Further Insights of Temperature-Time Events on the HED Parent Body Using U-Th-Pb Chronology of

Zircon-Bearing Noritic Diogenite Northwest Africa 10666

By

Christian Anthony Martinez

A thesis submitted to the Department of Earth and Atmospheric Sciences, College of Natural Science and Mathematics in partial fulfillment of the requirements for the degree of

Master of Science

in Geology

Chair of Committee: Thomas Lapen Committee Member: Alexander Robinson

Committee Member: David Mittlefehldt

University of Houston

May 2021

ACKNOWLEDGMENTS

I'd like to thank Christina Martinez, Dr. Robert Martinez, Gabriella Martinez, Frankie Martinez, and the rest of my family, Dr. Lapen, Dr. Minako Righter, Dr. Capuano, members of my committee, Upeople, friends, colleagues, and all of those who helped me in achieving the requirements to earn a Master of Science Degree from the University of Houston. Thank you for the friendships, professional relationships, guidance, emotional/financial support, and help along the way. I am eternally grateful and I would not have been able to do this without you all.

Abstract

Howardite, Eucrite, and Diogenites (HEDs) are a suite of achondrite meteorites believed to be derived from asteroid 4 Vesta and represent the largest suite of achondrites from a single parent body. The diogenites represent the lower crust of the parent body, but their igneous and metamorphic histories are not well understood. NWA 10666, which has been classified as a zircon bearing noritic diogenite was investigated by in situ U-Th-Pb and trace element analyses of trace and major phases, optical light and electron-beam petrologic analyses, and mineral thermometry to better constrain its igneous and metamorphic histories and its geochemical and petrologic relationships with other diogenite, eucrite, and cumulate eucrite specimens. NWA 10666 is moderately shocked, exhibits pyroxene compositions that are more ferroan than most other diogenite specimens, and contains minor and accessory phases: ilmenite, a silica polymorph, Ca-phosphate, and zircon.

Laser-ablation ICP-MS analyses of shock-fractured zircon and phosphate at UH yielded $^{207}Pb/^{20}6Pb - ^{204}Pb/^{238}U$ inverse isochron ages of 4542 ±20 Ma (MSWD = 0.3) and 4248 ±25 Ma (MSWD = 1.5), respectively. Trace element analyses of bulk rock indicates a slight positive Eu anomaly (Eu/Eu* = 1.2) and in situ rare-earth element (REE) analyses of pyroxene and plagioclase indicate REE equilibration at 1262 ± 8 °C (2SD). Fe-Mg exchange between OPX and CPX records an equilibration temperature of 850 °C. The U-Pb age of the shocked zircon is likely a minimum age for those grains indicating magmatism in the HED parent body was likely coeval with the main phase of eucrite magmatism at ~4555 Ma. Geochemical and petrologic data indicate that NWA 10666 is related to Yamato type-B diogenites, a group that may be compositionally transitional between cumulate eucrites and diogenites. The 4248 ±25 Ma age of Ca-phosphate is older than most Ar-Ar thermochronology that peak between 3.3 and 3.8 Ga.

Dates between 4.1 and 4.4 Ga are more common in higher temperature systems than Ar-Ar and may indicate that the Ar-Ar age cluster between 3.3-3.8 may reflect an overall waning impact intensity in the inner Solar System.

Table of Contents

Introduction	.1
1.1.1 HED meteorities	. 2
1.1.2 4 Vesta	. 3
1.1.3 Dawn Mission	. 3
1.1.4 Eucrites	. 4
1.1.4.1 Basaltic Eucrites	. 5
1.1.4.2 Cumulate Eucrites	. 7
1.1.5 Diogenites	. 9
1.1.6 Howardites	. 12
1.2 HED Ages	. 13
1.2.1 Long-lived chronometers	. 13
1.2.2 Short-lived chronometers	. 14
1.2.3 Al-Mg short-lived chronometer system	. 15
1.2.4 ⁵³ Mn- ⁵³ Cr system	. 15
$1.2.5 \ {}^{182}\text{Hf}-{}^{182}\text{W system}$. 16
1.2.6 Low-temperature chronometers (Ar-Ar and U-Pb in phosphate)	. 16
1.3 Project motivation	. 17
Sample Description	. 19
Sample Description	. 19 . 21
Sample Description	. 19 . 21 . 21
Sample Description	. 19 . 21 . 21
Sample Description	. 19 . 21 . 21 . 21 . 21
Sample Description	. 19 . 21 . 21 . 21 . 21 . 22
Sample Description	. 19 . 21 . 21 . 21 . 21 . 22 . 22
Sample Description Methods 3.1 Sample Preparation. 3.2 Electron-beam microanalyses. 3.2.1 Scanning Electron Microscope (SEM) 3.2.2 Electron probe microanalysis (EPMA) 3.3 Laser Ablation Inductively Coupled Plasma–Mass Spectrometry (LA-ICP-MS). 3.3.1 Trace element in situ analyses	. 19 . 21 . 21 . 21 . 21 . 22 . 22 . 23
Sample Description Methods 3.1 Sample Preparation 3.2 Electron-beam microanalyses 3.2.1 Scanning Electron Microscope (SEM) 3.2.2 Electron probe microanalysis (EPMA) 3.3 Laser Ablation Inductively Coupled Plasma–Mass Spectrometry (LA-ICP-MS) 3.3.1 Trace element in situ analyses 3.3.1.1 Ca-phosphate dating	. 19 . 21 . 21 . 21 . 21 . 22 . 22 . 23 . 23
Sample Description Methods 3.1 Sample Preparation 3.2 Electron-beam microanalyses 3.2.1 Scanning Electron Microscope (SEM) 3.2.2 Electron probe microanalysis (EPMA) 3.3 Laser Ablation Inductively Coupled Plasma–Mass Spectrometry (LA-ICP-MS) 3.3.1 Trace element in situ analyses 3.3.1.1 Ca-phosphate dating 3.3.1.2 Zircon dating	. 19 . 21 . 21 . 21 . 21 . 22 . 22 . 23 . 23 . 24
Sample Description Methods 3.1 Sample Preparation 3.2 Electron-beam microanalyses 3.2.1 Scanning Electron Microscope (SEM) 3.2.2 Electron probe microanalysis (EPMA) 3.3 Laser Ablation Inductively Coupled Plasma–Mass Spectrometry (LA-ICP-MS) 3.3.1 Trace element in situ analyses 3.3.1.1 Ca-phosphate dating 3.3.1.2 Zircon dating 3.4 Oxygen isotopes analyses	. 19 . 21 . 21 . 21 . 21 . 22 . 22 . 23 . 23 . 24 . 24
Sample Description Methods 3.1 Sample Preparation. 3.2 Electron-beam microanalyses. 3.2.1 Scanning Electron Microscope (SEM). 3.2.2 Electron probe microanalysis (EPMA) 3.3 Laser Ablation Inductively Coupled Plasma–Mass Spectrometry (LA-ICP-MS). 3.3.1 Trace element in situ analyses. 3.3.1.1 Ca-phosphate dating 3.3.1.2 Zircon dating 3.4 Oxygen isotopes analyses. 3.5 Bulk Chemistry.	. 19 . 21 . 21 . 21 . 22 . 22 . 23 . 24 . 24 . 25
Sample Description Methods 3.1 Sample Preparation 3.2 Electron-beam microanalyses 3.2.1 Scanning Electron Microscope (SEM) 3.2.2 Electron probe microanalysis (EPMA) 3.3 Laser Ablation Inductively Coupled Plasma–Mass Spectrometry (LA-ICP-MS) 3.3.1 Trace element in situ analyses 3.3.1.1 Ca-phosphate dating 3.4 Oxygen isotopes analyses 3.5 Bulk Chemistry 3.6 Thermometry	. 19 . 21 . 21 . 21 . 22 . 23 . 23 . 23 . 23 . 24 . 24 . 25 . 25

Results	
4.1 Petrography	
4.1.1 Orthopyroxene	
4.1.2 Clinopyroxene	
4.1.3 Plagioclase	

4.1.4 Oxides	
4.1.5 Phosphate	
4.1.6 Zircon	
4.2 Mineral Compositions	
4.2.1 Orthopyroxene	
4.2.2 Clinopyroxene	
4.2.3 Plagioclase	
4.2.4 Minor Phases	
4.3 U-Th-Pb Dating	
4.3.1 U-Th-Pb Data Phosphate	
4.3.2 U-Th-Pb Zircon	
4.4 Oxygen Isotopic Data	
4.5 Bulk Chemistry	
4.6 Thermometry.	
Discussion	
5.1 Comparison with other diogenites and cumulate eucrites	
5.1.1 Petrography/Petrology/Mineralogy	
5.1.2 Chemistry	
5.2 Age and Thermal History	
5.3 Parent Body Processes	
Conclusions	
Bibliography	

List of Figures and Tables

Figures

1 Models for 4 Vesta differentation	4
2 Basaltic eucrite LEW 88010	5
3 REE patterns of cumulate and basaltic eucrites & diogenites	7
4 Cumulate eucrite - Serra de Magé	8
5 Brecciated diogenite Johnstown	9
6 Pyroxene compositions of cumulate and basaltic eucrites & diogenites	10
7 Howardite Miller Range 11100	13
8 Ar-Ar ages of plagioclase from literature	17
9 NWA 10666 hosts zircons	19
10 X-ray composite chemical map of diogenite NWA 10666	20
11 Image of NWA 10666 (whole rock)	26
12 Low magnification image of NWA 10666 within silica epoxy	26
13 Chemical map of NWA 10666	27
14 X-ray composite chemical map of diogenite NWA 10666	28
15 Backscattered electron image of silica polymorph phase	29
16 Backscattered electron image of zircon in NWA 10666	30
17 Pyroxene composition quadrilateral of NWA 10666	31
18 Whole rock REE concentrations of NWA 10666	31
19 Plagioclase composition diagram of NWA 10666	32
20 False color chemical map of NWA 10666's phosphates	37
21 False color chemical map of NWA 10666's phosphates	37
22 Zircon and Ca-phosphates used for analyses	38
23 Pb-Pb inverse isochron diagram for Ca-phosphate	39
24 Backscattered electron image of zircon	42
25 Pb-Pb inverse isochron of zircon within NWA 10666	42
26 ²⁰⁷ Pb- ²⁰⁶ Pb weighted mean ages for three Ca-phosphates	43
27 HED oxygen isotope data	45
28 Bulk REE pattern of NWA 10666 compared to other HEDs	46
29 REE-in-plagioclase-clinopyroxene diagram	47
30 Pyroxene composition of NWA 10666 vs literature data of diogenites	50
31 Sm vs Hf log plot of NWA 10666 compared to other HEDs	52
32 Backscattered electron image of zircon	53
33 Compilation of various chronologic systems from literat	57
34 Schematic of a proposed fractionalization process within Vesta	58

Tables

1 Electron microprobe analyses of major phases in NWA 10666	34
1cont. Electron microprobe analyses of major phases in NWA 10666	35
2 Major and trace element abundances in NWA 10666	36
3a LA-ICP-MS U-Th-Pb data for Ca-phosphates in NWA 10666	41

3b LA-ICP-MS U-Th-Pb data for Ca-phosphates in NWA 10666	. 41
4a LA-ICP-MS U-Th-Pb data for zircon grain spots in NWA 10666	. 44
4b LA-ICP-MS U-Th-Pb data for zircon grain spots in NWA 10666	44

Chapter 1

Introduction

Howardites, eucrites, and diogenites (HEDs) are a clan of meteorites thought to be derived from asteroid 4 Vesta, which is located in the asteroid belt between Mars and Jupiter (McSween et al., 2013). The HED clan make up the largest suite of achondrite meteorites available for study from any solar system body, excluding the Moon (Mittlefehldt, 2015). Being so abundant, they provide clues of early planetary formation processes (e.g., Mittlefehldt, 2015 and references therein) as well as the timing and nature of impact processes (e.g., Bogard and Garrison, 2003; Cohen, 2013; Jourdan et al., 2020). Based on petrologic and chronologic analyses, the HED parent body underwent accretion and differentiation very early in solar system history (4563–4565 Ma) (e.g. Trinquier et al., 2008; Kleine et al., 2009; Schiller et al., 2011). Schiller et al., 2011 and Day et al., 2012 stated differentiation lasted 3-4 Myr after CAI formation through short lived chronometers, while Takahashi and Masuda, 1990 concluded a longer period of igneous activity of 50–100 Ma through long lived chronometers. Zhou et al., 2013 concluded that differentiation occurred during the first 50 Ma and was subjected to significant impacts, perhaps culminating between 4.1 and 3.3 Ga (e.g., Bogard and Garrison, 2003; Cohen, 2013). Nearly all HED meteorites show signs of thermal and/or impact metamorphism.

Diogenites are coarse-grained, mafic to ultramafic igneous rocks characterized as orthopyroxene-rich with smaller, but variable abundances of clinopyroxene, plagioclase, chromite, and olivine (Beck and McSween, 2010; Irving et al., 2014; Irving et al., 2016). Many diogenites are cataclastic although some samples such as (Dhofar 700) are poorly crushed. These specimens are important because they serve as records of lower crustal processes in the parent body (Mittlefehldt et al., 2012a). Constraints on the temperature-time histories of these lowercrustal materials have been difficult to constrain due to limited chronologic options for these typically mineralogically simple meteorites in addition to thermal equilibration/metamorphism that affected most diogenite and eucrite specimens.

NWA 10666 is one among a series of noritic and feldspathic diogenites (e.g., Type B diogenites; Mittlefehldt and Lindstrom, 1993) and the first reported zircon-bearing diogenite (Irving et al., 2014; Irving et al., 2016; Tanner et al., 2017). The specimen also contains Cl-apatite, making it well suited for combined chronologic and petrologic investigations. Zircon and apatite can be used for high and low temperature U-Th-Pb chronology due to the different resetting temperatures of each mineral. Zircon is not easily reset and will offer a robust crystallization age, while apatite resets at much lower temperatures and will present a low temperature constraint. Here, we present petrologic descriptions and analyses, geochemical data, and U-Th-Pb chronology of apatite and zircon to better constrain its igneous age, comparisons with other diogenite specimens, and its temperature-time history.

1.1.1 HED meteorites

Howardites, Eucrites, and Diogenites (HEDs) consist of ~62% of achondrites in the US Antarctic Meteorite Collection (McCoy et al., 2014). This suite provides clues of early planetary differentiation, early magmatism, and early impact processes. More than 1000 kg of HED meteorites had been processed before 2011.

1.1.2 4 Vesta

McCord et al., (1970) showed that the spectral reflectance of Vesta was similar to that of the basaltic eucrite Nuevo Laredo. It had been previously known that 4 Vesta was/is one of the largest known masses in the asteroid belt and appears to be covered by a basaltic crust, indicating that it has undergone extensive melting and differentiation (McCord et al., 1970; Keil, 2002; Russell et al., 2007; McSween et al., 2013 and references therein). However, not every scientist agrees that all HEDs come from 4 Vesta (e.g., Wasson and Chapman, 1996; Wasson, 2013; Schiller et al. 2011). Binzel and Xu (1993), observed smaller asteroids that were spectrally and dynamically linked to Vesta and referred to them as the "vestoids". Wasson (2013) concluded that basaltic reflection spectra are not unique enough to confirm all HEDs are from Vesta; a number of parent bodies like Vesta may have been produced in the same region of the Solar System. Oxygen isotopic compositions of HED meteorites as well as mesosiderites and IIIAB irons are essentially identical (Greenwood et al., 2017). These observations of asteroids in the inner Asteroid Belt led Wasson to believe that more than half of the V-type (basaltic) asteroids may not belong to the Vesta family.

1.1.3 Dawn Mission

In 2011, the Dawn mission orbited around 4 Vesta and the acquired data is consistent with it being a parent asteroid of the HEDs (McSween et al., 2013). Dawn conducted observations with high spatial resolution using framing cameras (FC) (Sierks et al., 2011), a visible and infrared mapping spectrometer (VIR) (De Sanctis et al., 2011) and a gamma ray and neutron detector (GRaND) (Prettyman et al., 2011). The mission showed spectra matches between the asteroid and meteorites, but it is still not confirmed that HEDs are in fact from 4 Vesta. Confirmation would come from direct sampling and subsequent isotopic fingerprinting.

1.1.4 Eucrites

Eucrites are hypothesized to represent the outer most layer (crust) of 4 Vesta (Figure 1). They contain pyroxene, calcic plagioclase, and minor amounts of chromite and accessory amounts of olivine, metal, silica, phosphates, and ilmenite (e.g. Duke and Silver, 1967 and references therein;



Figure 1. Models for 4 Vesta differentiation by a) (Righter and Drake 1997), and b) (Stopler, 1977). Illustration by: (Clenet et al., 2014)

Delaney et al., 1984a,b). Eucrites are separated into two igneous textural groups, the basaltic eucrites and the cumulate eucrites. They are also distinguished based on severity of secondary processes related to impact. These distinctions are unbrecciated, brecciated, and polymict eucrites. Eucrites can be unequilibrated, such as in basaltic eucrite NWA 5073 (Roszjar et al., 2011), or equilibrated evident in the homogenous compositions of major and minor phases. The presence or lack of equilibrated phases in eucrites indicates the various effects of thermal metamorphism.

1.1.4.1 Basaltic Eucrites

This group of eucrites are fine- to medium grained (<1– 2.5 mm) and primarily composed of pigeonite and calcic plagioclase (An₇₅₋₉₁; Figure 2). Most specimens are brecciated, with a fine-grained, fragmental matrix that surrounds lithic and mineral clasts. Original igneous textures of brecciated eucrites are mostly



Figure 2. False colored microscopic image of basaltic eucrite LEW 88010. Lathic texture of plagioclase (<1mm; light purple color) evidence of rapid cooling. Larger pyroxene (<1- 2mm). (Mayne et al, 2009)

preserved in lithic clasts. Those that are not brecciated, their igneous textures vary from finegrained vitrophyric with pyroxene microphenocrysts in a pyroxene microcrysts and plagioclasesilica glass groundmass (for example: ALHA 81001) to coarse-grained subophitic textures with fine-grained mesostatis (paired Pecora Escarpment (PCA) 91078, PCA 91245) (Howard et al., 2002; Mayne et al., 2009). An even fewer number of specimens of unbrecciated eucrites have been highly metamorphosed, leading them to be recrystallized into granoblastic textures (for example: EET 90020 and GRA 98098; Mayne et al., 2009). Minor and accessory phases in many eucrite specimens include: chromite, illmenite, silica, olivine, metal, phosphate, and zircon (e.g., Delaney et al., 1984a,b; Saiki et al., 1991; Mayne et al., 2009; Haba et al., 2014).

