1991). Although the geologic relationships and relative age separations between the CC and BOIC are obvious, the two legacy ages with errors for the CC could be interpreted as a near-singular crystallization age for all the CC plagiogranite plutons from north to south. In contrast, our new results presented below for five plutons particularly including those also sampled by previous studies, as well as our reevaluation of legacy ages and uncertainties now not only confirm the older ages but suggest a much more protracted interval of forearc silicic magmatism to explain the age dispersion determined.



Fig. 3.2 Detailed regional geologic map of northern (a) and southern (b) Coastal Complex respectively subjacent to the Table Mountain massif and Blow Me Down Mountain massif (Fig. 3.1) showing details of the main lithologies and tectonic features (modified from Casey et al., 1985 and Williams and Cawood, 1989). Note that yellow stars indicate approximate locations of plagiogranite samples analyzed in this study (for detailed GPS sample locations see Table 3.1). Sample CC-TR1-17ERS is spatially close to the location where trondhjemite 72-9 was sampled by Mattinson (1975a, b). Sample location of CC-BMDP1-17ERS is close to where trondhjemite 83GD-02 was taken by Jenner et al. (1991), and apparently both of them are from the Tortoise Mountain intrusion. Note that some samples were collected respectively close to each other to ensure a cogenetic origin.

It is notable that one revision of the CC definition (Comeau, 1972) involves subophiolitic allochthonous volcanic assemblages that are distributed widely in the Humber Arm Allochthon. They include the Skinner Cove Volcanic Assemblage (Strong, 1974; Baker, 1979) and other correlated and informally named sub-ophiolitic volcanic rocks (e.g., from Chimney Cove, Beverly Cove, Woods Island, Couchers, Fox River Island) (Williams and Cawood, 1989) that have strong to transitional alkalic nature (Strong, 1974; Malpas, 1976; Baker, 1979). There are also numerous undifferentiated sub-ophiolitic volcanic rocks mapped in the Bay of Islands region (see Fig. 3.1) that were, in part, previously interpreted to be part of the CC (Comeau, 1972, Karson and Dewey, 1978). Although always in faulted contact with the CC or BOIC assemblages, they are now excluded from the CC ophiolitic assemblage based on more recent geochronologic studies. These volcanic rocks are now generally recognized based on Sm-Nd and U-Pb zircon ages from the Skinner Cove type locality as allochthonous rift-related Ediacaran (ca. 550 Ma) volcanic rocks derived from the nearby Laurentian ocean-continental crust transition (Williams, 1975; McCausland et al., 1997; McCausland and Hodych, 1998; Cawood et al., 2001; Hodych et al., 2004; Hodych and Cox, 2007). They were erupted from the distal but transported to the ancient Laurentian passive margin, and in places tectonically accreted to the base of CC or BOIC ophiolitic slices in the allochthon as the lowest igneous crystalline slices below the upper CC and BOIC ophiolitic massifs and are commonly in tectonic contact with the welded metamorphic sole rocks with sharp metamorphic discontinuities (see discussions in Williams, 1973; Baker, 1979; Casey, 1980; Savci, 1988; Williams and Cawood, 1989; Dewey and Casey, 2013, 2015; Yan and Casey, 2020). All these volcanics are now excluded from the CC, as they are separate slices unrelated to the overlying CC and BOIC contiguous ophiolite forearc basement to the Notre Dame and not part of the uppermost crystalline thrust assemblage of the allochthon.

3.3.2 The Twillingate Granite pluton

The Twillingate Granite pluton in Notre Dame Subzone of the Dunnage Zone (Williams and St-Julien, 1982; Williams et al., 1988; Williams and Curries, 1995) in northern Central Newfoundland (Fig. 3.3) crops out dominantly on South Twillingate Island, as well as some other areas including North Twillingate Island, Burnt Island, Duck Island, Trump Islands, Black Island and the northwest part of New World Island (Payne, 1974; Williams and Payne, 1975). It has a batholithic dimension estimated to be 350 km² (Payne and Strong, 1979) and is situated in the Notre Dame Subzone, which is designated to be between the ophiolitic Baie Vert-Brompton Line to the west and the Red Indian Line to the east (Williams and St-Julien, 1982; Williams et al., 1988). The Twillingate Granite represents the northernmost exposed Taconic arc felsic intrusion in the Appalachian orogen. The Notre Dame arc is considered to be once adjacent to ophiolitic BOIC and CC forearc outlier klippe atop the Humber Arm and Hare Bay Taconic Allochthons (Dean, 1978; Nelson and Casey, 1979, Williams et al., 1988, Colman-Sadd et al., 1992; Kean et al., 1995, O'Brien, 2003, van Staal et al., 2007, Dewey and Casey, 2021) prior to collision and subsequent complex convergent tectonics, dismemberment and exhumation between the Baie Verte Line and outlier allochthons (Fig. 3.3).

Plutonic rocks from the Twillingate Granite show variable deformation intensity from massive and mildly foliated in the north to intensively foliated and mylonitic along its southeast contact near the Chanceport Fault. The batholithic intrusion consists of "sodic granites" (trondhjemites, granodiorites and felsites) that are geochemically enriched in Si and Na but depleted in K contents. The intrusion mineralogically is dominated by quartz and plagioclase (~90%) with minor mafics of amphibole and biotite, with rare or no K-feldspar (Strong and Payne, 1973; Payne, 1974; Williams and Payne, 1975; Payne and Strong, 1979). They are compositionally indistinguishable from rocks described as oceanic plagiogranite (see Koepke et al., 2007 for a summary) and are not significantly different from CC and BOIC plagiogranites, although they may have somewhat higher average K₂O with respect to the BOIC.

The Twillingate plagiogranites intrude the older Sleepy Cove pillow lava volcanic basement that has been correlated with the Lushs Bight volcanic terrane (the Lushs Bight Oceanic Tract) to the west in the Notre Dame Subzone (e.g., Swinden, 1996, Swinden et al., 1997, Zagorevski and van Staal, 2011). Thus, the age of the Twillingate Granite provides a minimum age for this primitive arc volcanic basement in the Notre Dame arc. Furthermore, the Twillingate Granite contains the same regional fabrics and similar but localized deformation trends (i.e., highly metamorphosed and deformed in the south to slightly or undeformed in the north). The close spatial distribution and similarities in structural fabric and deformation patterns with the Sleepy Cove suggests that they were temporally related products likely generated by the same period of early arc magmatic activity, which experienced a similar later deformation history (Williams and Payne, 1975) not always recognized in younger Notre Dame volcanics. The undated earlier Sleepy Cove volcanics also consist of areas of weakly to strongly deformed pillow lavas, which are dominantly arc tholeiitic to boninitic in compositions and largely devoid of epiclastics. They are similar to the Lushs Bight Oceanic Tract to the west that similarly contains sheeted dikes typical of oceanic crustal basements (Szybinski, 1995, Swinden, 1996; Swinden et al., 1997). These correlated volcanic units are thought to be the Cambrian basement foundation of the Notre Dame nascent arc linked to the contiguous CC ophiolitic forearc basement. Thus, the Lushs Bight-Sleepy Cove basements are likely near age equivalent to the Cambrian CC forearc basement (e.g., Nelson and Casey, 1979; van Staal et al., 2007; Dewey and Casey, 2013; 2015, 2021, Yan and Casey, 2020).

Spatially close to the Twillingate intrusion are the volcanic assemblages of the Moretons Harbour Group (Fig. 3.3). They are, however, interpreted to represent a younger more felsic and distinct volcanic/plutonic assemblages post-dating the Twillingate intrusion (Swinden, 1996; Swinden et al., 1997; O'Brien, 2003; Cutts et al., 2012) in contrast to more primitive pre-Twillingate SSZ Sleepy Cove volcanic basement. Cutts et al. (2012) showed that the Moretons Harbour Group, based on the U-Pb age of ca. 477 Ma from crosscutting trondhjemite intrusives, is likely to be significantly younger than the Sleepy Cove volcanics and Twillingate pluton in the Notre Dame arc sequence and may be correlated with the ca. 480 Ma Annieopsquotch Ophiolite Belt just to the west of the Red Indian Line that bounds the Notre Dame arc. The Moretons Harbor Group and Annieopsquotch Ophiolite Belt formed in between reported ages of the formation of BOIC and BVOT (ca. 489-488.3 Ma) (Yan and Casey, 2020) and the initial stages of obduction at ca. 470 Ma as provided by the age of the margin peripheral bulge migration, the first easterly derived distal margin flysch (Florian/Dapingian), arc derived ash layers and age of exhumation and erosion of the BOIC (Stevens, 1970; Nelson and Casey, 1979; Casey and Kidd, 1981; James and Stevens, 1986; Pohler and James, 1989; Casey and Dewey, 2013, 2015, 2021; Macdonald et al. 2017). The near-Laurentia position of the arc during the time of the Moretons Harbour Volcanic Group formation is consistent with Sm/Nd isotopic evidence showing continental influence and near-Laurentia paleomagnetic and palaeolatitudinal positions established (Swinden et al., 1997; van der Pluijim et al., 1990). Based on these cross-cutting relationships, the Twillingate Granite and older SSZ Sleepy Cove Group are interpreted to be the oldest Cambrian arc sequences that later were tectonically juxtaposed with younger deformed volcanics and dikes of the Moretons Harbour Group (e.g., Swinden, 1996).

Fig. 3.3 Regional geologic map of Twillingate Island of Notre Dame Subzone in northern Central Newfoundland, Canada, showing the three main lithologic groups of Moretons Harbour, Sleepy Cove and Twillingate Granite (after Williams and Currie, 1995). Note that South Twillingate Island is composed dominantly of "sodic granites" that are in fact mineralogically and chemically identical to oceanic plagiogranite (e.g., Koepke et al., 2007). From north to south, the Twillingate Granite pluton has been suggested to have experienced elevated grade of deformation (Strong and Payne, 1973; Payne, 1974; Williams and Payne, 1975; Williams et al., 1976). Yellow stars indicate estimate sampling locations in this study (detailed GPS sample locations see Table 3.1) whereas pink circles for samples from prior studies of Williams et al. (1976) and Elliott et al. (1991).



3.4 Sampling locations

To establish a more comprehensive geochronological understanding of the Coastal Complex (CC), we sampled several plagiogranite intrusions from north to south to establish an age or age range in the plutons and place a younger limit on the mafic volcanics and crust they intrude within the CC (see Table 3.1 for summary of detailed sample GPS locations). We also attempted to improve our understanding on the temporal and tectonic correlations between the CC and Twillingate Granite terranes to place more precise younger limits of the age of the Sleepy Cove volcanics. The Twillingate Granite is interpreted as one of the earliest oceanic island arc felsic plutons intruding into the Sleepy Cove volcanic basement in the juvenile stage of the Notre Dame arc (Williams et al. 1976; Nelson and Casey, 1979; Elliott et al., 1991). Four plagiogranite samples were collected from the northern CC including three from the Green Gardens Trail intrusion (CC-GG1-17ERS, CC-GG3-17ERS and CC-GG4-17ERS) and one from the Trout River intrusion (CC-TR1-17ERS) that was similarly sampled by Mattinson (1975a, b) (Figs. 3.1 and 3.2a). Seven samples were collected from the southern part of the CC in the Little Port area that included three from the Murray Mountain intrusion (CC-MM2-17ERS, CC-MM3-17ERS and CC-MM4-17ERS), three from the Southhead Lighthouse Trail intrusion (CC-LHT1-17ERS, CC-LHT1B-17ERS, CC-LHT5-17ERS) and one from the Tortoise Mountain intrusion in Blow Me Down Provincial Park (CC-BMDP1-17ERS) (Figs. 3.1 and 3.2b) that was similarly sampled by Jenner et al. (1991). From the Notre Dame Subzone in Central Newfoundland, three samples of the Twillingate Granite in South Twillingate Island (S.TW'G-1-17ERS, S.TW'G-2-17ERS and S.TW'G-5-17ERS) were collected to facilitate the age comparisons between the forearc and arc massif (Fig. 3.3).

Sample Label	Total Zircon Grains Collected	Zircon Type	Latitude (°)	Longitude (°)
Green Gardens Trail I	Intrusion, Northern CC (3 samples)		
CC-GG1-17ERS	20	Type 2	49.49867	-58.07512
CC-GG3-17ERS	30	Type 2	49.49920	-58.07502
CC-GG4-17ERS	30	Type 2	49.49873	-58.07495
Trout River Intrusion ,	, Northern CC (1 sample))		
CC-TR1-17ERS	20	Type 2	49.48591	-58.12274
Murry Mountain Intru	usion, Southern CC (3 sa	mples)		
CC-MM2-17ERS	22	Type 2	49.12831	-58.37106
CC-MM3-17ERS	35	Type 2	49.12822	-58.37087
CC-MM4-17ERS	39	Type 2	49.12822	-58.37087
Southhead Lighthouse	Trail Intrusion, Souther	rn CC (3 sam	nples)	
CC-LHT1-17ERS	27	Type 1	49.12612	-58.39805
CC-LHT1B-17ERS	17	Type 1	49.12607	-58.39804
CC-LHT5-17ERS	60	Type 1	49.12623	-58.39553
Tortoise Mountain Int	rusion, Southern CC (1 s	ample)		
CC-BMDP1-17ERS	75	Type 1	49.09127	-58.36525
Twillingate Granite, N	lotre Dame Subzone (3 sa	mples)		
S.TW'G-1-17ERS	23	Type 2	49.66057	-54.75795
S.TW'G-2-17ERS	31	Type 2	49.67006	-54.75795
S.TW'G-5-17ERS	37	Type 2	49.60225	-54.70303

Table 3.1 Summary of samples collected in this study

3.5 Analytical procedures

3.5.1 Zircon separation

Zircon grains were extracted from bulk rock samples by using conventional zircon separation techniques including crushing, sieving, free-fall magnetic separation, water and MI (Methylene Iodide) separation. A Franz Isodynamic separator was used to concentrate non-magnetic grains, among which individual zircon grains were handpicked under a polarizing microscope. Picks were regardless of zircon size and appearance to avoid potential artificial bias (Sláma and Košler, 2012; Košler et al., 2013). These handpicked grains were mounted in epoxy

resin and polished at 3000 grit to expose a flat inner surface, which was finally cleaned with 0.2%

HCl to reduce potential surface contamination.

The appearance of individual zircon crystals from each sample was examined with a petrographic microscope under plane polarized light (Fig. 3.4). Zircon grains collected could be divided into two different types (Type 1 and 2) based on their shape, size and texture. However, none of these grains shows petrographic evidence of inherited cores because oscillatory rim zoning was either not observed (e.g., Fig. 3.4c) or concordant with inner prismatic cores (e.g., Fig. 3.4f).

Fig. 3.4 Photomicrographs of representative zircon populations and crystals analyzed by LA-ICP-MS under plane polarized light from this study. Individual dates given in each photomicrograph are high precision ²⁰⁶Pb/²³⁸U dates (2s) with discordances indicated below within parentheses (red). Representative type 1 zircon including (a-c) typical zircon populations and single crystal of prismlike, transparent to semi-transparent, euhedral to subhedral appearance, and individual zircon grains with (d-e) murky brown domains and unknown mineral or fluid inclusions, and (f) concordant marginal oscillatory zoning and highly altered/damaged domains. Representative type 2 zircon including (g-h) typical zircon populations that are overall prism-like, semi-transparent to opaque, subhedral to anhedral, and individual zircon grains with (i) irregular and anhedral morphology and ubiquitous microfractures and inclusions, (j) typical elongated shape and welldeveloped metamict or alteration domains and microstructures, (k) marginal oscillatory zoning, and (l) anhedral shape with sponge-like surface and well-developed cracks.


Type 1 zircon grains are overall prism-like, transparent to semi-transparent, and euhedral to subhedral with rare or no inclusions (Fig. 3.4a-f). The long axes of type 1 zircon including broken and intact grains analyzed by LA-ICP-MS vary from approximately 200 to 400 microns with aspect ratios ranging between 2 and 5. Although microfractures are common, they appear to be randomly distributed, rarely cut through the entire zircon grain, and not to occur with narrow murky-brown or dark bands (e.g., Fig. 3.4d), indicating that these microfractures are more likely to have been induced by mechanical crushing during sample processing (e.g., Nasdala et al., 1996; Geisler et al., 2002; Takehara et al., 2018). Inclusions are rare, but if existing, they appear as black and dark brown pods and rods, or more common as colorless elongated rods of tens of microns length (e.g., Fig. 3.4e). Murky and dark brown domains likely originating by alteration are common but appear as isolated patches that only occupy part of the exposed (e.g., Fig. 3.4e and f). On Type 1 zircon, ablations spots could be easily isolated to clean, intact cores, away from cracks, alteration domains and unknown inclusions that may cause age mixing, Pb loss and/or common Pb contamination (see Table 3.1).

Type 2 zircon grains are overall semi-transparent to opaque and subhedral to anhedral with well-developed cracks, inclusions and alteration domains (Fig. 3.4g-l). Although still prism-like, type 2 zircon grains are characterized by irregular, subangular to subrounded edges. Compared to type 1, type 2 zircon is morphologically smaller and more elongated with brown to dark brown domains nearly occupying the entire exposed surfaces (e.g., Fig. 3.4j). The long axes of type 2 zircon grains including intact and broken crystals analyzed vary from approximately 100 to 700 microns with aspect ratios ranging between 1 and 7. Microfractures ubiquitously exist with murky-brown or dark bands (Fig. 3.4i-k) and suggest variable degrees of hydrothermal alteration along them. Inclusions are very common, and they appear as colorless, red, brown and/or dark brown pods and rods with their length varying from several to tens of microns (Fig. 3.4i-k). Because of the ubiquitous existence of cracks, murky brown domains and inclusions, as well as the relatively smaller size and elongated morphology, single spots analyzed by LA-ICP-MS on type 2 zircon can inevitably encompass parts of multiple domains and structures including rim, core, metamict and/or alteration region, inclusion, and microfracture that may yield complicated mixing results. Individual dates, particularly those highly discordant ones, revealed by single ablation spots, therefore, were used and interpreted with caution as they may reflect a combination result of age mixing, Pb loss and/or common Pb contamination. It is notable that zircon grains collected from the three samples of Twillingate Granite, although morphologically smaller, are apparently less altered than those from the CC samples (e.g., Fig. 3.4h vs. 3.4g) implying a more complicated tectonic/hydrothermal history. Furthermore, zircon grains from the three Twillingate samples do not show contrasting appearance nor distinct internal textures as observed by Williams et al. (1976), although one of them (S.TW'G-5-17ERS) is from moderately to highly deformed southern region, whereas the other two (S.TW'G-1-17ERS and S.TW'G-2-17ERS) from the relatively undeformed northern area of the intrusion (see Fig. 3.3).

3.5.2 LA-ICP-MS analysis

Zircon U-Pb isotopic analysis was carried out on a Varian 810 quadruple inductively coupled plasma-mass spectrometer (ICP-MS) equipped with a Photon Machines Excite 193 nm wavelength laser ablation system in the University of Houston ICP Lab. The overall LA-ICP-MS operational conditions and parameters, standard bracketing techniques, calibration and check standards chosen for data reduction, and data processing procedures are similar to those described in Yan and Casey (2020). Laser ablation operational parameters included a 25-µm ablation spot, a fluence of 3.95 J/cm² and a repetition rate of 10 Hz. A single LA-ICP-MS

acquisition lasted 60 seconds including background determination of the first 15 seconds, sample ablation time of the following 30 seconds with measurements of ²⁰²Hg, ²⁰¹Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, and ²³⁸U, and wash-out delay of the last 15 seconds before the next acquisition. The same standard bracketing techniques were employed for each analytical session by alternating between standards and unknowns. Specifically, a single analytical session starts with three analyses of standard Peixe followed by three analyses of standard FC5z, and the session ends with three analyses of FC5z followed by three analyses of Peixe. In between the starting and end standard suites, a group of 6-8 analyses (depending on availability of total zircon crystals picked for each sample) including one Peixe and one FC5z immediately followed by 4-6 unknowns were analyzed successively until all zircon grains from the same sample have been measured. Peixe with an accepted ID-TIMS value of 564 ± 4 Ma (Dickinson and Gehrels, 2003) was used as calibration standard and FC5z with an accepted ID-TIMS value of 1099.0 ± 0.6 Ma (Paces and Miller, 1993) as secondary standard. We conducted one shot per zircon crystal. The number of zircons (N) shots per sample were based on sample yields and availability of individual zircon crystals that could be picked (Table 3.1 and 3.2).

3.5.3 Data processing and screening

Raw isotopic intensities were reduced off-line by using GLITTER (Griffin, 2008) with Peixe being set as the "reference material". Each analytical session was reduced separately but with an identical protocol. In general, rise time interval of every single analysis from 0 to 14 seconds and 17 to 43 seconds were chosen respectively for background and sample signal intensity integration. A linear fit of background interpolation was applied. The initial 2 seconds after ablation starts and the final 2 seconds before the ablation ends were excluded purposely to avoid potential surface contamination and signal tail caused by washout of aerosol from the chamber,

respectively (e.g., Solari et al., 2010). It is important to note that integration intervals of background and sample signal intensity adopted in a single analytical session were required to be consistent relative to rise time to avoid any unintentional biasing caused by time drift and/or isotopic differentiation. After signal window determination, $^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$ ($^{235}U = ^{238}U/137.88$ after Jaffey et al., 1971) and $^{207}Pb/^{206}Pb$ ratios were then inspected in turn for each analysis to reject any with abnormal signals (i.e., multiple highly spiky points) that may be caused by the inclusions and/or cracks. A quadratic fit of calibration was used to correct fractionations of secondary standards and unknowns for every analytical session. No common Pb correction was performed. The corrected U-Pb isotopic ratios and dates are reported in Table A3.1-3.14 of Appendix with 2 sigma (2s) absolute uncertainties.

Analyses from every sample were plotted either in a Wetherill diagram to produce a concordia age or in a Tera-Wasserburg diagram to yield a lower intercept age. ²⁰⁶Pb/²³⁸U weighted mean age plots were also presented, but only accompanied with Wetherill plot because analyses of high discordance (e.g., datasets plot in Tera-Wasserburg plot) are at increased risk of being affected by common Pb contamination resulting in less geologically meaningful ages. If analyses from the same intrusions are repeatable, we integrated age results of different samples collected from the same plutons to produce a more precise composite concordia or intercept age. IsoplotR online version (Vermeesch, 2018) was used for plotting Wetherill or Tera-Wasserburg concordia age diagrams and ²⁰⁶Pb/²³⁸U weighted mean age diagrams, as well as for calculations of concordia ages, intercept ages and ²⁰⁶Pb/²³⁸U weighted mean ages. All uncertainties of individual analyses are reported at the 2s level. Age results calculated including concordia, intercept and weighted mean age by IsoplotR are presented at the 95% confidence interval (i.e., near 2s) with uranium decay constant errors included in uncertainty estimates (Mattinson, 1987; Ludwig, 2000; Horstwood et al., 2016). Model-2 solutions have been applied to some discordia lines and intercept age calculations when there was low probability of line fit (i.e., < 0.15) (see Ludwig, 2008). However, concordia or intercept age is preferentially reported in this study as they weigh both 206 Pb/ 238 U and 205 Pb/ 237 U or 207 Pb/ 206 Pb and 238 U/ 206 Pb ratio and thus, provide a more precise and more objective result (e.g., Spencer et al., 2016; Yan and Casey, 2020).

3.5.4 Secondary standard FC5z age results

FC5z with an accepted TIMS value of 1099.0 ± 0.6 Ma (Paces and Miller, 1993) was treated as check standard to independently evaluate the quality of every analytical session of this study. Furthermore, these FC5z age results from individual analytical sessions as well as the integration of all the 14 sessions reported in this study could also be used as supplements to the long-term standard record to assess the precision of U-Pb and Pb-Pb ages along with other interlaboratory analyses (Mattinson, 1987; Klötzli et al., 2009; Košler et al., 2013). The results are summarized in Table 3.2 and are plotted in Fig. 3.5. These analytical sessions yielded overall similar and comparable FC5z concordia age results of 1106.0 ± 11.0 Ma for CC-TR1-17ERS (N = 10), 1104.0 \pm 15.0 Ma for CC-GG1-17ERS (N = 10), 1097.0 \pm 6.4 Ma for CC-GG3-17ERS (N = 11), 1104.0 ± 13.0 Ma for CC-GG4-17ERS (N = 11), 1096.1 ± 5.3 Ma for CC-BMDP1-17ERS (N = 21), 1103.4 \pm 8.7 Ma for CC-LHT1-17ERS (N = 12), 1103.6 \pm 9.0 Ma for CC-LHT1B-17ERS (N = 9), 1100.4 ± 7.3 Ma for CC-LHT5-17ERS (N = 16), 1098.4 ± 5.7 Ma for CC-MM2-17ERS (N = 10), 1103.5 ± 7.0 Ma for CC-MM3-17ERS (N = 13), 1097.0 ± 11.0 Ma for CC-MM4-17ERS (N = 14), 1088.6 \pm 5.9 Ma for S.TW'G-1-17ERS (N = 10), 1099.0 \pm 13.0 Ma for S.TW'G-2-17ERS (N = 13) and 1092.1 \pm 7.6 Ma for S.TW'G-5-17ERS (N = 13), all of which are within 2% of the accepted value of 1099.0 \pm 0.6 Ma reported by Paces and Miller (1993). The MSWD (of concordance) of the 14 sessions vary from 0.0014 to 4.40 but dominantly lie between 0.2 and

2 (Table 3.2). We also obtained an integration standard result of all the 14 analytical sessions that yielded an extremely accurate concordia age of 1097.9 \pm 2.2 Ma and a nearly identical weighted mean age of 1098.1 \pm 2.4 Ma (N = 173) with a near unity MSWD (of concordance) of 1.2 comparable to the TIMS recommended 1099.0 \pm 0.6 Ma age. In general, ²⁰⁶Pb/²³⁸U weighted mean ages are less scattered, slightly older, less accurate, and have slightly higher errors when compared with their corresponding concordia age results.

Fig. 3.5 Concordia age offsets (%) for the replicate LA-ICP-MS measurements of secondary standard FC5z with respect to the accepted ID-TIMS $^{207}Pb/^{206}Pb$ age of 1099.0 ± 0.6 (Paces and Miller, 1993) for each sample analytical session and their integration as listed at the bottom (also see Table 3.2). Vertical bar length represents the 2-sigma error (2s %) uncertainty of the LA-ICP-MS concordia age during each of the analytical sessions and their integration. For each zircon reference material analyzed during a sample interval, age offset is generally within 1-2% of the accepted ID-TIMS age based on N between 9 and 21. Note the highly comparable and precise check standard age results of individual analytical sessions, and the extremely precise integration age of the 173 analyses from the 14 analytical sessions.



Table 3.2 Summarized U-Pb age results of secondary standard FC5z measured together with the 14 samples in each analytical session and integration of all the 14 analytical sessions. Uncertainties for concordia age and weighted mean age are both quoted at 95% confidence interval. Note N points depend on the total numbers of zircon analyzed for each sample (see standard-sample bracketing technique in Section 3.4.2). The accepted age for secondary standard FC5z is 1099.0 \pm 0.6 Ma (Paces and Miller, 1993) Accuracy (%) = |((Measured age)/(Accepted age) - 1)| * 100

Analytical session	N	Concordia age					Weighted mean age of ²⁰⁶ Pb/ ²³⁸ U				
		Age (Ma)	Error (Ma)	MSWD (of con.)	Probability	Accuracy (%)	Age (Ma)	Error (Ma)	MSWD	Probability	Accuracy (%)
CC-TR1-17ERS	10	1106.0	11.0	1.13	0.29	0.64	1109.0	13.0	0.18	1.00	0.91
CC-GG1-17ERS	10	1104.0	15.0	0.0014	0.97	0.45	1104.0	16.0	0.19	1.00	0.45
CC-GG3-17ERS	11	1097.0	6.4	0.36	0.55	0.18	1096.9	7.5	0.82	0.61	0.19
CC-GG4-17ERS	11	1104.0	13.0	1.70	0.19	0.45	1100.0	14.0	0.92	0.51	0.09
CC-MM2-	10	1098.4	5.7	1.50	0.23	0.05	1097.5	5.9	0.54	0.85	0.14
17ERS											
CC-MM3-	13	1103.5	7.0	0.22	0.64	0.41	1104.6	8.0	0.23	1.00	0.51
17ERS											
CC-MM4-	14	1097.0	11.0	0.89	0.34	0.18	1094.0	12.0	0.65	0.82	0.45
17ERS											
CC-LHT1-	12	1103.4	8.7	0.27	0.60	0.40	1105.0	10.0	0.21	1.00	0.55
17ERS											
CC-LHT1B-	9	1103.6	9.0	1.70	0.19	0.42	1100.0	14.0	1.3	0.25	0.09
17ERS											
CC-LHT5-	16	1100.4	7.3	4.40	0.037	0.13	1105.9	8.8	0.60	0.88	0.63
17ERS											
CC-BMDP1-	21	1096.1	5.3	0.049	0.82	0.26	1095.7	6.3	0.26	1.00	0.30
17ERS											
S.TW'G-1-	10	1088.6	5.9	0.095	0.76	0.95	1087.8	6.8	0.41	0.93	1.02
17ERS											
S.TW'G-2-	13	1099.0	13.0	1.60	0.20	0.00	1103.0	14.0	0.19	1.00	0.36
17ERS											
S.TW'G-5-	13	1092.1	7.6	0.096	0.76	0.63	1092.9	9.1	0.54	0.89	0.56
17ERS											
Integration	173	1097.9	2.2	1.20	0.27	0.10	1098.1	2.4	0.57	1.00	0.08

In summary, the individual analytical sessions, as well as the integration of the 14 analytical sessions, all yielded reliable secondary standard age results with the accuracy within 1% of the accepted TIMS values and uncertainty of both concordia and weighted mean age within 1.3% (Table 3.2). Scatter of the individual data points (e.g., error ellipses in concordia plots and error bars in weighted mean plots) and slightly older and younger age results of FC5z can also be attributed partially to its internal heterogeneity (of a natural zircon), matrix effects and ablation related processes (Black, 2005; Chang et al., 2006; Klötzli et al., 2009), that are irrelevant with respect to instrumental conditions or data reduction methods.

3.6 Zircon U-Pb LA-ICP-MS age results

New LA-ICP-MS ages are summarized below in Table 3.3. Some of these results were obtained from samples collected close to locations with previously published ID-TIMS-derived ages and uncertainties (see Figs. 3.1-3.3) that allow for direct comparison, re-examination and cross-checking. We have recalculated (see Table 3.4) the ages and uncertainties previously reported for the Coastal Complex (CC) and the Twillingate Granite with modern developed techniques and community-based data treatment standards. Yan and Casey (2020) addressed the significance and necessity to review and recalculate previously published legacy date/age results before proceeding to further comparisons or geologic application and interpretation. In the prior CC and Twillingate area, U-Pb zircon age results reported are all upper intercept ages yielded by poorly constrained discordia lines of very few (commonly 2 to 4) data points. Understandably, if fewer minerals are being dated or if there is only mild discordance, there is an increased likelihood that the points may fall on a straight line. The limited numbers of analyses also allow no redundant check of internal isotopic equilibrium and true co-genericity of the analyzed minerals (e.g., Ludwig, 2008; Heri et al., 2015). Furthermore, these discordia lines calculated would have low reliability

but very high probability of line fit especially 2-point discordias because any two points can fit a straight line (i.e., probability of line fit is always 1). In these cases where only two or a few analyses are available, the quality of single measurements will be extraordinarily important as any artificial bias or random artifacts introduced would readily propagate to the final age calculated, leading to high risk of producing age results with ambiguous geological meaning or unrealistic uncertainty assignments.

In some early studies, individual U-Pb and Pb-Pb isotopic ratios were not published (e.g., Williams et al., 1976 for Twillingate Granite in Notre Dame Subzone and Kurth et al., 1998 for the Western Lewis Hills in CC). In order to re-evaluate these discordia lines and intercept ages, we recalculated the isotopic ratios and errors based on the U-Pb and Pb-Pb ages reported. Considering early U-Pb zircon geochronological studies on samples from CC and Twillingate Granite were based on similar methods for sample processing and ID-TIMS measurements (e.g., Krogh, 1973, 1982; Krogh and Davis, 1975), we have assumed that individual U-Pb and Pb-Pb isotopic ratios and date uncertainties, if without specification in the original publications, were reported at the 2s level. It is notable that Elliott et al. (1991) only presented a range of uncertainties for ²⁰⁷Pb/²⁰⁶Pb (0.04-0.10%) and Pb/U ratio (0.02-0.29%) at 1s level. To simplify, we averaged the lowest and highest error, and then multiplied by 2 to calculate an uncertainty of 0.14% and 0.31% (2s error) respectively for ²⁰⁷Pb/²⁰⁶Pb and Pb/U isotopic ratios for our recalculations (see details below).

Many studies have emphasized the importance and necessity of more completely conducting error analysis and propagation during measurement and subsequent data reduction (e.g., Mattinson, 1987; Ludwig, 2000; Horstwood et al., 2016). Yan and Casey (2020) suggested consistent underestimation of age uncertainty results calculated without including uranium decay constant errors from prior ID-TIMS studies on the Bay of Islands Ophiolite Complex. Therefore, we also recalculated earlier ID-TIMS age and uncertainties from the Coastal Complex and Twillingate Granite by using IsoplotR (Vermeesch, 2018). Uncertainties recalculated by not including uranium decay constant errors are indicated without brackets whereas those recalculated by including uranium decay constant errors are reported within brackets. If only one age error is shown, this indicates that the intercept age errors with and without uranium decay constant errors included are almost equivalent. Furthermore, recalculations in IsoplotR show that the probability of discordia line fits for some prior datasets are very low (e.g., Fig. 3.10c), so Model-2 solution has been applied to construct more reliable discordia lines (see Vermeesch, 2018 for more details). Below we present our newly obtained LA-ICP-MS ages based on a larger population of zircon analyses and also review each prior ID-TIMS study, results of recalculating upper intercept ages and uncertainties with community-derived data treatment techniques, software and standards, and the recalculated age uncertainties with and without uranium decay constant errors included.

Table 3.3 Summarized U-Pb age results for each of the 14 plagiogranite samples, as well as composite age of cogenetic samples with similar ages and from the same pluton or intrusion. Uncertainties are quoted at 95% confidence interval. Bolded age indicates proposed age for each plagiogranite pluton

¹ Lower intercept age calculated within Tera-Wasserburg diagram

* Lower intercept age calculated by applying Model-2 solution (see Vermeesch, 2018)

			Concordia/Inter	Weighted mean age of ²⁰⁶ Pb/ ²³⁸ U				
Sample Label	N	Concordia (Ma)	Intercept ¹ (Ma)	MSWD	Probability	Age (Ma)	MSWD	Probability
Northern Coastal Comp								
CC-GG1-17ERS	20		$513.6 \pm 7.6^{*}$	2				
CC-GG3-17ERS	30	513.5 ± 4.3		0.7	0.4	514.3 ± 4.7	0.2	1.0
CC-GG4-17ERS	30	514.7 ± 3.9		0.7	0.4	514.3 ± 4.1	1.0	0.5
GG Composite	80		514.0 ± 2.8	0.8				
CC-TR1-17ERS	20		514.3 ± 7.9	1.0				
Southern Coastal Complex								
CC-MM2-17ERS	22		$512.1 \pm 7.5^{*}$	5.0				
CC-MM3-17ERS	35		514.2 ± 2.7	1.0				
CC-MM4-17ERS	39		511.1 ± 4.3	0.4				
MM Composite	96		$513.7 \pm 2.0^{*}$	2.0				
CC-LHT1-17ERS	27	504.2 ± 2.0		0.7	0.4	503.8 ± 2.2	1.1	0.4
CC-LHT1B-17ERS	17		$504.6\pm4.6^*$	2.0				
CC-LHT5-17ERS	60	503.8 ± 1.8		3.3	0.1	504.5 ± 1.9	0.46	1.00
LHT Composite	104		504.5 ± 1.5	0.8				
CC-BMDP1-17ERS	75	504.9 ± 1.6		0.4	0.5	504.7 ± 1.8	1.0	0.6
Twillingate Granite in Notre Dame Subzone								
S.TW'G-1-17ERS	23	504.7 ± 2.2		1.1	0.3	504.4 ± 2.4	1.4	0.1
S.TW'G-2-17ERS	31	502.4 ± 7.4		0.6	0.5	501.9 ± 7.6	1.1	0.4
S.TW'G-5-17ERS	37	504.0 ± 2.9		0.01	0.9	504.0 ± 3.1	1.6	0.02
S.TW'G Composite	91	504.3 ± 1.8		0.7	0.4	504.2 ± 1.9	1.3	0.02

3.6.1 Northern Coastal Complex

3.6.1.1 Green Gardens Trail Intrusion

Analyses of the two samples from the Green Gardens Trail (GG) intrusion yielded similar and comparable concordia and weighted mean age results (Table 3.3) respectively of 513.5 \pm 4.3 Ma and 514.3 \pm 4.7 Ma (N = 30) for CC-GG3-17ERS (Fig. 3.6a), and 514.7 \pm 3.9 Ma and 514.3 \pm 4.1 Ma (N = 30) for CC-GG4-17ERS (Fig. 3.6c). ²⁰⁶Pb/²³⁸U date histograms of the two samples show similar normal distribution pattern with both samples exhibiting identical relative probability peak at ca. 515 Ma (red dashed lines in Fig. 3.6d and f). However, four analyses from sample CC-GG1-17ERS are highly discordant with discordance of ~50%. Tera-Wasserburg diagram is accordingly presented yielding a lower intercept of 513.6 \pm 7.6 Ma (N = 20) (Fig. 3.6e). Because the three GG samples were collected from a single plagiogranite intrusion, we integrated all the 80 analyses and plotted them in a Tera-Wasserburg plot yielding a precise 3-sample composite lower intercept age of 514.0 \pm 2.8 Ma (N = 80) to represent crystallization age of this plagiogranite intrusion.

Fig. 3.6 Wetherill/Tera-Wasserburg and ranked 206 Pb/ 238 U weighted mean age plots, as well as 206 Pb/ 238 U date histograms, of samples collected from Green Gardens Trail intrusion (GG) in the north of Coastal Complex (Fig. 3.1 and 3.2a) for (a-b) CC-GG3-17ERS, (c-d) CC-GG4-17ERS and (e) CC-GG1-17ERS from the same plagiogranite intrusion, and (f) composite of the three GG samples yielding a lower intercept age of 514.0 \pm 2.8 Ma. Black error ellipses and black error bars for individual data points are shown at 2s level. Age results calculated by IsoplotR are presented at the at the 95% confidence interval with uranium decay constant errors included. Only lower intercept age has been reported in Tera-Wasserburg diagram as the upper intercept age is likely of limited geological significance (see text for discussion). Note symbols and age calculation criteria used here are the same for the following plots presented. Model-2 solution has been applied in (e) for discordia line and intercept age calculation because of the low probability of line fit (see Ludwig, 2008). In (f), the 3-sample composite age is calculated by including all the 80 analyses yielding a precise concordia age of 514.0 \pm 2.8 Ma to represent the crystallization age of this intrusion.



3.6.1.2 Trout River Intrusion

20 zircon grains were analyzed for sample CC-TR1-17ERS yielding a broad discordance range between 0.83% and 61%. These analyses, uncorrected for common Pb, were plotted along a single mixing line between common Pb and radiogenic end members in Tera-Wasserburg diagram yielding a lower intercept age of 514.3 ± 7.9 Ma (N = 20) to represent the crystallization age of this intrusion (Fig. 3.7a and Table 3.3). MSWD of the discordia line calculated is 1. Apparently, all the zircon analyses lie along a mixing line intersecting with the concordia curve at a high angle and no "younger" data points plot at the right-hand side of the discordia line presented, indicating that there is little or negligible radiogenic Pb loss, or alternatively, the Pb loss effect was somewhat overprinted by common Pb contamination.

Mattinson (1975a) also provided an ID-TIMS U-Pb age of the Coastal Complex by dating a single trondhjemite collected from a larger plagiogranite intrusion within mafic plutons of the "Trout River ophiolite" (see Fig. 3.2a). Two zircon fractions were analyzed by methods similar to those described by Krogh (1973), yielding two comparable 207 Pb/ 206 Pb dates of 507 ± 4 and 506 ± 7 Ma (2s error), and much younger 206 Pb/ 238 U dates of 489 and 480 Ma. Although Mattinson (1975a) noted a "normal" pattern of discordance for the two zircon analyses (i.e., the more-magnetic fractions contain more uranium and are slightly more discordant than the corresponding less-magnetic fractions), such "pattern" has not been reported by other studies from the same region (e.g., Mattinson, 1976; Dunning and Krogh, 1985; Jenner et al., 1991). A plagioclase fraction from the same trondhjemite was also analyzed and was used for common Pb correction in the two zircon fractions.

In the concordia plot presented by Mattinson (1975a), the two slightly discordant zircon fraction analyses are shown as points enclosed by hexagons representing errors estimated

at the 95% confidence level. Then the poorly constrained (two-point) discordia curve was constructed, yielding a "precise" upper intercept age of 508 ± 5 Ma but without uncertainty level indicated. Mattinson (1975a) did not report the lower intercept age because the discordia line was interpreted by him to be caused by multiple episodes of Pb loss or continuous Pb diffusion, and therefore the lower intercept may not have any geological significance. Our replotting in IsoplotR for the recalculated isotope ratios and errors yielded a slightly older, less precise upper intercept of 514 ± 31 Ma, and a lower intercept of 169 ± 403 Ma (MSWD = 1) (Fig. 3.7b and Table 3.4). We suggest that the much lower uncertainty of ± 5 Ma reported by Mattinson (1975a) is partly because of not including uranium decay constant errors typical of intercept age uncertainty reporting in older age reporting (e.g., Mattinson, 1987). It is important to note that, as mentioned before, the 2-point discordia recalculated here and presented by Mattinson (1975a) both are of doubtful reliability and thus, likely have limited geological significance. However, compared to the upper intercept age of 508 ± 5 Ma originally reported, our recalculated ca. 514 Ma age by using modern community-derived techniques appears to be more rational, and although low in precision is more comparable with our new LA-ICP-MS age of 515.8 ± 7.9 Ma from sample CC-TR1-17ERS (Fig. 3.7a) that was also collected from the same intrusion as the trondhjemite sampled by Mattinson (1975a) (see Figs. 3.1 and 3.2a).

Fig. 3.7 Age results for the two samples collected from the Trout River intrusion in northern CC (Fig. 3.1 and 3.2a) including (a) Tera-Wasserburg plot plagiogranite CC-TR1-17ERS analyzed in this study, and (b) Wetherill concordia diagram showing the individual data ellipses (2s error) and best-fit discordant line recalculated using IsoplotR for two zircon fraction analyses from trondhjemite of Mattinson (1975a) yielding an upper intercept age of 514 ± 31 Ma. Note a series of highly discordant zircon analyses (N = 20) from sample CC-TR1-17ERS produces a similar, but more precise lower intercept age of 514.3 ± 7.9 Ma. Note that the U-Pb isotopic ratios and uncertainties were not provided by Mattinson (1975a), so they are recalculated based on U-Pb dates and errors reported, which here are assumed to be $\pm 0.5\%$ (2s error) (see notes included below his Table 1). The overall similar and comparable age results of sample CC-TR1-17ERS analyzed in this study and our recalculation for trondhjemite 72-9 from Mattinson (1975a), as well as their intimate sampling location of a likely cogenetic origin, together indicate that the Trout River intrusion crystallized at 514.3 ± 7.9 Ma. However, it is important to note that because individual datasets of prior studies reported by Mattinson (1975a), Williams et al. (1976), Elliott et al. (1991), Jenner et al. (1991) and Kurth et al. (1998) only encompass very few analyses (2-4 data points), they lack statistical resolution resulting in doubtful reliability of the discordia lines and intercept ages calculated (see Ludwig, 2008 for details).



3.6.2 Southern Coastal Complex

3.6.2.1 Murray Mountain Intrusion

Zircon populations of the three samples from Murray Mountain intrusion (Fig. 3.2b) are dominated by type 2 zircon and yielded comparable intercept ages on Terra-Wasserburg plots (Table 3.3) respectively of 512.1 ± 7.5 Ma (N = 22) for CC-MM2-17ERS (Fig. 3.8a), 514.2 ± 2.7 Ma (N = 35) for CC-MM3-17ERS (Fig. 3.8b) and 511.1 ± 4.3 Ma (N = 39) for CC-MM4-17ERS (Fig. 3.8c). Because the three samples are from the same intrusion, we integrated all analyses to produce a more precise, composite intercept age of 513.7 ± 2.0 Ma (N = 96) to represent the crystallization age of this intrusion.



Fig. 3.8 Tera-Wasserburg plot for samples collected from Murray Mountain intrusion (MM) in the south of Coastal Complex (Fig.3.1 and 3.2b) for (a) CC-MM2-17ERS, (b) CC-MM3-17ERS, (c) CC-MM4-17ERS, and (d) composite of the three samples. Note zircon populations collected from these three samples are primarily composed of type 2 zircon (e.g., Fig 3.4g) yielding abundant highly discordant dates (i.e., discordance > 15%). Model-2 solution has been applied in (a) and (d) for discordia line and intercept age calculation because of the low probability of line fit (see Ludwig, 2008). In (d), a lower intercept age of 513.8 ± 2.8 Ma (N = 96) is calculated by integrating all analyses from the three cogenetic samples to represent the crystallization age of Murray Mountain intrusion in southern Coastal Complex.

3.6.2.2 Southhead Lighthouse Trail Intrusion

The three plagiogranites from Southhead Lighthouse Trail intrusion are dominated by type 1 zircon and yielded similar age results (Table 3.3) respectively of 504.2 ± 2.0 Ma (N = 27) for CC-LHT1-17ERS (Fig. 3.9a), 503.8 ± 1.8 Ma (N = 60) for CC-LHT5-17ERS (Fig. 3.9c) and 504.6 ± 4.6 Ma (N = 17) for CC-LHT1B-17ERS (Fig. 3.9e). We also produced the ²⁰⁶Pb/²³⁸U weighted mean ages of 503.8 ± 2.2 Ma (N = 27) for CC-LHT1-17ERS (Fig. 3.9a) and 504.5 ± 1.9 Ma (N = 60) for CC-LHT5-17ERS (Fig. 3.9c), which are consistent within error with each other and with their corresponding concordia ages. Furthermore, the relative probability of concordant ²⁰⁶Pb/²³⁸U dates of samples CC-LHT1-17ERS and CC-LHT5-17ERS both occur at ca. 505 Ma. Because the three samples are from the same intrusion, we similarly produced a more precise 3sample composite intercept age of 504.5 ± 1.5 Ma (N = 104) by including all analyses on a Terra-Wasserburg plot (Fig. 3.9f) to represent the crystallization age of this intrusion. Fig. 3.9 Wetherill/Tera-Wasserburg and ranked ²⁰⁶Pb/²³⁸U weighted mean age plots, together with ²⁰⁶Pb/²³⁸U date histogram, of samples collected from the Southhead Lighthouse Trail intrusion (LHT) in southern Coastal Complex (Fig. 3.1 and 3.2b) for (a-b) CC-LHT1-17ERS, (c-d) CC-LHT5-17ERS, (e) CC-LHT1B-17ERS, and (f) composite of the three samples. Note zircon populations collected from samples CC-LHT1-17ERS, CC-LHT1B-17ERS and CC-LHT5-17ERS are dominantly type 1 zircon (e.g., Fig. 3.4b) yielding mostly concordant dates with discordance $\leq 15\%$. Model-2 solution has been applied in (e) for discordia line and intercept age calculation because of the low probability of line fit (see Ludwig, 2008). Likewise, a 3-sample composite lower intercept age of 504.5 \pm 1.5 Ma is calculated to represent the crystallization age of the Southhead Lighthouse Trail intrusion.



3.6.2.3 Tortoise Mountain Intrusion

A large population of clean, euhedral, prismatic zircon grains have been collected and analyzed for the Tortoise Mountain (Blow Me Down Provincial Park) sample CC-BMDP1-17ERS, yielding an extremely precise concordia age of 504.9 ± 1.6 Ma and an identical weighted mean age of 504.7 ± 1.8 Ma (N = 75) (Fig. 3.10a and Table 3.3). 206 Pb/ 238 U dates show a narrow range and determine a typical normal distribution pattern with the peak of relative probability occurring at ca. 505 Ma (Fig. 3.10b), consistent with the concordia and weighted mean ages calculated.

Jenner et al. (1991) analyzed four zircon fractions from a single trondhjemite sample (83GD-02) by ID-TIMS also collected from the Tortoise Mountain intrusion in Blow Me Down Provincial Park (see Figs. 3.1 and 3.2b). They presented similar clustered ²⁰⁷Pb/²⁰⁶Pb dates including 504, 501 and 502 Ma for the three fractions with moderate U content (~350 ppm), and a slightly younger ²⁰⁷Pb/²⁰⁶Pb date of 498 Ma for the fraction with a relatively high U concentration (852 ppm). Two of the zircon fractions were physically abraded to mitigate Pb loss effects (Krogh, 1973, 1982), whereas the other two were not. Only ²⁰⁷Pb/²⁰⁶Pb dates without uncertainties were reported. However, the uncertainties of U-Pb and Pb-Pb isotopic ratios were provided. Based on this, 207Pb/206Pb date uncertainties were calculated here for zircon fractions as $\pm 2.2, \pm 2.1, \pm 1.9$ and \pm 2.0 Ma, respectively (Table 3.4). We also calculated the ²⁰⁶Pb/²³⁸U date with 2s error for each of the four zircon fractions respectively of 499.3 ± 1.4 Ma (No. 7, abraded), 498.1 ± 2.8 Ma (No. 8, abraded), 488.2 ± 1.6 Ma (No. 9, unabraded) and 474.2 ± 1.5 Ma (No. 10, unabraded) (Table 3.4). Because of the variable discordance of the four zircon fractions (discordance reported between 1.6 to 8%), they constructed a simple discordia line (reported 24% probability of fit), yielding an upper intercept age 505^{+3}_{-2} Ma to represent the sample crystallization age, and a lower intercept age of 106 ± 63 Ma. Using the same U-Pb isotopic ratios and uncertainties of four zircon fractions reported, we constructed a similar discordia line on the Wetherill concordia plot and calculated a similar upper intercept age of 503.6 ± 2.2 [± 2.3] Ma with a slightly younger lower intercept age of 94 ± 63 Ma (MSWD = 2) (Fig. 3.10c). Our recalculated uncertainty of ± 2.2 Ma without uranium decay constant errors included is nearly identical to the asymmetric error (+3/-2 Ma) originally reported by Jenner et al. (1991), as well as to our recalculated error of ± 2.3 Ma when uranium decay constant errors are included. The recalculated age of ca. 503.6 Ma, as well as the age of ca. 505 Ma originally reported by Jenner et al. (1991), are consistent and within error with our new LA-ICP-MS concordia age of 504.9 ± 1.6 Ma from sample CC-BMDP1-17ERS (Fig. 3.10a) that was also collected nearby from the same intrusion in the Blow Me Down Provincial Park (Figs. 3.1 and 3.2b). Therefore, we propose that the Tortoise Mountain plagiogranite intrusion in Little Port massif of the Coastal Complex crystallized at 504.9 ± 1.6 Ma.



Fig. 3.10 Age results for the two samples collected from the Tortoise Mountain intrusion of southern CC in Blow Me Down Provincial Park (Fig.3.1 and 3.2b) including (a) Wetherill and ranked ²⁰⁶Pb/²³⁸U weighted mean age plots and (b) ²⁰⁶Pb/²³⁸U date histogram for plagiogranite CC-BMDP1-17ERS analyzed in this study, and (c) Wetherill concordia diagram showing the individual data ellipses (2s error) and best-fit discordant line recalculated using IsoplotR for four zircon fraction analyses from trondhjemite of Jenner et al. (1991) yielding an upper intercept age of 503.6 \pm 2.2 [\pm 2.3] Ma. Note that age errors are shown both within brackets where uranium decay constant errors are included and without brackets where decay constant errors are not incorporated. Note selective domain analyses on a large population of primitive magmatic zircon (N = 75) from sample CC-BMDP1-17ERS yield an extremely precise concordia age of 504.9 \pm 1.6 Ma, and an identical weighted mean age of 503.6 \pm 2.3 Ma age recalculated for trondhjemite 83GD-02 that is apparently from the same intrusion reported by Jenner et al. (1991) (see Fig. 3.1 and 3.2b). Therefore, we suggest that the Tortoise Mountain intrusion formed at 504.9 \pm 1.6 Ma.

3.6.3 Western Lewis Hills massif, the southernmost part of the Coastal Complex

Although not sampled here, Kurth et al. (1998) collected two undeformed trondhjemites from the western part of the Lewis Hills massif, but without sample locations reported. Four "magmatic" zircon fractions from trondhjemite sample WLH 22 and three from WLH 15 were obtained, both of which have low U concentrations (50-170 ppm). Kurth et al. (1998) did not publish U-Pb and Pb-Pb isotopic ratios, nor provide descriptions for zircon grains analyzed. However, individual dates reported show variable, but low discordance of zircon fractions analyzed (calculated mild discordance from 0.02 to 0.31%) with a broad 206 Pb/²³⁸U date range from 490.2 to 507.8 Ma, but more clustered 207 Pb/²⁰⁶Pb dates between 498.5 and 504.8 Ma. Kurth et al. (1998) then constructed a discordia line for each of the two samples, yielding upper intercept ages of 503.7 ± 3.2 Ma (reported MSWD = 0.7) for WLH 22 and 500.6 ± 2.0 Ma (reported MSWD = 0.8) for WLH 15, without lower intercept ages reported. Because the two intercept ages were interpreted to be "indistinguishable", an average upper intercept age of 502 Ma was finally presented as the crystallization age of this trondhjemite suite from the WLH, but without assigned uncertainty.

To evaluate their results, we recalculated the U-Pb and Pb-Pb isotopic ratios and uncertainties based on the corresponding isotopic ages reported. Because Kurth et al. (1998) did not provide uncertainty level of U-Pb and Pb-Pb ages reported, the age uncertainties reported are assumed to be at 2 sigma level here. After entering recalculated isotopic ratios into IsoplotR, we calculated two upper intercept ages of 502.4 ± 4.3 [± 4.6] Ma (MSWD = 0.06) for sample WLH 15 (Fig. 3.11a) and 503.3 ± 1.9 Ma (MSWD = 3) for sample WLH 22, which are within error with each other (Fig. 3.11b). These two recalculated ages, although comparable with the ages originally reported, also indicate somewhat underestimation of age uncertainties reported in prior studies

likely because of not including uranium decay constant errors. Because the two samples are from the same trondhjemite intrusion, we integrated the 7 analyses yielding a composite upper intercept age of 502.7 ± 1.5 [± 2.1] Ma and a lower intercept age of 159 ± 90 Ma (MSWD = 1) (Fig. 11c). Compared to the simply averaged age result of 502 Ma, we propose that the pooled upper intercept age of 502.8 ± 2.1 Ma of the 7 cogenetic analyses that includes uranium decay constant errors is more appropriate and geologically meaningful. However, our calculation shows that the 7 analyses essentially plot on, or only slightly below the concordia curve, resulting in the discordia lines constructed for each and composite of the two samples sub-parallel (i.e., at very low angle) to the concordia curve (inset plots in Fig. 3.11). Therefore, these discordia lines calculated are less reliable because of the lack of any highly discordant data points. If zircon fractions analyzed are "magmatic" as originally described by Kurth et al. (1998), the oldest single ²⁰⁷Pb/²⁰⁶Pb date of 504.8 ± 0.3 Ma (Table 3.4) may also be an even more reasonable approximation for the crystallization age compared to the U-Pb dates and other younger ²⁰⁷Pb/²⁰⁶Pb dates of the same or cogenetic samples, although the multigrain dissolution technique used for ID-TIMS analysis is likely to some extent to always produce a mixed result (e.g., Mezger and Krogstad, 1997; Tichomirowa et al., 2019; Widmann et al., 2019). We also calculated a ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb weighted mean age respectively of 495.1 ± 1.2 Ma (MSWD = 20) and 500.2 ± 4.6 Ma (MSWD = 2.0) for sample WLH 15 (N = 3), 503.3 ± 1.1 Ma (MSWD = 13) and 503.1 ± 4.6 Ma (MSWD = 2.3) for sample WLH 22 (N = 4), and 499.6 \pm 0.9 Ma (MSWD = 34) and 501.8 \pm 4.5 Ma (MSWD = 4.4) for the 2-sample composite by combining all 7 analyses. Although $^{206}Pb/^{238}U$ age is preferentially reported relative to the ²⁰⁷Pb/²⁰⁶Pb age particularly for zircon younger than ~1 Ga (e.g., Spencer et al., 2016; Rioux et al., 2021), the more scattered, heterogeneous ²⁰⁶Pb/²³⁸U dates reported for the two Western Lewis Hills samples likely indicate variable extents of Pb loss. In

contrast, 207 Pb/ 206 Pb dates are more clustered and likely more resistant to Pb loss effects (e.g., Hansen and Friderichsen, 1989; Gehrels, 2011). Therefore, the 207 Pb/ 206 Pb weighted mean age of 501.8 ± 4.5 Ma calculated by integrating all the 7 analyses may have some geologic significance.

In summary, the 2-sample recalculated composite upper intercept age of 502.7 \pm 2.1 Ma (data of Kurth et al., 1998), the oldest single ²⁰⁷Pb/²⁰⁶Pb date of 504.8 \pm 0.3 Ma and the ²⁰⁷Pb/²⁰⁶Pb weighted mean age of 501.8 \pm 4.5 Ma are consistent within error with each other. However, as mentioned, the intercept age weighs both ²⁰⁶Pb/²³⁸U and ²⁰⁵Pb/²³⁷U ratio and thus, will provide a more precise and more objective result (e.g., Spencer et al., 2016; Yan and Casey, 2020). Therefore, we consider the 2-sample composite upper intercept age of 502.8 \pm 6.8 Ma calculated (Fig. 3.11c) is the best estimate for the crystallization age of the Western Lewis Hills massif in the southernmost Coastal Complex.



