

Petrology of the Paired Dominion Range 2010 Howardites: Indications of Magmatic Complexity on Asteroid Vesta

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Timothy Michael Hahn Jr.
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DEDICATION

To my supportive wife

Erika Hahn

My son born in the midst of academic chaos

Owen Hahn

And my beloved grandmother

Dianne Hahn

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ABSTRACT

A comprehensive petrologic and geochemical characterization of six paired howardites collected from the Dominion Range, Antarctica was conducted. These howardites are megaregolith samples from the asteroid 4 Vesta. Collectively, they contain an assortment of igneous rock fragments that indicate magmatic processes were capable of producing a variety of rock types; 21 chemically and texturally discrete basaltic eucrite, cumulate eucrite, and diogenite lithologies are recognized. The implications for remote-sensing observations of Vesta are discussed. The petrogenesis of two previously unrecognized lithologies are described in further detail: an evolved dacite that we propose is a residual melt from extensive crystallization, and a Mg-rich olivine-orthopyroxene and symplectite assemblage, which we interpret to represent the mantle of Vesta. Evidence suggests that complete melting of Vesta likely did not occur, and that partial melting and serial magmatism dominated the early magmatic history of Vesta. This research supports an evolving view that the differentiation and magmatic activity that occurred on Vesta was extremely complex.

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LIST OF ABBREVIATIONS AND SYMBOLS

^{26}Al	Radioactive isotope of aluminum
Ab	Albite
An	Anorthite
ANSMET	Antarctica Search for Meteorites
AU	Astronomical unit
CAI	Calcium Aluminum Inclusion
Cpx	Clinopyroxene
EDS	Energy-dispersive spectrometer
EMP	Electron Microprobe
En	Enstatite
Fo	Forsterite
Fs	Ferrosilite
$f\text{O}_2$	Oxygen fugacity
Ga	Billion years ago
GRaND	Gamma ray and neutron detector
GRO	Grosvenor Mountains
HED	Howardite-eucrite-diogenite
HREE	Heavy rare earth-element
ICP-MS	Inductively coupled mass spectrometer
IW	Iron-Wüstite
LREE	Light rare earth-element
MGNL	Main-group Nuevo Laredo
My	Million years
Opx	Orthopyroxene
Or	Orthoclase
PAP	Pouchou and Picchoir
PCA	Pecora Escarpment
QUE	Queen Alexandra
REE	Rare earth-element
VISNIR	Visible and near-infrared
WDS	Wave-dispersive spectrometer
Wo	Wollastonite
μm	Micron
σ	Sigma

INTRODUCTION

The formation of the terrestrial planets, those with a rocky surface composed primarily of silicate materials and a differentiated interior (Mercury, Venus, Earth, and Mars), has been a central theme of planetary science for nearly three centuries, beginning with the publication of the nebular hypothesis by Immanuel Kant in 1755. Although our own planet is familiar, our understanding of the formation and evolution of terrestrial planets from geological studies of Earth is incomplete. This is principally the result of active geologic processes that have operated since the Earth's formation and have obscured its early geologic history. Volcanic and sedimentary processes have produced a relatively young and complex surface, and the primordial crust has been recycled into the interior by plate tectonics. This enigmatic geologic history is not exclusive to Earth; Mercury, Venus, and Mars have all experienced, to varying degrees, resurfacing events (volcanism, erosion, and impact processes), which have erased the early history: in the case of Mercury (Marchi et al. 2013) and Mars the first few hundred million years, and in the case of Venus nearly the entire geologic record (Venus; average surface age <1 Ga; Bottke et al. 2016; Gilmore et al. 2014). Therefore, little insight is gained about the earliest evolution of these bodies through investigation of terrestrial planets. To further complicate matters, samples of the terrestrial planets, other than Earth, are limited or not available. How can we investigate these initial stages?

As it turns out, the formation of rocky and differentiated planetesimals was relatively common in the early Solar System (Greenwood et al. 2005). The accretion of nebular materials, mainly ferromagnesian silicates, metals, and sulfides, within the first few million years of the Solar System incorporated enough of the radioactive isotope ^{26}Al , a potent heat source, to melt planetesimals (Bizzarro et al. 2005). Segregation of Fe metal from silicate material resulted in the formation of iron cores and rocky mantles overlain by mostly basaltic crusts (McCoy et al. 2006). Contrary to early hypotheses, it was likely that these small differentiated bodies, rather than chondritic (primitive and unprocessed nebular materials), accreted to form the terrestrial planets. Therefore, the survival of these bodies provides a window into the early history of terrestrial planet formation.

The asteroid 4 Vesta (hereafter, Vesta), the second most massive asteroid with a diameter of ~500 km and a semi-major axis of 2.36 AU, is thought to be one of the few surviving protoplanets (Russell et al. 2012). Vesta was first discovered on March 29 in 1807 by Wilhelm Olbers, and has since been the target of extensive investigations (Russell and Raymond 2011). Interest in Vesta increased when McCord et al. (1970) recognized spectral similarities between the vestan surface and a basaltic meteorite (Nuevo Laredo), suggesting the first asteroid-meteorite link and evidence of a basalt-covered world. The eucrite Nuevo Laredo belongs to the most voluminous clan of achondritic meteorites (howardite-eucrite-diogenite; hereafter HED); therefore, it is obvious that complementary studies of Vesta and the HEDs can provide insights into the formation of the terrestrial planets. In 2007, the DAWN spacecraft departed for Vesta with the goal of characterizing its intrinsic properties such as shape, size, mass, and density, and mapping its surface geology (Russell and Raymond 2011; Russell et

al. 2012). Prior to the arrival of DAWN at Vesta, a wealth of knowledge had already been established due to decades of laboratory analyses of the HED meteorites.

The common oxygen isotopic composition of the HEDs has led investigators to conclude that nearly all of these meteorites originated on the same parent body (e.g. Clayton and Mayeda 1996; Greenwood et al. 2006), and they have provided geochemical and petrologic information regarding the evolution of their parent body, now generally accepted to be Vesta (McSween et al. 2013). Eucrites are meteoritic basalts or gabbros consisting primarily of pigeonite and plagioclase that formed as a direct result of volcanism, and occur as surface flows or shallow dikes (Duke and Silver 1967; Hsu and Crozaz 1996, 1997). Shallow plutonic samples are called cumulate eucrites, to distinguish them from basaltic eucrites. Diogenites are coarse-grained orthopyroxenites, harzburgites, and dunites, which resulted from crystallization at depth, presumably in the lower crust to upper mantle of their parent body (e.g. Mittlefehldt 1994; Ruzicka et al. 1997; Shearer et al. 1997). Howardites are brecciated mixtures of eucritic and diogenitic material that formed through impact gardening on the surface of Vesta (Bischoff et al. 2006). Analysis of trace element partitioning of Fe metal in eucrites has provided estimates of the core size (100 to 120 km; Ruzicka et al. 1997; Toplis et al. 2013); additionally, the presence of an Fe metal core indicates the body experienced melting and differentiation, prompting the development of a variety of geochemical and crystallization models. Governed in part by the degree of melting, these models invoke a variety of processes such as partial melting, complete melting (magma ocean models), melt extraction, volcanism, and plutonism (e.g. Mandler and Elkins-Tanton 2013; Neumann et al. 2014; Ruzicka et al. 1997; Stolper 1977). During the late 1990s and early 2000s an initial consensus emerged that seemed to suggest the HED parent body formed as a result of complete melting and solidification into a relatively simple layered structure consisting of a crust (eucrites), mantle (diogenites), and core. Surely this was an oversimplification, and further investigation of HEDs exposed complications, such as variations in trace-element concentrations of diogenites, that were inconsistent with a simple crystallization model (Barrat et al. 2008).

A major science objective of the DAWN spacecraft mission was to provide a test for various evolutionary models and strengthen the Vesta-HED connection (Russell and Raymond 2011). Certainly the observations made during the DAWN mission have provided valuable data on the composition and chronology of the surface, and firmer constraints on core size, but DAWN also revealed a complex surface morphology of deeply excavated impact basins, pervasive ejecta blankets, and linear troughs (De Sanctis et al. 2012; Marchi et al. 2012; Russell et al. 2012). Of special interest were two large, partially overlapping south-pole impact basins, Rheasilvia (thought to have formed at ~1 Ga) and Veneneia (at >2 Ga). The Rheasilvia impact likely was the source of most HED meteorites; dynamical simulations have suggested that it produced the V-type asteroids, located near the 3:1 resonance, which in turn provided a way to deliver HEDs to Earth (Marzari et al. 1996). Although invaluable information about Vesta has been gained, the DAWN mission was less successful at definitively constraining its differentiation.

Although initial views regarding the formation and evolution of Vesta were rather simplistic, new evidence suggests far more geologic and magmatic complexity. To

contribute to this effort, we have conducted a comprehensive petrologic and geochemical characterization of a suite of Antarctic howardites. These meteorites are “paired”, meaning that they were parts of the same fall and represented a larger pre-atmospheric meteoroid. These howardites formed through impact processes and contain rock fragments that provide some significant new insights into the magmatic evolution of Vesta. The main objective of the study was to quantify and interpret the geochemical and petrologic diversity of the clasts present in this complex breccia. Chapter 1 describes and classifies the clasts, compares the various meteorites in the pairing group with each other and with other large samples of the vestan regolith, and considers the implications for interpreting remote-sensing observations of Vesta. Chapters 2 and 3 describe in more detail two lithologies previously unrecognized in the HED collection. One study (Chapter 2) considers clasts that are interpreted to sample the vestan mantle, and the other (Chapter 3) considers clasts that extend the compositional range of vestan igneous rocks. Collectively, this research suggests that processes operating on Vesta, and by extension on other protoplanets, were complex.

Each of the three main chapters in this thesis has been submitted, or is in review, in the journal *Meteoritics and Planetary Science*. T. M. Hahn Jr. is the first author of each paper, reflecting his principal role in obtaining the data and interpreting the results.

Chapter 1: Petrologic Investigations of the Dominion Range

10 Howardites: Analogs for the Ancient Vestan Megaregolith

Disclosure: The following chapter is pending submission to the journal of *Meteoritics and Planetary Science* in July 2016, as a result of the primary author's graduate research. Co-authorship is shared with Nicole G. Lunning (National Museum of Natural History, Smithsonian Institution), Harry Y. McSween (UTK), Robert Bodnar (Virginia Tech, and Lawrence A. Taylor (UTK). Timothy M. Hahn Jr. prepared the manuscript. The content of the chapter contains the original submission materials in an unaltered form prior to co-author revisions.

ABSTRACT

We have characterized six paired howardites, collected from the Dominion Range, Antarctica during the 2010 ANSMET field season, using petrographic, electron microprobe, and laser ablation ICP-MS analyses. These howardites contain abundant lithic clasts of eucritic and diogenitic composition, as well as lithologies only recently recognized (dacite and Mg-rich harzburgite). Additionally, we identified secondary material (breccia-within-breccia and impact melt) derived from impact events. We describe the characteristics of the howardites, and the lithic clasts they contain, to (1) establish the range and scale of petrologic diversity, (2) recognize inter- and intra-sample mineralogical heterogeneity, and (3) confirm the initial pairing of these stones. We recognize a minimum of 21 individual lithologies represented by lithic clasts >1 mm, based on textural and geochemical analysis; however, more lithologies may be represented in comminuted mineral fragments. Large inter- and intra-sample variations exist between the meteorites, with distinct diogenite:eucrite and basaltic eucrite:cumulate eucrite ratios recognizable, which may be identifiable in Dawn data. We conclude these meteorites are pieces of the megaregolith, and have the potential to represent the largest sample of the vestan surface.

INTRODUCTION

Asteroid 4 Vesta, thought to represent an intact and differentiated protoplanet, was investigated by the Dawn spacecraft beginning on 16 July 2011 (Russell et al. 2012); observations have revealed a compositionally diverse surface, which records a geologically complex and violent collisional history (De Sanctis et al. 2012; Reddy et al. 2010; Ruesch et al. 2014; Russell et al. 2012). The howardite-eucrite-diogenite (HED) meteorite clan was first associated with Vesta based on visible and near-infrared (VISNIR) ground-based telescopic observations (McCord et al. 1970); Dawn's encounter has further strengthened the Vesta-HED connection by providing: (1) high-resolution VISNIR spectra that indicate similar pyroxene compositions to the HEDs, including an absence of nanophase Fe, (2) geochemical data signifying less heterogeneity than smaller asteroids, but consistent with HED meteorites, (3) crater size-frequency distributions that document an ancient surface (> 3-4 Ga) consistent with the ancient crystallization ages of eucrites and diogenites (McSween et al. 2013). Unfortunately, interpretations of remote sensing data may suffer from calibrations based on small HED samples; using larger samples may aid in solving this problem.

The modern surface of Vesta is covered by a 1-2 km-thick regolith, which is a consequence of large- and small-scale impacts, resulting in the comminution and redistribution of crustal and possibly mantle lithologies (Denevi et al. 2012a; Marchi et al. 2012; Marzari et al. 1996). Asteroid regoliths are often considered two-layer systems, with the near-surface representing the actively gardened portion containing solar wind-rich materials, and the underlying megaregolith (Warren et al. 2009). These portions of the regolith can be distinguished during remote-sensing observations based on physical and mineralogical characteristics (Denevi et al. 2012b). For example, the megaregolith is relatively more resistant to erosion, and therefore appears as prominent features on the surface that may have only recently been exposed (i.e. Arruntia crater; Thangjam et al. 2014; Thangjam et al. 2016). Howardites, which are impact-brecciated mixtures of vestan igneous lithologies, are analogs for both portions of the regolith (Fuhrman and Papike 1981; Pun et al. 1998); solar wind-rich howardites represent the surface regolith, while solar wind-poor and fragmental material denote the megaregolith (Bischoff et al. 2006; Cartwright et al. 2014; Cartwright et al. 2013).

Howardites are complex breccias composed of eucritic and diogenitic lithic clasts, in addition to comminuted mineral fragments, impact melts, and exogenous materials. Eucrites are basaltic rocks composed primarily of pigeonite and plagioclase (Hsu and Crozaz 1996, 1997; Mayne et al. 2009), thought to represent surface flows and shallow dikes (Duke and Silver 1967). Diogenites are orthopyroxenites, harzburgites, and dunites (e.g. Fowler et al. 1994, 1995; Shearer et al. 2010), thought to represent cumulates or residua during planetary differentiation (e.g. Mittlefehldt 1994; Righter and Drake 1997). A number of studies have systematically characterized howardites in an attempt to understand the diversity, heterogeneity, and properties of the vestan regolith, to allow better interpretation of Dawn's vestan data (Beck et al. 2015 and references therein). To increase the effective sample size, allowing a more representative view of the vestan surface, howardite pairing groups have been targeted for characterization studies. Recently, (Lunning et al. 2016) conducted a systematic study of the Grosvenor Mountain (GRO) 95 howardite pairing group (total mass ~212 g; pre-atmospheric radius 10-15 cm) which samples the surface regolith. (Beck et al. 2012) examined the Pecora Escarpment (PCA) 02 howardites (total mass ~135 g; pre-atmospheric radius 40-60 cm) representing the megaregolith.

As a complement to these studies, we have conducted a petrographic and geochemical investigation of the Dominion Range (DOM) 10 howardites (total mass ~1.1 kg) to quantify further the characteristics of the vestan megaregolith. Here we summarize the modal mineralogy and mineral compositions of lithic clasts, and provide a comparison to other howardite pairing groups. The DOM 10 howardites are among the most heterogeneous howardites, and have the potential to be the largest sample of the vestan surface in our collection. Additionally, we discuss characteristics of these meteorites that may have implications for spectroscopic studies of the vestan surface.

MATERIALS AND METHODS

Sample Selection

We examined six meteorites from a proposed howardite pairing group collected from the Dominion Range (DOM), Antarctica in 2010 (Table 1.1). The initial pairing of these stones was based on proximity of collection (1.5 km radius; Figure 1.1) and

petrographic similarities (Corrigan et al. 2011). During our preliminary investigation, we examined thin-sections from each stone in order to characterize petrologic and textural variations between samples, and confirm initial pairing (DOM 10838,6; 10100,8; 10120,6; 10837,7; 10105,6; 10839,6). We subsequently selected additional sections from three stones (DOM 10100,21; 10105,10; 10838,10) to quantify intra-sample variations.

Electron Microprobe (EMP)

A Cameca SX-100 EMP at the University of Tennessee was used to measure major- and minor-element abundances in minerals. Analyses were performed using a potential of 15 kV, beam current of 30 nA, and 1 μm beam for pyroxene, olivine, spinel, and ilmenite. Feldspar analyses were conducted at 15 kV and 10 nA, using a 7 μm spot size. Analyses of Fe metal were performed at 15 kV and 20 nA. Individual element count times varied from 20 to 60 s. Standard PAP corrections were applied. Natural and synthetic standards were utilized for calibrations, with analyses of standards deviating <1 % from known values.

Laser Ablation ICP-MS

Pyroxene trace-element concentrations were determined *in-situ* at Virginia Tech using an Agilent 7500ce inductively coupled plasma mass spectrometer (ICP-MS) equipped with an Excimer 193 nm ArF GeoLasPro laser for sample ablation. The spot size of each analysis was controlled by the availability of fracture- and inclusion-free areas (16-90 μm), with between 1 and 3 spots analyzed per grain. The NIST SRM610 reference glass was used as an external standard. At the beginning and end of each data collection period (~2 hours), the reference standard was analyzed to allow for drift correction. Prior to each analysis, approximately 60 s of He gas background signal was collected. Samples were ablated in a helium atmosphere at a repetition rate of 5 Hz for 20 to 60 s. Following ablation, the analyte was transported to the ICP-MS system via a helium-argon gas mixture. The LA ICP-MS lab at Virginia Tech has previously established 3 σ analytical precision for elements analyzed during the course of this study (Ce 0 to 5 %; Pr and Eu 5 to 10 %; La, Nd, Sm, Gd, Dy, Er, Yb, and Lu 10 to 20 %). To determine reproducibility, the NIST SRM610 was used as a reference, and USGS standards BCR-2G, BHVO-2G, BIR-1G, NKT-1G and NIST SRM612 and 614 were analyzed as “unknowns”. Standards were analyzed five times following routine analytical procedures. USGS standards BCR-2G, BHVO-2G, and BIR-1G are natural basalt glasses, and NKT-1G is a natural nephelinite. For data reduction purposes we utilized the SILLIS software program, which provides time-resolved signal analysis; this provides a method to evaluate erroneous portions of the signal due to contamination, whether from the surface or inclusions (Guillong et al. 2008). Therefore, only acceptable signals are used in the data reduction process.