Unequilibrated basaltic eucrites are those that have been less thermally influenced than the equilibrated counter parts. NWA 5073 is an uncommon, unmetamorphosed, and unbrecciated basaltic eucrite composed of coarse-grained zoned pyroxenes, plagioclase, and accessory phases such as chromite and fine-grained mesostatis (Roszjar et al., 2011). The unequilibrated grains display chemical 'zoning' from core to rim (Takeda and Graham, 1991). Unequilibrated pyroxenes have cores of magnesian pigeonite with low amounts of Ca, which then zone into ferroaugite or subcalcic ferroaugite compositions (Mittlefehldt, 2015). Plagioclase grains in Chervony Kut and Nuevo Laredo range compositionally (An ₇₅₋₉₄ and An₇₄₋₉₂, respectively) (Mayne et al., 2009; Warren and Jerde, 1987).

Global metamorphism on the eucrite parent body had caused most eucrites to have undergone some degree of metamorphism (Iizuka et al., 2015, 2019; Liao and Hsu, 2017; Kennedy et al., 2019; Koike et al., 2020; and others). Thermal metamorphic events discussed in chapter 5 caused original pigeonite to experience subsolidus exsolution of augite and the original Fe/Mg zonation became homogenized (Takeda and Graham, 1991). Equilibration could indicate prolonged periods at depth in the parent body or a prolonged metamorphic event or events. Some basaltic eucrites such as QUE 97052 are partially equilibrated where it contains igneous-zoned plagioclase and is thus unlikely to have experienced metamorphism extreme enough to have affected its igneous U-Pb systematics of, for example, zircon (Righter and Lapen, 2010; Righter et al., 2011).

Basaltic eucrites typically have a flat REE pattern with higher absolute values than cumulate eucrites or diogenites (Figure 3).

1.1.4.2 Cumulate Eucrites

Primarily composed of clinopyroxene and calcic plagioclase, these medium- to coarse-grained gabbroic specimens contain minor amounts of chromite, and accessory silica, phosphate, ilmenite, metal, troilite, and zircon (e.g. Delaney et al., 1984 a,b; Gomes and Keil, 1980).



and diogenites from literature. Blue=diogenites, green= cumulate eucrites, red= basaltic eucrites. (Mittlefehldt, 2015 and references therein)

Typical textures of unbrecciated cumulate eucrites are equigranular with subequal amounts of pyroxene and plagioclase grains 0.5–5 mm in width (Duke and Silver, 1967; Hess and Henderson, 1949; Lovering, 1975; Mayne et al., 2009; Mittlefehldt and Lindstrom, 1993; for example: Moore County and Moama). Serra de Magé represents a type-example cumulate eucrite exhibited through its cumulate texture (Figure 4). Most cumulate eucrite specimens are brecciated but a few are unbrecciated.

Compositions of cumulate eucrites are similar to basaltic eucrites. Plagioclase compositions are An_{91–95}, (Lovering, 1975; Mayne et al., 2009; Mittlefehldt, 1990; Mittlefehldt and Lindstrom, 1993; Treiman et al., 2004), a range that is generally more calcic than plagioclase in a basaltic eucrites. The primary igneous pyroxene from the majority of cumulate eucrites were pigeonite which produced exsolved augite lamellae hosted in orthopyroxene during slow cooling (Hess and Henderson, 1949; Harlow et al., 1979; Lovering, 1975; Mori and Takeda, 1981b;

Takeda et al., 1976). Silica is commonly present in many specimens including Moama, Moore County and Serra de Magé (Duke and Silver, 1967; Hess and Henderson, 1949; Lovering, 1975; Treiman et al., 2004). Treiman et al., 2004 concluded that some secondary silica-bearing veins in Sierra de Mage were precipitated from aqueous fluids.



Figure 4. Cross-polarized microscopic image of Serra de Magé consisting of almost entirely of pyroxene (gray with dark striations across grains). The other crystals in this image are plagioclase.

Equilibration of cumulate eucrites is evident in major phases pyroxene and plagioclase. Analyses of pyroxene from core to rim display compositions that are homogeneous in Fe/Mg, although the exact range varies from specimen to specimen (e.g. ALH 85001 pyroxene Mg# of 66.1 & Y-7991195 pyroxene Mg# of 42.6) (Mittlefehldt, 2015; Mittlefehldt and Lindstrom, 1993). Plagioclase (An₉₁₋₉₅) is also commonly compositionally homogenous (Lovering, 1975; Mayne et al., 2009; Mittlefehldt, 1990; Mittlefehldt and Lindstrom, 1993; Treiman et al., 2004).

Cumulate eucrites usually display a flat REE pattern with a positive Eu anomaly with lower overall REE abundances than basaltic eucrites (Figure 3). Binda is a polymict cumulate eucrite which leads to its unique REE pattern shown in Figure 3 (Delaney et al., 1983).

1.1.5 Diogenites

Diogenites are coarse-grained mafic to ultramafic rocks characterized by large abundances of magnesian orthopyroxene (Beck and McSween, 2010; Beck et al., 2013; Mason, 1963; Mittlefehldt, 1994a). They have smaller, but variable amounts of clinopyroxene,



Figure 5. Cross-polarized microscopic image of brecciated diogenite Johnstown. Johnstown's pyroxene grains (larger grain in FOV) have been rounded indicating primary igneous texture has been eliminated. Intragranular texture displays cracks indicating severe brecciation.

plagioclase, spinel, oxides, and olivine (Irving et al. 2014; 2016). Most diogenites have been brecciated to various degrees (Mason, 1963) although some diogenites, for example, GRO 95555, Tatahouine and Yamato Type A series (consisting of Y-74013, Y-74097, and Y-74136) are classified as "unbrecciated" (Mittlefehldt, 2015). However, other diogenites can show a high degree of brecciation. A typical diogenite that displays such high brecciation is Johnstown (Figure 5). Specimens with brecciated textures can be monomict or polymict. The coarse-grained nature of diogenites is traditionally interpreted to originate from within a plutonic layer deep inside the crust and are important records of lower crustal processes in their parent body (McSween et al., 2010; Zhang et al., 2020).

Unequilibrated diogenites such as Dhofar 700 and Y-74097 are rare. Dhofar 700 and Y-

74097 retain igneous core-to-rim compositional zoning in pyroxene indicating a lack of significant thermal metamorphic influence (Yamaguchi et al., 2011). Equilibrated diogenites typically have grains that are compositionally homogeneous in their major element concentrations. As the degree of metamorphism increases, primary textures and igneous petrologic information can be somewhat difficult to recognize and evaluate.

Most diogenites are primarily composed of large, subhedral orthopyroxene grains (~84 – 100 vol %), measuring up to 5cm in size set within a finegrained matrix of orthopyroxene (Mason, 1963; Bowman et al., 1997). In general, pyroxene



Figure 6. Pyroxene composition quad of cumulate and basaltic eucrites & diogenites compiled from literature (Mittlefehldt, 2015)

compositions of diogenites are typically more magnesian than basaltic and cumulate eucrites, although there is some overlap of pyroxene compositions between specimens classified as cumulate eucrites and diogenites (Figure 6). Orthopyroxene compositions in many diogenites have a narrow range of major element concentrations (Wo₁₋₃ En₇₂₋₇₆ Fs₂₃₋₂₅) and Mg # 74–77 (Domanik et al., 2004; Fowler et al. 1994; Mittlefehldt et al., 1998; Mittlefehldt 2000, 2015; Mittlefehldt and Lindstrom 1993). There is also a wide array of documented diogenites with varying orthopyroxene compositions. NWA 1461 and Meteorite Hills (MET) 00425 possesses the most magnesian orthopyroxene with Mg# of 86 and 84, respectively (Bunch et al., 2007; Barrat et al., 2010; Mittlefehldt, 2012a). Noritic diogenites, such as those in the Yamato Type B group (consisting of Y-75032, Y-791199, QUE 93009, and NWA 8321), are more ferroan than

typical diogenites, containing orthopyroxene with Mg# of 66 and 70, respectively (Mittlefehldt et al., 2012a; Fowler et al.,1994; Mittlefehldt and Lindstrom, 1993).

Typically, minor and accessory phases occur as inclusions within larger orthopyroxene grains (McSween et. al., 2010). Chromite and olivine are common minor minerals in diogenites ranging from 0 - 5 vol % (Bowman et al., 1997; Mittlefehldt, 1994a). Some diogenites described by Sack et al., (1991, 1994) contain significant amounts (40 - 50% vol) of olivine and have been described as "olivine diogenites". Dunitic specimen MIL 03443 was originally classified as a mesosiderite, but Beck et al., (2011) argue that this specimen should be reclassified and related to diogenites. Clinopyroxene occurs as ~1um thick exsolution lamellae in orthopyroxene, but discrete grains in the matrix or interstitial to orthopyroxene grains have also been found (Beck and McSween, 2010; Domanik et al., 2004; Mittlefehldt, 1994a, 2000). Clinopyroxene compositions are (Wo_{41-47.1} En_{41.7-47.6} Fs₆₋₁₄) (Mittlefehldt, 2015 and references therein) Plagioclase present in some diogenites ranges from trace constituents to > 5 vol%. Average plagioclase compositions range from An₈₁-An₉₁ (Mittlefehldt, 2015).

Accessory phases in typical diogenites include clinopyroxene ($\sim 0 - 3$ vol %), metal (<1 vol %), silica phase ($\sim 0 - 2$ vol %) and Ca-phosphates (<1 vol %) (Bowman et al., 1997; Mittlefehldt, 1994a). Silica is present in some diogenites and its distribution is highly variable even within a single diogenite specimen. It can occur as larger anhedral equant grains or as polycrystalline aggregates in the matrix (Mittlefehldt, 1994a). Metal inclusion "curtains" are frequent in orthopyroxene and exists as um-sized grains (Gooley and Moore, 1976). Phosphates are rare but grains in Bilanga and Roda are 5–10 µm size and are rich in light rare earth elements (Domanik et al., 2004, 2005; Mittlefehldt, 1994a). Ilmenite is a trace phase in some noritic diogenites (Delaney et al., 1984a,b; Mittlefehldt and Lindstrom, 1993; Mittlefehldt et al., 2012a) perhaps indicating shallow (< 10 km) levels of emplacement (e.g., Zhang et al., 2020).

Major element compositions of diogenites are strongly leveraged by the composition of the dominant pyroxene phase (Fredriksson et al., 1976; Fukuoka et al., 1977; Mittlefehldt, 1994a, 2003). Given the low partition coefficients for many incompatible trace elements in orthopyroxene (such as LREE), bulk rock compositions are generally depleted in incompatible trace elements relative to undifferentiated meteorites (Schwandt and McKay, 1998). Rare earth element data of diogenite whole rocks show the relatively low overall REE concentrations and relatively depleted light REE abundances (Figure 3) (Barrat

et al., 2008). These low concentrations, however, can be susceptible to contamination of LREE by hot desert/Antarctic weathering (e.g., Barrat et al., 1999, 2006), nugget effects from trace-element-rich phases that result in variations in trace element concentration determinations from one part of a specimen to another (such as in Johnstown; Floran et al., 1981), and/or contamination from foreign material in polymict specimens (Lomena et al., 1976; Mittlefehldt, 1994a). Therefore, the abundances of light REEs in pure orthopyroxene compared to a bulk rock measurement can differ significantly.

1.1.6 Howardites

Howardites are polymict breccias composed of diogenite and eucrite lithic clasts along with other debris from the rocks being subject to surface "gardening" (Figure 7) (Duke and Silver, 1967). They are the rocks that make up the surface and are split into two subtypes: regolithic howardites and fragmental howardites (Mittlefehldt et al., 2013b; Warren et al., 2009). Low degree of metamorphism has been reported for howardites such as Bholghati, Kapoeta and Frankfort (Mason and Wiik, 1966a, b; Reid et al., 1990). The howardites formed during gardening on the surface of the parent body. Howardites can be rich in noble gases compared to the other meteorites in the suite (e.g., Mazor and Anders, 1967) due to extensive surface exposure and implantation of solar wind ions.

1.2 HED Ages

1.2.1 Long-lived chronometers

for HED igneous lithologies as

The age of crystallization

Figure 7. Cross-polarized microscopic image of howardite Miller Range 11100. Fine-grained ground mass (black) along with other crushed up lithic fragments. Eucritic clasts are embedded throughout the rock. (Gregory et al., 2016)

determined by long-lived chronometer systems such as Rb-Sr, Sm-Nd, Pb-Pb demonstrate that magmatism on Vesta occurred early in Solar System history (e.g., Allègre et al., 1975; Birck and Allègre, 1978; Nyquist et al., 1986; Papanastassiou and Wasserburg, 1969; Smoliar, 1993; Tera et al., 1997). However, most eucrites and diogenites have been brecciated and/or thermally metamorphosed to a degree that has reset different geochronometers due to post-crystallization disturbances. The magnitude of isotopic disturbance depends on the relative diffusivities of the parent and daughter elements in the host material and the temperature-time history of the specimens (Mittlefehldt, 2015). Moore County and Serra de Magé are cumulate eucrites that yield Pb-Pb model ages (Tera et al., 1997) that are lower than the age of magmatism for the basaltic eucrites based on Rb-Sr data (Smoliar, 1993). Shock metamorphism in Johnstown and Tatahouine also displays lower ages than that of eucrite magmatism, leading to the potential resetting of the Rb-Sr chronometry systems (Takahashi and Masuda,1990). Overall, disturbances in isotopic systems have made it difficult to constrain the igneous histories of eucrites and diogenites.

U-Th-Pb in zircon systematics offers high temperature (>900°C) thermochronologic analysis due to slow Pb diffusion in zircon (Cherniak and Watson, 2001; Cherniak, 2010; Niihara, 2012; Zhou et al., 2013). Zircon has a relatively high closure temperature for Pb and is resilient to shock resetting (e.g. Cherniak, 2010) making zircon dating a reliable method for constraining the timing of suprasolidus processes, including igneous crystallization or partial melting. It is important to note that, with the exceptions of EET90020, Agoult, and perhaps Camel Donga (Zhou et al., 2013), most zircon ages of HEDs reflect igneous crystallization despite evidence for thermal metamorphism. It is critical to evaluate if shock deformation is present, as plastic deformation of zircon has been shown to facilitate mobility of trace elements, cause recrystallization, and if at sufficiently high temperature result in dissociation; all of these processes can affect U-Pb dates (e.g. Reddy et al., 2007; Cavosie et al., 2016).

1.2.2 Short-lived chronometers

Fine-scale experiments of the relative ages of events documenting Vestan differentiation history is provided by several short-lived chronometers. These short-lived chronometers systems: 26 Al- 26 Mg (t¹/₂= 0.717 Ma), 53 Mn- 53 Cr (t¹/₂= 3.7 Ma) and 182 Hf- 182 W (t¹/₂= 8.9 Ma) can be linked into an absolute age scale if an accurate, precise, and long-lived chronometer system, such as U-Pb, can be anchored to a reference meteorite (Mittlefehldt, 2015). Short-lived chronometers are important fine-scale chronometers for investigating the timing of differentiation of Vesta as well as to precisely date eucrites that formed while these short-lived isotope systems were extant.

1.2.3 Al-Mg short-lived chronometer system

Schiller et al., (2011) calculated that diogenites crystallized from 0.6 to 2.5 Myr after formation of CAIs. They also determined cumulate and basaltic eucrite reservoirs were formed between 2.1 and 2.8 Myr after CAI formation. Schiller et al., (2011) concluded that diogenite formation began within ~ 1Myr of solar system formation and was near complete solidification within the next ~3Myr. The correlations of ²⁶Mg abundance variations with incompatible lithophile element concentrations in diogenites suggest radiogenic ²⁶Mg ingrowth during silicate fractionation (Schiller et al., 2011). It is unclear if this correlation represents the timing of diogenite specimen crystallization or the formation of their sources. If the correlation represented the formation of diogenite sources, then diogenite material formed during secondary differentiation events.

Schiller et al., (2011) note that HEDs from an asteroid as big as Vesta cannot be explained by a magma ocean model. A magma ocean model cannot get to a point where diogenites were crystallizing in within 600,000 years (Schiller et al., 2011). However, these early variations in Al/Mg ratios associated with silicate fractionation during a magma ocean crystallization could have produced the variations in ²⁶Mg abundances that were inherited by subsequently produced igneous products (Schiller et al., 2011).

1.2.4 ⁵³Mn-⁵³Cr system

Shukolyukov and Lugmair (2002; and references therein) and Trinquier et al., (2008) investigated diogenites, cumulate eucrites and basaltic eucrites for their ⁵³Mn-⁵³Cr isotope systematics. They estimated the time of differentiation of the HED parent body to be 4565 ± 1 Ma (Shukolyukov and Lugmair, 2002) based on bulk rock Mn-Cr measurements that are

anchored to a 4557.8 ± 0.5 Ma Pb-Pb age of LEW 86010 (Lugmair and Galer, 1992).

1.2.5 ¹⁸²Hf–¹⁸²W system

The Hf-W system can constrain the timing of early metal-silicate fractionation on differentiated bodies because W, a moderately siderophile element, and Hf, a lithophile element, are strongly partitioned into metal and silicate, respectively (Mittlefehldt, 2015). Based on Hf-W measurements of eucrites and diogenites, core-mantle differentiation of Vesta is 2.5 ± 1.2 Myr after CAI formation (Touboul et al., 2008), which is statistically identical to the time of silicate differentiation based on the Mn-Cr system (Trinquier et al., 2008). These estimates are later than the time of silicate differentiation constrained from the Al-Mg, which indicates a time of 0.6 Myr after CAI (Schiller et al., 2011).

