FORMATION OF THE FINE SCALE RHYTHMIC LAYERING OF THE

STILLWATER COMPLEX, MONTANA

A Thesis Presented to

the Faculty of the Department of Earth and Atmospheric Sciences

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

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ABSTRACT

The Stillwater Complex (SC) is a Precambrian layered mafic intrusion which outcrops along the northern edge of the Beartooth Mountains in southwestern Montana. The SC is broken down into 5 zones, the Basal Series, the Ultramafic Series, the Lower Banded Series, the Middle Banded Series, and the Upper Banded Series. The focus in this study is on the fine scale rhythmic layering found in the Lower Banded Series of the SC. These fine scale rhythmic bands repeat a doublet pattern of alternating, millimeter- to centimeter-scale plagioclase and pyroxene bands. The pyroxene bands are usually 1 to 2 cm thick and separated by 2 to 4 cm thick plagioclase bands. The purpose of this study is to determine the mechanisms (i.e., physical or chemical) which formed the fine scale rhythmic bands of the SC. Utilizing a combination of full thin section quantitative element maps, EPMA major element and LA-ICP-MS trace element analyses of plagioclase and pyroxene, and various geothermometers and geospeedometers, we have determined the crystallization history of our sample. The calculated crystallization temperature for coexistent plagioclase and pyroxene is 1220±13°C based on rare earth element (REE) partitioning. The calculated temperatures based on Fe-Mg partitioning between coexisting pyroxene are ~835°C. Based on this difference in equilibration temperature, differences in REE and Fe-Mg diffusion rates, and geospeedometry models of Sun and Lissenberg (2018), the high temperature cooling rate is in the range of 0.0011 - 0.0102 °C/year. The rapid cooling rate indicates crystallization of plagioclase and pyroxene over a short time interval near the solidus temperature. Textural relationships and crystallization temperatures are inconsistent with compositional layering during crystallization and instead support sub-solidus equilibration and formation of the fine rhythmic layering in the Lower Banded Series.

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INTRODUCTION

Layered igneous intrusions have long been interpreted as evidence for crystal settling and fractional crystallization and these igneous piles serve as natural laboratories for the study of crystal-liquid dynamics and subsolidus textural and chemical equilibration. In addition to the petrologic implications of these igneous systems, their potential for hosting valuable resources, such as the platinum-group elements (PGEs; Wall et al. 2018), makes many of these intrusions economically important. The 2705 Ma Stillwater Complex (SC) in southeastern Montana is renowned for its deposits of chromium and PGEs, which are located in reefs throughout the complex.

The SC outcrops along the northern edge of the Beartooth Mountains and has an exposed area of ~180 km² with a maximum width of 8 km and a maximum length of 47 km (McCallum, 2002). It is composed mainly of chromite, olivine, orthopyroxene, clinopyroxene, and plagioclase that occur in variable proportions in distinct layers throughout the igneous section (McCallum, 2002). Overall the dominant ultramafic to mafic layered horizons are distinguished by mineralogy and are referred to, from the exposed base to top of section the Basal Series, Ultramafic Series, Upper, Middle, and Lower Banded Series (McCallum et al., 1980; Raedeke, 1982). Fine scale rhythmic layering (FSRL), defined by plagioclase-rich and pyroxene-rich layers within the Upper Banded Series, has been an enigmatic feature in the SC. Studies of the FSRL have been limited to mostly stratigraphic measurements (McCallum, 2002) and petrologic modeling (Boudreau, 2010). Here, we present an analysis of the FSRL of the SC to understand whether the layering was a result of sub-solidus diffusion, dissolution/re-precipitation reactions with migrating melts, or some other process. In addition, the thermal history of the FSRL is investigated through rare earth element partitioning and cation diffusion modeling between coexisting plagioclase and pyroxene (Sun and Liang, 2017; Sun and Lissenberg, 2018).

BACKGROUND AND GEOLOGIC SETTING

Layered Igneous Intrusions

Layered igneous intrusions (LIIs) are igneous complexes characterized by a succession of extensive, structurally and/or mineralogically distinct layers (Wager, 1953; Wager and Brown, 1967; Cox et al., 1981). Though layering is a characteristic feature of LIIs, it may be absent from large portions of any LII. In fact, very few of the many LIIs currently recognized across the world (Figure 1) exhibit layering throughout the entirety of their complexes. It is generally thought that the formation of LIIs requires a relatively large volume of relatively low viscosity magma that is able to cool down through the liquidus and precipitate several phase assemblages that accumulate without being contemporaneously disturbed by tectonic forces (Wager and Brown, 1967; Cox et al., 1981). Although layering can be found in igneous rocks across a range of compositions, most well developed LIIs are predominantly derived from ultramafic, mafic, or silica-undersaturated, alkaline intermediate parental magmas (Cox et al., 1981).

Wager and Brown (1967) categorize LIIs as closed or open systems according to inferences regarding their overall mechanism of magma supply and retention. In closed system LIIs (e.g., the Skaergaard Intrusion, Greenland), magma is rapidly emplaced in an apparent single injection event and undergoes crystallization with little or no loss of material from the magma chamber. In open system LIIs (e.g., the Isle of Rum intrusion, Scotland), magma is emplaced in multiple pulses with enough time between injection events to facilitate significant cooling, crystallization, and cumulate formation as well as potential magma migration and removal from the overall LII system. Although the observable portion of the SC in Montana, U.S.A., appears to have formed as a simple closed system, not all LIIs can be simply categorized as either closed or open systems. For example, the Bushveld Complex, South Africa, is inferred to have undergone some amount of magma replenishment, however. as has been found with other verv large



Figure 1: A map of the Earth illustrating the approximate locations of various layered igneous intrusions. The green box highlights the location of the SC.

continuous masses (e.g., the Great Dyke), the Bushveld could have resulted from the confluence of several initially separate intrusions (Cox et al., 1981).

Figure 2 presents an idealized model for the formation of closed system (e.g., Skaergaard) LIIs based on the work of Wager and Brown (1967). In this model, the first pulse of magma quickly cools or quenches to form a Border Group. The Border Group envelopes the complex and grades inwards from a chilled margin towards less quenched, but still relatively quickly cooled, rocks. As the shell continues to accrete inwards, the Layered Series forms as crystals accumulate along the floor of the more slowly cooling magma body. The inward accretion of the Marginal Border Group and upward accumulation of the Layered Series is contemporaneous with downward solidification of the Upper Border Group, facilitating the compositional correlation of units between each of these groups. The Sandwich Horizon represents a trapped volume of liquid between the advancing crystal fronts within the intrusion. Those rocks preserved in the Sandwich Horizon and the chilled margin of the Border Groups are likely to be the only rocks with liquid compositions (i.e., unmodified by



Figure 2: An idealized cartoon (not to scale) for the formation of closed system layered intrusions (*after* Wager and Brown, 1967). Arrows within the intrusion are indicative of solidification direction.

crystal settling) in the intrusion and are the most likely to not exhibit layering.

The layering in LIIs typically falls into one of three main categories: modal layering, phase layering, or cryptic layering. Modal layering is defined by a variation in the proportions of component minerals and can be uniform, graded or both. Phase layering is defined as modal layers in which the crystallization sequence may exhibit the appearance/disappearance of particular phases. Cryptic layering is defined by a gradual change in the chemical composition of various minerals of a sequence (Jones et al., 1960). Although it is often variable, the regularity, or pattern, of layering can be rhythmic (i.e., the layers repeat symmetrically) or intermittent (i.e., the layers are less regular and can consist of multiple types). Large scale rhythmic layers of a few meters are considered macrorhythmic and small scale rhythmic layering of a few centimeters is considered microrythmic (Cox et al., 1981).

The Stillwater Layered Igneous Intrusion

The SC layered mafic intrusion outcrops along the northern edge of the Beartooth Mountains in southwestern Montana (Figure 3). The complex is most commonly subdivided from bottom to top into 3 to 5 major units: the Basal Series, the Ultramafic Series, the Lower Banded Series, the Middle Banded Series, and the Upper Banded Series. The composite stratigraphic section in Figure 4 shows the major subdivision of the complex where "S" denotes sulfide-enriched zones, "A-K" denotes major chromitites and "P" denotes podiform concentrates of sulfide-rich materials. The most common primary minerals of the complex are olivine, orthopyroxene, clinopyroxene, inverted pigeonite, plagioclase, and chromite. Common minor and trace minerals are quartz, phlogopite, amphibole, apatite magnetite, ilmenite, and sulfide (McCallum, 2002). Zircon is also reported and has been used to most precisely constrain the age of the complex (Wall et al. 2018).