Fig. 3.11 Wetherill concordia diagrams for the Western Lewis Hills massif samples in the southernmost CC showing the individual data ellipses (2s error) and best-fit discordant lines recalculated using IsoplotR for analyses originally reported by Kurth et al. (1998) including (a) three zircon fractions from trondhjemite WLH 15 yielding an upper intercept age of 502.4 ± 4.3 [± 4.6] Ma, (b) four zircon fractions from trondhjemite WLH 22 yielding an upper intercept age of 503.3 ± 1.9 Ma, and (e) integration of the seven zircon fraction analyses from the two trondhjemites yielding an upper intercept age of 502.7 ± 1.5 [± 2.1] Ma. Note that the U-Pb isotopic ratios and uncertainties were not provided by Kurth et al. (1998), so they are recalculated based on U-Pb dates and errors reported. However, uncertainty level was not specified by Kurth et al. (1998), so here the date errors are assumed to be at 2s level for simplicity. The three recalculated upper intercept age of 502.7 ± 2.1 Ma, with uranium decay constant errors included, to be the best approximate of the crystallization age of Western Lewis Hills massif.

3.6.4 Twillingate Granite of Notre Dame Subzone

Although zircon populations of the three plagiogranites from Twillingate Granite are dominated by type 2 zircon showing pervasive alteration signatures (e.g., Fig. 3.4h), we still obtained similar and comparable concordia and weighted mean age results for all three samples (Table 3.3), respectively, of 504.7 \pm 2.2 Ma and 504.4 \pm 2.4 Ma (N = 23) for S.TW'G-1-17ERS (Fig. 3.12a), 502.4 \pm 7.4 Ma and 501.9 \pm 7.6 Ma (N =31) for S.TW'G-2-17ERS (Fig. 3.12c), and 504.0 \pm 2.9 Ma and 504.0 \pm 3.1 Ma (N = 37) for S.TW'G-5-17ERS (Fig. 3.12e). The three samples show similar normal ²⁰⁶Pb/²³⁸U date distribution patterns and identical relative probability peak at ca. 505 Ma (Fig. 3.12b, d and f). We produced a 3-sample composite age by integrating all the analyses yielding a precise concordia age of 504.3 \pm 1.8 Ma (N = 91) to represent the crystallization age of Twillingate Granite pluton, and a comparable weighted mean age of 504.2 \pm 1.9 Ma (Fig. 3.12g). Likewise, the ²⁰⁶Pb/²³⁸U dates define a similar normal distribution pattern with the peak occurring at ca. 505 Ma, similar to the three individual samples (Fig. 3.12h).

Fig. 3.12 Wetherill and ranked ²⁰⁶Pb/²³⁸U weighted mean age plots, as well as ²⁰⁶Pb/²³⁸U date histograms for the three "Twillingate Granites" of (a-b) S.TW'G-1-17ERS, (c-d) S.TW'G-2-17ERS and (e-f) S.TW'G-5-17ERS from the same pluton in South Twillingate Island of Notre Dame Subzone (Fig. 3.3), and (g-h) composite of the three South Twillingate samples interpreted as the crystallization age of the pluton. Note the three concordia ages, as well as the 3-sample composite age, are comparable and within error with each other including 504.7 \pm 2.2 Ma for S.TW'G-1-17ERS, 502.4 \pm 7.4 Ma for S.TW'G-2-17ERS, 504.0 \pm 2.9 Ma for S.TW'G-5-17ERS, and an extremely precise age of 504.3 \pm 1.8 Ma for the composite. Although zircon grains collected from the three Twillingate samples are dominantly composed of type 2 zircon showing significant alteration signatures, their analyses are essentially concordant producing a concordia age result for each of the three samples as well as their integration. Because all the three samples are from the same pluton, the 3-sample composite concordia age of 504.3 \pm 1.8 Ma is best to represent the crystallization age of the plagiogranite pluton cropping out nearly entire area of the South Twillingate Island in Notre Dame Subzone.



Williams et al. (1976) also collected two samples from the Twillingate Granite in South Twillingate Island for U-Pb zircon studies (Fig. 3.3). Sample WF-1-73 was collected from the moderately deformed central part of the pluton in Little Harbour and shows prominent foliation characterized by elongated, strained and recrystallized quartz phenocrysts, as well as low-grade metamorphic minerals including sericite, epidote and chlorite. Sample WF-2-73, in contrast, was collected from the northern margin of the pluton in Durrell's Arm where the deformation is mild or absent. Two non-magnetic zircon fractions were chosen from each of the two samples for isotopic analysis using the air abrasion methods of Krogh (1973). Because one fraction from sample WF-2-73 has too low radiogenic lead (reported 32.7%) compared to the other three (reported between 79.5% and 99.3%), Williams et al. (1976) treated the ${}^{207}Pb/{}^{235}U$ and ${}^{207}Pb/{}^{206}Pb$ ratios analyzed for this zircon fraction as "unreliable", and only presented the ²⁰⁶Pb/²³⁸U date for comparison purpose (i.e., not used for final age calculation) because ²⁰⁶Pb/²³⁸U ratio was considered to be less sensitive to non-radiogenic correction. Among the three analyses used for final age calculation, Williams et al. (1976) indicated that the high discordance of the zircon fraction that contains the highest U concentration of 2202.3 ppm would be caused by postcrystallization Pb loss because of radiation-induced structural damage. They did not report U-Pb and Pb-Pb isotopic ratios, nor uncertainties for individual dates, but assigned $\pm 1.5\%$ for U-Pb ages and $\pm 0.25\%$ for Pb-Pb ages at 2s uncertainty level. A three-point discordia was then constructed yielding an upper intercept age of 510^{+17}_{-16} Ma (1s error) and a lower intersection at the origin. Because the discordia line lay close to the concordia curve, Williams et al. (1976) suggested it was difficult to distinguish between episodic loss of Pb and continuous diffusion. However, they concluded that continuous diffusive loss is less possible because the data did not define a unique diffusion trajectory. Therefore, the upper intercept age of 510^{+17}_{-16} Ma (1s error) was interpreted to

be the crystallization age of the zircon, and the lower intercept to be caused by recent disturbance on U-Pb isotopic systems. Using the U-Pb isotopic ratios recalculated from the ages of three fractions reported, we also calculated a poorly constrained discordia line on the Wetherill concordia plot and a similar 2-sample composite upper intercept age of 509 ± 20 Ma with a lower intercept of 7.0 ± 40.2 Ma (MSWD = 50, Model-2 fit) (Fig. 3.13a). However, this discordia is constructed only based on three data points and has an extremely large MSWD of 50, we therefore regard this age as not reliable.
Fig. 3.13 Recalculated age results for analyses from the Twillingate pluton in Notre Dame Subzone. Wetherill concordia diagrams showing the individual data ellipses (2s error) and best-fit discordant lines recalculated using IsoplotR for analyses from the Twillingate pluton in Notre Dame Subzone of (a) the three zircon fractions including two from moderately deformed trondhjemite WF-1-73 (red) and one from undeformed trondhjemite WF-2-73 (green) of Williams et al. (1976) yielding an upper intercept age of 509 ± 20 Ma, and (b) three zircon fractions from the trondhjemite of Elliott et al. (1991) yielding an upper intercept age of $507.1 \pm 3.8 [\pm 3.9]$ Ma. Note that the U-Pb isotopic ratios and uncertainties were not provided by Williams et al. (1976), so they are recalculated based on U-Pb and Pb-Pb dates and errors reported, which were quoted at 2s level respectively as $\pm 1.5\%$ and $\pm 0.25\%$ (see their "Analytical Techniques" section). Elliott et al. (1991) did not publish uncertainties for individual isotopic ratios nor dates, but gave a range of 0.04-0.10% for Pb-Pb ratio and 0.02-0.29% for U-Pb ratio, both at 1s level. Here we averaged the highest and lowest uncertainty values and then multiplied by 2 to calculate an error at 2s level of 0.14% for Pb-Pb ratios and 0.31% for U-Pb ratios. Because of the low probability of line fit for discordia lines presented in (a), Model-2 fit has been applied to them (see Ludwig, 2008). Note the age of 509 ± 20 Ma from Williams et al. (1976) and 507.1 ± 3.9 Ma from Elliott et al. (1991), both with uranium decay constant errors included, are similar to each other, and also comparable and within larger error with our new LA-ICP-MS age of 504.3 ± 1.8 Ma.



Elliott et al. (1991) later analyzed three magnetic zircon fractions with relatively low U concentrations (80-275 ppm) from a coarse-grained Twillingate trondhjemite (84GD-06), yielding three comparable ²⁰⁷Pb/²⁰⁶Pb dates of 505, 506 and 501 Ma without uncertainties reported. They did not publish U-Pb and Pb-Pb isotopic ratio uncertainties, but did indicate an overall range of 0.04-0.10% for ²⁰⁷Pb/²⁰⁶Pb ratio and 0.02-0.29% for U-Pb ratio, both reported at 1 sigma level. They presented a 3-point discordia line (reported 54% probability of fit) with an upper intercept age of 507^{+3}_{-2} Ma (reported errors are quoted at 95% confidence level) that was interpreted to be the crystallization age of this sample. There was no lower intercept reported. Using the same three analyses from Elliott et al. (1991), we replotted these zircon results in IsoplotR and calculated a similar 3-point discordia, in which two of the data points are almost equivalent (i.e., overlap with each other). The discordia yielded an upper intercept age of $507.1 \pm 3.8 \pm 3.9$ Ma and a lower intercept of 109 ± 96 Ma (MSWD = 0.006) (Fig. 3.13b). This upper intercept age of 507.1 ± 3.9 Ma including uranium decay constant errors is also comparable and within error with the new more precise composite LA-ICP-MS age of 504.3 \pm 1.8 Ma presented here. It is notable that the recalculated uncertainties with (\pm 3.9 Ma) and without (\pm 3.8 Ma) uranium decay constant errors included are nearly identical to each other, and also similar to the original asymmetric error of +3/-2 Ma reported. The recalculated age of 507.1 ± 3.9 Ma from samples from Elliott et al. (1991), and our new LA-ICP-MS concordia ages for each sample of 504.7 ± 2.2 Ma, 502.4 ± 7.4 Ma and 504.0 \pm 2.9 Ma and resultant three-sample composite of 504.2 \pm 1.9 Ma are now all within the computed uncertainties of each other. We regard our new, more precise composite age to indicate that the Twillingate Granite crystallized at 504.2 ± 1.9 Ma. This therefore would represent a minimum age of the Sleepy Cove volcanics which the Twillingate granite intrudes (Szybinski, 1995; Swinden, 1996; Swinden et al., 1997). The geochemically and lithologically similar Lushs Bight volcanics

to the west with arc tholeiitic and boninitic pillow lavas and lack of epiclastics and felsic volcanics also have a minimum age of ca. 500 Ma (Szybinski, 1995). These ages place these basement volcanics of the Notre Dame arc terrane and the Twillingate granite within the same Early to Middle-Cambrian juvenile arc age range as the Coastal Complex forearc plagiogranites (ca.502.7-514.3 Ma). Table 3.4 Summarized and recalculated individual ${}^{207}\text{Pb}/{}^{235}\text{U}$, ${}^{206}\text{Pb}/{}^{238}\text{U}$ and ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ dates and uncertainties of the three prior ID-TIMS studies of Mattinson (1975a), Jenner et al. (1991) and Kurth et al. (1998) for the Coastal Complex, and the two of Williams et al. (1976) and Elliott et al. (1991) for the Twillingate pluton, together with reported ages and recalculated ages with and without uranium decay constant errors included for each study. Note that the italicized dates/ages and uncertainties indicate recalculated results in this study. Uncertainties of reported and recalculated ages are quoted at the 95% confidence interval unless otherwise noted with a superscript number, whereas the individual date uncertainties are (assumed to be) quoted at the 2s level. Discordance (%) is recalculated by $|({}^{206}\text{Pb}/{}^{238}\text{U}_{date})/({}^{207}\text{Pb}/{}^{235}\text{U}_{date}) - 1| * 100$

Zincon fraction	II	²⁰⁷ Pb/ ²³⁵ U		20	⁶ Pb/ ²³⁸ U	²⁰⁷ Pb/ ²⁰⁶ Pb		Discondorres		
/Sample label	(ppm)	Date (Ma)	Uncertainty (Ma)	Date (Ma)	Uncertainty (Ma)	Date (Ma)	Uncertainty (Ma)	(%)		
Trout River Regi	on, CC North, Mattin	son (1975	5a)							
Reported age: $508 \pm 5 \text{ Ma}^1$ Recalculated upper intercept age: $514 \pm 31 (N = 2)$										
znm/72-9	269 (²³⁸ U)	492	2.5	489	2.4	507	4	0.61		
zm/72-9	293 (²³⁸ U)	484	2.4	480	2.4	506	7	0.83		
Little Port Area,	CC South, Jenner et a	al. (1991)								
Reported age: 505	$^{+3}_{-2}$ Ma ¹ Recalculated	upper inte	ercept age: 503.6	$\pm 2.2 [\pm 2$	3] Ma (N = 4)					
7/83GD-02	325	500.1	1.3	499.3	1.4	504	2.2	0.17		
8/83GD-02	358	498.6	2.4	498.1	2.8	501	2.1	0.11		
9/83GD-02	401	490.6	1.4	488.2	1.6	502	1.9	0.49		
10/83GD-02	852	478.2	1.4	474.2	1.5	498	2.0	0.85		
Western Lewis H	ills, Southernmost CO	C, Kurth	et al. (1998)							
WLH 22 - Reporte	ed age: 503.7 ± 3.2 Ma	¹ Recalcı	ılated upper inter	cept age: 5	$03.1 \pm 4.3 [\pm 4.6]$	[Ma](N=4	()			
WLH 15 - Reporte	ed age: 500.6 ± 2.0 Ma	¹ Recalcu	lated upper interc	cept age: 50	$02.4 \pm 1.9 \ (N=3)$)				
Composite - Report	rted age: 502 Ma ¹	Recalcu	lated upper interc	cept age: 50	$2.8 \pm 1.5 \ [\pm 2.1]$	Ma] (N = 7))			
1/WLH 22	56.324	507.0	1.4	507.8	2.0	503.7	0.5	0.16		
2/WLH 22	166.666	504.5	1.3	504.7	2.0	503.9	0.3	0.04		
3/WLH 22	81.124	500.9	1.4	500.8	2.0	501.3	0.6	0.02		
4/WLH 22	64.782	500.8	1.3	499.9	2.0	504.8	0.3	0.18		
1/WLH 15	100.942	491.7	1.3	490.2	1.9	498.5	0.4	0.31		
2/WLH 15	132.623	498.5	1.3	497.9	1.9	501.4	0.3	0.12		
3/WLH 15	144.574	497.9	1.3	497.3	1.9	500.6	0.3	0.12		

Table 3.4 (continued)

Zircon fraction	Uconcentrations	²⁰⁷ Pb/ ²³⁵ U		²⁰⁶ Pb/ ²³⁸ U		²⁰⁷ Pb/ ²⁰⁶ Pb		Discordance			
/Sample label	(ppm)	Date (Ma)	Uncertainty (Ma)	Date (Ma)	Uncertainty (Ma)	Date (Ma)	Uncertainty (Ma)	(%)			
Twillingate, Williams et al. (1973)											
Reported age: 510^{+17}_{-16} Ma (1s error) Recalculated upper intercept age: 509 ± 20 Ma (N = 3)											
1/WF-1-73	2202.3	289	4.3	263	3.9	510	1.3	9.00			
2/WF-1-73	1321.6	470	7.1	467	7.0	483	1.2	0.64			
3/WF-2-73	564.9	507	7.6	502	7.5	529	1.3	0.99			
-/WF-2-73	504.4	-	-	499	7.5	-	-	-			
Twillingate, Elliott et al. (1991)											
Reported age: 507^{+3}_{-2} Ma Recalculated upper intercept age: $507.1 \pm 3.8 [\pm 3.9 \text{ Ma}] (N = 3)$											
1/84GD-06	80	501.8	1.2	500.9	1.5	505	3.5	0.18			
2/84GD-06	98	500.8	1.2	499.7	1.5	506	2.9	0.21			
3/84GD-06	275	483.7	1.2	480.0	1.4	501	2.9	0.78			

3.7 Discussion

We determined a precise crystallization age range of ca. 514.3-502.7 Ma for the forearc CC ophiolite plagiogranite intrusions by dating a series of samples (ca. 514.3-504.5 Ma) collected from discrete intrusions approximately along the regional strike of CC ophiolite (Figs. 3.1-3.2). We also included a recalculated age of 502.7 ± 2.1 Ma for the Western Lewis Hills massif by integrating seven U-Pb TIMS dates from two cogenetic trondhjemites originally reported by Kurth et al. (1998). The Early to Middle Cambrian age range of ca. 514.3-502.7 Ma of plagiogranite plutons within the CC likely suggests that the ancient Iapetus oceanic plate westward vergent subduction had initiated by at least ca. 514.3 Ma. It was then followed by a prolonged forearc magmatism history of at least ~12 Ma to produce the extensive CC forearc lithosphere intruded by plagiogranites above the subducting Iapetus oceanic plate. The forearc CC and contiguous Lushs Bight oceanic tract was then rifted in the latest Cambrian (Dewey and Casey, 2013, 2015) when spreading centers oriented at high angle and transforms at low angle to the existing trench nucleated within the forearc forming a trench-trench-ridge triple junction (Dewey and Casey, 2011). The CC was deformed within the forearc along a transform fault during the inception of the latest Cambrian supra-subduction zone (SSZ) spreading centers now represented by BOIC-Betts Cove-Point Rousse ophiolites of the Baie Verte Oceanic Tract (ca. 489-488.3 Ma) that were offset in a left lateral sense by these transforms within the forearc (see Dewey and Casey, 2013, 2015, 2021; Yan and Casey, 2020). The BOIC-CC boundary in the Lewis Hills massif is represented by a mid- to deep-crustal gabbroic gneisses and amphibolite with strong transformparallel low plunge linear crystal plastic fabrics in the WLH in contact with comparatively little deformed residual upper mantle and mafic-ultramafic transition zone of the BOIC in the ELH (Karson and Dewey, 1978, Casey and Karson, 1981; Karson, 1984). Stitching plutons and diabase

dikes from the BOIC intrude the older CC at ca. 488.3 Ma (Kurth et al., 1998; Kurth-Velz et al., 2004; Yan and Casey, 2020). The age and geochemical differences across the contact between highly-deformed lower crust of the CC (ca. 514.3-502.7 Ma) in the WLH and relatively less-deformed BOIC (ca. 488.3 Ma) mantle and plutonic rocks in the ELH that remains in autochthonous relationship is now well established (e.g., see also Kurth et al., 1998; Kurth-Velz et al. 2004).

We also obtained a precise 3-sample composite concordia age of 504.3 ± 1.8 Ma to represent the crystallization age of the Twillingate Granite pluton in Notre Dame Subzone. This pluton crops out most areas of the South Twillingate Island (Fig. 3.3) and intrudes the Sleepy Cove Group. It does not crosscut Moretons Harbour or Herring Neck Group volcanic rocks as previously thought that have been correlated stratigraphically with Lower to Middle Ordovician volcanics elsewhere in Notre Dame Bay (Payne 1974; Williams and Payne, 1975; Williams et al., 1976, Cutts et al., 2012). Although slightly younger than the ages of 510^{+17}_{-16} Ma and 507^{+3}_{-2} Ma reported by Williams et al. (1976) and Elliott et al. (1991), our new composite LA-ICP-MS concordia crystallization age of 504.3 \pm 1.8 Ma determined based on 91 individual concordant zircon analyses from three plagiogranites of the same pluton is more precise because of the large population of zircon grains analyzed and 0.7 MSWD calculated for final proposed ca. 504.3 Ma ages in this study. The new age is within error with the recalculated age and uncertainty results of prior studies (Fig. 3.14 and Table 3.4), suggesting that the Twillingate Granite pluton crystallized at ca. 504.3 Ma. This new age also overlaps with the end stages of CC forearc magmatism as the Notre Dame more felsic arc massif became established with major plutons like the Twillingate pluton covering in excess of ~180 km² in exposure, and likely extending offshore based on geophysical studies effectively doubling in area (Miller, 1970; Miller and Deutch, 1973; Payne

and Strong, 1979). Furthermore, the similarities in minerology, texture and chemistry of rocks from the CC and Twillingate Granite also indicate a similar subduction-related origin of the two terranes (e.g., Malpas et al., 1973; Payne, 1974; Williams and Payne, 1975; Malpas, 1976, 1979; Payne and Strong, 1979). The Coastal Complex and Twillingate Granite, therefore, are here interpreted to be a temporally related, once contiguous forearc-arc basement foundations that formed within a subduction zone initiated during the closure of the proto-Atlantic Ocean in Early Cambrian. The oldest plagiogranite intrusion age determined resides in the forearc CC is ca. 514.3 Ma, ~10 Ma older than the arc plutonism represented by the Twillingate batholith age of ca. 504.3 Ma. This is not uncommon as the subduction initiation and forearc magmatism may last for a short period of $< \sim 10-15$ Ma before the magmatic front stabilizes away from the trench and the stable magmatic island arc massif is built (e.g., Calvert et al., 2008; Ishizuka et al., 2011, 2018, 2020; Stern et al., 2012; Stern and Gerya, 2018; Hall, 2019; Reagan et al., 2019). The Twillingate batholith was later juxtaposed tectonically with younger plutons, dikes and volcanic rocks of the Ordovician arc represented by the adjacent Moretons Harbour and Herring Neck Group locally in fault contact (e.g., Malpas et al., 1973; Payne, 1974; Williams and Payne, 1975; Malpas, 1976, 1979; Payne and Strong, 1979, Swinden et al., 1997; Cutts et al., 2012).

Fig. 3.14 Compilation of age results from prior reported legacy ages (dashed lines), and our recalculated and new LA-ICP-MS age results from this study (solid lines) for various intrusions in Coastal Complex (CC) including (a) Green Gardens Trail intrusion of ca. 514.0 Ma and (b) Trout River intrusion of ca. 514.3 Ma from the Trout River region in northern CC, (c) Murray Mountain intrusion of ca. 513.4 Ma, (d) Southhead Lighthouse Trail intrusion of ca. 504.5 Ma and (e) Tortoise Mountain intrusion of ca. 504.9 Ma from Little Port area in southern CC, (f) Western Lewis Hills massif of ca. 502.7 Ma in the southernmost CC, and (g) for Twillingate Granite pluton of ca. 504.3 Ma in Notre Dame Subzone, as well as (h) suggested age of ca. 488.3 for BOIC ophiolite, ca. 488.5 Ma for Betts Cove ophiolite and ca. 489 Ma for Point Rousse ophiolite (Yan and Casey, 2020; Skulski et al., 2010). Note the geologic time scale is indicated at left side. Bold lines indicate suggested ages for each of the CC intrusions and Twillingate pluton in this study. Our ages calculated by pooling a large population of zircon have lower uncertainty but are still essentially within errors with the ages yielded from samples collected from the same intrusion/pluton. The uncertainties presented in age results from this study and our recalculated upper intercept ages all include the uranium decay constant errors. The single dot in (f) indicates an age of 502 Ma reported by Kurth et al. (1998) as they simply averaged the two upper intercept ages of two different samples from Western Lewis Hills massif without assigning error. ¹ U-Pb date uncertainties are assumed to be 0.5% at 2s level (see notes below Table 1 in Mattinson, 1975a).

² Uncertainty level (i.e., 1s or 2s) of 206 Pb/ 238 U and 207 Pb/ 206 Pb zircon date and sample preparation/measurement method are not provided in Kurth et al. (1998), so here we have assumed they were reported at 2s level.

³ Uncertainties of ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb dates are not provided by the study, so we recalculated their uncertainties based on the assumption that the U-Pb and Pb-Pb date uncertainties are assigned to be $\pm 1.5\%$ and $\pm 0.25\%$ at 2s level, respectively (see "Analytical Techniques" section in Williams et al., 1976).

⁴ Uncertainties of ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb isotopic ratios are not provided by the study, but reported a 1 sigma uncertainty range of 0.04-0.10% for ²⁰⁷Pb/²⁰⁶Pb ratio and 0.02-0.29% for U-Pb ratio (see "U/Pb ZIRCON RESULTS" section in Elliott et al., 1991). Therefore, here we averaged the lowest and highest error, and then multiplied by 2 to obtain an uncertainty of 0.14% and 0.31% (2s error) respectively for ²⁰⁷Pb/²⁰⁶Pb and Pb/U isotopic ratios.

⁵ Suggested ages of Baie Verte Oceanic Tract (BVOT) forearc ophiolites including new LA-ICP-MS U-Pb zircon age of 488.3 ± 1.5 Ma for BOIC ophiolite and recalculated age of 488.5 ± 8.0 Ma for Betts Cove Ophiolite (from Dunning and Krogh, 1985) in Yan and Casey (2020), and ca. 489 Ma age for Point Rousse ophiolite in Skulski et al. (2010).

r—	Caslasia Ti	Age (Ma) Vertical Dashed Line - Previously Reported Age (Ma) Vertical Solid Line - Previously Reported Age						Taconic Orogeny																
-	Geologic Time Scale		470	Northern	Northern Coastal Complex				Southern	Motre Dame Subzone	Obduction	Raio Vorto												
DOVICIAN	EARLY	FLOIAN		Trout Rive	r Region		Little Port Area W			Twillingate Granite	Initiation	Oceanic Tract												
				G1 34 ite	Z Mattins	A2 A3 A4 A4 te	T1 1B T5 ite	\downarrow	>	Villiams Elliott et al		\longleftrightarrow												
		TREMA-	1	G(G(posi	F (1975a	MM MM MM MM	LH HT LH LH	Q (1991)	Kurth et al. (1998)	2 2 2 2 2 2 2 2 2 2	U U													
			-480-	U		U	T T	8		S.T.V. S.T.V. S.T.V.	cti													
RI		DOCIAN		GC	-	MC	TC			G C C C C C C C C C C C C C C C C C C C	np													
0			L -	9		M	Southhead	Tortoise	Western Lewis Hills Massif	51 S	qn													
		AGE 10			Trout	Murray	Lighthouse Trail Intrusion	Mountain Intrusion	ca. 502.7 Ma	Ma 8.1	3 2	T												
		JIANGS- HANIAN	-490-	Green Gardens Trail Intrusion	River	Mountain	ca. 504.5 Ma	ca. 504.9 Ma	a a	4. T	ca. 489-488.3 Ma	1 .												
NN	FURON- GIAN			ca. 514.0 Ma	ca. 514.3 N	la ca. 513.4 Ma	Ma	4 6	Ma Ma Ma	2.4±	BVOT Forearc Spreading	Ma Ma												
							Ma 4.6 Ma 5 M	Ma 4+	9 M 9 M 5±2.1	Ma 9 M 8 M	Spreading	1.5												
	PA	PAIBIAN		9	Ma	Ma Ma	±2.0 4.4± ±1.8 ±1.5	: 1.6 ±2.0 1a	3±1.7±3 3±1.7±3 000.1	2.2 0±2 1.4		8.3±												
	Epoch 3 D	GUZHA-	L500-	.6 M	±5 Λ 3±	E7.5 Ma 4.0 h	4.24 1502 3.8=	1.9± 1.9± 1.9± 1.9± 1.9± 1.9±	503 03.3 503 502 02 N	4 .7± 4 .3 4 .3 Ma		, 48 Ma												
		NGIAN	500	6±7 5 Ма 1a Ма	3 ±	2.1₅ ±9.8 1.2±	4 50 50	504 505		507 507 507		plex ±8.0												
RI		DRUMIAN		513. ±4.3 1.9 N	514	+ 51 6.4 509 509	T	TI			Twillingate Arc	om] 8.5: e Op												
1B				1								1	1	1	1	1 13.5 13.5	T		+ + + +		-		Nascent	te C te48 uss
CAN		AGE 5	510	514 514 514			1		л I		Forearc-Arc CC and	iloli iloli t Ro												
		AGE 4		ΙΙΤŤ		<u>т</u> Г			/		Sleepy Cove- Lushs Bight	dq0 dq0 dq0												
											(?)	ads of the second secon												
	Epoch 2	AGE 3			[]	[]							$\left(\right)$		Subduction	Islaı is Co								
			AGE 3 -520-	1 ± 1					/		Initiation	Beti												
				T	Ia		Su	ggested CC for	♥ earc age range	Ч і ↓ –		Bay												
			1		of ca. 514.3-502.7 Ma in this study Suggested Twillingate arc																			
	TERRE-	AGE 2			14±.					504.3 ± 1.8 Ma in this study														
	NEUVIAN	41 mpm and 422 mm 440 20		(a)	(b) 5	(c)	(d)	(e) (f)	(g)		(h)												
			-530-																					

3.8 Conclusions

New LA-ICP-MS U-Pb dating of a large population of zircon grains from multiple samples collected from five different plagiogranite intrusions roughly along the structural strike of the Coastal Complex (CC) yielded a precise formation age range of ca. 514.3-504.5 Ma for the CC forearc lithosphere magmatic activity. This age range, combined with our recalculated 2-sample composite age of 502.7 \pm 2.1 Ma for the Western Lewis Hills massif (Kurth et al., 1998) in the southernmost CC, suggests a prolonged forearc magmatism until ca. 502.7 Ma of at least ~12 Ma to construct the CC forearc basement with extensive plagiogranite intrusions (Fig. 3.15). The oldest ca. 514.3 Ma age likely indicates that westward vergent subduction of ancient Iapetus oceanic crust adjacent to the Laurentian stable margin had initiated by at least ca. 514.3 Ma. We also determined a 3-sample composite concordia age of 504.3 ± 1.8 Ma for the Twillingate Granite in Notre Dame Subzone based on 91 individual LA-ICP-MS zircon analyses. This ca. 504.3 ± 1.8 Ma age is slightly younger than the legacy age results of 510^{+17}_{-16} Ma and 507^{+3}_{-2} Ma reported by Williams et al. (1976) and Elliott et al. (1991) but is more precise because of the large population of zircon grains analyzed and 0.7 MSWD calculated for the final proposed ca. 504.3 Ma age in this study. This age overlaps with youngest CC forearc plagiogranite magmatism and establishes the oldest age of a voluminously silicic magmatism of batholithic dimensions in the juvenile Notre Dame arc. It also provides a minimum age for the intruded arc tholeiitic and boninitic ophiolitic basement of Sleepy Cove volcanics, which is considered correlative with the Lushs Bight volcanics and sheeted dikes terrane. The correlative ages and similarities in minerology, texture and chemistry of rocks from the CC and Twillingate plagiogranites also indicate a similar subduction-related origin of the two terranes. The end-stage magmatism of Middle Cambrian of Coastal Complex and that of the Twillingate batholith are, therefore, temporally related as a once

contiguous forearc-arc system that formed in a supra-subduction zone (SSZ) environment during the initial closure of the proto-Atlantic Ocean Iapetus in Early to Middle Cambrian. The oldest plagiogranite intrusion age determined in this study for the CC of ca. 514.3 Ma is ~10 Ma older than the prominent arc plutonism represented by the Twillingate batholith crystallization age of ca. 504.3 Ma. The Twillingate batholith was later juxtaposed tectonically with younger plutons, dikes and volcanic rocks of Moretons Harbour and Herring Neck Group of the Cambro-Ordovician arc. The CC was deformed within the forearc along a transform fault during the inception of the latest Cambrian SSZ spreading centers now represented by BOIC-Betts Cove-Point Rousse ophiolites of the Baie Verte Oceanic Tract (ca. 489-488.3 Ma) that were offset in a left lateral sense by these transforms within the forearc. The composite forearc of the CC and BOIC locally in the Lewis Hills preserves the original autochthonous relationship in the Humber Arm Allochthon. They were initially obducted as a single basement sheet starting at ca. 470 Ma, almost ~20 Ma following the Baie Verte Oceanic Tract forearc accretion (e.g., BOIC) and ~45 Ma after the initial (oldest) CC forearc accretion. The ophiolitic welded forearc CC-BOIC basement composite was partially dismembered as the Humber Arm Allochthon was emplaced, except in the Lewis Hills where the contact is well preserved in autochthonous relationship between the older and younger ophiolitic forearc basements.

The age data also indicate that the CC forearc and subsequent Notre Dame Arc magmatic activity with westerly vergence persisted at least from oldest age in the CC of ca. 514.3 Ma to younger ages in the Snooks Arm Tuffs above the Betts Cove Ophiolite of the BVOT with an age of ca. 467 Ma (Skulski et al., 2010) and further to the age of youngest easterly derived ash layers recorded in flysch within the Humber Zone (i.e., to ca. 464.2 Ma) (Macdonald et al., 2017). These ages indicate volcanism was still underway as Taconic ophiolite obduction and convergence

were ongoing (MacDonald et al., 2017). The age gap between the oldest CC forearc age of ca. 514.3 Ma and Twillingate arc plutonism of ca. 504.3 Ma indicates that major silicic batholithdimension magmatism was initiated ~10 Ma after the earliest CC forearc plagiogranites, likely as a consequence of progressive eastward (current reference) migration of the volcanic arc front eastward during the arc building and stabilization phase ensued, best represented by the crystallization age of Twillingate batholith (ca. 504.3 Ma). The Notre Dame arc terrane remained magmatically active for the following ~40 Ma until at least ca. 464.2 Ma. The obduction initiated at ca. 470 Ma and was followed shortly after ca. 464 Ma by a brief hiatus in Notre Dame arc volcanism in response to the Taconic collision and convergence with the eastern Laurentian continental margin in the middle Ordovician. Volcanism and plutonism resumed after Iapetus slab detachment and a subduction polarity reversal forming an Andean-type margin as remnants of Iapetus were subducted (Fig. 3.15).

Fig. 3.15 Generalized geologic map and tectonic model for CC formation. (a) Generalized geologic and tectonic map modified after Dewey and Casey (2013) that includes the Humber Zone (former Laurentian stable margin and Taconic allochthons) and the Notre Dame Arc Subzone of the Dunnage Zone of the Western Newfoundland Appalachians (Williams, 1995) with updated ages (red) for Coastal Complex of ca. 514.3-502.7 Ma and Twillingate Granite of 504.3 ± 1.8 Ma. (b) Schematic 3D cross-section of the trench-forearc-arc-backarc system with subduction of the oceanic lithosphere adjacent to the Laurentian margin with lithosphere of supra-subduction zone forearc Bay of Islands of the Baie Verte Oceanic Tract (which also includes forearc Betts Cove and Pointe Rousse ophiolites of similar ages, and potentially the younger back arc Annieopsquatch ophiolite), and older composite forearc-arc basement of CC-Lushes Bight-Sleepy Cove. The older CC-Lushs Bight forearc formed at ca. 514.3-502.7 Ma, which was later rifted by the Baie Verte Oceanic Tract SSZ spreading centers at ca. 489-488.3 Ma. The Notre Dame arc represented by the Twillingate Granite pluton here initiated at ca. 504.3 Ma, overlapping the youngest CC forearc plagiogranite magmatism. The arc encroachment on the Laurentian margin results in ophiolite obduction over Laurentian Humber margin starting at ca. 470 Ma during the Taconic Orogeny. Note red color indicates new LA-ICP-MS U-Pb zircon (composite) ages suggested here and from Yan and Casey (2020) while blue ages indicate recalculated Betts Cove ophiolite age in Yan and Casey (2020) and proposed Point Rousse ophiolite age by Skulski et al. (2010).



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Zheng, Y.F., Gao, T.S., Wu, Y.B., Gong, B., Liu, X.M., 2007. Fluid flow during exhumation of deeply subducted continental crust: zircon U-Pb age and O-isotope studies of a quartz vein within ultrahigh-pressure eclogite. Journal of Metamorphic Geology 25, 267-283. Chapter 4 Petrogenesis of Bay of Islands Ophiolite Complex plagiogranites and silicic dikes by multi-stage Rayleigh fractionation of primitive and evolved melts with an intermediate stage of near-equilibrium fractionation of pore melts within a crystal-dominated mush

4.1 Introduction

The term "oceanic plagiogranite" was originally introduced to describe commonly present, but volumetrically small, leucocratic, silicic ($SiO_2 > 60$ wt.%) intrusive rocks collected in oceanic drill core and dredge and ophiolitic crust (Coleman and Peterman, 1975; Malpas, 1979; Aldiss, 1981; Lippard et al., 1986). Although lacking exact definition, these oceanic plagiogranites were suggested to be distinguished from their continental counterparts and other granitic rocks by having more depleted K₂O, lower Rb/Sr ratio and higher Na₂O and CaO content (Coleman and Peterman, 1975; Coleman and Donato, 1979). Even though "plagiogranite" was later more explicitly defined to describe a series of light-colored plutonic rocks consisting of oligoclase or andesine, quartz and less than 10% of mafic biotite and hornblende minerals or as a synonym for trondhjemite and leucocratic tonalite (Le Maitre et al., 2002), this definition is still somewhat defective because the corresponding rock suites within the oceanic and ophiolitic crust often also include diorite and quartz diorite of little or even no quartz present. Koepke et al. (2007) investigated over 300 analyses of oceanic plagiogranites from recent oceanic crusts and ophiolites. They recognized the significant compositional diversity of oceanic plagiogranites that were not fully realized in earlier studies. The "oceanic plagiogranite" definition was, therefore, expanded to include the whole suite of evolved, SiO₂-enriched (SiO₂ = \sim 52 to 80 wt.%) intrusive rocks within the plutonic sections of oceanic crust and ophiolite including trondhjemite, tonalite, quartz diorite

and diorite (see Koepke et al., 2007 for details). Oceanic plagiogranite or simply plagiogranite as used in this manuscript is inclusive of plutonic diorite, quartz diorite, tonalite and trondhjemite within the plutonic sections of ophiolite and oceanic crust, but here we also include for completeness related hypabyssal fine-grained compositional equivalents that include smaller quickly chilled dikes and veins of basaltic-andesitic, andesitic, dacitic and rhyodacitic compositions near the base of sheeted dike section. These dikes parallel the overall sheeted dike orientations (e.g., Fig. 4.3b) measured in the Bay of Islands Ophiolite Complex (Casey, 1980; Casey et al., 1983; Rosencrantz, 1980, 1983). The fine-grained silicic intrusions with major and limited trace elements were originally reported in Casey et al. (1985) and are interpreted to approximate silicic magmatic liquid compositions that form the basis for comparison of melt-like silicic compositions to their coarser-grained plagiogranite counterparts examined here.

The petrogenesis of plagiogranites has remained controversial with two main competing views. Some investigations support origins by partial melting of hydrated gabbroic or diabasic rocks (e.g., Flagler and Spray, 1991; Koepke et al., 2004, 2007; France et al., 2010) while others indicate they represent the residual melts after high degrees of fractionation of basaltic melts (e.g., Coleman and Peterman, 1975; Colemand and Donato, 1979; Spulber and Rutherford, 1983; Berndt et al., 2004). More broadly, four different mechanisms were proposed for genesis of silicic melt in segments of oceanic crust and ophiolites governed by different magmatic processes and supported by multiple experimental studies. These include 1) low-pressure (i.e., upper crust level) extreme differentiation of a primitive basaltic magma (e.g., Coleman and Peterman, 1975; Colemand and Donato, 1979; Spulber and Rutherford, 1983; Berndt et al., 2004; Koepke et al., 2018), 2) partial melting of hydrothermally altered or metamorphosed gabbroic or diabasic oceanic/ophiolitic crustal rocks within the conductive lid or magma chamber roof zone (e.g., Beard and Lofgren, 1991; Koepke et al., 2004, 2007; France et al., 2010, 2014), 3) immiscible segregations of silicic liquid from high Fe-Ti gabbroic rocks in shallow oceanic or ophiolitic crust (e.g., Rutherford et al., 1974; Dixon and Rutherford, 1979; Charlier and Grove, 2012; Charlier et al., 2013) and 4) mixing of (replenished) primitive basaltic magmas with felsic melts (e.g., Whalen and Curries, 1984; Tatsumi et al., 2008; Tatsumi and Suzuki, 2009). An additional mechanism, partial melting of metamorphic sole assemblages, the detached and deformed subducted slab at the base of ophiolite, has also been applied for some mantle penetrating plagiogranites within suprasubduction zone (SSZ) environments (e.g., Rollinson, 2014, 2015; Xu et al., 2017). More complex multi-stage models involving a combination of deeper in situ disequilibrium/equilibrium fractionation within cumulate pore spaces of gabbroic assemblages followed by segregation, mobilization and further fractionation processes of more evolved melts generated were proposed based on the nature of textural and compositional changes along the transition zone from layered to isotropic gabbro to sheeted dike unit in the BOIC (Casey, 1980; Carter, 1985). This combined, more complicated process will be specifically further evaluated in this study. Understandably, many investigators have surmised that single-process explanations on the compositional and textural variety of plagiogranites (or their associated gabbroic cumulates) are implausible, and a combination of two or more processes are not uncommonly proposed to explain these complexities within ophiolitic and oceanic crust (e.g., Rollinson, 2009; Wanless et al., 2010; Grimes et al., 2013; Marien et al., 2019).

In this study, we first examine the newly acquired geochemistry of BOIC plutonic plagiogranites and fine-grained dikes and integrate these data with existing chemical datasets also from the BOIC of compositions ranging from basaltic to felsic. The combined datasets show little evidence of commonly cited compositional gap in major element variation diagrams between BOIC basaltic and felsic samples that support a liquid immiscibility process, although samples of intermediate compositions appear to be sampled or analyzed less commonly. We have also modeled the process of partially melting a BOIC metamorphic sole amphibolite protolith composition, and our modeling results show significant melt composition mismatches with major and trace element geochemistry of BOIC felsic samples. Furthermore, plagiogranite and silicic dikes are commonly absent in the residual mantle and lower crustal sections of the BOIC ophiolite. Therefore, we have rejected the two models of liquid immiscibility and partial melting of metamorphic sole assemblages and only simulated the three of the four commonly proposed magmatic processes involving magma differentiation, partial melting (of magma chamber roof zone lithologies) and magma mixing primarily by using MELTS program (Ghiorso et al., 2002; Gualda et al., 2012; Ghiorso and Gualda, 2015). Then by comparing modeling results with the combined BOIC sample datasets of basaltic to felsic compositions with specific focus on immobile major and incompatible trace elements, we attempted to quantitatively evaluate the potential success or failure of each independent mechanism proposed for the formation of BOIC plutonic plagiogranites and felsic fine-grained dikes. Particularly, we established a multi-step sequential Rayleigh and equilibrium fractionation model to simulate the natural fractionation processes of primitive basaltic magmas within an oceanic magma chamber(s) involving crystal-rich much zone(s) where they can fractionally crystallize at the edges of a deeper chamber (estimated pressure of ~2.0 kb) and then enter a mid-crustal crystal-dominated three-phase saturated mush zone where they ascend, react and attempt equilibrium to fractionate at pressures between ~ 2.0 and 0.7 kb. As evolved magma is segregated from the mush and emplaced at shallower levels, it can potentially fractionate further within more silicic plutons just below the sheeted dikes (depth equivalent to pressure of ~ 0.7 kb). This stepwise fractionation model was designed to simulate a complete

magmatic evolution process from the deep initial primitive basaltic magmas to evolved intermediate two- or three-phase saturated melts to final highly evolved felsic melts saturated in quartz, plagioclase and amphibole at shallow depth within the BOIC plutonic crust. Furthermore, we also attempted to simulate roof zone partial melting of various gabbroic and diabasic protoliths analyzed from the BOIC and fractionate the initial low-degree, most silicic melts produced at ~5% melting to generate the more evolved melts that might be geochemically close to the compositions of highly evolved plagiogranites with $SiO_2 > 70$ wt.%. Magma mixing process was evaluated to assess the petrogenesis of certain intermediate dioritic and andesitic samples that fall off the dominant iron enrichment tholeiitic trends on the Alkalis-Iron-Magnesium (AFM) plot, by mixing primitive basaltic and more evolved plagiogranitic endmembers. This mixing process was specifically involved to investigate formation of BOIC intermediate samples that appear to have "apparent" calc-alkaline characteristics on AFM plots and are less likely to be produced by simple crystal fractionation and/or the partial melting processes.

4.2 Tectonic framework and sampling locations

The Bay of Islands Ophiolite Complex (BOIC) (Dewey, 1969; Stevens, 1970; Dewey and Bird, 1971; Williams, 1973), from north to south, includes the Table Mountain (TM) massif, the North Arm Mountain (NA) massif, the Blow Me Down Mountain (BMD) massif, and the eastern half of Lewis Hills (ELH) massif (Karson and Dewey, 1978; Casey et al., 1983, 1985; Casey and Dewey, 1984; Kurth et al., 1998) (Fig. 4.1). The BMD and NA massif expose relatively intact and complete ophiolitic stratigraphies, whereas the TM and ELH massif preserve only basal crustal and ultramafic portions that are largely devoid of plagiogranite (Williams, 1973; Karson and Dewey, 1978; Casey and Karson, 1981; Casey et al., 1983; Williams and Cawood, 1989). The BOIC has been variably interpreted in the past to have formed within an upper plate forearc, arc or back-arc supra-subduction zone (SSZ) spreading centers, primarily based on negative tantalum and niobium anomalies and tectonic interpretations of BOIC diabases, basalts and plagiogranites (Dewey and Bird, 1970, 1971; Casey and Dewey, 1984; Searle and Stevens, 1984; Elthon, 1991; Jenner et al., 1991; Kurth-Velz et al., 2004), as well as the BOIC-Coastal Complex structural and relative age relationships (Karson and Dewey, 1978; Nelson and Casey, 1979; Casey et al., 1983, 1985; Casey and Dewey, 1984; Dewey and Casey, 2013, 2015, 2021; Yan and Casey, 2020). Yan and Casey (2020) reviewed prior BOIC age studies and reported a new precise formation age of 488.3 ± 1.5 Ma based on some of the same plagiogranites presented here. They then specified the strong similarities between the new BOIC age and the recalculated ages of nearby Betts Cove and Point Rousse ophiolite, suggesting that the three ophiolites have likely formed along a contiguous set of supra-subduction zone spreading centers at high angles to a westward-facing (present-day coordinates) trench that collided with the Laurentian margin. Collectively, the three correlated Late Cambrian ophiolites are termed the Baie Verte Oceanic Tract (BVOT) (e.g., van Staal et al. 2007). These high-angle spreading centers were offset by large and small left-lateral offset transform faults, one of which juxtaposed the BOIC with the deformed and older Coastal Complex ophiolitic assemblage, that formed within the rifted forearc oceanic lithosphere of the Cambro-Ordovician Notre Dame arc of Central Newfoundland, illustrated in Karson and Dewey (1978), Nelson and Casey (1979), Casey and Dewey (1984), Dewey and Casey (2013, 2015, 2021) and Yan and Casey (2020).

Fig. 4.1 Generalized regional geologic map of the Bay of Islands region of Western Newfoundland, Canada, showing the main ophiolitic lithologic assemblages of the Bay of Islands Ophiolite Complex and the subjacent or autochthonous Coastal Complex (modified from Casey et al., 1985). The two red boxes within the North Arm Mountain (NA) massif and the Blow Me Down Mountain (BMD) massif indicate general locations where large and small plagiogranite bodies were mapped by Casey (1980), with detailed locations for the BMD massif included in Fig. 4.2 (derived from Casey and Karson, unpublished 1/15,000 maps). Sampling locations of plagiogranites are detailed in Casey (1980), Carter (1985), McNeil (1985), Kharas-Kumbatta (1988) and from the BMD massif (see Fig. 4.2) in the upper isotropic gabbroic unit, dike-gabbro transition zone and the base of the sheeted dike unit. Basalts, diabases and fine-grained silicic dikes shown in this study were sampled within the upper sections of the BMD and NA massif and were presented in Casey et al. (1985), McNeil (1985), Siroky et al. (1985) and Jenner et al. (1991).



Malpas (1976, 1979) first investigated the geochemistry of the BOIC trondhjemites, as well as their textural and structural characteristics, suggesting that these trondhjemites were generated by low-pressure crystallization of a wet differentiated basaltic magma within an oceanic spreading center. To explain their sodic nature, Malpas (1979) emphasized the importance of metasomatism by which the sea water may interact with the ophiolitic rocks to account for the gain or loss of some major and trace elements (e.g., Na). Subsequent studies provided more detailed geochemical analyses on a variety of ophiolitic rocks from BOIC including plagiogranites and silicic fine-grained dikes (Carter, 1985; Casey et al., 1985; Elthon, 1991; Jenner et al., 1991), gabbros (McNeil, 1985; Komor et al., 1987; Kharas-Khumbatta, 1988; Komor and Elthon, 1990), ultramafic rocks (Elthon et al., 1982, 1984) and diabasic and basaltic rocks (Suen et al., 1979; Casey et al., 1985; McNeil, 1985; Siroky et al., 1985; Elthon et al., 1986; Jenner et al., 1991). All these studies agreed that the BOIC plutonic assemblages were dominantly formed by low-pressure fractional crystallization, although acknowledging other processes including assimilation of gabbroic and basaltic xenoliths, magma mixing of replenishment melts, partial melting of gabbroic rocks and possibly higher-pressure crystallization of early cumulates may also be involved.

Within the BMD and NA massifs, nine ophiolitic units have been mapped at 1/15000 scale by Casey (1980), Rosencrantz (1980), Casey et al. (1981, 1983, 1985) and Casey and Karson (unpublished) including, from top to bottom, 1) basaltic pillow lava unit that includes volcanic breccias, minor jaspers and abundant mafic dikes at the base, 2) sheeted diabase dike unit that is mainly composed of diabases and strongly affected by passive greenschist to lower amphibolite facies alteration, 3) dike-gabbro transition that is composed of massive non-layered but vari-textured "isotropic gabbros" with > 10% diabase dikes in volume and that is strongly affected by static amphibolite to greenschist facies hydrothermal alteration and localized

amphibolite facies mylonites, 4) isotropic gabbro unit that is composed of the same massive nonlayered vari-textured gabbros with sparse diabase dikes and that is strongly affected by static amphibolite to greenschist facies alteration with localized amphibolite facies mylonites, 5) layered gabbro unit that includes gabbros, olivine gabbros, troctolites and anorthosites locally including layered hornblendites and hornblende gabbros or cut by narrow amphibolite to granulite facies mylonite zones and intrusive wehrlites and feldspathic dunites, 6) mafic-ultramafic transition that is composed of inter-layered mafic and ultramafic plutonic rocks and commonly tectonized during high temperature crystal-plastic deformation and localized mylonitization, 7) ultramafic unit that dominantly encompasses dunites with minor or abundant wehrlites, clinopyroxenites, websterites, minor chromites and olivine-rich harzburgites, which are strongly tectonized during high temperature crystal-plastic deformation, 8) residual harzburgite tectonite that is characterized by layered harzburgite with varying modal abundances and penetrative crystal-plastic deformation and commonly cross-cut by dikes of dunite and orthopyroxenite and 9) sub-ophiolitic dynamothermal metamorphic sole (Figs. 4.1 and 4.2). Silicic intrusions included within the BMD and NA massifs occur as large and small plagiogranite plutons of meter- to kilometer-scale and smaller pods and veins within the upper gabbroic unit and dike-gabbro transition zone. These intrusions also occur as fine-grained chilled dikes (< 0.5 m thick) within sheeted dike unit (Figs. 4.2 and 4.3) as would be expected if cogenetic with fractionation products of the more primitive ophiolite lower gabbroic assemblages (Casey, 1980). Xenoliths of gabbro, amphibolite and diabase within silicic intrusives are common (Fig. 4.3). These xenoliths mostly characterized by sharp contact margins in outcrop showing little to no evidence of internal partial melt pockets or strongly reactive boundaries. In thin section, quartz and partially altered euhedral plagioclase feldspar of variable sizes are common, but amphibole is sparse (Fig. 4.4). Plagioclase grains show normal

internal oscillatory zoning with concentric rings of higher and lower extinction angles (Fig. 4.4ad) that also show evidence of reactive/resorbed cores. This zoning indicates that plagioclase does not crystallize in equilibrium with interstitial melt and therefore evolves to more extreme compositions by interstitial fractional crystallization but is reactive with plagioclase cores because of changing chemico-physical conditions. Symplectic intergrowth of plagioclase with quartz is characterized by branching rods of quartz in plagioclase that are optically continuous (Fig. 4.4e and f). The roof zone vari-textured isotropic gabbros that are generally intimately associated with plagiogranites and fine-grained silicic intrusions in BOIC have been extensively altered as evidenced by the ubiquitous existence of static amphibole alteration/replacement of pyroxene in thin sections (Fig. 4.5). This implies that the presence of abundant hydrothermal fluids within BOIC ophiolitic roof zone were common. Shallow cyclic layering of hornblendite and oxide bearing gabbro also commonly exist (white arrows in Fig. 4.5) and in thin section, they show variable amounts of entrapped intercumulus melts and disequilibrium zoning (Fig. 4.5h-i). Fig. 4.2 Geologic map of the Blow Me Down Mountain massif with sampling locations including (a) Geological map of the allochthonous Blow Me Down Mountain massif generalized from Casey and Karson (unpublished 1/15,000 geologic maps), showing details of the main lithologies (including plagiogranite plutons) and tectonic features of the ophiolitic massif, (b) enlarged view of a portion of the geologic map (red box in a) including more details of dike-gabbro transition, plagiogranite plutons and locations sampled by J.F. Casey during the detailed 1/15,000 geological mapping in the early 1980s including four trondhjemites BMD.196-D, BMD.220-A, BMD.252-B and BMD.RTB.116-84-N.O. that were reported in Kharas-Khumbatta (1988) and seven fine-grained silicic intrusive dikes BMD 1085, BMD 2124B, BMD 2125B, BMD 2127A, BMD 2129A, BMD 2130A and BMD 2131 that were reported in Casey et al. (1985) that are indicated by yellow stars with labels, (c) enlarged view of a single plagiogranite pluton (red box in b) where the seven trondhjemites were sampled in this study (yellow stars with sample labels), and (d) legends for all the three geologic maps including nine main ophiolitic units, as well as underlying allochthonous sub-ophiolitic rift basalts and undifferentiated sedimentary/mélange slices. Note the close proximity of seven sample locations with labels (BMD-03-17Y through BMD-09-17Y) within a single plagiogranite pluton in (c), as well as one diorite (BMD-01-17Y) collected from a nearby large plagiogranite recent slide block at the base of the BMD cliff shown by a red star in (b) (all collected by us in 2017). Some samples have reported geochronology in Yan and Casey (2020). Latitude and longitude locations of each sample are provided in Appendix Table A4.1.



Fig. 4.3 Field outcrop photographs showing (a) sharp contact between isotropic gabbro and sheeted diabase dike unit (hammer for scale), (b) sheeted dike section of the Blow Me Down Mountain (BMD) massif showing lenticular sub-parallel fine-grained felsic rhyodacite dikes (white arrows) intruding thicker diabase dikes (lens cap for scale), (c) hornblende-plagioclase pegmatitic layer in upper layered gabbro unit of the BMD massif, (d) hornblende-plagioclase pegmatitic dike within isotropic gabbro unit of the BMD massif, (e) diorite intrusion with large and small diabase xenoliths characterized by irregular boundaries, (f) xenoliths including diabase/gabbro contact (white arrow), gabbro and diabase within trondhjemite intrusion, (g) plagiogranite roof zone intrusion with coarse isotropic gabbro and diabase xenoliths (note the sharp diabase/gabbro contact indicated by white arrow), and (h) trondhjemite intrusion with diabase xenoliths (also note the sharp boundary of xenoliths).



Fig. 4.4 Representative photomicrographs of plagiogranite from the Bay of Islands Ophiolite Complex showing the range of textures in a single plagiogranite sample. (a) and (b) Crosspolarized light (XPL) and plane-polarized light (PPL) image showing quartz (Qtz) and partially altered euhedral plagioclase feldspar (Pl) of variable sizes with normal continuous zoning of albitic rims on most grains, and scarce amphibole (Amp). Many plagioclase grains show internal oscillatory but discordant zoning with concentric rings of higher and lower extinction angles that are also showing evidence of reactive/resorbed cores (e.g., see Pl label). This zoning indicates that plagioclase does not crystallize in equilibrium with interstitial melt and therefore evolves to more extreme compositions by fractional crystallization or is reactive with plagioclase cores because of changing chemico-physical conditions (e.g., pressure, temperature, fluctuation in water contents, crystallinity and composition) likely induced by injection or replenishment of more primitive melt or fluid exsolution and addition. Also note very minor amphibole (Amp). (c) and (d) XPL and PPL image showing plagioclase (Pl), quartz (Qtz) and minor amphibole (Amp), and similar oscillatory zoning of plagioclase grain (center) with ghost of hopper growth zone (darker rim zone). (e) and (f) XPL and PPL image showing intergrowth of quartz (Qtz) and plagioclase (Pl) (yellow arrow) with branching rods of quartz in plagioclase that extinguish together. Note interstitial brown amphibole (Amp).





Fig. 4.5 Vari-textured roof zone gabbroic rocks showing static amphibole alteration/replacement of pyroxene and zoned igneous plagioclase and opaque iron oxides (a-f), shallow cyclic layering of hornblendite (white arrow in g) and oxide bearing gabbro (h-i). The ubiquitous existence of amphibole replacing pyroxene in meta-isotropic gabbros suggests that hydrothermal alteration was common in the roof zone gabbroic rocks above magma chamber in BOIC.