1.2.6 Low-temperature chronometers (Ar-Ar and U-Pb in phosphate)

The number of unequilibrated eucrites is few relative to those that were subjected to slow cooling and/or thermal metamorphism. Typically, metamorphic events, which are mostly attributed to impact processes, have been dated with the ³⁹Ar-⁴⁰Ar system, which has relatively low closure temperatures (T_c) in silicate minerals and glass compared to, for example, the U-Pb isotope system in zircon. Bogard (2011) showed that the HED suite contains evidence for significant Ar degassing in the period of about 4.1 to 3.3 Ga and Cohen (2013) determined Ar-Ar ages for impact-melt clasts from the howardites and concluded that the impact-melt clasts formed in a period between 3.3–3.8 Ga. Relatively few HED samples have Ar-Ar ages older than 4.1 Ga (Bogard, 2011), however in Figure 8, Kennedy et al., (2019) document Ar-Ar plateau

ages of plagioclase from eucrites to be between the ages of 4534 ±56 Ma to 4491 ±16 Ma. Bogard and Garrison (2003) showed that a suite of unbrecciated, metamorphosed basaltic eucrites and cumulate eucrites have Ar-Ar ages consistent with a single thermal event at 4.48 Ga.

Ar-Ar dating of eucrites has found a cluster of ages at 4.50 to 4.48 Ga perhaps related to cataclysmic bombardment, followed by a period of relatively few dates before a significant



Figure 8. Ar-Ar ages plateau ages of plagioclase modified from Kennedy et al. (2019). Robust ages (red) and possible ages (pink) showering cluster at 4.50 Ga and cluster from ~3.85 to ~3.47 Ga. Graph and data from Kennedy et al., 2017 and apatite data from Liao and Hsu, 2017

cluster of Ar-Ar ages between about 4.0 and 3.5 Ga (Bogard and Garisson, 2003; Cohen, 2013; Kennedy et al., 2019). Liao and Hsu (2017) obtained a series of apatite U-Pb ages NWA 8009 ranging from ~4.26 to ~4.14 Ga, a period of time where there are few Ar-Ar dates. Whether the data represent continuous, but waning, impact bombardment or events that represent punctuated increases in impact intensity are open questions.

1.3 Project motivation

The purpose of this project is to better constrain the temperature-time history of the HED parent body by analysis and characterization of a specimen that likely represents the interior of the HED parent body. This study investigates the physical and geochemical characteristics of noritic diogenite NWA 10666 with the end goal to further constrain igneous and early thermal histories of the HED parent body, which is likely to be asteroid 4 Vesta. The absolute duration of magmatism, however, remains an uncertain and complex problem.

There are two models for the formation history of diogenites and eucrites, a short formation interval (~4 Ma) as described by (Schiller et al., 2011; Day et al., 2012) and a longer formation interval (~100 Ma) (Takahashi and Masuda, 1990; Mittlefehldt et al., 1998, and references therein; Bouvier et al., 2015). Zhou et al., (2013) compared dates from several highclosure temperature (HCT) isotope systems suggesting magmatism in the HED parent body occurred in an interval spanning 50 Ma from the time of silicate differentiation, with an overall decreasing rate in magmatism over this period and an apparent peak in activity at about 4552 ± 9 Ma (Misawa et al., 2005; Righter et al., 2011). The two different models for early igneous activity demonstrate the need for further geochemical analyses to confirm whether dates in previous studies reflect igneous or metamorphic events.

The differences in the models is in part due to the limited igneous crystallization age data, particularly for diogenites. The meteorite record will be biased toward the most abundant periods of igneous activity requiring high numbers of analyses to document the ending stages of magmatism. Petrogenetic relationships between eucrites and diogenites remains uncertain.

The need for further characterizing lithologies that are compositionally transitional between diogenites and cumulate eucrites, such as specimens in Yamato Type B group, could help constrain when these materials formed and what processes were operative that produced eucrites and diogenites. NWA 10666 can be that necessary link between eucrites and diogenites. Its texture is consistent with an interior crustal origin, therefore offering potentially new information about the interior processes that are not achievable by extrapolating from typical eucrite or diogenite specimens.

Chapter 2

Sample description

NWA 10666 is one among a series of noritic and feldspathic diogenites and is the first reported zircon-bearing diogenite (Figure 9). Constraints on the temperature-time histories of lower-crustal materials have been difficult to obtain due to limited chronologic options for these typically mineralogically simple meteorites that have been affected by thermal equilibration/ metamorphism. Having



Figure 9. NWA 10666 hosting zircon grains $\sim 20 \,\mu\text{m}$ in diameter (red circles). OPX = orthopyroxene, Z = zircon, Ilm = ilmenite (Photo by Tanner et. al. 2017)

thermal equilibration/ metamorphism. Having zircon(s) large enough for analysis, makes this specimen well suited for combined chronologic and petrologic investigations.

Northwest Africa 10666 was not an observed fall and the whole specimen (46.83g) of the rock was purchased in Morocco in 2015. NWA 10666 is one among a series of noritic and feldspathic diogenite compositions described by Irving et al., (2014, 2016) and Tanner et al., (2017). It contains ~70–75% orthopyroxene that are 1 - 3 mm in the long dimensions (Fs _{34.9}. 35.0Wo_{1.9-2.1}, Fe/Mn = 30.3), ~5 – 8% clinopyroxene that are <0.1 - 0.3 mm (Fs_{14.8-14.9}Wo _{42.0-43.3}, Fe/Mn = 24.5), 15–20% calcic plagioclase that are 0.5 - 1 mm (An_{80.5}Or_{0.7} -An _{89.8}Or_{0.3}), ~1 – 2% oxides and sulfides that are <0.1 mm, as well as <1% accessory apatite and zircon grains that are <0.1 mm. Unlike typical diogenites, this specimen is poorly brecciated; however, the meteorite displays crosscuting fractures and cracks that are filled with an aggregate of fine-

grained silica (Tanner et. al., 2017).

A dominant orthopyroxene cumulate texture is characterized by larger, subhedral, interlocking OPX grains that contain clinopyroxene exsolution lamellae throughout the specimen (Figure 10). Areas of orthopyroxene that do not contain well-developed exsolution lamellae are more likely associated with larger, anhedral clinopyroxene grains. Larger grains of clinopyroxene occur as isolated grains sometimes poikilitically enclosed in orthopyroxene, but this is less common. The larger CPX grains are adjacent to large, interstitial plagioclase and ilmenite grains. Calcic plagioclase grains are anhedral and irregularly distributed. Grain boundaries between plagioclase and orthopyroxene are locally jagged. Iron sulfide occurs poikilitically as spheroidal grains (<0.1mm) (Tanner et al., 2017) enclosed in orthopyroxene and in some clinopyroxene. Cr-spinel grains have a bimodal size distributed (<0.1 mm; 4 mm) (Figure 10). Apatite grains are present, next to discrete clinopyroxene grains and primarily occur close to ilmenite throughout the specimen (Figure 10). The large ilmenites in NWA 10666 host over 10 zircons ranging from 20–60 µm and are present as anhedral to subhedral equant grains. Zircon grains are present as inclusions in and on the boundary of large and small ilmenite grains; texturally, not all zircon grains can be associated with exsolved components from ilmenite.



Figure 10. X-ray composite chemical map of diogenite NWA 10666 created by Tanner et al., (2017). Dark green= orthopyroxene, light green= clinopyroxene, gray/white= plagioclase, pink= ilmenite, brown= spinel, yellow= apatite. Elements combined (top right) used for map are arbitrarily assigned a color. Mineral phases with a certain color indicate the matching element color (ex: pink= Ti; pink =

Chapter 3

Methods

3.1 Sample Preparation

An intact piece of NWA 10666 (37.79g), an unpaired and oriented HED meteorite, was purchased through private dealers. It was cut in half and sectioned by an Isomet low-speed saw; one piece was mounted in epoxy and prepared into a ~2 mm thick polished section and the other material was saved for future analyses. The powdered gatherings produced from using the saw was collected and was used as a representative bulk rock powder.

3.2 Electron-beam microanalyses

3.2.1 Scanning Electron Microscope (SEM)

Backscatter electron (BSE) images and energy-dispersive X-ray (EDX) data were obtained using the JEOL JSM 7600 field emission scanning electron microscope at the NASA Johnson Space Center, with accelerating potential = 15kV and current = 30nA. Backscatter electron images were collected at NASA-JSC to identify mineral textures and setting within NWA 10666. Then compositional maps were produced from the EDX to generate chemical maps of NWA 10666. These maps were used to determine mineral compositions. Elements measured include Al, Ca, K, Ti, Si, Fe, and Mg which were used to identify minerals by their relative abundances and are used to produce chemical maps like in Figure 10. A mosaic chemical map of previously stated elements was generated using ImageJ to display mineral distributions in NWA 10666. The distribution of minerals and textures from these analyses were used to locate spots for electron probe microanalyses (EPMA).

3.2.2 Electron probe microanalysis (EPMA)

Major element concentrations of SiO₂, MgO, Na₂O, Al₂O₃, CaO, K₂O, TiO₂, V₂O₃, Cr₂O₃, FeO, NiO, MnO, Ce₂O₃, P₂O₅, SrO, and La₂O₃ were measured by EPMA using a JEOL JXA-8530F located at NASA-JSC. 139 spot analyses of pyroxene were taken at 15 kV accelerating potential, a beam current of 30 nA, 1.0 µm beam size, and 30s counting time. Only analyses that had element totals of 98.6–101.0 wt% were accepted. Spots that had an activation volume that included other phases resulting in mixed analyses were excluded. 131 oxides were measured at the same operating conditions that were used for analyses pyroxene. 79 plagioclase grains and 12 phosphate grains were analyzed at 15 kV, 20 nA beam current, 1.0 µm beam size, and 30s counting time. ZAF matrix corrections were applied to the data and the corrections were tested by analysis of standards as unknowns to ensure results are consistent and external/internal calibrations are correctly applied.

3.3 Laser Ablation Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS)

In situ major- and trace-element concentration and U-Th-Pb isotope analyses were obtained at the University of Houston (UH) using a Varian 810 quadrupole mass spectrometer coupled with a Photon Machines Excite excimer laser ablation system following methods outlined in Shaulis et al., (2010; 2017), Hui et al., (2011), Sarafian et al., (2017), and Lapen et al., (2017). The ~2 mm thick section was analyzed in two different sessions. The first was to conduct trace element in situ analyses and the second was to conduct in situ U-Th-Pb analyses of phosphate grains and a zircon grain found in the analyzed section.

3.3.1 Trace element in situ analyses

In situ chemical analyses of five orthopyroxene, clinopyroxene, and plagioclase grains (15 total) were performed in a single analytical session. Operation conditions were 50 µm diameter laser spot size with a 10 Hz repetition rate over 30s, a fluence of 3.95 J/cm2, and a He carrier gas flow rate of 0.43 L/min during these analyses. USGS glass standards BHVO-2G and BIR-1G were used as internal and external standards, respectively. Data reduction followed internal and external standardization following Lapen et al., (2017) and Hui et al., (2011) was carried out using the software package GLITTER, which allows for the integration of analyses without inclusions through visual recognition of anomalous peaks from time resolved graphical profiles of the data (Van Achterberg et al. 2001).

3.3.1.1 Ca-phosphate dating

The U-Th-Pb analyses of five apatite grains were performed using a 25 µm diameter laser spot size with a 10 Hz repetition rate, a fluence of 11.28 J/cm², and a He carrier gas flow rate of 0.93 L/min was used during the analyses. The analysis consisted of 20 s of background measurement followed by 30 s of sample ablation. Masses analyzed were ²⁰¹Hg, ²⁰²Hg, ²⁰⁴Pb+Hg, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, and ²³⁸U. Data reduction follow methods outlined in Shaulis et al. (2017) and Sarafian et al. (2017) where the Iolite addin to Igor Pro (ver. 6) was used to perform background corrections and report raw ²⁰⁴Pb/²⁰⁶Pb, ²⁰⁷Pb/²⁰⁶Pb, ²⁰⁶Pb/²³⁸U, ²⁰⁷Pb/²³⁵U, and ²⁰⁸Pb/²³²Th ratios. As explained in Shaulis et al. (2017), the ²⁰⁴Hg-corrected ²⁰⁴Pb/²⁰⁶Pb ratios are sometimes negative as a result of the ²⁰⁴Hg baseline measurement uncertainty propagation. These 'negative' ratios are within error of zero in both the phosphate and zircon analyses. A separate in-house spreadsheet was used to correct the raw data for instrumental element and isotopic fractionation as well as interferences from Hg (Shaulis et al., 2010; 2017; Sarafian et al., 2017). Bear Lake and Yates Mine apatite were used as standards for U-Pb and U-Th instrumental fractionation corrections. Instrumental mass fractionation of Pb isotopes were corrected with NIST 612 glass using the preferred GeoRem values (<u>http://georem.mpch-</u> mainz.gwdg.de/).

3.3.1.2 Zircon dating

In situ LA-ICP-MS analyses of zircon was performed with a 20 μ m diameter laser spot size on one zircon grain with a 10 Hz repetition rate, a fluence of 11.28 J/cm², and a He carrier gas flow rate of 0.93 L/min. FC5z (equivalent to FC1;1099.1 ± 0.5 Ma, Paces and Miller, 1993) and Plešovice (337.13 ± 0.37 Ma, Sláma et al., 2008) zircon standards are used to correct for instrumental elemental and isotopic fractionation and drift. Masses analyzed and data reduction methods are the same as for the apatite analyses.

3.4 Oxygen isotopes analyses

Oxygen isotopic analysis conducted for NWA 10666 was done by Dr. Karen Ziegler at the University of New Mexico. The analysis is reported in standard δ notation, where δ^{18} O has been calculated as: $\delta^{18}O = [(^{18}O/^{16}O)\text{sample} / (^{18}O/^{16}O)\text{ref} - 1] \times 1000 (\%)$ and similarly for $\delta^{17}O$ using the $^{17}O/^{16}O$ ratio, the reference being VSMOW: Vienna Standard Mean Ocean Water. $\Delta^{17}O$, which represents the deviation from the terrestrial fractionation line, has been calculated using the linearized format of Miller (2002): $\Delta^{17}O=1000\ln (1+\delta^{17}O/1000)-\lambda 1000\ln (1+\delta^{18}O/1000)$ where $\lambda = 0.528$, determined using 47 terrestrial whole-rock and mineral separate samples (Miller 2002; Miller et al. 1999; Kared et al., 2019).

3.5 Bulk Chemistry

A powdered sample (~100 mg) was obtained by collecting cutting dust from initial thick section preparation to perform bulk chemical analysis. The material was precisely weighed and digested as follows: 1) hotplate digestion in 4 ml of 29 M HF and 0.5 ml of 14 M HNO₃ in Teflon beakers to facilitate the breakdown of the majority of the silicates, 2) microwave digestion using the ultraWAVE in 4 ml of 14 M HNO₃, 1ml of 29 M HF, and 1ml of 12 M HCl to dissolve remaining materials, 3) hotplate digestion with 7 M HNO₃ to remove refractory fluoride complexes, and 4) repeated dissolution with 8 M HCl until the sample solutions were clear and no solid are detected after centrifuging. In between each step, the sample solutions were re-dissolved in 2% HNO₃ for trace element analysis. The sample was then analyzed by an Agilent 8800 QQQ-ICP-MS at the University of Houston. Chondrite normalization used values of Andrers and Grevesse (1989). USGS standards BIR-1 and BHVO-2 were used and tested as internal and external standards.

3.6 Thermometry

Plagioclase and clinopyroxene major and trace element compositions (wt.% and ppm, respectfully) of NWA 10666 measured by microprobe analysis and in situ LA-ICP-MS data were used as input values for the Sun and Liang (2017) REE-in-plagioclase-clinopyroxene thermometer. The thermometer is based on models of REE distributions between coexisting plagioclase and clinopyroxene. This method provides a robust assessment of equilibration temperatures because diffusion rates for LREE in pyroxene and plagioclase are much slower than those of divalent cations such as Fe^{2+} and Mg^{2+} in pyroxene (Sun and Liang, 2017; and

references therein). A two-pyroxene Fe^{2+} - Mg^{2+} exchange thermometer based on the calibration of Köhler and Brey (1990) and pyroxene compositions measured by EPMA were used to ascertain their equilibration temperature.

Chapter 4

Results

4.1 Petrography

NWA 10666 was found in the northwest Africa with a total mass of 46.83g. It is partly covered with a thin dark brownish-black, oriented fusion crust (Figure 11). Visual inspections of the specimen's sawn face identified the diogenite as having a coarse-grained orthocumulate texture and a noritic mineralogy. The coarse-grained nature (Figure 12) of NWA 10666 makes modal abundance estimates difficult; therefore, average modal abundance information should be referred to with caution. The chemical map of NWA 10666



Figure 11. Image of NWA 10666 (whole rock) before it was made into a thick section



Figure 12. Low magnification image of NWA 10666 within silica epoxy

(Figure 13) is composed of, in order of relative abundance: orthopyroxene, clinopyroxene, plagioclase, oxides (ilmenite and Ti-chromite), and accessory phosphates and zircons.

4.1.1 Orthopyroxene

Orthopyroxene (\sim 75 – 76 vol%) is the dominant and generally the coarsest mineral within NWA 10666 where OPX grains are 1 – 3 mm in the long dimension. In most cases, these grains are subhedral and interlocking. Exsolution lamellae of clinopyroxene within OPX occurs variably in nearly all OPX grains. Areas where the OPX does not contain well-developed lamellae are typically associated with larger irregular shaped CPX. The individual grain boundaries between OPX and plagioclase are locally jagged. Iron sulfide inclusions exists poikilitically and are in highest abundance where plagioclase is least abundant.



Figure 13. Chemical map of NWA 10666. Orthopyroxene ("opx", dark green), clinopyroxene ("cpx", yellow-green), plagioclase ("plag", white) oxides ("ox", magenta), and ("silica", blue)

4.1.2 Clinopyroxene

Clinopyroxene (~ 1.8 - 2.2 vol%) occurs mostly as irregular exsolution lamellae (<0.1 mm blebs) within orthopyroxene and locally as larger (0.1 - 0.3 mm) anhedral grains. The larger grains are locally associated with phosphate and ilmenite grains (Figure 14).