The Basal Series is an irregular sheet-like mass with a thickness of 60m to 400m composed of primarily orthopyroxenite with norite and sulfide-bearing assemblages; it also contains xenoliths of cordierite-pyroxene hornfels (Page, 1979; McCallum, 1996). The lower contact of the Basal Series is irregular and cuts across stratigraphic units which suggests the SC's emplacement is along an unconformity. The Basal series includes all igneous rocks below the first appearance of cumulus olivine.

The upper contact of the Basal Series is with the first cyclic unit of the Ultramafic Series which is subdivided into a lower Peridotite zone and an upper Bronzite zone. The base of the Ultramafic Series is defined as the first appearance of cumulus olivine and the upper boundary is defined by a horizon where plagioclase appears as a cumulus phase. The peridotite zone comprises a sequence of 20 cyclic units where each unit consists of peridotite, harzburgite, and







Figure 4: Composite stratigraphic section, Boudreau, 2016.

bronzite. The Bronzite zone of the Ultramafic Series is relatively uniform with a few thin layers of olivine and chromitites (McCallum, 2002).

The Banded Series overlies the Ultramafic Series and the contact in the south is represented by the northern portion of the Bluebird Thrust system. This unit contains all of the rocks with cumulus plagioclase as a major constituent and is split into the Lower Banded series, the Middle Banded series, and the Upper Banded series. The lower contact of the Lower Banded series is marked by the first appearance of cumulus plagioclase and the upper contact is marked as the base of the first thick anorthosite unit. The Lower Banded series is further subdivided into six zones; the Norite I, Gabbronorite I, Olivine-bearing I, Norite II, Gabbronorite II, and Olivine-bearing II (Figure 4). The J-M reef, located in the Olivine-bearing I zone of the Lower Banded Series, is economically significant because it is enriched in (PGEs) (McCallum, 2002). The plagioclase-rich Middle Banded Series has lithologies that are distinctly different from the Lower Banded series and the Upper Banded series. Plagioclase makes up 82 vol. % of the Middle Banded series with the most common cumulus mafic minerals being olivine and augite and a minor amount of cumulus orthopyroxene. The unique crystallization sequence for the Middle Banded series is as follows: olivine/plagioclase \rightarrow augite \rightarrow orthopyroxene. The plagioclase crystals are 2 to 3 times larger than those that appear in the Lower Banded series and the Upper Banded series and display complex zoning patterns. The Middle Banded series is split up into 4 zones: Anorthosite I, Olivine-bearing III, Olivine-bearing IV, and Anorthosite II. The Upper Banded Series is composed of a lower cyclic olivine-rich subzone (Olivine-bearing V) and an upper uniform gabbro subzone (Gabbronorite III) (McCallum, 2002).

Chronology of the Stillwater

Wall et al. (2018) constructed a framework for crystallization of the SC based on trace element geochemistry of zircon and U-Pb zircon-baddeleyite-titanite-rutile geochronology of 22



Figure 5: Schematic diagram showing emplacement and post-emplacement history of the Stillwater based on U-Pb dating. (a) At 2712 Ma is the beginning of magmatic activity w/ emplacement of Basal Series as well as sills and dikes. (b) At 2711 Ma is emplacement of upper portion of the Peridotite Zone and the entire Bronzitite zones. (c) At 2710 Ma a wide range of rock types are produced (lower Peridotite zone from repetitive MgO-rich magmas). During this time is also the emplacement of the Norite I zone of Lower Banded series and thick anorthosite layers of Middle Banded series. (d) At 2709 Ma the main magmatism of SW, including J-M reef including the rest of the Banded Series. (e) After 2709 Ma is the emplacement of swarms of mafic dykes and granophyres that crosscut the SW. (f) During the late Cretaceous the Laramide Orogeny uplifted and unroofed of the SW, resulting in the current exposure of the SW. (Wood et al., 2018)

samples through the magmatic stratigraphy. U-Pb data geochronological results, from Wall et al. (2018), indicate that the SC crystallized over a ~3 million-year interval from 2712 Ma to 2709 Ma. The dates from U-Pb data reveal that the intrusion was not constructed in strictly sequential order from the base (oldest) to the top (youngest), therefore the succession in the complex does not follow the stratigraphic law of superposition. Magmatic activity started at 2712 Ma with the emplacement of the Basal Series sulphide-bearing orthopyroxenites and norites. The lower contact of the Basal Series may have been emplaced along a fault of an unconformity due to the fact that it is not emplaced parallel to a stratigraphic horizon.

The second episode of magmatism started at 2711 Ma and produced the uppermost portion of the Peridotite zone from the J chromitites upwards, this includes the entirety of the Bronzitite zone. These rocks are out of sequence with respect to the underlying, younger Peridotite zone. During a 2710 Ma magmatic episode, a wide range of rock types were produced, including harzburgite, norite, and anorthosite. During this episode the lower two thirds of the Peridotite zone were formed by repetitive emplacement of MgO-rich magmas that cooled and differentiated to produce the cyclic units of this zone. The B and G chromitites of this unit were also formed during this episode (Figure 5). This lower package of ultramafic rocks can be interpreted as a sequence of sill-like injections of magma into already crystallized ultramafic rocks. During this same 2710 Ma episode magmas were intruding along the upper contact of the Bronzitite zone to form the Norite I layer of the Lower Banded Series; thick anorthosite units of the Middle Banded Series were also crystallized and are older than their underlying and overlying rock sequences. The anorthosites are lithologically distinct from the other plagioclase-rich lithologies of the Lower and Middle Banded series being made up of dominantly plagioclase grains that are on average two to three times larger than the plagioclase layers of the other series.

At 2709 Ma the main volume of magmatism of the Stillwater occurred. This included the first appearance of cumulus plagioclase Olivine-bearing Zone I and the J-M Reef of the Lower Banded Series as well as the rest of the Banded series. After 2709 Ma there is metamorphism and deformation with the emplacement of mafic dikes and granophyres. Finally, after that there is uplifting and unroofing of the Stillwater during the Laramide Orogeny, resulting in the exposure of the intrusion (Wall et al., 2018). A schematic diagram of the geochronology of the emplacement of Stillwater is shown in Figure 4.

Regional Context

The complex is in fault contact with Paleozoic sedimentary rocks to the north and intrusive/fault contact with Precambrian granites, granitic gneiss, and schist to the south (Figure 3) (Jones et al 1960). The complex is bound by the Mill Creek-Stillwater Fault Zone and West Boulder Fault which separate it from the main Beartooth Block and North Snowy block, respectively. The intrusive contact between the complex and the underlying metasedimentary rocks is exposed between the Boulder River and Chrome Mountain near Mountain View. The fault contact between the lower part of the complex and the hornfels of the contact aureole is located between Chrome Mountain and the West Fork of the Stillwater River. The eastern half of the complex contains a set of south-dipping thrust faults (Page and Nokleberg, 1974). Along the Bluebird Thrust, the complex is in contact with a younger quartz monzonite, with an age of 2803.43 ± 0.58 ma (Wall et al., 2018), which also intrudes the complex to the east of the Stillwater River. The Bluebird Thrust system has also juxtaposed Ultramafic Series rocks with Banded series rocks in the West Fork area along the northern part of the Bluebird Fault. To the east of the West Fork area, movement along this fault system has formed the Mountain View block by having rotated a large wedge of the Ultramafic Series. The Mountain View Block is bound by the Lake-Fye Fault to the north which merges with the Bluebird Thrust system to the west. About 1000 meters of the Ultramafic Series has been removed by the truncation of the chromite deposits of the Mountain View area by the Lake-Fye fault. The northern boundary of the complex is an angular unconformity until it reaches the Horseman Thrust between the West Fork and the Stillwater River. Horseman Thrust from the Picket Pin Creek to Little Rocky Creek is a contact of thrust slices that overlay the Paleozoic and Mesozoic sedimentary rocks. The part of the complex that is exposed covers an area of $\sim 180 \text{ km}^2$ with a maximum width of 8 km and a maximum length of 47 km. (McCallum, 2002).