In this study, we analyzed major and trace elements from seven trondhjemites, labeled through BMD-03-17Y to BMD-09-17Y, that were collected from a single plagiogranite pluton located ~200 m below the sheeted dike unit on the Blow Me Down Mountain massif (Fig. 4.2c). Each of the seven samples were chosen spatially separated from one another to cover a contiguous portion of the exposed area of the pluton (0.5 km in diameter) to assure they were cogenetic. Four of the seven trondhjemites have been dated using LA-ICP-MS U-Pb zircon dating technique yielding comparable age results of ca. 488 Ma (see Yan and Casey, 2020). We also analyzed an additional sample BMD-01-17Y collected from a nearby plagiogranite block spalled from a steep cliff at the base of the sheeted dike (red star in Fig. 4.2b) on the BMD massif. This

sample has a similar age of ca. 488 Ma, which gives us confidence in their overall cogenetic nature of the plagiogranites cropping out just below the sheeted dikes. Careful examination of these specimens presented shows that they all have undergone some extent of hydrothermal alteration (Fig. 4.4).

Here we provided new ICP-OES major element and triple-quadrupole (QQQ)-ICP-MS trace element data for these recently collected plagiogranites, as well as new trace element data for seven other fine-grained felsic/intermediate intrusive dikes from the sheeted dike sections reported in Casey et al. (1985) and four other coarse-grained plagiogranites also collected by J.F. Casey during mapping and reported in Kharas-Khumbatta (1988) from the BMD plutonic sections (Fig. 4.2b). More recently collected samples were located by GPS (Appendix Table A4.1), but earlier sample collections, although well-located on 1/15,000 geologic maps and air photos, were completed prior to the GPS availability. Therefore, these samples were relocated by matching their mapped locations on detailed geologic outcrop maps (Casey, unpublished) with Google Earth satellite topography and imagery (UTM projection) to provide an accurate estimate latitude and longitude location (see Appendix Table A4.1).

We integrated new bulk-rock major and trace elements together with earlier more abundant published, but fragmented, chemical major element datasets (supplemented with either limited XRF or more complete SIMS/ICP-MS trace element data) of compositions including basaltic, diabasic, andesitic, dacitic, rhyodacitic and plagiogranitic (Carter, 1985; Casey et al., 1985; McNeil, 1985; Siroky et al., 1985; Kharas-Khumbatta, 1988; Elthon, 1991; Jenner et al., 1991). They are evaluated and compared with major and trace element modeling results to comprehensively investigate the petrogenesis and evolution of the BOIC plutonic plagiogranites and fine-grained silicic dikes.

4.3 Analytical methods

4.3.1 Bulk rock geochemistry

The eight newly collected bulk plagiogranites were first trimmed to remove the outermost weathering surfaces and cut into smaller blocks by tungsten rock saw. Every block was carefully washed with Milli-Q water (resistivity of 18.2 M Ω .cm at 25 °C) and then dried in clean fume hood. The dried sample blocks were finally crushed by ceramic jaw crusher and pulverized by SPEX SamplePrep Shatterbox (series 8530). The powders of each sample were separately stored in pre-cleaned plastic bottles, similar to other archived sample powders analyzed from Casey et al. (1985) and Kharas-Khumbatta (1988) that are also included here. It is notable that all acids used (HNO₃, HCl and HF) for sample digestion described below were made from distilled strong acids by diluting with ultrapure 18.2 M Ω .cm Milli-Q water.

Analysis for major (Si, Al, Ca, Fe and Mg) and minor element (K, Mn, Na, Ti and P) was conducted using Agilent 725 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) at the University of Houston (UH) ICP lab, with similar sample preparation procedures described in Gao and Casey (2014). Loss on ignition (LOI) was calculated by using initial weight of the rock powder (dry after 12 hours at 100 °C in Lab-Line Oven) minus its final weight (ignited after 45 minutes at 1000 °C in Lindberg furnace), and then divided by the initial weight. After LOI determination, 0.2 g of the ignited sample powder was mixed with 1 g lithium metaborate and 0.1 ml non-wetting agent LiBr in a high purity graphite fusion crucible for the fusion process. The fusion process was conducted in the Lindberg furnace at 1000 °C for 20 minutes, after which the graphite crucible (with molten bead inside) was moved out of the furnace and onto a granite slab allowing it to sufficiently cool until a crystallized bead formed. The solidified bead was transferred into a 150 ml Teflon beaker and then filled with 50 ml 1N HNO₃ for dissolution on a hot plate

with magmatic stirring. After the bead completely dissolved, the solution was passed through ashless filter paper to filter out any carbon residue. The filtered solutions were finally diluted with 1N HNO₃ to 1:500 for measurement of K, Mn, Na, Ti and P, and to 1:5000 for Si, Al, Ca, Fe and Mg analysis by using the Agilent 725 ICP-OES at the UH ICP lab. Two procedural blanks (lithium metaborate only) and two USGS (United States Geological Survey) standards, BHVO-2 and SCO-1, were prepared simultaneously with rock samples by using the identical procedures. SCO-1 was used as primary standard to calibrate instrument-induced time drift and to calculate element concentrations, whereas BHVO-2 was treated as an unknown to independently assess the accuracy and precision of the entire analytical session. Major and minor element results of samples and secondary standard are together presented in Appendix Table A4.1 on a dry basis and only volatile-free totals ranging between 98.5 and 101% were reported. Reference values for BHVO-2 and SCO-1 are from Jochum et al. (2016) and Smith (1995), respectively (see Jochum et al., 2005 for reference data compilation). Repeat analyses of secondary standard BHVO-2 show high precision (i.e., RSD) within 1% for all elements.

For trace element (Li, Be, S, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Tb, Gd, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Pb, Th, and U) analysis (method modified from Gao et al., 2009), precisely weighted powdered samples (without ignition) of 100 mg were placed into pre-cleaned 20 ml PFA beakers with 4ml 24N HF and 0.5 ml 16N HNO₃. These beakers were tightly capped and heated on hot plate at ~120 °C for 12 hours. The samples were then dried at ~120 °C on a hot plate to evaporate the SiF4 but only to incipient dryness to avoid loss of any volatile elements. Then 2 ml 24N HF and 2 ml Aqua Regia (HCl : HNO₃ = 3:1) were added into the beakers and were heated on hot plate at ~120 °C for 3 hours. The solutions (and residues if any) were transferred to pre-cleaned

15 ml Teflon vessels for microwave digestion using single-reaction-chamber microwave (UltraWAVE by Milestone). The microwave digestion procedures were demonstrated by Casey et al. (2016) and Yang et al. (2017) for trace element analysis of organic samples and extended to bulk rock digestions. The UH ICP lab adapted the microwave for use of rock powders to achieve 100% recoveries for USGS standards to replace more traditional Parr bomb digestion systems. Specifically, the heating process and digestion procedure have been modified for rock powders using Teflon digestion vessels and strong acid mixtures of HF, HCl and HNO₃ with precision and accuracy of most critical trace elements < 5% including Zr and Hf that assures complete digestion of refractory zircon in a range of silicic USGS standards (Casey et al., in prep). After microwave digestion, the remaining residue and solution were completely transferred from each vessel back to their original 20 ml PFA beakers, dried to incipient dryness and then refluxed with 4 ml 16N HNO₃. The capped beakers were heated on a hot plate at ~120 °C for 12 hours and were again dried to incipient dryness but refluxed with 4 ml 12N HCl. The samples were repeatedly fluxed three times with 2 ml 8N HNO₃ to completely get rid of HF and HCl. After adding 4ml 8N HNO₃, the capped beakers were placed on a hot plate at a temperature of ~120 °C for 3 hours to allow the samples completely redissolve. The final clear solutions were transferred into pre-cleaned lowdensity polyethylene bottles and diluted with Milli-Q water to a dilution factor of 1:1000. These 1:1000 diluted solutions were analyzed by Agilent 8800 Triple Quadrupole-Inductively Coupled Plasma-Mass Spectrometer (QQQ-ICP-MS) at the UH ICP lab as well. More detailed information of QQQ-ICP-MS at UH ICP lab such as instrument operation and analysis conditions, background equivalent concentration and detection and quantitation limits of each element has been provided by Yang et al. (2017). One procedural blank and two USGS standards, BHVO-2 and SCO-1, were also prepared simultaneously with sample powders using the same procedures. Likewise, SCO-1

was used as the primary standard whereas the BHVO-2 was treated as secondary standard. Only trace elements with the relative standard deviation (RSD, assessed by BHVO-2) no higher than 10% were reported. Most trace elements have RSD of < 5%. Some elements including S, Ge, Se, Ag, Cd, W and Tl have higher RSD but still lower than 10%. Estimates of accuracy and precision are presented in Appendix Table A4.1. Reference values for BHVO-2 and SCO-1 are from Jochum et al. (2016) and Smith (1995), respectively. However, it is important to note that some elements including P, Mn and K in BOIC silicic samples analyzed in this study are lower than 0.1 wt.% that may not be appropriately treated as major/minor elements and precisely measured by ICP-OES. Therefore, these elements with concentrations ≤ 0.1 wt.% were analyzed again by QQQ-ICP-MS as trace elements but were finally converted to weight percent and reported as major/minor elements (highlighted with asterisk in Appendix Table A4.1).

4.3.2 Legacy geochemical datasets from the Bay of Islands Ophiolite Complex

To better understand the magmatic petrogenesis and evolution of the BOIC silicic intrusions, we also encompass some previously published datasets including those of fine-grained basalts, diabases, andesites, dacites, rhyodacites and their equivalent intrusive dikes, as well as plutonic plagiogranites, originally reported by Carter (1985), Casey et al. (1985), McNeil (1985), Siroky et al. (1985), Kharas-Khumbatta (1988), Elthon (1991) and Jenner et al. (1991). Older datasets that are not included in this manuscript are primarily from Malpas and his co-workers (e.g., Williams and Malpas, 1972; Malpas, 1976, 1979) because samples reported do not have clearly indicated locations, and also because the BOIC-CC (Coastal Complex) structural and tectonic framework for samples (Karson and Dewey, 1978; Casey and Dewey, 1984) had not been fully realized. Therefore, we are unable to relocate their samples with any accuracy and could not evaluate sample descriptions and field relations. Although Suen et al. (1979) clearly mapped each

sample, their basaltic and diabasic samples analyzed were described as porphyritic and have visible phenocrysts generally over 8% in volume. Therefore, samples from Suen et al. (1979) were not regarded as representatives of near-magmatic liquids and excluded as well.

All major elements and some trace elements (e.g., Ni, Y, Sr and Zr) of samples reported by Elthon (1991) are identical to those of diabases and basalts collected by J.F. Casey (reported in Casey et al., 1985; Siroky et al. 1985) and those of plagiogranites (reported in Carter, 1985). Therefore, we use our original field sample names and locations. Although Elthon (1991) simply designated different names for these samples, he did not provide or reference locations for each sample. Elthon (1991) did provide additional analyses of trace elements by INAA (instrumental neutron activation analysis) including Ta, Th and rare earth elements (REE) that are also used here. We compared the reproduced major and some trace element datasets in Elthon (1991) to assure that the analyses were exactly identical with prior publications. It showed that two samples named plagiogranite, two named quartz diorite and four named dolerite are respectively identical to two plagiogranites labeled 300C and 300G and two labeled 35Y and 50A reported in Carter (1985), and basalts and diabases labeled S141a, 4922a, 5000a and S111b that were collected by Casey (1980) and reported in Casey et al., (1985) and Siroky et al. (1985). Because the remnant samples are in our possession and the major element analyses were originally reported with appropriate and clear field sample labels, locations and descriptions, we retain the first published field sample names and chemistries reported in the original publications listed above for clarity. The INAA trace element data reported for these samples by Elthon (1991) were added to supplement our compiled database with other BOIC trace element data and used in modeling for completeness.

4.4. Analytical Results

4.4.1 Bulk rock geochemistry

Major elements of BOIC samples including those analyzed in this study and complied from prior available datasets are plotted versus MgO together with our modeling results (e.g., Fig. 4.11). We observe no compositional gap, that is commonly interpreted to be related to liquid immiscibility process (e.g., Dixon and Rutherford, 1979; Charlier et al., 2012, 2013), in major element variation diagrams between BOIC basaltic and felsic samples, although intermediate compositions appear to be sampled or analyzed less commonly. The more evolved compositions, however, show increasing scatter in SiO₂, Al₂O₃, CaO and Na₂O, with the latter two more subject to gains and losses during alteration. Understandably, tighter trends are obtained for immobile elements of TiO₂ and FeO* (total iron as FeO). Furthermore, the overall variation trends of TiO₂ and FeO* from BOIC basaltic to felsic compositions both suggest that Fe-Ti oxide minerals begin to crystallize as a large fraction when the magma MgO content reaches ~4-5 wt.%. When MgO is used as differentiation index, the BOIC diorites and trondhjemites are the most evolved melt-like magmatic products of similar extensive fractionation, but the diorites show systematically lower SiO₂ and FeO* and higher Al₂O₃ contents than those of trondhjemites suggesting that they may not be generated by strictly identical magmatic pathways.

New more extensive trace elements of each sample analyzed by QQQ-ICP-MS are presented for 19 samples in Appendix Table A4.1. They include seven trondhjemites and one diorite collected in 2017, four trondhjemites reported with limited XRF trace data in Kharas-Khumbatta (1988) and seven fine-grained dikes with limited XRF trace data from Casey et al. (1985). Selected elements are normalized to N-MORB values of Sun and McDonough (1989) except for vanadium that is from Gale et al. (2013) and are presented on multi-element and rareearth element (REE) variation diagrams in Fig. 4.6 with elements arranged in order from right to left by increasing mantle incompatibility (Sun and McDonough, 1989; Rollinson, 1993; Hoffman, 1997).

The primitive diabase BMD 1009B was used for modeling of primitive basalt fractionation because it shows a N-MORB-like REE pattern similar to other BOIC diabases and basalts but without significant Eu anomaly indicating an expected lack of plagioclase fractionation (black lines in Fig. 4.6). There is an overall growing negative Eu anomaly in more silica-enriched BOIC samples, which is a typical signature of fractional crystallization of cumulate plagioclase (e.g., Komor and Elthon, 1990). Extended trace element plots, however, also show negative Nb and Ta anomalies in diabase BMD 1009B, typical signatures for supra-subduction zone (SSZ) forearc, arc or back arc (also see Elthon, 1991; Jenner et al., 1991). Likewise, BOIC plutonic plagiogranites and silicic dike rocks analyzed show similar variation patterns and SSZ immobile element signatures, but there is nonsystematic scatter in mobile elements of Cs, Rb, K, Ba, Sr, Pb and Li, like CaO and Na₂O that reflect variable extents of hydrothermal alteration, element loss or gain at various levels in the upper stratigraphy or perhaps mild SSZ arc signatures (Fig. 4.6a and c) that are not completely distinguishable. Although variably affected by mobility, the predominant negative Sr anomalies both in silicic plutonic and dike rocks also likely reflect extensive plagioclase fractionation during magma evolution and are generally signatures of magmatic liquid compositions, as opposed to indicating any accumulative effects. Relative to the parental diabase BMD 1009B lacking anomalies, increasing negative V and Ti anomalies with increasing SiO₂ and decreasing MgO in more felsic rocks typically reflect Fe-Ti oxide crystal fractionation in evolved magmatic liquids, consistent with the variation trends of TiO₂ and FeO* in major element variation diagrams showing depleted trends from ~4-5 wt.% MgO samples toward more evolved felsic ones.

Strong Zr and Hf positive anomalies occur in one of the plutonic plagiogranites (BMD.252-B-84) and the two rhyodacitic dike rocks (BMD 2129A and BMD 2130A), likely indicating the effects of some zircon accumulation or small veins involved. The near-parallel REE variation patterns with progressively increasing abundances and slight enrichment of La/Sm ratios with lower MgO and higher SiO_2 of these coarse-grained silicic plutonic rocks are overall similar to those finegrained hypabyssal dikes with negative Nb and Ta anomalies. Therefore, it appears the BOIC silicic fine-grained dikes and plutonic plagiogranites are both melt-like in composition. Although rhyodacitic dike BMD 2130A is more enriched in HREEs that is different from all other samples characterized by relatively flat HREEs (Fig. 4.6d), such enrichment is in accordance with the anomalous Zr-Hf enrichment and perhaps caused by zircon accumulation and not a different magmatic lineage. In summary, the BOIC plutonic plagiogranites and silicic fine-grained intrusive dikes show strong geochemical equivalence suggesting that they all appear to represent nearmagmatic liquids that may be produced by extensive magma differentiation in a supra-subduction zone forearc environment (Nelson and Casey, 1979; Casey and Dewey, 1984, Dewey and Casey, 2011, 2013, 2015, 2021; Yan and Casey, 2020).

Fig. 4.6 N-MORB normalized multi-element and rare-earth element (REE) variation diagrams for (a) and (b) coarse-grained plutonic plagiogranites from this study and from Kharas-Khumbatta (1988), and (c) and (d) fine-grained intrusive dikes from Casey et al. (1985). The black line indicates the primitive diabase BMD 1009B chosen as the parental melt for following petrogenetic fractionation modeling. Note that elements are approximately arranged in decreasing order of lower mantle incompatibility from left to right (Sun and McDonough, 1989). N-MORB normalized element values are from Sun and McDonough (1989) except for vanadium that is from Gale et al. (2013). Element concentrations used here are analyzed by QQQ-ICP-MS in this study, except for a few potassium values which were originally measured by XRF with the major elements. Note that the primitive diabase BMD 1009B used in modeling shows a MORB-like REE pattern (i.e., parallel to mean N-MORB patterns and similar abundances to many primitive MORBs) with no significant Eu anomaly (e.g., Wanless et al., 2010) and that there is an overall growing negative Eu anomaly in BOIC more felsic samples typical of dacite to rhyodacite volcanic melts during progressive fractional crystallization. However, multi-element plots show negative Nb-Ta anomalies in diabase BMD 1009B, more typical signatures for supra-subduction zone (SSZ) forearc, arc, or back arc origin. BOIC felsic plutonic and dike rocks likewise show similar patterns and SSZ immobile element signatures, but there is nonsystematic scatter in fluidmobile elements of Cs, Rb, K, Ba, Sr, Pb and Li that reflect less distinguishable variable hydrothermal alteration or mild SSZ signatures. Although Sr is variably affected by fluid mobility (see positive Sr anomaly in diabase BMD 1009B), the predominantly negative Sr anomalies in more felsic samples likely reflect magma evolution trends during plagioclase fractionation both in more felsic plutonic and dike rocks. Increasingly negative Ti and V anomalies in more felsic rocks also typically reflect the effects of Fe-Ti oxide crystal fractionation in evolved magmatic liquids. Note rhyodacitic dike BMD 2125B and dacitic dike BMD 1085 show the highest negative Ti anomalies compared to other samples of similar SiO_2 or MgO, suggesting that they may have experienced more prolonged oxide mineral depletion effects (see Fig. 4.7). Some of the BOIC silicic samples show Zr-Hf positive anomalies, and the most significant positive anomaly occurs in the rhyodacitic dike rock BMD 2130A complemented with the enrichment in HREEs.



4.4.2 Geochemical discrimination diagrams

4.4.2.1 Lithology classification

In the SiO₂ vs. Zr/TiO₂ diagram of Winchester and Floyd (1977), fine-grained rocks of mafic composition plot within sub-alkaline basalt field (Fig. 4.7), in agreement with the original field description and chemical classification given by Casey et al. (1985) and Siroky et al. (1985). Several samples from these studies fall within andesite field (53-63 wt.% SiO₂), but as they are mainly fine-grained intrusive dikes within the sheeted diabase dike unit in the field, we refer them as andesitic dikes to denote their both textural and compositional characteristics, with samples of 52-57 wt.% SiO₂ specifically as basaltic andesitic dikes (see Appendix Table A4.1).

Two silicic fine-grained dike samples, BMD 2130A and BMD 2129A from Casey et al. (1985), have very high SiO₂ respectively of 72.98 wt.% and 72.57 wt.% that plot within rhyodacite and dacite field (Fig. 4.7). Accordingly, they are termed rhyodacitic dikes. Two other fine-grained dike samples BMD 2125B and BMD 1085 also from Casey et al. (1985) plot respectively within trachy-andesite and trachyte field. However, compositional data (very low K₂O) and spatial association with the other fine-grained silicic dikes intruding the basal sheeted diabase unit suggest they are not trachytic. On the Winchester and Floyd (1977) discrimination diagram the relatively high Zr/TiO₂ ratios, therefore, are probably caused by a combination effect of zircon accumulation and more extensive Fe-Ti oxide crystallization based on weak to moderate positive Zr and Hf anomalies and moderate to strong depletion of Ti in the normalized trace element patterns (Fig. 4.6), as well as based on very low K₂O content and Na₂O/K₂O ratio (Fig. 4.7) that are inconsistent with "true" trachytic compositions (also see Fig. 4.9). Thus, sample BMD 2125B and BMD 1085 in fact plot in the tholeiitic field and are more appropriately named andesitic and dacitic dike, respectively (black arrows in Fig. 4.7).



Fig. 4.7 SiO₂-Zr/TiO₂ classification diagram (Winchester and Floyd, 1977) for fine-grained volcanics and hypabyssal rocks including basalts and diabase intrusions classified as sub-alkaline basalt and diabase, andesite, basaltic andesite and andesitic, dacitic and rhyodacitic intrusive dikes collected from base of the sheeted dike unit or as dikes within the isotropic gabbro unit of the Bay of Islands Ophiolite Complex. Note that sample BMD 1085 and BMD 2125B (open black triangles with denoted K₂O contents) reported in Casey et al. (1985) respectively fall within more alkaline trachyte and trachy-andesite fields but have low K₂O showing typical tholeiitic characteristic (also see Fig. 4.9) that are likely caused by a combination effect of zircon accumulation and extensive Fe-Ti oxide depletion that elevates Zr/TiO₂ ratios (see Fig. 4.6).

For coarser-grained plutonic rocks, classification is based on CIPW normative (calculation procedures by Hollocher, 2004) compositions of albite, anorthite, orthoclase and quartz. Quartz-plagioclase-K-feldspar (QAP) diagram (Le Maitre et al., 2002) shows that the BOIC plagiogranites are composed of tonalites and trondhjemites with minor amounts of quartz diorites and diorites (Fig. 4.8a). However, further classification of the more silica-rich BOIC endmembers (i.e., samples in tonalite and trondhjemite field of Fig. 4.8a) on the anorthite-albite-orthoclase (An-Ab-Or) diagram (Fig. 4.8b, modified from Barker, 1979) shows that they are all

trondhjemites. Therefore, BOIC plutonic plagiogranites included in this study are dominantly composed of trondhjemites, with lesser intermediate compositions of quartz diorite and diorite (Fig. 4.8).



Fig. 4.8 CIPW normative rock classification ternary diagrams of (a) quartz-plagioclase-K-feldspar for coarse-grained plutonic plagiogranites (Le Maitre et al., 2002) with fields of tonalite & trondhjemite (quartz > 20%), quartz diorite (quartz = 5 to 20%) and diorite (quartz < 5%) and (b) anorthite-albite-orthoclase (An-Ab-Or) for quartz-rich plutonic rocks (after Barker, 1979). Note that only more felsic samples within tonalite & trondhjemite field of (a) are included in (b). The BOIC plagiogranites are dominantly composed of trondhjemites with lesser intermediate compositions of quartz diorite and diorite.

4.4.2.2 Magma series discrimination diagram

On the alkali-iron-magnesium (AFM) ternary diagram for discrimination of magmatic differentiation series, we plot the plutonic plagiogranites (Fig. 4.9a) and fine-grained dikes (Fig. 4.9b) with the calc-alkaline/tholeiitic boundary (purple line) included from Irvine and Baragar (1971). Most BOIC trondhjemites and quartz diorites and some diorites clearly follow a tholeiitic iron-enrichment trend (Fig. 4.9a). Fine-grained mafic basalts and diabases, although

clustered along the tholeiitic and calc-alkaline boundary, still exhibit a clear tholeiitic ironenrichment trend (e.g., Casey et al., 1985) and a typical compatible Fe-Ti enrichment trend with synchronous magnesium depletion (Fig. 4.9b). In contrast, some plutonic diorites and fine-grained hypabyssal dikes and volcanic samples of intermediate andesitic compositions show an "apparent" calc-alkaline trend characterized by equal consumption of iron and magnesium (i.e., constant FeO*/MgO ratio) with accumulation of alkalis (Fig. 4.9b). However, based on the overall low K₂O content of these silicic samples, they unlikely follow a true calc-alkaline series lineage (e.g., see Rickwood, 1989). In fact, BOIC samples of plagiogranitic, and esitic, dacitic and rhyodacitic compositions all plot within low-K tholeiitic series field, similar to oceanic plagiogranites from other oceanic crust and ophiolites (e.g., Coleman and Donato, 1979; Maniar and Piccoli, 1989; Koepke et al., 2007) but distinctive from A-type granite and Archean TTG (Tonalite-Trondhjemite-Granodiorite) suite of more typical calc-alkaline characteristics (Fig. 4.9c-d), even though metasomatic Na enrichment may play a role as suggested by Malpas (1976, 1979) In summary, the BOIC samples from basaltic to felsic compositions appear to dominantly follow a typical iron-enrichment tholeiitic trend, although some felsic samples appear to plot enigmatically within calc-alkaline field in AFM diagram (discussed below).

Fig. 4.9 Alkali-iron-magnesium (AFM) ternary diagram with calc-alkaline/tholeiitic boundary after Irvine and Baragar (1971) showing magma series discrimination diagrams for plutonic plagiogranites including trondhjemites, quartz diorites and diorites (a) and fine-grained basalts, diabases, andesites and andesitic, dacitic and rhyodacitic intrusive dikes (b), as well as SiO₂ vs. K₂O diagram with boundaries of shoshonite series, high-K calc-alkaline series, calc-alkaline series and low-K tholeiitic series from Peccerillo and Taylor (1976) for plutonic plagiogranites (c) and fine-grained basaltic to rhyodacitic hypabyssal dikes and volcanics. Fields for A-type granite (light blue shades) and Archean TTG (trondhjemite-tonalite-granodiorite, purple shades) are from Maniar and Piccoli (1989), whereas oceanic plagiogranite field is from Maniar and Piccoli (1989) and Koepke et al. (2007). Note that the combined dataset lacks compositional gaps in the dominant tholeiitic iron enrichment trends, although some of the fine-grained andesitic dikes and plutonic diorites fall "apparently" within the calc-alkaline (CA) field in (a-b) but lack higher K2O characteristics of CA volcanics and plot clearly within tholeiitic series field in (c-d), suggesting the BOIC samples from basaltic to felsic compositions are in fact following a typical ironenrichment tholeiitic variation trend. These silicic BOIC samples are similar to oceanic plagiogranites in other oceanic and ophiolitic crusts (e.g., Coleman and Donato, 1979; Maniar and Piccoli, 1989; Koepke et al., 2007), but distinctive from A-type granite and Archean TTG suite of more typical calc-alkaline characteristics.


4.4.2.3 Tectonic discrimination diagram

Pearce et al. (1984) suggested that felsic (SiO₂ \geq 56 wt.%) intrusive rocks can be subdivided into four main types including 1) ocean ridge granite (ORG) involving rocks from midocean ridges, SSZ forearc and back arc basin spreading centers and certain ophiolites, 2) volcanic arc granite (VAG), 3) within plate granite (WPG) and 4) collision granite (COLG) based on their Ta, Yb, Rb, Nb and Y concentrations. Because samples collected from the BOIC have undergone variable degrees of hydrothermal alteration that can significantly modify mobile element concentrations (e.g., Rb), here we only demonstrate diagrams constructed by using relatively immobile elements including Nb, Y, Ta and Yb to avoid potential bias.

Fig. 4.10 shows that the majority of BOIC felsic samples plots within the ORG field interpreted to indicate a spreading center origin, except one trondhjemite BMD.252-B from Kharas-Khumbatta (1988) and two fine-grained andesitic dikes 2124B and 2127A from Casey et al. (1985) that plot within VAG field. It is noteworthy that the three samples within VAG field have the lowest SiO₂ content compared to others of the same lithology and also plot in the calcalkaline field in AFM diagram (e.g., Fig. 4.24). However, all felsic samples included in Fig. 4.10 together show an apparent linear trend from the VAG to ORG field with an overall increasing SiO₂ content. This trend and the "apparent" calc-alkaline nature will be discussed further based on modeling results and addressed more specifically in the magma mixing section



Fig. 4.10 Felsic rock (SiO₂ \geq 56 wt.%) tectonic discrimination diagrams depicting Ta vs Yb (a) and Nb vs. Y (b) of Pearce et al. (1984) showing fine-grained felsic dikes and plutonic plagiogranites plot dominantly in the Ocean Ridge Granite (ORG) field that includes rocks from mid-ocean ridges, SSZ forearc and back arc basin spreading centers and certain ophiolites (Pearce et al., 1984). Note that the two quartz diorites (green diamonds) in (a) were originally reported by Carter (1985), but trace elements are from Elthon (1991). Three samples including two andesitic dikes (BMD 2124B and BMD 2127A, blue triangles) and one trondhjemite (BMD.252-B, red circle) are within the volcanic arc field (VAG), whereas all others dominantly plot in the ocean ridge field (ORG) in (a). However, the three VAG field samples have the lowest SiO₂ content compared to others of the same lithology. They together with other samples plotting within the ORG field show an apparent linear trend from the VAG to ORG field with an overall increasing SiO₂ content (see further discussion in magma mixing section).

4.5 Petrogenetic models

4.5.1 Direct partial melting of metagabbroic and diabasic rocks without or with post-partial melting fractional crystallization in magma chamber roof zone

4.5.1.1 Model justification and setup

Silicic melts can be produced by partially melting various parental materials, among which upper-crustal greenschist to amphibolite facies diabases/metagabbros are of special interests due to their intimate association with these melts in the roof zone of sub-axial magma chambers (e.g., Gillis and Coogan, 2002; Koepke et al., 2004, 2007; France et al., 2010, 2014; Fischer et al., 2016). Recent studies suggest that a dynamic axial magma chamber ubiquitously exists below intermediate and fast oceanic spreading centers involving a magma-dominated roof zone with multiple magma lenses, pockets or sills that act as the source for feeding upper pillow basalt and conduit sheeted dike units to form upper crust (e.g., Singh et al., 1998; France et al., 2009, 2014; Koepke et al., 2011), and also for crystallizing layered gabbroic units that form the lower crustal crystal-dominant mush zones commonly with entrained sill zones (e.g., Sleep, 1975; Dewey and Kidd, 1977; Detrick et al., 1987; Sinton and Detrick, 1992; Nicolas et al., 2009; Boudier and Nicolas, 2011; Marjanović et al., 2014; Lissenberg et al., 2019; Koepke and Zhang, 2020; Carbotte et al., 2021). The base of sheeted dike, therefore, can be regarded as a dynamically balanced interface or boundary layer with localized deformation between two contrasting convecting systems involving cooling (and hydrated) by hydrothermal fluid circulation penetrating through sheeted dike unit and potentially down into gabbroic sections, and heating (and partial melting) by the underlying axial magma lens (AML). The AML is sustained by episodic magma replenishment originating from lower mush zone or upper mantle (e.g., Boudier et al., 2000; Gillis and Coogan, 2002; Nicolas et al., 2003, 2008; Baker, 2009; France et al., 2009, 2010).

A common scenario proposed for genesis of felsic melts in the roof zone of magma chambers is by partial melting of previously hydrothermally altered sheeted dikes and upper gabbroic rocks in modern oceanic crust and in ophiolites (e.g., Gillis and Coogan, 2002; Koepke et al., 2004, 2005, 2007; France et al., 2010, 2014; Bindeman et al., 2012; Erdmann et al., 2015), although lower gabbroic section can also be melted if high-temperature amphibolite mylonite shear zones are present and act as conduits for hydrothermal fluids (Casey, 1980; Koepke et al., 2004). However, it is notable that low-potassium protoliths are necessarily required in particular to produce plagiogranitic composition typically with $K_2O < 1$ wt.% (e.g., Spulber and Rutherford, 1983; Koepke et al., 2004; France et al., 2010). Anatectic melts would further either solidify or crystallize in situ close to their protolith to form more evolved oceanic plagiogranites or may be recycled within the less evolved melt lens resulting in mixing, hybridization and contaminated MORB melts (Gillis and Coogan, 2002; Coogan et al., 2003; Rollinson, 2009; France et al., 2010, 2014; Grimes et al., 2013). Furthermore, the genesis of anatectic melts would be accompanied by a suite of residual (hornfels) assemblages with a typical granoblastic textures broadly recognized in the base of sheeted dike unit both in modern oceanic crust (e.g., Koepke et al., 2008; France et al., 2009) and in ophiolites (e.g., Rosencrantz, 1980; Coogan et al., 2003; Gillis, 2008; France et al., 2009).

Recent studies with specific focus on the chemical features and field relations of global intermediate and felsic samples have suggested partial melting of hydrated upper crust to be the most dominant process in oceanic and ophiolitic crust, by hydrous/dehydration melting of basic rocks underlying spreading centers in both subduction-unrelated (e.g., mid-ocean ridge) and subduction-related (e.g., forearc, arc and backarc) environments (see Furnes and Dilek, 2017 for a review). In the BOIC, lower sheeted dike and upper isotropic gabbro units have been strongly

affected by hydrothermal alteration to amphibolite to greenschist facies, many of which have little modified igneous textures, but some have fine granular textures deemed symptomatic of contact metamorphism suggested to indicate partial melting may be a common process. We, however, note that hornfels-like granular textures also can be interpreted as pure dehydrated metamorphic residue (e.g., Gillis and Roberts, 1999; France et al., 2010) or result from the igneous crystallization and simple heating (e.g., Gillis, 2008; France et al., 2009, 2010, 2014; Koepke et al., 2008, 2011) rather than residues of melting, and could be irrelevant to the melting process.

Deformation could effectively lead to the segregation, extraction and migration of these anatectic melts in the oceanic crust as the pore pressure will progressively elevate in response to increasing melting degree to induce local fractures (Petford et al., 2000; Bons et al., 2004; Brown, 2004, 2013; Clemens and Stevens, 2016). Recent studies suggest that very small increments of melting (< 1%) can cause significant increases of melt pore pressure of tens of MPa (e.g., Etheridge et al., 2021). These fractures can further merge with each other to form a connected fracture network to enhance the melt segregation and migration. This is in consistent with many field and geochemical studies suggesting that segregation of small degree partial melts is efficient and common (e.g., Le Fort, 1981; Holtz, 1989; Sawyer, 1991) and that accumulation of a large amount of melt fractions in the source is extremely unlikely (e.g., Etheridge et al., 2021). Therefore, partial melt, if it forms, is unlikely to accumulate in situ within the source, but appears as episodic pulses after every small amount of melting ($< \sim 1-5\%$) to form smaller pockets, dikes and veins close to the protolith, as proposed by many studies on the basis of major element compositions and corresponding natural samples (e.g., Koepke et al., 2004; France et al, 2009, 2010). However, we have sampled a 500 m diameter plagiogranite pluton in this study, not uncommon in the BOIC,

that appears still to require larger accumulations and sources of silicic melts (e.g., Fig. 4.2) suggesting that they may not be formed by a simple direct partial melting process.

pMELTS (Ghiorso et al., 2002) was utilized to quantitively simulate the partial melting process occurring at the roof zone of magma chamber (estimated equivalent pressure of ~0.7 kb) where felsic intrusions ubiquitously exist (e.g., Fig. 4.2) under relatively high-oxidation and high-water conditions of P = 0.7 kb, fo₂ = QFM+2 and H₂O = 2 wt.% (e.g., Beard and Lofgren, 1991; Koepke et al., 2004; France et al., 2010). The partial melting model presented here was conducted at an increasing temperature interval of 2 °C with a starting temperature of 600 °C to ensure that the starting melting point can be precisely recorded and an ending temperature of 1300 °C to completely melt the protolith (i.e., 100% liquid at the end). However, in natural environment melting beyond 50% is unlikely to occur (e.g., France et al., 2009, 2010) and thus, only melt compositions produced lower than 50% melting have been presented with models. It is notable that only low degree melts can approximate some plagiogranite major element compositions (e.g., Flagler and Spray, 1991; Koepke et al., 2004; France et al., 2010). Starting protolith materials used here include two BOIC statically altered (upper greenschist facies) diabases (BMD 1010AB and BMD 1017A), one statically altered (amphibolite facies) metagabbro (NA 76A) and one statically altered (amphibolite facies) oxide metagabbro (PM 169). These protoliths are considered to be representatives of the BOIC roof zone lithologies that could be potentially melted to form silicic intrusives. The metagabbros and diabases are all altered at greenschist to amphibolite facies statically, corresponding to the potential hydrated solid roof zone environment of magma chamber where evidence of extensive hydrothermal alteration exists (e.g., Fig. 4.5). Chemical compositions of these protoliths are from Casey et al. (1985) and J.F. Casey previously unpublished datasets (see Appendix Table A4.2). Trace element concentrations in partial melts were calculated by

assuming equilibrium melting prevailed (equation: $C_1 = C_0/[D(1 - F) + F]$; $C_1 = \text{concentration of}$ the element in the melt; $C_0 = \text{concentration of}$ the element in the parent; F = percentage of melt; D = bulk partition coefficient, similar, for comparison, to many other partial melting experimental and modeling studies (e.g., Flagler and Spray, 1991; Rapp et al., 1991; Koepke et al., 2004; France et al., 2010; 2014; Chen et al., 2019). Basaltic partition coefficients were used for calculations of any partial melts produced with SiO₂ < 53 wt.%, whereas andesitic partition coefficients for those melts with SiO₂ \geq 53 wt.% (Appendix Table A4.3).

Our modeling results show that, although various starting materials modeled, partial melting alone cannot reproduce the BOIC highly evolved felsic compositions with $SiO_2 >$ 70 wt.%. Therefore, the initial "evolved" silica-rich partial melts, normally produced at more limited ~5% melting values, were then molded to undergo Rayleigh fractional crystallization (equation: $C_1/C_0 = F^{(D-1)}$; C_1 = concentration of the certain element in the liquid; C_0 = concentration of the certain element in the parent; F = percentage of melt remaining; D = bulk partition coefficient of the certain element) by rhyolite-MELTS (Gualda et al., 2012; Ghiorso and Gualda, 2015), as an attempt to reproduce the more highly evolved intra-pluton compositions observed in BOIC felsic samples.

4.5.1.2 Direct hydrous partial melting of the altered metagabbros and diabases

Partially melting the roof zone protoliths from the BOIC is unlikely to reproduce the narrower sample trends observed in plagiogranite and silicic dike data from the BOIC and particularly compositions of those highly evolved plagiogranites of $SiO_2 > 75$ wt.% because of the mismatches between modeling results and natural sample geochemistries (Fig. 4.11, 4.12 and A4.1). Experimental melt compositions generated by partially melting a gabbroic rock (Koepke et al., 2004) at various temperatures shown by grey triangles in Fig. 4.11 are not very different from our partial melting modeling results of the two metagabbros. These modeling results all show clear mismatch with BOIC samples from the more felsic (e.g., trondhjemitic and dioritic) to andesitic melt compositions (e.g., enrichments of FeO*, TiO₂ and SiO₂ in natural BOIC felsic samples compared to modeled melts), and none of even the lowest degree melts can yield the lowest MgO and highest SiO₂ BOIC trondhjemites, which make up the majority of samples.

Modeled melting of BOIC diabases are the least capable in producing high SiO₂ and low MgO partial melts. Furthermore, no single melting trend derived from the four protoliths is capable of reproducing the range of Al₂O₃ contents or compositions of the most silicic samples. Likewise, melting trends derived from a hydrothermally altered diabase from France et al. (2010) (cross symbols in Fig. 4.11) also do not resemble the overall BOIC sample variation trends because experimental melts of intermediate compositions are low in Na₂O, TiO₂, and FeO* compared to BOIC intermediate samples. Particularly, the experimental results derived from the diabase (France et al., 2010) fail to reproduce BOIC sample Al₂O₃ composition as the melting line from felsic to intermediate only passes through a few BOIC samples and lack an overall match with the majority.

Enrichments in La, Y and La/Sm ratio in the highest SiO₂ BOIC samples are also not reproduced even by the lowest degree melts. Melting of plagioclase-rich metagabbro (24.31 wt.% Al₂O₃) NA 76A produces a melting trend on the La vs La/Sm plot that is too far away from the natural BOIC samples and cannot even be shown appropriately (Fig. 4.12c), nor does it match other melting trends (Fig. 4.12a and b) because of large residual plagioclase abundances. In summary, the compositional diversity of altered gabbroic and diabasic protoliths in the BOIC roof zone demonstrates significant mismatches in major elements, variations in modeled trace elements and lack of correlation with variation trends of the BOIC intermediate to silicic samples. Especially both major and trace element results of partial melting models fail to reproduce the highly evolved silica-enriched plagiogranites (Fig. 4.11, 4.12 and A4.1). Therefore, we suggest petrogenesis as a direct partial melt product of altered roof zone lithologies is unlikely to account for the genesis of BOIC plagiogranites and their fine-grained silicic dike equivalents, although it is commonly suggested to be the dominant process in many other oceanic crust and ophiolites (e.g., Koepke et al., 2004, 2005, 2007; France et al., 2010, 2013, 2014; Furnes and Dilek, 2017).

Fig. 4.11 Direct hydrous partial melting modeling results of various protoliths including two BOIC statically altered (upper greenschist facies) diabases (BMD 1010AB and BMD 1017A), one statically altered (amphibolite facies) metagabbro (NA 76A) and one statically altered (amphibolite facies) oxide metagabbro (PM 169) under low-pressure (i.e., 0.7 kb, roof zone melting), water-saturated ($H_2O = 2$ wt.%), oxidizing ($fo_2 = QFM+2$) conditions using pMELTS (Ghiorso et al., 2002). Note that only up to the first 50% melting and liquid compositions are shown as higher degrees of melting are unlikely to occur. Values at hatch marks along the partial melting trends (10%, 20%, 30%, 40% and 50%) indicate percentages of melt fractions produced by partial melting modeling; filled circle on each of the partial melting trend represents the ~5% partial melt used for future post-melting crystal fractionation (see Fig. 4.13 and 4.14). Grey triangles with adjacent melting temperatures represent liquid compositions from partial melting experiments on three oceanic cumulate gabbros drilled by ODP (Ocean Drilling Program) cruises witht temperatures of 1020, 980, 940 and 900 °C from Koepke et al. (2004). The apex of each triangle represents one of the three liquid compositions per each sample obtained at a particular temperature. Grey dashed lines with cross symbols indicate liquid compositions from partial melting experiments on a sample from hydrothermally altered sheeted dikes units at temperatures of 1030, 1000, 970, 955, 940, 910, 880 and 850 °C in France et al. (2010). Note similarities of prior experimental results with our modeling trends, but the much wider range of melt compositions modeled by choosing from the wide variety of roof zone lithologies. The individual melts derived by partially melting the altered roof zone lithologies fail to reproduce the BOIC SiO₂-enriched sample trends and in particular the compositions of highly evolved BOIC plagiogranites. FeO*: total Fe as FeO in this diagram and all subsequent modeling plots.



Fig. 4.12 Selected trace element modeling results of direct hydrous partial melting process including La and Y as representatives respectively of LREE and HREE vs. MgO, as well as La/Sm vs. La for direct hydrous partial melting models of the four (altered) protoliths used. Small hatch marks on each melting line indicate partial melts (F) produced at 10%, 20%, 30%, 40% and 50% melting of the protoliths; values at the left side of each melting line in (a) indicate mass percentages of the earliest melt produced; filled circles on each of the partial melting trend represent the ~5% partial melts used for future post-melting crystal fractionation (see Figs. 13-14). Note that partial melting fails to generally reproduce sample trace element trends nor do small melt fraction compositions (e.g., 1-15%) approach the most evolved samples even when various protoliths are used (also see Fig. A4.1). The two diabase melting lines do match some andesitic and dioritic sample compositions but still lack overall similar variation trends of the BOIC samples. Modeled melt trace elements of La and La/Sm ratio in gabbroic rock melting, the preferred lithology of Koepke et al. (2004), at low melting extent compositions are a mismatch with BOIC felsic rocks. Altered leucogabbro NA 76A melts are too depleted in both La and Y relative to the BOIC igneous samples. The diagram also shows direct melting of roof zone metabasites would produce a wide range of melt compositions dissimilar from BOIC felsic rocks.



4.5.1.3 Partial melting followed by crystal fractionation

In an attempt to accommodate production of melts with up to 70-75% SiO_2 that characterizes the BOIC trondhjemites, we fractionated the compositions of the more highly silicic low-degree partial melts produced at only ~5% melting to evolve modeled partial melts further by post-melting fractional crystallization. This was to promote further evolution and enrichment in SiO₂ of the partial melts rather than attempting to match the raw melting products as above. The combined modeling results of partial melting (solid lines) and corresponding subsequent postmelting fractional crystallization of the low-degree, SiO₂-enriched partial melts produced at ~5% melting (dashed lines) are presented in Figs. 4.13-4.15 (also see Fig. A4.2) with metagabbro and diabase melting and fractionation scenarios shown separately for clarity. Fractional crystallization of generated low-degree partial melts, however, still cannot reproduce the highly evolved (i.e., MgO < 0.5 wt.%) BOIC plagiogranite compositions as modeled melts are more depleted in FeO*, TiO₂ and Na₂O compared to BOIC plagiogranites of similar MgO content (Fig. 4.13). Furthermore, the overall combined variation trends of partial melting and post-partial melting fractional crystallization modeled also do not match BOIC sample trends from intermediate to felsic compositions (Fig. 4.13). Likewise, selected trace element modeling results of La and Y vs. MgO and La/Sm vs. La derived from the two metagabbros and one diabase BMD 1017A also indicate significant mismatches with BOIC samples presented, although melting and post-melting trends modeled from diabase BMD 1010AB understandably show some similarity in trace elements to the BOIC samples (Fig. 4.14 and Fig. A4.2). However, mismatches still persist with major element modeling results of diabase BMD 1010AB.

We then specifically demonstrate the combined REE modeling results of partial melting and post-melting fractionation model derived from two representative protoliths of metagabbro PM 169 and diabase BMD 1010AB to more comprehensively evaluate incompatible trace elements in the combined model (Fig. 4.15). Modeled partial melts derived from the metagabbro PM 169 (light grey field in Fig. 4.15a) have relatively flat REE variation patterns with no Eu anomaly at early anatectic melting stages, but for high-degree melts they have slightly positive Eu anomaly. REE abundances decrease with increasing degree of melting. The 5% partial melts modeled for post-melting fractionation is shown by the dotted line at the top of the light grey melting field. It is notable that none of the direct partial melts (light grey field in Fig. 4.15a) in the model match the elevated REE abundance of BOIC felsic samples superimposed (colored lines in Fig. 4.15a). Modeled fractionated 5% partial melts show increasing negative Eu anomalies during the post-melting fractionation stage. However, the most evolved modeled melt still only has a negative Eu anomaly of 0.54 (calculated as Eu-anomaly = $Eu_N/(Sm_N * Dy_N)^{0.5}$) that is significantly higher than those of BOIC plutonic plagiogranites (0.11-0.32, average 0.15) and their fine-grained silicic dike equivalents (0.14-0.27, average 0.21) reported in this study. Furthermore, BOIC felsic samples are all characterized by slight LREEs enrichments (La/Sm = 1.41-2.57) that were not successfully modeled by the combined partial melting and post-melting fractionation process (highest La/Sm = 1.47) using metagabbro PM 169 (Fig. 4.15a). Partial melts derived from the diabase BMD 1010AB also show overall flat REE variation patterns, but with very slight negative Eu anomalies (light grey field in Fig. 4.15b). However, the post-melting fractionation stages produced REE enrichment patterns with La/Sm of 1.74-2.09 and negative Eu anomaly value (~0.21) in late-stage modeled post-melting fractionated melts, similar to more felsic BOIC samples (La/Sm = 1.89-2.57 and Eu anomaly = 0.11-0.32) (Fig. 4.15b). Although some modeled major elements in partial melts derived from diabase BMD 1009B show significant mismatches with natural BOIC samples (see Fig. 4.13 and discussion above) suggesting melting process even combined with postmelting fractionation cannot reproduce BOIC plagiogranites, it may indicate that fractionation is necessary to account for trace element enrichments in highly evolved melts. We also include an experimental partial melt composition from France et al. (2014) produced at 955 °C (~40% melting) by partially melting a hydrothermally altered sheeted dike sample (yellow dashed line with cross symbols in Fig. 4.15b), which was reported to be the most plagiogranite-like in composition (see France et al., 2010, 2014). This experimental melt, although has very high melting degree, is somewhat compositionally similar to the BOIC diorites and andesitic dikes and our 5% diabase partial melt, but still very unlike the highly silica-enriched BOIC trondhjemites and rhyodacitic dikes presented here. Furthermore, the overall mismatches of experimental melt major element compositions from France et al. (2010) with BOIC sample trends presented in Fig. 4.11 suggest that direct partial melting of altered sheeted diabase dikes are unlikely to account for the formation of BOIC plagiogranites and their silicic fine-grained dike equivalents.

In summary, we conclude partial melting of altered gabbroic or diabasic rocks in the magma chamber roof zone of BOIC even if combined with post-melting fractionation, is unlikely to have produced these BOIC plutonic plagiogranites and their fine-grained silicic dike equivalents, particularly those highly enriched in silica contents ($SiO_2 > 70-75$ wt.%) due to the clear mismatches with modeled major and trace element trends, abundances and trace element enrichments, as well as with prior experimental studies (e.g., Koepke et al., 2004; France et al., 2010, 2014) (Figs. 4.11-4.15 and A4.1-4.2). Fig. 4.13 Combined partial melting and post-partial melting fractionation modeling results derived from two metagabbros (a-f) and two diabases (g-l). Melt compositions produced by partial melting are shown as solid lines with arrows beginning at 5% (marked as filled circles) and incremented at 10% to the end of 50% (indicated by hatch marks). Dashed lines with arrows represent melt compositions generated by fractional crystallization beginning at the composition represented by 5% melting (F= 5%, marked by filled circles). Note the modeled trends of partial melting followed by post-melting fractional crystallization derived from various lithologies have produced a range of more evolved melt compositions. In particular, they can reach the most evolved, SiO₂-enriched plagiogranite field when fractional crystallization effects are added to low-degree partial melts, but importantly post-melting fractionation still fails to strictly match compositional trends of other elements in felsic BOIC samples (e.g., much lower FeO* and TiO₂ in modeled melts). Similar mismatched results are exhibited by certain modeled trace elements shown in Fig. 4.14 and A4.2.



Fig. 4.13 (continued)



Fig. 4.14 Variation diagrams of selected trace elements of partial melting and post-melting fractionation modeling results derived from the four (altered) protoliths including two metagabbros (a-c) and two diabases (d-f). Note that only compositions produced from 5% (filled circles) to 50% melting incremented every 10% (hatch marks) are shown (solid lines with arrows). Crystal fractionation of 5% partial melts are shown by the dashed lines with arrows extending from the filled circles (i.e., F = 5%). Partial melting followed by postmelting fractionation fails to fit BOIC samples, and they collectively produce a range of compositions discordant to the sample trends except those derived from diabase BMD 1010AB (light green lines in d-f) that apparently fit the overall sample trends (also see Fig. A4.2). However, the significant mismatches of some major elements (e.g., FeO* in Fig. 4.13i) and REE variation patterns (Fig. 4.15) in modeling results with natural samples suggest that partial melting and post-melting fractionation process derived from diabase 1010AB also fails to reproduce BOIC silicic samples.



Fig. 4.15 N-MORB normalized rare-earth element (REE) variation diagrams for the partial melting and post-melting fractionation modeling results for (a) partial melting of oxide metagabbro PM 169 (light grey shaded area) followed by fractionation of the 5% partial melt compositions (dark grey shaded area) and (b) partial melting of diabase BMD 1010AB similarly followed by fractionation of the 5% partial melt compositions. Results derived from the two samples represent the closest fit, although poor, modeled melting lines and post-melting fractionation LLDs that could visually fit the sample trace element trends. However, the significant mismatches of major elements modeled in Fig. 4.13 suggest that the post-melting fractionation process is still unable to account for the petrogenesis of BOIC silicic samples. Note similar mismatches of certain major and trace elements were achieved for all partial melting modeling results examined and therefore, we view all partial melting models, including experimental partial melt data of Koepke et al. (2004) and France et al. (2010, 2014), as failing to adequately reproduce trace element trends and some major element trends of the BOIC sample data even if combined with post-melting fractionation. FLR: remaining fluid mass percentage during magma differentiation; F: melt mass percentage produced by partial melting; FX: fractional crystallization.



4.5.2 Single-stage Rayleigh fractional crystallization models

4.5.2.1 Model justification and setup

In the Bay of Islands region, early crystallization of basal dunites, wehrlites and clinopyroxenites containing low Ti and Na, high Mg-diopside (> 93%) in some ultramafic cumulate sections and their high-temperature crystal-plastic deformation were recognized and initially attributed to higher pressure crystallization (Casey, 1980; Elthon et al., 1982; Casey et al., 1983; Komor et al., 1985; Elthon et al., 1984) with lower pressure crystallization (~1-2 kb) for the layered gabbroic assemblages affected by fractionation-magma mixing processes (Komor et al., 1987; Komor and Elthon, 1990). Later other mechanisms of lower pressure crystallization of high-Mg diopside were recognized. However, Gaetani et al. (1993) suggested that low-pressure, highwater content basaltic magmas could achieve crystallization of high-Mg diopside in cumulate sections, whereas others suggested depleted boninitic melts (Varfalvy et al., 1996, 1997; Bédard et al., 1998; Bédard, 1999; Kurth-Velz et al., 2004) were responsible for early crystallization of high-Mg diopsides. Although boninites are inferred from cumulate mineral chemistry indirectly, no boninitic chemistries from the BOIC basaltic or diabasic rocks have yet been reported (Casey et al., 1985; Siroky et al., 1985; Jenner et al., 1991; Elthon, 1991) and the wide range of samples analyzed fit the BADR (Basalt-Andesite-Dacite-Rhyolite) tholeiitic series (e.g., Fig. 4.9), not the boninitic series trend of Pearce and Robinson (2010). A more recent suggestion from mid-ocean ridge studies is that low-pressure crustal reactive porous flow (e.g., Rampone et al., 2004; Lissenberg et al., 2013, 2016; Lissenberg and MacLeod, 2016; Dick et al., 2019) can lead to high Mg-diopside crystallization and will be further addressed in detail in Section 4.5.3.

Plutonic plagiogranites and fine-grained silicic dikes and veins mostly occur within or near 1) the upper non-layered vari-textured isotropic gabbro, 2) the isotropic gabbro-diabase transition zone, and 3) the commonly cannibalized boundary at the base of sheeted dikes in the BOIC (e.g., Figs. 4.2-4.3). Based on the thickness of the pillow basalt and sheeted diabase dike units, as well as the relative locations of plagiogranites and fine-grained silicic dikes to the two units in BOIC ophiolite, the averaged equivalent pressure to the depths of these felsic intrusives is roughly estimated to 0.7 kb, whereas the bulk of the fractional crystallization residues (mafic to ultramafic cumulates) derived from the BOIC basaltic melts exists from a range of in situ depths equivalent to approximately from 2.0 to 0.7 kb in the BOIC ophiolitic crust. Here our models cover a range of depths to simulate the potential influence of pressure on melt compositions during fractionation, but we, in the end, focus on the range of pressures between 2.0 (pale-MOHO depth) and 0.7 kb, the interval corresponding to depths where two- to three-phase saturated layered or isotropic gabbroic rocks are dominant, with the shallow pressure (~0.7 kb) corresponding to depths of the gabbro-sheeted dike transition where BOIC plagiogranites dominantly occur.

The typical range for MORB water content is 2300⁺³⁵⁰⁰₁₆₀₀ ppm (see a summary of PetDB database in Clog et al., 2013) with a suggested most common value of 0.27 wt.% (Kelley et al., 2019), although some ridge segments with E-MORB-type basalts that have higher values and some off-hot spot portions of the ridge glasses with up to 1.1 wt.% H₂O have been documented (Ligi et al., 2011). However, when corrected for crystal fractionation to equilibrium with the mantle (Fo₉₀ olivine), the water content in primary MORB magmas is estimated to 0.19 wt.% (Kelley et al., 2019). Therefore, we chose 0.2 wt.% as a representative estimate H₂O content in primitive MORB-like magma. Water content within magmas from supra-subduction zones or volcanic arc environments, like that inferred for the BOIC, could be higher and more variable due to the influx of volatiles dehydrated from the subducting slab (e.g., Wallace, 2005; Kelley and Cottrell, 2009; Grove et al., 2012; Plank et al., 2013; Cai et al., 2018). Furthermore, considering

that the BOIC plagiogranites commonly coexist with hydrothermally altered rocks in the shallow altered intrusive-extrusive crustal carapace that may be assimilated, we expect that the water content within magmas from BOIC in roof zones could potentially be enhanced and vary over a range above near MORB values of ~0.2 wt.% to potentially as high as ~6-8 wt.% observed in SSZ environments (e.g., Wallace, 2005; Zimmer et al., 2010). However, because of the strong iron enrichments trends (Fig. 4.9), we see little evidence for the very high values of water contents in BOIC primitive parental melts, in accordance with our modeling results shown below.