Lithologic Mapping

Lithologic distribution maps were produced for each thin-section to determine mineral abundances and variations in the distribution of lithologies (Beck et al. 2012; Lunning et al. 2016). Specifically, 10 elemental x-ray maps were collected in a series of two passes using a combination of wave- and energy-dispersive spectrometers (WDS:

Table 1.1. Summary of attributes for howardite pairing groups.

Meteorite	Section	Group	Subgroup	Dimensions (cm)	Weight (g)	Paired?	Reference
DOM 10100	,8 ,21	Howardite	Fragmental	6.5 x 7.0 x 5.0	426.0	✓	Corrigan et al. (2011) and this study
DOM 10838	,10 ,6	Eucrite ^a Howardite ^b	Brecciated Fragmental	2.75 x 3.0 x 2.5	31.9	✓	Corrigan et al. (2011) and this study
DOM 10105	,6 ,10	Howardite	Fragmental	4.0 x 3.5 x 2.25	40.9	✓	Corrigan et al. (2011) and this study
DOM 10120	,6	Howardite	Fragmental	5.0 x 3.0 x 3.0	65.7	✓	Corrigan et al. (2011) and this study
DOM 10837	,7	Howardite	Fragmental	7.5 x 6.0 x 5.0	471.4	✓	Corrigan et al. (2011) and this study
DOM 10839	,6	Howardite	Fragmental	4.0 x 3.75 x 2.5	58.7	✓	Corrigan et al. (2011) and this study
DOM 10103		Eucrite	Brecciated	6.0 x 3.0 x 3.0	71.6	?	Corrigan et al. (2011)
DOM 10350		Diogenite	Unbrecciated	3.5 x 2.5 x 2.0	27.3	?	Mittlefehldt et al. (2015)
GRO 95534	,4	Howardite	Regolithic	3.0 x 2.7 x 1.5	17.9	✓	Lunning et al. (2016)
GRO 95535	,11 ,16	Howardite	Regolithic	3.2 x 2.5 x 2.7	53.8	✓	Lunning et al. (2016)
GRO 95574	,17	Howardite	Regolithic	5.5 x 3.5 x 3.0	90.6	✓	Lunning et al. (2016)
GRO 95581	,7 ,14	Howardite	Regolithic	4.0 x 2.0 x 2.5	49.4	✓	Lunning et al. (2016)
GRO 95602	,10 ,13	Howardite	Regolithic	4.3 x 3.6 x 1.0	51.5	x	Lunning et al. (2016)
GRO 95633	,2	Howardite	Regolithic	4.7 x 2.5 x 3.0	58.1	x	Lunning et al. (2016)
GRO 95533	,18	Eucrite	Unbrecciated	13.7 x 7.1 x 5.8	613.2	x	Lunning et al. (2016)

^aClassification determined during this study by modal analysis.

^bInitial classification given to DOM 10838

Table 1.1. Continued.

Meteorite	Section	Group	Subgroup	Dimensions (cm)	Weight (g)	Paired?	Reference
PCA 02009	,7	Howardite	Fragmental	3.0 x 2.0 x 2.2	22.5	✓	Beck et al. (2012)
	,12						Beck et al. (2012)
PCA 02013	,6	Howardite	Fragmental	5.0 x 3.0 x 2.2	41.0	✓	Beck et al. (2012)
	,9						Beck et al. (2012)
PCA 02014	,6	Howardite	Fragmental	3.5 x 2.5 x 1.5	21.2	✓	Beck et al. (2012)
PCA 02015	,4	Howardite	Fragmental	3.5 x 2.5 x 1.5	16.8	✓	Beck et al. (2012)
	,7						Beck et al. (2012)
PCA 02018	,4	Howardite	Fragmental	2.0 x 1.2 x 1.0	3.1	✓	Beck et al. (2012)
PCA 02019	,4	Howardite	Fragmental	2.5 x 2.5 x 1.5	11.7	✓	Beck et al. (2012)
PCA 02008	,8	Diogenite	Fragmental	3.0 x 2.0 x 2.0	19.1	✓	Beck et al. (2010)

^aClassification determined during this study by modal analysis.

^bInitial classification given to DOM 10838

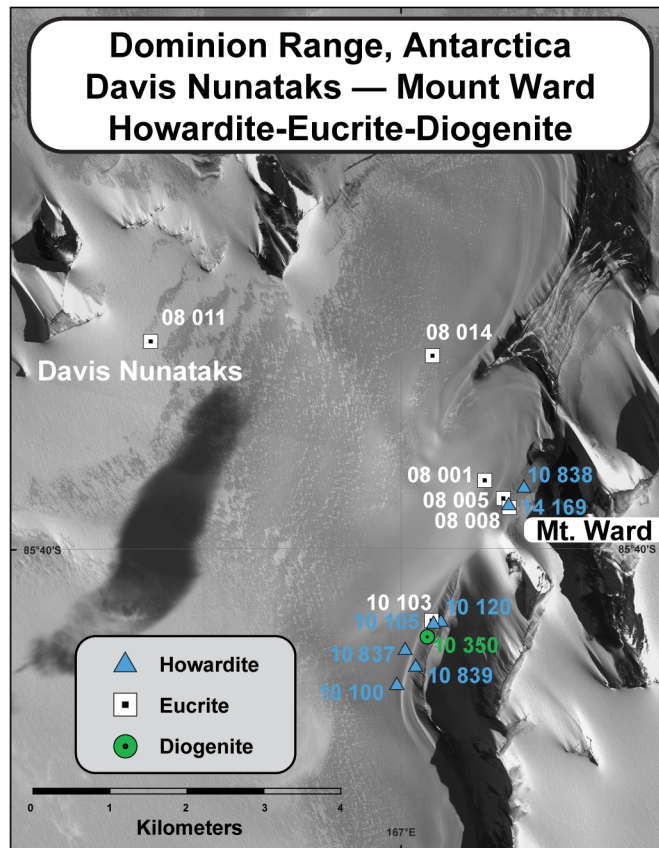


Figure 1.1 Meteorite Location Map

Locations of the six DOM 10 howardites collected during the 2010 ANSMET field season. All six stones were found within a 1.5 km radius. Location of a howardite (DOM 14169) collected during the 2014 field season is also shown. Additional HED finds (eucrites and diogenites) are also shown. Meteorite location map created and provided by John Schutt.

Fe, Mg, Si, Al, Ca, Cr, Ni, K, and EDS: Ti and S); these elements provide the compositional resolution needed to separate the various HED lithologies. A potential of 15 kV and a beam current of 30 nA with a 1 μm beam and 8 μm step-size were used during elemental mapping. Dwell times were 50 ms for all elements. A “geochemical information cube”, analogous to a multispectral image cube, was then created by combining elemental maps using remote-sensing software ENVI 4.2. Using point analyses, we then defined regions of interest (ROIs) for individual mineral phases. To allow for a direct comparison to data of (Lunning et al. 2016), we applied ROIs that were consistent between pairing groups. The sections were then classified using a minimum distance classification, where all pixels in the image (i.e. thin-section) are assigned to a specific mineral class based on their distance from ROI averages. Pixels that lie outside a set standard deviation for each class are deemed unclassified. Prior to classification we removed cracks and background from the image using a minimum value protocol, where pixels in the image that fall below a given threshold are not used during classification. Classifications were refined, by adjusting ROIs, until unclassified pixels were <10 %; lower values correspond to more reliable classifications. Classifications were validated using “ground-truth” analyses (point analyses). The beam- and step-sizes used during mapping constrain the resolution of the final classification image to 8 μm X 8 μm pixels; therefore, larger uncertainties are expected for small and minor phases because their classification is based only on a few pixels

RESULTS

Petrography

The DOM 10 howardites are composed of polycrystalline and polymineralic (lithic) clasts, in addition to secondary impact-derived breccia clasts (breccia-within-breccia), impact melts, and non-typical HED material, set in a fine-grained matrix of largely comminuted plagioclase and pyroxene. The abundance of lithic clasts varies between sections, with some containing less than 3 visible lithic clasts, while others include >15; lithic clasts are generally >1 mm in the longest dimension but can be up to 6 mm, although smaller clasts are observed. Textures within the lithic clasts include subophitic to ophitic, spherulitic, granular, and granoblastic, and range from very fine-grained (<0.1 mm) to coarse-grained (>5 mm). Three types of breccia clasts can be distinguished: diogenite- and eucrite-dominated breccias, as well as a breccia containing large abundant olivine mineral fragments. Impact melts are common, but not ubiquitous, in all thin-sections. Impact melt textures are vitrophyric and clast-rich. Two sections (10100,21 and 10105,10) contain shock melt veins that traverse the sections, with evidence of flow and crystallization at the margins, suggesting the rock was relatively coherent at the time of vein formation.

Geochemistry and Textures of Vestan Lithologies

In the ensuing sections, we present the major- and minor-element chemistry of mineral phases within lithic clasts and mineral fragments from the DOM 10 howardites; due to the large number of lithic clasts, only clasts >1 mm were examined. We attempt to separate lithologies first based on textures, followed by further separation based on mineralogy and chemistry. Where necessary, provide trace-element data of pyroxenes

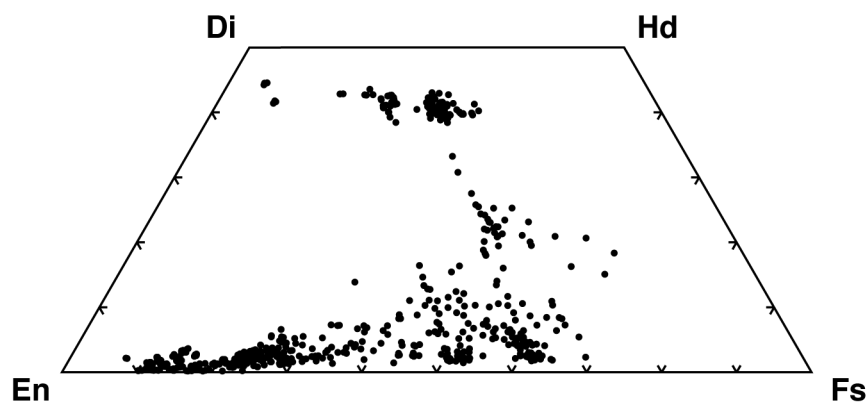
was used to refine our classification further. Pyroxene end-member compositions for the DOM 10 howardites are shown in Figure 1.2; REE patterns for pyroxenes measured in this study are displayed in Figure 1.3. In total, 21 separate lithologies are described including, 7 diogenites, 4 cumulate eucrites, 8 basaltic eucrites, and 2 formerly unrecognized lithologic types.

Diogenites

We identified five diogenite lithologies represented by lithic clasts and mineral fragments (>1 mm) based on mineral compositions and textures; we refer to these as diogenites type D1 through D5 (Table 1.2). Furthermore, we recognize two additional lithologies based on trace-element chemistry of orthopyroxene (types D6 and D7; Tables 1.2 and 1.3). Mineralogy of the diogenites varies from monomineralic polycrystalline (orthopyroxene) to a 4-phase assemblage of olivine, orthopyroxene, troilite, and FeNi metal. The textures observed in the diogenite clasts include fine-grained hypidiomorphic granular (Type D1; Figure 1.4), medium-grained granular (Types D2 and D4; Figures 1.4 and 1.5, respectively), coarse-grained granular (Type D3; Figure 1.5), fine-grained granoblastic (Type D5; Figure 1.6). Diogenites type D6 and D7 are mineral fragments that lack definitive textural context. The lithic clasts show variation in major- and minor-element concentrations consistent with previously identified diogenites (Table 1.2); the Mg# of pyroxenes span the complete range known for diogenites (66 to 85; Figure 1.7). Minor-element concentrations are correlated with major-element composition; In Figure 1.7, decreasing Mg# is positively correlated with Al₂O₃ and TiO₂ wt.%, while Cr₂O₃ wt.% is negatively correlated. These characteristic minor-element compositions aid in separating lithologies (i.e. Al₂O₃ wt.% vs. Mg#). We measured trace-element concentrations in 4 of the 7 lithologies (Figures 1.5 and 1.8; Table 1.3). Variations are observed in CI normalized concentrations, REE slope, and depth of Eu anomalies. For example, types D6 and D7 show an order of magnitude difference in CI-normalized concentrations and large variations in Eu/Eu* (Figure 1.8; 0.45 to 0.02).

Cumulate Eucrites

We recognized four cumulate eucrite lithologies within the DOM 10 howardites (Figure 1.9; Types C1 through C4). Classification of these clasts as cumulate eucrites is based on pyroxene chemistry and observed cumulate textures. Cumulate clasts consist dominantly of pyroxene and plagioclase, with accessory spinel, ilmenite, Fe metal, troilite, silica, and phosphates. Pyroxene has undergone varying degrees of exsolution to orthopyroxene-pigeonite and clinopyroxene pairs. We found zircon grains in the Type C4 cumulate eucrite clasts. Cumulate eucrites type C1 and C2 contain pyroxene compositions that lie within the range for typical cumulate eucrites (En₄₆₋₆₅); however, types C3 and C4 are more Fe-rich, although textures clearly suggest they are cumulate in origin (Table 1.4; Figure 1.9).



Key for Figures 4-6, 9-11, and 13

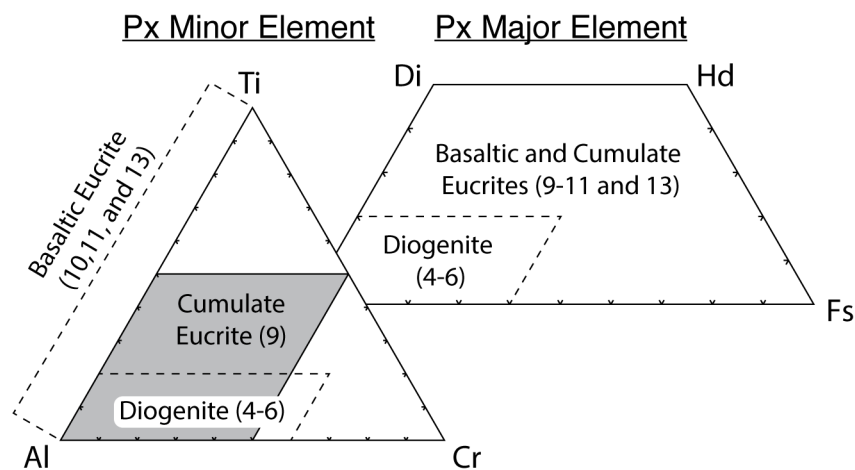


Figure 1.2 Representative Pyroxene Compositions in DOM 10 Howardites

Pyroxene compositions for the DOM 10 howardites. The compositions span the complete range for the HED meteorite clan. Below is the key for subsequent figures that display major- and minor-element concentrations for pyroxenes. To maximize space, only a subset of the diagram is shown for different HED lithologies. References to figures refer to those in Chapter 1.

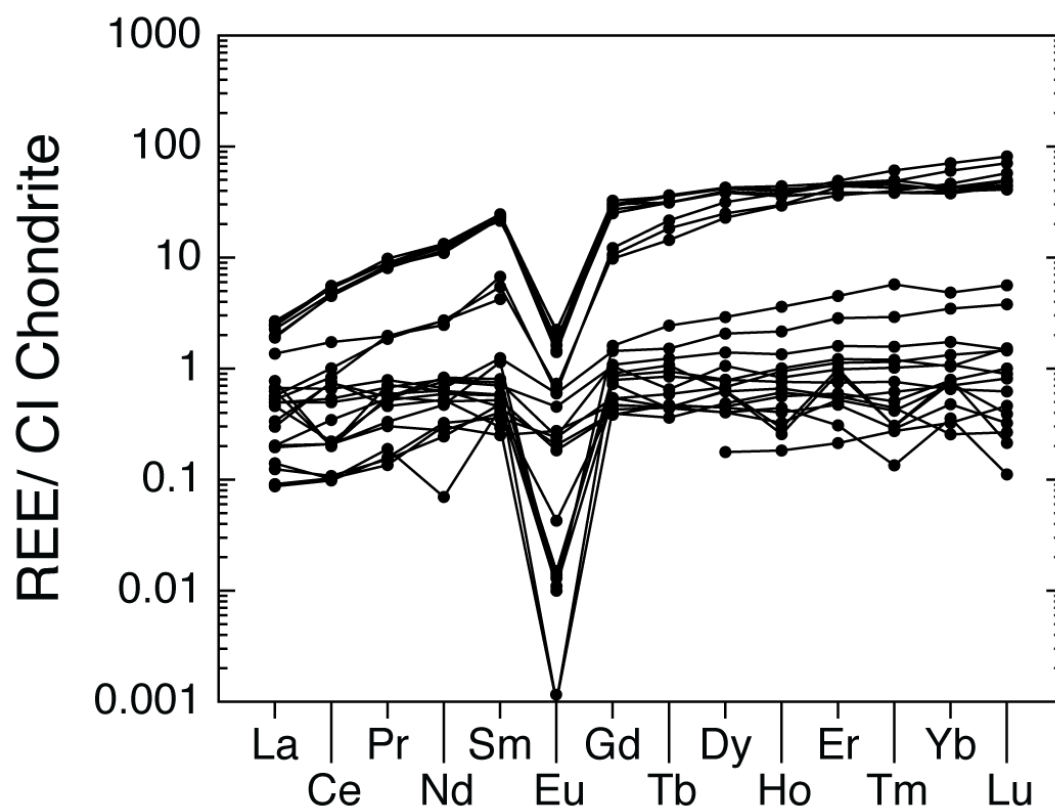


Figure 1.3 Rare Earth-Element Patterns of Pyroxenes

Rare earth-element chemistry of select pyroxenes in the DOM 10 howardites. Pyroxene trace-element compositions are consistent with eucritic and diogenitic meteorites; however, anomalies are observed, such as REE-enriched pyroxenes in some basaltic eucrite clasts. Data are normalized to CI chondrites (Anders and Grevesse 1989).