On the Beartooth block, there is preserved evidence for a major crust-forming event that occurred from ~3000 to 2740 Ma (Wooden and Mueller, 1989). This event produced the granodiorites and granites of the Long Lake Suite between 2780 and 2740 Ma. Isotopic data indicates that the intrusion of the Stillwater mafic magma at 2712 Ma is related to this major crust-forming event. Mafic dikes were emplaced throughout the Beartooth range and the complex which lead to low-grade regional metamorphism during the Proterozoic. In the late Proterozoic the area was uplifted, tilted towards the north, and eroded. Subsidence and sedimentation from the Middle Cambrian through the Lower Cretaceous covered the complex in a sequence of sedimentary rocks up to 3000 meters thick. Approximately 6 km of tectonic uplift associated with Laramide-style deformation, tilting and erosion during the late Cretaceous to early Tertiary exhumed the late Proterozoic erosional surface (Jones et al., 1960).

The banded series of the complex has been affected by five major high-angle reverse faults of Paleogene age that strike subparallel to the layering and dip steeply toward the northeast. The hanging walls of these faults have been elevated allowing for the preservation of Cambrian sedimentary rocks adjacent to the faults on the footwall block. The majority of the movement along these faults appears to be on planes coinciding with the igneous layering (Page and Nokleberg, 1974).

Layering occurs throughout the complex but only in a relatively minor proportion of rocks (McCallum, 2002). Outcrops typically exhibit modal uniformity with igneous laminations defined by preferred orientation of plagioclase and augite. Megalayers made up of anorthosites and bronzitite up to several hundreds of meters thick can be traced across the entire complex. Thinner layers of tens to hundreds of meters thick are present throughout the complex as well as the uncommon occurrence of modally-graded and rhythmic layering. Sized-graded and cross-bedded layers are rare. The fine scale rhythmic layering of the complex, composed of alternating

plagioclase- and pyroxene-rich layers, is considered to be an impressive example of rhythmic layering. There are also macrorhythmic layers preserved in the gabbronorites on Contact Mountain which exhibit upward grading over several meters from a pyroxene-rich base to a plagioclase-rich top (McCallum, 2002).

The complex contains important reserves of both base and noble critical metals. The sulfide-rich rocks of the Basal series, lower Ultramafic Series, and adjacent hornfels have been explored extensively since the late nineteenth century as a source of nickel and copper. The Ultramafic series also contains chromite-rich seams associated with the peridotites that have been extensively explored and were heavily mined in the Benbow, Mountain View, and Gish areas during wartime periods. The chromite deposits of the Stillwater represent 80% of the identified chromium reserves of the United States. Since the 1930's the complex was known to contain platinum and palladium minerals but the J-M reef was not discovered until 1973. The J-M reef is currently being mined in the Stillwater Valley and East Boulder plateau and is composed of disseminated sulfides in a narrow zone located within the lower part of the Banded series (McCallum, 2002).

The focus in this study is on the fine scale rhythmic layering found in the Gabbronorite-II Zone of the Lower Banded Series (Figure 6). These fine-scale rhythmic are composed of alternating, millimeter- to centimeter-scale plagioclase and pyroxene layers which can be rhythmically spaced. The pyroxene layers are usually 1 to 2 cm thick and separated by 2 to 4 cm thick plagioclase layers. The pyroxene often displays "doublets' of two closely- spaced layers separated by a thicker plagioclase layer (McCallum, 2002).



Figure 6: Outcrop of the fine scale rhythmic layering.



Figure 7: Layer spacing vs grain size in layered norites and gabbronorites, (Boudreau 1982).

The Formation of the Fine Scale Rhythmic Bands

The purpose of this study is to determine the physical or chemical mechanisms which lead to the formation of the fine scale rhythmic layering which occurs in the SC. The prevailing hypotheses involve sub-solidus diffusion and/or dissolution-reprecipitation from migrating melts.

Several previous investigations also suggest the fine scale rhythmic layering formed by periodic nucleation where it is proposed that the nucleation of new crystals occurs at a distance away from previously nucleated crystals because nucleation requires a finite amount of supersaturation in liquid before it can occur. This theory fails because it does not explain the pyroxene doublets that occur in the fine scale rhythmic layering. It also fails to explain the observed correlation between grainsize and layer spacing shown in Figure 6 which illustrates the relationship between spacing of layers in gabbroic and noritic rocks with orthopyroxene grain size. Figure 7



Figure 8: Qualitative model of how crystal ageing produces fine scale rhythmic layering. The figures on the left are an illustration showing the grain size distribution in a crystal + liquid assemblage. The graphs on the right display the solution concentration if it were a function of grain size. The arrows indicate the direction in which solution components are diffusing. (Boudreau, 2010)

suggests three general correlations: (i) layers of coarse grained rocks are further spaced than layers in finer grained rocks for a given modal abundance; (ii) for rocks of a given grain size, the spacing of mafic layers decreases with increasing modal abundance of pyroxene; and (iii) the overall trend extrapolates back to the origin. The last observation suggests that layering or patterns were not present at the time the crystals were undergoing nucleation (Boudreau 1982).

Crystal ageing (a.k.a, zone refining) is also suggested as a mechanism for explaining the crystallization of the fine scale rhythmic layering (Boudreau, 2010). Crystal ageing takes into account competitive particle growth, a theory of layer formation which maintains that once the initial period of nucleation and early growth is complete, a crystallizing system does not cease to react (Figure 8). The process of crystal ageing will allow the grains to continue to coarsen. Given an equal mass of larger crystals and smaller crystals, the larger crystals will have a lower free energy, because the contribution of surface free energy to the overall free energy of a crystal is always positive and the smaller crystals have a higher relative surface free energy than the larger crystals. The smaller crystals will have a higher solubility because they have a higher free energy. The crystal ageing process reduces the number of mineral grains and tends to produce a characteristic size distribution. Boudreau (2010) considers a crystallization of a single mineral phase from a solution in which crystal settling, other minerals, turbulent mixing, and other

mechanical effects are initially ignored to describe the manner in which crystal ageing occurs and could affect the layering. After crystallites initially form from a supersaturated solution, the crystals compete for components in the liquid of the crystallizing solution. (Boudreau, 2010)

Boudreau (2010) describes a given group of crystals that are marginally larger than those surrounding (Figure 8a). These crystals would be the earliest crystals to have nucleated in the case of an advancing crystal front. These larger crystals will continue to grow at the cost of the crystals that nucleated later and are smaller. Periodic layering can occur if this process repeats itself a distance away from the initial disturbance since the crystallization front is always advancing and there is always a gradient in the grain size across the front. In terms of favorable grain size, textural variations would continue to increase at the expense of the surrounding grains. An alternative mechanism could operate if the crystallites are numerous enough. Local solutions must increase to the higher equilibrium concentrations appropriate to their smaller size if the unfavored grains become smaller (Figure 8b). Initially favored grains will have accelerated growth due to this local high in concentration as well as cause solution components to diffuse into regions that had previously been unaffected by changes in their local environment. When the distal crystals experience the influx of component material they will begin to grow and the cycle repeats (Figure 8c). A local maximum in crystal size will induce a maxima in concentration nearby where grains are dissolving. This causes a flux of material to move outward to induce a new grain size maximum at a distance. This theory is explained as counterintuitive because layer formation is the result of crystal dissolution in the interlayer area even though the system may see an increase of crystallinity due to falling temperatures or diffusive influx of crystal components through the liquid. This competitive particle growth model only requires that crystals are not spatially uniform and that crystals in one location grow at the expense of grains elsewhere.

Crystal ageing has important implication on the crystallization behavior of layered intrusions. After grains nucleate crystal growth by solidification of liquid is limited by the rate that heat of crystallization is lost and may allow crystallites to remain very small and unstable in slowly cooled intrusions. While the crystal mass will increase only slowly with time, the crystal assemblages can continue to coarsen because the crystal ageing process is a largely neutral process in respect to overall heat budget. The growth of favored grains is compensated by the dissolution of thermally-equivalent unfavored grains that are smaller in size. This leads to the conclusion that the crystal ageing process can be significant in understanding the growth and segregation of grains in slowly cooled intrusions. (Boudreau, 2010)

METHODS

Sample Collection and Preparation

Samples have been collected from outcrops around the Stillwater Mine in Montana. This area was selected because along the mountain and in the valley, there are large outcrops of the fine-scale rhythmic layering. Samples have been collected from an outcrop along the road above the Stillwater Mine and in the valley near the mine. The sample from the outcrop displays the fine scale rhythmic doublets vertically as shown in Figure 3. The sample was roughly 14 inches by 5 inches by 4 inches. It was cut into 3x2 inch blocks with a tile saw, then cut into smaller chips that were mounted onto glass slides. From there an Ingram-Ward thin section cut-off saw and grinder was used to saw down the mounted samples and then grind down the mounted samples into ~70 micron thick thin sections for petrographic and chemical analysis.