In general, the most oxidizing conditions estimated for magmas evolved within subduction zone could reach quartz-fayalite-magnetite oxygen buffer (QFM) of +2 (Parkinson and Arculus, 1999; Rowe et al., 2009). Debret and Sverjensky (2017) further suggested that the breakdown of serpentinite could generate fluids with high oxygen fugacities (fo2) close to the hematite-magnetite (Hm-Mt) buffer, and mixing with these highly oxidized fluids released from the slab could therefore significantly increase the overall oxygen fugacity. However, Berry et al. (2018) suggested that the oxygen fugacities in magmas near mid-ocean ridges are only slightly above QFM buffer (i.e., QFM+0.1). Taking these extremes into consideration, oxygen fugacities used here to model the evolution of BOIC primitive melts to plagiogranites and silicic intrusive dikes are primarily approximated by quartz-fayalite-magnetite (QFM) buffer but vary in a relatively large range from QFM to Hm-Mt buffer. It is also important to note that 1) the variation of oxygen fugacity is affected by variation of water content in magmas (Feig et al., 2010), 2) the oxygen fugacity generally exhibits positive correlation with water content at shallow depth (Kelley and Cottrell, 2009), and 3) the water content (and hence oxygen fugacity) will progressively increase during magma fractionation as water has a bulk distribution coefficient of ~0.01 and likely behaves like an incompatible element to accumulate in magmatic melts (Michael, 1995;

Danyuschevsky et al., 2000; Dixon et al., 2002), all indicating that evolved felsic melt or primitive magma of high-water content could be involved in more oxidizing environments.

The rhyolite-MELTS program of version 1.1.0 (Gualda et al., 2012; Ghiorso and Gualda, 2015) was utilized to calculate the liquid lines of descent (LLDs) and fractionation products. We set up a series of univariate models for each of the three vital parameters including water (H₂O), oxygen fugacity (fo₂) and pressure (P) to separately investigate their potential influences on modeled LLDs derived from the same primitive diabase BMD 1009B. Although for a Paleozoic ophiolite, unfortunately all high-MgO diabases and basalts in our collection that could be used as parental melts in modeling are hydrothermally altered (Casey et al., 1985; Siroky et al., 1985). To minimize the compositional effects of alteration, we chose a potential parent using one of the most primitive BOIC diabases (sample BMD 1009B) from Casey et al. (1985), for which we have added additional ICP-MS trace element data (Appendix Table A4.2). This sample, BMD 1009B, was chosen because of the ~100 analyzed BOIC basalts and diabases in our collection, it has one of the highest MgO (9.80 wt.%) and Ni (189 ppm) contents and one of the lowest TiO₂ (0.76 wt.%) and Na₂O (2.04 wt.%) contents, as well as low Na₂O/CaO ratio (0.172), suggesting a primitive nature without strong Na metasomatism. These parameters are also very similar to those of fresh primitive MORB glasses (e.g., Lehnert et al., 2000; Jenner and O'Neill, 2012; Gale et al., 2013). In addition to its primitive nature, it also has a relatively low LOI (loss on ignition) of 1.81 wt.% when compared to the range of all altered basalts and diabases (0.67 to 9.96 wt.%, average = 2.96 wt.%). Furthermore, it does not show evidence of high degrees of Na metasomatism based on its low Na₂O/CaO ratio compared to other samples (e.g., Siroky et al., 1985, Casey et al., 1985). Likewise, this ratio is nearly identical to most values of fresh primitive MORB glasses reported (e.g., Lehnert et al., 2000; Jenner and O'Neill, 2012; Gale et al., 2013). Unfortunately, other primitive basalts and diabases analyzed do show more pronounced variation of Na₂O/CaO ratios due to introduction or removal of Na and Ca during metasomatism (e.g., albitization) and consequently, Na₂O and CaO, although displayed, are not as useful as other less mobile and effected major elements such as FeO*, TiO₂, Al₂O₃, SiO₂ and immobile trace elements for tracking LLD or melting trend. All crystal fractionation modeling was conducted at a decreasing temperature interval of 5 °C and with a starting temperature of 1300 °C to ensure that the parent would be liquid at the beginning of fractionation. A termination temperature of 600 °C was set for each run to allow the magma to continuously differentiate to small fractions of liquid remaining (FLR).

4.5.2.2 Effects of pressure on melt composition

As mentioned before, water content generally exhibits a positive correlation with oxygen fugacity at shallow depth. It is, therefore, more logical to have low oxygen fugacity accompanied by low water content, and vice versa. Although the pressures estimated for formation of ultramafic and mafic cumulates, as well as fine-grained silicic dikes and plutonic plagiogranites in the BOIC crust used here range approximately from 0.7 to 2.0 kb, we tested a much broader range from 0.7 to 10 kb to show a more comprehensive influence of pressure on LLDs calculated. To ensure a univariate modeling process, the influence of pressure was investigated at constant conditions of $fo_2 = QFM0$ and $H_2O = 0.2$ wt.%, and $fo_2 = QFM+3$ and $H_2O = 3$ wt.% respectively corresponding to a relatively reduced and a highly oxidizing environment using the same starting material of primitive diabase BMD 1009B.

Fig. 4.16 shows the representative modeled fractional crystallization LLDs of FeO* and Al₂O₃ vs. MgO by varying pressures from 0.7 to 10 kb at relatively reduced (Fig. 4.16a-b) and at highly oxidizing condition (Fig. 4.16c-d). Pressure has a key influence on Al₂O₃ contents in

melts and generally, lower pressure tends to deplete melt Al₂O₃ rapidly in the late-stage differentiation whereas higher pressure is likely to generate more Al₂O₃-enriched melt (Fig. 4.16b and d). These results at higher pressures are a better Al₂O₃ fit for silicic endmembers for both high and low QFM buffer but are a misfit for more mafic basalt and diabase trends where low pressure and low water content fractionation is a better fit. FeO* contents in derived melts are less susceptible to pressure change particularly under highly oxidizing, water-saturated conditions (e.g., fo₂ = QFM+3 and H₂O = 3 wt.%) where pressure has little or no effect on melt FeO* compositions and cannot fit the enrichment trends in BOIC basalts and diabases (Fig. 4.16c). As expected, modeled FeO* exhibits notably better matches in lower pressure runs with low water content and reduced condition (e.g., fo₂ = QFM0) (Fig. 4.16a).

In summary, lower pressure fractionation of a MORB-like magma (i.e., low water) under relatively reduced conditions can reproduce BOIC samples of mafic compositions but fails to match any of the BOIC silicic samples, whereas higher to moderate pressure fractionation of water-saturated magmas under more oxidizing conditions can account for the variability of Al₂O₃ enrichment in BOIC silicic samples but fails to reproduce the mafic sample trends (also see Fig. A4.3).



Fig. 4.16 Single-stage Rayleigh fractionation modeling results to assess effects of various pressures on liquid lines of descent (LLDs) modeled. Representative major oxide variation diagrams of FeO* and Al₂O₃ vs. MgO for BOIC basalts, diabases, andesites, plagiogranites and fine-grained intrusive dikes, as well as modeled LLDs for single-stage fractional crystallization derived from a primitive MORB-like BOIC diabase BMD 1009B (yellow stars) to assess various pressures using rhyolite-MELTS (Gualda et al., 2012; Ghiorso and Gualda, 2015). Pressures chosen include 0.7, 1, 2, 3, 5, 7 and 10 kb to simulate a wide range of depths from sheeted dike-gabbro transition to ~30 km depth with (a) and (b) run at fo₂ = QFM0 and H₂O = 0.2 wt.% (i.e., relatively reduced condition) and (c) and (d) run at fo₂ = QFM+3 and H₂O = 3 wt.% (i.e., highly oxidizing condition). Note oxygen fugacity commonly correlates positively with water content (Kelley and Cottrell, 2009; Feig et al., 2010; Zimmer et al., 2010). Variation diagrams of all major oxides for varying pressure, as well as water and oxygen fugacity, are presented in Appendix (see Figs. A4.3-4.5). Note that modeling results derived from high water content and oxidizing conditions fail to fit BOIC sample trends, whereas low water content and reduced conditions tend to fit better for basaltic to felsic sample trends.

4.5.2.3 Effects of initial water content on melt composition

We systematically changed the input parameters of initial water ranging between 0.2 and 8 wt.% in the parent rock composition to accommodate various tectonic settings including mid-ocean ridge and supra-subduction zone, to more comprehensively investigate the influence of water on variation trends of LLDs during fractional crystallization runs. To reduce potential influence from other variables, we used the same primitive diabase BMD 1009B as starting parent under constant pressure of 0.7 and 2 kb corresponding respectively to the approximately shallowest and deepest location where magma is likely to fractionate, and the same starting oxygen fugacity of QFM0 and QFM+3 corresponding respectively to the lowest and highest oxidizing condition that may have existed in the BOIC supra-subduction zone environment. Four extreme modeling conditions at two limiting pressures were accordingly established including P = 0.7 kb and fo₂ = QFM0, P = 0.7 kb and fo₂ = QFM+3, P = 2 kb and fo₂ = QFM0, and P = 2 kb and fo₂ = QFM+3. However, variation trends of LLDs modeled with H₂O ≥ 4 wt.% are almost indistinguishable from each other and thus, we only present LLDs modeled between 0.2 and 4 wt.% H₂O here.

Fig. 4.17 shows the representative fractional crystallization modeling results of varying water contents from 0.2 to 4 wt.% at the four extreme conditions. In the FeO* (as well as TiO₂ and V/Sc) vs. MgO plots it becomes clear that low initial water (e.g., 0.2-0.5 wt.% H₂O) in the primitive magma within a reduced condition is required to reproduce the basaltic ironenrichment trends observed in BOIC diabases and basalts (Fig. 4.17a and e; also see Appendix Fig. A4.4 for TiO₂). However, Al₂O₃ compositions calculated in melts under low-pressure fractionation runs (i.e., P = 0.7 kb, the plagiogranite intrusion depth equivalent) are consistently lower than all BOIC felsic samples and fail to reproduce the overall sample trends from basaltic to more felsic compositions, even though a wide variety of water contents has been considered (Fig. 4.17b and d). Enigmatically, water-saturated magmas (e.g., > 1 wt.% H₂O) are more likely to generate some silicic melts of high Al₂O₃ composition (17-20 wt.%), a typical feature of BOIC dioritic plagiogranites, but the modeled entire LLDs derived from these water-saturated magmas fail to match the natural basaltic and intermediate trends of the BOIC samples (Fig. 4.17f and h).

In summary, lower initial water in primitive magma is necessary to account for the BOIC basaltic and andesitic sample trends, whereas highly water-saturated magma appears to be required to reproduce those silicic melts particularly of dioritic compositions that have very high and variable Al₂O₃ enrichments (also see Fig. A4.4).

Fig. 4.17 Single-stage Rayleigh fractionation modeling results to assess effects of various water contents on LLDs modeled. Representative major oxide variation diagrams of FeO* and Al₂O₃ vs. MgO for BOIC basalts, diabases, andesites, plagiogranites and fine-grained intrusive dikes, as well as modeled LLDs for single-stage fractional crystallization derived from a primitive BOIC diabase BMD 1009B (yellow stars) at various water contents (0.2, 0.5, 1, 2, 3 and 4 wt.%) using rhyolite-MELTS. Pressures were chosen at 0.7 kb to correspond to the dike/gabbro contact (assuming ~2.5 km of water depth) and 2 kb to correspond with the depth of the base of the gabbroic crust in the BOIC. The LLDs are computed with water contents varying from 0 to 4 wt.% with (a) and (b) run at P = 0.7 kb and fo₂ = QFM0, (c) and (d) run at P = 0.7 kb and fo₂ = QFM+3, (e) and (f) run at P = 2 kb and fo₂ = QFM0, and (g) and (h) run at P = 2 kb and fo₂ = QFM+3.



4.5.2.4 Effects of redox state on melt composition

Likewise, we also established a univariate modeling process to investigate the potential influence of redox state on fractionation LLDs derived from the same primitive diabase BMD 1009B at constant pressures of 0.7 and 2 kb, and constant initial water contents of 0.2 and 3 wt.%. Accordingly, four extreme conditions were constructed including P = 0.7 kb and $H_2O = 0.2$ wt.%, P = 0.7 kb and $H_2O = 3$ wt.%, P = 2 kb and $H_2O = 0.2$ wt.% and P = 2 kb and $H_2O = 3$ wt.%. The oxygen fugacity was varied from QFM-1 to Hm-Mt buffer, a slightly broader range than discussed above that can completely cover the natural conditions from slightly reduced mid-ocean ridge to highly variable SSZ environments. Although a range of oxygen fugacity buffers were modeled, it becomes clear that high water and oxidizing conditions cannot reproduce iron enrichment trends in BOIC samples, and it should be noted that following the method of estimating oxygen fugacity for primitive basaltic magmas by Lee et al. (2005) using V/Sc ratios, these ratios for BOIC primitive basaltic and diabasic samples (~8.0-12.0 wt.% MgO) tightly cluster between ~5.7-6.6 and follow a flat trend along an olivine control line when plotted on an MgO vs. V/Sc diagram (Casey et al., in prep). This indicates that the most likely oxygen fugacity for primitive basaltic endmembers of the BOIC was MORB-like (close to QFM0). This may also imply a MORB-like low initial water content for BOIC primitive samples (also see further discussions of the method in Bucholz and Kelemen, 2019; Novella et al., 2020).

Modeling results shown in Fig. 4.18 indicate that oxygen fugacity (and water content) has a significant influence on melt FeO* content by directly affecting the crystallization of oxide minerals (e.g., Toplis and Carroll, 1995; Berndt, 2002; Berndt et al., 2004; Feig et al., 2010). The initiation of oxide mineral crystallization is indicated by the inflection point in each modeled LLD of FeO*. Magma that evolves within more oxidizing environments tends to
fractionate oxide minerals at earlier stage resulting in quicker depletion of Fe and Ti in melts. Particularly if evolving within a highly oxidizing environment (e.g., fo₂ = QFM+3 or Hm-Mt buffer), fractionated melts tend to show a steady depletion trend of FeO* independent of pressure and water content, a feature inconsistent with BOIC samples iron enrichment trends (Fig. 4.18c and g). It is also notable that TiO₂ appears to be less susceptible to the variation of oxygen fugacity compared to FeO* as the modeled LLDs of TiO₂ are overall similar under a given condition (see Fig. A4.5). This is probably because oxygen fugacities investigated here are mostly above QFM buffer (i.e., fo₂ above QFM0) where magnetite is crystallized as the dominant oxide phase (Toplis and Carroll, 1995). Al₂O₃ is not very susceptible to redox state because LLDs modeled with the same pressure and water content are overall similar to each other, although the oxygen fugacity varies from slightly reduced (QFM-1) to highly oxidized (Hm-Mt buffer) (Fig. 4.18b, d, f and h).

In summary, fractionation of MORB-like low water primitive magma within slightly reduced conditions can reproduce BOIC basaltic/diabasic compositions but fails to reproduce more silicic samples as the Al₂O₃ contents in modeled melts are consistently lower than those in BOIC silicic samples. Fractionation of water-saturated magma under a more oxidizing environment, in contrast, is more likely to produce the especially high Al₂O₃ felsic melts but does not fit more mafic basaltic/diabasic trends or the low Al₂O₃ trondhjemites (also see Fig. A4.5).

Fig. 4.18 Single-stage Rayleigh fractionation modeling results to assess effects of various redox states on LLDs modeled. Representative major oxide variation diagrams of FeO* and Al₂O₃ vs. MgO for BOIC basalts, diabases, andesites, plagiogranites and fine-grained intrusive dikes, as well as modeled LLDs for single-stage fractional crystallization derived from a primitive BOIC diabase BMD 1009B (yellow stars) using rhyolite-MELTS to assess various redox conditions ($fo_2 = QFM-1$, 0, +1, +2 and +3 and Hm-Mt buffer) to simulate MORB-like to supra-subduction zone environments where magmas can evolve from relatively reduced to highly oxidizing condition. (a) and (b) run at P = 0.7 kb and H₂O = 0.2 wt.%, (c) and (d) run at P = 0.7 kb and H₂O = 3 wt.%, (e) and (f) run at P = 2 kb and H₂O = 3 wt.%.



4.5.2.5 Selected best-fit fractionation LLDs for single-stage Rayleigh fractionation models

Based on all these univariate modeling results presented in Figs. 4.16-4.18 (including Appendix Figs. A4.3-4.5), a primitive MORB-like magma of low initial water (~0.2-0.5 wt.%) evolving within a low-pressure (≤ 2 kb), slightly reduced to oxidizing (fo₂ between QFM0 and QFM+2) environment may reproduce the overall variation trends, particularly the basaltic and highly silica-enriched (Al₂O₃ \leq 16 wt.% and SiO₂ \geq 70 wt.%) trondhjemite compositions observed in the BOIC samples, but no runs closely satisfy all critical element abundance trends in both basaltic/diabasic rocks and silicic plagiogranites and fine-grained dikes. Also evolved, but less silica-enriched diorites, in contrast, are better modeled at higher-pressure, highly oxidizing and water-saturated environment (e.g., P = 2 kb, fo₂ above QFM+2, H₂O \geq 2 wt.%), but these models cannot match basaltic/diabasic sample trends as a continuum to felsic samples. It is notable that the dominant major element variation trends (e.g., of FeO*, TiO₂, Al₂O₃, SiO₂) observed in BOIC basaltic (to intermediate) samples can only be reproduced under a reduced environment (i.e., fo₂ near QFM0, H₂O between 0.2 and 0.5 wt.%), which is consistent with V/Sc ratios (method of Lee et al., 2005).

We then specifically selected three most favorable conditions with LLDs calculated that appear to most closely match most of the BOIC samples of basaltic and felsic compositions (Fig. A4.6). However, comparison of melt major and trace element geochemistry, as well as meltassociated cumulate mineralogy between modeling results and natural BOIC samples from basaltic to felsic compositions suggests that none of the three best-fit models can simultaneously reproduce all the chemical features observed in BOIC from mafic to silicic samples (see Figs. A4.6-4.9 in Appendix for details). To summarize, the significant mismatches of some major and trace elements, as well as melt-associated cumulate mineralogy between modeling results and natural BOIC samples suggest that a single set of simple conditions are not able to reproduce the variable enrichments of Al₂O₃ typical in all BOIC highly silica-enriched plagiogranites, and/or they also are not able to match the overall sample variation trends from basaltic to highly felsic compositions. 4.5.3 Multi-stage Rayleigh and equilibrium fractionation models

4.5.3.1 Segregation, extraction and migration of fractionated Si-rich melts from crystal-rich mushes

During investigations on plutonic and volcanic sections of oceanic crust at sample, core and seismic scales, the idea of magma being stored in large liquid-rich regions (i.e. magma chambers) has evolved towards models of a sub-volcanic plumbing system that involves shallower, crystal-poor magma pockets, lenses or sills (e.g., the axial magma lens or AML) of limited sizes that are generally ~1-2 km wide and less than ~100 m thick (e.g., Detrick et al., 1987; Toomey et al., 1990, 1994; Kent et al., 1993a, b; Hussenoeder et al., 1996; Collier and Singh, 1997; Singh et al., 1998; Canales et al., 2006) and deeper, broader, low velocity zones comprising relatively more liquid-poor matrix-rich crystal mushes (e.g., Sinton and Detrick, 1992; Marsh, 2004; Ridley et al., 2006) estimated seismically to contain less than 18% melt (Crawford and Webb, 2002).

Observations from fast-spreading centers are consistent with some crystallization and evolution of a more primitive replenishing melt within the mush prior to the mixing with melt that may reside in the shallow liquid-dominant AML (e.g., Goss et al., 2010; Boudier and Nicolas, 2011; Wanless and Shaw, 2012; Lissenberg and MacLeod, 2016; Lissenberg et al., 2013, 2019). Replenishing melt may have undergone some near-perfect fractional to equilibrium crystallization within a crystal mush of troctolite, olivine gabbro or gabbro that potentially and ultimately assist in forming ad-, meso- and orthocumulate textures prior to replenishing the AML. Likewise, some primitive melt that is present in the lower plutonic mushes of the oceanic crust can be extracted and ultimately mix to become part of the melt-dominant AML undergoing boundary layer crystallization, but some may mix with the much larger melt-poor mush zones below the AML or alternatively segregate to intermediate plutonic levels to form smaller sill- and dike-like feeder channels within the mush zones (Lissenberg et al., 2019). Major crystallization is likely to occur at the AML margins and within the mush zones as residual pore melts solidify, with the relative extents of crystallization in each being dependent on starting porosity of cumulates, the nature of cooling, thermal and hydrothermal structure of the upper to lower crust and the volume and frequency of new magma pulses from the mantle delivered to shallow levels (e.g., Rubin and Sinton, 2007; Boudier and Nicolas, 2011; Zhang et al., 2014). Crystallization in the AML is likely to be near-perfect fractional crystallization whereas crystallization in the residual porosity of the mush may range from near-fractional (to produce orthocumulate textures) to near-equilibrium crystallization (textural equilibrium to produce textural near adcumulate-like textures) depending on the rate of heat extraction, intensity of the overlying and flank hydrothermal systems and whether the mush is melt-dominated or crystal-dominant (e.g., Campbell, 1987). However, slower cooling and crystallization are expected in the deeper mush zones that could lead to processes approaching modified equilibrium crystallization at the magma cumulate interface (true adcumulates) or trapped in situ melt or melt from porous flow through residual pore spaces left after cumulus processes were complete where the melt attempts to equilibrate with crystalline material of the mush matrix.

There may be a given fraction of the fractionated residual melt left in the mush after extensive crystallization that is added back to the AML (magma mixing) or that can be segregated into small discrete intrusions in the roof zone or deeper, but also result in significant allochthonous residual melt being 'trapped' within the mush zone. Return of some fraction of the interstitial melt from the mush zone to the eruptible melt in the AML, to higher level melt intrusions at the top of the plutonic mush complex or to AML flank intrusions can occur through numerous processes (compaction, tectonic deformation, compositional convection, mush zone disaggregation) and can be accomplished at various scales (see Holness et al., 2017 for a summary). These processes may impart the chemical signature (e.g., equilibrium clinopyroxene fractionation of primitive melts) but not necessarily a textural signature of in situ or cumulate crystallization if equilibrium is more complete (Casey and Karson, 1981; Langmuir, 1989; Nielsen and DeLong, 1992; O'Hara and Fry, 1996; Casey et al., 2007).

Fractional crystallization has long been considered the dominant mechanism for magma differentiation in ophiolitic and mid-ocean ridge magmatic systems, yet open-system plutonic igneous complexes like those of the Bay of Islands Ophiolite Complex (BOIC) also preserve evidence of replenishment, mixing, contamination, crystal-mush melt storage zones, porous reactive melt flow, crystallization-dissolution, melt hybridization and possible partial melting processes. Although intrusion of primitive hot reactive melt and percolation of evolved interstitial fractionated melt are two distinct processes that may occur in the lower oceanic crust, there is distinct evidence in the plutonic assemblages of the BOIC that documents primitive magma replenishment, late-stage percolating melts and small intrusions of differentiated melts, as well as in situ trapped fractionated melts in the gabbroic textures and geochemistry of three-phase saturated gabbroic assemblages that were clearly outlined in prior BOIC studies (Casey, 1980; Karson et al., 1984; Elthon et al., 1982, 1984; Komor et al., 1987; Komor and Elthon, 1990; Bédard and Hébert, 1996). For orthocumulate fractional crystallization, the concentration of an element in melt C_L , when the fraction of melt remaining is F, is given by a modified Rayleigh equation C_L = $C_l F^{(D'-1)(1-X)}$ where C_l is the initial concentration of the element in the melt, D' is the bulk

distribution coefficient, and X is the fraction of melt trapped between the cumulus grains (Campbell, 1987). The equilibrium equation can be modified in a similar way ($C_L =$ $\frac{C_l}{(1-X)[F(1-D')+D']}$). In the BOIC, however, lower plutonic section of extremely low abundances of incompatible elements suggest residual melts are scarce, and adcumulate is the dominant texture (e.g., Casey, 1980; Elthon et al., 1982, 1984; Komor et al., 1985, 1987; Komor and Elthon, 1990; Bédard and Hébert, 1996). We also distinguished a chemical-textural conforming adcumulates with very low incompatible trace element contents to from a textural-only adcumulates with nonconforming high incompatible element contents indicating trapped melt but equilibrium textures seen throughout the BOIC layered and isotropic gabbroic section. Although likely to be heterogeneously distributed, pore melts in crystal mushes may also have a wide range of chemical and mineralogical compositions, volumes in pore space and liquid chemistry from mafic (SiO₂poor, MgO-rich) to felsic (SiO₂-rich, MgO-poor) within ophiolitic and oceanic crust. The crystal mush model presents a view of plutons as crystal graveyards implying that the crystals are first separated from the silicate liquid (likely AML or deeper lenses) where they were crystallized but retained interstitial pore melt. The crystal mush model contrasts with the view of intrusive magma bodies forming adcumulates close to the magma body in which crystals communicate with chamber melts until diffusion from the main magma body allowing the cumulate primocrysts to undergo near-equilibrium crystallization eliminating the pore liquid. A newer model envisions a more dynamic system that upon cooling the crystal mush may experience different igneous differentiation processes, from equilibrium crystallization by diffusion with the larger adjacent mostly liquid magma body to more localized equilibrium to disequilibrium crystallization depending on temperature and cooling rate and fractionation histories of trapped or migrating residual pore melt undergoing reactive porous flow and fractionation of migrating melts creating

down-temperature zoning of cumulate primocrysts (normal zoning of primocrysts), zone refining, possible immiscibility in the pore melt (complex zoning), exsolution of water from the evolving pore melt (oscillatory zoning), mixing of fractionated melt with replenishing primitive pore melts percolating through the mush zone from below and/or decompression of melts (i.e., reverse zoning of primocrysts and symplectites).

To create an accumulation of crystals and layering in a more rigid threedimensional network, there has to be a mechanism that initially extracts the interstitial liquid from the already crystallized solids (i.e., crystal-melt segregation). Casey and Karson (1981) emphasized the relative importance of in situ crystallization in forming dominant adcumulates in the lower plutonic sections and well-formed cumulate layering, crescumulate-harrisitic textures, and cryptic layering reflecting replenishment relative to crystal settling mechanisms in the BOIC during igneous layering formation especially monomineralic layers of anorthosite, dunite or clinopyroxenite cumulates that of finely layered with non-cotectic or eutectic proportions (also see Elthon et al., 1984; Komor et al., 1985, 1987; Komor and Elthon, 1990). It is believed that with any of these mechanisms, an increase in the solid portion of the magma chamber occurs with either decreasing temperature or diffusion of melt from the main lens or liquid sills. This implies that the permeability will be lower with decreasing temperature or by means of adcumulate crystallization, in situ trapped residual melt crystallization (meso- and orthocumulates) and elimination of melt by replacement or compaction of the pore fluid. If there is pore melt left within the cumulates after reactive porous flow, it would lead to complex zoning relationships.

Magma migration in crystal mushes of solidifying cumulates can result in solidliquid disequilibrium and change the stable liquidus of the primocryst assemblages. This can substantially modify or cause dissolution-precipitation reactions and even form new diffuse layering in the crystal cumulate, as well as cause localized magma evolution (Boudreau and McCallum, 1992; Meurer et al. 1997; Boudreau, 1999; Huber et al., 2009; Namur et al., 2013; Leuthold et al. 2014). Casey and Karson (1981) and Casey et al. (1983) showed near vertical or strongly inclined layering occurred in the mid to upper layered gabbroic units of the BOIC, and this may imply that vertical melt migration may be common. Migration of fractionated interstitial liquid extracted from mushes may also be in evidence as the discordant veins and dikes of fractionated pegmatitic gabbroic rocks that include hornblende gabbro (lacking pyroxene informally called bojite) and gabbroic pegmatite of intermediate compositions, as well as discrete felsic plagiogranite plutons and more mafic non-layered roof zone vari-textured gabbroic veins (marked by variability in grain size and composition on thin section scales) located in the layered and isotropic gabbroic rocks (Casey, 1980; Rosencrantz, 1980; Karson et al., 1983; Bédard, 1991).

Here we attempted to assess whether a primitive MORB-like magma may evolve geochemically, through a series of crystallization, segregation and melt migration/extraction events, to form silicic endmember compositions similar to the BOIC plagiogranites and their finegrained dike equivalents. Depending on the thermal state, pressure, volume, rheology of the melt and intruded crust, the evolved melt would either 1) move rapidly (e.g., through channelized flow) to the shallow crust level or even reach the surface directly with only limited reaction/interaction with the mid-crustal crystal-dominated cumulates that they have passed through, or more commonly 2) stall and accumulate at middle crustal mushes likely acting as the source to episodically charge a shallower melt lens (e.g., Lissenberg et al., 2019).

Based on reviewing LLDs for various physical-chemical conditions and selecting models that potentially best fit the full range of basalts and diabases through more silicic finegrained dikes and plagiogranites (see Figs. 4.16-4.18 and Figs. A4.3-4.9), we established a simplistic and practicable model for each of the two cases. In case 1) we assumed that the primitive diabase BMD 1009B first undergoes some extent of fractional crystallization (FX) deep within the lower crust/upper mantle of slightly reduced environment with low water content (i.e., P = 2 kb, fo₂ = QFM0, H₂O = 0.3 wt.%; 1st stage), after which partially evolved melt rapidly ascends to shallower depth through the crystal mush zone but without significant interactions with the cumulates and continues to fractionate (at pressure of 0.7 kb equivalent to the depth of BOIC hypothesized AML; 2nd stage). Modeling results show that the following shallower pressure crystal fractionation processes (i.e., 2nd stage FX modeled at 0.7 kb), although starting from various extracted FLRs from the 1st stage fractionation, produced nearly identical LLD variation trends, all of which still show significant mismatches of Al₂O₃ contents with those in BOIC silicic samples (Fig. A4.10). This suggests that case 1) cannot directly account for the formation of BOIC plagiogranites and silicic fine-grained dikes.

For case 2), we constructed a practicable, discrete multi-stage Rayleigh and equilibrium fractionation model with a specific emphasis on the melt-crystal reaction as reactive porous melt migrating through a crystal-dominated gabbroic mush zone. Specifically, the multi-stage Rayleigh and equilibrium fractionation model begins with a certain extent of fractional crystallization (FX) of the primitive basaltic melt (parental sample BMD 1009B) that we assume results in early olivine + spinel and olivine + plagioclase + spinel or olivine + clinopyroxene + spinel +/- plagioclase cumulates to olivine + plagioclase + clinopyroxene cumulates observed in the lower BOIC plutonic sections. The early fractionated intercumulus melts or porous melt flow zones would be low-viscosity, basaltic to andesitic liquids of various FLRs generated under conditions of P = 2 kb, fo₂ = QFM0 and H₂O = 0.3 wt.% (1st stage Rayleigh fractionation) and are

assumed to buoyantly migrate upward through crystal-dominated mush networks created below the AML. They would eventually be extracted or aggregate as the more evolved melt-dominated mid-crustal lenses at shallower pressures, but in this case at intermediate depths (equivalent averaged pressure of 1.4 kb) in the plutonic assemblage. The creation of an intermediate depth sill with this aggregated melt, similar to low velocity lenses observed seismically along the East Pacific Rise (e.g., Detrick et al., 1987; Toomey et al., 1990, 1994; Hussenoeder et al., 1996; Singh et al., 1998; Marjanović et al., 2014), would then fractionate further (2nd stage). We treat this aggregated evolved melt as a new parent in the modeling with slightly higher water content (with abundance dictated by the 1st stage rhyolite-MELTS modeling results) that has resulted from prior Rayleigh fractionation. Because pressures are likely variable for the intermediate stages of mush equilibrium crystallization, a mean pressure of 1.4 kb was chosen to model further melt fractionation, but here we assumed an equilibrium fractionation model within the mush zone to better simulate fractionation process with interactions of surrounding two- (Ol + Pl), or more likely three-phase (Ol + Pl + Cpx) cumulates (for the 2^{nd} stage) as the second Cpx-bearing assemblage dominates the BOIC layered gabbroic plutonic sections evidence by textural adcumulates signifying near-equilibrium textures without significant zoning (e.g., Casey, 1980; Komor et al., 1987).

In the 2nd stage equilibrium fractionation, intermediate pressure of 1.4 kb is within the estimated depth-based pressure range (0.7-2 kb) of the gabbroic plutonic section in the BOIC ophiolite, but we realize realistically evolved melts can accumulate or fractionate at any depth in the plutonic section within the cumulate mush zone that is generally considered to be located below the liquid-dominated shallowest axial melt lens. Equilibrium fractionation models provide a clearly better fit for the LLDs of the BOIC natural samples from basaltic to felsic compositions (see below for details), and also fits textural data from the cumulates which show variable incompatible trace element abundances (correlatable with melt content) at the same bulk rock Mg# but a general lack of significant mineral zoning textures at mid-crustal levels, although obviously including solidified intercumulus melt in many sections (e.g., Fig. 4.5). Thus, the evolved melt produced in the 1st stage will partially solidify by equilibrium crystallization modeled at intermediate plutonic depths within the crystal mush (2nd stage equilibrium fractionation). Finally, we modeled a third stage with the evolved melt migrating upward towards the roof zone and then extracted into shallow evolved melt-dominated plutons of plagiogranite observed in the roof zone (equivalent P of 0.7 kb). At this pressure, it undergoes final low-pressure fractional crystallization (3rd stage Rayleigh fractionation).

Fractionation minerology of cumulates was examined to calculate the concentrations of trace elements in melts for Rayleigh fractional crystallization using equation $C_{l}/C_{o} = F^{(D-1)}$ (C_{l} = concentration of the certain element in the liquid; C_{o} = concentration of the certain element in the parent; F = percentage of melt remaining; D = bulk partition coefficient of the certain element) and for equilibrium fractionation using equation $C_{l}/C_{o} = [F (1 - D) + D]^{-1}$. Likewise basaltic partition coefficients were used for calculations of melts with $SiO_{2} < 53$ wt.%, whereas and esitic partition coefficients for those with SiO_{2} content ≥ 53 wt.% (see Table A4.3 in Appendix including partition coefficients and references used in this study).

4.5.3.3 Effects of 2nd stage equilibrium fractionation following 1st stage 2 kb Rayleigh fractionation on melt composition

We systematically investigated the influence of equilibrium fractionation process on melt composition at the intermediate averaged pressure of 1.4 kb by using a range of melt compositions with different FLR extractions varying from 90% to 20% produced in the 1st stage Rayleigh fractionation modeling as new parents for the 2nd stage equilibrium models (Fig. 4.19 and A4.11). It is clear that if using lower FLR melts from 1st stage as starting materials, the following equilibrium fractionation process tends to produce melts with lower SiO₂ and FeO* but higher Al₂O₃ contents compared to those starting with higher FLR melts. Furthermore, the variation trends modeled by using a range of FLRs from low to high that can overall bracket BOIC sample trends particularly of felsic compositions with regard to Al₂O₃ contents and other elements (Fig. 4.19). It is important to note that equilibrium fractionation process has pronounced effects on melt Al₂O₃ contents (Fig. 4.19c) by which the variability in Al₂O₃ enrichments typically observed in BOIC plagiogranites and silicic dikes can be successfully reproduced. This implies that the equilibrium fractionation of intercumulus residual or allochthonous melts within the middle crustal cumulates is a unique process required to generate BOIC plutonic plagiogranites and their finegrained dike equivalents that cannot be fulfilled by a single or a combination of any multiple fractional crystallization models. Furthermore, the equilibrium fractionation model fits many of the textural observations in the layered cumulate section, which typically exhibit unzoned or weakly zoned crystals but with variable amounts of bulk rock trace element contents at the similar Mg#s suggesting trapped or migrating melts have solidified in equilibrium with original primocrysts at high temperatures under slow cooling conditions as the textural ripening and solidification take place.

Fig. 4.19 Effects of 2^{nd} stage modeling of equilibrium fractionation (EX) process following 1^{st} stage 2 kb Rayleigh fractionation on LLDs modeled. Representative major oxide variation diagrams of SiO₂, FeO* and Al₂O₃ vs. MgO for BOIC basalts, diabases, andesites, plagiogranites and fine-grained intrusive dikes, as well as the modeled LLDs (colored lines) for equilibrium crystallization (EX) starting after a precursor period of fractional crystallization (FX) of parent BMD 1009B representing the new starting melt at various FLRs (fluid remaining) of 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90% (see Fig. A4.11 in Appendix for all oxide variation diagrams). Note that the starting FLRs used for each EX modeling run were derived from fractionally crystallizing primitive BOIC diabase BMD 1009B (black lines) under the condition of P = 2 kb, fo₂ = QFM0 and H₂O = 0.3 wt.% that reproduced most of the BOIC basaltic/diabasic compositions (also see black lines in Fig. A4.11). Starting from different FLRs (> ~30%), a wide range of melt compositions can be produced at the late stage by equilibrium fractionation within the mush zone (modeled at intermediate depths equivalent to an averaged pressure of 1.4 kb) and hence, bracket most of the felsic BOIC samples. In particular, fractional crystallization models alone fail to reproduce felsic high to low Al₂O₃ composition (e.g., see Appendix Figs. A4.3-4.9), but EX models with varying starting composition (FLRs) from a precursor fractional crystallization modeling reproduce this range, as well as other element trends (Fig. A4.11).



4.5.3.4 Multi-stage Rayleigh and equilibrium fractionation models

We specifically chose two representative equilibrium fractionation LLDs calculated by starting from melt compositions of FLR = 90% and 50% that best match the range of BOIC sample trends at the felsic end to construct two multi-stage Rayleigh and equilibrium fractionation models to comprehensively evaluate whether a primitive MORB-like magma may evolve geochemically, through a series of crystallization, segregation and migration/extraction events mostly occurred within the crystal mushes, to form silicic endmember compositions similar to the BOIC plagiogranites and their fine-grained dike equivalents. It is notable that the two new parental melt compositions of FLR = 90% and 50% used in the 2^{nd} stage equilibrium fractionation modeling were produced and dictated by the 1^{st} stage Rayleigh fractionation modeling and correspond respectively to two-phase (OI + PI) and three-phase (OI + PI + Cpx) saturation in the BOIC lower layered gabbroic plutonic sections (e.g., Casey, 1980; Komor et al., 1987).

We then added a 3^{rd} stage Rayleigh fractionation at shallowest pressure of 0.7 kb after 95% crystallization to the 2^{nd} stage equilibrium fractionation process that was modeled starting from FLR = 50% melt composition to establish a 3-stage Rayleigh and equilibrium fractionation model because the 3^{rd} stage of shallowest (0.7 kb) fractional crystallization is a necessity in order to produce the very high silica contents (> 70 wt.%) and trace element enrichments in modeled melts (green lines in Figs. 4.20-4.21 and A4.10) that are typically observed in BOIC trondhjemites. The 1^{st} Raleigh and 2^{nd} equilibrium fractionation processes reproduced the overall variation trends of BOIC samples from basaltic to andesitic compositions, with the 3^{rd} stage specially to reproduce the highly evolved, silica-enriched, relatively lower Al₂O₃ (~11-15 wt.%) trondhjemite compositions (green lines in Fig. 4.20). Likewise, in selected trace element diagrams of La and Y vs. MgO and La/Sm vs. La, the 3^{rd} stage is particularly required to

drive the modeled LLDs to trondhjemite sample fields that are typically most enriched in La and Y, as well as high La/Sm ratio compared to other BOIC silicic samples (green lines in Fig. 4.21 and Fig. A4.10). This is also consistent with the overall steadily increasing La (representative of LREE) and Y (representative of HREE) trends with decreasing MgO (i.e., towards higher differentiation degrees) indicating a dominant fractionation process (see Brophy, 2008, 2009). It is notable that the 3-stage model successfully reproduced the elevated immobile incompatible element abundance towards more felsic BOIC samples. Especially, the typical Th enrichment, negative Eu and Nb anomaly and slight light REE enrichments observed in BOIC plagiogranites and fine-grained dike equivalents are all simultaneously reproduced with an overall similar trace element variation pattern as BOIC natural samples superimposed (dark to light grey shaded areas vs. colored lines in Fig. 4.22a). Our modeling results further indicate that the BOIC plagiogranitic compositions start to be produced after ~60% fractionation within equilibrium fractionation stage while more highly silica-enriched trondhjemites were uniquely produced by very late-stage Rayleigh fractionation process (i.e., after 95% fractionation) (Fig. 4.22a). Mineral proportions modeled indicate an early 3-phase (Ol + Pl + Cpx) saturated melt of 1st stage is likely required before being able to enter mid-crustal gabbroic sections to undergo further equilibrium fractionation process to form the BOIC trondhjemite compositions (Fig. 4.23a).

The 2-stage Rayleigh and equilibrium fractionation model including a 1st stage Rayleigh fractionation followed by a 2nd stage equilibrium fractionation starting from melt composition of FLR = 90% is specifically constructed to account for the BOIC dioritic compositions with higher Al₂O₃ contents (purple lines in Figs. 4.20-4.21 and A4.10). However, rhyolite-MELTS program is somewhat incapable of extending to the extreme of 100% crystallinity (i.e., FLR = 0%) and thus, we extended the trajectories of modeled LLDs in the 2nd stage equilibrium fractionation assuming that melt in natural environment can completely crystallize, by which the most evolved diorite compositions with the highest Al₂O₃ contents can be reproduced (see purple dashed lines in Figs. 4.20-4.21 and A4.10). This model is unique to reproduce the very high Al₂O₃ BOIC dioritic compositions that cannot be fulfilled by any other magmatic processes modeled in this study. It requires a very early, low-degree Rayleigh fractionation (~10% fractionation) followed by a continuous equilibrium fractionation to the end (i.e., FLR = 0 wt.%) to produce the entire, variable Al₂O₃ trends observed from BOIC basaltic to dioritic compositions (purple lines in Fig. 4.20). Because of lacking Rayleigh fractionation at a later stage, the modeled trace elements of La and Y are less enriched compared to the 3-stage model, but clearly match more evolved BOIC diorite and some andesitic samples (note the extended purple dashed lines in Fig. 4.21). Furthermore, we suggest that by extending to the extreme of 100% crystallinity (Fig. 4.22b), the 2-stage model could produce a range of trace element compositions that bracket BOIC andesitic and dioritic samples. Mineral proportions modeled indicate very early segregation of 2phase (Ol + Pl) saturated melts is required and then, these evolved melts will enter mid-crustal gabbroic sections to undergo further equilibrium fractionation to the end (i.e., 100% crystallinity) (Fig. 4.23b). This is also consistent with the modeled LLDs shown in Fig. 4.19 as equilibrium fractionation of early segregated melts tend to enrich Al_2O_3 but deplete SiO₂ in late-stage melts whereas equilibrium fractionation of relatively late segregated melts is opposite.

However, crystallization of amphibole (and other hydrous solid phases) in the rocks we observed cannot be properly modeled by MELTS program (see Fig. A4.7 and 4.22). This is not surprising because thermodynamic models (e.g., MELTS program) have been realized to fail to predict the experimental phase relations under water-saturated conditions (Feig et al., 2006) in which abundant amphibole and other hydrous minerals are likely to form. In BOIC plagiogranites (dioritic to trondhjemitic composition), amphibole, although not in large volumes, is commonly present (e.g., Fig. 4.4; also see Carter, 1985), and we expect that the late-stage melt modeled can be further enriched in SiO₂ as a consequence of fractionation of amphibole observed as a fractionating phase in BOIC felsic samples.

In summary, we conclude that the BOIC plutonic plagiogranites and fine-grained silicic dikes were primarily generated by evolution of primitive MORB-like magmas through a series of Rayleigh-equilibrium or Rayleigh-equilibrium-Rayleigh fractionation processes within discrete liquid-dominated chambers and crystal-dominant mush plutonic sections. These melts were segregated from the crystal mush and finally emplaced in highly evolved liquid-dominated discrete magma chambers in roof zone of the shallower crust.

Fig. 4.20 The two selected 3-stage and 2-stage Rayleigh and equilibrium fractionation models for reproducing BOIC sample trends. The two models fit basaltic to plagiogranitic compositions (see text for details). Modeling is based on early 2 kb fractional crystallization (FX) followed by shallower pressure (1.4 kb) equilibrium fractionation (EX) of more evolved melt upon FLR = 50% (green solid line, 3-stage model) and FLR = 90% (purple solid line, 2-stage model). Specifically, we added a segregation and FX process at the end stage at 0.7 kb that fractionally crystallizes the EX melt at FLR = 5% (3-stage Rayleigh and equilibrium fractionation model) to reproduce the most evolved, SiO₂-enriched trondhjemitic compositions observed in the BOIC samples (see green lines in Fig. 4.21) For the 2-stage model (i.e., EX starting from FLR = 90%) that only includes a 1st Rayleigh and 2nd equilibrium fractionation, the inferred extended LLD trends (purple dashed line) match well with the high-Al diorite samples. Note equilibrium fractionation and also fractional crystallization processes calculated by rhyolite-MELTS sometimes cannot proceed to 100% crystallinity (i.e., FLR near 0%) and therefore, we extended the modeled LLDs (purple dashed arrow at FLR=3%) to assume all the melt can completely fractionate to FLR = 0%. We also indicated a potential mixing line (dashed grey lines with double arrow) between the primitive diabase BMD 1009B and the most evolved diorite sample showing that simple mixing between these two endmembers can produce a range of intermediate and dioritic compositions that are not apparently following the Rayleigh/equilibrium fractionation trends modeled (see magma mixing section for details).



Fig. 4.21 Selected trace element modeling results of the 2-stage and 3-stage Rayleigh and equilibrium fractionation models derived from the same primitive BOIC diabase BMD 1009B (yellow stars). Modeling results calculated from the two models both match well with the BOIC sample trends, but late-stage fractional crystallization is particularly required to account for the most highly evolved trondhjemite compositions (also see Fig. A4.10). Note both La and Y in BOIC samples show an overall steadily increasing trend with decreasing MgO (i.e., towards higher differentiation degrees) also indicating that fractionation is likely the dominant process to produce the sample trends (see Brophy, 2008, 2009).



Fig. 4.22 N-MORB normalized (Sun and McDonough, 1989) extended REE diagrams without fluid-mobile elements showing the 2stage and 3-stage Rayleigh and equilibrium fractionation modeling results (shaded areas). Trace elements presented for each sample are measured by QQQ-ICP-MS in this study. Dashed lines within the shaded areas indicate the first and last modeling melt produced that mimic the variation patterns of BOIC samples. Importantly, the 3rd stage fractional crystallization is essential to rapidly elevate trace element concentrations in modeled melt to reproduce those highly evolved BOIC trondhjemites. Note that in (b), although only the latest melt produced reaches the diorite composition, we expect further equilibrium fractionation of the last 3% melt can continue to produce more evolved BOIC diorite compositions, like what have been inferred for major oxides in Fig. 4.20.



Fig. 4.23 Main solid phases presented in the 2-stage and 3-stage Rayleigh and equilibrium fractionation models with FeO* vs. MgO diagrams for (a) the 3-stage model involving deep (2 kb) fractional crystallization (FX) followed by shallower (1.4 kb) equilibrium fractionation (EX) of evolved melt at FLR = 50% from the 1st stage and a final 3rd stage of FX of FLR = 5% melt from the 2nd stage at 0.7 kb, and (b) the two-stage model starting from deep (2 kb) FX followed by shallower (1.4 kb) EX of melt at FLR = 90% generated by the 1st stage FX assuming all the melt can completely crystallize (see inferred dashed lines with question marks on them). Squiggly lines indicate estimated appearance and proportion of pargasitic amphibole by Carter (1985) starting at ~2.97 wt.% MgO (also ~57 wt.% SiO₂). Red dashed line of 52 wt.% SiO₂ marks the composition transition from basaltic to basaltic andesitic. The 2nd stage EX modeling starts either at (a) olive-plagioclase-clinopyroxene eutectic or (b) olive-plagioclase cotectic as the lowest oceanic crust is dominantly made up of olivine + plagioclase and grading to olivine + plagioclase + clinopyroxene at shallower level where evolved melt can interact with the pre-crystallized crystals.



4.5.4 Mixing of primitive basaltic magma with evolved felsic plagiogranite: explaining intermediate apparent CA melt trends

4.5.4.1 Model justification and setup

Recent developed dynamic magma chamber model of a sub-volcanic plumbing system highlighted the significance and ubiquitous existence of mixing process occurred through the entire magma chamber, although in many cases this natural phenomenon is still considered to be a minor and supplementary mechanism in combination with fractional crystallization and/or partial melting (e.g., Coogan et al., 2000, 2001; Casey et al., 2007; Costa et al., 2010; Coogan and O'Hara, 2015). Magma mixing processes are well documented in plutonic sections in the BOIC by numerous chemical, isotopic, field and petrogenetic studies (e.g., Casey, 1980; Carter, 1985; Casey et al., 1985; Komor et al., 1985, 1987; Siroky et al., 1985; Elthon et al., 1986; Komor and Elthon, 1990; Jenner et al., 1991; Kurth et al., 1998; Kurth-Velz et al., 2004). In fact, mixing different magmas can produce a variety of chemical compositions simply depending on the compositions of two or more endmember materials and their proportions used for mixing. We attempted to model the mixing of primitive basaltic melts in the roof zone melt lens with silicic melts at the periphery of the melt lens. We specifically focus on an array of intermediate compositions including diorites and andesitic rocks that may form in unusual ways by mixing of a primitive basaltic melt with a highly evolved felsic melt generated in crystal mush zone. In binary diagrams, two-endmember mixing process will produce a linear mixing line between two endmember compositions and any composition on this line could be accordingly interpreted as formed by mixing. We suggest this mechanism will possibly explain the intermediate compositions that lie outside the dominant iron-enrichment tholeiitic trend.

4.5.4.2 Effects of mixing primitive and evolved magmas

In AFM ternary diagram of Fig. 4.24, we again demonstrate the modeled LLDs showing that diorite samples plotting deeply in the calc-alkaline field can be effectively produced by fractional crystallization followed by equilibrium crystallization within a MORB-like environment (Fig. 4.24a purple line). Alternately, simply mixing of a range from low to high Fe basaltic compositions with more evolved felsic magmas (gray dashed lines with double arrow in Fig. 4.24b) is another way to produce those calc-alkaline diorites and andesitic samples (also see Tatsumi and Suzuki, 2009). The three samples plotting within volcanic arc granite field in Fig. 4.10 could similarly be explained by mixing of relatively high Fe basaltic magmas with more evolved felsic compositions (Figs. 4.24-4.25). We specifically demonstrate tectonic discrimination diagram of Y vs. Nb (Pearce et al., 1984) including basaltic field of the BOIC diabases and basalts (blue shaded area) and the MORB glass field (gray shaded area) from Jenner and O'Neill (2012) acting as potential basaltic endmembers for mixing (Fig. 4.25). The mixing line (black solid line with double arrow in Fig. 4.25) between a primitive BOIC basaltic rock (or MORB glass) and a most evolved silicic dike sample shows that simple mixing can produce an apparent linear trend from the VAG to ORG field with an overall increasing SiO₂ content that includes samples within the VAG field, as well as those near the boundary between VAG and ORG field that have been frequently interpreted as a typical indicator of SSZ environment (e.g., Bonev and Stampfli, 2009). Furthermore, MORB glass fractionation especially when equilibrium fractionation is involved would produce similar trends to modeled LLDs derived from the diabase BMD 1009B and lead to a variety of felsic compositions within the ORG and anomalous ridge fields. Such variety of felsic endmember compositions, if mixed with more primitive BOIC basaltic/diabasic magmas outlined in Fig. 4.25, would also produce a wide range of intermediate compositions within VAG, ORG

and anomalous ridge fields. Therefore, magma mixing appears to be essentially involved to reproduce those "apparent" calc-alkaline and VAG samples of intermediate dioritic and andesitic compositions that are less likely to be directly generated by Rayleigh and/or equilibrium fractionation processes (Figs. 4.20, 4.24 and 4.25).

Fig. 4.24 AFM ternary diagrams with modeling results showing (a) modeled LLDs of the 2-stage and 3-stage Rayleigh and equilibrium fractionation models that could explain the overall variation trends and particularly those highly evolved diorite samples plotting deeply in the calc-alkaline field and (b) an alternative explanation of intermediate samples plotting in the calc-alkaline field that could be mixing of a range from low to high Fe basaltic compositions with more evolved felsic magmas. Note two possible examples of mixing vectors are shown with hatch marks incremented every 20% (0%, 20%, 40%, 60%, 80%, 100%) to indicate mass percentages of basaltic melts used for mixing. The three symbols (one circle and two triangles) highlighted by black arrows are the samples plotting within VAG field in Fig. 4.10 that could be specifically explained by magma mixing of relatively high Fe basaltic magmas with more evolved trondhjemite compositions.



Fig. 4.25 Felsic rock (SiO₂ \geq 56 wt.%) tectonic discrimination diagram of Nb vs. Y proposed by Pearce et al. (1984) with modeling results showing 25 BOIC fine-grained felsic dikes and plutonic plagiogranites, but we have included the basaltic field of the BOIC diabases and basalts (blue shaded area), which on average are more fractionated than parent diabase BMD 1009B. We also include the broader MORB glass field (gray shaded area) from Jenner and O'Neill (2012) for comparison. In the plot, we have included magma mixing lines between the averaged BOIC basaltic composition and a most evolved felsic dike (black solid line with double arrow) and the 2-stage and 3-stage Rayleigh and equilibrium fractionation modeling trends (green and purple line with arrow) derived from the primitive BOIC diabase BMD 1009B (yellow star). Fractionation of a range of BOIC basalts and diabases would produce similar trends to modeled LLDs derived from the diabase BMD 1009B and lead to felsic rocks within the ORG and anomalous ridge fields at late fractionation stages. Note that mixing of evolved felsic samples with BOIC MORB-like compositions can also produce samples within the VAG field or near the boundary between VAG and ORG field, that has in the past been specifically interpreted as an indicator of SSZ environment (e.g., Bonev and Stampfli, 2009).



4.6 Conclusions

Plagiogranites in the Bay of Islands Ophiolite Complex (BOIC) consists dominantly of trondhjemite with lesser intermediate compositions of quartz diorite and diorite. These plagiogranites generally occur as meter- to kilometer-scale plutons and smaller intrusive sills, dikes, pods and veins within the upper non-layered gabbroic units and at the cannibalized boundary with the lowermost sheeted dikes. Other fine-grained, sparsely-phyric compositionally similar silicic intrusions are located within the base of the sheeted dike unit as diabase-parallel dikes and include basaltic-andesitic, andesitic, dacitic and rhyodacitic compositions. These BOIC plutonic plagiogranites and silicic fine-grained dikes are all characterized by very low K₂O content of typical tholeiitic nature, similar to oceanic crust plagiogranites and those of other SSZ ophiolites, but distinctive from A-type granite and Archean TTG (Tonalite-Trondhjemite-Granodiorite) suite of more typical calc-alkaline characteristics. Furthermore, all these BOIC silicic samples exhibit overall similar geochemistry showing subparallel N-MORB normalized extended immobile trace element and REE variation patterns with negative Nb-Ta anomalies and slightly enriched Th. These patterns are also sub-parallel to the BOIC basaltic/diabasic assemblages and typical of supra-subduction zone (SSZ) forearc spreading tholeiitic environments. However, when compared to basaltic compositions, evolved felsic rocks have more significant negative Eu, Sr, Ti and V anomalies consistent with extensive crystal fractionation of plagioclase and Fe-Ti oxide minerals. The chemical similarities between coarse- and fine-gained silicic samples and their similar intrusive contact relationships both suggest that the plutonic plagiographies likely represent nearmagmatic liquid compositions without extensive accumulative effects (i.e., they are similar to their fine-grained dike counterparts compared here) but unlike BOIC mafic gabbroic cumulates which
typically have positive Sr and Eu anomalies reflecting plagioclase accumulation and either no, slight or large positive Ti and V anomalies (positive when accumulated oxide minerals are present).

We then combine our new major and trace geochemical analyses of plagiogranites and their equivalent fine-grained silicic dikes with prior geochemical datasets from basaltic to felsic compositions of the BOIC to conduct petrogenetic modeling of fractional and equilibrium crystallization, partial melting and magma mixing processes to quantitatively assess the petrogenesis of these felsic BOIC samples. The combined datasets show little evidence of commonly cited compositional gap in major element variation diagrams between BOIC basaltic and felsic samples that support a liquid immiscibility process, although intermediate compositions are sampled and analyzed less commonly. Examination of modeling results in particular of immobile major and incompatible trace elements suggests that BOIC silicic samples of tholeiitic characteristic were likely produced by fractionation of primitive basaltic magma with SSZ forearc feature that likely proceeded from deep-crustal fractional crystallization in magma chambers followed by initial melt entrapment and post-cumulate near-equilibrium crystallization reactions during migration through a mid-crustal cumulus mush zone. This combined process is wellpredicted by numerous dynamic oceanic magma chamber models in which primitive to evolved multi-saturated melts percolate upwards through reactive porous flow within the crystal mush zones and can efficiently account for the significant variability in the enrichment of Al₂O₃ observed in BOIC felsic samples.

The pervasive interactions between cumulus crystals and melts result in unzoned to weak marginal normal or reversed zoned primocrysts within the cumulate sections, except near the cooler roof zone where strong disequilibrium mineral zoning is present. The evolved melts within crystal mushes either solidify finally in situ or are extracted from residual intercumulus spaces within mushes likely to undergo further shallow fractional crystallization and/or mixing processes at high levels of the plutonic sections of ophiolite to form plagiogranites and felsic dikes. However, it is notable that the MELTS program fails to predict the fractionation of amphibole under water-saturated conditions. Amphibole is a common, although not in large volume, mineral observed in the BOIC plagiogranites. We suggest fractionation of amphibole can further concentrate melt SiO₂ content in late-stage magma fractionation. Partially melting the magma chamber roof zone lithologies can produce a large range of heterogenous melt compositions, some with some similarities to specific element groups and trends of intermediate to felsic rocks, but none conforms to the dominant high SiO₂ plagiogranites of the BOIC. Even if combined with postmelting crystal fractionation, these melts are unlikely to have produced BOIC high silica ($SiO_2 >$ 70 wt.%) samples due to the significant mismatches of some major and trace elements modeled. They also are unlike prior experimental study results and their overall geochemistries and variation trends. Magma mixing of primitive basalts and more felsic magmas appears to be another important process in the plutonic roof zone in producing certain intermediate dioritic to felsic compositions that apparently plot in the calc-alkaline field on AFM diagrams but lack overall characteristics of calc-alkaline melts (e.g., very low K₂O). Their intrusions as dikes within the sheeted dikes also likely indicates an immediately prior chamber expansion by replenishment with mixing with a more primitive melt.