Figure 14. X-ray composite chemical map of diogenite NWA 10666 created by Tanner et al., (2017). Dark green= orthopyroxene, light green= clinopyroxene, gray/white= plagioclase, pink= ilmenite, brown= spinel, yellow= apatite. Elements combined (top right) used for map are arbitrarily assigned a color. Mineral phases with a certain color indicate the matching element color (ex: pink= Ti; pink = ilmenite) is the most abundant element

4.1.3 Plagioclase

Calcic plagioclase occurs as porphyritic, anhedral and irregularly distributed grains. The smaller grains are 0.4 - 1.0 mm while the larger grains are 5.0 - 7.0 mm. Grain boundaries between the anorthite and adjacent orthopyroxene are locally jagged. Calcic plagioclase accounts for ~22% modal abundance within NWA 10666 and displays intragranular fractures. The modal abundance estimates of plagioclase can be highly variable due to the irregular and variable distribution within this coarse-grained specimen.
4.1.4 Oxides

The modal abundance of oxide minerals (including SiO₂) is <1 vol %. An anhedral silica polymorph grain (~1.7 mm in the long dimension) was observed in thick section and identified by x ray chemical mapping (blue area in Figure 13; Figure 15). It has plagioclase inclusions and is surrounded by plagioclase, ilmenite, and clinopyroxene grains. Secondary textures include extensive fracturing around the silica and silica fragments within larger fracture systems in the specimen. Ilmenite (<0.1 – 0.2 mm) typically



Figure 15. Backscattered electron image of silica polymorph phase surrounded by "ox"= oxides, "cpx" = clinopyroxene, "opx" = orthopyroxene, "plag"= plagioclase, within NWA 10666. Photo taken at NASA-JSC

occur as anhedral grains typically near plagioclase grains but can also be found as standalone grains near the larger clinopyroxene grains and chromite. Chromite (< 0.1 - 0.4 mm) exists as anhedral to subhedral equant grains. A large (3 – 4 mm) ilmenite was identified in Figure 13 (pink). Some ilmenite grains host multiple small zircon inclusions.

4.1.5 Phosphate

Phosphate (< 1 vol %) primarily occurs as < 0.1 mm long anhedral grains that are often associated with CPX (yellow area in Figure 14) but can also occur as smaller spherical inclusions within plagioclase grains. Intragranular fracturing is observed in every phosphate grain analyzed in this study.

4.1.6 Zircon

In the thick section studied here, approximately 5 zircon grains were identified within NWA 10666 that are larger than 0.01 mm, but smaller than 0.1 mm. This observation is in addition to the zircon identified in another section described by Tanner et al. (2017). Zircons in NWA 10666 are anhedral and many of



Figure 16. Backscattered electron image of largest (~0.1 mm) "Zr" = zircon with "ilm" = ilmenite surrounding it. Dark background is clinopyroxene

these grains are associated with phosphates or ilmenite. The largest zircon grain (~ 0.15 mm) is surrounded by a concentration of clinopyroxene, phosphate, ilmenites and plagioclase but has ilmenite inclusions (Figure 16). This zircon is fractured, and the density of fractures seems to increase from a relatively intact fragment on the left of figure 16 to more heavily damaged areas to the right. Ilmenite grains around the zircon also appear to be fractured in this image.

4.2 Mineral Compositions

4.2.1 Orthopyroxene

EMPA data (Table 1) analyzed major elements (Si, Mg, Al, Ca, K, Ti, V, Cr, Fe, Ni, and Mn). Orthopyroxenes in NWA 10666 show predominantly ferroan average compositions (Figure 17). Their compositional range is $Fs_{34.2-36.3} En_{61.6-63.8} Wo_{1.5-2.1}$ (Table 1). There is a slight variability for Al₂O₃ (0.33 – 0.52 wt.%), Cr₂O₃ (0.13 – 0.31 wt.%), CaO (0.76 – 4.06 wt.%), and TiO₂ (0.22 – 0.38 wt.%). Some of the relatively high CaO values may be mixed analyses with

CPX. The Fe/Mn ratio of the orthopyroxenes range from 27.62 - 31.85.

Trace element

concentrations

determined by LA-ICP-

MS (Table 2) were

used to calculate REE



Figure 17. Pyroxene composition quadrilateral of NWA 10666 (green dots)

patterns and also to compare similarity of major element oxide percentages to those determined by EMPA. Chondrite-normalized REE patterns are shown in Figure 18 and show a typically LREE-depleted pattern.

Open symbols in Figure 18 are maximum values. Mixed analyses of OPX and CPX was identified by measured Ca concentrations. The averaged chemical data for OPX do not include analyses where the Ca wt% is >

1.0.



Figure 18. REE concentrations. Red: OPX, Blue: plag, Green: CPX, Black: bulk rock from analysis of whole rock powder, Open circle: maximum value

4.2.2 Clinopyroxene

Clinopyroxene in NWA 10666 also display a dominantly ferroan composition compared to other diogenites from literature. Table 1 and Figure 17 reveal a compositional range of $Fs_{12.9}$. 14.9 En41.3-42.8 W043.2-44.9. The Fe/Mn ratio of the clinopyroxenes range from 22.15 – 25.95 (see Table 1 for more detail). Trace element concentrations of clinopyroxene determined by LA-ICP-MS found in (Table 2) were compared to the clinopyroxene EPMA data (Table 1) to ensure precision and accuracy of the two datasets. Mixed analyses of CPX and OPX by LA-ICP-MS was detected by monitoring Ca. Data with less than ~12 wt % Ca are not included in averaged CPX chemical data.

4.2.3 Plagioclase

Plagioclase feldspar in NWA 10666 has a composition of An_{80.5-89.8} Or_{0.3-0.7} (Figure 19 and Table 1). There is narrow variability for Na₂O (1.10 - 2.24 wt.%), CaO (16.73 - 18.28 wt.%), and K₂O (0.06 - 0.14 wt.%). Sodium and potassium oxides were not measured by LA-ICP-MS data for plagioclase, but CaO ranged from 16.58 - 17.80 wt.%, which primarily agrees with the microprobe data.



Figure 19. Calcium plagioclase composition diagram of NWA 10666. (n= 79)

4.2.4 Minor Phases

EMPA data of chromite displayed a Cr_2O_3 range of 42.94 - 52.30 wt.%, Al₂O₃ range of 5.81 - 11.25 wt.% (Table 1). MgO range is 1.62 - 3.28 wt.%. The Mg# (=100 Mg/ (Mg + Fe), atomic) values of chromite show variation, from 7.81 - 16.27. Cr# (=100 Cr/ (Cr + Al), atomic) range was determined to be 75.19 - 83.22. The chromites contain low amounts of TiO₂ (2.48 - 14.32 wt.%) and V₂O₃ (<0.72 wt.%). Ilmenite was also measured and their Mg# values of were determined to show a small variation, ranging from 13.77 - 14.17. They possessed a narrow range in TiO₂ of 53.89 - 54.64 wt.%.

Ca-phosphates measured possess an MgO oxide wt% of 2.97 - 3.41, Na₂O oxide wt% of 0.12 - 0.60, and CaO oxide wt% 43.54 - 45.15. The Ca-phosphates are low in F and Cl so the dominant anion species will be O or OH. The number of anions on the basis of 26 Oxygen ions show that magnesium is a major consituent (0.78 - 0.88). The composition of the Ca-phosphates are consistent with Ca-merrilite given the MgO oxide wt%.

			Pyrox	enes			Fe	eldspars	
	Н	igh- Ca		Ι	.ow- Ca				
Ν		37			102			79	
Oxide wt%	Min	Max	Average	Min	Max	Average	Min	Max	Average
SiO_2	52.30	53.30	52.79	52.44	54.07	53.25	45.04	47.10	45.96
MgO	14.23	14.87	14.43	20.56	22.72	22.04	< 0.01	0.04	0.02
Na ₂ O	0.12	0.60	0.16	< 0.01	1.44	0.05	1.10	2.24	1.35
Al_2O_3	0.58	0.85	0.72	0.33	0.52	0.39	34.28	35.89	35.22
CaO	20.64	21.97	21.27	0.76	4.06	1.20	16.73	18.28	17.72
K ₂ O	< 0.01	0.02	< 0.01	< 0.01	0.03	< 0.01	0.06	0.14	0.09
TiO ₂	0.34	0.55	0.46	0.22	0.38	0.26	< 0.01	0.05	0.01
V_2O_3	< 0.01	0.05	0.03	< 0.01	0.03	0.01			
Cr ₂ O ₃	0.27	0.41	0.36	0.13	0.31	0.18			
FeO	8.03	9.17	8.81	20.01	22.73	21.88	0.02	0.56	0.10
NiO	< 0.01	0.03	< 0.01	< 0.01	0.04	< 0.01			
MnO	0.34	0.40	0.36	0.66	0.78	0.72	< 0.01	0.03	< 0.01
Total	98.85	100.24	99.42	98.61	100.98	100.01	99.22	100.96	100.47
		n	umber of ions	s on the basis of 26 (O)					
Si	8.53	8.62	8.57	8.54	8.64	8.60	6.76	7.01	6.84
Mg	3.46	3.60	3.49	5.01	5.43	5.31	< 0.01	0.01	< 0.01
Na	0.04	0.19	0.05	< 0.01	0.45	0.02	0.32	0.66	0.39
Al	0.11	0.16	0.14	0.06	0.10	0.07	6.02	6.27	6.18
Ca	3.59	3.79	3.70	0.13	0.70	0.21	2.67	2.91	2.83
K	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	0.01	0.03	0.02
Ti	0.04	0.07	0.06	0.03	0.05	0.03	< 0.01	0.01	< 0.01
V	< 0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01			
Cr	0.04	0.05	0.05	0.02	0.04	0.02			
Fe	1.09	1.25	1.20	2.70	3.08	2.95	< 0.01	0.07	0.01
Ni	0.00	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01			
Mn	0.05	0.05	0.05	0.09	0.11	0.10	< 0.01	< 0.01	< 0.01
Total	17.25	17.38	17.30	17.29	17.61	17.32	16.25	16.46	16.27
Wo	0.43	0.45	0.44	0.02	0.08	0.02			
En	0.41	0.43	0.42	0.59	0.64	0.63			
Fs	0.13	0.15	0.14	0.32	0.36	0.35			
Fe/Mn	22.15	25.95	24.02	27.62	31.85	29.97	80.52	89.79	87.43
Mg#	76.56	73.52	74.48	65.40	62.92	64.23			

Table 1. Electron microprobe analyses (wt.%) of major phases in NWA 10666

		probe analyse	Oxides		10000			Ca-phopl	nate	
	C	hromite		II	lmenite					
Ν		120			11		Ν	12		
Oxide wt%	Min	Max	Average	Min	Max	Average	Oxide wt%	Min	Max	Average
SiO_2	< 0.01	0.19	0.03	0.01	0.03	0.02	F	< 0.01	< 0.01	< 0.01
MgO	1.62	3.28	2.68	3.64	3.77	3.71	Na ₂ O	0.08	0.84	0.66
Na ₂ O	< 0.01	0.22	0.02	< 0.01	0.03	0.02	MgO	2.97	3.41	3.23
Al_2O_3	5.81	11.25	9.17	< 0.01	0.01	< 0.01	SiO_2	0.03	0.13	0.07
CaO	< 0.01	0.28	0.04	< 0.01	0.01	< 0.01	CaO	43.54	45.15	44.14
K ₂ O	< 0.01	0.07	< 0.01	< 0.01	0.03	< 0.01	SO3	< 0.01	0.13	0.04
TiO ₂	2.48	14.32	3.77	53.89	54.64	54.11	Ce_2O_3	0.55	1.04	0.85
V_2O_3	0.44	0.71	0.56	< 0.01	< 0.01	< 0.01	Cl	0.01	0.14	0.04
Cr_2O_3	42.94	52.30	50.48	0.06	0.11	0.08	P_2O_5	44.25	46.02	45.36
FeO	29.98	34.92	31.70	40.48	40.73	40.63	SrO	< 0.01	< 0.01	< 0.01
NiO	< 0.01	0.04	< 0.01	< 0.01	0.05	0.02	FeO	0.41	1.64	0.82
MnO	0.61	0.73	0.66	0.82	0.87	0.84	La_2O_3	0.23	0.43	0.34
Total	98.02	100.27	99.14	99.34	100.28	99.68	Total	94.33	96.94	95.55
			Oxygen=	26			Oxygen = 26			
Si	< 0.01	0.05	0.01	< 0.01	0.01	< 0.01	F	< 0.01	< 0.01	< 0.01
Mg	0.56	1.11	0.91	1.16	1.19	1.18	Na	0.03	0.28	0.22
Na	< 0.01	0.10	0.01	< 0.01	0.01	0.01	Mg	0.78	0.88	0.83
Al	1.54	2.99	2.47	< 0.01	< 0.01	< 0.01	Si	0.01	0.02	0.01
Ca	< 0.01	0.07	0.01	< 0.01	< 0.01	< 0.01	Ca	8.10	8.28	8.18
K	< 0.01	0.02	< 0.01	< 0.01	0.01	< 0.01	S	< 0.01	0.02	0.01
Ti	0.42	2.42	0.65	8.65	8.69	8.67	Ce	0.03	0.07	0.05
V	0.08	0.14	0.11	0.04	0.05	0.04	Cl	< 0.01	0.04	0.01
Cr	7.62	9.47	9.13	0.01	0.02	0.01	Р	6.59	6.67	6.64
Fe	5.67	6.81	6.07	7.20	7.26	7.24	Sr	< 0.01	< 0.01	< 0.01
Ni	< 0.01	0.01	< 0.01	< 0.01	0.01	< 0.01	Fe	0.06	0.23	0.12
Mn	0.12	0.14	0.13	0.15	0.16	0.15	La	0.01	0.03	0.02
Total	18.96	19.58	19.50	17.28	17.33	17.30	Total	16.02	16.19	16.10
Cr#	75.19	83.22	78.79							
Mg#	7.81	16.27	13.14	13.77	14.17	14.00				

 Table 1 cont. Electron microprobe analyses (wt.%) of major phases in NWA 10666

 Oxides

	min	max	Average	min	max	Average	min	max	Average
	Orthop	yroxene (n=	=5)	Clinop	yroxene (n=	=5)	Plagi	oclase (n=5)	
wt. %									
SiO_2	52.77	54.20	53.73	52.96	54.12	53.43	45.09	45.89	45.58
MgO	22.19	23.48	23.07	15.54	22.77	18.25	0.02	0.03	0.03
Al_2O_3	0.37	0.39	0.39	0.45	0.83	0.63	33.32	35.04	34.31
CaO	1.19	2.99	1.71	3.04	23.50	15.91	16.58	17.80	17.22
TiO ₂	0.24	0.28	0.26	0.31	0.49	0.39	0.01	0.02	0.01
Cr_2O_3	0.20	0.28	0.23	0.25	0.46	0.36	b.d.	<i>b.d.</i>	b.d.
NiO	0.002	0.002	0.002	0.002	0.004	0.003	b.d.	<i>b.d.</i>	b.d.
MnO	0.87	0.93	0.89	0.45	0.87	0.60	0.002	0.004	0.003
ppm by v	weight								
Р	27.28	28.96	32.00	28.06	142.37	82.87	86.76	86.76	86.76
Sc	22.97	28.22	28.11	35.68	86.00	62.33	1.35	1.49	1.42
Co	16.03	16.82	16.39	7.58	16.02	10.63	<i>b.d.</i>	<i>b.d.</i>	<i>b.d.</i>
Cu	11.54	13.23	20.89	15.74	114.40	48.03	2.60	6.09	4.31
Zn	5.86	6.19	5.97	2.57	6.91	4.38	<i>b.d.</i>	<i>b.d.</i>	b.d.
Ga	b.d.	b.d.	b.d.	<i>b.d.</i>	b.d.	b.d.	2.71	6.18	4.06
Ge	2.86	2.86	2.35	<i>b.d.</i>	b.d.	b.d.	b.d.	b.d.	b.d.
Rb	b.d.	b.d.	b.d.	0.40	0.4	0.40	b.d.	b.d.	b.d.
Sr	0.36	1.49	1.97	2.15	7.72	6.11	182.00	194.60	188.39
Y	3.86	6.46	5.81	8.02	33.19	22.36	0.19	0.42	0.30
Zr	3.83	5.30	6.45	7.72	75.22	33.49	h d	b d	b d
Nb	0.06	0.06	0.10	0.12	0.20	0.15	h d	h d	b d
Sn	1 75	1 97	1.89	1 41	13 10	6.80	2 99	2 99	2 99
Ba	0.51	6.26	6.04	1 32	4 16	3 11	74 77	78 75	77.81
La	0.06	0.20	0.07	0.06	1 11	0.64	0.32	1.00	0.64
Ce	0.00	0.00	0.10	0.00	3 32	1 91	0.52	1.00	1 20
Dr	0.02	0.03	0.10	0.15	0.64	0.41	0.71	0.22	0.14
Nd	0.05 h d	0.05 h d	0.05 h d	0.05	3.0	2 41	0.32	0.22	0.14
Sm	0.08	0.08	0.u.	0.21	2.58	2.41	0.52 h.d	0.97 h.d	0.37 h.d
Fu	0.08 h d	0.08 h d	0.17 h.d	0.24	0.00	0.07	<i>D.u.</i> 1 30	1.72	1 AA
Gd	0.13	0.35	0.30	0.04	1 48	2.53	0.14	0.14	0.14
Th	0.15	0.00	0.00	0.56	1.40	0.52	0.14 b.d	0.14 h d	6.14 h.d
10 Dv	0.00	0.09	0.09	1.08	6.22	0.32	0.00	0.0	0.00
Dy Ho	0.44	0.92	0.78	0.20	1.20	0.82	0.09	0.03	0.09
110 En	0.13	0.20	0.21	0.30	2.50	0.85	0.02	0.03	0.02
Er	0.50	0.83	0.73	0.96	5.30	2.20	0.07	0.07	0.07
1 m Nh	0.10	0.10	0.13	0.10	0.49	0.33	<i>D.a.</i>	<i>D.a.</i>	<i>D.a.</i>
YD	0.68	1.11	0.88	1.22	2.50	1.8/	0.09	0.09	0.09
Lu	0.13	0.22	0.16	0.21	0.39	0.29	<i>b.d.</i>	b.d.	b.d.
Ht	0.12	0.24	0.22	0.49	4.65	1.97	<i>b.d.</i>	b.d.	<i>b.d.</i>
la	<i>b.d.</i>	b.d.	b.d.	0.02	0.03	0.02	<i>b.d.</i>	<i>b.d.</i>	<i>b.d.</i>
Pb	0.10	0.10	0.16	0.19	0.44	0.34	0.13	0.13	0.13
Th	0.04	0.04	0.06	0.02	0.13	0.07	<i>b.d.</i>	<i>b.d.</i>	<i>b.d.</i>
U	0.01	0.02	0.03	0.01	0.09	0.04	0.03	0.03	0.03

 Table 2. Major and trace element abundances in NWA 10666 determined by LA-ICP-MS analysis (oxides in wt.%, other elements in ppm)

Table 2. Minimum, maximum, and average ranges of LA-ICP-MS analysis for major and trace element abundances of orthopyroxene, clinopyroxene, and plagioclase based on an Si standard. (n=#) represents number of samples used. "b.d." = below detection limit. Spot size= 50 μ m

4.3 U-Th-Pb Dating

4.3.1 U-Th-Pb Data Phosphate

A total of four LA-ICP-MS analyses were made on four Ca-phosphate grains, each larger than 35µm in their smallest dimension in the section. Phosphates 1 & 8 were surrounded by plagioclase and Phosphates 6 & 7 were surrounded by pyroxene (figures 20, 21, and 22).