Major Element Analysis

Full thin section quantitative element maps (see Appendix 1) and mineral spot analyses were collected using the Zeiss Sigma HD Analytical SEM (ASEM) outfitted with dual Oxford

Instruments 1050 mm² active area X-MaxN EDS detectors at the Cardiff University School of Earth and Ocean Sciences in Cardiff, UK. Individual, standardized spot analyses of plagioclase and pyroxene were all collected with a 20 kV accelerating voltage, a beam current of 2.5 nA, and a spot size of 5 µm. The beam current was measured with a stage mounted Faraday cup. However, due to known difficulties in calibrating stage mounted faraday cups with known current sources (Newbury, 2006), the repeatability was estimated on the independent EDS measurement of the integrated X-ray counts from a pure Cu standard, and was found to be better than 0.2% relative. Each EDS spectrum was collected over a 30s live time using both detectors. The raw data were processed using the internal XPP matrix correction (Pouchou and Pichoir, 1991) of the Oxford Instruments Aztec Software package with oxygen being calculated by stoichiometry. These conditions that were used for spot analyses were also used for element map collection, with dwell times of 20 ms per pixel and a step-size of 20 µm. Further mineral major element data was collected on the EPMA-1720HT Electron Probe Microanalyzer (EPMA) at the Shimadzu Center for Environmental, Forensics, and Material Science within the Shimadzu Institute for Research Technologies at the University of Texas at Arlington using a combination of natural and synthetic standards. An accelerating voltage of 15 kV and a beam current of 10 nA was used for all analyses. Pyroxene was analyzed with a 5 μ m focused beam, and plagioclase was analyzed with a 5 μ m defocused beam. A series of tables which include the statistics as well as a list of the standards and dwell times used for the pyroxene and plagioclase analyses as well as can be found in Appendix 2.

Trace Element Analysis

Using the data from the Analytical SEM and EPMA, suitable locations were chosen for trace element analyses by laser-ablation inductively-coupled plasma mass spectrometry (LA-ICPMS). Trace elements were measured in-situ using a Varian 810 quadrupole ICP-MS coupled to a PhotonMachines Analyte.193 ArF laser ablation instrument at the University of Houston. A

circular spot sizes of 50 and 80 microns were selected utilizing 240 ~4 ns laser pulses at a rate of 8 Hz with a fluence of 2.99 J/cm². Each analysis was preceded by a gas blank of ~18 s. Spots were taken linearly along a slide to get a relative cross section of trace element data across two pyroxene doublets including the plagioclase between said doublets. Trace element analyses include masses ²⁵Mg, ²⁹Si, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁹Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷³Yb, and ¹⁷⁵Lu. All trace element data were corrected for laser and ICP-MS element fractionation with internal standards Mg for pyroxene and Ca for plagioclase. Data reduction was performed with GLITTER software (Griffin et al. 2008). USGS certified reference materials BHVO-2 and BIR-1 were used as calibration standards.

Element Modelling, geothermometry, and geospeedometry

The major and trace element analyses were used as input into the REE-in-plagioclaseclinopyroxene (Sun and Liang, 2017), the REE-Mg combined geospeedometer (Sun and Lissenberg, 2018), and the two-pyroxene thermometer of Brey and Kohler (1990). For these models, the full dataset as well as calculated averages and reintegrated orthopyroxene and clinopyroxene analyses were used as inputs.

RESULTS

Plagioclase grains range in diameter from as small as 0.5 mm to as large as 5 mm, and pyroxene grains range in diameter from 0.3 mm or smaller to upwards of 3.5 mm; on average, pyroxene grains are much smaller in size than plagioclase grains. The plagioclase grains are subhedral while the pyroxenes are more anhedral. The average modal percentage for plagioclase is ~77% while pyroxenes are ~19% with clinopyroxene at ~13.7% and orthopyroxene at ~5.3%. This cumulate rock displays textures commonly associated with mesocumulates, possibly adcumulates, with the pyroxenes appearing as interstitial material.

A summary of major element analyses for plagioclase and pyroxene are provided in Tables 1 and 2 and a summary of LA-ICP-MS analyses for the REEs is provided in Table 3. Major element data from the EPMA spot analysis and the element maps generated from the Analytical SEM (Figures 9 & 10) have been used to determine that the plagioclase has an average anorthite (An = $100 \times Ca / Ca + Na$) content of An₈₀, with a range of An₇₈ to An₈₄ which can be seen in Figure 10a. The pyroxenes are found to have an average Mg# (Mg# = $100 \times Mg / Mg + Fe^{2+}$) of 75 with a range of 67 to 78, shown in Figure 10b. Based on the element map of Mg# in pyroxene (Figure 9b) there are two pyroxenes present in the samples. Some of the pyroxenes display well-defined exsolution lamellae as seen in Figure 9, while the plagioclase displays minor compositional zoning. The reverse zoning in the plagioclase seen in Figure 9 shows that the rims typically have a higher An content than the cores.

Before employing the REE-in-plagioclase-clinopyroxene (Sun and Liang, 2017) and the REE-Mg combined geospeedometer (Sun and Lissenberg, 2018) reintegrated pyroxene values were calculated. Reintegrated pyroxene values were calculated from modal mineral percentages of plagioclase, clinopyroxene, and orthopyroxene. To calculate the reintegrated pyroxene compositions, we used the modal mineral percentage as volume in p=m/V (p=density, m=mass, V=volume) and then solved for mass, the masses of their respective mineral were then normalized. Once normalized the major element and REE data was multiplied by the normalized mass values and totaled.

Results from the REE-in-plagioclase-clinopyroxene thermometer are shown in Figure 13, the top graph shows the temperature for the average composition of the plagioclase and pyroxene within the sample and the bottom graph shows temperatures for the average compositions with reintegrated pyroxene. The average composition yielded a temperature of 1194±34°C and the reintegrated pyroxene composition yielded a temperature of 1220±13°C. From the temperature

Table 1: EPMA	Spot Analy	sis of pyro	xene in Wt.	%						
Point	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	MgO	CaO	Na_2O	Total
Opx8	53.35	0.24	0.98	0.12	20.35	0.35	24.56	1.10	0.01	101.05
0px9	52.65	0.26	0.96	0.10	20.59	0.35	24.48	1.04	0.00	100.43
OpxAvg	53.00	0.25	0.97	0.11	20.47	0.35	24.52	1.07	0.01	100.74
CpxI	52.80	0.36	1.68	0.27	7.47	0.16	14.97	22.64	0.21	100.56
Cpx2	52.43	0.46	1.81	0.25	8.21	0.19	14.97	22.08	0.21	100.59
Cpx3	52.81	0.48	1.82	0.24	7.83	0.15	15.00	22.17	0.21	100.71
Cpx4	52.44	0.47	1.92	0.21	8.62	0.15	15.41	21.12	0.21	100.55
Cpx5	52.21	0.50	1.80	0.20	8.44	0.20	15.07	21.59	0.22	100.23
Cpx6	52.49	0.43	1.81	0.22	9.12	0.17	15.52	20.41	0.19	100.36
Cpx7	51.76	0.51	1.80	0.23	7.81	0.16	14.86	22.35	0.22	99.70
Cpx12	50.79	0.46	2.08	0.27	7.87	0.16	14.96	21.84	0.24	98.67
Cpx15	51.22	0.44	2.26	0.25	7.72	0.15	14.77	22.21	0.23	99.25
Cpx16	51.57	0.45	2.00	0.26	8.40	0.19	15.03	21.36	0.20	99.46
Cpx18	52.92	0.33	1.48	0.18	7.39	0.17	15.01	22.57	0.19	100.24
Cpx19	51.73	0.48	1.89	0.23	7.82	0.17	14.79	22.48	0.22	99.80
Cpx20	52.02	0.50	1.84	0.25	90.6	0.18	15.55	20.62	0.21	100.22
Cpx2I	51.67	0.49	1.86	0.23	7.90	0.17	15.18	21.58	0.21	99.28
Cpx22	50.67	0.42	2.50	0.22	8.10	0.17	14.85	21.49	0.19	98.61
CpxAvg	51.97	0.45	1.90	0.23	8.12	0.17	15.06	21.77	0.21	99.88

inversions shown in Figure 11 we can also see that the reintegrated pyroxene T_{REE} exhibits comparatively less error.