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Chapter 5 The BOIC subcreted dynamothermal metamorphic sole

5.1 Introduction

The dynamothermal metamorphic sole is welded to the base of each of the four Bay of Islands Complex ophiolitic massifs that form the once contiguous uppermost crystalline thrust sheet of the Taconic Humber Arm Allochthon in Western Newfoundland as part of the Northern Appalachians (Fig. 5.1) (Malpas et al., 1973; Williams and Smyth, 1973; Malpas, 1976, 1979; McCaig, 1983; Casey and Dewey, 1984; Savci, 1988; Cawood and Suhr, 1992; Suhr and Cawood, 1993; Fergusson and Cawood, 1995; Dewey and Casey, 2013, 2015). A similar metamorphic sole is also preserved to the north beneath the St. Anthony Ophiolite Complex of the Taconic Hare Bay Allochthon on the northern peninsular of Newfoundland (Jamieson, 1979, 1980, 1981, 1986; Jamieson and Strong, 1981; Dewey and Casey, 2013, 2015). Although ~190 km separated, the two sole assemblages show comparable inverted metamorphic gradients and similar polyphase deformation intensity decreasing structurally downward (Williams and Smyth, 1973; Jameison, 1980; McCaig, 1983; Savci, 1988). Dewey and Casey (2013) showed that the dynamothermal metamorphic sole lies immediately below a porphyroclastic to mylonitic shear zone (100 m in thickness) in the ophiolitic basal ultramafic section (their unit 2). They then recognized a more complete transect of metabasic and metasedimentary sole section (their units 5-13) of up to 1360 m thickness below these basal ultramafic rocks, although acknowledging no locality in these exposed areas includes all units in a single section. These metamorphic rocks include a downward progression of two-pyroxene-garnet granulites, garnet amphibolites, upper to lower amphibolite facies rocks and upper to lower greenschist facies assemblages. They are underlain by anchimetamorphic mafic pillow lavas and mélanges with more pelitic matrices. The metabasic

rocks within the sole have MORB to OIB affinities (Dewey and Casey, 2013, 2015), whereas metasediment compositions vary between metapelites, metasandstones and volcanoclastic rocks. All the metamorphic sole units, therefore, show a clear downsection gradient of P-T-d (pressure-temperatures-deformation) conditions varying from the upper level uppermost two-pyroxene garnet granulites and garnet amphibolites to intermediate amphibolites and greenschists and finally to lower metasediments (see a summary in Dewey and Casey, 2013). The peak metamorphism, estimated based on the two-pyroxene garnet granulites located near the ophiolite basal porphyroclastic to mylonitic residual lherzolite and harzburgite mantle-sole contact, represents temperature of > 800-900 °C and pressure of 8.5-11 kb, whereas lower amphibolite and greenschist facies appear to be metamorphosed by lower temperature of 300-600 °C and pressure of < 3-5 kb (Jamieson, 1980, 1981; McCaig, 1983; Savci, 1988). Therefore, there is both an inverted temperature and pressure gradient downsection through the sole (Casey and Dewey, 1984; Savci, 1988; Dewey and Casey, 2011, 2013).

Fig. 5.1 Generalized regional geologic map of allochthonous ophiolitic rocks of the Bay of Islands region of Western Newfoundland, Canada showing the dynamothermal metamorphic sole assemblages at the base of the four BOIC massifs (modified from Casey et al., 1985). Note blue stars indicate sampling locations from the base of the North Arm Mountain (NA) massif (see an enlarged satellite view of 2017 sample locations in Fig. 5.2) and prior Blow Me Down Mountain (BMD) massif sample location analyzed in this study.



Thermochronological studies (Dallmeyer and Williams, 1975) on metamorphic sole rocks yielded an ⁴⁰Ar-³⁹Ar amphibole age of ca. 469 Ma (see Nelson and Casey, 1979 for recalculation based on new K decay constant). Largely based on this age, as well as structural and some chemical studies, the metamorphic sole was proposed to be generated during obduction onto the Laurentian continental margin which is stratigraphically dated by the early ophiolitic detritus in flysch on allochthonous slope-rise deposits as Dapingian (e.g., Stevens, 1970; Lindholm and Casey, 1989; Dewey and Casey, 2015), implying that the overlying BOIC ophiolite was still hot (e.g., Malpas, 1979). However, Yan and Casey (2020) reported a crystallization age of ca. 488.3 Ma for the BOIC ophiolite lying directly above the sole. This indicates that, if the sole age is true, the BOIC oceanic lithosphere was in a subduction setting for ~20 Ma with older cold Iapetus nearmargin lithosphere subducting prior to obduction onto the continental margin. Therefore, it would be incapable of producing the sole metabasic two-pyroxene-garnet granulites (estimated temperature of > 800-900 °C by McCaig, 1983; Savci, 1988) ~20 Ma after its formation. We estimate given the current thickness of the ophiolite that the base of the ophiolite would be below sole temperatures within ~5 Ma. Furthermore, the estimated pressure of 8.5-11 kb for the twopyroxene-garnet granulites indicates an equivalent depth of $\sim 25-35$ km, which cannot be simply accommodated by the thickness of BOIC ophiolite that varies only from ~10-12 km in thickness (e.g., Casey et al., 1981; 1985; Cawood and Suhr, 1989). A complicating factor for the BOIC sole ca. 469 Ma age is that the sole exposed at the base of St. Anothony Ophiolite Complex in the northern extremity of Taconic Allochthon that is correlated with the BOIC ophiolite emplacement age has yielded a much older 40 Ar- 39 Ar age of 489 ± 5 Ma (see recalculation in Dunning and Krogh, 1985). This age is similar to the BOIC crystallization age of ca. 488.3 Ma (Yan and Casey, 2020). Therefore, it would indicate an early sole formation age close to the age of the Baie Verte Oceanic Tract (BVOT) (ages of ca. 489-488.3 Ma; Yan and Casey, 2020) including both the Taconic Bay of Islands Ophiolite Complex and St. Anthony Ophiolite Complex, but ~20 Ma prior to the actual obduction of Taconic ophiolitic allochthons. It is also notable that such young metamorphic sole ages as the BOIC (i.e., ~20 Ma younger than the directly overlying ophiolite) have not been reported in other sole assemblages. For example, the metamorphic sole beneath Semail ophiolite is interpreted to be near coincident or only slightly younger than the overlying ophiolite (e.g., Rioux et al., 2013, 2016, 2021). Therefore, the often-cited recalculated ca. 469 Ma age of Dallmeyer and Williams (1975) for the metamorphic sole subcreted to the base of BOIC ophiolite may not be appropriate. Tectonic evolutionary models established based on this age to explain the sole formation, accordingly, may need further revision. Here we hypothesize a likely older sole formation age (e.g., Casey and Dewey, 1984; Savci, 1988; Dewey and Casey, 2013, 2015, 2021) and undertake a preliminary LA-ICP-MS U-Pb zircon study of sole rocks with samples collected during past field mapping by J.F. Casey and new samples jointly collected in 2017 on a transect through the North Arm basal sole rocks (Fig. 5.1 and 5.2). This study will be the first test of the thermochronological ⁴⁰Ar-³⁹Ar age in the last 45 years. We present a three-sample study here to be followed up at a later date with additional sample studies from the present collection.

To accommodate the issues mentioned on these age relationships, Dewey and Casey (2013, 2015) hypothesized a new model suggesting that the sole was produced nearsimultaneously with the overlying ophiolite by the metamorphism of MORB- and OIB-like rocks and accreted metasediments originating from the subducting plate. These subcreted metamorphic rocks beneath the supra-subduction zone BOIC ophiolite forearc basement were progressively attached during exhumation by flattening the overlying plate in a subduction zone (Casey and Dewey, 1984; Savci, 1988; Dewey and Casey, 2013, 2015, 2021). Dewey and Casey (2013, 2015) further implied that the forearc BOIC basement together with the basal subcreted metamorphic sole were transported in an oceanic subduction setting for ~20 Ma prior to the final obduction (ca. 470 Ma). The final stage of emplacement resulted in the generation of more pelitic matrix lower greenschist facies and anchimetamorphic mélanges proximal to the continental margin marking the base of the sole as final emplacement in the allochthon between ca. 470-460 Ma onto the Laurentian margin. This obduction stage may partly account for the enigmatic ⁴⁰Ar-³⁹Ar amphibole age of ca. 469 Ma determined over 45 years ago but is unlikely to represent the hot subcretion of granulite and amphibolite stage of sole formation. However, the lack of more detailed U-Pb geochronological studies since this early Ar thermochronological study of the BOIC high-temperature metamorphism in 1975 has inhibited further understanding of these ambiguities and confirmation and development of newer model proposed (e.g., Dewey and Casey, 2015, 2021).

In this chapter, we first conduct bulk-rock major and trace element analyses on a contiguous set of samples collected from just below the NA massif basal ophiolitic mantle-sole contact to the lower more pelitic matrix greenschist facies (see Table A5.1). These data will be combined with more analyses to understand the protoliths and metamorphism history of the BOIC metamorphic sole and will contribute to a larger database (Dewey and Casey, 2015, unpublished datasets) to assess protoliths accreted in subsequent papers. Furthermore, we specifically choose three samples including two from the NA massif (Fig. 5.1 and 5.2) and one from the BMD massif (Fig. 5.1) to conduct a preliminary age study of sole samples. LA-ICP-MS U-Pb zircon depth-profiling analysis on unpolished zircon grains were conducted to assess the high temperature (Tc of zircon is ~900 °C) metamorphism ages. The preliminary study reported is part of a larger study planned for a range of sole samples collected from the BOIC sole in 2017 and over the last 35 years.

5.2 Sampling locations

To comprehensively characterize the protoliths of the metamorphic sole assemblage subcreted to the base of Bay of Islands Ophiolite Complex, we analyzed 17 samples that were collected from the base of North Arm Mountain (NA) massif (Fig. 5.1 and 5.2). Each of the 17 samples was chosen separately from one another to cover largest continuous portion of the exposed area of the metamorphic sole assemblage (Fig. 5.2). Two of the samples, NA-S13-17Y and NA-S18-17Y, were specifically chosen for zircon analysis to determine both the high temperature (~900 °C) metamorphism age (i.e., rim age) and the inherited protolith age (i.e., core age). Sample NA-S18-17Y was collected close to the ophiolite basal porphyroclastic to mylonitic residual lherzolitic mantle-sole contact that is suggested to be directly related to highest temperature metamorphism (e.g., Savci, 1988; McCaig, 1983; Dewey and Casey, 2013, 2015). Sample NA-S13-17Y is located in the middle level of the sole assemblage that may have only undergone somewhat lower temperature amphibolite facies metamorphism, which may not significantly affect the inherited zircons separated. Sample NA-S14-17Y is an intrusive vein within sample NA-S13-17Y. Sample NA-S18-17Y and NA-S19-17Y were collected from the same locality, but NA-S19-17Y is at a higher level in the sole nearer to the basal ophiolite ultramaficsole contact.

We also analyzed another sample B.12.7.2F collected close to the ophiolite mantlesole contact of the Blow Me Down Mountain massif in order to provide additional age constraint on the high temperature metamorphism within the sole.



Fig. 5.2 Enlarged view (Google Earth satellite image) of a portion of the North Arm Mountain massif within the basal dynamothermal metamorphic sole (see the blue star in Fig. 5.1) showing the detailed sampling locations of the 17 samples we collected in 2017 (yellow pins with sample labels). The sole sample traverse is progressively upward from the shoreline from lower amphibolites to granulites just below the peridotite-sole contact (NA-S01-17Y to NA-S19-17Y). Detailed GPS locations of each sample are provided in Appendix Table A5.1. Note samples NA-S18-17Y and NA-S13-17Y are specifically chosen for zircon U-Pb study.

5.3 Method

5.2.1 Bulk rock geochemistry

The newly collected bulk metamorphic sole rocks were first trimmed to remove the outermost weathering surfaces and cut into smaller blocks by tungsten rock saw. Every block was carefully washed with Milli-Q water and then dried in clean fume hood. These dried sample blocks were crushed by ceramic jaw crusher followed by pulverization using SPEX SamplePrep
Shatterbox (series 8530). Finally, the powders of each sample were separately stored in precleaned plastic bottles for future geochemistry analysis.

Loss on ignition (LOI) was calculated by using initial weight of the rock powder (dry after 12 hours at 100 °C in Lab-Line Oven) minus its final weight (ignited after 45 minutes at 1000 °C in Lindberg furnace), and then divided by the initial weight. After LOI determination. the ignited powders were then dissolved by 2N nitric acid following procedures described in Chapter 4. The solutions were finally diluted to 1:500 for measurement of K, Mn, Na, Ti and P, and to 1:5000 for Si, Al, Ca, Fe and Mg analysis by using Agilent 725 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) at the University of Houston (UH) ICP lab. Major element results of the 17 samples and secondary standard are together presented in Appendix Table A5.1 on a dry basis and only volatile-free totals that range between 98.5 and 101% were reported. Reference values for BHVO-2 and SCO-1 are from Jochum et al. (2016) and Govindaraju (1994), respectively (see Jochum et al., 2005 for standard chemical data compilation). BHOV-2 was used as primary standard to calibrate instrument-induced time drift while SCO-1 was served as an unknown to independently evaluate the accuracy and precision of the entire analysis. Repeat analyses of secondary standard SCO-1 show high precision (i.e., RSD) within 1.5%.

Single-reaction-chamber microwave (UltraWAVE by Milestone) with strong acid (HF-HCl-HNO₃) was used for digestion of powdered samples for trace element analysis of rock samples with lab-established bulk-rock powder heating processes and digestion procedures. After microwave digestion, the remaining materials were completely transferred to Teflon beakers, and were dissolved by repeatedly adding nitric and hydrochloric acids followed by drying on hotplate in a clean fume hood to completely remove fluoride residues (see Chapter 4 for detailed procedures). The final clear solutions were diluted to 1:1000 and then were analyzed by Agilent

8800 Triple Quadrupole-Inductively Coupled Plasma-Mass Spectrometer (QQQ-ICP-MS) at the UH ICP lab as well. Only trace elements with RSD (assessed by SCO-1) no higher than 15% were reported, although most elements were withing 5% RSD (Table A5.1). Likewise, BHOV-2 was used as primary standard for correction while SCO-1 was treated as secondary standard to monitor the accuracy and precision of the entire run. Reference values for BHVO-2 and SCO-1 are from Jochum et al. (2016) and Govindaraju (1994), respectively.

5.2.2 Zircon depth profiling of unpolished zircon

Bulk samples were processed by conventional zircon separation techniques including crushing, sieving, free-fall magnetic separation, water separation and MI (Methylene Iodide) separation. A Franz Isodynamic separator was used to concentrate non-magnetic grains, among which individual zircon grains were handpicked under a polarizing microscope regardless of their size and appearance to avoid potential artificial bias (Sláma and Košler, 2012; Košler et al., 2013). These handpicked grains were placed on a glass slide using double-sided tape for zircon depth-profiling analysis. It is notable that every zircon was carefully adjusted under a petrographic microscope to ensure that a flat grain surface is upfacing and parallel to the glass slide. The depth profiling technique was used on unpolished grains to obtain laser analyses of any metamorphic rim analyses while potentially drilling into zircon cores that could be inherited igneous or detrital zircons.

Zircon U-Pb depth-profiling analysis was carried out on a new Analytik Jena (PlasmaQuant MS Elite) inductively coupled plasma-mass spectrometer (ICP-MS) purchased in 2020 and equipped with a Photon Machines Excite 193 nm wavelength laser ablation system in the University of Houston ICP Lab. Laser ablation operational parameters included a 25- μ m ablation spot, a fluence of 3.95 J/cm², a repetition rate of 8 Hz and a burst count of 320 shots. A

single LA-ICP-MS acquisition lasted 70 s including background determination of the first 15 s, sample ablation time of the following 40 s with measurements of ²⁰²Hg, ²⁰¹Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, and ²³⁸U, and wash-out delay of the last 15 s before the next acquisition. Ablation rate of 0.58 μ m/s is assumed at energy of 3.95 J/cm² (Kelley et al., 2014; Gutiérrez-González et al., 2015). Pleisovice with an accepted ID-TIMS value of 337.13 \pm 0.37 Ma (Sláma et al. 2008) was used as calibration standard for corrections of instrument fractionation and time drift whereas FC5z with an accepted ID-TIMS value of 1099.0 \pm 0.6 Ma (Paces and Miller, 1993) as secondary standard to independently monitor the accuracy and precision of the entire run. Raw U-Th-Pb intensity data were reduced using Iolite (Paton et al., 2011), followed by further correction and calibration using an in-house U-Pb age data reduction Excel spreadsheet (Shaulis et al., 2010). Common Pb correction was not performed due to interference from Hg (see Shaulis et al., 2010, 2017 for discussion).

LA-ICP-MS depth profiling of unpolished zircon is an effective method to date micron thick metamorphic zircon rims that can yield reliable U-Pb ratios within ~1 μ m thickness (equivalent of ~2 s ablation time estimated here) intervals from zircon rims to interiors and avoiding mixing older age domains (Cottle et al., 2009; Kelly et al., 2014). Therefore, the first 2 s (~1.2 μ m drilling thickness) after ablation starts was specifically used for integration and calculation of zircon outermost rim age, which is regarded as the best estimation for the high temperature metamorphic age of zircon. It is notable that because of the short integration interval used here, the individual analyses commonly come out with larger errors (e.g., Fig. 5.3a). However, a more precise concordia or weighted mean age could still be achieved by pooling a large population of LA-ICP-MS U-Pb single rim-core zircon analyses (e.g., Yan and Casey, 2020). Here we applied a discordance filter of 15 (calculated as the log ratio distance to the maximum likelihood composition on the concordia curve; see Vermeesch, 2021 for details) for concordia and weighted mean age calculation to exclude ages that may have been affected by Pb loss and/or common Pb contamination.

The last ~ 27 s ablation interval (i.e., $\sim 11-38$ s) was used for estimation of the interior (inherited) core age, if unlike the rim age, and it appears to have determined a relatively flat plateau in the time-resolved spectra distinct from the rim age (e.g., Fig 5.3a). However, if the rim age appears to be indistinguishable from the core age (i.e., no different signal plateaus observed), we then used the entire integration interval of 2-38 s for age calculation (e.g., Fig. 5.3b) because a long ablation time interval for the interior age calculation could effectively mitigate the signal variation and random spikes likely caused by heterogeneous alteration, inclusions and/or microstructures that were ubiquitously observed in zircon grains analyzed here. These secondary structures, understandably, are very abundant in metamorphic/altered parts of the zircon grains analyzed and cannot be avoided during the LA-ICP-MS analysis. Kernel density estimate (KDE) and cumulative age distribution (CAD) diagrams are specifically presented because the core analyses could include a wide variety of inherited ages (for example detritus in a single sample) resulting in ambiguous or meaningless intercept, concordia and weighted mean ages calculated. Calculations of concordia, intercept and weighted mean ages, as well as plotting of Wetherill/Tera-Wasserburg, kernel density estimate (KDE) and cumulative age distribution (CAD) diagrams, were conducted using IsoplotR online version (Vermeesch, 2018). Reduced data are shown in Table A5.2-5.6. Individual isotopic ratios and dates are reported at the 2 sigma (2s) level whereas the final calculated concordia, weighted mean and intercept age are presented at 95% confidence interval.

Fig. 5.3 Representative unpolished zircon grains and their rim-to-interior variations in LA-ICP-MS raw ²⁰⁶Pb/²³⁸U signal. Note that sample B.12.7.2F is dominated by metamorphic zircons of rounded to subrounded shape and have interiors without obvious zoning yielding no significant rim vs. interior variation or distinct rim plateau. Zircons in sample NA-S13-17Y and NA-S18-17Y, however, are subhedral with inherited internal zoning and appear to have very young rims with heterogeneous thicknesses that are tentatively interpreted to indicate post-final emplacement low-temperature young rims originating possibly during a later Salinic deformation episode.



5.4 Preliminary results and conclusions

5.4.1 Bulk rock geochemistry

Selected elements are normalized to N-MORB values (Gale et al., 2013) and demonstrated in Fig. 5.4 to investigate the potential protoliths of the 17 metamorphic sole samples analyzed here. Approximately these samples can be divided into three groups based on the overall element variation patterns particularly those of immobile incompatible ones. Five samples are depleted in heavy rare earth elements but with moderate to strong positive Sr and Eu anomalies and either positive or negative Ti anomalies (Fig. 5.4a and b). These features and their overall similar variation patterns suggest that they may be derived from similar protoliths of gabbroic rocks with high plagioclase content. Eight samples have overall comparable N-MORB normalized (Gale et al., 2013) immobile incompatible trace element patterns that are bracketed by the lower and upper bound of MORB composition (Fig. 5.4c and d) similar to those described in Dewey and Casey (2015) from the Blow Me Down Mountain massif sole assemblage and other North Arm Mountain massif sole metabasites. This may indicate that the protoliths of these samples are also MORB-like composition but varying from D-MORB to E-MORB. The slight negative Ti and V anomaly but positive Eu and Sr anomaly observed in the eight samples suggest that they may have undergone some extent of Ti-Fe oxide fractionation and plagioclase accumulation before being metamorphosed. However, all the eight samples have significant negative Nb anomalies indicating they may have been somewhat contaminated by continental sediments or arc detritus as deformed rocks analyzed have complex and isoclinally folded laminations. Four samples show nearly identical variation pattern as the Post-Archean Australian Shale (PAAS) in particular of immobile elements, suggesting that they are metapelites with shale-like protoliths that are PAAS-like in composition. It appears the immobile elements of these protoliths have not been significantly

modified by later metamorphism (Fig. 5.4e and f). It is notable that all the samples analyzed here show prominent positive U and Pb anomaly likely indicating either pre-sole metamorphic or synmetamorphic subduction fluid mobility of U and Pb or a strong continental contamination (e.g., wind-blown brown pelagic clays) by the subducting sediment intrafolial laminations (Fig. 5.4).

Fig. 5.4 N-MORB normalized multi-element incompatible element variation diagrams with (a, c and e) and without (b, d and f) fluidmobile elements for the 17 metamorphic sole rocks from the base of NA massif. Preliminarily, they are interpreted to be divided into three different groups based on their overall elemental variation patterns. Group 1 samples (a-b) are mafic in composition and highly depleted in middle and heavy REEs that likely represent meta-cumulate gabbroic protoliths. Group 2 samples (c-d) are also mafic in composition but lie within the bounds of E-MORB to D-MORB-like metabasalt protoliths. Group 3 samples (e-f) appear to almost exactly match Post-Archean Australian Shales (PAAS) and are interpreted to represent pelitic protoliths in the lower to middle part of the transect. N-MORB, E-MOEB, D-MORB and upper and lower MORB bound values plotted are from Gale et al. (2013). Plotted Post-Archean Australian Shale (PAAS) values are from Taylor and Mclennan (1985).



5.4.2 U-Pb depth profiling of unpolished zircon

5.4.2.1 Sample B.12.7.2F

Zircon grains collected from sample B.12.7.2F are likely metamorphic zircons as they are relatively small in size and dominantly with rounded to subrounded shapes with no obvious internal concentric zoning (e.g., Fig. 5.3c). Every analysis appears to only have one single sample signal plateau and therefore, the integration interval of 2-38 s during ablation time for each analysis was used for age calculation. A total of 100 zircon grains were separated and analyzed for sample B.12.7.2F. Unfortunately, only 41 analyses yielded error correlation values between the ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U ratios within 0-1 that are suitable for further age calculations. We suggest that the large population of outliers (i.e., 59 analyses out of the 0-1 error correlation range) are likely caused by the overall rounded to subrounded shape of these unpolished zircons (e.g., Fig. 5.3c) because the laser was not able to be focused on a clear, flat, upfacing surface. This unfocused problem could result in uneven ablation rate (and heterogeneous sample inputs) and hence, unknow elemental fractionation issues that finally result in unexpected large errors of some elements (e.g., ²⁰⁷Pb) measured during the entire run. However, as mentioned, we still observed a single flat sample signal plateau (e.g., ²⁰⁶Pb/²³⁸U ratio) for each analysis (e.g., Fig. 5.3b) likely indicating inherited cores within these zircons are absent or rare. These zircons, therefore, will be later mounted and polished and analyzed again to presumably provide more precise age results by analyzing a polished flat surface.

Here we provided some preliminary results based on the 41 analyses with error correlation values of 0-1 by applying a discordance filter of 15. These analyses yielded comparable concordia and weighted mean ages respectively of 491.8 ± 6.0 Ma (MSWD = 1.3) (Fig. 5.5a) and 492.0 ± 6.0 Ma (MSWD = 1.9) (Fig. 5.5b). Furthermore, they determined an age peak in KDE plot

of ca. 490 Ma, consistent with the concordia and weighted mean ages calculated. It is notable that, as mentioned, zircon grains collected from this sample show typical metamorphic zircon appearance and no different signal plateaus were observed in each zircon depth-profiling analysis. This may indicate somewhat high temperature metamorphism (i.e., above ~800-900 °C) that is similar to the highest metamorphism temperature estimated for two-pyroxene-garnet granulite facies. Therefore, we suggest the zircon age of 491.8 \pm 6.0 Ma determined for sample B.12.7.2F represents the highest temperature metamorphism age near the ophiolite-sole contact. Notable, this 491.8 \pm 6.0 Ma age of metamorphism is within error of the age of crystallization of the BOIC plagiogranites (ca. 488.3 Ma, Yan and Casey, 2020).



Fig. 5.5 LA-ICP-MS U-Pb zircon depth-profiling age results for sample B.12.7.2F including (a) Wetherill concordia plot and (b) ranked weighted mean concordia age plot yielding a comparable ca. 491.8 Ma age for the high temperature sole at the base of BMD massif, and (c) kernel density estimate (KDE) plot by using an integration interval of 2-38 s of the entire ablation time from rim to core. Note discordance filter of 15 has been applied. These analyses yielded highly comparable concordia and weighted mean age respectively of 491.8 \pm 6.0 Ma and 492.0 \pm 6.0 Ma, consistent with the peak of ca. 490 Ma shown in KDE plot. The 491.8 \pm 6.0 Ma age for the rim analysis is within error of the BOIC crystallization age of 488.3 \pm 1.5 Ma. Concordia and weighted mean ages are reported at 95% confidence interval.

5.4.2.1 Sample NA-S13-17Y

Ten zircon grains were collected and analyzed for sample NA-S13-17Y and most of the analyses, both from the rim and interior, are highly discordant (discordance > 100). Therefore, they are plotted on a Tera-Wasserburg diagram yielding a younger less precise rim age of 491.5 \pm 42.3 Ma compared to an older more precise core age of 503.5 \pm 12.5 Ma (Fig. 5.6). However, the large error of 42 Ma calculated based on the rim analyses may indicate this age likely has limited geologic significance and may involve mixed ages. It is notable that zircon grains from sample NA-S13-17Y analyzed show variable degrees of common Pb contamination for both outermost rim and interior. This indicates that secondary structures related to alteration and/or metamorphism may even have affected the innermost part of zircons resulting in their overall heterogeneous natures. Although the rim age is similar to sample B.12.7.2F from the Blow Me Down massif sole, the large age error limits its reliability. However, the interior inherited age with smaller error is within the age of possible arc detritus contributed to the trench from the Notre Dame forearc-arc terrane with forearc-arc magmatism that initiated at least by ca. 514.3 Ma and lasted until at least ca. 463 Ma.



Fig. 5.6 Tera-Wasserburg plot for plotting core analyses of sample NA-S13-17Y yielding an intercept age of 503.5 ± 12.5 Ma. Rim analyses, however, yielded a much less precise age of 491.5 \pm 42.3 Ma that may not have geological significance (not shown). The 503.5 ± 12.5 Ma age for the core analysis is similar and comparable with the latest CC plagiogranite magmatism age and the Twillingate Granite intrusion age (ca. 504.3 Ma).

5.4.2.2 Sample NA-S18-17Y

Sixty-six zircon grains were analyzed for sample NA-S18-17Y that is located immediately below the ophiolite-sole contact. Likewise, by applying a discordance filter of 15, we obtained an age results of 492.8 ± 5.6 Ma for Wetherill concordia age but a slightly younger age of 487.3 ± 5.8 Ma for weighted mean age (Fig. 5.7). Because these ages were calculated by only including relatively concordant, outermost rim analyses, they are also regarded as the representatives of high temperature metamorphism ages. It is notable that the concordia and weighted mean ages presented here are still comparable and within error of the age of 491.8 ± 6.0 Ma calculated for BMD sample B.12.7.2F that was similarly derived from just below the mantle-

sole contact. The high temperature metamorphism age of 492.8 ± 5.6 Ma (NA-S18-17Y rim) and 491.8 ± 6.0 Ma (B.12.7.2F) are both within error of the BOIC crystallization age of 488.3 ± 1.5 Ma (Yan and Casey, 2020) and are also highly comparable and consistently within error with each other. However, as the analyses from sample B.12.7.2F determined a more concentrated age peak, we then take the 491.8 ± 6.0 Ma age (B.12.7.2F) as the best estimation for the high temperature sole formed near-simultaneously with accretion of the BOIC ophiolite as suggested by Dewey and Casey (2013, 2015).



Fig. 5.7 Wetherill concordia plot yielding age of 492.8 ± 5.6 Ma and weighted mean plot yielding a similar age of 487.3 ± 5.8 Ma (using concordia dates) for NA sample NA-S18-17Y rim analyses. A similar discordance filter of 15 has been applied for age calculations. Blue bars on weighted mean plot indicate outliers removed from the weighted mean age calculation by applying a generalized Chauvenet Criterion (see Vermeesch, 2018).

When plotting the interior core analyses on Wetherill plot, the data ellipses are essentially concordant (all have discordance < 10) but are more dispersed than the rim analyses, yielding a concordia age of 509.0 ± 1.9 Ma (Fig. 5.8). A similar, but slightly older age of 513.4 ± 2.0 Ma is calculated for the weighted mean age of concordia dates (Fig. 5.8). Because the dispersion spreads along the concordia curve (and in weighted mean plot) spanning a broad age

range of 399.7-612.8 Ma, rather than concentrated in a narrower field, the concordia and weighted mean age calculated here may have ambiguous or limited geological meaning in terms of a single age. Therefore, we presented the core analyses in kernel density estimate (KDE) plot, similarly with a discordance filter of 15, to show the age distribution patterns (Fig. 5.9a). We also integrate the core (Fig. 5.9a) and rim (Fig. 5.9b) analyses to show a more comprehensive age distribution spectra (Fig. 5.9c), by which the metamorphism history may be better understood.



Fig. 5.8 Wetherill concordia plot yielding age of 509.0 ± 1.9 Ma and weighted mean plot yielding a slightly older age of 513.4 ± 2.0 Ma (using concordia dates) for NA sample NA-S18-17Y core analyses. These core analyses are essentially concordant (i.e., discordance < 10) and show significant dispersion in both Wetherill and weighted mean plots with a broad age range of 399.7-612.8 Ma indicating that the single concordia and weighted mean age calculated here may not be geologically meaningful. Blue bars on weighted mean plot indicate outliers removed from the weighted mean age calculation by applying a generalized Chauvenet Criterion (see Vermeesch, 2018).

Understandably, rim analyses include a somewhat higher percentage of younger dates that yield a younger mean than the core analyses (Fig. 5.7 vs. 5.8), whereas the core analyses appear to contain more older inherited dates, although date ranges for both cores and rims are very similar (Fig. 5.9a and b). Rim analyses span a wider age range of ca. 440-540 Ma with most

analyses concentrated at ca. 490 Ma and another two peaks at ca. 450 and 525 Ma (Fig. 5.9b). Core analyses, in contrast, has a narrower age range with most analyses clustering between ca. 500-540 Ma and two peaks occurring at ca. 505 and 530 Ma (Fig. 5.9a). When superimposed the rim and core analyses, a composite KDE plot shows clearly four peaks at ca. 450, 490, 505 and 525 Ma (Fig. 5.9c).

We interpreted the oldest peak of ca. 525 Ma with a range between ca. 550-510 Ma to represent the oldest range of inherited core ages related to the downgoing slab and detachment to the base of the ophiolite. Furthermore, both rim and core analyses have the same peak of ca. 525 Ma, although a discordance filter has been applied. This may indicate that some of the zircons may not have been seriously affected by the high temperature metamorphism. The ca. 525 age peak with a range of ca. 550-510 Ma also encompasses the age range of ancient oceanic crust (e.g., Iapetus oceanic crust) which started accretion adjacent to the Laurentian margin with possible intraplate seamounts of various age at ca. 550 with spreading continuing at least to the ca. 514.3 Ma (initiation of Early Cambrian subduction and potentially younger) indicating a prolonged igneous and sediment detritus accumulation history. We take subduction as initiating at least by ca. 514.3 Ma based on the oldest CC plagiogranite magmatism ages reported in Chapter 3.

The ca. 505 Ma age peak appears to occur within a narrow age range of ca. 510-500 Ma (Fig. 5.9a and c). This ca. 505 Ma age peak is not different from the intercept age of ca. 503.5 Ma calculated from sample NA-S13-17Y core analyses, both of which are also comparable to the youngest CC plagiogranite magmatism and Twillingate batholith crystallization age ranges (see Chapter 3). The ca. 503.5 or 505 Ma age represents post-Notre Dame arc formation and is close to the extinction time of Notre Dame CC forearc magmatism. It is notable that the ca. 503.5 age is calculated based on sample NA-S13-17Y core analyses (Fig. 5.6), and the ca. 505 Ma age peak with a narrow age range of ca. 510-500 Ma also dominantly comes from the sample NA-S18-17Y core analyses (Fig. 5.9a) indicating that they likely represent inherited ages rather than metamorphism ages.

We interpreted the ca. 490 Ma age peak, or more precise 491.8 ± 6.0 Ma age, as representative of the high temperature sole forming metamorphic age best characterized by the rim analyses from sample NA-S18-17Y presented here. The youngest ca. 450 Ma age peak is dominantly contributed by rim analyses and may indicate a post-obduction and emplacement lowtemperature hydrothermal and structurally related disturbance (e.g., dissolution-reprecipitation and/or hydrothermal alteration) that dominantly affects the outermost zircon rim areas. In a related low-temperature (U-Th)/He thermochronology and thermal history ongoing study at the University of Southern California by Ryley Collins and Emily Cooperdock of same zircons separated from the BOIC plagiogranites that are reported in Yan and Casey (2020) of Chapter 2, the ophiolitic allochthon is shown to undergo slow cooling due to post-Taconic exhumation or isotherm relaxation.

Ophiolitic ZHe ages ranged from ca. 324 to 427 Ma with an approximate closing temperature of 150-160 °C (R. Collins, personal communication), suggesting that the youngest U-Pb ages reported here in the zircon rims of sole rocks overlap and may be the result of the slightly later Late Ordovician-Silurian Salinian Orogen deformation-hydrothermal events (see Williams and Cawood, 1989; Cawood et al., 1994) known to have affected the allochthons. The Silurian Salinic deformation is interpreted to have initiated in Central Newfoundland by ca. 455 Ma and spread to Western Newfoundland characterized by cooling and exhumation of Taconic metamorphic terranes by ca. 434-425 Ma (van Staal et al., 2014). This is the exact range of the

youngest U-Pb dates measured here. These late disturbances in the Humber Arm Allochthon may also, in part, help to explain the younger ⁴⁰Ar-³⁹Ar ages of ca. 469 Ma for the sole rocks.

Fig. 5.9 Kernel density estimate and cumulative age distribution diagrams for (a) rim, (b) core and (c) rim and core composite analyses (discordance filter of \leq 15 applied) of NA sample NA-S18-17Y. Note that rim analyses include a somewhat higher percentage of younger dates that yield a younger mean than the core analyses. The core analyses, in turn, appear to contain more older inherited dates, although date ranges for both cores and rims are very similar. This result shows that often-reported single-grain TIMS analyses for metamorphic sole ages for this sample would likely yield an older mixed age, rather than a true sole metamorphic age. Note that maximum dates with 3 or more dates are also not older than ~550 Ma, which is regarded as the oldest age of Iapetus Ocean formation adjacent to Laurentia. Overall, this result is consistent in the dates for all three samples presented in this chapter indicating a lack of Grenville detritus from the Laurentian margin in the early sole formation protoliths.



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Chapter 6 Summary and conclusions

In this dissertation, age relationships of ophiolitic rocks in Western Newfoundland and an arc batholith in Central Newfoundland are investigated in the northernmost part of the Appalachians. The study is conducted to understand age relationships in the earliest pre-terminal collision of a juvenile to mature island arc formed within the Iapetus Ocean to its final collision with the Laurentia continental margin. Based on new LA-ICP-MS U-Pb dating of a large population of zircon grains collected from several ophiolitic plagiogranite plutons, as well as by reviewing and recalculating legacy age results using modern developed and communityrecommended data treatment techniques, we reported a more precise composite age of 488.3 ± 1.5 Ma based on 5 samples from two plutons in the Bay of Islands Ophiolite Complex (BOIC). We also reported a range of ages from several plutons of ca. 514.3-502.7 Ma from the Coastal Complex (CC) ophiolite. Both ophiolitic assemblages are located within the Humber Arm Allochthon of Western Newfoundland and represent different stages of forearc accretion during forearc-arc development. We also reported here a new 504.3 \pm 1.8 Ma age for the Twillingate batholith in Notre Dame Subzone of northern Central Newfoundland representing the earliest large silicic pluton in the Notre Dame arc.

To reexamine the age of the BOIC metamorphic sole formation and inherited ages included within the sole we examined two samples including one granulite and one amphibolite as a preliminary study. We obtained an age of 491.8 ± 6.0 Ma for the granulite metamorphism, temperature (Tc of zircon is ~900 °C) within the peak metamorphic part of the dynamothermal metamorphic sole subcreted just below the peridotite at the base of BOIC ophiolite. These new ages, in combination of our recalculated ages, allow a much more precise tectonic evolutionary

model to be constructed for ophiolites of the Humber Arm allochthon and early magmatism in Notre Dame arc in Western and Central Newfoundland. Here we primarily follow the temporal tectonic evolutionary model originally proposed in Dewey and Casey (2011, 2013, 2015, 2021) but with new age constraints on the development of the Early Cambrian island arc and forearc and the mid to late Cambrian rifting of the early forearc and arc system with formation of the older Coastal Complex-Lushs Bight-Sleepy Cove lithosphere and the younger Baie Verte Oceanic Tract, as well as the formation of the sole at the initiation of subduction beneath the newly accreted BOIC forearc, to the final collision and emplacement of the Taconic Humber Arm Allochthon ophiolites and Notre Dame arc onto the Cambro-Ordovician Laurentian passive continental margin during the Middle Ordovician (Fig. 6.1 and 6.2).

Fig. 6.1 Schematic three-dimension cross-section of the trench-forearc-arc-back arc system with subduction of the oceanic lithosphere adjacent to the Laurentian margin with lithosphere of supra-subduction zone Bay of Islands of the Baie Verte Oceanic Tract (which includes forearc Betts Cove and Pointe Rousse ophiolites of same ages, and potentially the younger back arc Annieopsquatch ophiolite). The Baie Verte oceanic tract spreading centers are oriented approximately orthogonal to the trench and left stepping transforms were approximately parallel requiring a trench-ridge-ridge triple junction in the front of the forearc (Dewey and Casey, 2011, 2013, 2015). Instantaneous subduction initiation beneath the spreading centers and hot sole subcretion of the downgoing oceanic lithosphere is shown to form metamorphic soles (cooling starting at ca. 491.8 Ma) below the Baie Verte oceanic tract. The ophiolites of the Baie Verte oceanic tract start to form at ca. 489 Ma, which involved rifting of the older CC-Lushs Bight forearc (formed early at ca. 514.3-502.7 Ma). The arc encroachment on the Laurentianmargin results in ophiolite obduction over Laurentian Humber margin starting at ca. 470 Ma during the Taconic Orogeny. Note red color indicates new LA-ICP-MS U-Pb zircon (composite) ages suggested here and from Yan and Casey (2020) while blue ages indicate recalculated Betts Cove ophiolite age in Yan and Casey (2020) and proposed Point Rousse ophiolite age by Skulski et al. (2010).



Fig. 6.2 Tectonic evolutionary model for development of Taconic Humber Arm Allochthon and Notre Dame Arc during the Taconic collision and obduction with the Laurentia continental margin (modified from Dewey and Casey, 2021). Note the ages (red) are determined from Chapters 2, 3 and 5.



Fig. 6.2 (continued)


The ancient peri-Laurentian westerly-vergent subduction initiated at least by ca. 514.3 Ma based on the earliest CC ages in the forearc plagiographies. This was followed by a prolonged early forearc-arc magmatic period of at least ~11.6 Ma that lasted to at least ca. 502.7 Ma. During the ~11.6 Ma long forearc-arc magmatism period, the Coastal Complex (CC)-Lushs Bight (LB)-Sleepy Cove (SC) ophiolitic assemblages representing a composite forearc-arc terrane were gradually established. This was accompanied by the eastward migration (i.e., away from the trench) of magmatic front (i.e., more intense active arc activity). At ca. 504.3 Ma, a stable magmatic island arc massif, represented by the Twillingate batholith, was built. These terranes including CC-LB forearc and Notre Dame arc (e.g., SC volcanics and Twillingate batholith) comprise the oldest, primitive Notre Dame forearc-arc basement formed above a subduction zone. The forearc magmatic activity in the CC appears to have ceased by ca. 502.7 Ma and therefore, overlaps with the intrusion of the Twillingate plagiogranite batholith. Volcanism persisted during this early stage of arc evolution that lasted at least ~25 Ma from ca. 514.3-489 Ma (Fig. 6.1) until the inception of the BVOT forearc-arc rifting, which represents a new phase of magmatism for the Notre Dame forearc and arc that partly built a new, younger basement.

The Baie Verte Oceanic Tract (BVOT) spreading initiated at least by ca. 490-488.3 Ma and resulted in the formation of supra-subduction zone (SSZ) trench-proximal Bay of Islands Ophiolite Complex (BOIC) (ca. 4883. Ma), as well as the trench-distal, arc-proximal Betts Cove (ca. 488.5 Ma) and Point Rousse (ca. 489 Ma) ophiolites along a set of supra-subduction zone forearc spreading centers offset by trench-parallel transform faults. These spreading centers were linked to a trench-trench-spreading center triple junction to the northwest and were likely offset by many long trench-parallel transforms (Fig. 6.1). The younger once-contiguous BVOT oceanic crust was generated by rifting the older Notre Dame forearc-arc lithosphere. It is notable that rifting

and transform margins of the BVOT resulted in the juxtaposition of the younger BOIC with the older CC, with a direct igneous contact between the BOIC and CC preserved and exposed in the Lewis Hills massif (Karson and Dewey, 1978).

Plagiogranites within the BOIC gabbro-dike transition zone of the oceanic crust were dominantly derived by fractionation of primitive MORB-like BOIC forearc tholeiitic basalts within a SSZ forearc. These felsic rocks originated from deep-crustal fractional crystallization of primitive mantle-derived magmas within the ophiolitic crust. Cumulate mushes derived from early fractionation and the entrapped post-cumulate melts likely reacted by equilibrium crystallization. This process resulted in evolved melts migrating upwards by reactive porous flow through the mid-crustal gabbroic crystal-rich gabbroic mushes. The more evolved melts finally segregated to shallow plutons just below the sheeted dike to either solidify, undergo further fractional crystallization or mix with more primitive magmas that triggered shallower silicic dike intrusions observed in the BOIC ophiolite.

The BVOT ophiolites accretion (ca. 489-488.3 Ma) and hot subcretion (ca. 491.8 Ma) of sole rocks to the BOIC as spreading proceeded were essentially simultaneous (Fig. 6.1 and 6.2) downdip of a three-plate trench-trench-spreading center triple junction proposed by Dewey and Casey (2011, 2013), a triple junction model modified from Casey and Dewey (1984). The sole was produced by the metamorphism of MORB- and OIB-like rocks and sediments originating from the subducting plate and subcreted to the overlying SSZ forearc BOIC ophiolite as exhumation by flattening of the subducting plate occurred (Fig. 6.2).

The composite forearc-arc basement including the older CC-LB-SC terrane and younger BVOT was obducted starting at ca. 470 Ma, ~20 Ma after BOIC seafloor spreading in the forearc and sole subcretion (Fig. 6.2). The ophiolitic welded composite forearc CC-BOIC

basement was partially dismembered during obduction and final emplacements onto the Laurentia continental margin, In the Lewis Hills, however, the BOIC-CC contact is still preserved in autochthonous igneous relationship between the older deformed and younger little-deformed ophiolitic basements. The obduction was followed shortly after ~460 Ma by a hiatus in Notre Dame arc volcanism in response to the Taconic collision and convergence with the eastern Laurentian continental margin in the middle Ordovician (ca. 470-460 Ma). Volcanism and plutonism resumed after Iapetus slab detachment and a subduction polarity reversal forming an Andean-type margin as remnants of Iapetus were subducted (Fig. 6.2).

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Appendix

A 1			Isotopic	ratios					Isotopic Age	es (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
BMD01_01	0.05806	0.00262	0.61622	0.02856	0.07703	0.00238	531.70	98.56	478.30	14.24	487.50	17.94
BMD01_02	0.05546	0.00198	0.60853	0.02328	0.07963	0.00232	430.60	77.32	493.90	13.88	482.60	14.70
BMD01_03	0.05531	0.00246	0.62146	0.02854	0.08154	0.00252	424.70	96.74	505.30	14.98	490.80	17.86
BMD01_04	0.05719	0.00196	0.65626	0.02464	0.08328	0.00244	498.30	74.74	515.70	14.52	512.30	15.10
BMD01_06	0.05909	0.00256	0.63996	0.02872	0.07860	0.00244	570.50	92.64	487.80	14.56	502.30	17.78
BMD01_07	0.05844	0.00296	0.64136	0.03288	0.07965	0.00258	546.20	108.52	494.10	15.40	503.10	20.34
BMD01_08	0.05681	0.00258	0.61716	0.02886	0.07884	0.00248	483.60	98.74	489.20	14.78	488.10	18.12
BMD01_09	0.05599	0.00262	0.59341	0.02868	0.07692	0.00244	451.80	102.16	477.70	14.62	473.00	18.28
BMD01_10	0.05591	0.00236	0.60076	0.02672	0.07799	0.00242	448.40	92.14	484.10	14.44	477.70	16.94
BMD01_11	0.05548	0.00244	0.59266	0.02722	0.07753	0.00242	431.50	95.66	481.30	14.52	472.60	17.36
BMD01_12	0.05712	0.00276	0.63874	0.03172	0.08116	0.00262	495.50	105.80	503.10	15.60	501.50	19.66
BMD01_13	0.05624	0.00266	0.59979	0.02932	0.07739	0.00248	461.30	103.66	480.60	14.88	477.10	18.60
BMD01_14	0.05711	0.00290	0.60724	0.03162	0.07716	0.00254	495.30	111.20	479.20	15.18	481.80	19.98
BMD01_15	0.05753	0.00302	0.63190	0.03388	0.07971	0.00266	511.60	114.14	494.40	15.84	497.30	21.08
BMD01_16	0.05482	0.00282	0.58137	0.03080	0.07696	0.00254	404.80	111.94	478.00	15.24	465.30	19.78
BMD01_17	0.05672	0.00276	0.60277	0.03042	0.07712	0.00252	480.00	106.14	478.90	15.02	479.00	19.28
BMD01_18	0.05752	0.00312	0.61431	0.03396	0.07751	0.00262	511.10	117.80	481.20	15.66	486.30	21.36
BMD01_19	0.05623	0.00314	0.60447	0.03434	0.07800	0.00266	460.80	122.78	484.20	15.90	480.10	21.72
BMD01_20	0.05631	0.00302	0.60306	0.03310	0.07772	0.00262	463.80	117.88	482.50	15.62	479.20	20.96
BMD01_21	0.05729	0.00314	0.62333	0.03496	0.07894	0.00268	502.40	119.74	489.80	16.02	491.90	21.86
BMD01_22	0.05644	0.00320	0.62611	0.03604	0.08049	0.00276	469.00	123.72	499.10	16.46	493.70	22.50
BMD01_23	0.05846	0.00358	0.63070	0.03890	0.07828	0.00278	547.10	131.40	485.80	16.56	496.50	24.22
BMD01_24	0.05831	0.00358	0.65442	0.04038	0.08144	0.00288	540.60	132.88	504.70	17.18	511.20	24.78
BMD01_25	0.05559	0.00316	0.59921	0.03452	0.07821	0.00268	435.60	123.28	485.40	16.02	476.70	21.92
BMD01_29	0.05700	0.00378	0.63187	0.04164	0.08042	0.00292	490.90	144.02	498.60	17.46	497.30	25.92
BMD01_30	0.05881	0.00396	0.64940	0.04336	0.08010	0.00294	560.20	143.34	496.70	17.54	508.10	26.70
BMD01_31	0.05791	0.00394	0.62071	0.04184	0.07775	0.00286	526.10	146.62	482.70	17.08	490.30	26.22
BMD01_33	0.05803	0.00444	0.62680	0.04680	0.07835	0.00304	530.50	163.84	486.30	18.12	494.10	29.20

Table A2.1 LA-ICP-MS analysis results of sample BMD-01-17Y. GPS Location: 49.07123N, 58.26468W

Table A2.1 (continued)

A 1 . 11			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	207 Pb/ 235 U	2s
BMD01_34	0.05479	0.00400	0.58806	0.04216	0.07785	0.00294	403.80	158.36	483.30	17.58	469.60	26.96
BMD01_35	0.05769	0.00416	0.63285	0.04466	0.07957	0.00298	517.60	154.14	493.60	17.82	497.90	27.76
BMD01_38	0.05653	0.00446	0.61980	0.04726	0.07952	0.00310	472.60	171.62	493.30	18.50	489.70	29.62
BMD01_05	0.05960	0.00242	0.62603	0.02670	0.07623	0.00232	589.20	86.88	473.60	13.92	493.60	16.68
BMD01_26	0.05760	0.00352	0.66210	0.04068	0.08339	0.00294	514.30	132.14	516.30	17.50	515.90	24.86
BMD01_27	0.05530	0.00360	0.58152	0.03770	0.07629	0.00276	424.10	140.92	473.90	16.48	465.40	24.20
BMD01_28	0.05578	0.00388	0.65565	0.04518	0.08527	0.00316	443.30	151.04	527.50	18.78	512.00	27.70
BMD01_32	0.05966	0.00588	0.66943	0.06384	0.08139	0.00354	591.30	206.52	504.40	21.08	520.40	38.82
BMD01_36	0.05842	0.00492	0.68642	0.05570	0.08523	0.00344	545.50	178.56	527.20	20.46	530.60	33.54
BMD01_37	0.06090	0.00558	0.68318	0.06014	0.08137	0.00344	635.70	191.22	504.30	20.50	528.70	36.28
BMD01_39	0.05747	0.00462	0.60196	0.04650	0.07598	0.00298	509.10	171.62	472.10	17.86	478.50	29.46
BMD01_40	0.05732	0.00474	0.60561	0.04798	0.07664	0.00304	503.30	178.94	476.00	18.26	480.80	30.34

			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	207 Pb/ 235 U	2s
BMD03_03	0.05817	0.00410	0.65155	0.04516	0.08114	0.00298	535.60	151.96	503.00	17.76	509.40	27.76
BMD03_04	0.05701	0.00266	0.61385	0.02942	0.07800	0.00250	491.40	102.66	484.20	14.94	486.00	18.52
BMD03_08	0.05624	0.00348	0.60383	0.03706	0.07780	0.00276	461.00	135.00	483.00	16.52	479.70	23.46
BMD03_10	0.05655	0.00316	0.61946	0.03470	0.07938	0.00272	473.30	121.42	492.40	16.28	489.50	21.76
BMD03_11	0.05636	0.00352	0.60061	0.03726	0.07723	0.00278	465.90	135.84	479.50	16.66	477.60	23.64
BMD03_12	0.05600	0.00346	0.60428	0.03728	0.07820	0.00282	452.00	134.90	485.40	16.82	479.90	23.60
BMD03_14	0.05555	0.00366	0.60494	0.03950	0.07892	0.00292	434.30	143.24	489.70	17.46	480.40	24.98
BMD03_15	0.05714	0.00388	0.60808	0.04072	0.07713	0.00290	496.40	147.02	478.90	17.34	482.30	25.70
BMD03_17	0.05595	0.00436	0.60802	0.04632	0.07876	0.00318	450.00	168.02	488.70	18.98	482.30	29.24
BMD03_21	0.05652	0.00494	0.60405	0.05128	0.07745	0.00334	472.30	188.84	480.90	20.04	479.80	32.46
BMD03_22	0.05671	0.00514	0.62666	0.05506	0.08008	0.00354	479.60	195.34	496.60	21.12	494.00	34.38
BMD03_23	0.05697	0.00556	0.62298	0.05876	0.07925	0.00366	489.70	209.12	491.70	21.86	491.70	36.76
BMD03_24	0.05652	0.00546	0.61519	0.05754	0.07889	0.00364	472.00	208.46	489.50	21.70	486.80	36.18
BMD03_25	0.05651	0.00586	0.60334	0.06036	0.07736	0.00374	471.90	223.08	480.40	22.34	479.40	38.22
BMD03_26	0.05595	0.00638	0.61108	0.06708	0.07914	0.00404	450.10	244.78	491.00	24.12	484.20	42.28
BMD03_28	0.05627	0.00620	0.62175	0.06588	0.08006	0.00402	462.30	236.88	496.50	24.00	490.90	41.26
BMD03_29	0.05528	0.00624	0.59866	0.06492	0.07847	0.00400	423.40	242.90	487.00	23.94	476.40	41.24
BMD03_30	0.05730	0.00710	0.61709	0.07308	0.07803	0.00424	502.50	262.56	484.40	25.40	488.00	45.88
BMD03_31	0.05709	0.00714	0.62615	0.07482	0.07946	0.00436	494.50	265.56	492.90	26.02	493.70	46.72
BMD03_32	0.05508	0.00706	0.59698	0.07300	0.07852	0.00438	415.30	274.48	487.30	26.16	475.30	46.42
BMD03_33	0.05716	0.00740	0.62593	0.07724	0.07933	0.00446	497.10	274.20	492.20	26.62	493.60	48.24
BMD03_06	0.05697	0.00316	0.59675	0.03316	0.07590	0.00258	489.70	121.10	471.60	15.48	475.20	21.08
BMD03_07	0.05604	0.00318	0.58382	0.03326	0.07549	0.00260	453.50	124.00	469.20	15.56	466.90	21.32
BMD03_27	0.05817	0.00632	0.61750	0.06458	0.07692	0.00384	535.60	230.48	477.70	22.92	488.30	40.54
BMD03_34	0.05771	0.00774	0.60725	0.07758	0.07623	0.00440	518.50	282.26	473.60	26.32	481.80	49.02
BMD03_01	0.05294	0.00554	0.55549	0.05672	0.07601	0.00318	326.30	228.94	472.20	19.02	448.60	37.02
BMD03_02	0.06091	0.00296	0.62691	0.03098	0.07456	0.00242	636.10	102.90	463.60	14.50	494.20	19.34
BMD03_05	0.06038	0.00346	0.65828	0.03766	0.07899	0.00272	617.30	121.54	490.10	16.22	513.60	23.06

Table A2.2 LA-ICP-MS analysis results of sample BMD-03-17Y. GPS Location: 49.04860N, 58.26880W

Table A2.2 (continued)

A			Isotopic	ratios			Isotopic Ages (Ma)						
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s	
BMD03_09	0.05467	0.00302	0.59472	0.03306	0.07882	0.00270	398.90	119.96	489.10	16.08	473.90	21.06	
BMD03_13	0.05390	0.00360	0.58341	0.03852	0.07845	0.00292	366.60	146.74	486.90	17.40	466.60	24.70	
BMD03_16	0.06207	0.00476	0.67604	0.05070	0.07894	0.00316	676.50	159.74	489.80	18.94	524.40	30.72	
BMD03_18	0.05464	0.00420	0.60309	0.04544	0.08000	0.00322	397.40	166.42	496.10	19.16	479.20	28.78	
BMD03_19	0.06244	0.00526	0.67078	0.05490	0.07787	0.00330	689.10	174.50	483.40	19.68	521.20	33.36	
BMD03_20	0.05397	0.00470	0.58593	0.04964	0.07868	0.00336	369.90	189.12	488.20	20.10	468.30	31.78	
BMD03_35	0.06184	0.00594	0.69967	0.06496	0.08199	0.00376	668.70	199.00	508.00	22.40	538.60	38.80	