Table 1.2. Representative pyroxene and olivine compositions from diogenites in the DOM 10 howardites (wt.% oxide).

Type	D1				D2		D3		D4		D5		D6		D7	
Phase	Px		Ol		Px		Px		Px		Px		Px		Px	
	n=13		n=10		n=5		n=5		n=8		n=5		n=3		n=3	
Oxide																
SiO ₂	55.2	(3)	37.5	(1)	54.3	(8)	54.0	(2)	54.6	(17)	54.1	(1)	54.5	(<1)	55.6	(1)
TiO ₂	<0.03		<0.03		0.08	(3)	0.07	(1)	0.09	(9)	n.d.		0.12	(1)	0.06	(1)
Al ₂ O ₃	0.23	(10)	<0.03		0.59	(7)	0.54	(2)	0.50	(24)	0.23	(3)	0.77	(3)	0.99	(2)
Cr ₂ O ₃	0.18	(10)	<0.03		0.59	(14)	0.60	(3)	0.74	(43)	0.30	(5)	0.64	(2)	0.85	(1)
FeO	14.9	(3)	24.8	(3)	16.7	(26)	15.8	(1)	15.2	(48)	18.6	(2)	14.4	(3)	9.48	(5)
MnO	0.62	(4)	0.56	(1)	0.54	(7)	0.55	(1)	0.51	(17)	0.63	(2)	0.44	(1)	0.36	(<1)
MgO	28.5	(4)	37.0	(1)	26.1	(19)	26.3	(1)	27.4	(42)	25.5	(1)	27.5	(1)	31.1	(1)
CaO	0.49	(10)	<0.03		1.11	(1)	1.13	(1)	0.88	(44)	0.67	(3)	1.01	(2)	1.05	(1)
Total	100.2		100.0		100.1		99.0		99.9		100.0		99.5		99.5	
En	76.6	(7)			71.9	(44)	73.1	(1)	74.7	(90)	70.0	(3)	75.7	(4)	83.7	(<1)
Fs	22.4	(5)			25.9	(42)	24.6	(1)	23.6	(81)	28.7	(3)	22.3	(4)	14.3	(<1)
Wo	0.93	(2)			2.20	(2)	2.26	(3)	1.76	(93)	1.32	(5)	2.01	(3)	2.03	(3)
Mg#	77.3	(6)	72.7	(2)	73.5	(45)	74.8	(1)	75.9	(85)	70.9	(3)	77.3	(4)	85.4	(<1)
Fe/Mn	24.0	(13)	43.9	(17)	30.2	(14)	28.6	(1)	29.7	(14)	29.4	(9)	32.0	(12)	25.5	(1)

* Values in parentheses represent 1 standard deviation.

Table 1.3. Rare earth-element chemistry of selected diagenite lithologies (ppb).

	Type 3	1 σ	Type 4	1 σ	Type 6	1 σ	Type 7	1 σ
La	36	(7)			29	(7)	158	(16)
Ce	62	(6)			65	(6)	395	(29)
Pr	18	(3)			14	(3)	70	(7)
Nd					111	(36)	303	(57)
Sm	67	(11)			70	(21)	183	(31)
Eu	11	(2)					33	(7)
Gd	78	(24)			106	(26)	283	(42)
Tb	13	(4)			21	(4)	55	(6)
Dy	112	(24)	43	(6)	166	(26)	501	(48)
Ho	32	(5)	10	(2)	52	(5)	120	(11)
Er	91	(13)	34	(5)	179	(15)	452	(38)
Tm	14	(4)	7	(2)	28	(4)	71	(8)
Yb	123	(18)	53	(7)	216	(18)	563	(50)
Lu	19	(7)	11	(3)	35	(6)	92	(10)
Eu/Eu*	0.49				0.02		0.45	

*Missing data values were either below the detection limit or produce poor statistics (i.e. $[1\sigma/\text{concentration}] \cdot 100 > 40$)

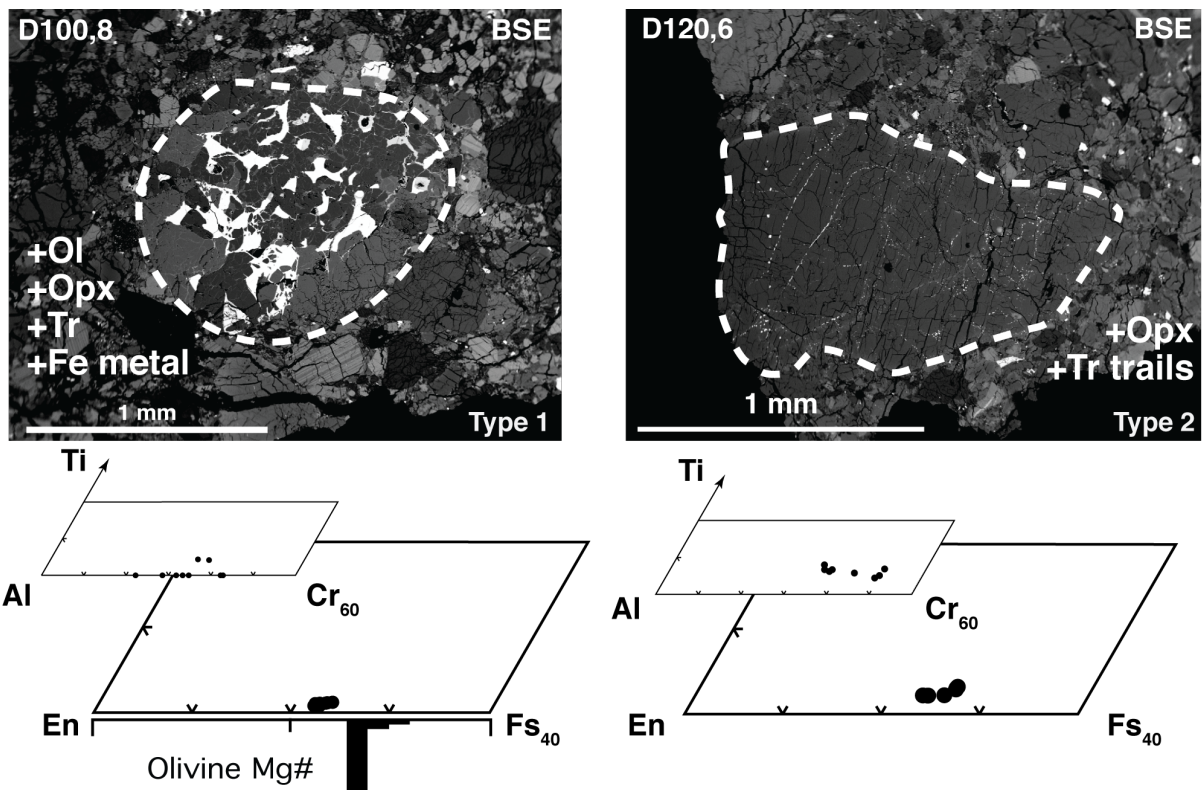


Figure 1.4 Examples of Types 1 and 2 Diogenites

Examples of types D1 and D2 diogenite lithic clasts observed in the DOM 10 howardites. Insets show pyroxene major- and minor-element trends. Where appropriate, olivine composition (Mg#) is shown. See Figure 1.2 for key.

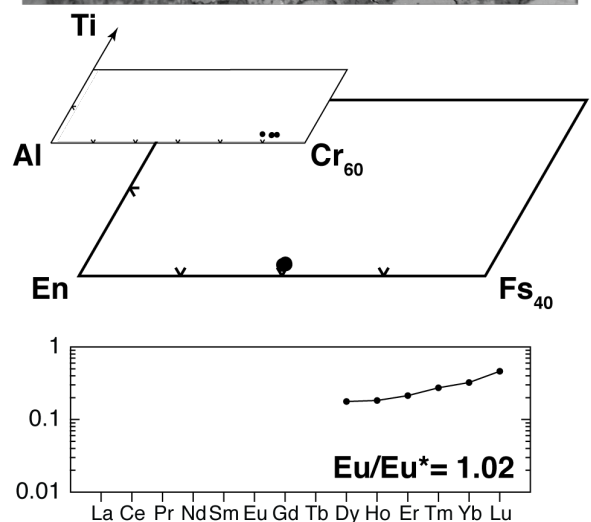
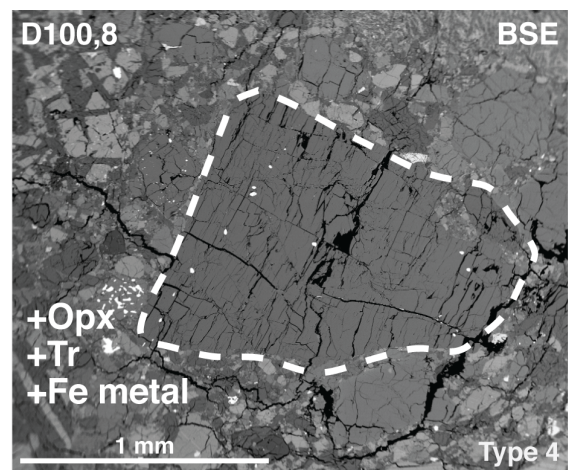
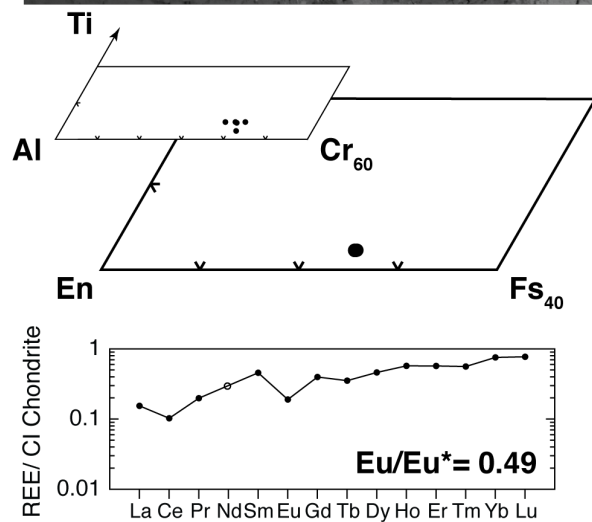
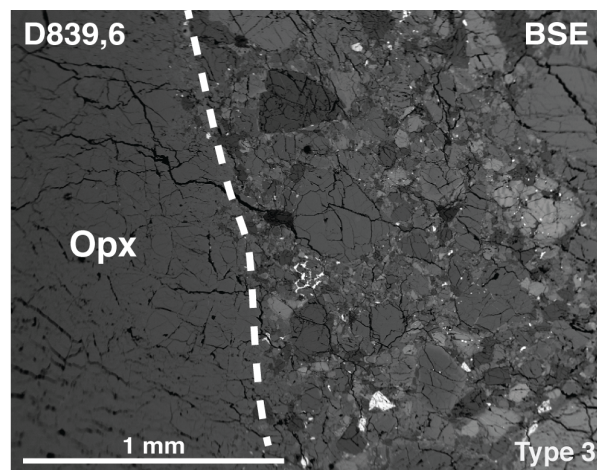


Figure 1.5 Examples of Types 3 and 4 Diogenites

Examples of types D3 and D4 diogenite polycrystalline clasts are shown, along with pyroxene major- and minor-element compositions. Pyroxene REE patterns are shown below the corresponding lithology. Eu/Eu* for type D4 diogenite calculated from detection limits. REE data are normalized to CI chondrites (Anders and Grevesse 1989). See Figure 1.2 for key.

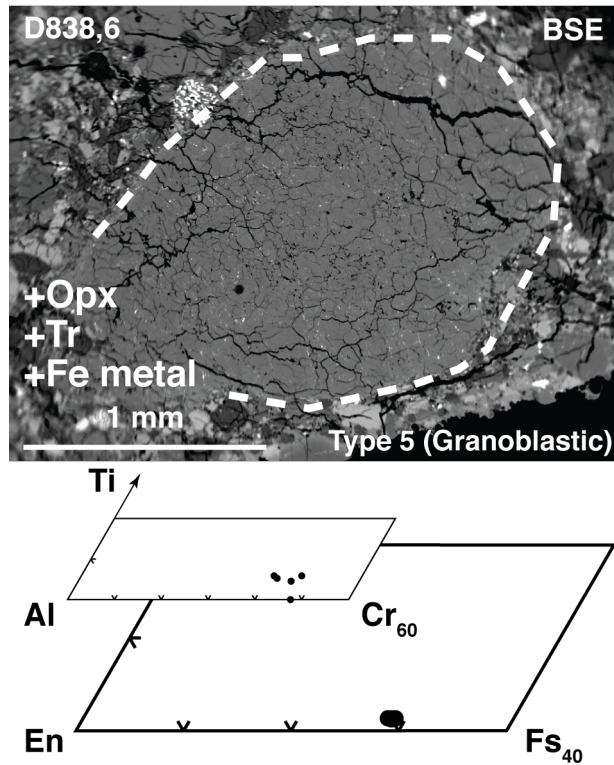


Figure 1.6 Type 5 Granoblastic Diogenite

Type D5 diogenite polymineralic lithic clast example. Pyroxene major- and minor-element composition are shown below. Granoblastic textures are not shown in this figure because BSE images display composition, and not necessarily accurate textures. See Figure 1.2 for key.

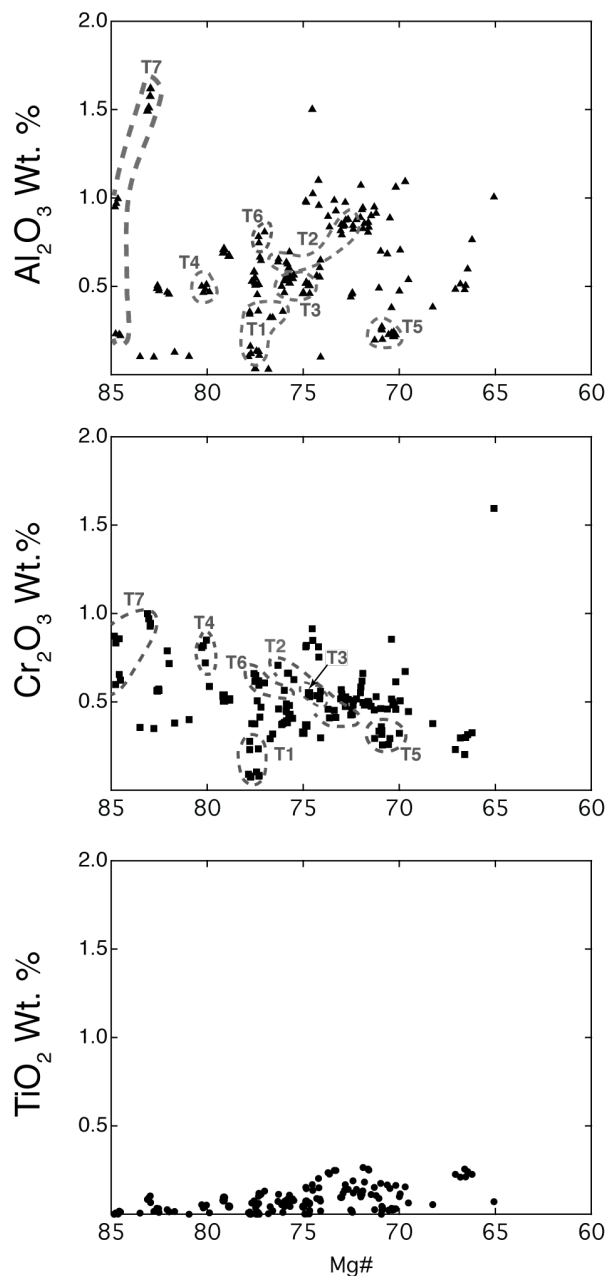


Figure 1.7 Minor-Element Variations in Diogenite Pyroxene

Minor-element concentrations vs. Mg# in diogenite pyroxenes. Variations in minor-element chemistry can be used to distinguish lithologies. Specifically, Al_2O_3 and Cr_2O_3 are more useful for classification because large variations are observed. Compositional range for individual diogenite types shown in figure. Note outliers are present suggesting more diversity exists; however, without additional mineralogical or textural information, it is difficult to distinguish between discrete lithologies and continuous compositional trends.