Point	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	Total
Plag1	48.10	32.56	0.46	0.02	16.02	2.14	0.07	99.37
Plag2	48.27	32.98	0.43	0.03	16.06	2.06	0.06	99.90
Plag3	48.92	33.13	0.45	0.03	16.02	2.19	0.06	100.80
Plag4	47.96	32.98	0.50	0.04	15.74	2.37	0.11	99.69
Plag5	48.11	33.13	0.43	0.03	15.68	2.34	0.09	99.80
Plag6	47.56	33.49	0.44	0.03	16.15	2.13	0.10	99.90
Plag7	47.73	33.29	0.97	0.22	15.39	2.30	0.09	99.98
Plag8	48.36	32.76	0.43	0.04	16.01	2.17	0.11	99.88
Plag9	48.61	32.68	0.47	0.04	15.82	2.26	0.10	99.96
Plag10	48.78	33.21	0.51	0.04	15.99	2.14	0.10	100.75
Plag11	48.69	33.23	0.46	0.05	15.88	2.20	0.09	100.59
Plag12	48.58	33.15	0.60	0.05	15.48	2.28	0.08	100.21
Plag13	47.45	34.14	0.50	0.04	16.44	1.98	0.06	100.61
Plag14	47.23	33.71	0.44	0.01	16.69	1.76	0.04	99.88
Plag15	48.42	32.90	0.42	0.04	15.72	2.31	0.09	99.89
Plag16	48.49	33.00	0.48	0.03	15.67	2.36	0.08	100.11
Plag17	47.03	34.25	0.45	0.03	16.68	1.63	0.09	100.16
Plag18	47.74	33.86	0.47	0.03	15.95	2.12	0.08	100.26
Plag19	47.93	33.93	0.48	0.03	15.93	2.22	0.09	100.62
Plag20	48.11	33.08	0.47	0.02	15.95	2.15	0.06	99.83
Plag21	48.73	33.26	0.42	0.04	16.23	2.01	0.08	100.77
Plag22	47.12	34.11	0.43	0.02	16.83	1.68	0.09	100.29
Plag23	48.77	33.57	0.43	0.03	15.89	2.13	0.11	100.94
Plag24	48.46	33.52	0.44	0.03	15.77	2.24	0.08	100.54
Plag25	48.04	33.68	0.42	0.03	15.98	2.24	0.08	100.48
Plag26	48.46	33.01	0.41	0.03	16.20	2.07	0.08	100.26
Plag27	48.59	33.01	0.49	0.03	15.77	2.30	0.10	100.28
PlagAvg	48.16	33.32	0.48	0.04	16.00	2.14	0.08	100.21

Table 2: EPMA Analysis of Plagioclase in Wt. %

<u> </u>	ζ				Ē	ç	Ē	ė	, H	Ē	Ē	1	
3	1	5	DN	NI	FU	3	9	ĥП	PI	Er		χD	FI
3.880		0.689	4.120	1.510	0.241	1.840	0.380	2.580	0.580	1.780	0.243	1.520	0.252
3.880		0.674	3.840	1.160	0.249	2.240	0.409	2.560	0.545	1.430	0.175	1.480	0.233
3.670		0.696	3.590	1.380	0.279	1.860	0.379	2.660	0.564	1.830	0.195	1.420	0.219
3.820		0.784	4.160	1.670	0.323	2.250	0.439	2.680	0.526	1.590	0.243	1.740	0.279
3.620		0.709	3.640	1.390	0.230	2.310	0.356	2.530	0.570	1.470	0.244	1.590	0.294
3.910		0.781	4.180	1.140	0.178	2.220	0.456	2.850	0.618	1.770	0.256	1.730	0.261
3.610		0.758	3.820	1.430	0.245	2.230	0.382	2.410	0.599	1.780	0.212	1.670	0.253
3.640		0.651	3.160	1.270	0.257	2.210	0.354	2.520	0.482	1.410	0.214	1.430	0.228
4.220		0.713	3.610	1.290	0.292	2.050	0.330	2.310	0.571	1.620	0.254	1.650	0.279
3.560		0.625	3.350	1.260	0.282	1.800	0.346	2.220	0.502	1.520	0.225	1.580	0.184
2.920		0.558	2.800	1.070	0.268	1.400	0.306	1.910	0.386	1.300	0.234	1.110	0.203
3.680		0.678	3.760	1.640	0.205	2.010	0.356	2.810	0.647	1.480	0.202	1.790	0.247
4.350		0.786	4.160	1.520	0.199	2.280	0.433	2.750	0.606	1.550	0.248	1.490	0.279
4.680		0.896	4.010	1.730	0.297	2.280	0.411	2.960	0.682	1.830	0.312	1.950	0.273
3.960		0.689	3.960	1.220	0.238	2.180	0.442	2.880	0.602	1.360	0.237	1.600	0.304
'							0.039	0.173	0.051	0.287	0.070	0.493	0.106
1			,				0.033	0.212	0.059	0.346	0.055	0.539	0.102
1.639	~	0.163	0.607	0.088	0.256	0.079	0.010	0.046	0.007			0.017	
1.67_{4}	-	0.183	0.623	0.114	0.294	0.071	0.007	0.047	0.004	0.015	,		
1.678	~	0.174	0.582	0.088	0.280	0.077	0.007	0.045	0.007	0.022	,		
1.557	~	0.175	0.605	0.101	0.277	0.087	0.007	0.031	0.006	0.015	0.005		0.006
1.710	_	0.171	0.585	0.096	0.284	0.054	0.006	0.018	0.007	0.012	,	·	,
1.72(0	0.183	0.638	0.077	0.298	0.085	0.005	0.033	0.010	0.011	,		
1.64	0	0.176	0.565	0.091	0.271	0.041	0.009	0.041	0.007	0.019	0.004		0.006
1.69(_	0.175	0.650	0.108	0.276	0.107	0.010	0.046	0.006	0.011		0.014	
1.67(_	0.171	0.627	0.079	0.285	0.088	0.006	0.037	0.006	0.021	,	0.010	
1.63(_	0.171	0.570	0.089	0.274	0.067	0.007	0.050	0.005	0.012			ı
1.54	_	0.171	0.604	0.103	0.280	0.073	0.008	0.045	0.004	0.020	ī	0.017	ī
1.56	0	0.157	0.590	0.074	0.265	0.061	0.011	0.044	0.005			0.013	ı
1.72	0	0.186	0.627	0.078	0.287	0.100	0.010	0.030	0.006	0.019	0.003		
1.81	0	0.182	0.603	0.092	0.258	0.080	0.007	0.038	0.007		0.004		
1.66	0	0.179	0.594	0.093	0.277	0.072	0.00	0.038	0.006	0.013	- 000	- 10 - 0	
1.67	0	0.177	0.624	0.089	0.278	0.063	0.006	0.037	0.005	0.019	0.003	0.017	,
1.81	0	0.183	0.671	0.078	0.307	0.087	0.007	0.033	0.008	0.012	,	0.019	·
1.66(_	0.178	0.570	0.074	0.255	0.085	0.004	0.022	0.009	0.013		0.015	ı
1.70	0	0.174	0.590	0.076	0.281	0.057	0.007	0.034		0.021			0.005
1.66(_	0.179	0.595	0.082	0.268	0.069	0.005	0.032	0.004	·	0.003	,	,
1.74	0	0.176	0.624	0.098	0.289	0.089	0.006	0.033	0.009	0.013	0.003	ī	ī
1.80(0	0.189	0.658	0.074	0.269	0.092	0.010	0.047	0.004	0.012	0.004	0.014	
1.76(_	0.186	0.635	0.096	0.295	0.081	0.008	0.036	0.004	0.019	,	0.011	
1.690	_	0.176	0.642	0.097	0.282	0.086	0.007	0.040	0.007	0.012	,	·	ī
1.680	_	0.175	0.617	0.088	0.262	0.082	0.009	0.036	0.008		,		0.006
1.66(_	0.179	0.637	0.117	0.285	0.084	0.009	0.040	0.008	0.018			
1.650	_	0.177	0.594	0.091	0.273	0.069	0.010	0.038	0.007	0.018	-		-
	Ĺ												



Figure 9: Element maps of S1_1-3 displaying (A) An content in plagioclase and (B) Mg# in pyroxene. Exsolution lamellae of orthopyroxene are visible with lower Mg# compared to clinopyroxene.



Figure 10: Histograms of (A) An in plagioclase and (B) Mg# in pyroxene derived from elements maps of S1_1-3 provided in Figure 9.