			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	$^{207}Pb/^{206}Pb$	2s	²⁰⁷ Pb/ ²³⁵ U	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
BMD04_01	0.05660	0.00206	0.60777	0.02392	0.07780	0.00232	475.40	80.46	483.00	13.90	482.20	15.12
BMD04_02	0.05690	0.00250	0.61343	0.02792	0.07812	0.00244	487.10	95.58	484.90	14.58	485.70	17.56
BMD04_03	0.05662	0.00256	0.60893	0.02846	0.07793	0.00246	476.00	99.46	483.80	14.68	482.90	17.96
BMD04_04	0.05678	0.00262	0.64349	0.03062	0.08212	0.00260	482.50	101.00	508.70	15.52	504.50	18.92
BMD04_08	0.05691	0.00294	0.61895	0.03228	0.07881	0.00260	487.50	113.12	489.00	15.48	489.20	20.26
BMD04_09	0.05835	0.00346	0.63796	0.03764	0.07923	0.00274	542.80	127.10	491.50	16.36	501.00	23.32
BMD04_10	0.05575	0.00292	0.60805	0.03222	0.07903	0.00262	442.30	114.32	490.30	15.62	482.30	20.34
BMD04_11	0.05833	0.00380	0.61816	0.03962	0.07679	0.00276	541.60	140.54	476.90	16.54	488.70	24.86
BMD04_14	0.05590	0.00352	0.61647	0.03836	0.07992	0.00284	447.90	137.14	495.60	16.98	487.60	24.10
BMD04_15	0.05686	0.00344	0.62641	0.03758	0.07984	0.00280	485.30	132.32	495.10	16.72	493.90	23.46
BMD04_16	0.05667	0.00386	0.62880	0.04200	0.08040	0.00298	478.00	148.80	498.50	17.76	495.30	26.18
BMD04_17	0.05752	0.00398	0.61804	0.04180	0.07786	0.00290	511.20	149.40	483.30	17.36	488.60	26.24
BMD04_18	0.05501	0.00400	0.58890	0.04164	0.07758	0.00296	412.40	157.26	481.70	17.68	470.20	26.62
BMD04_19	0.05695	0.00402	0.61247	0.04208	0.07794	0.00294	488.90	153.06	483.80	17.54	485.10	26.50
BMD04_20	0.05720	0.00446	0.61890	0.04674	0.07840	0.00310	498.90	168.40	486.60	18.54	489.20	29.32
BMD04_21	0.05531	0.00446	0.60042	0.04666	0.07866	0.00318	425.10	173.86	488.10	18.98	477.50	29.60
BMD04_22	0.05822	0.00456	0.63619	0.04808	0.07919	0.00316	537.50	168.10	491.30	18.84	499.90	29.84
BMD04_23	0.05792	0.00478	0.62747	0.04978	0.07850	0.00322	526.60	176.56	487.20	19.24	494.50	31.06
BMD04_24	0.05809	0.00486	0.61866	0.04964	0.07718	0.00320	532.70	178.84	479.30	19.10	489.00	31.14
BMD04_26	0.05678	0.00548	0.61053	0.05612	0.07793	0.00352	482.20	207.84	483.70	21.00	483.90	35.38
BMD04_27	0.05767	0.00560	0.62887	0.05802	0.07903	0.00358	516.90	206.78	490.30	21.38	495.40	36.16
BMD04_28	0.05536	0.00534	0.60779	0.05566	0.07957	0.00360	426.40	207.72	493.50	21.44	482.20	35.16
BMD04_29	0.05831	0.00576	0.64039	0.05992	0.07958	0.00366	540.90	210.08	493.60	21.80	502.50	37.10
BMD04_31	0.05667	0.00626	0.61923	0.06452	0.07919	0.00392	478.00	236.90	491.30	23.44	489.40	40.46
BMD04_32	0.05620	0.00622	0.59985	0.06242	0.07736	0.00384	459.30	237.76	480.30	22.96	477.10	39.62
BMD04_33	0.05505	0.00646	0.59472	0.06564	0.07828	0.00404	414.30	250.98	485.90	24.10	473.90	41.78
BMD04_34	0.05599	0.00650	0.61266	0.06678	0.07930	0.00408	451.60	248.68	491.90	24.32	485.20	42.04

Table A2.3 LA-ICP-MS analysis results of sample BMD-04-17Y. GPS Location: 49.04861N, 58.26885W

Table A2.3 (continued)

A 1 1 11			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
BMD04_06	0.05558	0.00298	0.58591	0.03160	0.07639	0.00254	435.30	116.48	474.50	15.18	468.30	20.24
BMD04_07	0.05738	0.00300	0.59526	0.03140	0.07517	0.00248	505.70	113.86	467.20	14.88	474.20	20.00
BMD04_12	0.05639	0.00328	0.59899	0.03460	0.07697	0.00264	467.00	126.60	478.00	15.86	476.60	21.98
BMD04_13	0.05761	0.00346	0.61053	0.03634	0.07680	0.00268	514.50	129.84	477.00	16.06	483.90	22.92
BMD04_30	0.05571	0.00590	0.58324	0.05858	0.07587	0.00362	440.60	228.22	471.40	21.74	466.50	37.56
BMD04_05	0.05991	0.00290	0.63260	0.03126	0.07652	0.00246	600.30	103.24	475.30	14.78	497.70	19.44
BMD04_35	0.05456	0.00636	0.60401	0.06610	0.08023	0.00414	394.10	251.28	497.50	24.70	479.80	41.84
BMD04_25	0.05944	0.00514	0.63828	0.05296	0.07782	0.00328	583.30	182.70	483.10	19.66	501.20	32.82

			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
BMD07_01	0.05543	0.00240	0.60177	0.02606	0.07868	0.00224	429.30	93.86	488.20	13.38	478.40	16.52
BMD07_02	0.05673	0.00232	0.61082	0.02528	0.07803	0.00220	480.30	90.18	484.40	13.10	484.10	15.94
BMD07_03	0.05713	0.00254	0.60895	0.02698	0.07725	0.00222	495.90	97.38	479.70	13.30	482.90	17.02
BMD07_04	0.05637	0.00236	0.61249	0.02584	0.07875	0.00222	466.20	92.44	488.60	13.30	485.10	16.28
BMD07_05	0.05654	0.00252	0.64737	0.02876	0.08297	0.00240	473.00	98.18	513.90	14.26	506.90	17.72
BMD07_06	0.05793	0.00284	0.62741	0.03036	0.07849	0.00234	526.80	106.48	487.10	14.02	494.50	18.94
BMD07_07	0.05666	0.00278	0.62152	0.03000	0.07950	0.00238	477.50	106.98	493.10	14.18	490.80	18.78
BMD07_08	0.05710	0.00312	0.63703	0.03402	0.08086	0.00252	494.60	119.56	501.20	15.06	500.50	21.10
BMD07_09	0.05748	0.00346	0.61050	0.03548	0.07697	0.00252	509.50	130.24	478.00	15.04	483.90	22.38
BMD07_10	0.05663	0.00352	0.62176	0.03730	0.07957	0.00264	476.50	135.98	493.50	15.74	491.00	23.36
BMD07_11	0.05685	0.00350	0.62110	0.03690	0.07918	0.00262	484.90	134.48	491.20	15.62	490.50	23.12
BMD07_12	0.05730	0.00368	0.60806	0.03758	0.07690	0.00260	502.60	139.32	477.60	15.54	482.30	23.74
BMD07_13	0.05870	0.00412	0.62635	0.04210	0.07732	0.00274	556.20	149.82	480.10	16.40	493.80	26.28
BMD07_14	0.05618	0.00416	0.59830	0.04220	0.07718	0.00280	458.60	160.14	479.30	16.80	476.20	26.80
BMD07_15	0.05615	0.00420	0.60587	0.04314	0.07820	0.00288	457.90	161.20	485.30	17.16	481.00	27.28
BMD07_16	0.05835	0.00486	0.66795	0.05266	0.08296	0.00326	542.90	177.16	513.80	19.40	519.50	32.06
BMD07_17	0.05694	0.00490	0.61126	0.04970	0.07779	0.00312	488.60	185.70	482.90	18.64	484.40	31.32
BMD07_18	0.05696	0.00414	0.61842	0.04284	0.07867	0.00284	489.50	157.62	488.20	16.98	488.90	26.88
BMD07_19	0.05824	0.00510	0.63653	0.05258	0.07921	0.00322	538.00	187.16	491.40	19.18	500.20	32.62
BMD07_20	0.05718	0.00506	0.62403	0.05208	0.07908	0.00322	498.10	190.80	490.60	19.30	492.40	32.56
BMD07_21	0.05686	0.00520	0.60099	0.05182	0.07660	0.00320	485.30	197.30	475.80	19.14	477.90	32.86
BMD07_22	0.05985	0.00602	0.62254	0.05880	0.07538	0.00336	598.10	210.90	468.50	20.16	491.40	36.80
BMD07_23	0.05578	0.00578	0.60548	0.05886	0.07866	0.00358	443.40	223.32	488.10	21.38	480.70	37.24
BMD07_24	0.05929	0.00618	0.66928	0.06538	0.08180	0.00374	577.70	219.06	506.90	22.32	520.30	39.78
BMD07_25	0.05652	0.00616	0.60119	0.06118	0.07707	0.00364	472.20	233.68	478.60	21.76	478.00	38.80

Table A2.4 LA-ICP-MS analysis results of sample BMD-07-17Y. GPS Location: 49.04776N, 58.26870W

A 1			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	$^{207}Pb/^{206}Pb$	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s	$^{206}Pb/^{238}U$	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
BMD08_01	0.05754	0.00384	0.62268	0.04110	0.07843	0.00284	512.00	143.86	486.70	17.02	491.50	25.72
BMD08_03	0.05711	0.00412	0.62104	0.04424	0.07880	0.00298	495.40	156.64	488.90	17.76	490.50	27.72
BMD08_06	0.05592	0.00584	0.59806	0.06060	0.07748	0.00354	448.80	224.88	481.10	21.20	476.00	38.50
BMD08_07	0.05708	0.00514	0.61761	0.05438	0.07838	0.00334	494.00	194.04	486.50	19.90	488.30	34.14
BMD08_08	0.05651	0.00532	0.60720	0.05564	0.07783	0.00340	471.80	203.08	483.20	20.28	481.80	35.16
BMD08_09	0.05795	0.00562	0.63931	0.06032	0.07991	0.00354	527.60	206.38	495.60	21.18	501.90	37.36
BMD08_10	0.05761	0.00570	0.61505	0.05916	0.07732	0.00348	514.70	210.60	480.10	20.78	486.70	37.18
BMD08_11	0.05678	0.00648	0.61673	0.06822	0.07866	0.00388	482.40	244.12	488.10	23.22	487.80	42.84
BMD08_12	0.05652	0.00666	0.61409	0.07004	0.07868	0.00398	472.30	252.08	488.20	23.72	486.10	44.06
BMD08_13	0.05724	0.00692	0.61661	0.07206	0.07801	0.00400	500.30	256.52	484.30	23.96	487.70	45.26
BMD08_14	0.05760	0.00726	0.62641	0.07626	0.07876	0.00416	514.20	266.10	488.70	24.92	493.90	47.60
BMD08_15	0.05802	0.00734	0.62957	0.07694	0.07858	0.00416	530.00	266.40	487.70	24.90	495.80	47.94
BMD08_16	0.05697	0.00818	0.62250	0.08606	0.07913	0.00462	489.80	303.14	490.90	27.54	491.40	53.86
BMD08_18	0.05780	0.00876	0.64183	0.09358	0.08042	0.00488	521.90	316.86	498.70	29.18	503.40	57.88
BMD08_19	0.05668	0.00884	0.62301	0.09334	0.07960	0.00494	478.50	328.76	493.70	29.52	491.70	58.40
BMD08_20	0.05767	0.00918	0.63381	0.09686	0.07960	0.00502	516.90	332.20	493.70	30.00	498.50	60.20
BMD08_21	0.05784	0.01028	0.64830	0.11020	0.08119	0.00560	523.30	368.24	503.20	33.38	507.40	67.88
BMD08_23	0.05688	0.01054	0.63827	0.11296	0.08129	0.00580	486.30	386.30	503.80	34.54	501.20	70.02
BMD08_24	0.05726	0.01104	0.61653	0.11322	0.07800	0.00574	501.10	399.14	484.20	34.34	487.70	71.12
BMD08_25	0.05771	0.01132	0.63787	0.11908	0.08008	0.00598	518.50	404.06	496.60	35.68	501.00	73.82
BMD08_26	0.05699	0.01240	0.61246	0.12630	0.07788	0.00634	490.50	448.26	483.50	37.94	485.10	79.54
BMD08_27	0.05818	0.01290	0.62487	0.13106	0.07785	0.00644	535.80	452.42	483.30	38.50	492.90	81.90
BMD08_29	0.05768	0.01338	0.62816	0.13762	0.07895	0.00678	517.20	473.20	489.80	40.56	494.90	85.84
BMD08_02	0.05630	0.00394	0.59063	0.04074	0.07602	0.00282	463.60	151.40	472.30	16.90	471.30	26.00
BMD08_04	0.05623	0.00422	0.59799	0.04410	0.07707	0.00296	460.50	162.24	478.60	17.72	476.00	28.02
BMD08_05	0.06140	0.00460	0.66549	0.04898	0.07853	0.00302	653.30	156.50	487.40	18.02	518.00	29.86
BMD08_17	0.05899	0.00868	0.63084	0.08940	0.07745	0.00460	566.80	305.46	480.90	27.54	496.60	55.66

Table A2.5 LA-ICP-MS analysis results of sample BMD-08-17Y. GPS Location: 49.04762N, 58.26837W

Table A2.5 (continued)

			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s
BMD08_22	0.06296	0.01150	0.66970	0.11692	0.07705	0.00544	706.90	366.60	478.50	32.56	520.50	71.10
BMD08_28	0.05909	0.01334	0.63040	0.13458	0.07732	0.00650	570.50	456.82	480.10	38.86	496.30	83.82

Laboratory &	
Sample Prenaration	
Laboratory name	Laser Ablation MC-ICP-MS Laboratory
Sample type/mineral	Trondhjemite/zircon
Sample preparation	Conventional zircon separation and mount procedure designed by
	Chisholm et al. (2014)
Imaging	Microscopic view provided by Chromium 2.3 (v. 2018.1.29.0)
Laser ablation system	
Make, Model & type	Teledyne Photon Machines Excite 193 nm ArF laser
Ablation cell &	HelEx II, in-house built volume cell comes with three $D = \sim 2.3$ cm
volume	and two D = ~ 1.1 cm rounded sample holders, and two $\sim 7.4*2.3$ rectangular sample holders
Laser wavelength	193 nm
(nm)	
Pulse width (ns)	4 ns
Fluence (J.cm ⁻²)	3.95 J.cm ⁻²
Repetition rate (Hz)	10 Hz
Ablation duration (secs)	30 secs
Spot diameter (µm) nominal/actual	25 μm / 25 μm
Sampling mode /	Static spot ablation
Carrier gas	100% He in the cell
Cell carrier gas flow	0 6-0 7 1/min
(l/min)	
ICP-MS	
Instrument	
Make, Model & type	Varian Model 810 Quadrupole ICP-MS
Sample introduction	Ablation aerosol only
RF power (W)	1300W
Make-up gas flow	No make-up gas flow
(l/min)	
Detector	All digital, extended range, scaling pulse detector developed by
	ETP Electron Multipliers
Masses measured	201, 202, 204, 206, 207, 208, 232, 238
Integration time per	10000 µs for 201, 202, 206, 208, 232, 238
peak/dwell times	20000 µs for 204
(µs); quadrupole	50000 μs for 207

Table A2.6 Data reporting information for LA-ICP-MS U-Th-Pb data

settling time	
between mass jumps	
Total integration	~30 secs
time per output	(N.B. this should represent the time resolution of the data)
datapoint (secs)	0004
'Sensitivity' as	>80%
useful yield (%,	((ions detected/atoms sampled)*100; Schaltegger <i>et al.</i> 2015)
element)	
IC Dead time (ns)	20 ns
Data Processing	
Gas blank	~15s prior to each ablation
Calibration strategy	Peixe used as primary calibration material, FC5z used as secondary standard
Reference Material	Peixe: 564 + 4 Ma (Dickinson and Gehrels, 2003)
info	FC5z: 1099.0 \pm 0.6 Ma (Paces and Miller, 1993)
Data processing	GLITTER (Griffin, 2008) for data reduction
package used /	Isoplot (Ludwig, 2008) for plotting and age calculations
Correction for LIEF	
Mass discrimination	Mass bias correction for all ratios normalized to primary
	calibration reference material
Common-Pb	No common Pb correction applied to the data.
correction,	
composition and	
uncertainty	
Uncertainty level &	Isotopic ratios and dates reduced by GLITTER are given as 2s
propagation	absolute but final reported ages calculated by Isoplot are at 2s
	absolute for concordia age and 95% confidence interval for
	weighted mean age. Propagation is by quadratic fit.
Quality control /	Accessed by FC5z concordia age of each analytical session:
Validation	BMD-01-17Y: 1098.4 ± 6.4 Ma, 2s error, N = 15, MSWD (of
	concordance) = 3.9, probability (of concordance) = 0.049;
	BMD-03-17Y: 1103.0 ± 8.3 Ma, 2s error, N = 14, MSWD (of
	concordance) = 3.3, probability (of concordance) = 0.070;
	BMD-04-17Y: 1106.5 \pm 7.8 Ma, 2s error, N = 14, MSWD (of
	concordance) = 4.0, probability (of concordance) = 0.046;
	BMD-07-17Y: 1107.5 ± 8.4 Ma, 2s error, N = 11, MSWD (of
	concordance) = 4.8, probability (of concordance) = 0.029;
	BMD-08-17Y: 1112.0 ± 11.0 Ma, 2s error, N = 13, MSWD (of
	concordance) = 0.79 , probability (of concordance) = 0.38 .
Other information	N/A

Fig. A2.1 Concordia and ${}^{206}Pb/{}^{238}U$ weighted mean age plots for secondary standard FC5z measured during each sample analytical session for (a) BMD-01-17Y, (b) BMD-03-17Y, (c) BMD-04-17Y, (d) BMD-07-17Y and (e) BMD-08-17Y, and (f) integration standard result of all five analytical sessions. Black error ellipses (\bigcirc) for individual data point are given at 1s level, whereas computed concordia age error ellipses (\bigcirc) and weighted mean age (\bigcirc) are calculated by Isoplot and indicated at 2s level. Note that error bars in weighted mean plots are listed in order of measuring sequence.



A 1			Isotopic	ratios			_			Isotopic Ag	es (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	$^{206}Pb/^{238}U$	2s		²⁰⁷ Pb/ ²⁰⁶ Pb	2s	$^{206}Pb/^{238}U$	2s	²⁰⁷ Pb/ ²³⁵ U	2s
1	0.05768	0.00896	0.63017	0.09458	0.07917	0.00432		517.50	324.76	491.20	25.84	496.20	58.90
2	0.06212	0.00221	0.68557	0.02412	0.08005	0.00294		678.13	75.95	496.40	17.54	530.13	14.53
3	0.06322	0.02230	0.70011	0.24114	0.08024	0.00910		715.70	671.72	497.50	54.26	538.90	144.02
4	0.05889	0.02000	0.65277	0.21648	0.08031	0.00876		563.10	665.08	498.00	52.32	510.20	133.00
5	0.05643	0.00814	0.62538	0.08718	0.08033	0.00416		468.40	306.14	498.10	24.80	493.20	54.46
6	0.05838	0.01618	0.65492	0.17674	0.08129	0.00730		543.90	554.56	503.80	43.52	511.50	108.44
7	0.05789	0.00233	0.65466	0.02721	0.08202	0.00192		525.64	88.21	508.15	11.45	511.34	16.70
8	0.05865	0.01110	0.66834	0.12248	0.08258	0.00528		554.00	388.40	511.50	31.44	519.70	74.54
9	0.07234	0.00334	0.82585	0.03785	0.08280	0.00294		995.58	93.82	512.79	17.48	611.31	21.05
10	0.05846	0.00236	0.67967	0.03491	0.08432	0.00197		547.15	88.08	521.84	11.73	526.58	21.11
11	0.06436	0.00310	0.75784	0.04414	0.08540	0.00198		753.39	101.79	528.30	11.75	572.76	25.50
12	0.06003	0.01098	0.71769	0.12692	0.08664	0.00538		604.80	372.90	535.60	31.96	549.30	75.02
13	0.06057	0.02282	0.72492	0.26706	0.08672	0.01050		624.00	722.94	536.10	62.30	553.60	157.20
14	0.05707	0.01142	0.68715	0.13306	0.08725	0.00584		493.70	413.96	539.30	34.60	531.10	80.08
15	0.05670	0.02060	0.69122	0.24538	0.08833	0.01030		479.20	717.08	545.60	61.06	533.50	147.32
16	0.05609	0.02188	0.68387	0.26092	0.08835	0.01108		455.40	766.44	545.70	65.60	529.10	157.34
17	0.71995	0.05829	23.69048	1.47935	0.23865	0.01630		4771.07	116.12	1379.69	84.81	3255.74	60.91
18	0.64526	0.05062	23.59118	1.29139	0.26516	0.01898		4613.37	113.37	1516.21	96.72	3251.65	53.37
19	0.76965	0.07261	34.60463	3.34582	0.32609	0.03116		4866.59	134.71	1819.40	151.50	3627.43	95.70
20	0.70211	0.03994	36.95435	1.82650	0.38173	0.02063		4735.05	81.72	2084.37	96.24	3692.32	48.90

Table A3.1 LA-ICP-MS analysis results of sample CC-GG1-17ERS

A			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s	$^{206}Pb/^{238}U$	2s	²⁰⁷ Pb/ ²⁰⁶	Pb 2s	206Pb/238U	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s
1	0.05947	0.00480	0.68812	0.05494	0.08386	0.00340	584.40	170.34	519.10	20.18	531.70	33.04
2	0.05489	0.00560	0.62051	0.06174	0.08197	0.00380	407.70	220.18	507.90	22.64	490.20	38.68
3	0.05626	0.00602	0.63503	0.06608	0.08185	0.00392	461.80	230.42	507.20	23.38	499.20	41.04
4	0.05530	0.00604	0.64765	0.06878	0.08493	0.00414	424.10	234.20	525.50	24.54	507.00	42.38
5	0.05604	0.00636	0.65247	0.07174	0.08443	0.00422	453.70	243.12	522.50	25.02	510.00	44.08
6	0.05762	0.00658	0.65961	0.07298	0.08302	0.00416	515.00	242.14	514.10	24.78	514.40	44.66
7	0.05764	0.00714	0.66649	0.07952	0.08386	0.00444	515.70	261.32	519.10	26.44	518.60	48.46
8	0.05901	0.00738	0.66302	0.07998	0.08148	0.00436	567.30	261.44	505.00	25.98	516.50	48.84
9	0.05552	0.00714	0.63503	0.07858	0.08294	0.00452	433.10	274.86	513.60	26.90	499.20	48.80
10	0.05690	0.00750	0.64565	0.08188	0.08229	0.00458	486.90	279.94	509.80	27.22	505.80	50.52
11	0.05712	0.00474	0.65808	0.05392	0.08351	0.00342	495.50	178.82	517.00	20.38	513.40	33.02
12	0.05510	0.00738	0.62269	0.08002	0.08196	0.00460	416.10	286.06	507.80	27.40	491.50	50.08
13	0.05489	0.00790	0.62192	0.08564	0.08216	0.00486	407.70	306.90	509.00	28.98	491.00	53.62
14	0.06081	0.00900	0.69839	0.09874	0.08328	0.00504	632.70	303.60	515.60	30.04	537.80	59.04
15	0.05588	0.00854	0.64582	0.09406	0.08380	0.00520	447.30	323.12	518.80	30.90	505.90	58.04
16	0.05684	0.00874	0.65053	0.09528	0.08298	0.00516	484.70	323.70	513.90	30.78	508.80	58.62
17	0.05481	0.00910	0.63076	0.09942	0.08344	0.00552	404.50	351.60	516.60	32.82	496.60	61.90
18	0.05428	0.00918	0.63228	0.10148	0.08445	0.00566	382.70	359.62	522.60	33.68	497.50	63.14
19	0.05528	0.00958	0.65094	0.10684	0.08538	0.00584	423.30	365.28	528.10	34.66	509.10	65.72
20	0.05671	0.01006	0.64462	0.10820	0.08241	0.00574	479.60	371.40	510.50	34.22	505.20	66.80
21	0.05881	0.01152	0.67235	0.12382	0.08287	0.00626	560.10	400.78	513.30	37.22	522.10	75.18
22	0.05843	0.01198	0.67481	0.12962	0.08371	0.00654	545.90	418.82	518.30	38.94	523.60	78.58
23	0.05955	0.01280	0.69397	0.13940	0.08447	0.00686	587.30	435.36	522.70	40.76	535.20	83.56
24	0.05949	0.01364	0.70157	0.14962	0.08547	0.00730	585.10	462.20	528.70	43.40	539.70	89.28
25	0.05760	0.00494	0.65050	0.05498	0.08186	0.00342	514.20	183.64	507.20	20.40	508.80	33.82
26	0.05885	0.00524	0.67197	0.05876	0.08277	0.00354	561.60	188.26	512.60	21.06	521.90	35.68
27	0.05775	0.00542	0.66467	0.06110	0.08344	0.00368	520.10	200.02	516.60	21.88	517.50	37.26

Table A3.2 LA-ICP-MS analysis results of sample CC-GG3-17ERS

Table A3.2 (continued)

A 1			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	$^{206}\text{Pb}/^{238}\text{U}$	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
28	0.05656	0.00534	0.64245	0.05934	0.08235	0.00364	473.80	203.56	510.10	21.68	503.80	36.68
29	0.05578	0.00542	0.64013	0.06072	0.08320	0.00374	443.40	209.46	515.20	22.26	502.40	37.60
30	0.05837	0.00576	0.66321	0.06388	0.08238	0.00374	543.70	208.60	510.30	22.32	516.60	39.00

			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
1	0.05866	0.00366	0.65012	0.04088	0.08031	0.00260	554.50	133.46	498.00	15.56	508.60	25.16
2	0.06179	0.00400	0.70021	0.04558	0.08211	0.00272	667.00	135.94	508.70	16.18	538.90	27.22
3	0.05853	0.00434	0.66824	0.04928	0.08274	0.00288	549.60	157.86	512.40	17.10	519.60	30.00
4	0.05868	0.00400	0.66344	0.04538	0.08194	0.00276	555.10	145.46	507.70	16.44	516.70	27.70
5	0.05556	0.00388	0.62391	0.04378	0.08137	0.00276	434.70	152.02	504.30	16.48	492.30	27.38
6	0.06197	0.00496	0.72698	0.05786	0.08502	0.00310	673.20	166.64	526.00	18.42	554.80	34.02
7	0.05639	0.00484	0.62039	0.05286	0.07974	0.00298	467.10	186.16	494.50	17.84	490.10	33.12
8	0.05732	0.00494	0.64585	0.05538	0.08167	0.00308	503.40	185.38	506.10	18.32	505.90	34.16
9	0.05775	0.00490	0.65497	0.05540	0.08221	0.00308	520.10	181.56	509.30	18.36	511.50	34.00
10	0.05899	0.00516	0.68035	0.05918	0.08361	0.00320	566.60	184.80	517.60	19.00	527.00	35.76
11	0.05684	0.00538	0.67455	0.06358	0.08604	0.00344	484.60	203.88	532.10	20.44	523.50	38.54
12	0.06462	0.00656	0.75476	0.07602	0.08468	0.00356	762.00	207.34	524.00	21.16	571.00	43.98
13	0.05339	0.00576	0.61344	0.06566	0.08331	0.00356	345.40	233.70	515.90	21.20	485.70	41.32
14	0.05758	0.00602	0.68864	0.07178	0.08673	0.00370	513.30	222.80	536.20	21.90	532.00	43.16
15	0.05508	0.00744	0.63473	0.08498	0.08360	0.00420	415.30	288.92	517.60	24.96	499.00	52.78
16	0.05627	0.00794	0.65315	0.09140	0.08421	0.00442	462.30	300.20	521.20	26.22	510.40	56.14
17	0.05768	0.00814	0.67781	0.09482	0.08526	0.00446	517.20	295.96	527.40	26.52	525.50	57.38
18	0.05907	0.00890	0.67425	0.10052	0.08281	0.00456	569.60	312.12	512.90	27.10	523.30	60.96
19	0.06285	0.00966	0.72691	0.11040	0.08391	0.00472	703.20	311.20	519.40	28.02	554.70	64.92
20	0.05816	0.00972	0.69214	0.11416	0.08635	0.00516	535.10	347.16	533.90	30.60	534.10	68.50
21	0.05867	0.00980	0.67964	0.11224	0.08405	0.00502	554.80	345.08	520.20	29.84	526.60	67.84
22	0.05631	0.01018	0.64911	0.11556	0.08363	0.00532	463.90	378.70	517.70	31.60	507.90	71.16
23	0.05882	0.01174	0.68766	0.13452	0.08480	0.00582	560.60	407.36	524.70	34.60	531.40	80.94
24	0.05415	0.01094	0.62349	0.12352	0.08352	0.00580	377.30	425.46	517.10	34.46	492.00	77.24
25	0.05403	0.01124	0.63973	0.13020	0.08587	0.00610	372.30	437.50	531.10	36.24	502.10	80.64
26	0.05679	0.01210	0.64854	0.13508	0.08283	0.00602	482.60	440.54	513.00	35.80	507.60	83.20
27	0.05871	0.01338	0.68600	0.15206	0.08473	0.00650	556.20	461.86	524.30	38.62	530.40	91.58

Table A3.3 LA-ICP-MS analysis results of sample CC-GG4-17ERS

Table A3.3 (continued)

A 1			Isotopic	ratios						Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	20	⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
28	0.05680	0.01356	0.65469	0.15152	0.08356	0.00666		483.30	489.30	517.30	39.56	511.40	92.98
29	0.05134	0.01304	0.59303	0.14580	0.08373	0.00690		256.20	535.96	518.40	41.02	472.80	92.94
30	0.05597	0.01400	0.63987	0.15450	0.08287	0.00684		450.90	512.52	513.20	40.70	502.20	95.66

			Isotopic	ratios					Isotopic Age	es (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
1	0.13162	0.02132	1.52697	0.23118	0.08415	0.00574	2119.60	270.92	520.80	34.10	941.30	92.90
2	0.18862	0.02984	2.15514	0.30772	0.08288	0.00644	2730.10	249.22	513.30	38.40	1166.70	99.02
3	0.05378	0.00604	0.62481	0.06792	0.08427	0.00366	361.70	242.88	521.60	21.78	492.90	42.44
4	0.06313	0.01192	0.70511	0.12906	0.08101	0.00472	712.80	377.66	502.20	28.12	541.80	76.86
5	0.05996	0.00566	0.73983	0.06692	0.08950	0.00378	602.10	197.76	552.60	22.34	562.30	39.06
6	0.05997	0.00904	0.66977	0.09732	0.08102	0.00428	602.30	310.58	502.20	25.58	520.60	59.18
7	0.06774	0.01010	0.77887	0.11150	0.08340	0.00454	860.60	295.24	516.40	27.04	584.80	63.64
8	0.05953	0.00792	0.66394	0.08458	0.08090	0.00414	586.50	276.20	501.50	24.68	517.00	51.60
9	0.06720	0.01110	0.77895	0.12308	0.08409	0.00502	844.00	326.16	520.50	29.88	584.90	70.26
10	0.06039	0.01000	0.71014	0.11242	0.08530	0.00508	617.70	338.40	527.70	30.14	544.80	66.74
11	0.14182	0.02884	1.64619	0.31290	0.08420	0.00690	2249.50	331.74	521.20	41.08	988.10	120.06
12	0.05651	0.01184	0.62199	0.12570	0.07985	0.00530	471.60	434.62	495.20	31.60	491.10	78.70
13	0.05442	0.00980	0.61045	0.10506	0.08137	0.00514	388.50	380.60	504.30	30.62	483.80	66.24
14	0.27630	0.07168	3.91241	0.89872	0.10272	0.01328	3342.20	378.78	630.30	77.60	1616.30	185.76
15	0.20002	0.04498	2.49911	0.51600	0.09064	0.00884	2826.40	345.12	559.30	52.30	1271.80	149.74
16	0.05593	0.01240	0.65769	0.13894	0.08531	0.00644	449.30	458.58	527.70	38.30	513.20	85.10
17	0.05297	0.01130	0.60450	0.12246	0.08280	0.00624	327.30	451.34	512.80	37.14	480.10	77.50
18	0.07023	0.01494	0.78077	0.15678	0.08066	0.00628	935.00	408.18	500.00	37.44	585.90	89.40
19	0.10866	0.02686	1.28668	0.29968	0.08591	0.00776	1777.00	419.94	531.30	46.04	839.80	133.08
20	0.18164	0.04852	2.33264	0.57638	0.09317	0.01012	2667.90	411.24	574.30	59.74	1222.30	175.60

Table A3.4 LA-ICP-MS analysis results of sample CC-TR1-17ERS

Analysis			Isotopic r	atios					Isotopic Ag	es (Ma)		
#	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
1	0.05840	0.00243	0.66303	0.02448	0.08234	0.00219	544.88	90.77	510.07	13.02	516.47	14.95
2	0.05554	0.00210	0.62984	0.02197	0.08225	0.00209	433.91	84.05	509.55	12.46	496.00	13.69
3	0.06217	0.00647	0.78087	0.08838	0.09109	0.00385	679.97	222.29	562.01	22.76	585.98	50.43
4	0.05480	0.00487	0.66332	0.06832	0.08779	0.00213	404.12	198.83	542.44	12.63	516.64	41.73
5	0.52518	0.03358	13.04558	0.75397	0.18016	0.01014	4313.49	93.88	1067.84	55.37	2682.95	54.56
6	0.63342	0.05771	22.19406	1.66885	0.25412	0.01800	4586.60	131.85	1459.70	92.53	3192.26	73.18
7	0.55701	0.03327	18.81769	1.00033	0.24502	0.01350	4399.66	87.29	1412.75	69.90	3032.52	51.30
8	0.07102	0.00323	0.78112	0.03583	0.07977	0.00203	958.01	92.86	494.74	12.14	586.12	20.43
9	0.07072	0.00265	0.80076	0.02825	0.08212	0.00259	949.39	76.62	508.76	15.43	597.26	15.93
10	0.65628	0.05864	20.22307	1.46876	0.22349	0.01573	4637.83	128.97	1300.29	82.89	3102.09	70.38
11	0.63554	0.04492	20.65762	1.06740	0.23574	0.01461	4591.43	102.27	1364.53	76.21	3122.67	50.08
12	0.06334	0.00303	0.71735	0.03289	0.08214	0.00169	719.59	101.63	508.90	10.09	549.10	19.45
13	0.29144	0.10145	4.55300	1.74413	0.11330	0.00634	3425.31	541.00	691.91	36.70	1740.71	330.07
14	0.06956	0.01424	0.81103	0.16831	0.08457	0.00210	915.26	421.33	523.33	12.51	603.03	94.64
15	0.52876	0.11533	12.15482	2.56749	0.16672	0.01060	4323.45	320.04	994.02	58.58	2616.43	200.75
16	0.05704	0.01156	0.63636	0.13114	0.08092	0.00268	492.93	446.76	501.60	15.99	500.05	81.55
17	0.40056	0.08927	7.52784	1.63883	0.13630	0.00893	3911.19	335.04	823.71	50.67	2176.31	197.59
18	0.53594	0.14403	15.26851	6.03388	0.20662	0.02924	4343.23	393.91	1210.81	156.25	2832.14	395.45
19	0.06285	0.01329	0.72721	0.15544	0.08392	0.00422	703.08	450.05	519.49	25.12	554.92	91.63
20	0.05647	0.00236	0.62692	0.03537	0.08052	0.00237	470.76	92.70	499.24	14.13	494.18	22.08
21	0.05728	0.00245	0.68037	0.03838	0.08614	0.00248	502.42	94.30	532.69	14.73	527.00	23.19
22	0.05762	0.00206	0.64524	0.02707	0.08121	0.00170	515.50	78.63	503.35	10.16	505.55	16.71

Table A3.5 LA-ICP-MS analysis results of sample CC-MM2-17ERS

A 1			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	$^{206}Pb/^{238}U$	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
1	0.05478	0.00150	0.62735	0.01898	0.08299	0.00218	403.20	60.48	514.00	13.04	494.40	11.84
2	0.05718	0.00174	0.65248	0.02124	0.08269	0.00222	498.10	66.48	512.10	13.24	510.00	13.06
3	0.05711	0.00212	0.64746	0.02482	0.08216	0.00230	495.20	81.14	509.00	13.74	506.90	15.30
4	0.05561	0.00154	0.62288	0.01900	0.08117	0.00214	436.40	60.40	503.10	12.82	491.60	11.88
5	0.05539	0.00148	0.64423	0.01910	0.08428	0.00222	427.80	58.78	521.60	13.20	504.90	11.80
6	0.05533	0.00162	0.65289	0.02078	0.08550	0.00230	425.50	64.56	528.90	13.62	510.30	12.76
7	0.05516	0.00168	0.64252	0.02096	0.08441	0.00228	418.60	66.58	522.40	13.56	503.90	12.96
8	0.05395	0.00174	0.61949	0.02120	0.08321	0.00228	368.80	72.14	515.20	13.54	489.50	13.30
9	0.05565	0.00218	0.63226	0.02528	0.08233	0.00236	438.00	85.02	510.00	14.02	497.50	15.72
10	0.05581	0.00188	0.62441	0.02216	0.08107	0.00224	444.60	73.46	502.50	13.36	492.60	13.84
11	0.05726	0.00220	0.64766	0.02544	0.08196	0.00234	501.10	84.16	507.80	13.92	507.00	15.68
12	0.05451	0.00192	0.64187	0.02356	0.08532	0.00238	392.20	77.46	527.80	14.14	503.50	14.58
13	0.05515	0.00190	0.61675	0.02232	0.08104	0.00226	418.10	75.80	502.30	13.44	487.80	14.02
14	0.05498	0.00228	0.64727	0.02732	0.08531	0.00248	411.40	91.08	527.70	14.76	506.80	16.84
15	0.05457	0.00284	0.60143	0.03098	0.07986	0.00248	394.70	113.88	495.30	14.80	478.10	19.64
16	0.05681	0.00238	0.64371	0.02736	0.08210	0.00240	483.50	91.72	508.60	14.32	504.60	16.90
17	0.05566	0.00234	0.64048	0.02728	0.08337	0.00244	438.60	91.38	516.20	14.52	502.60	16.90
18	0.05748	0.00252	0.64881	0.02870	0.08179	0.00242	509.50	95.84	506.80	14.48	507.70	17.68
19	0.05452	0.00224	0.63111	0.02640	0.08387	0.00244	392.50	90.28	519.20	14.50	496.80	16.44
20	0.05469	0.00266	0.62085	0.03014	0.08224	0.00252	400.10	105.64	509.50	15.02	490.40	18.88
21	0.05595	0.00266	0.65255	0.03102	0.08450	0.00258	450.10	103.60	522.90	15.30	510.00	19.06
22	0.05556	0.00274	0.63369	0.03106	0.08263	0.00254	434.60	107.12	511.80	15.16	498.40	19.30
23	0.08165	0.00520	0.96302	0.05918	0.08544	0.00300	1237.20	122.12	528.50	17.86	684.90	30.62
24	0.05624	0.00288	0.63904	0.03248	0.08232	0.00258	461.00	112.66	509.90	15.32	501.70	20.12
25	0.05684	0.00338	0.63820	0.03708	0.08133	0.00270	484.80	129.76	504.10	16.04	501.20	22.98
26	0.05641	0.00330	0.65605	0.03758	0.08425	0.00276	467.60	127.60	521.40	16.46	512.20	23.04
27	0.05548	0.00334	0.63173	0.03714	0.08248	0.00274	431.20	130.84	510.90	16.32	497.20	23.12

Table A3.6 LA-ICP-MS analysis results of sample CC-MM3-17ERS

Table A3.6 (continued)

			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	$^{206}\text{Pb}/^{238}\text{U}$	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
28	0.05540	0.00326	0.63799	0.03672	0.08342	0.00274	428.00	127.86	516.50	16.32	501.10	22.76
29	0.05526	0.00346	0.62436	0.03802	0.08183	0.00276	422.70	135.76	507.10	16.46	492.60	23.78
30	0.07495	0.00476	0.86315	0.05312	0.08341	0.00284	1067.20	124.84	516.50	16.88	631.80	28.94
31	0.05641	0.00372	0.64045	0.04098	0.08224	0.00284	467.60	143.26	509.50	16.90	502.60	25.36
32	0.05612	0.00374	0.65551	0.04234	0.08461	0.00292	456.60	144.72	523.60	17.38	511.90	25.96
33	0.05652	0.00424	0.65181	0.04694	0.08354	0.00306	472.10	163.60	517.20	18.18	509.60	28.86
34	0.06006	0.00480	0.69301	0.05292	0.08359	0.00316	605.70	168.46	517.50	18.82	534.60	31.74
35	0.40028	0.04282	7.95752	0.66582	0.14403	0.01130	3910.10	156.30	867.40	63.64	2226.20	75.48

A			Isotopic	ratios					Isotopic Age	es (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	$^{206}Pb/^{238}U$	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
1	0.05731	0.00458	0.64707	0.05038	0.08185	0.00300	502.90	172.28	507.20	17.90	506.70	31.06
2	0.06682	0.00184	0.76934	0.02114	0.08341	0.00186	832.10	56.68	516.40	11.02	579.40	12.14
3	0.05893	0.00508	0.65794	0.05504	0.08093	0.00310	564.60	182.08	501.70	18.48	513.40	33.70
4	0.05750	0.00514	0.64519	0.05610	0.08134	0.00320	510.30	191.68	504.10	19.02	505.50	34.62
5	0.06099	0.00562	0.69100	0.06190	0.08212	0.00328	639.00	192.46	508.80	19.54	533.40	37.18
6	0.05814	0.00610	0.66658	0.06788	0.08311	0.00360	534.40	222.84	514.60	21.40	518.60	41.36
7	0.05589	0.00264	0.63614	0.02918	0.08246	0.00210	447.70	102.80	510.80	12.50	499.90	18.10
8	0.06206	0.00696	0.70772	0.07692	0.08265	0.00374	676.30	230.96	511.90	22.28	543.40	45.74
9	0.05887	0.00680	0.67709	0.07586	0.08335	0.00386	562.40	242.24	516.10	22.92	525.00	45.92
10	0.05928	0.00708	0.68010	0.07878	0.08315	0.00394	577.30	249.64	514.90	23.42	526.80	47.60
11	0.08607	0.01158	1.01590	0.13242	0.08553	0.00442	1339.80	249.30	529.10	26.22	711.90	66.70
12	0.05990	0.00830	0.72122	0.09680	0.08725	0.00460	600.10	286.60	539.20	27.30	551.40	57.10
13	0.05881	0.00838	0.67776	0.09356	0.08351	0.00450	560.00	296.34	517.10	26.78	525.40	56.62
14	0.05857	0.00858	0.67307	0.09554	0.08327	0.00458	551.30	304.84	515.60	27.30	522.60	57.98
15	0.06202	0.00938	0.69210	0.10132	0.08086	0.00456	674.70	307.82	501.30	27.26	534.10	60.80
16	0.06161	0.01036	0.69879	0.11372	0.08219	0.00506	660.50	341.38	509.20	30.12	538.10	67.96
17	0.06376	0.01100	0.72920	0.12170	0.08286	0.00520	733.70	345.72	513.20	31.00	556.10	71.46
18	0.05715	0.00176	0.65683	0.02016	0.08327	0.00190	496.80	67.40	515.60	11.34	512.70	12.36
19	0.06290	0.01142	0.72384	0.12712	0.08337	0.00546	705.00	364.62	516.20	32.54	552.90	74.88
20	0.08042	0.01508	0.96930	0.17546	0.08733	0.00590	1207.30	348.50	539.70	35.02	688.10	90.46
21	0.05914	0.01214	0.65602	0.12992	0.08037	0.00584	572.30	417.70	498.30	34.90	512.20	79.66
22	0.05963	0.00190	0.68960	0.02186	0.08379	0.00194	590.30	68.40	518.70	11.54	532.60	13.14
23	0.08474	0.01792	1.06867	0.21772	0.09137	0.00686	1309.60	385.04	563.60	40.50	738.10	106.86
24	0.06232	0.01340	0.73381	0.15220	0.08531	0.00648	685.10	428.76	527.80	38.44	558.80	89.14
25	0.06239	0.01374	0.71588	0.15190	0.08313	0.00644	687.60	438.02	514.80	38.32	548.20	89.88
26	0.07857	0.01770	0.90759	0.19676	0.08370	0.00662	1161.20	416.48	518.20	39.34	655.80	104.74
27	0.06307	0.00202	0.72422	0.02312	0.08320	0.00194	710.70	67.44	515.20	11.50	553.20	13.62

Table A3.7 LA-ICP-MS analysis results of sample CC-MM4-17ERS

Table A3.7 (continued)

			Isotopic	ratios					Isotopic Age	es (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
28	0.06459	0.01588	0.72009	0.17010	0.08078	0.00690	760.90	479.88	500.80	41.22	550.70	100.40
29	0.05919	0.01486	0.67886	0.16354	0.08311	0.00724	573.90	503.58	514.60	43.08	526.10	98.92
30	0.06431	0.01650	0.74979	0.18446	0.08448	0.00750	751.80	499.62	522.80	44.64	568.10	107.04
31	0.05812	0.01522	0.70007	0.17560	0.08728	0.00790	533.80	527.80	539.40	46.84	538.80	104.88
32	0.05665	0.00186	0.64864	0.02128	0.08296	0.00194	477.30	72.88	513.80	11.54	507.60	13.10
33	0.07124	0.01904	0.80023	0.20472	0.08139	0.00750	964.40	502.48	504.40	44.76	597.00	115.48
34	0.05881	0.01702	0.67934	0.18748	0.08371	0.00832	560.10	574.98	518.20	49.46	526.40	113.36
35	0.05899	0.01740	0.69884	0.19640	0.08584	0.00868	566.90	584.48	530.90	51.54	538.10	117.38
36	0.06301	0.01896	0.74473	0.21328	0.08565	0.00884	708.60	582.08	529.70	52.44	565.20	124.12
37	0.06057	0.01890	0.71973	0.21340	0.08611	0.00920	623.90	609.90	532.50	54.56	550.50	126.00
38	0.05844	0.00208	0.67319	0.02364	0.08347	0.00200	546.30	76.46	516.80	11.88	522.70	14.34
39	0.06645	0.00240	0.76237	0.02716	0.08313	0.00200	820.70	74.26	514.80	11.92	575.40	15.64

A			Isotopic	ratios			_			Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	207 Pb/ 235 U	2s	$^{206}Pb/^{238}U$	2s		²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s
1	0.05583	0.00258	0.63317	0.03419	0.08225	0.00130		445.79	102.57	509.51	7.73	498.07	21.26
2	0.05692	0.00324	0.64232	0.04255	0.08184	0.00143		488.53	125.54	507.09	8.53	503.74	26.32
3	0.05871	0.00364	0.64594	0.04473	0.07980	0.00149		556.25	135.09	494.92	8.87	505.97	27.60
4	0.05561	0.00339	0.61688	0.04250	0.08046	0.00164		436.72	135.85	498.86	9.77	487.89	26.69
5	0.05590	0.00341	0.62535	0.04313	0.08114	0.00153		448.23	135.40	502.93	9.11	493.19	26.95
6	0.05782	0.00159	0.65826	0.02162	0.08257	0.00157		523.03	60.26	511.42	9.35	513.55	13.24
7	0.05771	0.00222	0.64146	0.02416	0.08062	0.00144		518.68	84.59	499.82	8.59	503.21	14.95
8	0.05816	0.00201	0.65624	0.02744	0.08183	0.00172		535.81	75.73	507.06	10.24	512.31	16.83
9	0.05701	0.00288	0.64766	0.04489	0.08239	0.00208		491.94	111.39	510.39	12.37	507.04	27.67
10	0.05654	0.00352	0.63253	0.04825	0.08114	0.00233		473.59	137.63	502.92	13.87	497.67	30.02
11	0.05652	0.00314	0.63633	0.04453	0.08165	0.00217		472.95	122.97	505.97	12.96	500.03	27.64
12	0.05659	0.00818	0.61973	0.10322	0.07942	0.00276		475.69	319.58	492.68	16.48	489.68	64.80
13	0.05593	0.00794	0.63590	0.10562	0.08246	0.00284		449.59	315.18	510.79	16.91	499.76	65.65
14	0.05722	0.00579	0.63493	0.06932	0.08048	0.00209		499.99	223.02	498.98	12.46	499.16	43.08
15	0.05733	0.00564	0.64586	0.06919	0.08171	0.00195		504.17	216.57	506.31	11.63	505.93	42.71
16	0.05870	0.00655	0.66765	0.07859	0.08249	0.00384		556.17	243.22	510.94	22.87	519.29	47.89
17	0.05598	0.00859	0.63120	0.10044	0.08178	0.00169		451.64	340.58	506.71	10.10	496.84	62.60
18	0.05749	0.00566	0.62846	0.06773	0.07928	0.00184		510.44	216.30	491.83	11.01	495.13	42.25
19	0.05682	0.00592	0.64493	0.07215	0.08232	0.00263		484.47	229.99	509.98	15.69	505.36	44.57
20	0.05811	0.00396	0.64553	0.04534	0.08057	0.00210		533.76	149.17	499.55	12.52	505.72	27.99
21	0.05725	0.00286	0.64802	0.03022	0.08210	0.00155		501.10	110.13	508.63	9.24	507.26	18.62
22	0.05883	0.00317	0.66084	0.03316	0.08147	0.00199		560.88	117.27	504.88	11.84	515.13	20.28
23	0.05593	0.00188	0.63200	0.02316	0.08196	0.00249		449.47	74.69	507.80	14.84	497.34	14.41
24	0.05789	0.00198	0.63411	0.02320	0.07945	0.00238		525.51	75.09	492.82	14.19	498.65	14.42
25	0.05671	0.00234	0.63343	0.02608	0.08101	0.00208		480.40	91.31	502.12	12.42	498.23	16.21
26	0.05701	0.00268	0.64366	0.03042	0.08189	0.00202		491.83	103.83	507.39	12.02	504.57	18.79
27	0.05750	0.00173	0.64005	0.01901	0.08074	0.00173		510.66	66.07	500.51	10.33	502.34	11.77

Table A3.8 LA-ICP-MS analysis results of sample CC-LHT1-17ERS

A 1			Isotopic	ratios					Isotopic Age	s (Ma)		
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s
1	0.06870	0.00462	0.77120	0.05172	0.08137	0.00280	889.80	135.74	504.30	16.74	580.50	29.64
2	0.05791	0.00284	0.65644	0.03342	0.08215	0.00256	526.00	105.98	509.00	15.24	512.40	20.50
3	0.05992	0.00258	0.69039	0.03178	0.08350	0.00252	600.70	91.98	517.00	15.02	533.00	19.10
4	0.05925	0.00254	0.69039	0.03180	0.08443	0.00254	576.40	92.14	522.50	15.16	533.00	19.10
5	0.06090	0.00300	0.68349	0.03544	0.08131	0.00254	635.80	104.62	503.90	15.16	528.90	21.38
6	0.05965	0.00338	0.67057	0.03902	0.08144	0.00264	590.90	120.38	504.70	15.80	521.10	23.72
7	0.05874	0.00304	0.64374	0.03472	0.07939	0.00250	557.60	110.62	492.50	14.98	504.60	21.46
8	0.07085	0.00452	0.81118	0.05224	0.08295	0.00284	953.10	127.60	513.70	16.94	603.10	29.28
9	0.06033	0.00324	0.68652	0.03836	0.08245	0.00264	615.30	113.94	510.70	15.68	530.70	23.10
10	0.06421	0.00462	0.72920	0.05252	0.08228	0.00292	748.50	148.20	509.70	17.44	556.10	30.84
11	0.06125	0.00416	0.65565	0.04498	0.07756	0.00268	648.10	142.86	481.50	16.04	512.00	27.58
12	0.05903	0.00446	0.66721	0.05040	0.08190	0.00296	568.30	160.64	507.40	17.58	519.00	30.70
13	0.06476	0.00508	0.73598	0.05696	0.08237	0.00300	766.60	160.88	510.20	17.86	560.10	33.32
14	0.20854	0.01652	2.91206	0.22674	0.10122	0.00374	2894.20	125.76	621.50	21.88	1385.00	58.86
15	0.06060	0.00586	0.70808	0.06526	0.08472	0.00338	625.20	201.82	524.20	20.08	543.60	38.80
16	0.06316	0.00688	0.74366	0.07664	0.08538	0.00366	713.70	223.50	528.10	21.76	564.50	44.62
17	0.05885	0.00638	0.67580	0.06888	0.08327	0.00354	561.70	227.70	515.60	21.06	524.20	41.74

Table A3.9 LA-ICP-MS analysis results of sample CC-LHT1B-17ERS

A		Isotopic ratios								Isotopic Ages (Ma)						
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s		²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s			
1	0.05982	0.00330	0.66218	0.03540	0.08021	0.00222		597.20	117.24	497.40	13.28	515.90	21.62			
2	0.05610	0.00226	0.62414	0.02582	0.08069	0.00236		456.10	87.70	500.20	14.08	492.40	16.14			
3	0.05598	0.00322	0.62855	0.03502	0.08135	0.00226		451.40	124.98	504.20	13.52	495.20	21.84			
4	0.05876	0.00306	0.65642	0.03324	0.08096	0.00220		558.00	111.74	501.80	13.14	512.40	20.38			
5	0.05581	0.00226	0.63064	0.02620	0.08196	0.00240		444.40	87.98	507.80	14.30	496.50	16.32			
6	0.05754	0.00266	0.64794	0.02912	0.08160	0.00212		511.70	100.40	505.70	12.68	507.20	17.94			
7	0.05657	0.00248	0.64907	0.02886	0.08321	0.00250		474.20	96.40	515.30	14.82	507.90	17.78			
8	0.05237	0.00260	0.58003	0.02882	0.08034	0.00248		301.40	110.70	498.10	14.78	464.50	18.52			
9	0.05768	0.00298	0.64590	0.03248	0.08114	0.00220		517.50	112.16	502.90	13.12	506.00	20.04			
10	0.05552	0.00300	0.62517	0.03352	0.08166	0.00260		433.10	117.32	506.00	15.56	493.10	20.94			
11	0.05500	0.00274	0.63127	0.03056	0.08317	0.00222		412.30	107.72	515.00	13.20	496.90	19.02			
12	0.05803	0.00268	0.64869	0.02924	0.08100	0.00212		530.60	100.34	502.10	12.64	507.70	18.00			
13	0.05478	0.00266	0.61749	0.03020	0.08175	0.00254		403.40	106.48	506.60	15.12	488.30	18.96			
14	0.05889	0.00274	0.67119	0.03056	0.08258	0.00218		563.20	99.96	511.50	12.94	521.40	18.56			
15	0.05495	0.00310	0.61488	0.03428	0.08116	0.00264		410.10	122.00	503.00	15.76	486.60	21.56			
16	0.05669	0.00308	0.64752	0.03422	0.08277	0.00228		478.80	118.10	512.60	13.62	507.00	21.10			
17	0.05673	0.00326	0.63691	0.03628	0.08142	0.00270		480.50	126.16	504.60	16.10	500.40	22.50			
18	0.05637	0.00308	0.63595	0.03390	0.08175	0.00228		466.20	120.00	506.60	13.54	499.80	21.04			
19	0.05554	0.00312	0.63741	0.03548	0.08324	0.00274		433.80	122.04	515.40	16.32	500.70	22.00			
20	0.05854	0.00380	0.65468	0.04168	0.08111	0.00284		549.90	138.74	502.80	16.88	511.40	25.58			
21	0.05728	0.00284	0.64496	0.03114	0.08159	0.00220		502.00	108.06	505.60	13.12	505.40	19.22			
22	0.05593	0.00322	0.62831	0.03588	0.08148	0.00272		449.20	125.64	504.90	16.20	495.00	22.38			
23	0.05790	0.00310	0.64262	0.03356	0.08042	0.00224		525.80	116.00	498.60	13.34	503.90	20.76			
24	0.05592	0.00364	0.63198	0.04032	0.08197	0.00288		448.80	141.48	507.90	17.18	497.30	25.08			
25	0.05671	0.00404	0.62861	0.04374	0.08040	0.00294		479.40	155.20	498.50	17.54	495.20	27.28			
26	0.05654	0.00284	0.63061	0.03104	0.08082	0.00220		472.80	110.22	501.00	13.10	496.50	19.32			
27	0.05795	0.00364	0.64736	0.03940	0.08095	0.00240		527.60	134.46	501.80	14.28	506.90	24.28			

Table A3.10 LA-ICP-MS analysis results of sample CC-LHT5-17ERS

Table A3.10 (continued)

	Isotopic ratios							Isotopic Ages (Ma)							
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²³⁵ U	2s			
28	0.05479	0.00354	0.62111	0.03952	0.08222	0.00290	403.70	140.42	509.30	17.24	490.50	24.76			
29	0.05586	0.00362	0.62274	0.03926	0.08078	0.00240	446.50	140.98	500.80	14.26	491.60	24.56			
30	0.05669	0.00388	0.65051	0.04364	0.08322	0.00300	478.80	149.48	515.30	17.90	508.80	26.84			
31	0.05672	0.00366	0.63383	0.03966	0.08097	0.00240	480.00	140.60	501.90	14.36	498.50	24.66			
32	0.05705	0.00402	0.64444	0.04434	0.08192	0.00300	493.00	152.84	507.60	17.90	505.00	27.38			
33	0.05478	0.00464	0.62380	0.05124	0.08259	0.00332	403.10	183.22	511.60	19.72	492.20	32.04			
34	0.05777	0.00336	0.64505	0.03664	0.08092	0.00234	520.60	125.88	501.60	13.98	505.40	22.62			
35	0.05621	0.00450	0.63065	0.04898	0.08137	0.00320	460.00	174.28	504.30	19.06	496.50	30.50			
36	0.05773	0.00322	0.65705	0.03570	0.08247	0.00234	519.50	120.36	510.80	13.98	512.80	21.88			
37	0.05950	0.00382	0.66042	0.04128	0.08043	0.00244	585.30	136.56	498.70	14.54	514.90	25.24			
38	0.05591	0.00524	0.64437	0.05834	0.08359	0.00360	448.30	202.68	517.50	21.40	505.00	36.02			
39	0.05804	0.00338	0.64370	0.03660	0.08036	0.00234	531.00	126.02	498.30	13.96	504.60	22.62			
40	0.05800	0.00528	0.64890	0.05700	0.08113	0.00346	529.50	194.30	502.90	20.60	507.80	35.10			
41	0.05738	0.00368	0.64950	0.04046	0.08203	0.00248	505.60	138.64	508.20	14.76	508.20	24.90			
42	0.06018	0.00366	0.66786	0.03968	0.08042	0.00240	609.90	129.12	498.60	14.28	519.40	24.16			
43	0.05824	0.00374	0.65511	0.04104	0.08151	0.00248	538.20	138.92	505.10	14.76	511.60	25.18			
44	0.05734	0.00548	0.64718	0.05954	0.08185	0.00360	504.20	204.56	507.20	21.44	506.70	36.70			
45	0.05569	0.00622	0.61797	0.06624	0.08047	0.00388	439.80	240.08	499.00	23.10	488.60	41.58			
46	0.05686	0.00358	0.64321	0.03948	0.08198	0.00248	485.30	137.20	507.90	14.74	504.30	24.40			
47	0.05775	0.00628	0.63871	0.06650	0.08021	0.00382	520.20	230.34	497.40	22.84	501.50	41.20			
48	0.05791	0.00406	0.64283	0.04382	0.08044	0.00254	526.00	150.50	498.70	15.12	504.10	27.08			
49	0.05607	0.00610	0.63932	0.06672	0.08270	0.00398	454.60	233.82	512.20	23.64	501.90	41.32			
50	0.05541	0.00616	0.62185	0.06608	0.08139	0.00396	428.60	239.00	504.40	23.60	491.00	41.36			
51	0.05697	0.00672	0.65534	0.07384	0.08342	0.00426	489.80	251.68	516.50	25.28	511.80	45.28			
52	0.05779	0.00187	0.64256	0.02033	0.08056	0.00124	521.70	69.63	499.50	7.42	503.90	12.57			
53	0.05580	0.00692	0.62607	0.07388	0.08137	0.00428	444.10	264.96	504.30	25.56	493.60	46.14			
54	0.05692	0.00728	0.63175	0.07694	0.08050	0.00434	487.60	271.98	499.10	25.88	497.20	47.88			