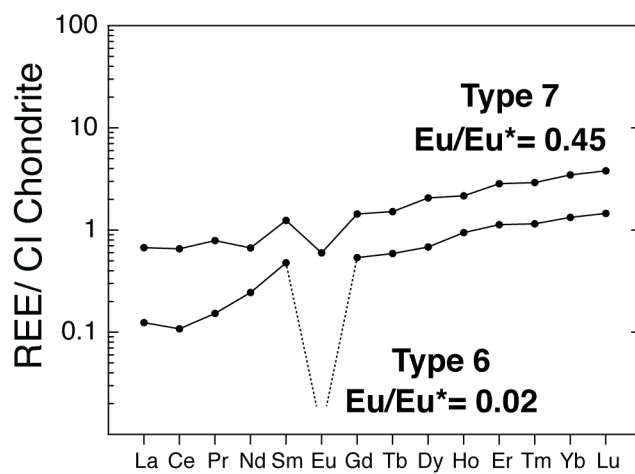


Figure 1.8 Rare Earth-Element Patterns of Types D6 and D7 Diogenite Pyroxene

Rare earth element patterns for diogenite mineral fragments (types D6 and D7). Note the large variations in Eu anomalies, suggesting plagioclase crystallized from diogenite parent magmas, but to various extents. Data are normalized to CI chondrites (Anders and Grevesse 1989)

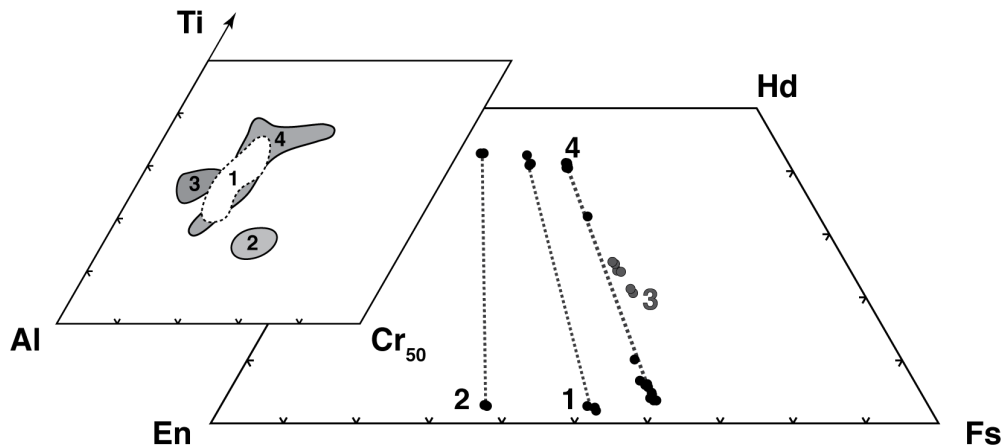
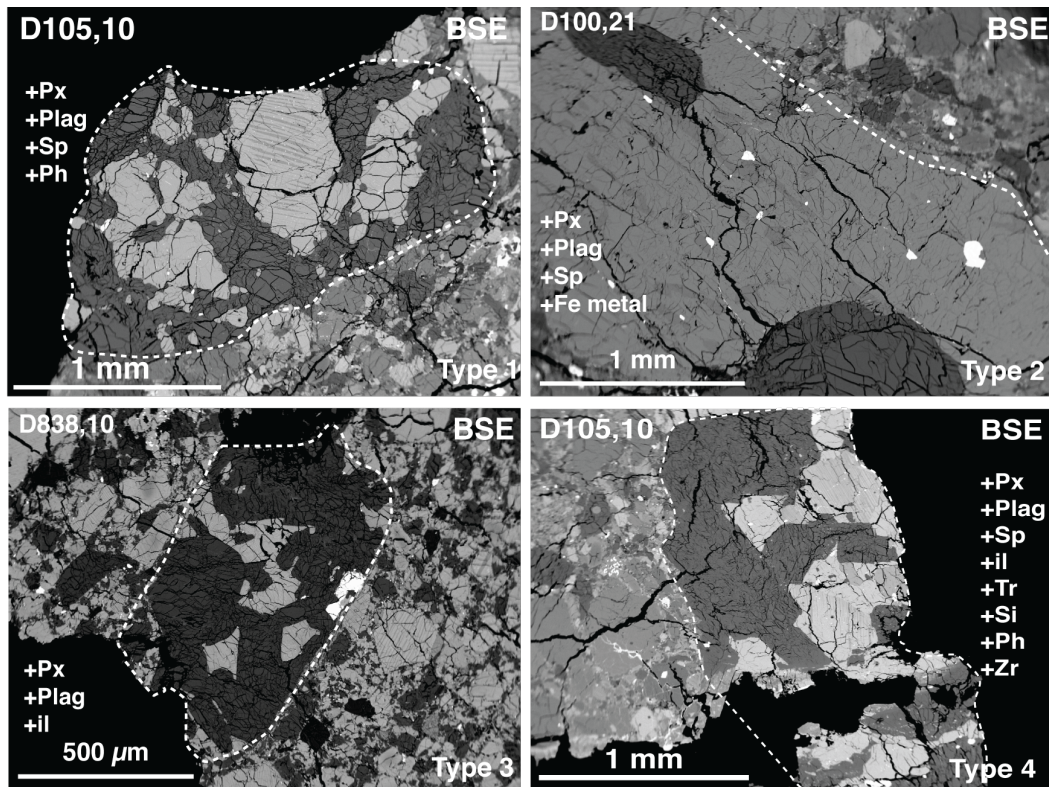


Figure 1.9 Cumulate Eucrite Clasts

Examples of cumulate eucrite lithic clasts. Corresponding pyroxene end-member and minor-element concentrations are shown below. To reduce clutter, only end-member compositions that define the tie-line are shown, as analyses in between are caused by beam overlap on the EMP. Type C1 cumulate eucrites displays cumulate textures and pyroxene compositions consistent with typical cumulate eucrites. Type C2 cumulate eucrite contains pyroxene compositions consistent with more Mg-rich cumulate eucrites; however, cumulate textures are less obvious. Fe-rich cumulate eucrite lithic clasts (types C3 and C4) are found, for which the composition of pyroxenes lies within the basaltic eucrite field; however, obvious cumulate textures are observed. We therefore classify these samples as cumulate eucrites based on textural considerations, rather than compositional. See Figure 1.2 for key.

Basaltic Eucrites

At least eight basaltic eucrite types are distinguishable in the DOM 10 howardites (Figures 1.10 and 1.11; Table 1.5; Types B1 to B8). The basaltic eucrite polymineralic clasts show textures ranging from granoblastic to ophitic; regardless of texture, all but one basaltic eucrite contain exsolution lamellae (type B8; Figure 1.11). Pyroxene exsolution lamellae tend to be more pronounced in clasts exhibiting granoblastic textures, while subophitic to ophitic clasts contain pyroxene with submicron exsolution lamellae. Basaltic eucrites type B1 through B4 all exhibit granoblastic textures; pyroxene major-element chemistry is consistent with typical basaltic eucrites ($En_{<45}$) and pyroxene minor-element concentrations show only limited variation (Figures 1.10 and 1.11). Basaltic eucrites type B5 and B6 exhibit subophitic and ophitic textures, respectively (Figure 1.11); although texturally these two clasts are similar, the pyroxene chemistry, both major- and minor-element, suggest they are chemically discrete (Table 1.5; Figure 1.11). Pyroxene compositions of type B7 basaltic eucrites are intermediate between types B5 and B8 are only observed in 10838,10 and occur as individual grains distributed throughout the section. Figure 1.11 displays the type specimen for this lithology, in addition to pyroxene major- and minor-element compositions. Pyroxene of type B8 basaltic mineral fragments is strongly zoned with Mg-rich cores and Ca-rich rims (Table 1.5). Additionally, variations in core to rim compositions are observed from grain to grain, as shown in Figure 1.11.

Mg-rich harzburgites

We identified Mg-rich lithic clasts, similar to those described by (Lunning et al. 2015b), consisting of intergrown olivine and pyroxene (harzburgite; Figure 1.12). These clasts were subjected to a further detailed investigation (Hahn et al. *In Review-b*). Here we only briefly describe the major-, minor-, and trace-element chemistry of the clasts. Olivine and pyroxene in the harzburgite clasts show a wide variation in major-element chemistry (Mg#s 82 to 92). Minor-element correlations in pyroxene show increasing Al/Cr ratios with near constant Ti concentrations. Associated with the harzburgite clasts are euhedral to subhedral grains of FeNi metal, and a ubiquitous association of chromite-orthopyroxene symplectites (Figure 1.12). Trace-element concentrations in Mg-rich pyroxene are variably depleted relative to CI chondrites and are LREE-enriched.

Dacite

We identified a basaltic eucrite-like clast consisting of pyroxene, plagioclase, and quartz, with minor amounts of troilite, FeNi metal, ilmenite, and phosphates. Unlike typical basaltic eucrites, the primary pyroxene is augite, which occurs as large (> 1mm) oikocrysts (Figure 1.13). Moreover, quartz is a major, rather than minor, phase within the clast (~30 %). Pyroxene major- and minor-element chemistry is consistent with basaltic eucrites; however, REE abundances and the presence of primary augite suggest a more evolved origin (Figure 1.13). A more complete characterization of this lithology is given by (Hahn et al. *In Review-a*).

Table 1.4. Representative pyroxene compositions in cumulate eucrite lithic clasts (wt.% oxide).

Type	C1				C2				C3		C4			
Phase	Pigeonite		Cpx		Pigeonite		Cpx		Pigeonite		Pigeonite		Cpx	
	n=4		n=3		n=5		n=1		n=7		n=3		n=4	
Oxide														
SiO ₂	50.7	(1)	51.2	(3)	52.6	(2)	52.4	(4)	49.2	(1)	49.7	(1)	50.9	(2)
TiO ₂	0.22	(5)	0.42	(2)	0.22	(2)	0.33	(1)	0.64	(5)	0.20	(3)	0.41	(5)
Al ₂ O ₃	0.27	(9)	0.75	(7)	0.53	(5)	0.86	(5)	0.97	(6)	0.23	(6)	0.68	(11)
Cr ₂ O ₃	0.11	(2)	0.26	(4)	0.33	(2)	0.48	(4)	0.25	(5)	0.09	(1)	0.28	(4)
FeO	30.8	(7)	14.2	(5)	23.1	(2)	10.0	(1)	26.3	(13)	34.3	(8)	17.2	(2)
MnO	0.88	(6)	0.45	(2)	0.79	(1)	0.41	(1)	0.84	(3)	1.05	(1)	0.52	(2)
MgO	16.0	(4)	12.3	(1)	21.7	(2)	14.6	(2)	10.5	(3)	12.3	(1)	10.5	(1)
CaO	1.22	(19)	20.1	(3)	1.51	(4)	21.1	(2)	10.6	(10)	2.25	(67)	19.6	(2)
Total	100.2		99.7		100.7		100.3		99.3		100.1		100.1	
En	46.8	(9)	35.5	(2)	60.7	(1)	41.3	(3)	32.0	(8)	37.0	(2)	30.6	(1)
Fs	50.7	(13)	23.0	(7)	36.3	(2)	15.9	(3)	44.9	(21)	58.1	(14)	28.3	(2)
Wo	2.55	(38)	41.6	(9)	3.02	(9)	42.9	(1)	23.2	(23)	4.88	(15)	41.1	(3)
Mg#	48.0	(11)	60.7	(6)	62.6	(2)	72.2	(5)	41.6	(12)	39.0	(5)	52.0	(1)
Fe/Mn	34.7	(20)	31.8	(22)	28.8	(2)	24.1	(4)	30.7	(11)	32.4	(7)	32.7	(13)
An	90 to 93				94 to 95				88 to 92		88 to 91			

* Values in parentheses represent 1 standard deviation.

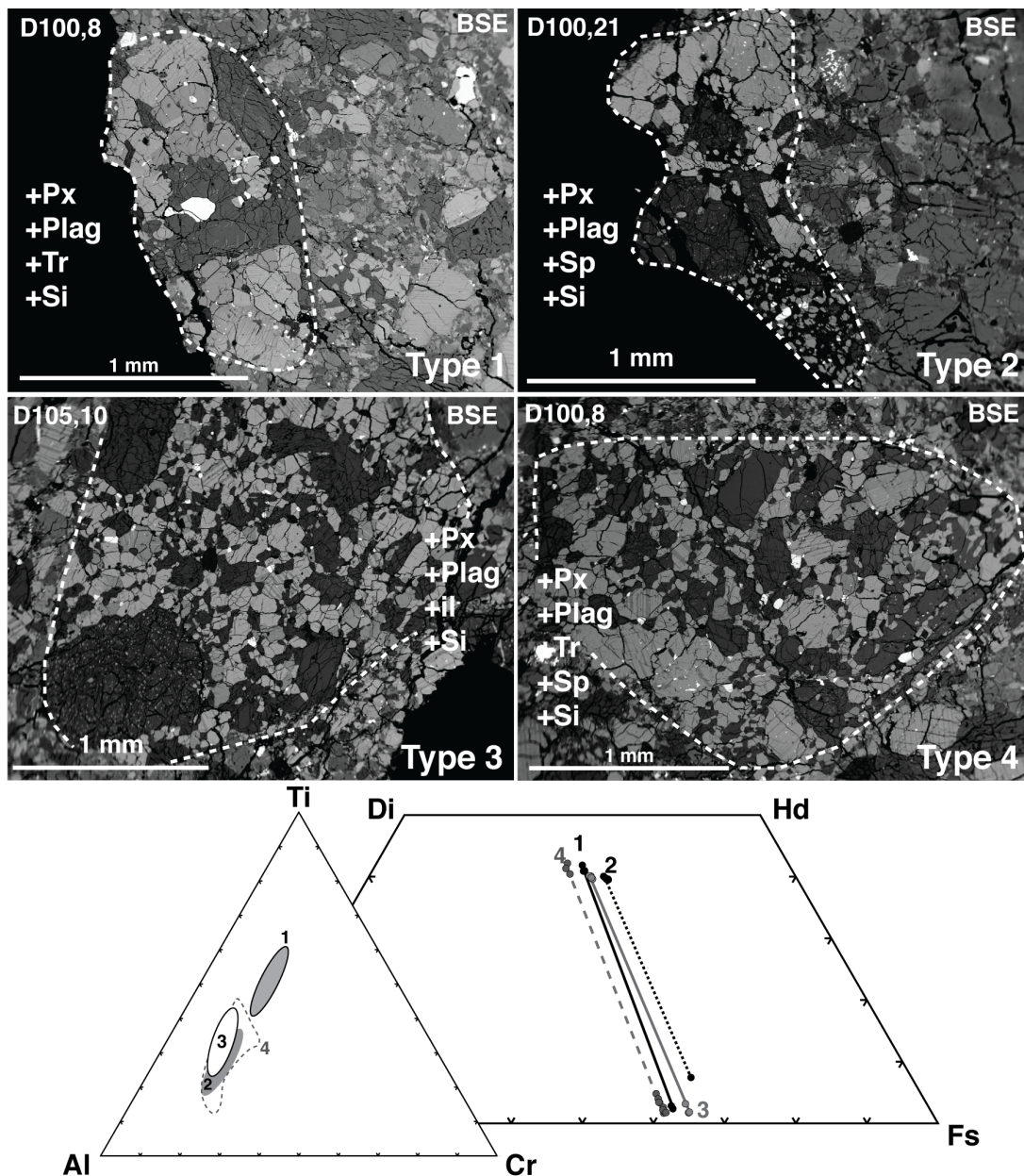


Figure 1.10 Granoblastic Basaltic Eucrite Clasts

Basaltic eucrite lithic clasts with granoblastic textures (types B1 through B4). Pyroxene major- and minor-element compositions shown below. To reduce clutter, only end-member compositions that define the tie-line are shown, as analyses in between are caused by beam overlap on the EMP. See Figure 1.2 for key.

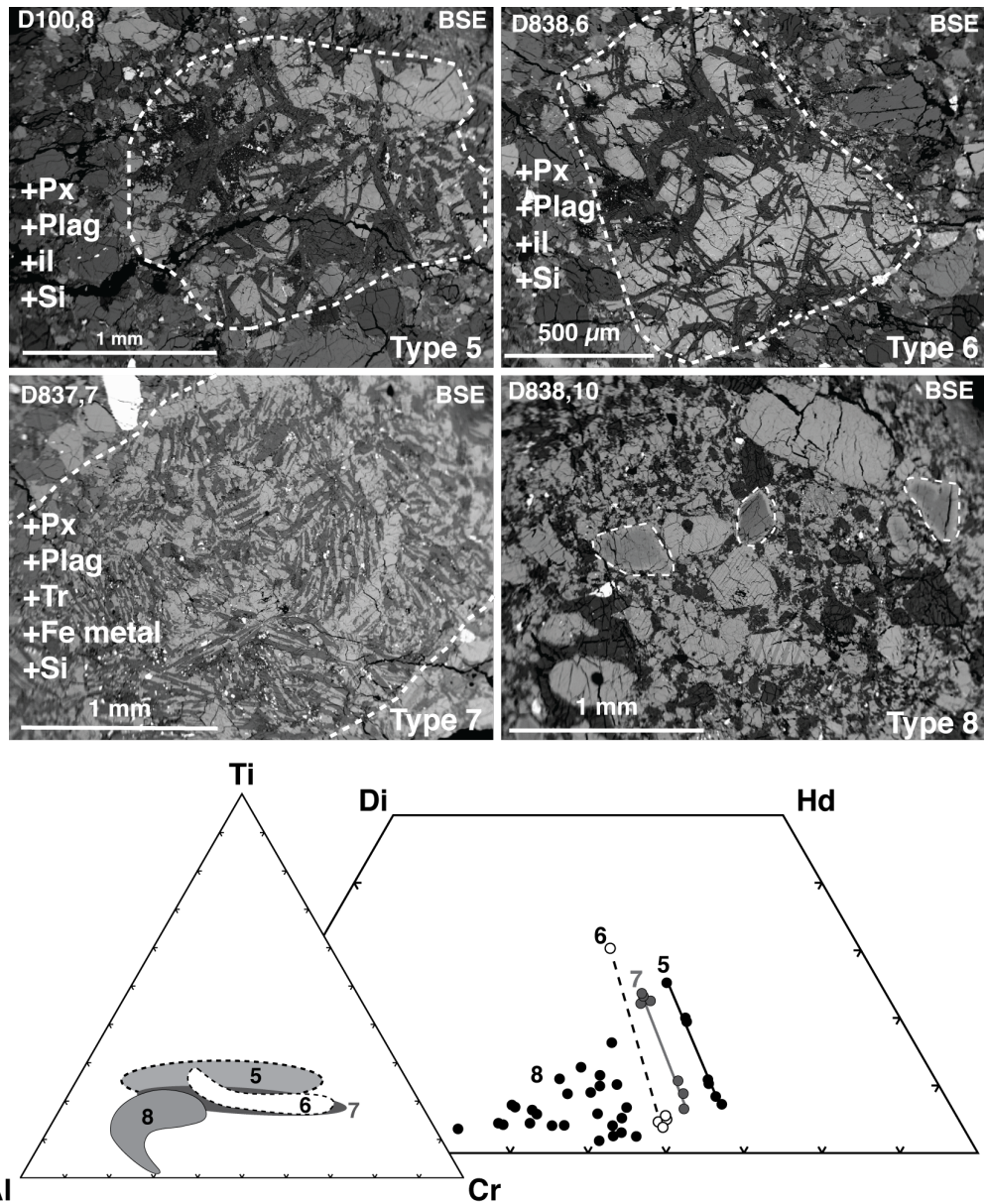


Figure 1.11 Types 5-8 Basaltic Eucrite Clasts

Types B5 through B8 basaltic eucrite lithic clasts and mineral fragments. Pyroxene major- and minor-element compositions are shown below. To reduce clutter, only end-member compositions that define the tie-line are shown, as analyses in between are caused by beam overlap on the EMP. Basaltic eucrites types B5 and B6 show subophitic and ophitic textures, respectively. Spherulitic textures are observed in the type B7 basaltic eucrite clasts. Basaltic eucrite type B8 is zoned, and only occurs as mineral fragments in section 10838,10. See Figure 1.2 for key.