Figure 11: Results of the REE-in-Plagioclase-Pyroxene Thermometer (Sun and Liang, 2017) for the (A) Average plagioclase and Pyroxene and (B) Average plagioclase and reintegrated OPX and CPX.

DISCUSSION

Plagioclase-Pyroxene Equilibrium

Trace element data collected from LA-ICP-MS analysis, specifically rare earth element (REE) data, are in equilibrium for plagioclase and pyroxene. This can be deduced because the samples are texturally mature, the REE are homogenous throughout the samples, the exsolution lamellae within the pyroxenes, and the REE thermometry (see below). Figure 12 shows variations in REE concentrations horizontally across a sample, the values near 22 mm and 33 mm are pyroxene bands and the values in the middle are plagioclase. The values are homogenous throughout the sample with respect to the minerals. The plagioclase trend among these REE graphs is relatively linear with no large change in concentration across the sample; the pyroxenes are also relatively similar throughout the sample. The higher concentrations of LREEs in the pyroxenes are due to the fact that LREEs (with the exception of La) are more compatible in pyroxene than in plagioclase. The only other REE more compatible in plagioclase than pyroxene is Eu, which can occur as a 2+ valence state. This is anomaly is common because Eu^{2+} is more compatible with plagioclase where is can substitute for Ca^{2+} (Sinha, 2012). Thus, Eu displays a negative anomaly for clinopyroxene and a positive anomaly for plagioclase as seen in the REE diagrams in Figure 13.

Pyroxene Exsolution

Based on the solubility of diopside and enstatite, two-pyroxene geothermometry is a reliable method for estimating equilibrium temperatures in coexisting clinopyroxene and orthopyroxene (e.g., Wood and Banno, 1973; Wells, 1977; Brey and Kohler, 1990). One of the most widely used two-pyroxene geothermometers is the Brey and Kohler (1990) geothermometer



Figure 12: Graphs showing concentration of REE with respect to horizontal distance across the samples. Note that the Y-axis in A is concentration while in B it is logarithmic for the sake of clearing up the plots.

(B&K) which employs more realistic pyroxene compositions to provide a revised calibration of previous two-pyroxene thermometers (Wood and Banno, 1973; Wells, 1977). The B&K thermometer has been chosen because it has been calibrated over a wider composition and temperature range and is a more recent calibration. Previous authors (e.g., Harder and Russell, 2006) have also shown that the temperatures calculated with the Wells (1977) thermometer from sample mineral pairs are consistently lower than and higher than the calculated B&K temperatures below 900°C and above 980°C, respectively.



Figure 13: A) Comparison of REE in plagioclase and clinopyroxene, B) concentration ratio of REE in plagioclase vs clinopyroxene.

Pressures of 1.5 to 3.0 kbar have been assumed for the B&K thermometer based on the pressures employed in previous models (e.g., Helz, 1995, McCallum, 1988) for the development of the SC. After examining the effect of the chosen pressure on the resulting temperature for the B&K thermometer it was found that an increase or decrease of 1kbar in pressure resulted in an equivalent increase or decrease in temperature of about 2.5°C. Therefore, the choice in pressure

	Ave	rage				Pa	irs			
	CPX	0PX	Px1-CPX	Px8-OPX	Px2-CPX	Px9-OPX	Px3-CPX	Px10-OPX	Px4-CPX	Px11-OPX
c.p.f.u. ^A										
Si	1.938	1.934	1.944	1.942	1.933	1.929	1.943	1.944	1.932	1.922
AI	0.078	0.042	0.073	0.042	0.078	0.041	0.079	0.043	0.084	0.041
Cr	0.007	0.003	0.008	0.003	0.007	0.003	0.007	0.004	0.006	0.003
Ï	0.012	0.007	0.010	0.007	0.013	0.007	0.013	0.006	0.013	0.008
Fe ^{TOTAL}	0.247	0.627	0.230	0.619	0.253	0.631	0.241	0.628	0.266	0.629
Fe ^{2+ B}	0.219	0.554	0.204	0.561	0.215	0.547	0.225	0.575	0.231	0.533
Fe ^{3+ B}	0.029	0.073	0.026	0.059	0.038	0.084	0.016	0.053	0.035	0.096
\mathbf{Mg}	0.828	1.336	0.822	1.333	0.822	1.337	0.823	1.332	0.847	1.340
\mathbf{Mn}	0.005	0.010	0.005	0.011	0.006	0.011	0.005	0.010	0.005	0.010
Ca	0.868	0.040	0.893	0.043	0.872	0.041	0.874	0.033	0.834	0.045
Na	0.015	0.000	0.015	0.001	0.015	0.000	0.015	0.000	0.015	0.001
molar ratios										
$Mg^{\mu c}$	77.0	68.1	78.1	68.3	76.5	67.9	77.4	68.0	76.1	68.1
En	42.6	66.7	42.3	66.8	42.2	66.6	42.5	60.9	43.5	66.5
\mathbf{Fs}	12.7	31.3	11.8	31.1	13.0	31.4	12.4	31.5	13.6	31.2
Wo	44.7	2.0	45.9	2.1	44.8	2.0	45.1	1.6	42.8	2.2
Brey & Kohle.	r (1990) The	ermometry								
P (kbar)	1.5	3	1.5	3	1.5	ю	1.5	б	1.5	3
$T(^{\circ}C)$	833.4	837.2	782.6	786.1	825.6	829.4	819.7	823.4	890.1	894.1

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^A Cations per formula unit on the basis of 6 oxygens ^B Fe^{2+} and Fe^{3+} calculated according to the method of Droop (1987) ^C Mg# = 100 x Mg / Mg + Fe^{TOTAL}

should not significantly affect the resulting temperatures and our interpretations of them. Temperatures were calculated using EPMA analyses of four orthopyroxenes and four adjacent clinopyroxenes as well as averages of both phases. The results of the B&K thermometer calculations, represented in Table 4, range from ~780°C to 895°C with the average of the orthopyroxene and clinopyroxene resulting in a temperature of ~835°C.

REE-Thermometry and Geospeedometry

A high temperature thermal history for the Stillwater can be deduced by combining the REE-in-plagioclase-clinopyroxene thermometer of Sun and Liang (2017) and the geospeedometer of Sun and Lissenberg (2018) which utilizes differential Mg closure temperatures and REE diffusion between plagioclase and clinopyroxene. The REE-in-plagioclase-clinopyroxene thermometer was developed out of the temperature- and composition-dependent REE partitioning between coexisting plagioclase and clinopyroxene. This thermometer utilizes parameters from lattice strain models for REE partitioning in both plagioclase and pyroxene (Liang et al. 2013; Sun and Liang, 2014) which are calibrated against experimentally-determined mineral-melt partitioning data (Sun and Liang, 2012; Sun et al., 2017). Two elements with different diffusivities and distinct closure temperatures could be utilized together to constrain a cooling rate and initial temperature. Through numerical simulations of diffusion in plagioclase-clinopyroxene systems, Sun and Liang (2017) showed that REEs preferentially record near-crystallization temperatures due to their slow diffusion rates, while Mg records the initial crystallization temperatures of rocks from rapidly cooling magmas. There are several factors that may influence the accuracy of Sun and Liang's REE-exchange thermometer with an interpretation of the crystallization sequence being the most significant especially in highly evolved magmas. To reduce this influence, a careful petrographic analysis and in situ core/rim chemical analysis is necessary. Other factors that may have an influence include analytical errors of REE in plagioclase and uncertainties in the estimated pressure

and water content of the sample (Sun and Liang, 2017). Trace element data for the plagioclase and pyroxene, taken from LA-ICP-MS spot analysis, was input into Sun's (2017) REE-in-plagioclaseclinopyroxene thermometer (Figure 11).

Sun and Liang (2017) applied their REE-in-plagioclase-clinopyroxene thermometer to 70 mafic cumulate rocks, using 34 cumulate rocks from the Sept Iles layered intrusion in Canada and 36 cumulate rocks from the Bushveld Complex in South Africa. The Sept Iles samples had a range of anorthite content from An₄₈₋₆₈ and an Mg# of 66-78, while the Bushveld samples were similar in composition, they did have a slightly wider range of An content from An₄₅₋₇₆ and Mg# of 47-84. Weight percentages for the Sept Iles were taken from Namur et al. (2010): SiO₂ 48.56 wt%, TiO₂ 2.85 wt%, and MgO 5.47 wt%. The Bushveld weight percentages were taken from Davies and Cawthorn (1984): SiO₂ 49.72 wt%, TiO₂ 0.81 wt%, and MgO 6.08 wt%. Sept Iles sample DC-9-2410, a troctolite, was most similar to our Stillwater samples with an An/Mg# of 68/78. This troctolite had a T_{REE} of 1133±10°C. Of the Bushveld sample B07-008 (VanTongeren & Mathez 2013) and sample 2446.8 (Tanner et al. 2014) are the most similar to the samples taken from the Stillwater with an An/Mg# of 76/78 and 70/70, respectively. The B07-008 anorthosite had a T_{REE} of 1196±19°C and the 2446.8 gabbro had a T_{REE} of 1154±20°C.