Table A3.10 (continued)

Analysis #		Isotopic ratios							Isotopic Ages (Ma)						
	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²⁰⁶ Pt	2s	206Pb/238U	2s	207 Pb/ 235 U	2s			
55	0.05868	0.00203	0.65907	0.02224	0.08139	0.00130	555.20	73.69	504.40	7.72	514.00	13.61			
56	0.05655	0.00191	0.63404	0.02096	0.08125	0.00128	473.20	73.81	503.60	7.61	498.60	13.02			
57	0.05745	0.00854	0.64619	0.09064	0.08158	0.00494	508.20	311.88	505.50	29.42	506.10	55.90			
58	0.05708	0.00730	0.65366	0.07948	0.08305	0.00448	494.10	271.34	514.30	26.70	510.70	48.80			
59	0.05579	0.00806	0.62264	0.08504	0.08095	0.00478	443.50	306.66	501.80	28.50	491.50	53.22			
60	0.05651	0.00816	0.63577	0.08662	0.08159	0.00484	471.90	305.68	505.60	28.80	499.70	53.78			

A		Isotopic ratios								Isotopic Ages (Ma)						
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s	²⁰⁶ Pb/ ²³⁸ U	2s		²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s			
1	0.05784	0.00188	0.63913	0.02190	0.08009	0.00214		523.40	70.76	496.70	12.72	501.80	13.56			
2	0.05647	0.00214	0.62449	0.02392	0.08013	0.00206		470.20	83.46	496.90	12.34	492.70	14.96			
3	0.05692	0.00204	0.62316	0.02308	0.07934	0.00216		488.00	78.38	492.20	12.86	491.80	14.44			
4	0.05762	0.00210	0.63585	0.02360	0.07996	0.00204		515.10	79.78	495.90	12.22	499.70	14.64			
5	0.05558	0.00210	0.61011	0.02382	0.07955	0.00218		435.50	82.54	493.50	13.06	483.60	15.02			
6	0.05647	0.00210	0.64125	0.02420	0.08229	0.00212		470.20	82.02	509.70	12.60	503.10	14.98			
7	0.05708	0.00190	0.63290	0.02210	0.08037	0.00216		493.80	72.58	498.30	12.84	497.90	13.74			
8	0.05890	0.00220	0.65338	0.02480	0.08039	0.00208		563.30	80.56	498.40	12.36	510.60	15.24			
9	0.05746	0.00212	0.63047	0.02368	0.07951	0.00204		508.80	81.08	493.20	12.18	496.40	14.74			
10	0.05604	0.00192	0.61829	0.02228	0.07997	0.00216		453.50	75.02	495.90	12.86	488.80	13.98			
11	0.05767	0.00212	0.65214	0.02440	0.08195	0.00210		516.90	80.34	507.80	12.52	509.80	15.00			
12	0.05761	0.00274	0.65236	0.03100	0.08207	0.00240		514.50	103.26	508.50	14.32	509.90	19.06			
13	0.05751	0.00222	0.65761	0.02570	0.08286	0.00216		510.90	84.62	513.20	12.80	513.20	15.74			
14	0.05865	0.00218	0.64386	0.02440	0.07956	0.00204		554.00	80.28	493.50	12.22	504.70	15.08			
15	0.05769	0.00234	0.64349	0.02662	0.08083	0.00228		517.80	88.44	501.10	13.56	504.50	16.46			
16	0.05916	0.00232	0.66546	0.02674	0.08152	0.00228		572.90	84.22	505.20	13.58	517.90	16.30			
17	0.05690	0.00270	0.62815	0.02976	0.08000	0.00234		487.10	102.76	496.10	14.00	494.90	18.56			
18	0.05680	0.00242	0.63121	0.02688	0.08054	0.00214		483.00	93.14	499.30	12.78	496.80	16.72			
19	0.05880	0.00274	0.64867	0.03038	0.07995	0.00234		559.60	100.32	495.80	14.02	507.70	18.72			
20	0.05760	0.00234	0.64654	0.02646	0.08135	0.00214		514.10	88.80	504.20	12.74	506.30	16.32			
21	0.05752	0.00264	0.65020	0.02996	0.08192	0.00240		511.10	100.00	507.60	14.26	508.60	18.44			
22	0.05626	0.00248	0.63985	0.02808	0.08242	0.00222		461.90	96.78	510.60	13.18	502.20	17.38			
23	0.05638	0.00276	0.62401	0.03024	0.08021	0.00222		466.70	107.70	497.40	13.24	492.40	18.90			
24	0.05739	0.00256	0.65769	0.02960	0.08304	0.00240		506.30	97.60	514.20	14.32	513.20	18.14			
25	0.05714	0.00230	0.64393	0.02606	0.08168	0.00214		496.20	87.04	506.10	12.70	504.70	16.10			
26	0.05664	0.00278	0.64165	0.03144	0.08209	0.00244		476.80	107.34	508.60	14.58	503.30	19.44			
27	0.06254	0.00276	0.69394	0.03052	0.08041	0.00216		692.80	92.80	498.60	12.94	535.20	18.30			

Table A3.11 LA-ICP-MS analysis results of sample CC-BMDP1-17ERS
Table A3.11 (continued)

			Isotopic	ratios			Isotopic Ages (Ma)						
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	207	Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
28	0.05837	0.00314	0.65964	0.03518	0.08190	0.00252		543.60	115.66	507.40	15.02	514.40	21.52
29	0.05774	0.00266	0.64598	0.02956	0.08108	0.00220	:	519.90	100.02	502.50	13.16	506.00	18.24
30	0.05636	0.00280	0.63253	0.03132	0.08133	0.00244	4	465.60	109.28	504.10	14.56	497.70	19.48
31	0.05844	0.00272	0.65307	0.03020	0.08100	0.00222	:	546.20	100.34	502.10	13.20	510.40	18.56
32	0.05640	0.00314	0.63640	0.03500	0.08176	0.00256	4	467.40	121.86	506.60	15.22	500.10	21.72
33	0.05780	0.00284	0.64997	0.03142	0.08150	0.00226	:	522.00	106.04	505.10	13.50	508.50	19.34
34	0.05543	0.00278	0.63548	0.03166	0.08307	0.00250	4	429.50	108.72	514.40	14.90	499.50	19.66
35	0.05779	0.00294	0.64366	0.03232	0.08073	0.00228	:	521.50	110.40	500.50	13.56	504.60	19.96
36	0.05875	0.00322	0.66702	0.03608	0.08227	0.00256		558.00	117.26	509.60	15.30	518.90	21.98
37	0.06197	0.00304	0.67875	0.03284	0.07938	0.00220	(673.10	103.24	492.40	13.20	526.00	19.86
38	0.05892	0.00320	0.66235	0.03562	0.08146	0.00254	-	564.20	116.40	504.80	15.14	516.10	21.76
39	0.05776	0.00290	0.65651	0.03244	0.08237	0.00230	-	520.60	108.82	510.30	13.68	512.50	19.88
40	0.05800	0.00358	0.64351	0.03898	0.08040	0.00264	-	529.30	133.58	498.50	15.76	504.50	24.08
41	0.05909	0.00322	0.66535	0.03542	0.08161	0.00236	-	570.30	116.36	505.70	14.04	517.90	21.58
42	0.05825	0.00340	0.67152	0.03850	0.08354	0.00268	:	538.40	126.34	517.20	15.96	521.60	23.38
43	0.05708	0.00306	0.66071	0.03470	0.08389	0.00240	4	494.20	117.38	519.30	14.28	515.00	21.22
44	0.05842	0.00318	0.65320	0.03468	0.08104	0.00234	-	545.50	116.60	502.30	13.90	510.40	21.30
45	0.05728	0.00360	0.65194	0.03996	0.08247	0.00272	-	501.80	136.06	510.90	16.26	509.70	24.56
46	0.05819	0.00342	0.64805	0.03706	0.08072	0.00240	-	536.20	127.34	500.40	14.32	507.30	22.84
47	0.05631	0.00332	0.64033	0.03654	0.08242	0.00244	4	463.80	128.64	510.50	14.54	502.50	22.62
48	0.06127	0.00422	0.70669	0.04730	0.08357	0.00290	(648.80	144.72	517.40	17.30	542.80	28.14
49	0.05723	0.00384	0.64281	0.04202	0.08138	0.00280	-	500.00	145.68	504.40	16.64	504.00	25.98
50	0.05704	0.00362	0.64914	0.03970	0.08248	0.00252	4	492.50	137.94	510.90	15.04	508.00	24.44
51	0.05644	0.00388	0.64664	0.04322	0.08301	0.00288	4	469.10	150.30	514.10	17.14	506.40	26.64
52	0.05722	0.00366	0.64657	0.03978	0.08190	0.00252	4	499.40	138.62	507.50	15.00	506.40	24.52
53	0.05583	0.00410	0.63532	0.04526	0.08246	0.00296	4	445.10	159.68	510.80	17.62	499.40	28.10
54	0.05704	0.00360	0.63143	0.03836	0.08022	0.00244	4	492.70	137.38	497.50	14.62	497.00	23.88

Table A3.11 (continued)

			Isotopic ratios				Isotopic Ages (Ma)					
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
55	0.05659	0.00386	0.64953	0.04236	0.08319	0.00264	474.80	148.80	515.10	15.66	508.20	26.08
56	0.05621	0.00398	0.63418	0.04292	0.08176	0.00264	460.00	153.70	506.60	15.70	498.70	26.66
57	0.05532	0.00448	0.62783	0.04884	0.08224	0.00312	425.10	174.88	509.50	18.56	494.70	30.46
58	0.05775	0.00464	0.65486	0.05068	0.08217	0.00312	520.00	172.30	509.10	18.54	511.50	31.10
59	0.05563	0.00400	0.62981	0.04314	0.08206	0.00266	437.20	156.24	508.40	15.86	496.00	26.88
60	0.05724	0.00472	0.65089	0.05150	0.08240	0.00316	500.20	177.38	510.40	18.86	509.00	31.68
61	0.05747	0.00482	0.65090	0.05250	0.08207	0.00320	509.20	180.36	508.50	19.02	509.00	32.28
62	0.05493	0.00506	0.63484	0.05580	0.08375	0.00344	409.30	198.70	518.50	20.48	499.10	34.66
63	0.05713	0.00454	0.63813	0.04784	0.08096	0.00276	495.90	171.62	501.80	16.50	501.10	29.66
64	0.05622	0.00534	0.64814	0.05868	0.08353	0.00350	460.40	205.16	517.20	20.84	507.30	36.16
65	0.05781	0.00546	0.66272	0.05974	0.08306	0.00348	522.50	201.26	514.40	20.76	516.30	36.48
66	0.05813	0.00566	0.66227	0.06154	0.08256	0.00354	534.10	207.70	511.40	21.06	516.00	37.60
67	0.05663	0.00460	0.65373	0.04992	0.08367	0.00290	476.30	176.18	518.00	17.20	510.80	30.66
68	0.05768	0.00568	0.64059	0.06010	0.08048	0.00348	517.30	209.88	499.00	20.72	502.70	37.20
69	0.05601	0.00474	0.63926	0.05078	0.08271	0.00292	452.50	183.14	512.30	17.40	501.80	31.46
70	0.05668	0.00596	0.65384	0.06514	0.08358	0.00378	478.50	225.50	517.50	22.46	510.80	40.00
71	0.05650	0.00600	0.63013	0.06344	0.08081	0.00368	471.30	228.36	501.00	21.96	496.20	39.52
72	0.05681	0.00508	0.64266	0.05338	0.08198	0.00298	483.50	192.60	507.90	17.78	504.00	33.00
73	0.05690	0.00514	0.64594	0.05430	0.08227	0.00302	487.00	194.96	509.60	17.98	506.00	33.50
74	0.05611	0.00614	0.63883	0.06614	0.08250	0.00384	456.20	234.58	511.00	22.84	501.60	40.98
75	0.05697	0.00524	0.65259	0.05548	0.08301	0.00306	489.70	197.72	514.10	18.24	510.10	34.08

			Isotopic	ratios			Isotopic Ages (Ma)					
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
1	0.05806	0.00203	0.66204	0.02160	0.08270	0.00179	531.92	203.51	512.25	27.34	515.86	34.05
2	0.05846	0.00158	0.64608	0.01815	0.08016	0.00181	546.92	161.55	497.07	26.87	506.07	28.33
3	0.05734	0.00188	0.64225	0.02139	0.08124	0.00179	504.57	181.63	503.51	26.93	503.70	33.30
4	0.05657	0.00203	0.64518	0.02228	0.08272	0.00144	474.67	188.64	512.35	21.93	505.51	34.76
5	0.05800	0.00175	0.64498	0.02057	0.08066	0.00128	529.64	174.97	500.04	19.11	505.38	32.08
6	0.05620	0.00243	0.61802	0.02411	0.07975	0.00163	460.43	221.01	494.63	24.07	488.60	36.96
7	0.05580	0.00161	0.63047	0.02254	0.08195	0.00147	444.24	142.58	507.77	22.20	496.39	34.84
8	0.06220	0.00528	0.67535	0.05384	0.07875	0.00275	680.95	617.60	488.65	40.20	523.96	85.52
9	0.05669	0.00203	0.64158	0.02388	0.08208	0.00137	479.62	190.05	508.51	20.82	503.29	37.17
10	0.05671	0.00224	0.64395	0.02444	0.08235	0.00134	480.44	209.67	510.13	20.42	504.75	38.10
11	0.05711	0.00426	0.63546	0.05413	0.08070	0.00239	495.80	407.53	500.29	35.66	499.49	83.96
12	0.05641	0.00410	0.63937	0.05414	0.08220	0.00248	468.62	377.09	509.25	37.61	501.91	84.18
13	0.05817	0.00499	0.63869	0.06195	0.07964	0.00277	536.10	503.71	493.95	40.81	501.50	96.30
14	0.05634	0.00410	0.61211	0.05230	0.07880	0.00247	465.64	374.98	488.97	36.03	484.89	79.89
15	0.05528	0.00420	0.61798	0.05397	0.08108	0.00258	423.60	358.66	502.54	38.66	488.58	82.77
16	0.05317	0.00449	0.60658	0.05919	0.08274	0.00306	336.08	321.72	512.46	46.72	481.40	90.08
17	0.05766	0.00491	0.65457	0.06215	0.08234	0.00282	516.74	483.12	510.07	42.80	511.29	97.55
18	0.05621	0.00413	0.62282	0.05346	0.08036	0.00244	460.72	374.96	498.27	36.22	491.61	82.25
19	0.05621	0.00512	0.63182	0.06508	0.08152	0.00223	460.70	464.96	505.20	33.53	497.23	100.73
20	0.05778	0.00324	0.64099	0.04634	0.08045	0.00244	521.62	320.50	498.82	36.26	502.92	72.12
21	0.05674	0.00492	0.63436	0.06246	0.08108	0.00206	481.49	461.13	502.59	30.88	498.81	96.82
22	0.05539	0.00466	0.62520	0.06105	0.08186	0.00200	427.99	401.68	507.23	30.19	493.10	94.09
23	0.05521	0.00474	0.62991	0.06210	0.08275	0.00208	420.62	402.84	512.53	31.80	496.04	95.99

Table A3.12 LA-ICP-MS analysis results of sample S.TW'G-1-17ERS

Analysis		Isotopic ratios					Isotopic Ages (Ma)						
#	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s		²⁰⁷ Pb/ ²⁰⁶ Pb	2s	$^{206}\text{Pb}/^{238}\text{U}$	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s
1	0.06836	0.01960	0.78185	0.21960	0.08294	0.00566		879.40	542.72	513.70	33.66	586.50	125.14
2	0.05032	0.02742	0.53435	0.28854	0.07701	0.00636		209.90	1065.62	478.20	38.12	434.70	190.94
3	0.05573	0.02242	0.60694	0.24030	0.07900	0.00712		441.40	789.34	490.10	42.58	481.60	151.84
4	0.06737	0.01606	0.74404	0.17368	0.08010	0.00490		849.10	459.86	496.70	29.24	564.80	101.12
5	0.06558	0.03802	0.74494	0.42558	0.08238	0.00882		793.10	1025.88	510.30	52.58	565.30	247.64
6	0.05378	0.03280	0.60943	0.36782	0.08220	0.00814		361.60	1144.10	509.20	48.48	483.20	232.06
7	0.06060	0.02694	0.64000	0.28050	0.07660	0.00656		625.10	836.64	475.80	39.30	502.30	173.68
8	0.05184	0.02634	0.55493	0.27886	0.07765	0.00670		278.40	992.30	482.10	40.02	448.20	182.10
9	0.06081	0.02630	0.66588	0.28370	0.07942	0.00684		632.70	815.46	492.70	40.88	518.20	172.92
10	0.05484	0.01966	0.60275	0.21312	0.07973	0.00592		405.50	715.96	494.50	35.32	479.00	135.02
11	0.05421	0.01454	0.60516	0.15976	0.08097	0.00526		379.70	553.12	501.90	31.42	480.50	101.06
12	0.06287	0.02492	0.65484	0.25516	0.07555	0.00646		703.90	746.74	469.50	38.68	511.50	156.56
13	0.05410	0.02634	0.59218	0.28482	0.07941	0.00724		375.00	942.50	492.60	43.22	472.30	181.64
14	0.06646	0.03134	0.76109	0.35320	0.08307	0.00814		821.00	855.52	514.40	48.48	574.60	203.64
15	0.06170	0.01994	0.67317	0.21350	0.07915	0.00632		663.70	625.90	491.00	37.78	522.60	129.56
16	0.07503	0.02958	0.79286	0.30592	0.07666	0.00736		1069.30	704.66	476.10	44.06	592.80	173.26
17	0.05038	0.01860	0.64294	0.23388	0.09257	0.00764		212.60	760.18	570.70	45.04	504.10	144.54
18	0.06651	0.02056	0.73524	0.22214	0.08019	0.00674		822.60	586.40	497.20	40.22	559.60	129.98
19	0.05997	0.01440	0.71903	0.16812	0.08697	0.00664		602.70	480.92	537.60	39.42	550.10	99.30
20	0.05744	0.02254	0.71992	0.27724	0.09092	0.00860		507.90	763.92	561.00	50.82	550.60	163.68
21	0.05043	0.01994	0.58118	0.22604	0.08359	0.00770		214.90	806.44	517.50	45.78	465.20	145.16
22	0.06447	0.03158	0.74517	0.35868	0.08383	0.00914		757.20	892.80	519.00	54.34	565.40	208.70
23	0.07098	0.02336	0.81359	0.26062	0.08314	0.00792		956.70	608.72	514.80	47.08	604.50	145.92
24	0.05381	0.01888	0.61323	0.21060	0.08266	0.00766		362.90	707.56	512.00	45.60	485.60	132.56
25	0.05188	0.02322	0.59224	0.26020	0.08280	0.00858		280.00	889.14	512.80	51.06	472.30	165.94
26	0.05454	0.02438	0.61777	0.27068	0.08215	0.00874		393.20	872.10	509.00	52.10	488.40	169.90
27	0.06215	0.02820	0.68201	0.30240	0.07958	0.00896		679.30	844.64	493.60	53.48	528.00	182.56

Table A3.13 LA-ICP-MS analysis results of sample S.TW'G-2-17ERS

Table A3.13 (continued)

Analysis #			Isotopic	ratios			Isotopic Ages (Ma)					
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
28	0.04953	0.02768	0.52634	0.28872	0.07707	0.00930	172.80	1095.70	478.60	55.62	429.40	192.06
29	0.05490	0.02214	0.58796	0.22968	0.07766	0.00870	408.20	794.40	482.10	52.04	469.60	146.86
30	0.05401	0.02880	0.62661	0.32678	0.08413	0.01032	371.40	1019.46	520.70	61.36	494.00	203.98
31	0.05062	0.03592	0.56600	0.39530	0.08108	0.01104	223.50	1325.42	502.60	65.80	455.40	256.30

A			Isotopic	ratios			Isotopic Ages (Ma)					
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s	$^{206}Pb/^{238}U$	2s	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	$^{207}\text{Pb}/^{235}\text{U}$	2s
1	0.06174	0.00814	0.71048	0.09194	0.08339	0.00350	665.00	270.40	516.30	20.80	545.00	54.58
2	0.05329	0.00650	0.59702	0.07160	0.08118	0.00320	341.10	263.22	503.20	19.10	475.30	45.52
3	0.05563	0.00384	0.63752	0.04380	0.08304	0.00276	437.30	149.80	514.30	16.38	500.80	27.16
4	0.05534	0.00638	0.60912	0.06926	0.07976	0.00310	425.70	248.16	494.70	18.46	483.00	43.70
5	0.05536	0.00364	0.61307	0.04022	0.08025	0.00264	426.40	142.84	497.60	15.76	485.50	25.32
6	0.05333	0.00548	0.60625	0.06132	0.08237	0.00308	342.80	223.64	510.30	18.34	481.20	38.76
7	0.05798	0.00372	0.64351	0.04114	0.08042	0.00266	528.80	138.20	498.60	15.84	504.50	25.42
8	0.05338	0.00442	0.60045	0.04930	0.08151	0.00284	344.80	181.94	505.20	16.96	477.50	31.28
9	0.06083	0.00588	0.66972	0.06358	0.07978	0.00302	633.10	201.52	494.80	18.02	520.50	38.66
10	0.05690	0.00276	0.63927	0.03180	0.08141	0.00252	486.90	105.58	504.50	14.98	501.90	19.70
11	0.06029	0.00424	0.65713	0.04582	0.07898	0.00272	613.90	148.60	490.00	16.26	512.90	28.08
12	0.05735	0.00578	0.65644	0.06508	0.08294	0.00318	504.50	215.60	513.60	18.96	512.40	39.90
13	0.05613	0.00294	0.64789	0.03448	0.08364	0.00264	457.10	114.44	517.80	15.70	507.20	21.24
14	0.04886	0.00592	0.58195	0.06962	0.08630	0.00340	141.20	273.04	533.60	20.14	465.70	44.68
15	0.06586	0.00822	0.73321	0.08918	0.08067	0.00354	801.80	250.90	500.10	21.14	558.40	52.24
16	0.06026	0.00674	0.66825	0.07322	0.08035	0.00324	612.90	232.70	498.20	19.38	519.70	44.56
17	0.05572	0.00496	0.62354	0.05466	0.08108	0.00300	441.00	191.70	502.60	17.90	492.10	34.18
18	0.05747	0.00484	0.66807	0.05544	0.08423	0.00310	509.20	181.12	521.30	18.48	519.50	33.74
19	0.06365	0.00734	0.75888	0.08534	0.08638	0.00368	730.00	235.12	534.10	21.86	573.40	49.26
20	0.05891	0.00456	0.64541	0.04918	0.07937	0.00288	563.90	164.24	492.40	17.24	505.60	30.34
21	0.05884	0.00416	0.66671	0.04664	0.08209	0.00290	561.10	150.52	508.60	17.28	518.70	28.42
22	0.05474	0.00754	0.61343	0.08300	0.08119	0.00350	401.70	294.52	503.20	20.84	485.70	52.24
23	0.06026	0.00860	0.66485	0.09290	0.07994	0.00368	612.80	294.42	495.70	21.92	517.60	56.66
24	0.05933	0.00738	0.64695	0.07876	0.07900	0.00346	579.20	259.58	490.10	20.70	506.60	48.56
25	0.05624	0.00580	0.60824	0.06136	0.07835	0.00322	461.00	222.02	486.30	19.22	482.40	38.74
26	0.05991	0.00546	0.65927	0.05896	0.07971	0.00318	600.40	191.66	494.40	18.98	514.20	36.08
27	0.05647	0.00462	0.64864	0.05230	0.08321	0.00316	470.00	177.54	515.30	18.82	507.60	32.20

Table A3.14 LA-ICP-MS analysis results of sample S.TW'G-5-17ERS

Table A3.14 (continued)

			Isotopic	ratios			Isotopic Ages (Ma)						
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁷ Pb/ ²³⁵ U	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ F	Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
28	0.05881	0.00570	0.66126	0.06272	0.08145	0.00332	5	60.20	204.32	504.80	19.84	515.40	38.34
29	0.06287	0.00850	0.69115	0.09120	0.07964	0.00374	7	03.80	275.28	494.00	22.36	533.50	54.76
30	0.05503	0.00558	0.61292	0.06096	0.08069	0.00336	4	13.20	218.64	500.20	20.10	485.40	38.36
31	0.05877	0.00540	0.63375	0.05734	0.07812	0.00318	5	58.50	194.52	484.90	19.02	498.40	35.64
32	0.05774	0.00558	0.63261	0.06020	0.07936	0.00334	5	19.80	205.68	492.30	19.94	497.70	37.44
33	0.05905	0.00708	0.68071	0.08014	0.08350	0.00398	5	68.90	250.66	517.00	23.70	527.20	48.42
34	0.05636	0.00630	0.66157	0.07300	0.08503	0.00394	4	65.70	240.02	526.10	23.44	515.60	44.62
35	0.05657	0.00662	0.64281	0.07452	0.08231	0.00396	4	74.00	250.54	509.90	23.60	504.00	46.06
36	0.05672	0.00688	0.62831	0.07544	0.08024	0.00396	4	79.90	259.00	497.50	23.58	495.00	47.04
37	0.05873	0.00710	0.65518	0.07834	0.08080	0.00398	5	57.30	253.06	500.90	23.76	511.70	48.06

Table A4.1 Major and trace element geochemistry, lithologies and GPS locations of plutonic plagiogranites and fine-grained intrusive dikes from the Blow Me Down Mountain Massif, together with average results of secondary standard BHVO-2

Abbreviations: F.G.: fine-grained; BDL: below detection limit; Ref.: reference value (see Section 4.3.1); Ave.: average value

¹ Samples and major elements are from Casey et al. (1985); trace elements are measured by QQQ-ICP-MS in this study

 2 Samples and major elements are from Kharas-Khumbatta (1988); trace elements are measured by QQQ-ICP-MS in this study.

³ Pre-1995 sample latitude and longitude locations were obtained by matching outcrop locations of the pre-1995 1/15000 geologic and sampling maps with the Google Earth locations (UTM projection)

* Elements were measured as trace elements by QQQ-ICP-MS in this study, but then transferred to wt.% and reported as major elements due to their very low concentrations (≤ 0.1 wt.%) originally reported in Casey et al. (1985)

Sample	BMD-01-17Y	BMD-03-17Y	BMD-04-17Y	BMD-05-17Y	BMD-06-17Y
Lithology	Diorite	Trondhjemite	Trondhjemite	Trondhjemite	Trondhjemite
Latitude (°)	49.07123	49.04860	49.04861	49.04858	49.04787
Longitude (°)	-58.26468	-58.26880	-58.26885	-58.26899	-58.26874
Major oxides ((wt.%)				
SiO ₂	58.78	78.37	76.34	76.07	76.48
TiO ₂	0.44	0.13	0.14	0.17	0.15
Al_2O_3	18.96	12.58	12.99	13.43	12.89
$Fe_2O_3(t)$	2.95	2.55	2.25	2.68	2.52
MnO	0.04	0.03	0.05	0.06	0.04
MgO	2.08	0.13	0.12	0.23	0.22
CaO	8.40	0.35	0.67	0.90	0.45
Na ₂ O	7.04	6.34	6.10	6.48	6.32
K ₂ O	0.09	0.14	0.80	0.30	0.30
P_2O_5	0.06	0.02	0.02	0.03	0.02
Total	98.84	100.63	99.50	100.36	99.39
LOI	2.23	1.08	0.66	0.90	0.76
Trace element	s (ppm)				
Li	4.67	0.872	0.757	0.983	2.05
Be	1.01	1.47	1.89	2.73	1.50
S	180	9.73	11.7	1.03	3.11
Sc	12.2	6.62	8.09	7.96	7.94
V	70.9	0.804	0.434	0.730	0.552
Cr	58.7	0.029	0.099	0.019	0.029
Co	10.5	7.70	4.39	7.46	6.85
Ni	20.0	0.219	BDL	0.007	0.058
Cu	1.54	1.26	0.433	2.22	3.87
Zn	12.5	25.0	48.4	47.0	68.6
Ga	20.4	18.7	22.7	22.5	22.2
Ge	0.775	1.08	1.30	1.27	1.18
As	0.098	1.40	0.123	0.165	4.68
Se	BDL	0.012	BDL	BDL	0.003
Rb	0.253	0.955	7.90	2.77	2.07
Sr	78.6	39.8	42.2	75.5	55.7
Y	47.5	66.0	101	98.0	78.7
Zr	187	208	283	241	248
Nb	4.00	4.57	5.96	5.02	5.44

Sampla	BMD 01 17V	BMD 03 17V	BMD 04 17V	BMD 05 17V	BMD 06 17V
Lithology	Diorita	Trondhiamita	Trondhiamita	Trondhiomite	Trondhiamita
Littiology	10 07122			10.04959	10.04787
Latitude (1)	49.07125	49.04800	49.04801	49.04838	49.04/8/
	-38.20408	-38.20880	-38.20885	-38.20899	-38.20874
Trace element	s (ppm)	0.160	0.752	0.202	0.000
Мо	0.132	0.162	0.753	0.393	0.288
Ag	0.060	0.066	0.079	0.062	0.072
Cd	0.029	0.032	0.050	0.050	0.147
Sn	0.678	1.76	1.84	2.29	1.43
Sb	0.024	0.037	0.022	0.022	0.069
Cs	0.020	0.010	0.024	0.020	0.026
Ba	72.2	35.1	169	84.4	63.7
La	10.1	15.8	21.4	18.9	18.2
Ce	25.6	33.7	52.6	45.0	42.4
Pr	3.67	6.09	7.53	6.86	6.61
Nd	17.0	28.6	34.2	31.9	30.2
Sm	5.04	8.36	9.94	9.27	8.57
Eu	1.21	1.25	1.34	1.63	1.43
Gd	6.52	9.75	12.6	12.1	10.4
Tb	1.23	1.75	2.35	2.19	1.91
Dy	8.20	11.7	16.0	14.5	12.7
Но	1.82	2.58	3.56	3.22	2.82
Er	5.48	7.82	10.7	9.52	8.52
Tm	0.849	1.24	1.67	1.42	1.33
Yb	5.61	8.17	11.0	9.03	8.81
Lu	0.830	1.25	1.67	1.37	1.34
Hf	5.29	6.91	9.32	7.67	7.55
Та	0.271	0.391	0.493	0.443	0.390
W	0.064	0.240	0.167	0.215	0.206
T1	0.001	0.008	0.043	0.012	0.012
Pb	0.508	1.47	2.87	1.86	2.48
Th	1.82	3.00	3.92	3.34	3.06
U	0.983	1.50	2.12	1.82	1.77

Table A4.1 (continued)

Sample	BMD-07-17Y	BMD-08-17Y	BMD-09-17Y	BMD.RTB. 116-84-N.O. ¹	BMD.196-D ¹
Lithology	Trondhjemite	Trondhjemite	Trondhjemite	Trondhjemite	Trondhjemite
Latitude (°)	49.04776	49.04762	49.04786	49.001312 ³	49.057920^3
Longitude (°)	-58.26870	-58.26837	-58.26781	-58.311457 ³	-58.266325^3
Major oxides (wt.%)				
SiO ₂	75.65	76.79	77.54	76.50	76.26
TiO ₂	0.15	0.14	0.14	0.20	0.17
Al_2O_3	13.22	13.01	12.61	14.01	12.76
$Fe_2O_3(t)$	2.28	2.27	2.37	2.45	4.04
MnO	0.04	0.05	0.04	0.01^{*}	0.01^{*}
MgO	0.15	0.13	0.17	0.52	0.46
CaO	0.33	0.78	0.62	1.13	0.57
Na ₂ O	6.78	5.89	6.17	5.40	5.44
K_2O	0.11	0.91	0.26	0.34	0.14^{*}
P_2O_5	0.02	0.02	0.01	0.11	0.02^{*}
Total	98.71	99.99	99.94	100.67	99.86
LOI	1.03	0.75	0.95		
Trace elements	s (ppm)				
Li	1.53	1.19	0.985	1.28	1.83
Be	1.34	1.85	1.54	1.30	1.57
S	23.0	BDL	4.77	30.2	50.4
Sc	7.34	7.49	5.91	8.89	6.47
V	0.622	0.407	0.336	2.75	1.38
Cr	0.039	0.052	0.063	24.3	33.2
Co	4.01	4.66	3.66	3.80	1.03
Ni	0.731	0.152	0.058	6.00	3.03
Cu	1.12	0.415	1.03	2.03	2.22
Zn	43.6	66.6	44.3	1.65	15.0
Ga	21.7	22.2	23.0	16.4	18.4
Ge	1.15	1.24	1.55	0.789	0.763
As	3.54	0.209	0.144	0.374	0.719
Se	0.019	BDL	0.008	0.004	0.004
Rb	0.948	10.8	2.12	1.85	1.08
Sr	24.8	41.4	54.3	179	40.0
Y	72.4	121	98.5	89.4	57.7
Zr	224	245	388	309	247
Nb	5.93	6.24	6.17	5.47	5.29

Table A4.1 (continued)

Sample Label	BMD-07-17Y	BMD-08-17Y	BMD-09-17Y	BMD.RTB. 116-84-N.O. ¹	BMD.196-D ¹
Lithology	Trondhjemite	Trondhjemite	Trondhjemite	Trondhjemite	Trondhjemite
Latitude (°)	49.04776	49.04762	49.04786	49.001312 ³	49.057920^3
Longitude (°)	-58.26870	-58.26837	-58.26781	-58.311457 ³	-58.266325^3
Trace elements	s (ppm)				
Mo	0.136	0.105	0.255	0.695	1.41
Ag	0.077	0.069	0.106	0.084	0.081
Cd	0.077	0.039	0.063	0.054	10.3
Sn	2.09	1.78	1.44	0.582	0.777
Sb	0.066	0.032	0.016	0.018	0.047
Cs	0.017	0.042	0.023	BDL	0.001
Ba	17.6	162	66.7	27.1	58.8
La	17.6	20.9	27.3	16.4	13.2
Ce	44.4	49.5	61.3	42.7	41.4
Pr	6.39	7.47	9.01	5.59	4.53
Nd	28.9	34.7	40.7	27.4	22.0
Sm	8.18	10.4	11.0	8.70	6.62
Eu	1.13	1.42	1.44	1.80	1.06
Gd	9.91	14.1	13.4	10.8	7.38
Tb	1.84	2.60	2.42	2.06	1.35
Dy	12.2	17.6	16.3	14.0	9.29
Но	2.69	3.97	3.68	3.56	2.40
Er	8.09	11.8	11.3	9.70	6.92
Tm	1.26	1.77	1.77	1.68	1.29
Yb	8.43	11.4	11.7	9.18	7.56
Lu	1.28	1.73	1.83	1.40	1.18
Hf	7.25	8.74	11.3	9.22	8.12
Та	0.425	0.514	0.419	0.465	0.494
W	0.160	0.171	0.137	0.095	0.071
Tl	0.006	0.061	0.010	BDL	BDL
Pb	1.92	2.81	1.84	BDL	1.14
Th	3.41	3.77	4.39	2.90	3.41
U	1.72	2.09	2.65	2.00	1.78

Table A4.1 (continued)

Sample	BMD.220-A ¹	BMD.252-B ¹	2130A ²	2129A ²	1085 ²
Lithology	Trondhjemite	Trondhjemite	F.G. Dacitic Dike	F.G. Dacitic Dike	F.G. Dacitic Dike
Latitude (°)	49.032614 ³	49.012273 ³	49.027490^3	49.027499^3	49.040323 ³
Longitude (°)	-58.273687^3	-58.280409^{3}	-58.307822^3	-58.306149 ³	-58.286125^3
Major oxides ((wt.%)				
SiO_2	74.64	69.45	72.98	72.57	63.83
TiO ₂	0.19	0.25	0.23	0.29	0.24
Al_2O_3	13.35	15.59	13.90	13.68	18.53
$Fe_2O_3(t)$	3.78	4.06	4.42	4.20	4.35
MnO	0.07^{*}	0.04^{*}	0.04^{*}	0.04^{*}	0.07^{*}
MgO	0.35	0.58	0.63	0.53	0.43
CaO	1.26	3.54	0.53	0.78	0.59
Na ₂ O	5.05	6.32	7.81	7.28	11.03
K_2O	0.86	0.03^{*}	0.06^{*}	0.04^{*}	0.04^{*}
P_2O_5	0.02^{*}	0.15	0.03^{*}	0.06^{*}	0.02^{*}
Total	99.57	100.02	100.63	99.48	99.12
LOI			1.22	1.13	0.70
Trace element	s (ppm)				
Li	1.91	1.62	4.35	2.97	0.778
Be	1.40	1.09	1.50	1.20	2.26
S	20.9	34.1	1978	123	62.5
Sc	7.66	6.56	10.3	8.22	6.88
V	0.580	4.13	2.26	6.74	0.874
Cr	13.7	22.4	45.5	34.1	6.32
Co	0.561	2.17	9.12	3.53	21.8
Ni	3.09	4.02	3.82	2.99	0.966
Cu	4.71	6.47	27.6	156	23.8
Zn	94.4	35.4	28.7	15.7	138
Ga	18.5	15.9	21.5	20.7	34.1
Ge	0.874	0.403	0.748	1.19	2.00
As	1.19	0.161	0.951	0.338	0.271
Se	BDL	BDL	0.162	0.159	0.021
Rb	7.56	0.144	0.355	0.249	0.289
Sr	76.1	44.2	26.5	38.3	40.6
Y	94.5	30.0	48.3	72.6	112
Zr	287	156	298	298	543
Nb	4.88	2.69	5.50	6.10	11.7

Table A4.1 (continued)

Sample Label	BMD.220-A ¹	BMD.252-B ¹	2130A ²	2129A ²	1085 ²
Lithology	Trondhjemite	Trondhjemite	F.G. Dacitic Dike	F.G. Dacitic Dike	F.G. Dacitic Dike
Latitude (°)	49.032614 ³	49.012273 ³	49.027490 ³	49.027499 ³	49.040323 ³
Longitude (°)	-58.273687^3	-58.280409^3	-58.307822^3	-58.306149^3	-58.286125^3
Trace elements	(ppm)				
Mo	1.09	1.06	1.81	1.04	1.78
Ag	0.094	0.054	0.082	0.093	0.172
Cd	0.118	0.035	0.215	0.286	1.09
Sn	2.36	1.16	1.80	2.40	4.18
Sb	0.068	0.022	0.104	0.070	0.133
Cs	0.033	BDL	0.006	0.004	0.006
Ba	146	13.7	6.40	5.00	10.3
La	19.8	6.37	7.81	17.3	36.0
Ce	46.3	16.7	18.6	42.0	91.0
Pr	6.07	1.94	2.62	5.98	12.7
Nd	28.4	9.13	12.6	27.1	55.1
Sm	8.46	2.79	4.11	7.77	14.0
Eu	1.37	1.11	0.882	1.54	2.42
Gd	10.7	3.50	5.48	9.50	16.0
Tb	2.01	0.65	1.09	1.76	3.04
Dy	13.5	4.46	7.84	11.9	20.8
Но	3.40	1.15	1.90	2.69	4.59
Er	9.14	3.19	6.38	8.32	14.1
Tm	1.56	0.561	1.08	1.31	2.25
Yb	8.43	3.13	7.56	8.83	15.4
Lu	1.28	0.498	1.22	1.36	2.35
Hf	9.10	4.40	8.26	8.76	15.1
Та	0.447	0.246	0.365	0.392	0.967
W	0.134	0.055	0.134	0.122	19.3
Tl	0.030	BDL	0.005	0.007	0.005
Pb	5.33	1.42	0.705	0.800	2.15
Th	2.89	1.59	2.11	3.51	5.67
U	1.83	0.996	1.15	1.65	3.03

Table A4.1 (continued)

Sample	2125B ²	2124B ²	2127A ²	2131 ²		BHVO-2	
Lithology	F.G. Andesitic Dike	F.G. Andesitic Dike	F.G. Basaltic Andesitic Dike	F.G. Basaltic Andesitic Dike	Secondary standar (N=5)		dard
Latitude (°)	49.027775 ³	49.027600^3	49.027846 ³	49.027357 ³			
Longitude (°)	-58.301572 ³	-58.300602 ³	-58.303761 ³	-58.309303 ³	Ref.	Ave.	RSD (%)
Major oxides	s (wt.%)						
SiO_2	60.56	57.42	56.53	54.79	49.6	49.73	0.34
TiO ₂	0.66	1.23	1.13	1.47	2.731	2.72	0.67
Al_2O_3	17.58	16.12	16.42	15.43	13.44	13.44	0.50
$Fe_2O_3(t)$	6.05	9.72	9.37	11.77	12.39	12.47	0.26
MnO	0.08^{*}	0.13	0.18	0.20	0.169	0.17	0.91
MgO	1.40	3.94	5.21	5.73	7.257	7.31	0.34
CaO	3.65	4.21	4.14	4.29	11.4	11.44	0.29
Na ₂ O	9.19	6.98	6.77	6.28	2.219	2.21	0.16
K ₂ O	0.13	0.36	0.54	0.18	0.513	0.51	0.55
P_2O_5	0.16	0.12	0.11	0.14	0.2685	0.27	0.93
Total	99.46	100.23	100.40	100.28	99.99	100.28	
LOI	1.47	1.89	3.09	3.97			
Trace elemen	nts (ppm)						
Li	0.972	3.32	5.31	8.57	4.5	4.60	3.65
Be	1.30	0.729	0.612	0.633	1.076	1.06	4.65
S	38.7	6.64	1886	1674	164	151	6.86
Sc	13.6	25.4	25.6	34.0	31.83	27.9	4.69
V	41.9	215	176	351	318.2	307	4.82
Cr	14.3	17.5	40.0	17.5	287.2	281	4.14
Co	10.4	27.5	27.1	36.5	44.89	41.2	4.31
Ni	3.14	8.55	16.0	16.5	119.8	128	3.76
Cu	53.9	2.88	56.0	58.1	129.3	126	4.27
Zn	30.3	29.9	68.5	100	103.9	92.6	4.26
Ga	22.8	17.0	16.8	17.8	21.37	17.5	3.07
Ge	1.15	0.946	0.968	1.55	1.623	1.29	7.17
As	1.18	0.257	0.605	1.58	0.7	0.588	3.40
Se	0.011	0.014	0.424	0.229	0.18	0.141	9.47
Rb	0.376	3.15	3.08	1.82	9.261	8.55	3.94
Sr	44.3	136	140	136	394.1	398	4.00
Y	67.5	30.7	29.1	35.8	25.91	26.4	1.73

Table A4.1 (continued)

Sample Label	2125B ²	2124B ²	2127A ²	2131 ²	BHVO-2			
Lithology	F.G. Andesitic Dike 49 027775 ³	F.G. Andesitic Dike 49 027600 ³	F.G. Basaltic Andesitic Dike 49 027846 ³	F.G. Basaltic Andesitic Dike 49 027357 ³	Check standard (N=5)			
Longitude (°)	-58.301572^3	-58.300602^3	-58.303761 ³	-58.309303^3	Ref.	Ave.	RSD (%)	
Trace elemen	nts (ppm)							
Zr	278	107	99.8	86.7	171.2	164	1.70	
Nb	5.89	2.86	2.94	2.17	18.1	17.2	1.93	
Мо	2.01	1.37	0.867	0.978	4.07	4.87	3.62	
Ag	0.108	0.037	0.037	0.067	0.089	0.083	7.67	
Cd	0.091	0.159	0.171	0.043	0.152	0.072	6.09	
Sn	1.68	1.48	1.76	1.13	1.776	1.81	2.74	
Sb	0.065	0.046	0.094	0.357	0.1034	0.087	4.84	
Cs	0.001	0.017	0.035	0.017	0.0996	0.094	1.56	
Ba	11.7	37.7	37.3	23.2	130.9	119	2.52	
La	16.0	6.05	6.89	5.22	15.2	13.7	3.49	
Ce	40.9	15.0	16.8	14.3	37.53	37.1	2.59	
Pr	5.85	2.25	2.49	1.95	5.339	4.87	1.67	
Nd	27.5	10.9	12.1	10.4	24.27	23.2	1.54	
Sm	8.06	3.36	3.68	3.71	6.023	5.74	2.76	
Eu	1.99	1.12	1.21	1.23	2.043	1.93	4.14	
Gd	10.1	4.42	4.74	4.29	6.207	5.73	2.61	
Tb	1.79	0.788	0.843	0.80	0.9392	0.868	2.78	
Dy	11.7	5.17	5.54	5.78	5.28	4.94	2.87	
Но	2.58	1.13	1.19	1.41	0.9887	1.04	2.81	
Er	7.68	3.31	3.54	3.76	2.511	2.39	2.58	
Tm	1.18	0.495	0.527	0.595	0.3349	0.355	2.71	
Yb	7.79	3.19	3.46	3.60	1.994	1.85	1.55	
Lu	1.21	0.500	0.529	0.569	0.2754	0.253	1.24	
Hf	8.02	3.05	2.99	2.94	4.47	4.33	2.20	
Та	0.404	0.170	0.172	0.239	1.154	1.19	2.79	
W	0.298	0.214	0.160	1.43	0.251	0.277	7.47	
Tl	0.003	0.012	0.007	0.002	0.0224	0.021	6.30	
Pb	2.21	0.605	2.09	2.03	1.653	1.46	3.70	
Th	2.75	1.12	0.951	0.573	1.224	1.24	2.43	
U	1.46	0.739	0.549	0.334	0.412	0.406	2.20	

Table A4.1 (continued)

Table A4.2 BOIC starting materials used in this study for petrogenetic fractionation modeling (BMD 1009B, a primitive high MgO and low TiO₂, Na₂O diabase), and for partial melting modeling that includes two metagabbroic rocks (PM 169 and NA 76A), two diabases (BMD 1010AB and BMD 1017A) and one sole amphibolite (7.11.2A). Note that chemical compositions of each sample are from unpublished ICP-MS and ICP-OES datasets of J.F. Casey, except for major elements of samples BMD 1009B and BMD 1017A reported in Casey et al. (1985) n.d. - not determined

Sample	1009B	PM 169	NA 76A	1010AB	1017A	7.11.2A
	Diabase	Oxide Gabbro	Gabbro	Diabase	Diabase	Amphibolite
Major oxides	s (wt.%)					_
SiO_2	48.03	43.42	46.21	48.53	50.87	47.67
TiO_2	0.76	4.43	0.11	0.66	1.34	1.39
Al_2O_3	17.87	12.13	24.31	22.88	15.30	15.13
$Fe_2O_3(t)$	8.31	16.38	5.31	6.15	10.52	11.76
MnO	0.12	0.22	0.08	0.10	0.18	0.31
MgO	9.80	7.51	10.68	6.56	7.15	5.19
CaO	11.85	12.64	9.71	12.40	10.31	13.82
Na ₂ O	2.04	2.17	1.76	2.31	4.05	3.59
K ₂ O	0.12	0.11	0.96	0.29	0.04	0.08
P_2O_5	0.07	0.05	0.03	0.08	0.12	0.42
Total	98 97	99.06	99.16	99.96	99.88	99.36
LOI	1 81	1 97	3 97	2 32	3 43	n d
Trace elemen	nts (ppm)	1.97	5.97	2.32	5.15	11.01.
Li	2.72	n.d.	n.d.	3.64	6.22	52.1
Rb	1.27	n.d.	n.d.	2.87	0.432	0.944
Sr	138	170	222	285	203	106
Y	20.0	21.4	1.08	14.1	33.5	22.6
Zr	41.2	46.0	2.00	43.5	111	86.5
Nb	0.656	n.d.	n.d.	0.724	1.96	6.20
Cs	0.026	n.d.	n.d.	0.048	0.004	0.812
Ba	11.0	n.d.	n.d.	23.3	12.2	109
La	1.58	0.947	0.498	1.43	3.71	16.2
Ce	5.66	3.95	1.49	4.37	10.7	34.8
Pr	0.783	n.d.	n.d.	0.792	1.89	4.22
Nd	4.80	4.87	0.501	4.25	9.6	16.3
Sm	1.77	2.00	0.146	1.54	3.46	3.65
Eu	0.75	0.98	0.247	0.633	1.23	0.753
Gd	2.57	2.81	0.017	2.11	4.63	3.88
Tb	0.461	n.d.	n.d.	0.365	0.809	0.614
Dy	3.18	3.67	0.165	2.37	5.29	4.33
H0 Er	0.002	n.d.	n.d.	0.511	1.10	0.788
El Vh	1.92	1.0.	0.056	1.49	3.37	2.20
I U I U	0.287	1.90 n.d	0.050 n d	0.218	0.506	0.339
Hf	1 11	n.d.	n.d.	1.04	2.60	1 99
Та	0.048	n.d.	n.d.	0.233	0.122	0.275
Pb	0.248	n.d.	n.d.	0.195	0.404	3.39
Th	0.107	n.d.	n.d.	0.080	0.337	2.75
U	0.069	n.d.	n.d.	0.047	0.227	0.753

Elemen	nen Basaltic composition											
t	Olvine	Ref.	Срх	Ref.	Opx	Ref.	Plag	Ref.				
Th	7.00E-06	Halliday et al., 1995	0.0021	Halliday et al., 1995	0.0001	McKenzie & O'Nions, 1991	0.13	Dunn & Sen, 1994				
U	9.00E-06	Halliday et al., 1995	0.001	Halliday et al., 1995	0.0001	McKenzie & O'Nions, 1991	0.051	Dunn & Sen, 1994				
Nb	0.00005	Halliday et al., 1995	0.0089	Halliday et al., 1995	0.003	Keleman & Dunn, 1992	0.045	Dunn & Sen, 1994				
La	0.0004	McKenzie & O'Nions, 1991	0.0515	Hauri et al., 1994	0.0008	Green et al., 2000	0.27	McKenzie & O'Nions, 1991				
Ce	0.0005	McKenzie & O'Nions, 1991	0.098	McKenzie & O'Nions, 1991	0.0016	Green et al., 2000	0.2	McKenzie & O'Nions, 1991				
Sr	0.00004	Halliday et al., 1995	0.091	Halliday et al., 1995	0.007	McKenzie & O'Nions, 1991	1.4	Dunn & Sen, 1994				
Nd	0.001	McKenzie & O'Nions, 1991	0.21	McKenzie & O'Nions, 1991	0.0056	Green et al., 2000	0.14	McKenzie & O'Nions, 1991				
Zr	0.001	Halliday et al., 1995	0.26	Halliday et al., 1995	0.02	Keleman & Dunn, 1992	0.048	Rollinson, 1993				
Hf	0.0029	Halliday et al., 1995	0.33	Halliday et al., 1995	0.01	McKenzie & O'Nions, 1991	0.051	Rollinson, 1993				
Sm	0.0013	McKenzie & O'Nions, 1991	0.26	McKenzie & O'Nions, 1991	0.015	Green et al., 2000	0.11	McKenzie & O'Nions, 1991				
Eu	0.0016	McKenzie & O'Nions, 1991	0.31	McKenzie & O'Nions, 1991	0.03	Green et al., 2000	0.73	McKenzie & O'Nions, 1991				
Dy	0.0017	McKenzie & O'Nions, 1991	0.33	McKenzie & O'Nions, 1991	0.077	Green et al., 2000	0.055	McKenzie & O'Nions, 1991				
Y	0.0082	Halliday et al., 1995	0.47	Halliday et al., 1995	0.062	Lofgren et al. 2006	0.013	Dunn & Sen, 1994				
Yb	0.0015	McKenzie & O'Nions, 1991	0.28	McKenzie & O'Nions, 1991	0.22	Green et al., 2000	0.031	McKenzie & O'Nions, 1991				
Lu	0.0015	McKenzie & O'Nions, 1991	0.28	McKenzie & O'Nions, 1991	0.22	Green et al., 2000	0.025	McKenzie & O'Nions, 1991				

Table A4.3 Partition coefficients used in calculation of trace element concentration for fractionation and partial melting. Values with star (*) are interpolated by averaging the nearest neighbors

Table A4.3 (continued)

	Andesit	ic composition										
Element	Ol	Ref.	Срх	Ref.	Opx	Ref.	Plag	Ref.	Mag	Ref.	Ilm	Ref.
Th	0.020	Luhr & Carmichael, 1980	0.01	Klein et al., 2000	0.14	Luhr & Carmichael, 1980	0.19	Dunn & Sen, 1994	0.42	Luhr & Carmichael, 1980	0.00055	Zack & Brumm, 1998
U	0.040	Dunn & Sen, 1994	0.0075*		0.46*		0.34	Dunn & Sen, 1994	0.56*		0.0082	Zack & Brumm, 1998
Nb	0.11	Ewart & Griffin, 1994	0.0050	Klein et al., 2000	0.78	Ewart & Griffin, 1994	0.033	Dunn & Sen, 1994	0.7	Haskin et al. 1966	2	Rollinson, 1993
La	0.020	Luhr & Carmichael, 1980	0.14	Luhr & Carmichael, 1980	0.03	Luhr & Carmichael, 1980	0.21	Luhr & Carmichael, 1980	0.45	Luhr & Carmichael, 1980	0.000029	Zack & Brumm, 1998
Ce	0.010	Luhr & Carmichael, 1980	0.51	Schnetzler & Philpotts, 1970	0.33	Luhr & Carmichael, 1980	0.30	Schnetzler & Philpotts, 1970	0.42	Luhr & Carmichael, 1980	0.000054	Zack & Brumm, 1998
Sr	0.070	Ewart & Griffin, 1994	0.28	Ewart & Griffin, 1994	0.13	Ewart & Griffin, 1994	2.7	Dunn & Sen, 1994	0.49		0.00027*	
Nd	0.020	Luhr & Carmichael, 1980	0.65	Schnetzler & Philpotts, 1970	0.43	Luhr & Carmichael, 1980	0.24	Schnetzler & Philpotts, 1970	0.55	Luhr & Carmichael, 1980	0.00048	Zack & Brumm, 1998

Table A4.3 (continued)

	Andesit	ic composition										
Element	Ol	Ref.	Срх	Ref.	Opx	Ref.	Plag	Ref.	Mag	Ref.	Ilm	Ref.
Zr	0.020	Luhr & Carmichael, 1980	0.33	Ewart & Griffin, 1994	0.13	Ewart & Griffin, 1994	0.00090	Dunn & Sen, 1994	0.59*		0.29	Zack & Brumm, 1998
Hf	0.020	Luhr & Carmichael, 1980	0.34	Luhr & Carmichael, 1980	0.22	Luhr & Carmichael, 1980	0.017*		0.62	Luhr & Carmichael, 1980	0.38	Zack & Brumm, 1998
Sm	0.010	Luhr & Carmichael, 1980	0.78	Luhr & Carmichael, 1980	0.43	Schnetzler & Philpotts, 1970	0.203	Schnetzler & Philpotts, 1970	0.55	Luhr & Carmichael, 1980	0.00059	Zack & Brumm, 1998
Eu	0.030	Luhr & Carmichael, 1980	0.68	Schnetzler & Philpotts, 1970	0.42	Schnetzler & Philpotts, 1970	0.55	Dunn & Sen, 1994	0.42	Luhr & Carmichael, 1980	0.009	Zack & Brumm, 1998
Dy	0.10	Luhr & Carmichael, 1980	1.46	Schnetzler & Philpotts, 1970	0.56	Schnetzler & Philpotts, 1970	0.034	Dunn & Sen, 1994	0.58	Luhr & Carmichael, 1980	0.01	Zack & Brumm, 1998
Y	0.072	Ewart & Griffin, 1994	1.38*		0.56*		0.034*		0.53*		0.0045	Zack & Brumm, 1998
Yb	0.030	Luhr & Carmichael, 1980	1.30	Schnetzler & Philpotts, 1970	0.56	Schnetzler & Philpotts, 1970	0.033	Schnetzler & Philpotts, 1970	0.47	Luhr & Carmichael, 1980	0.17	Zack & Brumm, 1998
Lu	0.080	Luhr & Carmichael, 1980	1.40	Luhr & Carmichael, 1980	0.68	Schnetzler & Philpotts, 1970	0.034	Schnetzler & Philpotts, 1970	0.44	Luhr & Carmichael, 1980	0.084	Zack & Brumm, 1998

Fig. A4.1 Selected trace element modeling results of La, Sm, Y, Zr and Th vs. MgO, as well as La/Sm vs. La for partially melting the two metagabbros and two diabases. Small hatch marks on each melting line indicate partial melts (F) produced at 10%, 20%, 30%, 40% and 50% melting of the protoliths; value beside each melting line in (a) indicates mass percentage of the earliest melt produced; filled circle on each of the partial melting trend represents the ~5% partial melt used for future post-melting crystal fractionation. Note that partial melting does not reproduce sample trace element trends nor extend to the most evolved samples even various protoliths have been used, although the diabase melting lines match some andesitic and dioritic compositions.