Figure 20. False color chemical map of NWA 10666. Orthopyroxene ("opx", dark purple), clinopyroxene ("cpx", bright pink), plagioclase ("plag", darker pink) Caphosphate ("phos", yellow), and zircon/interference ("zrc" green). "1" = Phosphate 1, "6" = Phosphate 6, "7" = Phosphate 7



Figure 21. False color chemical map of NWA 10666. Orthopyroxene ("opx", dark purple), clinopyroxene ("cpx", bright pink), plagioclase ("plag", darker pink) Ca-phosphate ("phos", yellow), and zircon/interference ("zrc" green). "8" = Phosphate 8

phosphates contain uranium and thorium concentrations of 22 – 33 ppm and 1499 – 2568 ppm,

respectfully. The U-Th-Pb isotope compositions are listed in Table 3a & 3b. The ²⁰⁷Pb- ²⁰⁶Pb

ages of the four spots are 4267 ± 41 , 4240 ± 65 , 4238 ± 33 , and 4313 ± 38 Ma and these data

yield a weighted mean age of 4271 ± 28 Ma with an MSWD= 2.6.

Figure 22 a, b, c, d, e. Xray chemical map of thick section for NWA 10666. The locations of the zircon and Caphosphates are highlighted by red and cyan boxes. images of the locations are also shown. Zrc is in red box. Phos 1, 6, and 7 are in red box. Phos 8 in cyan box. red circl= 25µm diameter. cpx -clinopyroxene, opx- orthopyroxene, plag - plagioclase, phos - Ca-phosphate, zrc - zircon



Given the potential for common Pb contamination, especially along cracks, the Pb data is presented as a 204 Pb/ 206 Pb – 207 Pb/ 206 Pb inverse isochron (Figure 23) which yields an intercept age of 4248 ± 25 Ma (MSWD = 1.5). This is slightly younger but within uncertainty of the 207 Pb- 206 Pb weighted mean age, indicating that the effects of common Pb are not a significant issue. The U-Pb data yield a concordia intercept age of 4271 ± 28 Ma (MSWD = 2.6), also identical

within uncertainty with the weighted average ²⁰⁷Pb-²⁰⁶Pb and inverse isochron ages. Despite the overlapping ages, the age determined by the inverse isochron method is regarded as the most accurate as it addresses



Figure 23. Pb-Pb inverse isochron diagram for Ca-phosphate. Black line = best line between radiogenic and common Pb, blue curves = 2σ error envelope for the best-fit mixing line, red ellipses = measured data

any issues with common Pb. 232 Th- 208 Pb ages are 4103 \pm 120, 4350 \pm 254, 4203 \pm 108, and 4259 \pm 111 Ma with a weighted average of 4202 \pm 63 Ma, also identical to the Pb-Pb and U-Pb ages.

Analyses of phosphate standards were used to assess the accuracy and reproducibility of the method. The measured common Pb-corrected ${}^{238}U{}^{-206}Pb$ age for Yates Mine apatite is 909 +/- 56 Ma (n = 10). This agrees with Th-Pb age determinations of 913 +/- 7 Ma for Barfod et al. (2005) and U-Pb determinations of 932 +/- 12 Ma for Chew et al. (2011). The measured ${}^{238}U{}^{-206}Pb$ and ${}^{232}Th{}^{-208}Pb$ ages for Madagascar apatite are 483 +/- 12 and 486 +/- 10 Ma (n = 2), respectively. These agree with mean U-Pb ages of 485–475 Ma; Thomson et al. (2012) and

Chew et al. (2014). Thus, the instrumental elemental fractionation of U-Pb and Th-Pb are accurately corrected. Repeated analyses of NIST 612 glass (n = 10) yielded a measured $^{206}Pb/^{204}Pb$ ratio of 17.11 ± 1.15 (2SD) which is identical to the value of 17.094 ± 0.003 (2SD; Woodhead and Hergt, 2001). These data indicate that the 204 Hg on 204 Pb isobaric interferences and Pb isotopic measurements are accurately corrected.

Table 3a. LA-ICP-MS U-Th-F	b data for	Ca-phospha	ttes in NWA 10)666.											
														$^{206} Pb/^{238} U$	
Analysis #	U ppm	Th ppm	$^{204}Pb/^{206}Pb$	2%SD	207 Pb/ 206 Pb	2%SD	$^{207}Pb/^{235}U$	2%SD	$^{206}Pb/^{238}U$	2%SD	rho	²⁰⁸ Pb/ ²³² Th	2%SD	Age (Ma)	2SD
NWA10666 Phosphate 1	33	2568	0.0001	06	0.5087	2.8	71.79	5.2	1.046	4.4	0.85	0.2251	3.2	4618	144
NWA10666 Phosphate 6	28	1506	-0.0027	320	0.4996	4.4	76.59	11	1.137	10	0.92	0.2401	6.4	4900	351
NWA10666 Phosphate 7	28	2120	0.0001	55	0.4991	2.2	67.23	4.0	1.002	3.2	0.83	0.2311	2.9	4478	102
NWA10666 Phosphate 8	22	1499	0.0021	53	0.5249	2.6	65.97	4.1	0.9241	3.1	0.79	0.2346	2.9	4222	96
Table 3b. LA-ICP-MS 1	J-Th-Pb	age data fo	or Ca-phosph	ate in N ¹	WA 10666.								I		
													l		

	$^{206}\text{Pb}/^{238}$	U	$^{207}\text{Pb}/^{23}$	5U	207 Pb/ 206	Pb	208 Pb/ 232	'Th
Analysis #	Age (Ma)	2SD	Age (Ma)	2SD	Age (Ma)	2SD	Age (Ma)	2SD
NWA10666 Phosphate 1	4618	144	4354	53	4267	41	4103	120
NWA10666 Phosphate 6	4900	351	4418	112	4240	65	4350	254
NWA10666 Phosphate 7	4478	102	4288	40	4238	33	4203	108
NWA10666 Phosphate 8	4222	96	4269	41	4313	38	4259	111
			Weighted a	average	4267	20	4202	63

Table 3a & Table 3b. using NIST 612 and standard Yates Mine and Madagascar apatites. Pb isotope compositions corrected using NIST 612 and GeoRem isotopic values. U/Pb and Th/Pb instrumental fractionation corrected the measured common Pb-corrected ²³⁸U-²⁰⁶Pb age for Yates Mine apatite is 909 +/- 56 Ma (n = 10). This agrees with age determinations of 913 +/- 7 Ma for Barfod et al. (2005) and 932 +/- 12 Ma for Chew et al. (2011). "The measured ²³⁸U-²⁰⁶Pb and ²³²Th-²⁰⁸Pb ages for Madagascar apatite are 483 +/- 12 and 486 +/- 10 Ma (n = 2), respectively. These agree with mean U-Pb ages of 485–475 Ma; Thomson et al. (2012) and Chew et al. (2014).

4.3.2 U-Th-Pb Zircon

Three U–Th-Pb analyses were conducted on a large (~100µm) fragmented zircon grain (Figure 24) within the thick section of NWA 10666. This zircon is adjacent to anhedral ilmenite grains and has ilmenite inclusions. The



Figure 24. Backscattered electron image of zircon (bright) surrounded by ilmenite (darker gray) within NWA 10666. Red circles indicate three 20 μ m spot locations for LA-ICP-MS analysis

three measurements of the U-Th-Pb isotope compositions are listed in Table 4a & 4b. The U and

Th concentrations of zircon are very low, ranging from 9 - 11 ppm and 0.3 - 0.4 ppm,

respectively (Table 5a). The three analyses yielded 207 Pb- 206 Pb ages of 4532 ± 34 Ma, 4566 ± 36 Ma, and 4570 ± 40 Ma producing a 207 Pb- 206 Pb weighted average age of 4555 ± 21 Ma (MSWD = 1.4) (Figure 25). Because the analyzed zircon is heavily fractured, common Pb contamination

= 1.4) (Figure 25). Because the analyzed zircon is heavily fractured, common Pb contamination

- A ²⁰⁴Pb/²⁰⁶Pb -
- ²⁰⁷Pb/²⁰⁶Pb inverse

along cracks is possible.

isochron yields an age of 4542 ± 20 Ma (MSWD = 0.29), slightly younger than, but statistically identical to the weighted average ²⁰⁷Pb/²⁰⁶Pb age (Figure





Figure 25. Pb-Pb inverse isochron of zircon within NWA 10666. Black line = best line between radiogenic and common Pb, blue curves = 2σ error envelope for the best-fit mixing line, red ellipses = measured data

common Pb contamination is not an issue that with the data. A U-Pb concordia upper intercept age of 4576 ± 29 (MSWD = 0.09) is determined; 2 out of 3 data points are reversely discordant. Based on the fractured nature of the zircon and potential for Pb contamination, the inverse isochron age of 4542 ± 20 is interpreted to be the most accurate age of zircon crystallization.

Analysis of external zircon standards Plešovice (337.13 ± 0.37 Ma; Sláma et al., 2008) and zircon megacryst from Rio de Peixe, Brasil (564 ± 4 Ma; Dickenson and Gehrels, 2003; Shaulis et al., 2010) as unknowns were used to assess the accuracy of the corrections for instrumental elemental and mass fractionation. Six U-Pb analyses each of Plešovice and Peixe zircons yielded U-Pb concordia ages of 340.8 ± 2.5 and 558 ± 6.4 Ma, respectively.



Figure 26. ²⁰⁷Pb- ²⁰⁶Pb ages (red) for three analyses with the weighted mean age (green)

Table 4a. LA-ICP-MS U-Pb da	ta for zirco	n grain spo	ots in NWA 10666													
											²⁰⁶ Pb/ ²³⁸ U		²⁰⁷ Pb/ ²³⁵ U		²⁰⁷ Pb/ ²⁰⁶ Pb	
Analysis #	U ppm	Th ppm	²⁰⁴ Pb/ ²⁰⁶ Pb 2%SD	²⁰⁷ Pb/ ²⁰⁶ Pb	2%SD	²⁰⁷ Pb/ ²³⁵ U	2%SD	²⁰⁶ Pb/ ²³⁸ U	2%SD	rho	Age (Ma)	2SD	Age (Ma)	2SD	Age (Ma)	SD
NWA10666 zircon 1-1	11	0.3	-0.0008 160	0.6100	2.4	98.78	4.0	1.150	2.7	0.82	4938	94	4674	40	4532	34
NWA10666 zircon 1-2	10	0.4	0.0034 100	0.6247	2.5	96.74	4.1	1.118	3.1	0.80	4842	105	4653	41	4566	36
NWA10666 zircon 1-3	6	0.9	0.0029 141	0.6263	2.7	87.29	4.2	1.005	3.0	0.75	4490	66	4550	42	4570	40
Table 4b. LA-ICF	-MS U	-Pb dai	ta for zircon g	ırain spot	s in N	WA 1066	9									
	306	338		ē	120 - 201			c	202	206						

	²⁰⁶ Pb/ ²³⁸ U		²⁰⁷ Pb/ ²³⁵ U		²⁰⁷ Pb/ ²⁰⁶ Pb	
•	Age (Ma)	2SD	Age (Ma)	2SD	Age (Ma)	2SD
zircon 1-1	4938	94	4674	40	4532	34
zircon 1-2	4842	105	4653	41	4566	36
zircon 1-3	4490	66	4550	42	4570	40

Table 4a & 4b. U-Pb analysis on three spots on a single ${\sim}100\mu m$ zircon

4.4 Oxygen Isotopic Data

Oxygen isotopic composition on acid-washed subsamples: δ^{17} O: 1.709 ± 0.012 (2 σ), 1.659 ± 0.01 (2 σ), 1.811 ± 0.012 (2 σ); δ^{18} O: 3.759 ± 0.004 (2 σ), 3.662 ± 0.006 (2 σ), 3.983 ± 0.0028 (2 σ); Δ^{17} O: -0.276 ± 0.002 (2 σ), -0.275 ± 0.002 (2 σ), -0.292 ± 0.002 (2 σ) per mil. The δ^{17} O values were in majority agreement within HED uncertainty and Δ^{17} O values were lower than the diogenites analyzed by Greenwood et al., 2017 which were 1.527 ± 0.212 (2 σ) and -0.229 ± 0.016 (2 σ), respectfully (Figure 27). The values retrieved from NWA 10666 is unlike diogenites recorded by Greenwood et al., (2014, 2017) (n = 44) which display a high level of isotopic homogeneity with respect to Δ^{17} O. However, this may be due to systematic bias that may be present in laboratory analyses.

Wiechert et al., 2004 concludes that the HEDs which have been sampled for oxygen isotopic analyses may not be representative of an entire parent body because there are resolvable

differences in several samples such as Caldera, Ibitira, Pasamonte, and ALHA 78132 which fall outside of the 2σ error (95% confidence). They note that the deviations in the oxygen isotopes could reflect intrinsic heterogeneities within the HED parent body due to incomplete mixing at an early change, or



Figure 27. NWA 10666 oxygen data compared to oxygen isotopic composition of HEDs (n = 144). Central zone (labelled "1"): $\pm 2\sigma$ precision for eucrite and diogenite falls only (n = 26). Intermediate zone (labelled "2"): $\pm 2\sigma$ precision for eucrite, cumulate eucrite and diogenite falls and finds (n= 105). Outer zone (labelled "3"): $\pm 2\sigma$ precision for howardites and polymict eucrites (n=39). EFL= Eucrite Fractionation Line: average Δ^{17} O for 26 eucrites and diogenites falls = -0.240 ± 0.014 (2σ) (Greenwood et al., 2017)

incomplete admixing at a late stage.

Comparing Δ^{17} O can be misleading because there is not yet a consensus of which reference line should be chosen for defining Δ^{17} O (Greenwood et al., 2017). Some authors determine λ using values from the fractionation line determined by terrestrial samples (e.g.Miller, 2002; Spicuzza et al., 2007; Pack et al., 2013), while others use the high temperature equilibrium limit value of .5305 (Wiechert et al., 2004; Pack and Herwartz, 2014).

4.5 Bulk Chemistry

Major and trace element data of bulk rock powder collected from NWA 10666 are listed in Table 2. The bulk rock REE data average ~3.5*chondrite with a positive Eu concentration anomaly (Eu/Eu*) of 1.2

(Figure 28). The positive Eu anomaly is likely associated with the presence of plagioclase in the rock. The REE pattern of NWA 10666 (Figure 28) is similar to that of Binda, which is a polymict cumulate eucrite, and the Type B diogenite Y-75032, suggesting perhaps a common process that



Figure 28. Bulk REE pattern of NWA 10666 (solid black line & green circle). The reference chondrite is from Anders and Grevesse (1989). Also shown are the REE patterns of typical diogenites, cumulate and basaltic eucrites found in literature (Mittlefehldt, 2015)

produced these specimens. It is unclear which lithology was analyzed for Binda or whether the analysis mixed lithologies, so the chemical similarities may be coincidental. The positive Eu anomaly in NWA 10666 is perhaps unique among diogenites, but common among cumulate eucrites (suggestive of plagioclase accumulation).

4.6 Thermometry

Equilibration temperatures of NWA 10666 using REE in plagioclase-clinopyroxene and two-pyroxene Fe-Mg exchange thermometry was calculated from the mineral chemical data in Figure 18. Two-pyroxene thermometry yielded 850° C (Köhler and Brey, 1990) and REE in plagioclase-clinopyroxene thermometry yielded 1262 ± 4 (1 σ) °C. Due to the low concentration of the heavy REEs in plagioclase, the REE data used for the temperature calculations are La, Ce, Pr, Nd, Eu and Gd; only a maximum concentration of Sm was determined for plagioclase. Two

approaches were used to calculate the composition of pyroxene used in the calculations. The first approach assumed that the CPX (~2 vol%) was in REE equilibrium with plagioclase yielding a temperature of 1262 °C. The second approach attempted to reintegrate the pyroxenes into a single phase; this pyroxene composition yielded spurious values in excess of 1500 °C.

The D value of a given element is defined by the concentration ratio of that



NWA 10666: $T_{(REE)} = 1262\pm4$ °C

Figure 29. REE-in-plagioclase-clinopyroxene displaying initial igneous crystallization temperature range of the coexisting minerals. D= partition coefficient, A and B are coefficients corresponding to the changes of entropy and enthalpy

element into the two minerals (Sun and Liang, 2017). Plagioclase and clinopyroxene REE partition coefficients (D) in NWA 10666 were as followed: La=0.788, Ce= 0.470, Pr= 0.254, Nd= 0.173, Eu= 18.90, and Gd= 0.039. A clinopyroxene Mg# of 74 and plagioclase composition of An₈₇ were used as input parameters to the calibration of Sun and Liang (2017). The *A* term is a constant that accounts for compressibility as well as Poison's ratio of a given crystal (Stosh, 1982). The *B* term is another constant that accounts for charge balance whenever trace and major ions possess different valency (Onuma et al. 1968). For this experiment where the exchange reaction was temperature sensitive, *A* and *B* were calibrated experimentally (Sun and Liang, 2017). Based on the computations outlined in Sun and Liang (2017), the linearity of the REE data in Figure 29 support REE equilibration between CPX and plagioclase.