When the REE-in-plagioclase-clinopyroxene thermometer is combined with the Mgexchange thermometer, a geospeedometer is produced which can numerically solve for the initial crystallization temperatures and cooling rates for an individual sample. The coupled Mg-REE speedometer utilizes diffusion coefficients, partitioning coefficients, mineral proportions, and grain radii of the clinopyroxene and plagioclase. The initial temperatures of cumulus rocks can be seen as the mean temperatures of cumulus crystallization because of their simple cooling histories prior to crystallization. Potential issues with cooling rates and temperatures calculated from Sun and Lissenberg (2018) will be offset by using average mineral compositions to better represent the bulk closure concentrations as the speedometer utilizes mean quantities based on bulk diffusion of Mg and REE between coexisting plagioclase and clinopyroxene. Plagioclase zoning is another potential issue but, as noted by Sun and Lissenberg (2018), using an averaged composition for normally zoned plagioclase results in about a ~20°C overestimate in bulk Mg closure temperatures.

Sun and Lissenberg also developed a new Mg-exchange thermometer since a previous Mgexchange thermometer, from Faak et al. (2015), had strong dependencies on silica activities that could only be calculated from existing activity models and was calibrated for 1100-1200°C for plagioclase with 50-80 mol% anorthite. Since Fe and Mg in gabbros resets by diffusion at much lower temperatures, a new Mg-exchange thermometer is required. The basis of Sun and Lissenberg's (2018) new Mg-exchange thermometer is the temperature-sensitive exchange of an element between coexisting minerals, in this case Mg exchange between plagioclase and pyroxene coupled with Ca. By describing the Mg-exchange simply, it allows for the development of a thermometer independent of silica activities even though silica activities are not necessarily negligible and may have an effect on the mineral major compositions and equilibrium phase relations. The Mg partition coefficient used in this thermometer takes into account changes in enthalpy, volume, and entropy as well as the activity of Ca of the Ca-bearing component and the activity of the Mg-bearing component. The Ca component in plagioclase is a function of anorthite content as well as temperature, the Mg component is similar. Since Mg is very incompatible with plagioclase it can be difficult to measure. The use of a lattice strain model for trace element partitioning between plagioclase and silicate melt can assist in the calibration of the plagioclaseclinopyroxene Mg partitioning model. Sun and Lissenberg's (2018) new Mg-Exchange thermometer has been able to yield temperatures ranging from $800-1430^{\circ}C \pm 50^{\circ}C$ across a wide range of mineral assemblages coexisting with plagioclase, clinopyroxene, and melt, thus being suitable for our samples.

The Mg-REE coupled speedometer takes into account mineral composition, relative grain radii (size), and relative mineral modes (volume). The cooling rates are sensitive to Mg bulk closure temperatures and the Mg bulk closure temperatures are sensitive to variations in plagioclase with respect to anorthite composition and the size and volume of plagioclase. Larger plagioclase grains or a greater abundance of plagioclase leads to higher Mg bulk closure temperatures. Mg bulk closures are more responsive than REE bulk closures to changes in cooling rate, composition, mineral mode, and grain radii because Mg has much faster diffusivities in plagioclase and clinopyroxene.

A pressure of 2.0 kbar, or 0.2 GPa, was selected based on pressures used in previous models (e.g., Helz 1995, McCallum 1988) for the development of the SC and above in this study. Using EPMA and LA-ICP-MS analysis of adjacent plagioclase and clinopyroxene grains, as well as orthopyroxene grains, temperatures have been calculated utilizing Sun and Liang (2017). Our reintegrated pyroxene values and average pyroxene and plagioclase values were used with the Sun and Lissenberg (2018) geospeedometer. Plagioclase and clinopyroxene grain radii were measured with plagioclase radii ranging from .3mm to 1.125mm and clinopyroxene radii ranging from 0.21mm to 0.65mm. Mineral modes were also measured with percentages of 77% and 15% (19% for the reintegrated average) for plagioclase and clinopyroxene, respectively. Anorthite content of 78-81% were used across the samples with 78% being used for the reintegrated and averaged samples. The geospeedometer for the sample average and the reintegrated average are shown in Figure 14 showing a calculated cooling rate of log(°C/year) = -2.01 and -2.17, respectively. In these figures you can also see that once again the reintegrated (WeightedPx) has a smaller error range.



Figure 14: Results from the Sun and Lissenberg (2018) geospeedometer. These graphs show the difference in REE and Mg bulk closure temperatures plotted against REE bulk closure temperatures. The upper red boundary shows the maximum differences in the bulk closure temperatures between the REE and Mg thermometers. Cooling rates are represented by the blue curves. The initial temperature curves start with the red circles and follow up the red curves. The top graph displays the results of the geospeedometer for the average compositions of plagioclase and pyroxene in the samples. The bottom graph shows the results of the geospeedometer for the reintegrated pyroxene.

Elastic Strain Model

An elastic strain model has been applied to the trace element data collected from the plagioclase and pyroxene within our samples (Figure 15). Partition coefficients (between plagioclase and pyroxene) were calculated for 3+ ions with a coordination of VI and VIII between

the plagioclase and pyroxene. The theoretical foundation for trace element partitioning was laid by Goldschmidt in 1937. Goldschmidt recognized that the ions of trace elements will enter specific lattice sites in minerals. He proposed that the main variables controlling this partitioning are the charge and size of the trace ion relative to the charge and size of the lattice site, which varies with mineral composition. Ions that have lower partition coefficients do not fit well into lattice sites compared to others because of an energy penalty and charge mismatch. In general the elastic strain model follows Goldschmidt's (1937) rules for ionic substitution, primarily that ions of the same charge and similar radius will enter into a crystal lattice with equal ease. Lattice strain models are based on the premise that trace ions are charged point defects in a dielectric, elastic continuum.

Disruption of this lattice around the charged point defect is diminished by relocating the neighboring ions and distributing the surplus electrostatic energy throughout the lattice. The elastic strain energy for accommodating ions that are too large for a site is roughly the same as accommodating ions that are too small for a site by about the same amount. That is, the elastic strain energy is approximately symmetrical around an optimum ionic size. Since elastic strain energy is inversely correlated with the logarithm of the partition coefficient it should vary almost parabolically with ionic radius. The ion that fits the lattice site with the least amount of strain has the maximum partition coefficient. This near parabolic relationship between partition coefficients and iconic radii is not enough to explain the variability in partition coefficients. When the ions of interest have a different charge than the cation that is normally located at a lattice site electrostatic work is done. The optimum size of the lattice site varies inversely with cation charge. If an ion is of a different charge than that of the ion that normally occupies a lattice site, then a charge-compensating defect is required elsewhere in the lattice (Blundy and Wood 2003).



Figure 15: Lattice Strain model using partition coefficients calculated from element data gathered from inch scale banding samples.

Comparison of Geothermometry and Zircon Temperatures

Using the Ti-in-zircon geothermometers of Ferry and Watson (2007), Wall et al. (2018) provided zircon crystallization temperatures of 890°C to 870°C for rocks from the Lower Banded series, Ultramafic series, and Basal series. Our calculated temperatures fall in the middle of the range of temperatures for the entire SC as analyzed by Wall et al. (2018) (e.g., 990-720°C), which

are inferred to indicate that zircons crystallized over a wide minimum temperature range within each sample from initial zircon saturation temperatures at <10% interstitial melt down to nearsolidus temperatures; hence, the zircons should track near-solidus temperatures of the cumulates. The calculated two-pyroxene equilibration temperatures, Table 4, predominantly fall below the near-solidus temperature range determined by Wall et al (2018); therefore, the orthopyroxene is likely not magmatic and is instead likely a result of sub-solidus exsolution from the clinopyroxene. Our REE-in-plagioclase (Sun and Liang 2017) thermometer which yielded crystallization temperatures around 1200°C are much higher than Wall et al's (2018) Ti-in-zircon thermometry for the Stillwater.