Table 1.5. Representative pyroxene compositions in basaltic eucrite lithic clasts (wt.% oxide).

Type	B1				B2				B3				B4			
Phase	Pigeonite		Cpx		Pigeonite		Cpx		Pigeonite		Cpx		Pigeonite		Cpx	
	n=2		n=3		n=1		n=5		n=6		n=7		n=13		n=4	
Oxide																
SiO ₂	49.4	(1)	50.2	(3)	48.6	50.0	(3)		49.3	(3)	50.6	(2)	49.2	(3)	50.4	(3)
TiO ₂	0.21	(6)	0.50	(9)	0.28	0.36	(5)		0.17	(2)	0.46	(5)	0.18	(3)	0.37	(2)
Al ₂ O ₃	0.17	(1)	0.73	(13)	0.28	0.61	(6)		0.17	(2)	0.62	(7)	0.17	(3)	0.58	(2)
Cr ₂ O ₃	0.10	(1)	0.30	(6)	0.11	0.26	(4)		0.07	(2)	0.27	(3)	0.09	(3)	0.27	(7)
FeO	35.9	(3)	17.7	(5)	35.5	20.1	(2)		35.6	(9)	18.2	(4)	35.9	(5)	17.2	(4)
MnO	1.07	(1)	0.52	(2)	1.03	0.54	(1)		1.07	(3)	0.53	(2)	1.05	(5)	0.47	(2)
MgO	12.0	(1)	9.93	(20)	10.3	9.06	(2)		11.8	(5)	10.1	(3)	12.0	(2)	10.0	(5)
CaO	1.26	(20)	19.4	(2)	3.88	18.8	(2)		1.70	(50)	19.0	(2)	1.19	(4)	19.7	(8)
Total	100.1		99.4		99.9	99.8			100.2		100.2		99.1		99.0	
En	36.2	(1)	29.4	(2)	31.1	26.8	(2)		35.8	(12)	29.8	(7)	36.3	(5)	29.6	(5)
Fs	61.0	(4)	29.4	(6)	60.4	33.2	(5)		60.5	(20)	30.0	(8)	61.1	(9)	28.5	(9)
Wo	2.74	(40)	41.3	(7)	8.45	39.9	(3)		3.70	(11)	40.2	(3)	2.6	(8)	41.9	(12)
Mg#	37.2	(2)	50.0	(4)	34.0	44.7	(5)		37.2	(15)	49.8	(12)	37.3	(5)	51.0	(7)
Fe/Mn	33.4	(3)	33.3	(18)	34.3	36.6	(13)		33.0	(10)	34.2	(14)	33.9	(13)	36.6	(5)
An	74 to 83				79 to 83				86 to 90				85 to 90			

* Values in parentheses represent 1 standard deviation.

Table 1.5. Continued.

Type	B5		B6		B7		B8				
Phase	Pigeonite n=7		Pigeonite n=4		Cpx n=1	Pigeonite n=9		Core n=5		Rim n=4	
Oxide											
SiO ₂	48.7	(6)	49.2	(5)	50.0	48.4	(6)	51.6	(5)	50.2	(5)
TiO ₂	0.31	(1)	0.30	(14)	0.23	0.59	(57)	0.19	(9)	0.29	(10)
Al ₂ O ₃	0.39	(2)	0.25	(8)	0.33	0.49	(19)	0.94	(33)	0.77	(28)
Cr ₂ O ₃	0.44	(3)	0.60	(49)	0.35	0.74	(48)	0.61	(44)	0.39	(14)
FeO	33.2	(34)	33.8	(2)	22.5	29.9	(32)	23.2	(18)	28.7	(23)
MnO	1.02	(10)	1.01	(2)	0.71	0.86	(9)	0.73	(7)	0.83	(6)
MgO	9.35	(30)	12.5	(3)	10.7	10.8	(5)	19.9	(13)	15.2	(13)
CaO	6.66	(32)	2.39	(3)	14.5	7.36	(32)	2.62	(65)	3.40	(20)
Total	100.1		100.1		99.4	99.2		99.9		99.9	
En	28.5	(1)	37.8	(7)	31.8	32.9	(14)	57.2	(37)	45.1	(35)
Fs	56.9	(60)	57.1	(5)	37.4	51.1	(56)	37.4	(29)	47.7	(41)
Wo	14.6	(70)	5.18	(73)	30.8	16.1	(68)	5.39	(13)	7.2	(42)
Mg#	33.5	(17)	39.8	(6)	45.9	39.3	(19)	60.4	(33)	48.6	(34)
Fe/Mn	32.2	(5)	32.9	(6)	30.9	34.2	(8)	31.5	(35)	34.4	(18)
An	81 to 84		83 to 88			77 to 98					

* Values in parentheses represent 1 standard deviation.

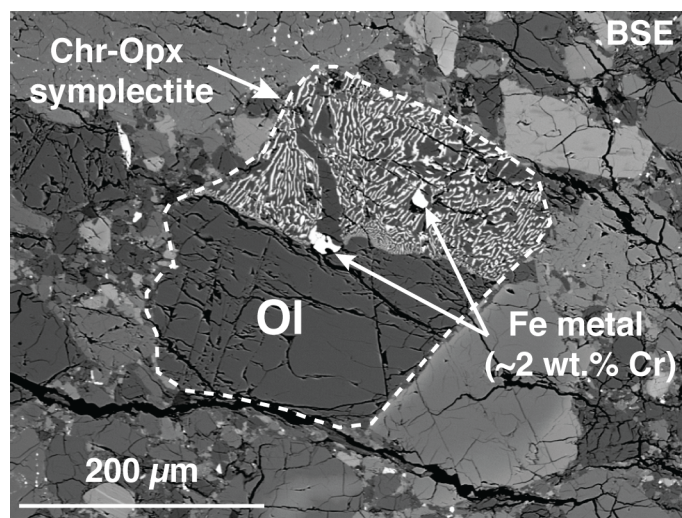


Figure 1.12 Example of Harzburgite Lithology

Example of harzburgitic-dunitic lithology identified by (Hahn et al. *In Review-b*) in the DOM 10 howardites. This lithology is an assemblage of olivine, pyroxene, and Fe metal, with an associated chromite-orthopyroxene symplectite. The Mg#s for olivine and pyroxene within the clasts range from 82 to 92.

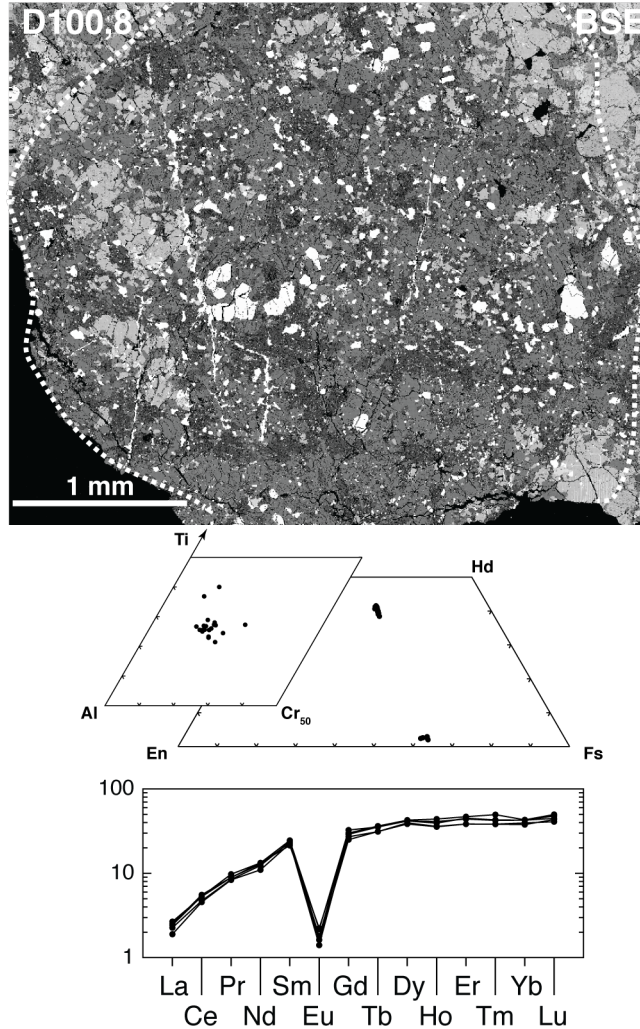


Figure 1.13 Example of Dacite Lithology

Dacite clast identified in the DOM 10 howardites by (Hahn et al. *In Review-a*). The clast is dominated by plagioclase, quartz, and primary augite. Accessory Fe metal, ilmenite, phosphates, pigeonite, troilite, and K-feldspar are also observed. Pyroxene end-member and minor-element compositions, as well as REE data are shown below. This lithology is hypothesized to represent residual melt pockets in the vestan crust. Data for REEs were normalized to CI chondrites (Anders and Grevesse 1989).

Lithologic Distribution Maps

Mineral modes for all nine thin-sections were determined using the mapping procedure described previously, and distribution maps of lithologies are shown in Figures 1.14, 1.15, and 1.16. Large variations in mineral abundances are observed between different meteorites; large intra-sample variations were also found (Table 1.6). For example, eucritic minerals comprise ~40 % and ~84 % of 10839,6 and 10838,10, respectively. However, these same variations are observed in sections cut from the same stone, where 10838,6 contains ~36 % eucritic minerals (Figure 1.15; Table 1.6). Similar intra-sample variations are observed in 10100,8 and 10100,21; however, the two sections cut from 10105 show nearly identical modal mineralogy (Table 1.6). Differences in eucrite and diogenite ratios suggest three distinct breccia clasts have likely been sampled (10:1; 4:1; 1:1; Table 1.6; Figure 1.17), and further support is given by basaltic and cumulate eucrite ratios. Furthermore, a breccia clast identified in 10838,6 contains only diogenitic minerals, suggesting a fourth breccia has been sampled.

DISCUSSION

Pairing of the Dominion Range 10 Howardites

We studied, in detail, the geochemistry of the DOM 10 howardites in order to confirm their initial pairing. As stated previously, all six meteorites were found within an approximately 1.5 km radius. Additionally, we identified petrographic characteristics that support the initial pairing of these stones. First, the DOM 10 howardites contain a diverse array of lithologies relating to eucritic and diogenitic rock types; we have shown that these are shared lithologies between the various meteorites. For example, type D2 diogenites are observed in 10837,7, 10120,6, 10105,6, and 10838,6. Second, we have identified an Mg-rich harzburgite-dunite lithology with a unique 2-phase symplectite of chromite and orthopyroxene that is common in each stone. Therefore, although the modal mineralogy of each stone varies widely between sub-samples, we conclude that the six stones in the DOM 10 howardite pairing group are indeed paired. We attribute the intra-sample mineralogical diversity to reflect the sampling of different breccia clasts within the pairing group.

Future cosmogenic nuclide analyses of the DOM 10 howardites could provide a more concrete conclusion as to the pairing of these stones. Additionally, such studies might incorporate howardite DOM 14169, eucrite DOM 10103, and diogenite DOM 10350 (also found within 1.5 km radius of DOM 10 howardites). Although we did not examine these meteorites during the course of this study, their preliminary petrographic descriptions (Corrigan et al. 2011) are similar to the DOM 10 howardites or, in the case of the eucrite and diogenite samples, share similar textures and mineral chemistry to lithic clasts in the DOM 10 howardites. For instance, diogenite DOM 10350 shares the same coarse-grained tabular orthopyroxenes, with similar compositions to type D3 diogenites examined here. We hypothesize that DOM 10350 may represent a large “plucked” lithic clast during atmospheric entry, although additional studies will be needed to support this suggestion.

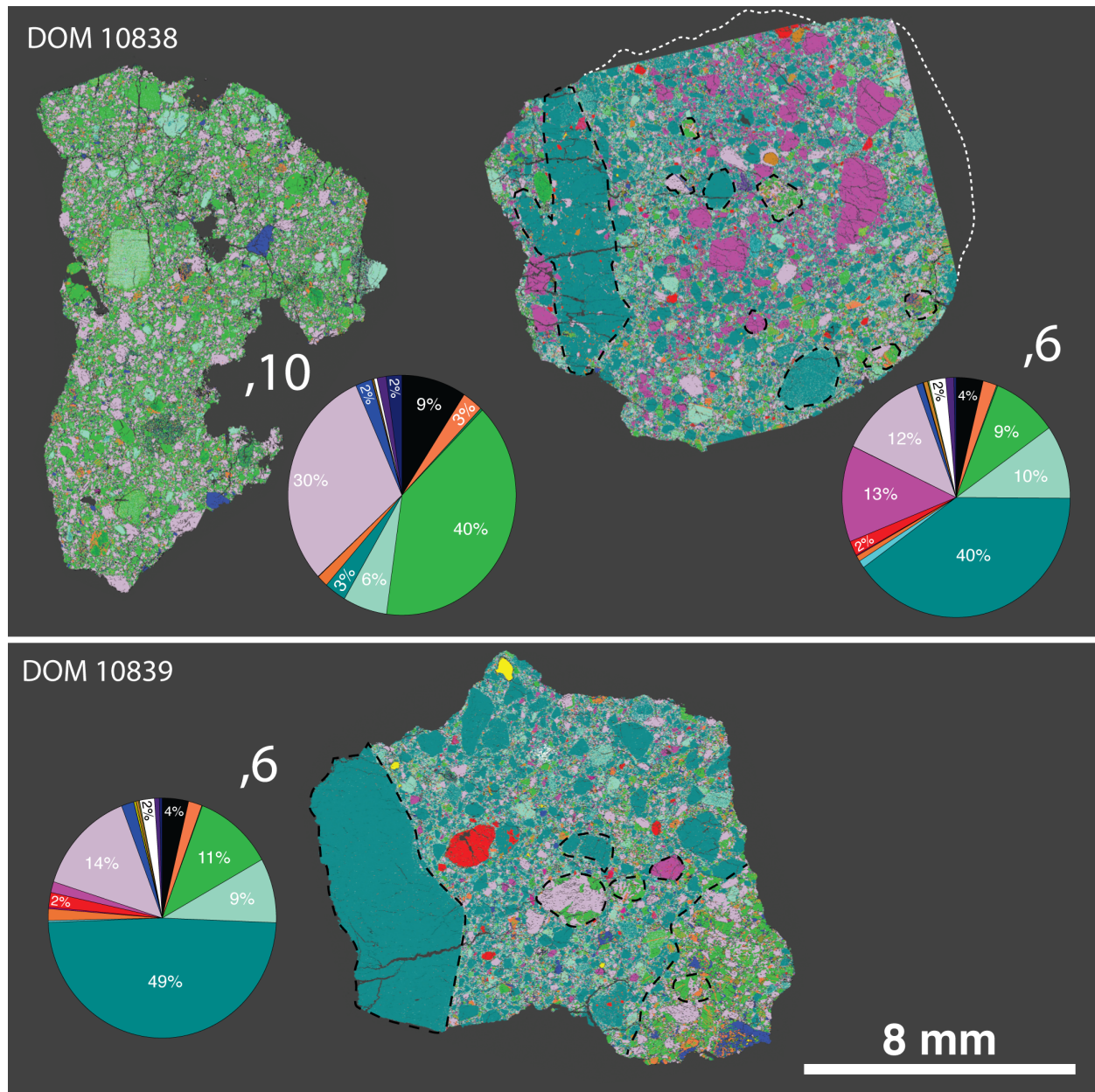


Figure 1.15 Lithologic Distribution Maps of DOM 10838 and 10839

Lithologic distribution maps for DOM 10838 and 10839. Corresponding legend is shown in Figure 1.14. Note that 10839,6 contains eucrite- and diogenite-rich areas; the eucrite-rich breccia clast is found in the lower right portion of the section. The two sections cut from 10838 contain large intra-sample variations in mineralogy (i.e. 9% and 40% basaltic eucrite in 10838,6 and 10838,10, respectively). Section 10838,6 also contains a large (>8 mm) breccia clast with only diogenitic minerals (left).