Fig. A4.2 Variation diagrams of selected modeled trace elements of La, Sm, Y and Zr vs. MgO, as well as La/Sm vs. La, showing BOIC basalts, diabases, andesites, plagiogranites and fine-grained intrusive dikes, together with combined partial melting and post-melting fractionation modeling results derived from the four protoliths including two metagabbros (a-e) and two diabases (f-j). Note that only compositions produced from 5% (filled circles) to 50% melting incremented every 10% (hatch marks) are shown (solid lines with arrows). Post-melting Rayleigh fractionation of 5% partial melts are shown by the dashed lines with arrows extending from the filled circles (i.e., F = 5%). Although the post-melting fractionation reproduce some BOIC felsic samples, the combined modeling results of melting and post-melting fractionation processes collectively produce a range of compositions discordant to the sample trends. Furthermore, the significant mismatches of major elements modeled with BOIC samples (e.g., Fig. 4.13i) suggest that partial melting even if combined with post-melting fractionation, fails to reproduce these highly evolved felsic BOIC plagiogranites and the overall variation sample trends from intermediate to felsic composition.





Fig. A4.3 Fig. A4.3 Major oxide variation diagrams vs. MgO for BOIC basalts, diabases, andesites, plagiogranites and fine-grained intrusive dikes, as well as modeled liquid lines of descent (LLDs) for fractional crystallization derived from a primitive BOIC diabase BMD 1009B (yellow stars) at various pressures using rhyolite-MELTS (Gualda et al., 2012; Ghiorso and Gualda, 2015). Pressures chosen include 0.7, 1, 2, 3, 5, 7 and 10 kb to simulate a wide range of depths from near surface to deep mantle at runs of (a-f) fo₂ = QFM0 and H₂O = 0.2 wt.% (i.e., relatively reduced condition) and (g-l) fo₂ = QFM+3 and H₂O = 3 wt.% (i.e., highly oxidized condition) because oxygen fugacity commonly correlates positively with water content (see main text for details). FeO*: total Fe as FeO in this diagram and all subsequent modeling plots.



Fig. A4.3 (continued)



Fig. A4.4 Major oxide variation diagrams vs. MgO for BOIC basalts, diabases, andesites, plagiogranites and fine-grained intrusive dikes, as well as modeled LLDs for fractional crystallization derived from a primitive BOIC diabase BMD 1009B (yellow stars) at various water contents (0.2, 0.5, 1, 2, 3 and 4 wt.%) using rhyolite-MELTS. Pressures were chosen at 0.7 kb to correspond to the dike/gabbro contact (assuming ~2.5 km of water depth) and at 2 kb to correspond with the depth of the base of the gabbroic crust in the BOIC. The LLDs are computed by assuming initial water contents varying in the primitive magma from 0 to 4 wt.% with (a-f) P = 0.7 kb and fo₂ = QFM0, (g-l) P = 0.7 kb and fo₂ = QFM+3, (m-r) P = 2 kb and fo₂ = QFM0, and (s-x) P = 2 kb and fo₂ = QFM+3.



Fig. A4.4 (continued)



Fig. A4.4 (continued)



Fig. A4.4 (continued)



Fig. A4.5 Major oxide variation diagrams vs. MgO for BOIC basalts, diabases, andesites, plagiogranites and fine-grained intrusive dikes, as well as modeled LLDs for fractional crystallization derived from a primitive BOIC diabase BMD 1009B (yellow stars) using rhyolite-MELTS at various redox conditions (fo₂ = QFM-1, 0, +1, +2 and +3, and Hm-Mt buffer) to simulate supra-subduction zone environment where magmas can exist from relatively reduced to highly oxidizing condition. (a-f) P = 0.7 kb and $H_2O = 0.2$ wt.%, (g-l) P = 0.7 kb and $H_2O = 3$ wt.%, (m-r) P = 2 kb and $H_2O = 0.2$ wt.%, and (s-x) P = 2 kb and $H_2O = 3$ wt.%.


Fig. A4.5 (continued)



Fig. A4.5 (continued)



Fig. A4.5 (continued)



Fig. A4.6 The three selected best-fit LLDs by crystal fractionation and their conditions of 1) P = 0.7 kb, fo₂ = QFM0 and H₂O = 0.3 wt.% (blue lines), 2) P = 2 kb, fo₂ = QFM0 and H₂O = 0.3 wt.% (black lines), and 3) P = 2 kb, fo₂ = QFM+3 and H₂O = 3 wt.% (orange lines) for reproducing BOIC sample trends for major oxide variations vs. MgO, together with BOIC basalts, diabases, andesites, plagiogranites and fine-grained intrusive dikes. The LLDs for fractional crystallizations were modeled using rhyolite-MELTS. Note the former two low-water, slightly reduced conditions are necessary to reproduce the overall variation trends and particularly those basaltic and trondhjemitic compositions observed in BOIC samples (blue and black lines), whereas the latter high-pressure, highly oxidizing condition is required to reproduce diorite compositions (orange lines). However, in specific of Al₂O₃ composition in (d), late-stage melts calculated with the former two conditions (blue and black line) are consistently lower than BOIC felsic samples whereas the LLD produced under the latter condition (orange line) fails to match the basaltic and andesitic sample trend, together suggesting that single-stage fractional crystallization is unlikely the way to produce the overall sample trends from basaltic to felsic determined by the majority of BOIC samples.



Fig. A4.7 Cumulative percentage of main fractionated solid phases in the three selected best-fit conditions of (a) P = 0.7 kb, fo₂ = QFM0 and H₂O = 0.3 wt.%, (b) P = 2 kb, fo₂ = QFM0 and H₂O = 0.3 wt.%, and (c) P = 2 kb, fo₂ = QFM+3 and H₂O = 3 wt.%. Dashed lines with question marks indicate estimated appearance of pargasitic amphibole by Carter (1985) at ~2.97 wt.% MgO (also ~57 wt.% SiO₂). Red dashed line of 52 wt.% SiO₂ marks the composition transition from basaltic to basaltic andesitic. The BOIC cumulate assemblage is dominated by the sequence of olivine, plagioclase and clinopyroxene (e.g., Casey, 1980; Elthon et al., 1982, 1984; Komor et al., 1985, 1987; Komor and Elthon, 1990) indicating that highly oxidizing environment represented by (c) is unlikely the way to produce the BOIC lower ophiolitic sections.





Fig. A4.8 Trace element modeling results of La, Sm, Y, Zr and Th vs. MgO, as well as La/Sm vs. La for the three selected best-fit single-stage Rayleigh fractionation models derived from a primitive BOIC diabase BMD 1009B (yellow star). Note modeling results calculated from the three selected conditions appear to match some of the BOIC sample trends, but the significant mismatches of the major elements suggest that single-stage Rayleigh fractionation still fails (Fig. A4.6).



The Three Selected Best-Fit Rayleigh Fractional Crystallization (FX) Models





Fig. A4.9 N-MORB normalized (Sun and McDonough, 1989) extended REE diagrams without fluid-mobile elements showing the three selected best-fit fractional crystallization modeling results (shaded grey areas) derived from the BOIC primitive diabase BMD 1009B (black solid line) at runs of (a) P = 0.7 kb, fo₂ = QFM0, H₂O = 0.3 wt.%, (b) P = 2 kb, fo₂ = QFM0, H₂O = 0.3 wt.%, and (c) P = 2 kb, fo₂ = QFM+3, H₂O = 3 wt.%. Trace elements presented for each sample are measured by QQQ-ICP-MS in this study. Dashed lines within the shaded areas indicate the first modeling melt produced that mimics the variation patterns of the BOIC samples. Note that in (c), no negative Eu anomalies were produced during modeling, suggesting melt with lower initial water content is the preferable source for producing BOIC plagiogranites and their fine-grained dike equivalents. However, major element modeling results indicate that the three models all fail to reproduce the overall sample trends.





Fig. A4.10 Major oxide variation diagrams vs. MgO for BOIC basalts, diabases, andesites, plagiogranites and fine-grained intrusive dikes, as well as the modeled LLDs (colored lines) for subsequent shallow (0.7 kb) fractional crystallization (FX) starting from various FLRs (fluid remaining) of 20%, 30%, 40%, 50%, 60% and 70%. The starting FLRs used for FX modeling are calculated from fractionally crystallizing a primitive BOIC diabase BMD 1009B (black lines) at P = 2 kb, fo₂ = QFM0 and H₂O = 0.3 wt.%. Note that even though a variety of FLRs has been used as stating compositions, all these subsequent LLDs modeled at shallow depth (0.7 kb) are indistinguishable from each other. Particularly as shown in (d), the late-stage melts calculated show consistently lower Al₂O₃ contents than those of BOIC felsic samples.



Fig. A4.11 Major oxide variation diagrams vs. MgO for BOIC basalts, diabases, andesites, plagiogranites and fine-grained intrusive dikes, as well as the modeled LLDs (colored lines) for the following shallower (1.4 kb) equilibrium crystallization (EX) starting from various FLRs (fluid remaining) of 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90%. Note that the starting FLRs used for each EX modeling are calculated from fractionally crystallizing a primitive BOIC diabase BMD 1009B (black lines) at P = 2 kb, fo₂ = QFM0 and H₂O = 0.3 wt.% that can reproduce most of the BOIC basaltic compositions (see the black lines). Starting from different FLRs (> ~30%), a wide range of melt compositions can be produced particularly at relatively late differentiation stage that bracket most of the felsic BOIC samples. It is notable that the enrichments of Al₂O₃ observed in BOIC felsic samples are successfully reproduced by the equilibrium fractionation that cannot be fulfilled by a single or a combination of multiple fractional crystallization processes.



Fig. A4.12 Selected trace element modeling results of La, Sm, Y, Zr and Th vs. MgO, as well as La/Sm vs. La for the 2-stage and 3-stage Rayleigh and equilibrium fractionation models derived from a primitive BOIC diabase BMD 1009B (yellow star). Modeling results calculated from the two models both match well with the BOIC sample trends, but late-stage fractional crystallization is required to account for those highly evolved trondhjemite compositions. Note both La and Y in BOIC samples show an overall steadily increasing trend with decreasing MgO (i.e., towards higher differentiation degree) also indicating that fractionation is the dominant process (see Brophy, 2008, 2009).







	NA-S01-	NA-S02-	NA-S03-	NA-S04-	NA-S05-	NA-S06-
	17Y	17Y	17Y	17Y	17Y	17Y
Lat. (°)	49.20633	49.20635	49.20638	49.20643	49.20644	49.20648
Long. (°)	-58.03138	-58.03141	-58.03138	-58.03139	-58.03141	-58.03143
Major elem	ents (wt.%)					
SiO ₂	57.58	59.43	57.08	49.09	49.73	49.07
TiO ₂	0.97	1.14	1.11	1.13	1.33	1.16
Al ₂ O ₃	18.57	16.78	18.00	16.80	15.57	18.27
$Fe_2O_3(t)$	8.46	9.21	9.25	10.30	10.41	12.62
MnO	0.18	0.22	0.17	0.21	0.20	0.21
MgO	3.33	3.56	3.39	6.15	6.13	4.41
CaO	4.32	3.74	4.67	11.72	9.96	8.56
Na ₂ O	2.36	2.81	2.07	2.80	3.80	3.80
K ₂ O	3.94	3.16	3.57	1.18	1.26	1.57
P2O5	0.15	0.27	0.21	0.11	0.18	0.18
Total	99.86	100.31	99.51	99.47	98.56	99.84
LOI	1.88	2.49	2.05	1.60	1.33	1.89
Trace element	nts (ppm)					
Li	53.9	57.7	66.2	21.5	15.7	48.7
Be	2.41	1.98	2.41	0.883	1.07	0.491
В	44.3	16.3	50.7	15.0	20.2	17.2
Sc	24.2	22.7	26.9	36.9	15.5	44.5
V	126	198	131	192	251	192
Cr	172	111	127	811	161	1188
Co	28.8	32.3	30.7	58.8	45.2	81.4
Ni	64	63	55	250	107	283
Cu	71.8	102	61.2	83.8	55.0	53.0
Zn	108	116	109	65.3	79.6	90.7
Ga	25.2	22.6	24.4	15.3	15.3	18.2
Ge	1.97	1.77	1.71	1.18	0.721	1.15
As	0.495	0.618	0.638	3.22	0.730	13.0
Se	0.373	1.03	0.272	0.211	0.122	0.190
Rb	125	93.1	112	27.0	10.9	24.4
Sr	231	261	230	272	86	326
Y	29.8	30.9	32.4	23.8	8.00	27.3
Zr	145	156	151	64.6	94.4	55.8
Nb	14.0	17.4	14.1	2.48	6.40	1.02

Table A5.1 Major and trace elements of the 17 metamorphic sole samples

	NA-S01-	NA-S02-	NA-S03-	NA-S04-	NA-S05-	NA-S06-
	17Y	17Y	17Y	17Y	17Y	17Y
Lat. (°)	49.20633	49.20635	49.20638	49.20643	49.20644	49.20648
Long. (°)	-58.03138	-58.03141	-58.03138	-58.03139	-58.03141	-58.03143
Trace element	nts (ppm)					
Mo	1.75	3.48	1.55	0.102	0.724	0.058
Ag	0.098	0.131	0.076	0.058	0.066	0.019
Cd	0.183	0.528	0.149	0.221	0.442	0.141
In	0.129	0.102	0.125	0.079	0.067	0.068
Sn	2.65	1.83	2.43	0.796	1.06	0.641
Sb	0.061	0.032	0.067	0.262	0.113	0.454
Cs	5.42	4.48	5.18	0.761	0.237	1.21
Ba	789	825	784	539	369	306
La	41.0	38.9	38.4	3.43	2.55	2.05
Ce	89.3	86.1	83.0	10.9	6.72	5.53
Pr	10.2	9.72	9.55	1.55	0.873	1.13
Nd	39.1	38.0	37.2	8.43	4.11	6.98
Sm	7.44	7.53	7.37	2.82	1.15	2.76
Eu	1.60	1.57	1.70	1.36	0.437	1.07
Gd	6.44	6.69	6.57	3.72	1.37	3.96
Tb	0.967	1.00	0.999	0.652	0.232	0.720
Dy	5.60	5.86	5.84	4.21	1.47	4.69
Но	1.12	1.17	1.19	0.878	0.313	1.02
Er	3.07	3.22	3.26	2.44	0.87	2.90
Tm	0.449	0.467	0.472	0.360	0.129	0.428
Yb	3.04	3.09	3.08	2.30	0.794	2.76
Lu	0.435	0.456	0.448	0.337	0.120	0.407
Hf	3.81	4.05	4.04	1.76	2.43	1.76
Та	0.890	1.13	0.889	0.166	0.346	0.109
W	0.818	0.685	0.798	0.236	0.299	0.186
T1	0.950	0.680	0.781	0.235	0.200	0.156
Pb	22.1	22.4	21.7	2.23	6.50	0.555
Th	12.3	10.7	10.8	0.291	0.372	0.058
U	2.74	4.30	2.50	0.144	0.760	0.144

Table A5.1 (continued)

	NA-S07-	NA-S08-	NA-S09-	NA-S10-	NA-S11-	NA-S12-
Let $(^{\circ})$	1 / Y 40 20651	1 / Y 40 20652	1 / Y 40 20652	1 / Y 40 20657	1 / Y 40 20661	1 / Y 40 20662
Lat. () Long $(^{\circ})$	49.20031 58.02142	49.20032	49.20033	49.20037	49.20001 58.03144	49.20002
Major eleme	-38.03143	-38.03148	-38.03148	-38.03143	-38.03144	-38.03144
SiO2	50.25	40.51	51 44	53.06	50.70	40.71
31O ₂	1.27	49.31	1 47	1.46	1.07	49.71
1102	1.37	0.94	1.47	1.46	1.27	1.00
Al ₂ O ₃	18.20	17.34	17.29	14.35	15.45	15.12
$Fe_2O_3(t)$	11.07	10.31	11.45	11.41	9.95	10.65
MnO	0.19	0.19	0.20	0.23	0.19	0.20
MgO	4.14	6.62	4.38	6.10	4.88	7.77
CaO	9.09	10.28	5.88	8.70	3.61	11.17
Na ₂ O	4.47	2.93	4.85	2.43	3.43	2.43
K ₂ O	0.82	1.70	1.49	1.75	1.58	1.25
P2O5	0.21	0.11	0.23	0.18	0.34	0.12
Total	99.81	99.92	98.66	99.67	100.40	99.40
LOI	2.83	1.84	1.99	1.44	3.56	1.41
Trace element	nts (ppm)					
Li	57.3	23.9	38.0	21.7	64.7	19.5
Be	0.589	0.527	0.773	1.36	1.66	0.812
В	6.62	12.3	12.7	14.1	25.4	19.1
Sc	41.7	34.7	44.5	38.5	25.2	30.2
V	202	192	208	272	265	185
Cr	531	853	338	191	202	961
Co	57.7	58.3	53.4	41.8	33.7	61.8
Ni	181	232	112	79	90	351
Cu	100	88.4	97.9	32.1	95.2	97.0
Zn	80.0	65.7	85.4	92.4	130	72.9
Ga	17.7	14.9	18.2	17.4	20.9	14.9
Ge	1.26	0.990	1.30	1.28	1.70	0.963
As	8.15	3.30	2.52	2.13	0.541	2.89
Se	0.315	0.073	0.291	0.193	1.49	0.087
Rb	12.4	37.2	30.5	38.7	37.2	32.4
Sr	343	214	260	214	245	200
Y	31.5	23.7	33.0	29.3	32.4	22.4
Zr	93.3	47.1	108	96.0	149	45.8
Nb	4.10	1.26	5.25	7.38	16.5	1.46

Table A5.1 (continued)

	NA-S07-	NA-S08-	NA-S09-	NA-S10-	NA-S11-	NA-S12-
	17Y	17Y	17Y	17Y	17Y	17Y
Lat. (°)	49.20651	49.20652	49.20653	49.20657	49.20661	49.20662
Long. (°)	-58.03143	-58.03148	-58.03148	-58.03143	-58.03144	-58.03144
Trace elemer	nts (ppm)					
Mo	0.123	0.119	0.958	0.854	5.06	0.156
Ag	0.049	0.074	0.068	0.069	0.17	0.062
Cd	0.161	0.242	0.340	0.391	0.978	0.287
In	0.089	0.055	0.106	0.104	0.101	0.076
Sn	1.05	0.705	1.32	1.66	2.17	0.762
Sb	0.551	0.222	0.174	0.126	0.041	0.429
Cs	1.02	0.788	0.775	0.951	1.29	0.836
Ba	147	770	531	896	1057	501
La	5.06	3.33	8.73	9.99	31.5	3.37
Ce	14.5	8.82	21.4	24.7	71.3	6.73
Pr	2.19	1.17	3.15	3.19	8.07	1.07
Nd	11.4	6.65	15.1	14.6	32.2	6.31
Sm	3.60	2.44	4.29	3.98	6.65	2.37
Eu	1.34	1.06	1.37	1.57	1.58	1.24
Gd	4.54	3.44	5.17	4.78	6.31	3.39
Tb	0.786	0.615	0.888	0.812	0.971	0.605
Dy	5.07	4.06	5.63	5.20	5.87	3.94
Но	1.12	0.880	1.20	1.09	1.17	0.844
Er	3.12	2.51	3.41	3.14	3.32	2.40
Tm	0.459	0.371	0.495	0.470	0.493	0.358
Yb	2.94	2.34	3.15	2.99	3.21	2.29
Lu	0.433	0.353	0.470	0.451	0.473	0.340
Hf	2.38	1.50	2.75	2.63	3.80	1.50
Та	0.362	0.155	0.401	0.550	1.04	0.139
W	0.261	0.241	0.244	0.573	0.815	0.517
Tl	0.116	0.241	0.205	0.260	0.272	0.282
Pb	2.84	2.65	4.08	11.3	17.1	3.39
Th	0.369	0.193	1.60	1.90	8.54	0.166
U	0.161	0.083	1.08	1.12	5.80	0.151

Table A5.1 (continued)

	NA-S13- 17Y	NA-S14- 17Y	NA-S17- 17Y	NA-S18- 17Y	NA-S19- 17Y
Lat. (°)	49.20662	49.20662	49.20711	49.20713	49.20713
Long. (°)	-58.03159	-58.03159	-58.03045	-58.03043	-58.03043
Major eleme	nts (wt.%)				
SiO ₂	54.29	54.06	54.18	53.74	51.43
TiO ₂	1.10	0.90	0.29	0.33	1.12
Al ₂ O ₃	15.50	23.25	13.16	14.34	18.21
$Fe_2O_3(t)$	9.00	3.98	6.54	6.20	7.68
MnO	0.19	0.08	0.13	0.13	0.11
MgO	6.44	2.00	11.59	11.12	7.77
CaO	8.47	10.35	11.54	10.25	9.25
Na ₂ O	4.16	5.39	2.47	2.21	2.96
K ₂ O	0.97	0.29	0.69	1.68	1.86
P_2O_5	0.11	0.16	0.04	0.03	0.13
Total	100.22	100.47	100.62	100.04	100.54
LOI	1.21	1.73	1.42	1.60	2.11
Trace element	nts (ppm)				
Li	10.5	15.3	13.8	11.7	22.3
Be	0.796	0.541	0.472	0.830	0.520
В	16.5	4.65	8.12	16.1	55.0
Sc	32.2	8.21	37.3	48.1	15.3
V	209	83.7	174	171	202
Cr	264	99	1128	722	150
Co	36.3	17.7	40.3	37.5	36.7
Ni	53	32	187	179	103
Cu	12.8	5.31	17.1	2.18	39.0
Zn	64.4	25.4	40.3	43.3	37.8
Ga	14.1	21.8	9.04	11.2	13.2
Ge	0.972	0.463	0.648	0.811	0.559
As	0.655	4.40	0.421	0.423	0.490
Se	0.047	0.102	0.014	0.022	0.030
Rb	23.6	6.18	14.2	54.2	22.5
Sr	299	279	108	282	162
Y	25.7	6.61	8.79	16.2	4.92
Zr	78.1	42.9	4.50	16.4	66.3
Nb	2.89	2.76	1.05	2.39	6.16

Table A5.1 (continued)

	NA-S13-	NA-S14-	NA-S17-	NA-S18-	NA-S19-
	17Y	17Y	17Y	17Y	17Y
Lat. (°)	49.20662	49.20662	49.20711	49.20713	49.20713
Long. (°)	-58.03159	-58.03159	-58.03045	-58.03043	-58.03043
Trace element	nts (ppm)				
Mo	0.181	0.058	BDL	0.012	0.119
Ag	0.032	0.082	0.009	0.010	0.052
Cd	0.193	0.055	0.211	0.439	0.200
In	0.081	0.035	0.050	0.098	0.058
Sn	1.29	0.541	0.735	0.975	0.696
Sb	0.083	0.720	0.129	0.084	0.088
Cs	1.60	0.085	0.463	1.93	0.294
Ba	654	61.2	81.1	207	95.8
La	4.26	5.38	1.34	7.42	2.10
Ce	12.7	11.1	3.00	18.7	8.13
Pr	1.86	1.21	0.445	2.45	0.740
Nd	9.62	4.97	2.31	10.0	3.44
Sm	3.16	1.15	0.863	2.45	0.914
Eu	1.19	1.04	0.427	0.731	0.353
Gd	4.07	1.27	1.31	2.59	1.02
Tb	0.711	0.198	0.233	0.447	0.158
Dy	4.54	1.16	1.58	2.87	0.970
Но	0.975	0.228	0.340	0.584	0.187
Er	2.75	0.610	0.959	1.64	0.506
Tm	0.406	0.081	0.138	0.245	0.071
Yb	2.64	0.534	0.921	1.56	0.431
Lu	0.395	0.075	0.133	0.222	0.065
Hf	2.15	1.13	0.234	0.542	1.61
Та	0.281	0.351	0.228	0.219	0.353
W	0.257	0.689	0.196	0.235	0.271
Tl	0.132	0.046	0.150	0.341	0.319
Pb	7.83	19.8	3.89	6.88	4.19
Th	0.955	0.476	0.279	0.799	0.150
U	0.583	0.159	0.660	0.560	0.134

Table A5.1 (continued)

Table A5.1 (continued	(1
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	SCO-1								
	Chec	k standa	rd (N=4)						
	Ref.	Ave.	RSD (%)						
Major eleme	ents (wt.%))							
SiO ₂	68.622	69.20	0.37						
TiO ₂	0.686	0.66	1.29						
Al ₂ O ₃	14.942	14.48	0.68						
$Fe_2O_3(t)$	5.618	5.41	0.21						
MnO	0.058	0.06	1.42						
MgO	2.973	2.85	0.82						
CaO	2.864	2.73	0.39						
Na ₂ O	0.984	0.91	1.12						
K ₂ O	3.028	2.97	0.55						
P_2O_5	0.225	0.23	1.35						
Total	100.00	99.49							
LOI		6.86							
Trace eleme	nts (ppm)								
Li	45	47.0	2.56						
Be	1.84	1.81	4.00						
В	72	75.7	14.90						
Sc	10.8	12.6	3.87						
V	131	134	1.15						
Cr	68	68.8	2.00						
Co	10.5	11.8	2.13						
Ni	27	28.0	1.84						
Cu	28.7	28.8	1.73						
Zn	103	110	1.90						
Ga	15	17.9	1.53						
Ge	1	1.24	7.35						
As	12.4	13.0	1.46						
Se	0.89	1.08	7.76						
Rb	112	117	1.71						
Sr	174	170	0.32						
Y	26	24.1	1.67						
Zr	160	182	1.62						
Nb	11	12.0	1.28						

	SCO-1									
	Che	ck standa	urd (N=4)							
	Ref.	Ave.	RSD (%)							
Trace eleme	nts (ppm))								
Mo	1.37	1.01	3.44							
Ag	0.134	0.158	6.33							
Cd	0.14	0.276	4.53							
In	0.11	0.096	10.18							
Sn	3.7	3.56	1.40							
Sb	2.5	2.69	6.91							
Cs	7.8	8.50	4.45							
Ba	570	600	1.10							
La	29.5	30.5	1.70							
Ce	62	62.3	1.33							
Pr	6.6	7.23	1.18							
Nd	26	27.9	0.95							
Sm	5.3	5.44	1.00							
Eu	1.19	1.21	1.42							
Gd	4.6	4.76	0.75							
Tb	0.7	0.712	1.10							
Dy	4.2	4.17	0.84							
Но	0.97	0.851	0.91							
Er	2.5	2.42	1.12							
Tm	0.42	0.366	1.20							
Yb	2.27	2.44	1.06							
Lu	0.34	0.368	0.91							
Hf	4.6	4.84	1.76							
Та	0.92	0.784	3.18							
W	1.4	1.38	10.64							
Tl	0.72	0.792	5.51							
Pb	31	35.5	1.10							
Th	9.7	9.64	1.25							
U	3	3.09	1.81							

Table A5.1 (continued)

A		Isotopic ratios						Isotopic Ages (Ma)				
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s %	²⁰⁷ Pb/ ²³⁵ U	2s %	²⁰⁶ Pb/ ²³⁸ U	2s %	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
B_01	0.05355	15.99581	0.57679	16.14796	0.07812	6.59291	352.06	361.44	484.91	30.80	462.40	60.05
B_05	0.05628	9.99825	0.59228	9.20533	0.07632	5.03660	463.58	221.56	474.12	23.02	472.32	34.78
B_07	0.06308	28.13054	0.68084	30.21477	0.07828	8.24442	711.06	597.96	485.82	38.58	527.28	124.90
B_100	0.05823	12.08390	0.65152	11.69244	0.08115	5.29388	538.46	264.36	502.97	25.61	509.41	46.87
B_12	0.05236	12.14344	0.58118	12.10586	0.08050	4.55729	301.10	276.89	499.13	21.89	465.22	45.21
B_13	0.05601	15.21315	0.61962	14.45981	0.08024	5.49020	452.63	337.76	497.55	26.29	489.61	56.23
B_15	0.09367	23.20523	1.04707	24.40398	0.08107	7.51295	1501.52	438.65	502.51	36.32	727.43	127.41
B_29	0.05087	14.40010	0.52870	14.01709	0.07537	4.84647	235.08	332.28	468.45	21.90	430.94	49.26
B_32	0.05718	18.96920	0.65830	17.47035	0.08350	7.48077	498.51	417.83	516.97	37.16	513.58	70.53
B_37	0.06014	34.46648	0.60974	41.46422	0.07354	8.90379	608.49	745.17	457.43	39.32	483.40	160.81
B_38	0.04042	26.88089	0.44872	26.19175	0.08052	6.61391	-324.10	690.39	499.21	31.77	376.38	82.55
B_42	0.08084	14.72857	0.88150	13.78153	0.07909	6.38476	1217.45	289.62	490.69	30.17	641.79	65.65
B_44	0.03647	43.27529	0.42707	46.00584	0.08492	7.57918	-595.25	1175.27	525.42	38.24	361.09	140.69
B_50	0.06082	13.46389	0.69070	14.38701	0.08236	7.86700	632.91	289.91	510.22	38.59	533.22	59.75
B_52	0.05520	25.07004	0.59730	24.15313	0.07848	8.72221	420.17	559.74	487.07	40.92	475.52	91.96
B_53	0.11631	44.10757	1.22572	45.61143	0.07644	15.83059	1900.19	792.78	474.81	72.47	812.39	260.63
B_54	0.06604	16.52436	0.74591	15.28176	0.08192	9.38561	807.56	345.81	507.58	45.81	565.85	66.39
B_56	0.06209	23.99523	0.69280	23.29626	0.08092	9.84277	677.33	512.88	501.62	47.50	534.48	97.10
B_58	0.10645	18.75668	1.13373	16.95491	0.07725	9.71324	1739.41	343.82	479.67	44.90	769.53	91.72
B_61	0.09363	18.97968	0.96426	18.38881	0.07469	8.66141	1500.65	358.82	464.37	38.81	685.50	91.91
B_62	0.06012	18.06673	0.67963	18.15855	0.08199	7.40337	607.88	390.64	507.98	36.16	526.55	74.74
B_64	0.07786	43.05221	0.88447	46.16229	0.08239	9.06684	1143.28	855.77	510.37	44.49	643.40	223.54
B_65	0.09363	20.03061	1.04949	18.38881	0.08130	8.23112	1500.61	378.69	503.86	39.89	728.63	95.90
B_66	0.04928	20.03061	0.55992	19.60248	0.08241	6.92917	161.02	468.50	510.50	34.01	451.48	71.56
B_69	0.06110	26.60349	0.68650	26.38280	0.08149	8.10400	642.84	571.89	504.99	39.36	530.70	109.47
B_70	0.06012	19.15605	0.67882	17.11735	0.08190	9.95680	607.77	414.20	507.42	48.59	526.06	70.39
B_73	0.06701	21.47097	0.76393	20.55454	0.08268	8.06399	838.17	447.15	512.09	39.70	576.28	90.63

Table A5.2 LA-ICP-MS U-Pb depth profiling of sample B.12.7.2F. Integration interval: 0-38 s

Table A5.2 (continued)

		Isotopic ratios					Isotopic Ages (Ma)					
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s %	²⁰⁷ Pb/ ²³⁵ U	2s %	²⁰⁶ Pb/ ²³⁸ U	2s %	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
B_78	0.06898	17.30652	0.78024	15.82713	0.08203	7.90602	898.19	357.03	508.25	38.64	585.62	70.55
B_79	0.05321	31.57090	0.59543	30.35645	0.08115	9.67913	337.94	715.17	503.00	46.84	474.33	115.53
B_80	0.07884	13.95351	0.81574	12.79362	0.07505	7.68558	1168.00	276.36	466.48	34.59	605.67	58.43
B_81	0.05912	28.59558	0.60600	28.11377	0.07434	8.66457	571.70	622.07	462.23	38.65	481.03	108.12
B_82	0.06405	20.36981	0.78484	18.98903	0.08887	8.57456	743.34	430.72	548.84	45.11	588.24	84.98
B_87	0.06701	23.57796	0.71341	22.04910	0.07722	8.42543	837.95	491.05	479.51	38.93	546.77	93.48
B_89	0.03843	33.36762	0.41885	34.29548	0.07905	7.82665	-455.50	880.22	490.44	36.96	355.23	103.15
B_90	0.07292	35.16767	0.79968	34.55515	0.07954	7.90736	1011.65	712.93	493.38	37.56	596.65	157.15
B_91	0.06109	25.90521	0.66699	25.41095	0.07918	8.31311	642.45	556.91	491.25	39.32	518.88	103.60
B_92	0.06109	21.08917	0.66662	21.18439	0.07914	6.86067	642.44	453.38	490.99	32.43	518.66	86.24
B_93	0.07193	20.67184	0.71553	20.21601	0.07215	6.64139	983.94	420.84	449.08	28.81	548.02	85.82
B_95	0.05577	16.23579	0.60755	17.05456	0.07901	6.07091	443.20	361.05	490.22	28.66	482.02	65.54
B_96	0.06503	15.46869	0.70680	14.99840	0.07883	6.26133	775.32	325.40	489.12	29.49	542.85	63.15
B_97	0.07587	18.42873	0.73631	17.77326	0.07039	6.74855	1091.60	369.13	438.49	28.61	560.25	76.68

A 1 · //			Isotopic	ratios				Isotopic Ages (Ma)				
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s %	²⁰⁷ Pb/ ²³⁵ U	2s %	²⁰⁶ Pb/ ²³⁸ U	2s %	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
NA13_03	0.31416	26.80837	4.30232	22.77459	0.09932	20.85428	3541.47	413.13	610.44	121.48	1693.81	189.82
NA13_04	0.24819	24.40467	3.62360	21.23862	0.10589	22.24814	3173.28	386.72	648.82	137.35	1554.73	170.60
NA13_05	0.21201	24.62642	2.53743	24.82300	0.08680	27.11977	2920.95	398.57	536.61	139.66	1282.83	182.74
NA13_08	0.47847	31.64670	14.40246	60.01866	0.21831	43.53683	4176.23	468.22	1272.95	503.94	2776.59	644.37
NA13_09	0.06367	25.62489	0.76949	23.61469	0.08765	30.32707	730.66	542.96	541.65	157.59	579.47	104.64
NA13_10	0.24792	33.08384	3.08191	29.66701	0.09016	16.22681	3171.55	524.32	556.47	86.51	1428.20	231.36
NA13_11	0.07162	10.02549	0.73885	14.26136	0.07482	15.18821	975.27	204.37	465.11	68.16	561.73	61.61
NA13_14	0.18840	22.70806	2.98983	35.56046	0.11509	47.83912	2728.29	373.94	702.26	318.56	1405.03	277.27
NA13_17	0.30075	43.42544	3.79765	41.05182	0.09158	25.47997	3474.07	672.47	564.89	137.83	1592.25	342.36
NA13_19	0.05425	7.73094	0.63931	11.75508	0.08548	10.91736	381.26	173.79	528.73	55.42	501.88	46.58

Table A5.3 LA-ICP-MS U-Pb depth profiling of sample NA-S13-17Y. Integration interval: 0-2 s

Analysis #		Isotopic ratios							Isotopic Ages (Ma)						
	²⁰⁷ Pb/ ²⁰⁶ Pb	2s %	²⁰⁷ Pb/ ²³⁵ U	2s %	²⁰⁶ Pb/ ²³⁸ U	2s %	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s			
NA13_03	0.18031	8.13686	2.33160	8.25973	0.09379	9.70520	2655.70	134.91	577.89	53.65	1221.97	58.76			
NA13_04	0.37667	16.14688	5.78595	12.77385	0.11141	14.04242	3818.45	244.19	680.92	90.75	1944.31	111.03			
NA13_05	0.27589	16.22980	3.64517	11.64629	0.09583	11.44432	3339.81	253.85	589.90	64.52	1559.45	93.06			
NA13_08	0.22058	4.22031	3.19838	6.44744	0.10516	5.43284	2984.91	67.93	644.60	33.33	1456.77	49.91			
NA13_09	0.05762	3.89107	0.62682	5.84503	0.07889	5.67387	515.53	85.46	489.50	26.75	494.11	22.87			
NA13_10	0.07129	7.44985	0.83415	8.59838	0.08486	5.51969	965.73	152.09	525.08	27.83	615.91	39.73			
NA13_11	0.05304	4.01683	0.59781	7.45547	0.08175	6.93742	330.32	91.12	506.57	33.80	475.84	28.33			
NA13_14	0.33332	17.77998	5.00024	14.40819	0.10880	11.41766	3632.43	272.26	665.77	72.22	1819.36	122.51			
NA13_17	0.28086	13.21561	4.25924	12.27448	0.10999	9.79704	3367.74	206.27	672.66	62.58	1685.52	101.27			
NA13_19	0.05806	3.63177	0.64429	4.79685	0.08048	3.91023	532.03	79.54	499.00	18.78	504.96	19.09			

Table A5.4 LA-ICP-MS U-Pb depth profiling of sample NA-S13-17Y. Integration interval: 11-38 s

A 1 . 11		Isotopic Ages (Ma)										
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s %	²⁰⁷ Pb/ ²³⁵ U	2s %	$^{206}Pb/^{238}U$	2s %	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
NA18_01	0.06005	14.42868	0.67826	11.36437	0.08191	15.95632	605.52	312.10	507.53	77.88	525.72	46.67
NA18_02	0.06028	9.22043	0.71169	15.27884	0.08563	13.89055	613.57	199.18	529.65	70.63	545.75	64.59
NA18_03	0.06949	13.41234	0.69758	13.21771	0.07281	10.49841	913.23	276.05	453.06	45.93	537.34	55.20
NA18_04	0.05573	5.69074	0.63089	14.31698	0.08210	13.95038	441.69	126.58	508.66	68.23	496.65	56.29
NA18_05	0.06387	6.73859	0.88451	10.68807	0.10044	12.71290	737.31	142.63	616.99	74.80	643.42	50.98
NA18_06	0.05598	13.18175	0.60558	13.55910	0.07846	8.38018	451.45	292.72	486.94	39.30	480.77	51.97
NA18_07	0.05908	18.21448	0.64889	15.75590	0.07966	14.19753	570.09	396.35	494.07	67.53	507.79	63.04
NA18_08	0.05905	16.00848	0.56218	14.64221	0.06905	9.42347	568.79	348.42	430.45	39.24	452.95	53.55
NA18_09	0.05480	7.74540	0.60095	12.20073	0.07954	7.62327	403.95	173.42	493.37	36.21	477.84	46.53
NA18_10	0.05613	11.69903	0.67672	14.92864	0.08745	10.10504	457.37	259.52	540.42	52.38	524.79	61.25
NA18_11	0.06353	9.68021	0.76493	10.46157	0.08732	12.02261	726.07	205.26	539.69	62.24	576.85	46.07
NA18_14	0.05776	8.53668	0.61781	16.84682	0.07758	15.42700	520.55	187.33	481.66	71.60	488.47	65.41
NA18_16	0.05590	10.18229	0.55617	11.64034	0.07216	19.42598	448.36	226.23	449.16	84.29	449.03	42.27
NA18_17	0.05432	8.10358	0.66431	8.92639	0.08870	10.16712	384.25	182.07	547.85	53.40	517.25	36.19
NA18_18	0.05750	7.03204	0.66720	7.45103	0.08416	11.52440	510.65	154.57	520.91	57.67	519.01	30.29
NA18_19	0.05534	18.56484	0.63892	12.08538	0.08374	22.24240	425.80	414.09	518.42	110.81	501.64	47.87
NA18_20	0.06230	10.12281	0.61220	13.41558	0.07127	12.63873	684.33	216.12	443.82	54.21	484.95	51.77
NA18_21	0.06103	17.72562	0.75465	11.93873	0.08969	16.99609	640.14	381.21	553.69	90.18	570.92	52.18
NA18_22	0.05732	9.72866	0.59641	5.16523	0.07547	8.31766	503.69	214.10	469.03	37.63	474.95	19.60
NA18_23	0.05313	9.10941	0.52612	7.35122	0.07182	8.52949	334.21	206.49	447.14	36.85	429.23	25.74
NA18_25	0.05579	9.35444	0.53524	9.58983	0.06958	9.85142	444.06	207.99	433.63	41.31	435.28	33.96
NA18_26	0.05692	9.46278	0.68956	6.46914	0.08787	9.27976	488.27	208.80	542.92	48.32	532.53	26.81
NA18_27	0.05526	13.53654	0.68640	15.68383	0.09010	20.72138	422.57	302.11	556.10	110.41	530.64	64.91
NA18_28	0.05639	17.22979	0.63608	15.56351	0.08181	9.63778	467.88	381.52	506.89	46.98	499.88	61.51
NA18_29	0.05502	15.47047	0.66644	15.06779	0.08785	14.76778	413.16	345.83	542.78	76.88	518.55	61.26
NA18_30	0.06031	16.68555	0.59123	18.05940	0.07110	11.75382	614.54	360.38	442.81	50.30	471.65	68.24
NA18_31	0.06243	18.95021	0.67765	20.24944	0.07872	28.12624	688.89	404.28	488.50	132.34	525.35	83.24

Table A5.5 LA-ICP-MS U-Pb depth profiling of sample NA-S18-17Y. Integration interval: 0-2 s

Table A5.5 (continued)

			Isotopic	ratios			Isotopic Ages (Ma)					
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s %	²⁰⁷ Pb/ ²³⁵ U	2s %	²⁰⁶ Pb/ ²³⁸ U	2s %	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
NA18_32	0.05808	14.36487	0.65660	17.53174	0.08199	25.57171	532.74	314.56	508.01	124.94	512.53	70.67
NA18_34	0.05535	11.93161	0.70747	18.72988	0.09269	26.12562	426.58	266.10	571.45	142.89	543.24	78.96
NA18_35	0.05582	15.03579	0.65382	18.41925	0.08495	26.34127	445.25	334.24	525.60	132.97	510.83	74.07
NA18_36	0.06015	8.76459	0.69284	20.21053	0.08355	24.49170	608.83	189.48	517.26	121.75	534.51	84.18
NA18_37	0.05572	8.25130	0.59738	24.21863	0.07776	30.21605	441.13	183.56	482.74	140.56	475.57	92.22
NA18_38	0.05388	8.69433	0.54073	20.90021	0.07278	22.24702	366.19	195.97	452.89	97.30	438.90	74.61
NA18_40	0.05654	7.63283	0.62100	19.54969	0.07965	22.96534	473.79	168.84	494.05	109.23	490.47	76.19
NA18_43	0.05543	12.83608	0.59581	26.01114	0.07796	17.16522	429.50	286.13	483.95	80.03	474.57	98.92
NA18_44	0.05427	12.82689	0.58254	22.10161	0.07785	13.71784	382.27	288.30	483.29	63.87	466.09	82.79
NA18_45	0.05369	10.83099	0.63740	21.29420	0.08611	13.94115	357.96	244.48	532.47	71.25	500.70	84.36
NA18_46	0.05383	12.14078	0.64358	15.08318	0.08671	10.12599	364.06	273.75	536.04	52.08	504.52	60.04
NA18_47	0.05536	7.93088	0.56156	8.96860	0.07357	9.36216	426.66	176.87	457.65	41.36	452.54	32.76
NA18_48	0.05449	13.81239	0.61128	12.35052	0.08136	14.61049	391.38	309.95	504.24	70.87	484.36	47.61
NA18_49	0.05448	10.13682	0.55706	10.02730	0.07415	11.39144	391.12	227.48	461.13	50.70	449.61	36.44
NA18_50	0.05782	12.11674	0.61158	15.09765	0.07671	19.93378	523.12	265.77	476.44	91.55	484.56	58.24
NA18_52	0.05647	9.21537	0.56540	11.62086	0.07262	12.22945	470.77	203.96	451.93	53.38	455.03	42.64
NA18_53	0.05895	13.29835	0.65819	20.19022	0.08098	12.26438	565.17	289.61	501.97	59.23	513.50	81.55
NA18_54	0.05961	11.73187	0.85559	13.83377	0.10409	6.82174	589.59	254.45	638.34	41.46	627.71	64.85
NA18_55	0.06582	13.95036	0.66943	23.11677	0.07376	12.50884	800.70	292.27	458.79	55.40	520.37	94.39
NA18_56	0.05703	10.25009	0.70913	14.24547	0.09019	16.94409	492.60	226.00	556.64	90.37	544.23	60.08
NA18_57	0.05502	14.83361	0.68845	9.61041	0.09075	14.87994	413.13	331.60	559.96	79.81	531.87	39.81
NA18_58	0.05120	10.78057	0.64382	11.93903	0.09120	17.45351	249.94	248.09	562.61	94.04	504.67	47.51
NA18_59	0.05436	11.52044	0.55990	13.15621	0.07471	20.08168	385.82	258.77	464.45	89.99	451.46	47.98
NA18_61	0.05571	11.35890	0.52869	27.75843	0.06883	21.44238	440.65	252.71	429.13	89.02	430.94	97.78
NA18_62	0.05428	11.36791	0.65025	29.56771	0.08689	25.97087	382.50	255.49	537.13	133.86	508.63	118.84
NA18_63	0.05399	15.91645	0.61911	33.24034	0.08316	23.43302	370.74	358.46	514.98	115.99	489.29	129.76
NA18_64	0.05629	12.57358	0.71361	27.30688	0.09194	20.18925	463.83	278.61	567.02	109.60	546.89	115.97

Table A5.5 (continued)

Analysis #			Isotopic	ratios		Isotopic Ages (Ma)						
	²⁰⁷ Pb/ ²⁰⁶ Pb	2s %	²⁰⁷ Pb/ ²³⁵ U	2s %	²⁰⁶ Pb/ ²³⁸ U	2s %	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
NA18_65	0.05658	12.78435	0.66833	28.25639	0.08567	23.59358	475.27	282.72	529.86	120.03	519.70	115.43
NA18_66	0.05365	15.21050	0.55054	12.15267	0.07442	15.38765	356.52	343.43	462.73	68.71	445.35	43.84
NA18_67	0.05462	13.89159	0.67421	9.61055	0.08953	13.74684	396.55	311.44	552.76	72.82	523.27	39.32
NA18_68	0.05462	18.19523	0.61929	10.63744	0.08223	17.96143	396.84	407.91	509.40	87.98	489.40	41.33
NA18_69	0.06305	17.57492	0.81495	7.72064	0.09374	16.39448	709.93	373.65	577.64	90.59	605.22	35.21
NA18_70	0.05674	13.01993	0.53363	20.66224	0.06821	15.07575	481.60	287.62	425.33	62.05	434.22	73.13
A 1 . II		Isotopic Ages (Ma)										
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Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s %	²⁰⁷ Pb/ ²³⁵ U	2s %	206Pb/238U	2s %	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	²⁰⁶ Pb/ ²³⁸ U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
NA18_01	0.05703	3.21942	0.66531	8.98517	0.08461	6.28789	492.79	70.98	523.56	31.62	517.86	36.46
NA18_02	0.05862	2.91984	0.71292	9.07483	0.08821	6.47236	552.99	63.72	544.92	33.82	546.48	38.37
NA18_03	0.05641	4.34659	0.65757	4.76053	0.08455	3.44764	468.36	96.24	523.23	17.33	513.13	19.18
NA18_04	0.05650	4.06468	0.78493	5.13931	0.10076	3.84398	472.01	89.94	618.87	22.68	588.29	22.95
NA18_05	0.06029	4.76019	0.82901	7.69944	0.09973	4.58877	614.00	102.82	612.81	26.83	613.06	35.45
NA18_06	0.05845	3.26795	0.62874	3.40028	0.07802	4.47566	546.50	71.40	484.31	20.88	495.31	13.33
NA18_07	0.05854	2.94397	0.63408	2.69327	0.07856	3.70947	549.95	64.28	487.52	17.42	498.63	10.61
NA18_08	0.05663	2.54339	0.67357	2.68619	0.08626	3.44199	477.26	56.23	533.38	17.62	522.88	10.98
NA18_09	0.05613	2.56179	0.71411	3.10877	0.09228	3.46835	457.38	56.83	568.99	18.89	547.18	13.15
NA18_10	0.05562	2.58055	0.68434	2.76515	0.08924	3.24938	437.16	57.45	551.03	17.16	529.39	11.41
NA18_11	0.05729	2.51821	0.70276	3.31837	0.08897	3.06456	502.69	55.43	549.43	16.14	540.44	13.91
NA18_13	0.05538	6.52256	0.59981	4.57512	0.07856	4.76326	427.50	145.44	487.49	22.36	477.11	17.42
NA18_14	0.05717	2.60885	0.68327	3.75729	0.08669	3.61445	497.97	57.47	535.91	18.59	528.75	15.49
NA18_15	0.05716	3.07504	0.67829	3.65064	0.08606	3.04435	497.70	67.74	532.22	15.55	525.74	14.98
NA18_16	0.05672	2.93400	0.68099	3.21296	0.08707	2.33592	480.72	64.82	538.21	12.06	527.37	13.22
NA18_17	0.05791	2.73225	0.75856	4.27035	0.09500	4.01903	526.41	59.90	585.04	22.48	573.18	18.71
NA18_18	0.05671	2.93400	0.65209	3.49813	0.08340	3.43997	480.22	64.83	516.38	17.07	509.77	14.02
NA18_19	0.05700	3.23910	0.63229	3.25512	0.08045	3.82577	491.59	71.43	498.81	18.36	497.52	12.80
NA18_20	0.05769	2.89316	0.71058	3.51128	0.08933	3.56755	518.12	63.51	551.56	18.86	545.09	14.81
NA18_21	0.05578	2.50013	0.68399	4.88303	0.08894	2.97550	443.46	55.60	549.27	15.67	529.18	20.14
NA18_22	0.05806	3.50427	0.64949	5.74953	0.08113	4.56145	532.00	76.75	502.88	22.07	508.17	22.99
NA18_23	0.05576	2.81226	0.62142	5.27161	0.08083	3.27377	442.90	62.54	501.05	15.78	490.74	20.52
NA18_25	0.05695	3.07947	0.64882	5.11976	0.08264	2.56495	489.41	67.94	511.83	12.62	507.75	20.46
NA18_26	0.05472	5.76053	0.67165	7.74849	0.08902	3.80156	400.83	129.05	549.74	20.03	521.72	31.62
NA18_27	0.05710	5.79188	0.60104	8.08476	0.07634	4.42884	495.49	127.64	474.24	20.25	477.90	30.83
NA18_28	0.05577	5.51430	0.62451	7.95709	0.08121	4.47042	443.38	122.62	503.34	21.65	492.67	31.07
NA18_29	0.05699	5.65534	0.65897	7.53919	0.08386	3.65591	491.22	124.72	519.11	18.23	513.98	30.42

Table A5.6 LA-ICP-MS U-Pb depth profiling of sample NA-S18-17Y. Integration interval: 11-38 s

Table A5.6 (continued)

		Isotopic Ages (Ma)										
Analysis #	²⁰⁷ Pb/ ²⁰⁶ Pb	2s %	²⁰⁷ Pb/ ²³⁵ U	2s %	²⁰⁶ Pb/ ²³⁸ U	2s %	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	206Pb/238U	2s	²⁰⁷ Pb/ ²³⁵ U	2s
NA18_30	0.05709	5.72069	0.67675	7.74522	0.08598	4.13289	494.85	126.09	531.72	21.09	524.81	31.75
NA18_31	0.05726	7.09053	0.59131	8.07475	0.07490	5.12017	501.56	156.10	465.59	23.00	471.71	30.48
NA18_32	0.05705	7.02770	0.69659	7.56886	0.08855	4.25755	493.62	154.93	546.96	22.33	536.75	31.56
NA18_33	0.05556	6.81408	0.68161	8.06576	0.08898	4.73987	434.75	151.75	549.49	24.97	527.75	33.21
NA18_34	0.05635	6.75796	0.56063	7.76118	0.07216	4.68498	466.12	149.69	449.16	20.33	451.94	28.32
NA18_35	0.05555	6.98798	0.55756	8.85837	0.07280	6.16079	434.36	155.64	452.99	26.95	449.94	32.21
NA18_36	0.05711	7.40305	0.72422	3.49054	0.09198	8.92221	495.66	163.14	567.22	48.45	553.15	14.89
NA18_37	0.05581	7.58773	0.67359	3.34412	0.08754	8.80392	444.80	168.69	540.95	45.68	522.90	13.67
NA18_38	0.05580	7.58773	0.71266	3.31112	0.09262	8.73418	444.62	168.69	571.02	47.73	546.32	13.99
NA18_39	0.05848	7.60454	0.48055	4.73045	0.05960	9.09589	547.82	166.10	373.17	32.98	398.45	15.59
NA18_40	0.05738	7.45040	0.68429	2.86782	0.08649	8.60064	506.31	163.89	534.73	44.14	529.37	11.83
NA18_41	0.05637	3.86894	0.61060	3.92341	0.07856	4.77688	467.06	85.68	487.51	22.43	483.94	15.10
NA18_43	0.05646	4.17790	0.63468	3.65524	0.08153	4.48543	470.60	92.47	505.22	21.80	499.01	14.41
NA18_44	0.05685	4.05893	0.63496	3.77250	0.08100	4.31473	485.91	89.60	502.08	20.84	499.18	14.88
NA18_45	0.05536	3.99162	0.64336	3.25470	0.08428	4.14926	426.88	89.02	521.63	20.79	504.38	12.94
NA18_46	0.05583	3.60764	0.64152	3.79038	0.08334	3.75136	445.65	80.19	516.01	18.60	503.25	15.04
NA18_47	0.05712	3.24181	0.54288	3.67471	0.06894	4.55234	496.01	71.44	429.74	18.93	440.32	13.13
NA18_48	0.05751	2.52788	0.62218	3.51666	0.07847	4.13333	511.08	55.56	486.96	19.39	491.21	13.70
NA18_49	0.05661	2.96729	0.68521	2.95672	0.08779	3.82222	476.41	65.61	542.43	19.88	529.92	12.21
NA18_50	0.05581	2.70856	0.66823	3.46585	0.08683	4.26120	444.96	60.21	536.78	21.95	519.64	14.10
NA18_51	0.05699	2.67370	0.64899	3.57979	0.08260	4.00671	491.02	58.97	511.60	19.71	507.86	14.31
NA18_52	0.05678	2.81790	0.59528	4.44252	0.07603	4.68168	483.19	62.23	472.39	21.32	474.23	16.83
NA18_53	0.05569	2.85377	0.60982	4.54145	0.07942	5.08819	440.06	63.50	492.65	24.13	483.45	17.47
NA18_54	0.05747	3.37405	0.55127	5.00517	0.06957	5.44569	509.64	74.18	433.56	22.83	445.83	18.06
NA18_55	0.05786	2.57900	0.63360	3.79112	0.07942	4.17249	524.58	56.55	492.64	19.79	498.33	14.93
NA18_56	0.05665	6.98292	0.66409	8.32726	0.08502	3.87799	477.98	154.35	526.01	19.59	517.11	33.76
NA18_57	0.05655	7.03870	0.61498	8.43674	0.07888	4.64343	473.94	155.70	489.41	21.88	486.69	32.63

Table A5.6 (continued)

Analysis #		Isotopic Ages (Ma)										
	²⁰⁷ Pb/ ²⁰⁶ Pb	2s %	²⁰⁷ Pb/ ²³⁵ U	2s %	206Pb/238U	2s %	²⁰⁷ Pb/ ²⁰⁶ Pb	2s	$^{206}\text{Pb}/^{238}\text{U}$	2s	²⁰⁷ Pb/ ²³⁵ U	2s
NA18_58	0.05674	6.93147	0.68500	8.03977	0.08755	3.34583	481.53	153.12	541.06	17.36	529.79	33.20
NA18_59	0.05644	7.03999	0.66817	8.31972	0.08586	4.15523	469.78	155.84	531.00	21.18	519.60	33.85
NA18_61	0.05454	2.46720	0.61932	4.35788	0.08235	4.88983	393.57	55.34	510.14	23.98	489.42	16.92
NA18_62	0.05731	3.08300	0.59134	4.58952	0.07483	5.20661	503.56	67.85	465.20	23.37	471.72	17.32
NA18_63	0.05691	3.24595	0.54899	4.92777	0.06996	5.28104	488.16	71.62	435.92	22.26	444.34	17.74
NA18_64	0.05899	3.16230	0.64216	4.30553	0.07895	4.98149	566.67	68.85	489.88	23.50	503.64	17.10
NA18_65	0.05611	2.56067	0.63951	4.26595	0.08265	4.56231	456.91	56.81	511.95	22.45	502.00	16.90
NA18_66	0.05629	2.65027	0.64053	4.11497	0.08252	3.34123	464.00	58.72	511.17	16.42	502.64	16.32
NA18_67	0.05659	2.80124	0.64137	3.99270	0.08220	3.23816	475.53	61.95	509.25	15.86	503.15	15.84
NA18_68	0.05718	2.38805	0.68889	4.94956	0.08738	3.73745	498.45	52.60	540.02	19.36	532.13	20.50
NA18_69	0.05718	2.22586	0.56957	5.11239	0.07225	4.14193	498.34	49.03	449.69	17.99	457.73	18.84
NA18_70	0.05552	1.87316	0.57572	4.73082	0.07521	3.79240	433.28	41.73	467.44	17.10	461.71	17.55