Chapter 5

Discussion

5.1 Comparison with other diogenites and cumulate eucrites

5.1.1 Petrography/Petrology/Mineralogy

Diogenites are generally regarded as cumulate rocks that formed in a magma ocean and/or large discreet magma chambers based on their mineralogical and geochemical distinctions (Mittlefehldt 1994a; Barrat et al., 2008; Zhang et al., 2020). Dominantly composed of orthopyroxene, diogenites are characterized by their coarse-grained textures which suggest slow cooling. Because many diogenite specimens exhibit brecciation and/or metamorphic recrystallization, the primary igneous textures of many diogenite specimens have been significantly obscured (e.g., Barrat et al., 2008). NWA 10666's cataclastic texture (shock stage = moderate) does not significantly obscure the primary igneous textures. NWA 10666 is equilibrated, as evidence by the major phase minerals exhibiting a general homogenous composition (e.g., Hewins 1980; Berkley and Boynton 1992; Mittlefehldt 1994b; Fowler et al. 1994; Bowman et al. 1999). It contains a number of crushed phases and evidence of maskelynite (Cavosie personal communication). Olivine diogenites described by Sack et al., (1991) contain "significant" (~35%) amounts of olivine. No olivine was observed in NWA 10666, exemplifying the large mineralogical variation within specimens classified as diogenites. The presence of ilmenite and silica polymorph phase(s) in NWA 10666 and Y-75032 (Type B diogenite as indicated by Mittlefehldt and Lindstrom, 1993) suggest that perhaps an intercumulus melt was trapped. The same can be said about cumulate eucrites where ilmenite and silica are commonly found (Mittlefehldt and Lindstrom, 1993). However, cumulate eucrites contain less orthopyroxene and are richer in clinopyroxene and plagioclase. Overall, most diogenites have textures consistent with dynamic crystal-liquid processes, such as accumulation, likely associated with fractional crystallization processes of a liquid of unknown scale. Basaltic eucrite textures are fine- to medium- grained, suggestive of more rapid cooling perhaps related to surface/near surface emplacement.

Unequilibrated diogenites such as Dhofar 700 and Y-74097 are rare. These unequilibrated diogenites display compositional zoning in pyroxenes from core to rim due to the lack of significant thermal metamorphic imprint (Yamaguchi et al., 2011). These specimens are important because they possible indicate derivation from shallow intrusions. Equilibrated diogenites are more typically found and usually display grains that are homogeneous with respect to the major elements. As degree of metamorphism increases, primary textures and igneous petrologic information can be difficult to evaluate as they tend to be obscured/destroyed.

Based on pyroxene data compiled from Mittlefehldt (2015), NWA 10666 displays pyroxene compositions that are transitional between diogenites and cumulate eucrites (Figure 30). Some Yamato-series diogenites



Figure 30. Pyroxene composition quadrilateral of NWA 10666 (green dots) vs literature data of diogenites (blue), cumulate eucrites (green), and basaltic eucrites (red) determined by Mittlefehldt, (2015)

such as Y-75032, Y-791000, Y-791199, and Y-791422 also display similar transitional pyroxene compositions, evident through their pyroxene assemblage/ compositional range and average Mg# of ~66 (Takeda and Mori, 1985), which is identical to OPX compositions in NWA 10666. The average FeO/MnO ratio of OPX is ~30, similar to that of other diogenites (e.g., Mittlefehldt 1994b). The plagioclase compositions range from An 80.5 - 89.8, identical to those in Y-791199 (An₈₂₋₉₀) and slightly lower than the those in Y-791422 (An₈₈₋₉₃). The An content of plagioclase in Y-75032 ranges from 78 - 87; Takeda and Mori (1985) interpreted the An trend in Y-75032 as the product of plagioclase crystallization in a trapped intercumulus liquid.

The temperature recorded by the plagioclase-clinopyroxene REE thermometer is $1262 \pm 4 (1\sigma)$ °C, a temperature that may indicate igneous conditions. The good linearity of the REE data in Figure 29 support REE equilibration and show no evidence for secondary disturbances and/or re-equilibration. However, it is unlikely that the CPX is an igneous phase. Texturally, the CPX appears to have exsolved from the host low-Ca pyroxene, and thus would not be

equilibrating with plagioclase during igneous conditions. Additionally, the calculated temperature of 1262 °C is higher than temperatures of plagioclase stability in magmatic systems predicted by experiments of eucrite compositions (e.g., Stolper, 1977). In chondritic systems, the temperature of plagioclase stability is also significantly below the calculated temperatures REE temperatures (e.g., Jurewicz et al., 1993; 1995). Thus, it is likely that the plagioclase is not in chemical equilibrium with the exsolved CPX yielding calculated temperatures that very likely overestimate the actual thermal conditions.

Fe-Mg partitioning between coexisting OPX and CPX which yielded an equilibration temperature of 850°C (Brey and Köhler, 1990) suggests that protracted cooling and/or thermal equilibration occurred after igneous crystallization and emplacement. The Ca-Fe-Mg equilibration between OPX and CPX can occur without resulting in diffusive equilibration of 3+ and 4+ cations, allowing the two-pyroxene thermometer to record low temperatures (Mittlefehldt, 1994a). Two-pyroxene thermometry of Type B diogenites, Roda, and Johnstown yielded an equilibration temperature of 980°C, 850°C, and 650°C, respectively (Mittlefehldt, 1994a).

5.1.2 Chemistry

Bulk chemical analyses of major and minor/trace elements help to further frame the context of distinguishing eucrites and diogenites from each other and relating them to their parent body. As indicated in (Figure 31) refractory highly incompatible elements (e.g., Sm and Hf) show that diogenites (blue) tend to have lower concentrations of incompatible elements, whereas cumulate eucrites and basaltic eucrites have higher concentrations of incompatible elements, elements, respectively. There is substantial compositional overlap between the specimens

classified as diogenites and those classified as cumulate eucrites. The incompatible element concentration data of NWA 10666 plots within the range of cumulate eucrites, indicating compositions much more incompatible trace element rich than most other diogenites. Due to its similarities in composition and mineralogy, NWA 10666 should be classified as a Type B diogenite or 'transitional diogenite' as



Figure 31. Sm vs Hf log plot of NWA 10666 compared to other diogenites and eucrites found in literature. Values are chondrite normalized. Two points of NWA 10666 plotted since two trace element samples were analyzed (~1:500) & (~1:1000) dilution factor.

defined as having compositions transitional between cumulate eucrite and diogenites.

5.2 Age and Thermal History

The relatively evolved composition of NWA 10666 greatly expands the options for chronology in this specimen. The U-Pb isotope system in zircon has a closure temperature of ~900°C assuming a roughly 50 µm average size and a slow cooling rate of 1–100°C /Myr (Cherniak and Watson, 2001; Cherniak et al., 1991). Thus, zircon can provide robust age information of igneous or very high-temperature metamorphic processes. U-Th-Pb in apatite has a closure temperature of 450–550°C under a slow cooling rate of 1–100°C/Myr (Cherniak, 2010). Thus, records of high temperature and "moderately high-temperature" events could be documented which could likely be missed or overwritten in other radiometric systems that could be prone to mineral reactions and/or diffusive exchange.

Zircons have not been recorded in any other specimen classified as a diogenite, so we compared the new U-Pb in zircon data with literature data of cumulate and basaltic eucrites. The zircon in NWA 10666 is unlikely to be an exsolution phase since it is not hosted exclusively in ilmenite (Figure 32).



Figure 32. Backscattered electron image of zircon (bright) surrounded by ilmenite (darker gray) within NWA 10666.

Despite the minerals being equilibrated, the cumulate igneous texture is inconsistent with largescale recrystallization that may have resulted in zircon precipitation, though this scenario cannot be completely ruled out. The zircon age of 4542 ± 20 Ma is identical within uncertainty to U-Pb in zircon ages of polymict eucrite Y-75011 (4550 ± 9 Ma), metamorphosed eucrite Y-792510 (4545 ± 18 Ma), granulitic eucrites A881388 (4555 ± 54 Ma) and A881467 (4558 ± 13 Ma) and an impact-melted eucrite Padvarninkai (4556 ± 15 Ma) (Misawa et al., 2005). Overall, the U-Pb zircon age of NWA 10666 is identical within uncertainty to that of many eucrites, suggesting that magmatic processes were occurring at about 4.55 Ga. According to Hf-W measurements of zircon conducted by Roszjar et al. (2016) on unbrecciated eucrites, magmatism on Vesta could have lasted until 4.53 Ga.

The Pb-Pb apatite age 4248 ± 25 Ma and the concordance of Pb-Pb, U-Pb, and Th-Pb dates indicate that the phosphate in NWA 10666 was either precipitated at that time or subjected to conditions, such as recrystallization, that caused it to expel all accumulated radiogenic Pb. Given that there is no evidence that igneous processes occurred as late as 4.25 Ga, impact processes are a likely heat source that resulted in the precipitation or recrystallization of apatite

(e.g., Liao and Hsu et al., 2017). The ²⁰⁷Pb-²⁰⁶Pb phosphate ages of NWA 10666 match within uncertainty of ²⁰⁷Pb-²⁰⁶Pb ages for four merrillites in Juvinas (basaltic eucrite) of 4200 \pm 49 Ma (MSWD= 0.59) but fall outside the range of ²⁰⁷Pb-²⁰⁶Pb age for three apatites in Juvinas at 4552 \pm 85 Ma (mean square weighted deviation (MSWD =0.48) (Koike et. al., 2020). NWA 8009 (eucrite) and Béréba (eucrite) have also recorded thermal metamorphic events within the ~4.25 -4.1 Ga causing a complete reset of U-Pb in the apatite grains (Liao and Hsu, 2017; Zhou et al., 2011). The U-Pb data for the phosphates and zircon indicate that initial magmatic crystallization occurred around 4542 \pm 20 Ma and a subsequent thermal/impact metamorphic event happened about 300 m.y. afterwards.

5.3 Parent Body Processes

Any model of Vesta's early evolution is subject to four major constraints: chronological, thermal, petrological/chemical, and physical. A multi-step evolution of the diogenite parent body (EPB) was first presented by Righter and Drake (1997) and then refined by Mandler and Elkins-Tanton (2013). The first step is accretion and heating. The heating of Vesta, which was accreted from smaller objects, can be explained by early ²⁶Al decay (Shukolyukov and Lugmair 1993; Quitté et al. 2011; Schiller et al. 2011). Heat released from radioactive decay may have caused planet-scale melting (magma ocean), allowing for efficient metal-silicate fractionation. Early metal silicate fractionation is evident in Hf-W isotopic compositions (Jacobsen, 2005; Kleine et al., 2009; Kleine and Walker, 2017) and siderophile element compositions of eucrites (Palme and Rammensee 1981; Righter and Drake 1997). Step two consists of different cooling mechanisms and rates that lead to the crystallization of a magma ocean. The heat budget of a growing EPB is controlled by surficial processes because all heat loss occurs at the surface (Mandler and Elkins-

Tanton, 2013). Step three is more cooling and melt extraction that produces a crust and leaves behind depleted residues. Compositional trends indicative of contamination and/or fractional crystallization (e.g., Barrat et al., 2007) and the complex nature of a planetary igneous system preclude further refinements of the processes as they relate to NWA 10666, except that these igneous processes were very early (4.54 Ga). In addition, the cumulate texture of NWA 10666 is consistent with deep emplacement and the chemically transitional nature of it may suggest petrogenetic linkages between cumulate eucrites and diogenites.

Periods of high impact flux on 4 Vesta have been documented where thermochronometers such as U-Pb in Ca-phosphates or Ar-Ar in silicates have been either partially or completely reset (Liao and Hsu, 2017; Bogard and Garrison, 2003). These periods of high impact flux on EPB have contributed to global metamorphism. The data points to metamorphic events being likely related to multiple processes. The chronology suggests that metamorphism related to impact processes likely waned in intensity with time. Observations made by Iizuka et al., 2015, 2019; Liao and Hsu, 2017; Kennedy et al., 2019; Koike et al., 2020; and others have identified a thermal metamorphic event at ~4500 Ma through Pb-Pb and K-Ar systems. After this major event, another but less intense series of events occurred at ca. 4300 -4100 Ma identified through U-Pb of phosphates (Liao and Hsu, 2017; Zhou et al., 2011) and silicates (Galer and Lugmair, 1996; Tera et al., 1997) and Ar-Ar in plagioclase (Kunz et al., 1995; Kennedy et al. 2019) in brecciated eucrites. Figure 33 shows a compilation of multiple chronologic systems including U-Pb in zircon, silicates, and phosphates; K-Ar in whole rock (WR), melt, and silicate; and Hf-W in zircon (Koike et al., 2020 and references therein). K-Ar in plagioclase data record younger bombardment of the Vestan parent body at 3.85 - 3.47 Ga (Kennedy et al., 2019). The lack of ~3.85 Ga ages in U-Pb phosphate ages indicate that this

bombardment episode may not have been sufficiently energetic to reset U-Pb in phosphate. On the other hand, thermal events that could reset the U-Pb system in phosphate would have very likely resulted radiogenic Ar being expelled from the silicate minerals. Thus, the U-Pb phosphate data may be uncovering a period bombardment that predates a Vestan cataclysm (3.3 - 3.8 Ga;e.g., Cohen, 2013). The Pb-Pb phosphate ages in NWA 10666 fall within the same time frame as a documented episode of metamorphism found in impact age spectra of the moon (~4.1 – 4.2 Ga) (Morbidelli et al., 2012; Hopkins and Mojzsis, 2015; Norman et al., 2016). This implies that an intense widespread bombardment happened within the inner solar system at 4.1 through ~4.25 Ga (Liao and Hsu, 2017).

Metamorphism has affected most if not all materials from the HED parent body (McSween et al., 2010). Different chronometers have different sensitivities to these thermal events and/or changes involving recrystallization/metamorphic reaction. The most commonly used chronometers that are susceptible to thermal events in the range of 300-550° are Ar-Ar and U-Pb in phosphate. The Pb-Pb phosphate age of 4248 ± 25 Ma in NWA 10666 is similar to phosphate ages in NWA 8009, Stannern, Béréba, and Juvinas (Figure 33; modified from Koike et al., 2020). The 4.1 - 4.5 Ga ages of U-Pb in Ca-phosphate in eucrites and diogenites indicate a high impact/thermal flux on Vesta during this time period (Koike et al., 2020; Liao and Hsu, 2017; Zhou et al., 2011).

The U-Th-Pb analyses of the zircons in eucrites, and now NWA 10666, suggest initial peak magmatism on the Eucrite Parent Body (EPB) occurred ~4550 Ma. This age indicates that crystallization began at or within ~16-18 Myr of the age of CAI formation (4567.2 ± 0.6 Ma; Efremovka CAIs, Amelin et al., 2002). The Pb-Pb zircon ages indicate a time where Vesta had already accreted, melted, developed a metallic core, and underwent magmatic crystallization near

the surface (Mandler and Elkins-Tanton et al., 2013). Heat source models by (Ghosh and McSween 1998; Gupta and Sahijpal 2010) have attempted to understand the thermal histories on Vesta through ²⁶Al decay, but fine details of modeling have yet to adequately deal with parameters such as heat transfer or impact heating of the upper boundary.



Figure 33. Compilation of various chronologic systems from literature showing a concentration of dates at ~4500 Ma and ~4300 Ma. Overall, there is a waning trend of dates recorded after ~4300 Ma (modified from Koike et al., 2020)

Because thermal modeling still needs work to implement the complex parameters, petrogenetic modeling is seen as the more useful approach to understanding EPB evolution. The two main models to explain lithologic differences in HEDs can broadly be separated into: partial melting vs fractional crystallization of a magma ocean. Diogenites are orthopyroxene cumulates which means their crystallization process must leave residual liquid. The less dense residual liquid will therefore be on top (e.g. shallower depths) of the originally crystallized diogenites and continue this trend upwards to the surface (Figure 34) (Mandler and Elkins-Tanton, 2013). NWA 10666 is an orthopyroxene cumulate that follows this fractionalization trend between ordinary



Figure 34. Schematic of a proposed fractionalization process within Vesta showing residual liquid from diogenite formation must crystallize at shallower levels in Vesta. Heavy minerals (e.g. olivine, orthopyroxene) will sink/sit at the bottom and lighter minerals (e.g. clinopyroxene, plagioclase) will form on top of the pile.

diogenites and cumulate eucrites. However, the issue with the magma ocean model is that it can't explain extreme incompatible trace element concentrations (Mittlefehldt, 1994a; Fowler et al., 1994). Stolper's (1977) partial melting model suggested that diogenites could form from partial melting of a Vestan mantle that was depleted from previous partial melting to form eucrites. The melt's composition would be close to pure orthopyroxene and would crystallize as plutons without leaving a eucritic residual liquid. Stolper supported this claim by comparing Type B diogenites to Sioux County (eucrite) and noting their similar Mg#, alluding to diogenites formed from similar parent melts. A silica phase in Sioux County appeared after about 70% of the melt had crystallized in his experiment. Therefore, it can be inferred that NWA 10666's silica phase is from a trapped liquid late in the crystallization process. Ilmenite is also commonly a late accessory phase in most eucrites and its existence in NWA 10666, Y-75032, and Y-79199 also point towards trapped liquids (Mittlefehldt and Lindstrom 1993).

Chapter 6

Conclusions

NWA 10666 is compositionally and perhaps petrologically related to Yamato type-B diogenites. NWA 10666 has average pyroxene compositions of (Wo_{2.4}En_{62.7}Fs_{34.9} and Wo_{44.1}En_{41.6}Fs_{14.3}) and average plagioclase compositions of (An_{87.9}). Yamato type-B diogenites have average pyroxene compositions of (Wo_{1.7}En_{64.9}Fs_{33.4} and Wo_{41.5}En_{44.5}Fs_{14.0}) and average plagioclase compositions of (An_{88.6}). Yamato type-B diogenites are compositionally transitional between cumulate eucrites and diogenites (Mittlefehldt and Lindstrom, 1993).