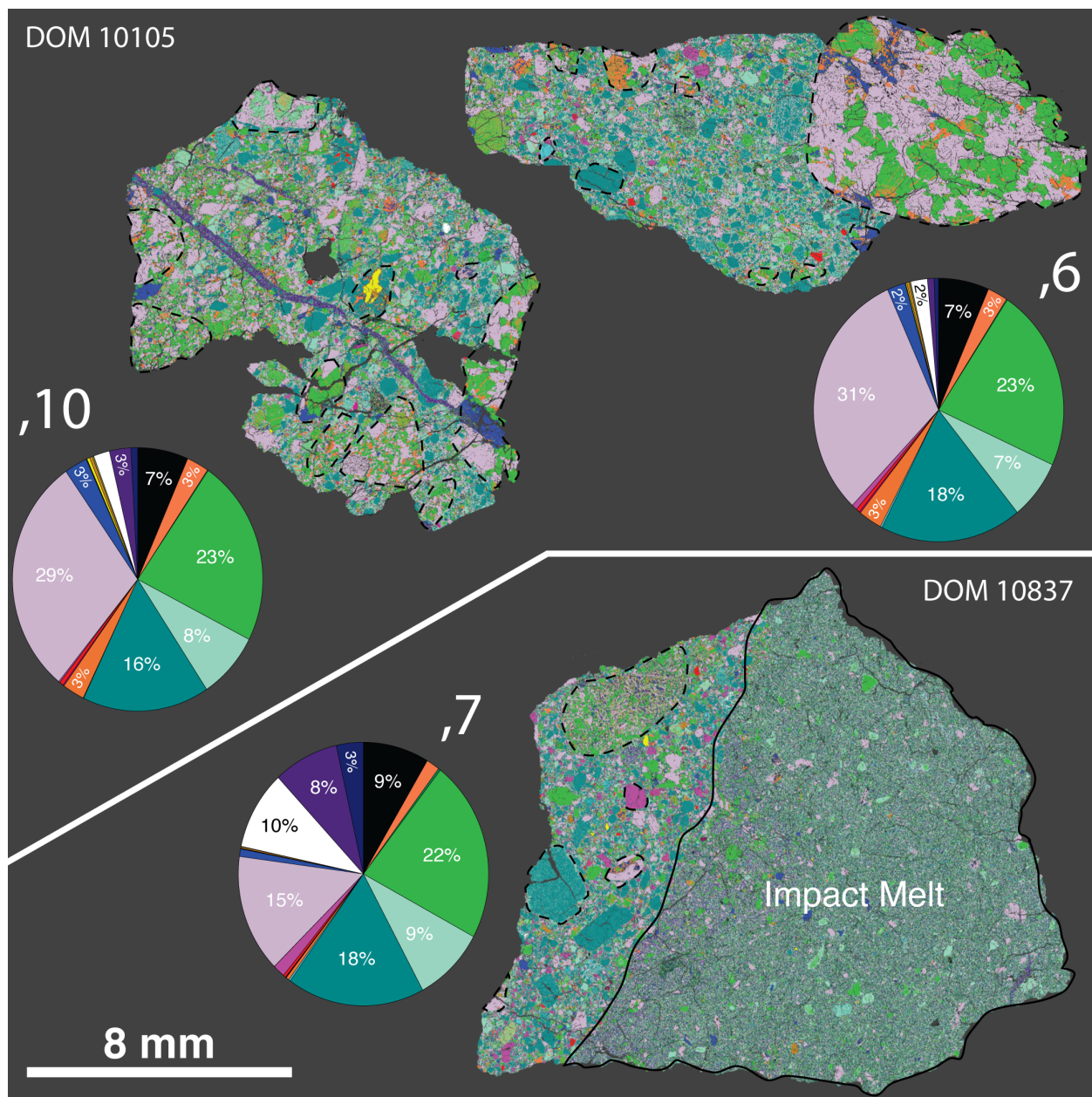


Figure 1.16 Lithologic Distribution Maps of DOM 10105 and 10837

Lithologic distribution maps for DOM 10105 and 10837. Section 10837,7 is dominated by a clast-laden impact melt.

Table 1.6. Mineral modes determined for thin-sections from the DOM 10 howardites.

		DOM 10838,6	DOM 10838,10	DOM 10100,8	DOM 10100,21
Euclite	Clinopyroxene	2.0	2.9	3.2	2.8
	Fe-rich pyroxene	0.2	0.3	0.2	0.1
	Basaltic pyroxene	9.2	39.7	21.2	9.6
	Cumulate pyroxene	9.9	6.3	9.0	15.9
	High Fe-Ca pyroxene	0.8	1.6	3.3	0.7
	Plagioclase	12.3	30.2	26.4	14.7
	Silica	1.0	2.4	4.6	1.1
	Ilmenite	0.1	0.1	0.3	0.2
	K-feldspar	b.d.	b.d.	b.d.	b.d.
	Phosphate	b.d.	b.d.	0.1	b.d.
	Olivine Fo ₁₆₋₆₀	0.1	0.1	0.1	0.2
Diogenite	Diogenite pyroxene	40.0	3.1	13.7	35.7
	Olivine Fo ₆₁₋₇₉	2.0	b.d.	0.6	2.5
	Metal and troilite	0.1	b.d.	0.7	0.2
	Chromite	0.6	0.2	0.3	0.8
Harzburgite mantle	Olivine Fo ₈₀₋₉₂	13.0	b.d.	1.1	3.0
	Orthopyroxene En ₈₅₋₈₈	1.0	b.d.	0.2	0.6
	Symplectite	0.1	b.d.	b.d.	b.d.
Exogenic	Olivine Fo _{>98}	b.d.	b.d.	b.d.	b.d.
	CM components	0.3	2.2	1.4	0.4
	Fusion crust	2.4	0.4	3.1	3.3
	Impact melts	1.1	1.3	2.0	3.9
	Unclassified	3.8	9.2	8.4	4.6
	Euclitic Minerals	35.5	83.6	68.5	45.2
	Diogenite Minerals	42.5	3.3	14.6	38.9
	Basaltic:Cumulate ^a	48:52	86:14	70:30	38:62
	Plag/(Plag+Euclite Px)	36.6	38.0	44.0	34.1
	Euclite:diogenite ^a	49:51	97:3	82:18	59:41
	Euclite minerals/ (Euclite+Diogenite minerals) ^b	45.5	96.2	82.4	53.7

^aCalculated using the procedure described by Lunning et al. (2016).

Table 1.6 Continued.

		DOM 10105,10	DOM 10105,6	DOM 10120,6
Eucrite	Clinopyroxene	2.9	2.6	2.4
	Fe-rich pyroxene	0.1	0.1	0.1
	Basaltic pyroxene	23.0	22.6	8.5
	Cumulate pyroxene	8.2	7.4	15.5
	High Fe-Ca pyroxene	2.9	3.1	1.0
	Plagioclase	29.4	31.2	15.6
	Silica	3.0	2.4	1.0
	Ilmenite	0.2	0.2	0.1
	K-feldspar	b.d.	b.d.	b.d.
	Phosphate	0.1	b.d.	b.d.
	Olivine Fo ₁₆₋₆₀	0.1	0.2	0.2
Diogenite	Diogenite pyroxene	16.4	18.3	42.2
	Olivine Fo ₆₁₋₇₉	0.5	0.5	1.5
	Metal and troilite	0.4	0.2	0.3
	Chromite	0.4	0.3	0.6
Harzburgite mantle	Olivine Fo ₈₀₋₉₂	0.2	0.7	1.5
	Orthopyroxene En ₈₅₋₈₈	0.1	0.2	0.3
	Symplectite	b.d.	b.d.	b.d.
Exogenic	Olivine Fo _{>98}	b.d.	b.d.	b.d.
	CM components	0.9	0.6	0.3
	Fusion crust	2.1	2.2	3.6
	Impact melts	2.8	0.9	1.1
	Unclassified	6.5	6.5	4.0
	Eucritic Minerals	69.8	69.6	44.5
	Diogenite Minerals	17.3	19.1	44.3
	Basaltic:Cumulate ^a	74:26	75:25	35:65
	Plag/(Plag+Eucrite Px)	46.3	48.8	37.1
	Eucrite:diogenite ^a	79:21	77:23	53:47
	Eucrite minerals/ (Eucrite+Diogenite minerals) ^b	80.2	78.5	50.1

^aCalculated using the procedure described by Lunning et al. (2016).

Table 1.6 Continued.

		DOM 10837,7	DOM 10839,6	Weighted Average
Eucrite	Clinopyroxene	1.7	1.9	2.4
	Fe-rich pyroxene	0.3	0.1	0.2
	Basaltic pyroxene	22.3	11.2	19.1
	Cumulate pyroxene	9.3	8.7	9.5
	High Fe-Ca pyroxene	0.4	1.6	1.6
	Plagioclase	14.5	14.3	20.5
	Silica	0.9	1.8	2.0
	Ilmenite	b.d.	0.2	0.1
	K-feldspar	b.d.	b.d.	0.0
	Phosphate	b.d.	b.d.	0.0
	Olivine Fo ₁₆₋₆₀	0.1	0.2	0.1
Diogenite	Diogenite pyroxene	17.8	48.8	25.3
	Olivine Fo ₆₁₋₇₉	0.4	2.0	1.0
	Metal and troilite	0.1	0.3	0.2
	Chromite	0.2	0.3	0.4
Harzburgite mantle	Olivine Fo ₈₀₋₉₂	1.6	1.5	2.7
	Orthopyroxene En ₈₅₋₈₈	0.2	0.3	0.3
	Symplectite	b.d.	b.d.	0.0
Exogenic	Olivine Fo _{>98}	b.d.	b.d.	0.0
	CM components	3.5	0.4	1.3
	Fusion crust	9.7	2.1	3.8
	Impact melts	8.4	0.7	2.9
	Unclassified	8.5	3.7	6.4
	Eucritic Minerals	49.6	39.9	55.6
	Diogenite Minerals	18.3	51.1	26.7
	Basaltic:Cumulate ^a	71:29	56:44	67:33
	Plag/(Plag+Eucrite Px)	30.1	39.5	39.6
	Eucrite:diogenite ^a	78:22	45:55	69:31
	Eucrite minerals/ (Eucrite+Diogenite minerals) ^b	73.0	43.9	67.6

^aCalculated using the procedure described by Lunning et al. (2016).

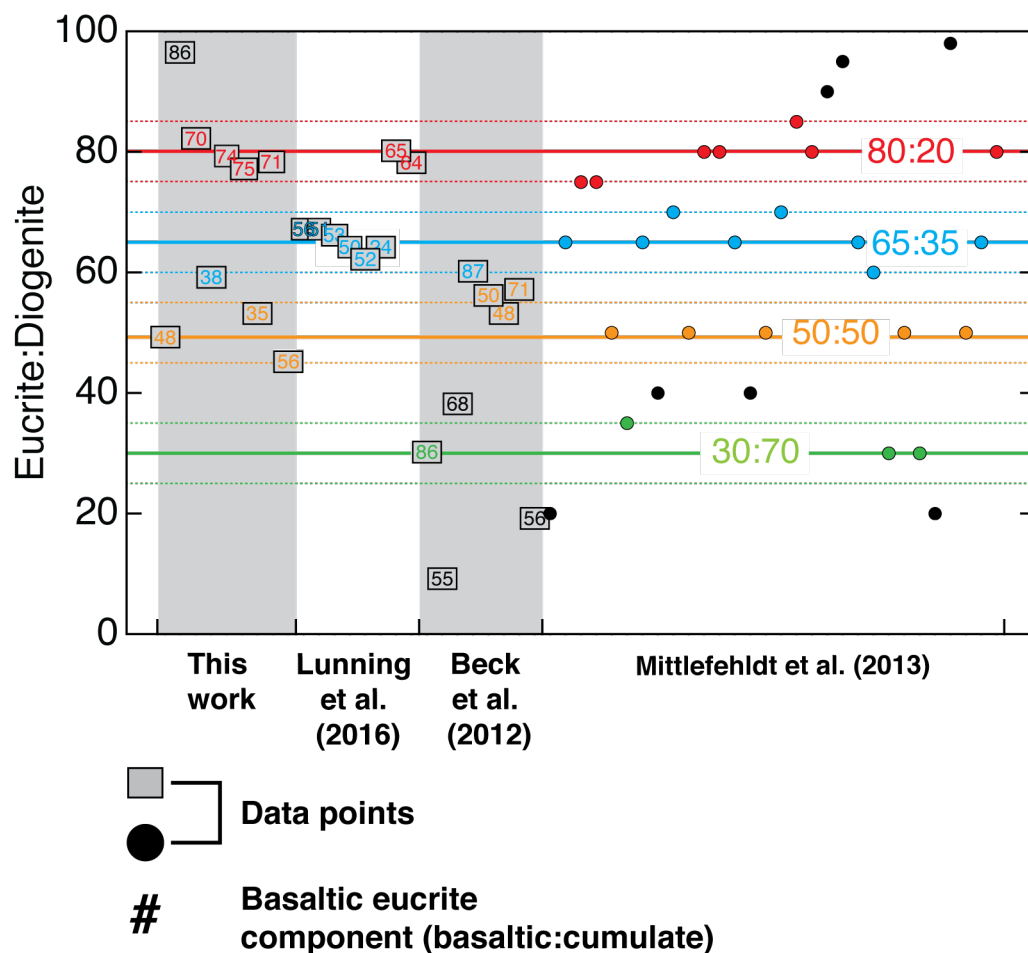


Figure 1.17 Characteristic Mineral Ratios in Howardites

Calculated ratios of the abundances of eucrite to diogenite for various HEDs, with corresponding basaltic eucrite to cumulate eucrite ratios shown as a number inside each data point. Eucrite:diogenite ratios for (Cartwright et al. 2013) were calculated from petrographic and bulk chemical analysis, and the basaltic eucrite:cumulate eucrite ratio cannot be determined. Solid colored lines depict average eucrite:diogenite ratios that appear frequently, and may represent original values of various source terrains. Data values shown in black fall between the common ratios, which may be the result of error or misrepresentation of the data due to large clasts that dominated thin sections (i.e. DOM 10105,6; Fig. 1.16).

The heterogeneity of the meteorite samples on thin-section scale indicates that characterization of a single section from a megaregolithic howardite is insufficient to capture a representative mineralogical sample, and that characterization of multiple sections is needed. Although this observation has been made before (Lunning et al. 2015a), the DOM 10 howardites exceed previously recognized heterogeneity and lithologic diversity in howardites.

Recognition of Distinct Lithologies

The six howardites collected during the 2010 field season from the Dominion Range sample numerous lithologies that provide fundamental information regarding the geological evolution of the asteroid Vesta. We have identified 21 petrologically distinct lithologic types: 8 basaltic eucrites, 4 cumulate eucrites, 7 diogenites, Mg-rich harzburgite-dunite, and an evolved dacite lithology; a summary of their characteristic is given in Table 1.7. An additional component is impact melt. We have attempted to associate each lithic clast with a specific meteorite for which major- and minor-element chemistry of pyroxenes are similar, although other aspects may not necessarily be consistent (i.e. texture; Fowler et al. 1995; Lunning et al. 2015b; Mayne et al. 2009; Mittlefehldt and Lindstrom 2003; Shearer et al. 2010; Takeda and Graham 1991; Warren and Jerde 1987). However, we note that some lithologies appear to be absent from the meteorite collection (i.e. dacite and Fe-rich cumulates); this indicates a few lithic clasts likely sample previously unrecognized lithologies on Vesta, and therefore provide further constraints on geologic processes. Specifically, evolved dacite and Fe-rich cumulate eucrite clasts that show the relationships and compositional boundaries between eucrite classes are not distinct. For instance, type 3 cumulate eucrite clasts show unambiguous cumulate textures, yet the pyroxenes are well within the basaltic eucrite compositional field (Figure 1.9). This provides evidence that melts more evolved than basaltic eucrites should exist on Vesta, which would be capable of producing these Fe-rich cumulates.

Comparison with Other Howardite Pairing Groups

Pecora Escarpment 02 howardites and diogenites

Beck et al. (2012) investigated petrologic variations in the PCA 02 howardite and diogenite pairing group. Cosmogenic nuclide analysis suggests these meteorites represent a pre-atmospheric meteoroid approximately 1 meter in diameter. Beck et al. (2012) demonstrated that the PCA 02 howardites and diogenites contain silicate material with compositions covering all known HED lithologies, and the diversity of the lithologies implies they originated from a variety of source regions. These meteorites are interpreted as samples of the megaregolith, implying that meter-scale diversity exists in the regolith. The DOM 10 howardites contain numerous lithologies (>21 petrologic types), and the abundance of large lithic clasts indicates, like the PCA 02 howardites and diogenites, an origin from the immature megaregolith on Vesta. Specifically, preservation of large mineral and lithic clasts (>1 mm) implies the DOM 10 howardites experienced minimal impact gardening. However, in comparison to the PCA 02 howardites and diogenites, the DOM 10 howardites appear to have sampled a greater variety of lithologies. Although no cosmic-ray exposure data are available for

Table 1.7. Summary of lithologic diversity in the DOM 10 howardites.

Classification	Lithologic type	Texture	Identifying characteristics	Meteorite association
Basaltic eucrite				
	B1	Granoblastic	Px major- and minor-element composition; plagioclase composition	Haraiya (Takeda and Graham 1991)
	B2	Granoblastic	Px major-element composition	Nuevo Laredo (Warren and Jerde 1987)
	B3	Granoblastic	Px major-element and plagioclase composition	EET 90020 (Mayne et al. 2009)
	B4	Granoblastic	Px major-element and plagioclase composition	LEW 85353; LEW 85305 (Mayne et al. 2009)
	B5	Subophitic	Texture; Px and plagioclase major-element composition	Nuevo Laredo (Warren and Jerde 1987)
	B6	Ophitic	Texture; Px major-element composition	PCA 82501 (Mayne et al. 2009)
	B7	Spherulitic	Texture and Px and plagioclase major-element composition	QUE 99658 (Mayne et al. 2009)
	B8	N/A	Zoned composition	None
Cumulate Eucrite				
	C1	Granoblastic	Texture; pyroxene major- and minor-element composition	Moore County (Mayne et al. 2009)
	C2	Cumulate poikilitic	Texture; pyroxene major- and minor-element composition	Serra de Mage; Moama (Mayne et al. 2009)
	C3	Orthocumulate	Texture; pyroxene major- and minor-element composition	None
	C4	Orthocumulate	Texture; pyroxene major- and minor-element composition; plagioclase composition	Y-791195 (Mittlefehldt and Lindstrom 2003)

Table 1.7. Continued.

Classification	Lithologic type	Texture	Identifying characteristics	Meteorite association
Diogenite	D1	Granular	Texture, mineralogy, and Px composition	LAP 03569 (Shearer et al. 2010)
	D2	Fragmental	Texture and major- and minor-element chemistry	LAP 03979 (Shearer et al. 2010)
	D3	Fragmental	Texture and major- and trace-element composition	Aioun El Atrouss (Fowler et al. 1994,1995)
	D4	Fragmental	Major- and trace-element Px composition	Tatahouine (Fowler et al. 1994,1995)
	D5	Granoblastic	Texture and Px major-element composition	LEW 88008 (Fowler et al. 1994,1995)
	D6	Fragmental	Px trace-element chemistry	ALHA 77256 (Fowler et al. 1994,1995)
	D7	Fragmental	Px trace-element chemistry	MET 00425 (Shearer et al. 2010; Fowler et al. 1995)
Mg-rich harzburgite-dunite		Inequigranular	Major-, minor-, and trace-element chemistry of Ol and Px; symplectite association	Ol and Px in GRO 95 howardites (Lunning et al. 2015)
Dacite		Subophitic to granular	Mineralogy, Px major- and trace-element chemistry	None

the DOM 10 howardites, the collective mass of the 6 howardites (~1.1 kg) is a factor of 8 larger than the PCA 02 howardites and diogenites, and therefore collectively might represent the largest piece of the vestan megaregolith in our collection, which has been thoroughly characterized; subsequent radionuclide analyses are needed to support this hypothesis.