By assuming the zircon age of 2710 Ma from Wall et al. (2018) and using the T_{Mg} (944°C), T_0 (1235°C), and the calculated cooling rate (log(°C/year) = -2.23) from the Sun and Lissenberg (2018) geospeedometer we can determine the approximate starting time of high-temperature crystallization of our samples to be ~2710.05 Ma. For comparison, our calculated cooling rates (0.0011 - 0.0102 °C/year) are lower than Sun and Lissenberg's (2018) calculated cooling rates for Hess Deep gabbros (0.003 – 10.2°C/year). MOR crust likely has faster cooling rates due to the combination of hydrothermal cooling above the axial melt lens and conductive/advective cooling by reactive porous flow below the melt lens (Zhang et al. 2014). Taking into account the whole dataset of calculated cooling rates for our samples we find a range of initial crystallization ages from 2710.05 Ma to 2710.08 Ma (within uncertainty of the U-Pb dates). This suggests that the plagioclase and pyroxene which constitute the FSR layering crystallized and then cooled over a period of ~0.0407 Ma, which is consistent with the model of SC formation proposed by Wall et al (2018).

CONCLUSIONS

Layered igneous intrusions are natural laboratories for studying differentiation processes and the petrogenesis of magmas as they preserve the crystalline products of fractionation. This study has produced an in depth investigation of the fine-scale rhythmic layering found in the Lower Banded Series of the SC in an attempt to better understand the mechanisms (i.e., physical or chemical) which formed the layering. Utilizing a combination of full thin section quantitative element maps, EPMA major element and LA-ICP-MS trace element analyses of plagioclase and pyroxene, and the methods developed by Sun and Liang (2017) and Sun and Lissenberg (2018), we have determined the high temperature geothermal history for the SC, specifically the plagioclase-pyroxene system of the fine-scale rhythmic layering. These methods yielded temperatures ranging from 1177°C to 1245°C, with cooling rates ranging from $\log(°C/year) = -$ 1.236 to -2.693. This range of temperatures is much higher than those from Wall et al. (2018). Our results show that the approximate starting time of high temperature crystallization of our samples is to be 2710.05 Ma with a calculated cooling rate of 0.0011 - 0.0102 °C/year. Our calculated crystallization for coexistent plagioclase and pyroxene is higher $(1220\pm13^{\circ}C)$ than the calculated temperatures for a two pyroxene system (~835°C) suggesting that the plagioclase crystallized first with the clinopyroxene crystallizing later. Both temperatures are below their respective solidus. These temperature data in concert with the textural data (Figure 7; Boudreau, 1982), suggests the formation of the fine-scale rhymithic layering was in large part due to sub-solidus diffusion.

Further, this study displayed the applicability of Sun and Liang's (2017) REE-inplagioclase-clinopyroxene thermometer and Sun and Lissenberg's (2018) geospeedometer to a gabbroic sample.

APPENDIX 1: ELEMENT MAPS

Ratio maps and histograms of Mg# in pyroxene and An in plagioclase derived from the element maps collected for this study are presented in the following pages. The software which was developed by Loocke and Lissenberg (in prep) for processing the element maps collected by their QACD (Quantitative Assessment of Compositional Distribution) technique can be found at www.qacd-quack.com. This study has displayed the applicability of Loocke's (in prep) QACD method in developing high resolution element maps of gabbroic rocks from a LII, as well as determining bulk major element compositions. This method allowed for simple major element analysis and data representation in the form of quantitative element maps, which allowed for quick determination of Mg#'s of pyroxene grains and An content of feldspar grains and their chemical distributions within the samples.

























































APPENDIX 2: ELECTRON MICROPROBE METHODS

All analyses were performed on the Shimadzu EPMA-1720HT in the Shimadzu Center for Environmental, Forensics, and Material Science at the University of Texas at Arlington during the Spring of 2018. The compositions of all synthetic and natural standards, and the analytical conditions for each phase used for analysis can be found in the below tables. The collected data was corrected for absorption, atomic number, and fluorescence (ZAF) effects by the software provided by Shimadzu. The Shimadzu software package applied a ZAF correction to the data after collection. The elemental weight percent data were converted to weight percent oxides assuming five oxygens for plagioclase and six oxygens for the pyroxenes.

St	anda	ards	used	in	for	EPN	LA	anal	yses.
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Name	SiO ₂	Al ₂ O ₃	TiO ₂	Cr ₂ O ₃	Fe ₂ O ₃	FeO	MgO	MnO	CaO	Na ₂ O	K ₂ O	NiO	V_2O_5
Anorthoclase	66.44	20.12				0.2			0.87	9.31	2.35		
Augite (Cr)	50.48	8.03	0.51	0.85	1.04	3.77	17.32	0.12	17.3	0.84	< 0.01		
Augite	50.73	8.73	0.74		1.08	5.37	16.65	0.13	15.82	1.27	0		
Chromite		9.92		60.5		13.04	15.2	0.11	0.12				
Diopside	55.81	0.11				0.25	17.79	0.04	25.28	0.25			
Gahnite		55.32				1.97		0.34					
Ilmenite			45.7		11.6	36.1	0.31	4.77					
Magnetite			0.17	0.26	67.07	30.60	0.05	< 0.01					
Microcline	64.24	18.3	0.02		0	0.04	0.03	0.04	0.02	1.3	15.14		
Olivine (San Carlos)	40.81					9.55	49.42	0.14	< 0.05			0.37	
Plagioclase	51.25	30.91	0.05		0.34	0.15	0.14	0.01	13.64	3.45	0.18		
Pyrope	41.46	23.73	0.47			10.68	18.51	0.28	5.17				
V^*													99.8

*Denotes a synthetic standard.

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	Flowert	Chandoud	Channel	Pe	eak	В	ackgroun	ds
	Element	Standard	(Crystal)	λ (nm)	Time (s)	λ_1 (nm)	λ_2 (nm)	Time (s)
-	Mg	Augite (Cr)	CH1/RAP	0.9896	30	1.0371	0.9418	15
	Al	Augite (Cr)	CH1/RAP	0.8335	30	0.8824	0.7835	15
	Fe	Augite	CH3/LIF	0.1936	30	0.2055	0.1815	15
	Si	Diopside	CH4/ADP	0.7123	40	0.7244	0.7004	20
	Ca	Diopside	CH4/ADP	0.3361	30	0.3457	0.3237	15
	Ti	Ilmenite	CH3/LIF	0.2749	30	0.2888	0.2648	15
	Na	Plagioclase	CH1/RAP	1.1920	20	1.2424	1.1444	10
	Κ	Microcline	CH4/ADP	0.3743	30	0.3858	0.3638	15
	Cr	Chromite	CH3/LIF	0.2290	30	0.2390	0.2210	15
	Mn	Pyrope	CH3/LIF	0.2101	30	0.2200	0.2000	15

Pyroxene analytical conditions used on the University of Arlington Shimadzu EPMA-1720HT EPMA. The analyses used a accelerating potential of 15 kV and a beam current of 20 nA with a beam size of 1 μ m. Abbreviations for the crystals are as follows: RAP = Rubidium Acid Pthalate, PET = Pentaerythritol, LIF = Lithium Fluoride, ADP = ammonium dihydrogen phosphate.

Plagioclase analytical conditions used on the University of Arlington Shimadzu EPMA-1720HT EPMA. The analyses used a accelerating potential of 15 kV and a beam current of 10 nA with a beam size of 5 μ m. Abbreviations for the crystals are as follows: RAP = Rubidium Acid Pthalate, PET = Pentaerythritol, LIF = Lithium Fluoride, ADP = ammonium dihydrogen phosphate.

F 1	Ctour lour l	Channel	Pe	eak	Ba	ackgroun	ds
Element	Standard	(Crystal)	λ (nm)	Time (s)	λ_1 (nm)	λ_2 (nm)	Time (s)
Na	Anorthoclase	CH1/RAP	1.1925	20	1.241	1.141	10
Mg	Diopside	CH1/RAP	0.9905	30	1.0398	0.9398	15
Ca	Anorthite	CH4/ADP	0.3356	30	0.3459	0.3259	15
Al	Plagioclase	CH1/RAP	0.8347	30	0.8833	0.7853	15
Si	Plagioclase	CH4/ADP	0.7122	30	0.7224	0.7024	15
Fe	SC-Olivine	CH3/LiF	0.1935	30	0.2036	0.1836	15
К	Microcline	CH4/ADP	0.3738	20	0.3841	0.3641	10

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