The 4542 ± 20 Ma zircon age is coeval with eucrite U-Pb zircon ages. Eucrites such as polymict eucrite Y-75011 (4550 ± 9 Ma), metamorphosed eucrite Y792510 (4545 ± 18 Ma), granulitic eucrites A881388 (4555 ± 54 Ma) and A881467 (4558 ± 13 Ma) and an impact-melted eucrite Padvarninkai (4556 ± 15 Ma) have zircon U-Pb ages that overlap with NWA 10666 within uncertainty (Misawa et al., 2005).

The 4248 ± 25 Ma Ca-phosphate age is older than most Ar-Ar thermochronology. This is due to the fact Ar-Ar thermochronometers reset easier than U-Pb in phosphates due to the low temperature reset nature of Ar-Ar systematics (Bogard, 1995; Bogard and Garrison, 2003). Dates between 4.1 - 4.4 Ga are more commonly recorded in higher-temperature systems than in Ar-Ar.

EPB metamorphic events (collisions to EPB) between 4.0 - 4.5 Ga wouldn't have had enough energy to reset U-Pb in zircon (indicative from most eucritic igneous zircons being ~4.5Ga) but would be able to reset the Ca-phosphates. Presumably lower energy events (<4.0 Ga) were able to reset the Ar-Ar dates in silicates, but not U-Pb in phosphates. The 3.3 - 3.8 Ga may reflect an overall waning impact intensity in the inner Solar System. Thus, U-Pb in phosphates may be a window into determining the timing of metamorphic events between igneous crystallization and Ar-Ar dates that indicate impact cataclysm.

Bibliography

Allègre C. J., Birck J. L., Fourcade S., Semet M. P., (1975) Rubidium-87/ Strontium-87 age of Juvinas basaltic achondrite and early igneous activity in the solar system. Science 187(4175), 436–438.

Amelin Y., Krot A. N., Hucheon I. D., Ulyanov A. A., (2002) Lead isotopic ages of chondrules and calcium-aluminum-rich inclusions. Science 297(5587), 1678–1683.

Barfod G. H., Krogstad E. J., Frei R., Albarède F., (2005) Lu-Hf and PbSL geochronology of apatites from Proterozoic terranes: A first look at Lu-Hf isotopic closure in metamorphic apatite. Geochimica Et Cosmochimica Acta, 69(7), 1847-1859.

Barrat J. A., Gillet Ph., Lesourd M., Blichert-Toft J., Poupeau G. R. (1999) The Tatahouine diogenite: Mineralogical and chemical effects of sixty-three years of terrestrial residence. Meteoritics & Planetary Science 34(1), 91–97.

Barrat J. A., Beck P., Bohn, M., Cotten J., Gillet P., Greenwood R. C., Franchi I. A., (2006) Petrology and geochemistry of the fine-grained, unbrecciated diogenite Northwest Africa 4215. Meteoritics & Planetary Science 41(7), 1045–1057.

Barrat J. A., Yamaguchi A., Greenwood R. C., Benoit, M., Cotten J., Bohn, M., Franchi I. A., (2008) Geochemistry of diogenites: still more diversity in their parental melts. Meteoritics & Planetary Science 43(11), 1759–1775

Barrat, J. A., Yamaguchi, A., Greenwood, R. C., Bohn, M., Cotton, J., Benoit, M., Franchi, I. A., (2007) The Stannern trend eucrites: contamination of main group eucritic magmas by crustal partial melts. Geochimica Et Cosmochimica Acta 71(16), 4108–4124

Barrat J. A., Yamaguchi A., Zanda B., Bollinger C., Bohn M., (2010) Relative chronology of crust formation on asteroid Vesta: insights from the geochemistry of diogenites. Geochimica Et Cosmochimica Acta 74(21), 6218–6231.

Beck A. W., McSween H. Y., (2010) Diogenites as polymict breccias composed of orthopyroxenite and harzburgite. Meteoritics & Planetary Science 45(5), 850–872.

Beck A. W., Mittlefehldt D. W., McSween H. Y., Rumble III D., Lee C.-T. A., Bodnar R. J., (2011) MIL 03443, a dunite from asteroid 4 Vesta: evidence for its classification and cumulate origin. Meteoritics & Planetary Science 46(8), 1133–1151.

Beck A. W., McCoy T. J., Sunshine J. M., Viviano C. E., Corrigan C. M., Hiroi T., Mayne R. G., (2013) Challenges in detecting olivine on the surface of 4 Vesta. Meteoritics & Planetary Science 48(11), 2155–2165.

Berkley J. L., Boynton N. J., (1992) Minor/major element variation within and among diogenite and howardite orthopyroxenite groups. Meteoritics, 27(4), 387-394.

Binzel R. P., Xu S. (1993) Chips off of Asteroid 4 Vesta: Evidence for the Parent Body of Basaltic Achondrite Meteorites. Science, 260(5105), 186-191.

Birck J. L., Allègre C. J., (1978) Chronology and chemical history of the parent body of basaltic achondrites studied by the ⁸⁷Rb-⁸⁷Sr method. Earth and Planetary Science Letters, 39(1), 37–51.

Bogard D. D., (1995) Impact ages of meteorites: A synthesis. Meteoritics, 30(3), 244-268

Bogard D. D., Garrison D. H., (2003) ³⁹Ar-⁴⁰Ar ages of eucrites and thermal history of asteroid 4 Vesta. Meteoritics & Planetary Science 38, 669–710.

Bogard D. D., (2011) K-Ar ages of meteorites: clues to parent-body thermal histories. Geochemistry 71(3), 207–304.

Bouvier A., Blichert-Toft J., Boyet M., Albarede F., (2015) ¹⁴⁷Sm-¹⁴³Nd and ¹⁷⁶Lu-¹⁷⁶Hf systematics of eucrite and angrite meteorites. Meteoritics & Planetary Science 50(11), 1896–1911.

Bowman L. E., Papike J. J., Spilde M. N., (1999) Diogenites as asteroidal cumulates: Insights from spinel chemistry. American Mineralogist 84, 1020–1026

Bowman L.E., Spilde M.N., Papike J.J., (1997) Automated energy dispersive spectrometer modal analysis applied to the diogenites. Meteoritics & Planetary Science 32(6), 869–875.

Bunch T., Irving A., Wittke J., Kuehner S., Rumble D., (2007) Distinctive magnesian, protogranular, and polymict diogenites from Northwest Africa, Oman, and United Arab Emirates. Meteoritics & Planetary Science 42, A27.

Cavosie A. J., Timms N. E., Erickson T. M., Hagerty J. J., Hörz F., (2016) Transformations to granular zircon revealed: twinning, reidite, and ZrO2 in shocked zircon from Meteor Crater (Arizona, USA). Geology 44(9), 703–706

Cherniak D. J., (2010) Diffusion in accessory minerals: zircon, titanite, apatite, monazite and xenotime. Reviews in Mineralogy and Geochemistry, 72, 827-869.

Cherniak D. J., Lanford W. A., Ryerson F. J., (1991) Lead diffusion in apatite and zircon using ion implantation and Rutherford Backscattering techniques. Geochimica Et Cosmochimica Acta 55(6), 1662–1673.

Cherniak D. J., Watson E. B., (2001) Pb diffusion in zircon. Chemical Geology 172, 5-24.

Chew D. M., Petrus J. A., Kamber B. S., (2014) U–Pb LA–ICPMS dating using accessory mineral standards with variable common Pb. Chemical Geology 363, 185–199.

Chew D. M., Sylvester P. J., Tubrett M. N., (2011) U-Pb and Th-Pb dating of apatite by LA-ICPMS. Chemical Geology 280(1-2), 200–216.

Clenet H., Jutzi M., Barrat J., Asphaug E. I., Benz W., Gillet P., (2014) A deep crust-mantle boundary in the asteroid 4 Vesta. Nature, 511(7509), 303-306.

Cohen B. A., (2013) The Vestian cataclysm: impact-melt clasts in howardites and the bombardment history of 4 Vesta. Meteoritics & Planetary Science 48(5), 771–785.

Day J. M. D., Walker R. J., Qin L. P., Rumble D., (2012) Late accretion as a natural consequence of planetary growth. Nature Geoscience. 5(9), 614-617.

De Sanctis M. C., Ammannito E., Migliorini A., Lazzaro D., Capria M. T., McFadden L., (2011) Mineralogical characterization of some V-type asteroids, in support of the NASA Dawn mission. Monthly Notices of the Royal Astronomical Society, 412(4), 2318-2332.

Delaney J. S., Prinz M., Nehru C. E., Stokes C. P., (1984a) Allan Hills A81001 Cumulate Eucrites and Black Clasts from Polymict Eucrites. 15th Lunar & Planetary Science Conference, Abstract #1108.

Delaney J. S., Prinz M., Takeda H., (1984b) The polymict eucrites. Proceedings of the 15th Lunar & Planetary Science Conference, C251-C288.

Delaney J. S., Takeda H., Prinz M., Nehru C. E., Harlow G. E., (1983) The nomenclature of polymict basaltic achondrites. Meteoritics 18, 103–111.

Domanik K., Kolar S., Musselwhite D., Drake M. J., (2004) Accessory silicate mineral assemblages in the Bilanga diogenite: a petrographic study. Meteoritics & Planetary Science 39, 567–579

Domanik K., Sideras L., Drake M., (2005) Olivine and Ca-phosphates in the diogenites Manegaon and Roda. 36th Lunar & Planetary Science Conference, Abstract #2128.

Duke M. B., Silver L. T., (1967) Petrology of eucrites, howardites and mesosiderites. Geochimica Et Cosmochimica Acta 31, 1637–1665.

Floran R. J., Prinz M., Hlava P. F., Keil K., Spettel B., Wänke H. (1981) Mineralogy, petrology, and trace element geochemistry of the Johnstown meteorite: a brecciated orthopyroxenite with siderophile and REE-rich components. Geochimica Et Cosmochimica Acta 45(12), 2385-2391

Fowler G. W., Papike J. J., Spilde M. N., Shearer C. K., (1994) Diogenites as asteroidal cumulates: insights from orthopyroxene major and minor element chemistry. Geochimica Et Cosmochimica Acta 58, 3921–3929.

Fredriksson K., Noonan A., Brenner P., Sudre C., (1976) Bulk and major phase composition of eight hypersthene achondrites. Meteoritics 11, 278–286.

Fukuoka T., Boynton W. V., Ma M.-S., Schmitt R. A., (1977) Genesis of howardites, diogenites, and eucrites. Proceedings of the 8th Lunar and Planetary Science Conference, 187–210.

Galer S. J. G., Lugmair G. W., (1996) Lead isotope systematics of non-cumulate eucrites. Meteoritics & Planetary Science 31(Suppl.), A47–A48.

Ghosh A., McSween H. Y., (1998) A thermal model for the differentiation of asteroid 4 Vesta, based on radiogenic heating. Icarus 134, 187–206.

Gomes C. B., Keil K., (1980) Brazilian Stone Meteorites. University of New Mexico Press, Albuquerque, NM.

Gooley R., Moore C. B., (1976) Native metal in diogenite meteorites. American Mineralogist 61, 5–6.

Greenwood R. C., Barrat J. A., Yamaguchi A., Franchi I. A., Scott E.R.D., Bottke W. F., Gibson J. M., (2014) The oxygen isotope composition of diogenites: Evidence for early global melting on a single, compositionally diverse, HED parent body. Earth and Planetary Science Letters, 390, 165–174.

Greenwood R. C., Burbine T. H., Miller M. F., Franchi I. A., (2017) Melting and differentiation of early-formed asteroids: The perspective from high precision oxygen isotope studies. Geochemistry, 77(1), 1–43.

Gupta G., Sahijpal S., (2010) Differentiation of Vesta and the parent bodies of other achondrites. Journal of Geophysical Research 115(E8).

Haba M. K., Yamaguchi A., Horie K., Hidaka H., (2014) Major and trace elements of zircons from basaltic eucrites: implications for the formation of zircons on the eucrite parent body. Earth and Planetary Science Letters, 387, 10–21.

Harlow G. E., Nehru C. E., Prinz M., Taylor G. J., Keil K., (1979) Pyroxenes in Serra de Magé; cooling history in comparison with Moama and Moore County. Earth and Planetary Science Letters, 43, 173–181.

Hess H. H., Henderson E. P., (1949) The Moore County meteorite: a further study with comment on its primordial environment. American Mineralogist 34, 494–507.
Hewins R. H., (1980) Subdivision of diogenites into chemical classes. 11th Lunar and Planetary Science Conference, 44143.

Hopkins M. D., Mojzsis S. J. (2015) A protracted timeline for lunar bombardment from mineral chemistry, Ti thermometry and U–Pb geochronology of Apollo 14 melt breccia zircons. Contributions to Mineralogy and Petrology 169, 30

Howard L. M., Domanik K. J., Drake M. J., Mittlefehldt D. W., (2002) Petrology of Antarctic Eucrites PCA 91078 and PCA 91245. 33rd Lunar & Planetary Science Conference, Abstract #1331.

Hui H., Peslier A. H., Lapen T. J., Shafer J. T., Brandon A. D., Irving A. J., (2011) Petrogenesis of basaltic shergottite Northwest Africa 5298: Closed system crystallization of an oxidized mafic melt. Meteoritics & Planetary Science, 46(9).

Iizuka T., Jourdan F., Yamaguchi A., Koefoed P., Hibiya Y., Ito K. T. M., Amelin Y., (2019) The geologic history of Vesta inferred from combined 207Pb/206Pb and 40Ar/39Ar chronology of basaltic eucrites. Geochimica Et Cosmochimica Acta 267, 275–299.

Iizuka T., Yamaguchi A., Haba M. K., Amelin Y., Holden P., Zink S., Huyskens M. H., Ireland T. R., (2015) Timing of global crustal metamorphism on Vesta as revealed by high-precision U-Pb dating and trace element chemistry of eucrite zircon. Earth and Planetary Science Letters, 409, 182–192.

Irving A. J., Kuehner S. M., Fujihara G., Ralew S., Sipiera P. P., (2014) Noritic diogenites Northwest Africa 6928 and Northwest Africa 8367: Diversity in mineralogy of ancient magma ocean cumulates on the diogenite parent body. 77th Meteoritical Society Meeting. Abstract# 5199.

Irving A. J., Kuehner S. M., Wittke J. H., Tait K. T., (2016) Noritic diogenites and feldspathic diogenites: Evolved ancient cumulates potentially related to mesosiderites and not to any eucrites. 47th Lunar and Planetary Science Conference, Abstract #2264.

Jacobsen S. B., (2005) The Hf-W isotopic system and the origin of the Earth and Moon. Annual Review of Earth and Planetary Sciences 33, 531–570.

Jourdan F., Kennedy T., Benedix G. K., Eroglu E., Mayer C., (2020) Timing of the magmatic activity and upper crustal cooling of differentiated asteroid 4 Vesta. Geochimica Et Cosmochimica Acta 273, 205–225.

Jurewicz A. J. G., Mittlefehldt D. W., Jones J. H., (1993) Experimental partial melting of the Allende (CV) and Murchison (CM) chondrites and the origin of asteroidal basalts. Geochimica Et Cosmochimica Acta 57, 2123–2139.

Jurewicz A. J. G., Mittlefehldt D. W., Jones J. H., (1995) Experimental partial melting of the St, Severin (LL) and Lost City (H) chondrites. Geochimica Et Cosmochimica Acta 59, 391–408.

Kared R., Moine B. N., Seddiki A., Cottin J. Y., Greenwood R. C., Franchi I. A. (2019) Petrology, mineralogy, and geochemistry of the olivine diogenite NWA 4255: New insights into the magmatic evolution of asteroid 4 Vesta. Arabian Journal of Geosciences, 12(14).

Keil K., (2002) Geological history of asteroid 4 Vesta: The "smallest terrestrial planet". In Asteroids III (W. Bottke, A. Cellino, P. Paolicchoi and R.P. Binzel, eds.), University of Arizona Press, Tucson, pp. 573–584.

Kennedy T., Jourdan F., Eroglu E., Mayers C., (2019) Bombardment history of asteroid 4 Vesta recorded by brecciated eucrites: large impact event clusters at 4.50 Ga and discreet bombardment until 3.47 Ga. Geochimica Et Cosmochimica Acta 260, 99–123.

Kleine T., Touboul M., Bourdon B., Nimmo F., Mezger K., Palme H., Yin Q. Z., Jacobsen S. B., Halliday A. N., (2009) Hf-W chronology of the accretion and early evolution of asteroids and terrestrial planets. Geochimica Et Cosmochimica Acta 73, 5150–5188.

Kleine T., Walker R. J., (2017) Tungsten isotopes in planets. Annual Review of Earth and Planetary Sciences 45, 389–417.

Koike M., Sano Y., Takahata N., Iizuka T., Ono H., Mikouchi T. (2020) Evidence for early asteroidal collisions prior to 4.15 Ga from basaltic eucrite phosphate U–Pb chronology. Earth and Planetary Science Letters, 549, 116497.

Köhler T., Brey G., (1990) Calcium exchange between olivine and clinopyroxene calibrated as a geothermobarometer for natural peridotites from 2 to 60 kb with applications. Geochimica Et Cosmochimica Acta 54(9), 2375-2388.

Kunz J., Trieloff M., Bobe K. D., Metzler K., Stöffler D., Jessberger E. K., (1995) The collisional history of the HED parent body inferred from ⁴⁰Ar-³⁹Ar ages of eucrites. Planetary Space Science 43, 527–543.

Lapen T. J., Righter M., Andreasen R., Irving A. J., Satkoski A. M., Beard B. L., Nishiizumi K., Jull A. J., Caffee M. W., (2017) Two billion years of magmatism recorded from a single Mars meteorite ejection site. Science Advances 3.2

Liao S., Hsu W. (2017) The petrology and chronology of NWA 8009 impact melt breccia: Implication for early thermal and impact histories of Vesta. Geochimica Et Cosmochimica Acta 204, 159–178.