The PCA 02 howardites and diogenites are dominated by diogenitic and olivine-rich impact-melt clasts with eucritic material interspersed, whereas the DOM 10 howardites show no clear lithologic dominance, with ratios of eucrite to diogenite ranging from 10:1 to 1:1 (Table 1.6). Unlike the DOM 10 howardites, the PCA 02 howardite and diogenite pairing group displays only small intra-sample mineralogical dissimilarities (i.e. 15 % to 25 % variation in total eucrite and diogenite minerals); in contrast, the DOM 10 howardites can show >50 % variations in eucrite and diogenite mineralogy within a single stone. We observed a single thin-section (10100,8) of breccia-within-breccia where one side is eucrite-rich and contains no Mg-rich olivine mineral fragments, and the other side is dominated by diogenite clasts and contains Mg-rich olivines (Figure 1.14). In contrast, section 10838,6 contains a breccia clast containing only diogenite minerals (Figure 1.15). DOM 10837,7 is dominated by a large impact melt clast (Figure 1.16). The DOM 10 howardites are evidence that extreme heterogeneity exists in the megaregolith, and offer insights into regolith composition that may be detectable in Dawn data.

Grosvenor Mountains 95 howardites

Lunning et al. (2016) conducted a petrologic study of the GRO 95 regolithic howardites. These howardites appear to be plagioclase-depleted relative to eucritic pyroxene (Fuhrman and Papike 1981; Lunning et al. 2016), suggesting plagioclase may be more easily comminuted or melted by impact processes, which could serve as an indicator of regolith maturity. Lunning et al. (2016) also considered that granular sieving could be the dominant process, which would suggest mature terrains might be underlain by megaregolith that is enriched in plagioclase. The GRO 95 howardites also show a ~2:1 eucrite:diogenite ratio, which may be indicative of mature regolith (Warren et al. 2009; Figure 1.17). Additionally, Lunning et al. (2016) noted the broad range in the ratio of basaltic eucrite to cumulate eucrite (2:1 to 1:3), indicating unrecognized diversity of eucritic lithologies in the regolith, which may potentially be resolvable by the Dawn spacecraft (Beck et al. 2015).

The GRO 95 howardites are finer-grained, with smaller and less abundant polymineralic clasts than the DOM 10 howardites; this is consistent with separate origins for these meteorites in the surface regolith and megaregolith, respectively (Bischoff et al. 2006). Because the DOM 10 howardites are megaregolithic and relatively texturally immature, we expected to see plagioclase in abundances consistent with or enriched relative to eucritic pyroxene in unbrecciated eucrites (1:1; Mayne et al. 2009); instead, we observed depletions in plagioclase similar to the GRO 95 howardites (Figure 1.18a). Only DOM 10105 contains plagioclase and eucritic pyroxene in a 1:1 ratio, which is likely caused by the high abundance and large size of eucritic lithic clasts (Figure 1.16). This observation seems inconsistent with a granular sieving hypothesis (Lunning et al. 2016). The observed plagioclase depletion remains an enigmatic feature of howardites, apparently occurring in both the surface regolith and megaregolith. The

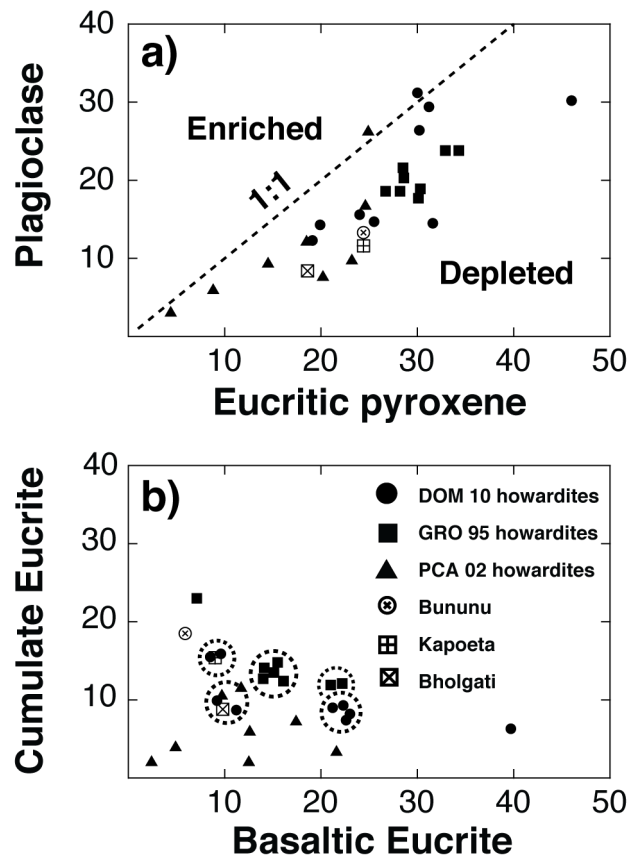


Figure 1.18 Plagioclase Depletion and Euclite Ratios

a) Plot of plagioclase vs. euclitic pyroxene in thin-sections from the DOM 10, PCA 02, and GRO 95 howardite pairing groups. The large regolithic howardites Bununu, Kapoeta, and Bholgati are also shown. Only a few sections appear to contain plagioclase and euclitic pyroxenes in the same ratio as in unbrecciated euclites (1:1, Mayne et al. 2009); all others are depleted in plagioclase relative to euclitic pyroxene. b) Cumulate vs. basaltic euclite abundances in the same meteorites. Sections from each pairing group appear to cluster around particular values, possibly reflecting original ratios before brecciation. Data for PCA 02 howardites from Beck et al. (2012), and for all other howardites from Lunning et al. (2016)

GRO 95 howardites also display a more limited range in proportions of eucritic to diagenitic minerals, with distinct clusters at 4:1 and 2:1 (Figure 1.17), which may suggest they have evolved towards a more homogenized composition due to impact gardening; a broader range in eucritic and diagenitic mineral proportions are observed in the DOM 10 howardites, offering further support that they represent immature regolith.

Lunning et al. (2016) noted variations in the ratio of basaltic and cumulate eucrite material in regolithic howardites – this is an important observation, and we argue, the most significant. When comparing modal analyses for the PCA 02 and DOM 10 megaregolithic howardites, with that of regolithic howardites GRO 95, Kapoeta, Bununu, and Bholgati, we found that the abundance ratios of basaltic eucrite to cumulate eucrite appear to form clusters (Figure 1.18b). We hypothesize that these clusters may represent original basaltic eucrite and cumulate eucrite ratios in the source regions, and that subsequent smaller impacts have acted to homogenize those portions in the surface regolith, and left the same ratios in the underlying megaregolith. Indeed, the DOM 10 howardites contain at least three breccia types with distinctive mineralogy, two of which contain basaltic eucrite:cumulate eucrite ratios identical to Kapoeta and Bholgati.

Implications for Remote Sensing

Developing a data set for rigorous interpretation of Dawn's remote-sensing data of Vesta has been an important objective of some recent HED studies (e.g. Beck et al. 2015; Mittlefehldt et al. 2013). Identification and mapping of eucrite, diogenite, and howardite terrains on the vestan surface have been based on VIR pyroxene absorption bands (De Sanctis et al. 2012) and GRaND neutron absorption characteristics (Prettyman et al. 2013); however, separation of HED subgroups has proven more difficult. Nevertheless, Beck et al. (2015) have shown that principal component analysis of measurables from the GRaND instrument are capable of further differentiating between HED meteorite subgroups (i.e. basaltic vs. cumulate eucrites). The identification of substantial large- and small-scale mineralogical variations, both basaltic eucrite:cumulate eucrite and eucrite:diogenite ratios, within megaregolith analogs have important implications for remote sensing observations of the vestan surface. Specifically, the observation of distinctive eucrite:diogenite ratios, in combination with the array of basaltic eucrite:cumulate eucrite ratios, make the DOM 10 howardites ideal candidates for spectral calibration studies. Such investigations might make it possible to map these lithologic units on the vestan surface, which has the potential to advance our understanding of the regolith. As suggested by Warren et al. (2009), the modern regolith of Vesta may be the result of a single large impact around 1 Ga; this would have been the sole source of diagenitic components to the regolith, and subsequently smaller impacts would have acted to homogenize the regolith towards a 2:1 eucrite to diogenite ratio. The various eucrite to diogenite ratios in the DOM 10 howardites could thus represent original ratios in numerous ancient source regions. More recent impacts may have excavated this ancient material, which may be resolvable in the Dawn data. We have also reported variations in olivine abundance (1 to 15 %; Table 1.6), composition, and grain size, which is useful for interpreting diagenitic lithologies containing variations in olivine content (Beck et al. 2015).

CONCLUSIONS AND SUMMARY

Petrologic investigations of the DOM 10 howardites have revealed an array of lithic clasts with compositions covering the complete spectrum of HED meteorites, in addition to lithologies not represented in the meteorite collection. The abundance and large size of lithic clasts indicates these meteorites were part of the megaregolith on Vesta. In total, 21 lithologies were identified as clasts, and more may be represented in comminuted mineral fragments. The identification of unique diogenite:euclite and cumulate:basaltic ratios within breccia clasts likely represents the original ratios within the source regions sampled, may be identifiable by the Dawn spacecraft. Collectively, the DOM 10 howardites have the potential to represent the largest piece of the vestan megaregolith, and therefore could be useful to interpret Dawn data of relatively fresh regions on Vesta, which may expose the underlying vestan megaregolith.

Chapter 2: Mg-rich Harzburgites from Vesta: Mantle Residua or Cumulates from Planetary Differentiation?

Disclosure: The following chapter was submitted to the journal of *Meteoritics and Planetary Science* in November 2015, as a result of the primary author's graduate research. Co-authorship is shared with Nicole G. Lunning (National Museum of Natural History, Smithsonian Institution), Harry Y. McSween (UTK), Robert Bodnar (Virginia Tech, and Lawrence A. Taylor (UTK). Timothy M. Hahn Jr. prepared the manuscript. The content of the chapter contains the original submission materials in a form that has undergone only minor revisions.

ABSTRACT

We have conducted petrographic, electron microprobe, and laser ablation ICP-MS analyses of Mg-rich harzburgite clasts in howardites, which we conclude are samples of the vestan mantle. Key chemical and petrologic characteristics of these rocks provide tests for differentiation models. Our results indicate the mantle of Vesta formed through partial melting (>50 %), which left behind a harzburgite and possibly dunite residuum. The Mg-rich clasts are composed of orthopyroxene and olivine, with minor clinopyroxene, FeNi metal, and distinctive pyroxene-chromite symplectites. Major- and trace-element compositions of the Mg-rich lithic clasts (Mg# 82-89 of co-existing olivine and pyroxene) suggest variable amounts of melting within the mantle. The symplectites are spatially located along mineral grain boundaries suggesting a possible secondary formation process: interaction with a metasomatic melt, as recently proposed for lunar symplectites. The rare earth element composition of Mg-rich orthopyroxene appears to have been altered by interaction with the symplectite-forming melt. The Ni/Co and low Ni concentrations in Mg-rich olivine further support formation in the vestan mantle. The occurrence of FeNi metal containing ~2 wt. % Cr within the mantle assemblage indicates a very reducing environment (<<IW).

INTRODUCTION

Differentiation was a common occurrence in planetesimals that accreted before the decay of ^{26}Al in the early solar system (Bizzarro et al. 2005). Although differentiated bodies were likely raw materials for the formation of the terrestrial planets, few such bodies survive as intact protoplanets (Goldstein et al. 2009). Evidence for extensive differentiation can be seen in the variety of achondrites and iron meteorites that display evidence for varying degrees of partial melting and fractionation, as well as different bulk compositions and redox states (e.g. Burbine et al. 2002 and references therein; Mittlefehldt et al. 1998). Of these bodies, Vesta – commonly accepted as the howardite-eucrite-diogenite (HED) parent body (McSween et al. 2013) – is the best characterized and most completely sampled (e.g. Buratti et al. 2013; De Sanctis et al. 2012; McCoy et al. 2015; McSween et al. 2013; Russell et al. 2012). Differentiation models envisioned for the HED parent body fall into two camps: partial melting to form plutons and erupted lavas (Stolper 1977), and global-scale melting to form a magma ocean (e.g. Righter and Drake 1997; Ruzicka et al. 1997). More recently, models that feature a shallow magma ocean (Neumann et al. 2014) or continuous extraction of magmas during melting which precluded a magma ocean (Wilson and Keil 2012) have been proposed. Due to the low

survival rates of small differentiated bodies, one would expect meteorite collections to contain samples from all portions of a differentiated body (crust, mantle, and core) (Burbine et al. 1996). Although crusts and cores are well sampled, only a handful of studies have identified potential mantle samples (Floss 2002; Lunning et al. 2015b). However, developing a complete understanding of these samples typically is hampered by their relatively small size, lack of petrologic context, and unknown parent body association.

The HED meteorite group records one of the earliest differentiation events (7-20 Ma after CAI formation) of a protoplanetary body within the solar system (Blichert-Toft et al. 2002; Misawa et al. 2005; Quitté et al. 2000). The HED meteorites represent the silicate portion of Vesta, certainly the crust and possibly the upper mantle (e.g. Mandler and Elkins-Tanton 2013; Ruzicka et al. 1997). Diogenites, which are orthopyroxenites, harzburgites, and dunites (Beck and McSween 2010; Beck et al. 2011), formed either as cumulates from a magma ocean (Ruzicka et al. 1997 and references therein) or in crustal magma chambers (e.g. Beck and McSween 2010; Mandler and Elkins-Tanton 2013; Mittlefehldt et al. 2012). The eucrites are basaltic or gabbroic cumulate rocks that formed as shallow intrusions and surface flows (Hsu and Crozaz 1996, 1997; McCarthy et al. 1973). Howardites are polymict breccias that formed through impact mixing of eucrites and diogenites, along with unique and minor igneous lithologies and exogenic materials (e.g. Fuhrman and Papike 1981).

Lunning et al. (2015b) identified Mg-rich, monomineralic olivine and pyroxene mineral fragments within howardites from the Grosvenor Mountains, Antarctica (GRO 95), and discussed evidence supporting their formation in the vestan mantle. Unfortunately, the rarity of the mineral fragments, lack of petrologic context, and redistribution of trace elements, as indicated by Ce anomalies, hampered interpretation. Additionally, meteorite QUE 93148 (a small 1.1 g stone), originally classified as a lodranite (Mason 1995), exhibits features that suggest a possible relation to the HED meteorites, and specifically the mantle of the HED parent body (Floss 2002; Goodrich and Delaney 2000). Such features include oxygen isotope composition, primitive major-element composition, Fe/Mn in olivine and pyroxene, and low trace element abundances.

We have conducted a further search of howardites for Mg-rich components to substantiate the findings of Lunning et al. (2015b) and Floss (2002). Here we identify harzburgite lithic fragments, synonymous with Mg-rich lithic fragments, within the Dominion Range, Antarctica (DOM 10) howardite pairing group that are remarkably similar in major- and minor-element systematics to the Mg-rich mineral fragments of the paired GRO 95 howardites and QUE 93148, although we find some differences in trace-element composition. These rock clasts allow us to evaluate the hypothesis that these Mg-rich minerals are from the HED parent body mantle using a more robust data set. These rocks lead us to propose a model for the petrogenesis of Mg-rich components in howardites, and to consider implications of our model for the differentiation and remote sensing observations of Vesta.

Our study suggests that no current differentiation model can account for all the requirements of the HED meteorites (chemical, physical, thermal, and chronological), and therefore, this work should serve as a foundation for constraining future differentiation models.

MATERIALS AND METHODS

Samples

We analyzed thin-sections from six stones of a proposed howardite pairing group collected from the Dominion Range, Antarctica (DOM 10105,6; 10100,8; 10120,6; 10837,7; 10838,6; 10839,6), hereafter designated by the first letter of their location and the last four identification numbers (i.e. DOM 10100,8 = D100,8). These six stones were initially thought to be paired, based on close proximity (within a circle of 2 km radius; John Schutt and Ralph Harvey, pers. comm. 2015) during collection and on petrographic similarities (Corrigan et al. 2011).

The howardites are complex breccias that record small-scale heterogeneity and display an array of lithic clasts. Their matrices consist of comminuted pyroxene and plagioclase grains ranging in size from 0.5-5.0 mm, which host clasts of eucrite, diogenite, granitoid, and impact-melt (Hahn et al. 2015a; Hahn et al. 2015b; Lunning et al. 2015a). In addition, they contain harzburgite rock clasts with Mg-rich olivine, orthopyroxene, and associated phases in non-brecciated equilibrium (igneous or metamorphic) contact, ranging in size from 50-500 μm , and mineral fragments of such clasts, ranging from 0.1-2 mm (e.g. Figure 2.1). The harzburgite clasts also contain unusual symplectites composed of orthopyroxene and chromite (Figure 2.1a). The proportion of the Mg-rich clasts and their monomineralic equivalents vary significantly between sections (1-11 modal %; Lunning et al. 2015a).

Electron Microprobe Analysis

Major- and minor-element chemistry was determined for individual phases using wave-dispersive (WDS) and energy-dispersive (EDS) spectrometers on a Cameca SX-100 electron microprobe (EMP) at the University of Tennessee. Individual point analyses on olivine and pyroxene were conducted with a potential of 15 kV, a beam current of 30 nA, and a 1 μm spot size. High beam-current analyses (20 kV and 100 nA) were also conducted in an attempt to lower detection limits and increase precision for P, Ni, Mn, and Ti. However, certain elements remained below detection limits. Instead, we opted to use an average of several analyses performed on the same grain when calculating elemental ratios (i.e. Fe/Mn), which provided adequate results. Count times for individual elements varied from 20-50 s for low beam-current analyses (i.e. 15 kV and 30 nA). Standard PAP corrections were used. Natural and synthetic samples were analyzed for calibration purposes.