Lomena I. S. M., Touré F., Gibson E. K., Clanton U. S., Reid A. M., (1976) Aïoun el Atrouss: a new hypersthene achondrite with eucritic inclusions. Meteoritics 11, 51–57

Lovering J. F., (1975) The Moama eucrite - a pyroxene-plagioclase adcumulate. Meteoritics 10, 101–114.

Lugmair G. W., Galer S. J. G., (1992) Age and isotopic relationships among the angrites Lewis Cliff 86010 and Angra dos Reis. Geochimica Et Cosmochimica Acta 56, 1673–1694.

Mandler B. E., Elkins-Tanton L. T. (2013) The origin of eucrites, diogenites, and olivine diogenites: Magma ocean crystallization and shallow magma chamber processes on Vesta. Meteoritics & Planetary Science, 48(11), 2333–2349.

Mason B., (1963) The hypersthene achondrites. American Museum Novitates 2155, 1–13.

Mason B., Wiik H. B., (1966a) The composition of the Bath, Frankfort, Kakangari, RoseCity, and Tadjera meteorites. American Museum Novitates 2272, 1–24.

Mayne R. G., McSween H. Y., McCoy T. J., Gale A., (2009) Petrology of the unbrecciated eucrites. Geochimica Et Cosmochimica Acta 73, 794–819.

Mazor E., Anders E., (1967) Primordial gases in the Jodzie howardite and the origin of gas-rich meteorites. Geochimica Et Cosmochimica Acta 31, 1441–1456.

McCord T. B., Adams J. B., Johnson T. V., (1970) Asteroid Vesta: Spectral reflectivity and compositional implications. Science 168,1445–1447.

McCoy T. J., Beck A. W., Prettyman T. H., & Mittlefehldt D. W., (2014) Asteroid (4) Vesta II: Exploring a geologically and geochemically complex world with the Dawn Mission. Geochemistry, 75(3), 273–285.

McSween H. Y., Binzel R. P., De Sanctis M. C., Ammannito E., Prettyman T. H., Beck A. W., Reddy V., Le Corre L., Gaffey M. J., Raymond C. A., Russell C. T., and the Dawn Science Team. (2013) Dawn, the Vesta-HED connection, and the geologic context for eucrites, diogenites, and howardites. Meteoritics & Planetary Science 48.

McSween H. Y., Mittlefehldt D. W., Beck A. W., Mayne R. G., McCoy T. J., (2010) HED meteorites and their relationship to the geology of Vesta and the dawn mission. Space Science Review 163, 141–174.

Miller M. F., (2002) Isotopic fractionation and the quantification of 17O anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. Geochimica Et Cosmochimica Acta 66(11), 1881–1889

Miller M. F., Franchi I. A., Sexton A. S., Pillinger C. T., (1999) High-precision d17O isotope measurements of oxygen from silicates and other oxides: methods and applications. Rapid Communications in Mass Spectrometry 13, 1211–1217

Misawa K., Yamaguchi A., Kaiden H., (2005) U-Pb and 207Pb-206Pb ages of zircons from basaltic eucrites: implications for early basaltic volcanism on the eucrite parent body. Geochimica Et Cosmochimica Acta 69, 5847–5861.

Mittlefehldt D. W., (2003) 1.11 Achondrites. In Treatise on geochemistry, volume 1: Meteorites, comets, and planets, edited by Davis A. M. Oxford: Elsevier-Pergamon. pp. 291–324

Mittlefehldt D. W., (2015) Asteroid (4) Vesta: I. The howardite-eucrite-diogenite (HED) clan of meteorites. Geochemistry, 75(2), 155-183.

Mittlefehldt D.W., (1990) Petrogenesis of mesosiderites: I. origin of mafic lithologies and comparison with basaltic achondrites. Geochimica Et Cosmochimica Acta 54, 1165–1173.

Mittlefehldt D.W., (1994a) The genesis of diogenites and HED parent body petrogenesis. Geochimica Et Cosmochimica Acta 58, 1537–1552.

Mittlefehldt D.W., (1994b) ALH84001, a cumulate orthopyroxenite member of the SNC meteorite group. Meteoritics, 29, 214–221.

Mittlefehldt D.W., (2000). Petrology and geochemistry of the Elephant Moraine A79002 diogenite: a genomict breccia containing a magnesian harzburgite component. Meteoritics & Planetary Science 35, 901–912.

Mittlefehldt D. W., Beck A. W., Le C. A., McSween H. Y., Buchanan, P. C., (2012a). Compositional constraints on the genesis of diogenites. Meteoritics & Planetary Science 47(1), 72–98.

Mittlefehldt D. W., Herrin J. S., Quinn J. E., Mertzman S. A., Cartwright J. A., Mertzman K. R., Peng Z. X., (2013b). Composition and petrology of HED polymict breccias: the regolith of (4) Vesta. Meteoritics & Planetary Science 48, 2105–2134.

Mittlefehldt D.W., Lindstrom M. M., (1993). Geochemistry and petrology of a suite often Yamato HED meteorites. Antarctic Meteorite Research 6, 268.

Mittlefehldt D. W., McCoy T. J., Goodrich C. A., Kracher A., (1998) Non-chondritic meteorites from asteroidal bodies. In: Papike, J.J. (Ed.), Planetary Materials. Mineralogical Society of America, Washington, DC, USA, pp. 1–195.

Morbidelli A., Marchi S., Bottke W., Kring D., (2012) A sawtooth-like timeline for the first billion years of lunar bombardment. Earth and Planetary Science Letters, 355-356, 144-151.

Mori H., Takeda H., (1981b) Evolution of the Moore County pyroxenes as viewed by an analytical transmission electron microprobe (ATEM). Meteoritics 16, 362–363.

Niihara T., (2012) Uranium-lead age of baddeleyite in shergottite Roberts Massif 04261:

Implications for magmatic activity on Mars. Journal of Geophysical Research: Planets 117(E2)

Norman M., Taylor L., Shih C. Y., Nyquist L., (2016) Crystal accumulation in a 4.2 Ga lunar impact melt. Geochimica Et Cosmochimica Acta 172, 410–429

Nyquist L. E., Takeda H., Bansal B. M., Shih C. Y., Wiesmann, H., Wooden, J.L., (1986) Rb-Sr and Sm-Nd internal isochron ages of a subophitic basalt clast and a matrix sample from the Y75011 eucrite. Journal of Geophysical Research 91, 8137–8150.

Onuma N., Higuchi H., Wakita H., Nagasawa H., (1968) Trace element partition between two pyroxenes and the host lava. Earth and Planetary Science Letters, 5, 47–51.

Paces J. B., Miller J. D., (1993) Precise U-Pb ages of Duluth Complex and related mafic intrusions, northeastern Minnesota: New insights for physical, petrogenetic, paleomagnetic and tectono-magmatic processes associated with the 1.1 Ga Midcontinent Rift system. Journal of Geophysical Research, 98, 3,997–14,013.

Pack, A., Gehler, A., Süssenberger, A., (2013) Exploring the usability of isotopically anomalous oxygen in bones and teeth as palaeo-CO2-barometer. Geochimica Et Cosmochimica Acta 102, 306–317.

Palme H., Rammensee W., (1981) The significance of W in planetary differentiation processes: Evidence from new data on eucrites. Proceedings of the 12th Lunar & Planetary Science Conference, pp. 949–964

Papanastassiou D. A., Wasserburg G. J., (1969) Initial strontium isotopic abundances and the resolution of small time differences in the formation of planetary objects. Earth and Planetary Science Letters, 5, 361–376.

Prettyman T. H., Feldman W. C., Mcsween H. Y., Dingler R. D., Enemark D. C., Patrick D. E., Reedy R. C., (2011) Dawn's Gamma Ray and Neutron Detector. Space Science Reviews, 163(1-4), 371-459.

Quitté G., Latkoczy C., Schönbächler M., Halliday A. N., and Günther D., (2011) ⁶⁰Fe-⁶⁰Ni systematics in eucrite parent body: A case study of Bouvante and Juvinas. Geochimica Et Cosmochimica Acta 75, 7698–7706.

Reddy S. M., Timms N. E., Pantleon W., and Trimby P., (2007) Quantitative characterization of plastic deformation of zircon and geological implications: Contributions to Mineralogy and Petrology, 153, 625–645.

Reid A. M., Buchanan P., Zolensky M. E., Barrett R. A., (1990) The Bholghati howardite: petrography and mineral chemistry. Geochimica Et Cosmochimica Acta 54, 2161–2166.

Righter K., Drake, M. J. (1997) A magma ocean on Vesta: Core formation and petrogenesis of eucrites and diogenites. Meteoritics & Planetary Science, 32(6), 929–944.

Righter M., Lapen T. J., (2010) Petrology, mineralogy and mineral chemistry of Antarctic monomict eucrites CMS 04049 and QUE 97053. 41st Lunar & Planetary Science Conference, Abstract #2629

Righter M., Lapen T. J., Shaulis B., (2011) U-Pb and 207Pb-206Pb ages of zircons from basaltic eucrites. 42nd Lunar & Planetary Science Conference, Abstract #2740

Roszjar J., Metzler K., Bischoff A., Barrat J. A., Geisler T., Greenwood R. C., Franchi I. A., Klemme S., (2011) Thermal history of Northwest Africa 5073—A coarse-grained Stannern-trend eucrite containing cm-sized pyroxenes and large zircon grains. Meteoritics & Planetary Science 46, 1754–1773.

Roszjar J., Whitehouse M. J., Srinivasan G., Mezger K., Scherer E. E., Van Orman J. A., Bischoff A., (2016) Prolonged magmatism on 4 Vesta inferred from Hf–W analyses of eucrite zircon. Earth and Planetary Science Letters, 452, 216–226.

Russell C., Barucci M., Binzel R., Capria M., Christensen U., Coradini A., Zuber M., (2007) Exploring the asteroid belt with ion propulsion: Dawn mission history, status and plans. Advances in Space Research, 40(2), 193–201.

Sack R. O., Azeredo W. J., Lipschutz, M. E., (1991) Olivine diogenites: the mantle of the eucrite parent body. Geochimica Et Cosmochimica Acta 55, 1111–1120.

Sack R. O., Azaredo W. J., Lipschutz M. E., (1994) Erratum to R. O. Sack, W. J. Azaredo, and M. E. Lipschutz (1991) Olivine diogenites: the mantle of the eucrite parent body. Geochimica Et Cosmochimica Acta 55, 1111–1120.

Saiki K., Takeda H., Tagai T., (1991) Zircon in magnesian, basaltic eucrite Yamato 791438 and its possible origin. Proceedings of the 22nd Lunar & Planetary Science Conference, pp. 341–349

Schiller M., Baker J., Creech J., Paton C., Millet M. A., Irving A. J., Bizzarro M., (2011) Rapid timescales for magma ocean crystallization on the howardite-eucrite-diogenite parent body. The Astrophysical Journal, 740(1).

Schwandt C. S., McKay G. A., (1998) Rare earth element partition coefficients from enstatite/melt synthesis experiments. Geochimica Et Cosmochimica Acta 62(16), 2,845–2,848.

Shaulis B., Lapen T. J., Toms A., (2010) Signal linearity of an extended range pulse counting detector: Applications to accurate and precise U-Pb dating of zircon by laser ablation quadrupole ICP-MS. Geochemistry, Geophysics, Geosystems, 11(11).

Shaulis B. J., Righter M., Lapen T. J., Jolliff B. L., Irving A. J., (2017) 3.1 Ga Crystallization age for magnesian and ferroan Gabbro lithologies in the Northwest Africa 773 clan of lunar meteorites. Geochimica Et Cosmochimica Acta, 213, 435–456.

Shukolyukov A., Lugmair G. W., (1993) ⁶⁰Fe in eucrites. Earth and Planetary Science Letters 119, 159–166.

Shukolyukov A., Lugmair G.W., (2002) Chronology of asteroid accretion and differentiation. In: Bottke, W.F., Cellino, A., Paolicchi, P., Binzel, R. (Eds.), Asteroids III. University of Arizona Press, Tucson, pp. 687–695.

Sierks H., Keller H. U., Jaumann R., Michalik H., Behnke T., Bubenhagen F., Büttner I., Carsenty U., Christensen U., Enge R., Fiethe B., Gutiérrez Marqués P., Hartwig H., Krüger H., Kühne W., Maue T., Mottola S., Nathues A., Reiche K. U., Richards M. L., Roatsch T., Schröder S. E., Szemerey I., Tschentscher M., (2011) The Dawn framing camera. Space Science Review 163, 263–327.

Sláma J., Košler J., Condon D. J., Crowley J. L., Gerdes A., Hanchar J. M., Whitehouse M. J., (2008) Plešovice zircon — A new natural reference material for U–Pb and Hf isotopic microanalysis. Chemical Geology, 249(1–2), 1–35.

Smoliar M. I., (1993) A survey of Rb-Sr systematics of eucrites. Meteoritics 28, 105–113.

Spicuzza, M. J., Day, J. M. D., Taylor, L. A., Valley, J. W., (2007) Oxygen isotope constraints on the origin and differentiation of the Moon. Earth and Planetary Science Letters, 253, 254–265.

Stolper E. M., (1977) Experimental petrology of eucritic meteorites. Geochimica Et Cosmochimica Acta 41, 587–611.

Sun C., Liang Y., (2017) A REE-in-plagioclase–clinopyroxene thermometer for crustal rocks. Contributions to Mineralogy and Petrology, 172(4).

Takahashi K., Masuda A., (1990) Young ages of two diogenites and their genetic implications. Nature 343, 540–542.

Takeda H., Graham A. L., (1991) Degree of equilibration of eucritic pyroxenes and thermal metamorphism of the earliest planetary crust. Meteoritics 26, 129–134.

Takeda H., Miyamoto M., Ishii T., Reid A., (1976) Characterization of crust formation on a parent body of achondrites and the moon by pyroxene crystallography and chemistry. Proceedings of the 7th Lunar & Planetary Science Conference, 3535–3548.

Takeda H., Mori H. (1985) The diogenite-eucrite links and the crystallization history of a crust of their parent body. Journal of Geophysical Research, 90(S02).

Tanner T. B., Jeffcoat C. R., Righter M., Berger E. L., Lapen T. J, Irving A. J., Kuehner S. M., Fujihara G., (2017) Petrology of Zircon-bearing Diogenite Northwest Africa 10666. 48th Lunar & Planetary Science Conference, Abstract #2714.

Tera F., Carlson R. W., Boctor N. Z., (1997) Radiometric ages of basaltic achondrites and their relation to the early history of the solar system. Geochimica Et Cosmochimica Acta 61, 1713–1731.

Thomson S. N., Gehrels G. E., Ruiz J., Buchwaldt R., (2012) Routine low-damage apatite U-Pb dating using laser ablation-multicollector- ICPMS. Geochemistry, Geophysics Geosystems 13.

Touboul M., Kleine T., Bourdon B., (2008) Hf-W Systematics of Cumulate Eucritesand the Chronology of the Eucrite Parent Body. 39th Lunar & Planetary Science Conference, Abstract #2336.

Treiman A. H., Lanzirotti A., Xirouchakis D., (2004) Ancient water on asteroid 4 Vesta: evidence from a quartz veinlet in the Serra de Magé eucrite meteorite. Earth and Planetary Science Letters, 219, 189–199.

Trinquier A., Birck J. L., Allègre C. J., Göpel C., Ulfbeck D., (2008) ⁵³Mn-⁵³Cr systematics of the early Solar System revisited. Geochimica Et Cosmochimica Acta 72, 5146–5163.

Van Aachterbergh E., Ryan C. G., Jackson S. E., Griffin W., (2001) Data reduction software for LA-ICP-MS. Mineralogical Association of Canada, Series 29, 239–243.

Warren P. H., Jerde E. A., (1987) Composition and origin of Nuevo Laredo trend eucrites. Geochimica Et Cosmochimica Acta 51, 713–725.

Warren P. H., Kallemeyn G. W., Huber H., Ulff-Møller F., Choe W., (2009) Siderophile and other geochemical constraints on mixing relationships among HED-meteoritic breccias. Geochimica Et Cosmochimica Acta 73, 5918–5943.

Wasson J. T., (2013) Vesta and extensively melted asteroids: Why HED meteorites are probably not from Vesta. Earth and Planetary Science Letters 381, 138–146.

Wasson J. T., Chapman C. R., Grogan K., Dermott S. F., (1996) Possible formation of the Vestafamily asteroids and the main IRAS dust band by an oblique impact on Vesta. 27th Lunar & Planetary Science Conference, Abstract 27, 1387–1388

Wiechert U. H., Halliday A. N., Palme H., Rumble D., (2004) Oxygen isotope evidence for rapid mixing of the HED meteorite parent body. Earth and Planetary Science Letters, 221, 373–382.

Woodhead J. D., Hergt J. M., (2001) Strontium, Neodymium and Lead Isotope Analyses of NIST Glass Certified Reference Materials: SRM 610, 612, 614. Geostandards and Geoanalytical Research, 25(2–3), 261–266

Yamaguchi A., Barrat J. A., Ito M., Bohn M., (2011) Posteucritic magmatism on Vesta: Evidence from the petrology and thermal history of diogenites. Journal of Geophysical Research: Planets 116(E8)

Zhang, A.-C., Kawasaki N., Bao H., Liu J., Qin L., Kuroda M., Gao J.-F., Chen L.-H., He Y., Sakamoto N., Yurimoto H., (2020) Evidence of metasomatism in the interior of Vesta. Nature Communications, 11(1)

Zhou Q., Yin Q. Z., Bottke B., Claeys P., Li X. H., Wu F. Y., Li Q. L., Liu Y., Tang G. Q., (2011) Early basaltic volcanism and late heavy bombardment on Vesta: U–Pb ages of small zircons and phosphates in eucrites. 42nd Lunar & Planetary Science Conference, p. 2575.

Zhou Q., Yin Q. Z., Young E. D., Li X. H., Wu F. Y., Li Q. L., Liu Y., and Tang G. Q., (2013) SIMS Pb-Pb and U-Pb age determination of eucrite zircons at <5 mm scale and the first 50 Ma of the thermal history of Vesta. Geochimica Et Cosmochimica Acta 110, 152–175.