Laser Ablation ICP-MS

Trace-element analyses were conducted *in situ* at Virginia Tech with an Agilent 7500ce inductively coupled plasma mass spectrometer (ICP-MS). An Excimer 193 nm ArF GeoLasPro laser ablation system was used to ablate material from the sample. Laser spot sizes ranged from 16 to 90 μm . Only fracture-free areas were chosen for analysis, but the coarse grain size permitted, on average, 3 to 4 analyses per grain. The NIST SRM610 reference glass was used as an external standard. Before and after data collection, the NIST standard was analyzed twice in order to allow for drift correction. Before sample ablation was initiated, approximately 60 s of He gas background was collected. Sample ablation times varied from 20-60 s; however, during

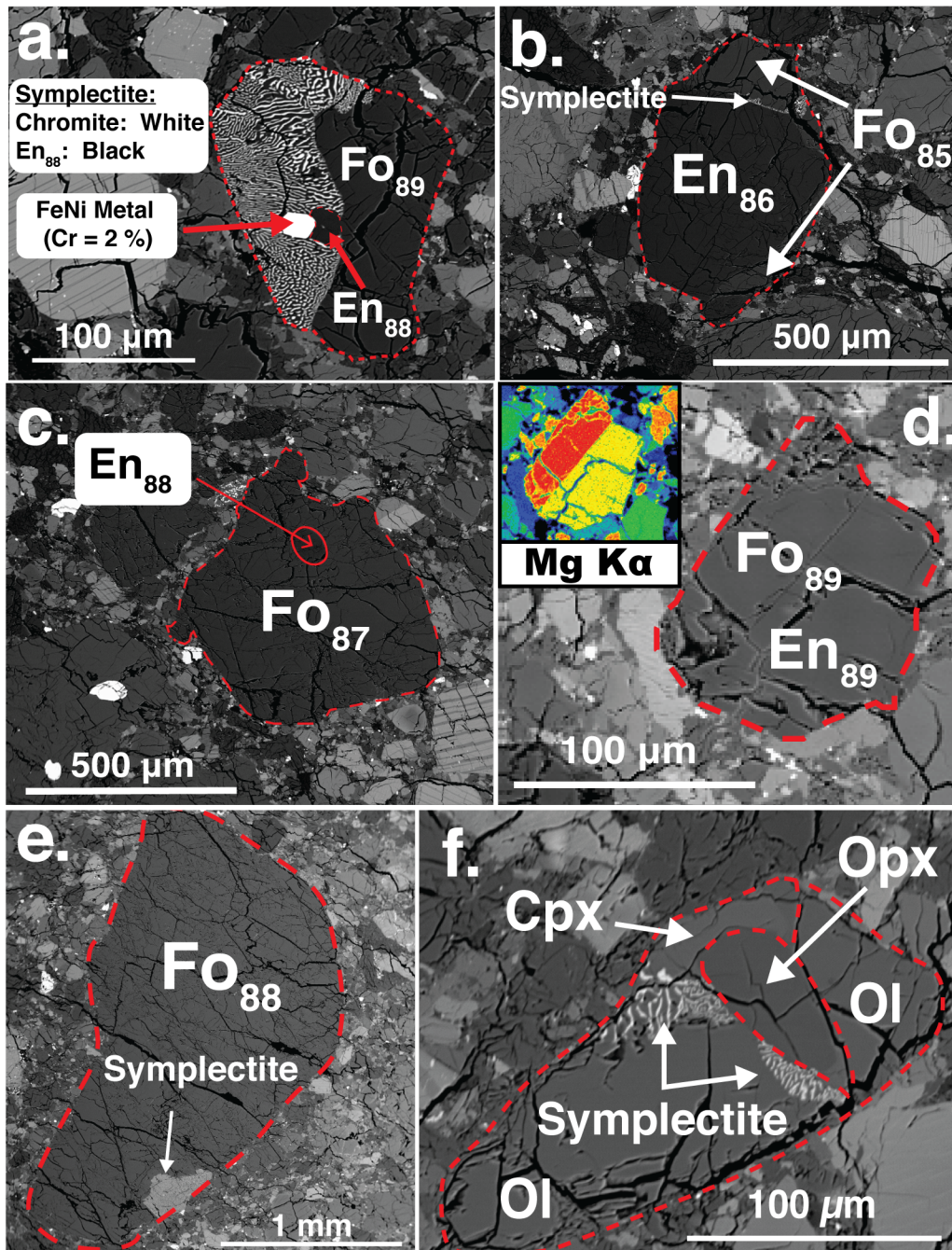


Figure 2.1 Mg-rich Harzburgite Clasts

Backscattered electron (BSE) images of Mg-rich lithic clasts in the DOM 10 howardite pairing group. Olivines and orthopyroxenes occur in non-brecciated contact. There is little contrast between olivine and pyroxene in BSE images, which makes distinguishing these grains difficult. Chromite-orthopyroxene symplectites are common in these clasts.

the data reduction process only adequate signals were used; that is, signals with low noise and no obvious evidence of contamination. After sample ablation, the analyte was carried by a mixture of He and Ar gas to the ICP-MS. Analytical precisions for elements analyzed during the course of this study have been previously established by the LA ICP-MS lab at Virginia Tech. The 3σ precision, relative to NIST 612, provides results mostly in the range of 5-10 %, but can be as high as 10-20 % for elements like REE and Sc, respectively. For a detailed description of analytical precision and protocols, see <http://www.geochem.geos.vt.edu>

For the data reduction process, we used the method employed by (Lunning et al. 2015b). Because detection limits are dependent on a multitude of factors, each detection limit varies for every element. Therefore, where trace-element concentrations are below detection limits, we report the detection limits for the specific element calculated for that analysis. For calculation purposes, i.e. Eu/Eu^* , we choose to use detection limits and report the data as such.

Bulk Composition Reconstruction for Symplectites

We conducted detailed EMP investigations and quantitative x-ray mapping of symplectites in Mg-rich clasts in order to estimate the bulk composition, which aids in the interpretation of formation mechanisms. By combining EMP point analyses, modal abundance of phases, and representative density calculations for phases based on mineral chemistry, we calculated the bulk composition of symplectites. For modal abundance measurements of phases in symplectites, which are assumed as volume % for reconstruction purposes, we use elemental x-ray maps, in conjunction with remote sensing software (ENVI 4.2) to allow for precise modal abundance determinations. For comparison, we conducted (semi-quantitative) broad beam EMP analyses of symplectites using 20 μm defocused beams.

Numerical Modeling

In order to evaluate our petrogenetic hypothesis for the Mg-rich harzburgite clasts, we conducted numerical melting experiments using the alphasELTS front-end (Smith and Asimow 2005) of the MELTS program (Ghiorso and Sack 1995). For our starting composition we used the predicted bulk-silicate composition of Vesta that best satisfies the oxygen isotope and Fe/Mn constraints (0.75 H/0.25 CM chondrite) as determined by Toplis et al. (2013). Our models were run at the IW buffer and a pressure of 500 bars, a reasonable estimate for melt production in the vestan mantle (Righter and Drake 1997), and assumed equilibrium melting. We investigated the effect of fractional melting; however, the resulting mineralogy of the residuum is indistinguishable. Data from our models are presented below and the implications are discussed.

RESULTS

Petrography

Mg-rich olivine and pyroxene occur as monomineralic, polymineralic, and monomineralic polycrystalline fragments as large as 2 mm in longest dimension (Figure 2.1), surrounded by a matrix that contains a variety of lithic fragments belonging to the HED meteorite group. The Mg-rich grains of interest (olivine and pyroxene), along with associated phases, are minor components (1 to 2 modal %) of the analyzed sections, except for section D838,6, where Mg-rich olivine and pyroxene comprise ~11 modal % of the section. The abundance of Mg-rich pyroxene is generally an order of magnitude less than Mg-rich olivine (0.1 to 0.8 and 1 to 11 modal %, respectively).

The majority of comminuted mineral fragments are heavily fractured, small, and monomineralic. Lithologies of large grain size are likely to be broken into fragments that lack textural context. We have, however, identified several lithic clasts that contain primary olivine and pyroxene in non-brecciated (igneous or metamorphic) contact (e.g. Figures 2.1b and 2.1d). The Mg-rich olivine grains commonly show evidence for high degrees of shock metamorphism (i.e. undulatory extinction, planar fractures, and weak to moderate mosaicism). All olivine and pyroxene fragments are relatively free of mineral inclusions.

Associated with Mg-rich olivine and pyroxene grains, including monomineralic, polymineralic, and monomineralic polycrystalline, are symplectites of chromite and orthopyroxene, with occasional clinopyroxene and FeNi metal (Figure 2.2), which are similar to symplectites in the lunar Mg-suite lithologies, QUE 93148, and some terrestrial mafic intrusions (Elardo et al. 2012 and references therein). Symplectites vary in size from 10-400 μm in the longest dimension. Often, symplectites occur along olivine-pyroxene and olivine-olivine grain boundaries (e.g. Figures 2.1b, 2.1f). Contact relationships between olivine and symplectite are irregular, whereas pyroxene-symplectite boundaries are planar (Figures 2.1b and 2.2). The chromite lamellae within symplectites are variable in thickness (Figure 2.2).

Mineral Chemistry

We report major-, minor-, and trace-element chemistry for Mg-rich olivine and pyroxene grains, together with compositions of diogenite olivine and pyroxene for comparison. We define diogenite olivine and pyroxene as having Mg#s <80 and <85, respectively. Below we report a subset of representative analyses; a more complete data set is given in the online appendix. All coexisting Mg-rich olivine and pyroxene in lithic clasts have equilibrium compositions (Figure 2.3), indicating that olivine and pyroxene were co-genetic over a wide compositional range (Mg# 82-92).

Olivine

Olivine shows significant variation in major-element composition but is less variable in minor-element concentrations. For example, the Mg#s of olivine grains range from 80-92 with Fe/Mn of 34-44 (Tables 2.1 and 2.1A; Figure 2.4). During our investigation, we identified olivine grains with Mg#s of typical diogenite (Mg# <80),

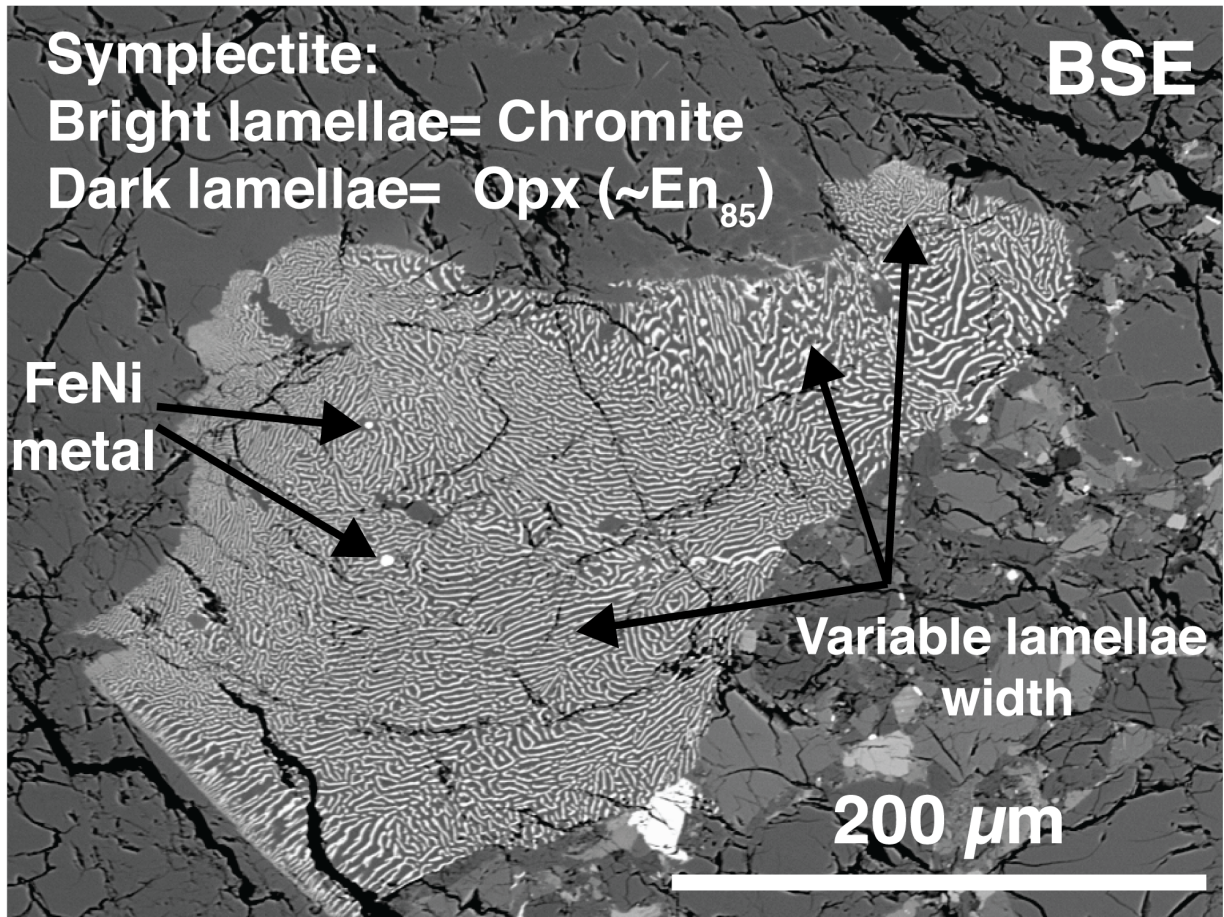


Figure 2.2 Chromite-Orthopyroxene Symplectite

Enlarged view of symplectite in Figure 2.1e, illustrating the variable thickness in chromite lamellae. The apparent differences, however, are likely a result of sectioning and orientation in three dimensions. Boundaries between the symplectite and olivine are both planar and irregular.

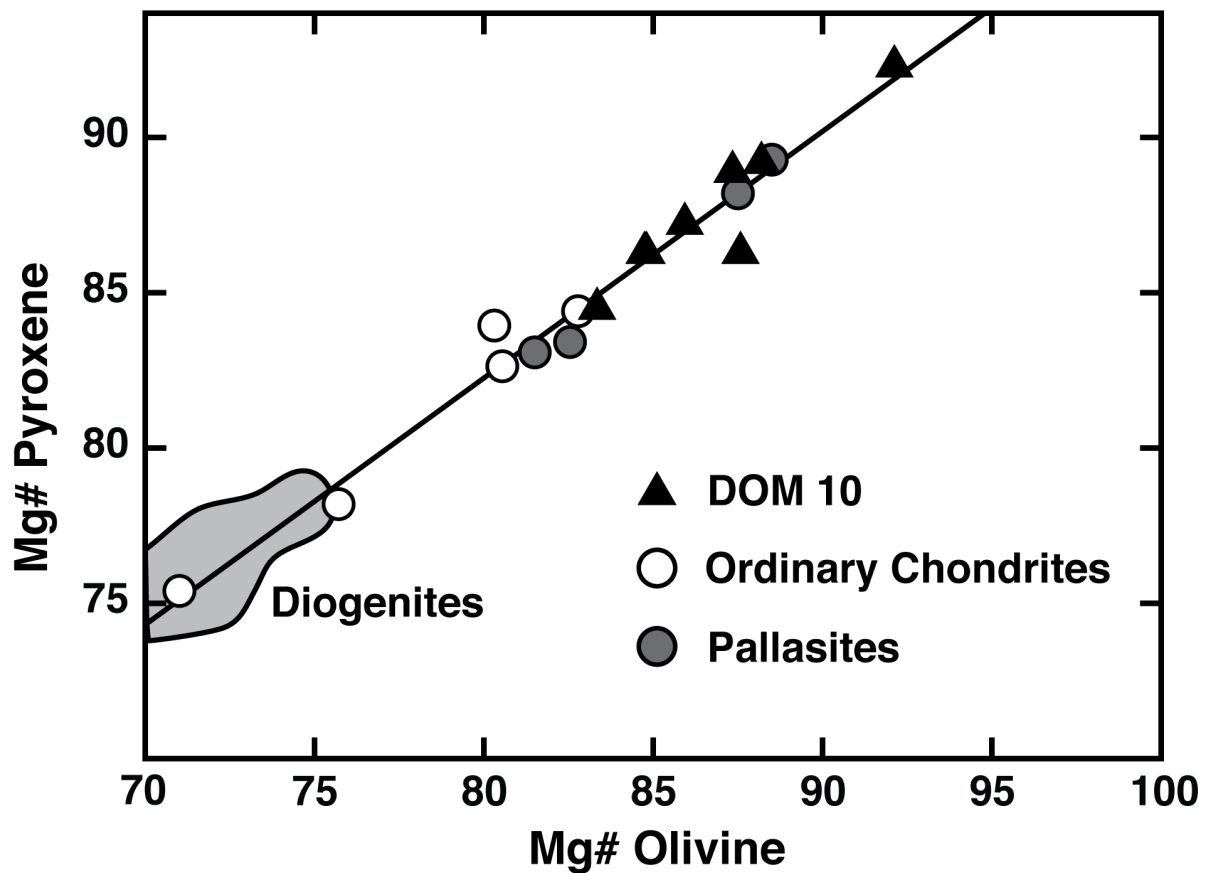


Figure 2.3 Co-existing Olivine and Pyroxene Grains

Plot of Mg#s in coexisting orthopyroxene and olivine (filled triangles) in lithic clasts. The regression line for equilibrated olivine and pyroxene is based on H, L, and LL ordinary chondrites (Mittlefehldt et al. 1998) and pallasites (Buseck 1977). Gray field is the compositional range of olivine and pyroxene in HEDs (Beck et al. 2010).

which report along side Mg-rich olivine grains in Table 2.1, for comparison. We note that there are compositional gaps between Mg-rich and diagenitic olivines (Figure 2.4). Minor-element concentrations in olivine are low for Al_2O_3 and Cr_2O_3 (<0.2 wt.%), and TiO_2 concentrations are below EMP detection limits (i.e. <0.03 wt.%; Tables 2.1 and 2.1A). Each olivine grain is compositionally homogeneous throughout, and as determined by high intensity x-ray mapping of P in olivine grains, no relict zonation is apparent. Additionally, there is no correlation between Cr_2O_3 and Mg# in the olivine, which suggests a decoupling between major and minor elements, even for elements with relatively low diffusion rates (Mittlefehldt 1994).

Pyroxene

Major-element compositions of Mg-rich pyroxene grains are more restricted than Mg-rich olivine grains, with Mg#s ranging from 85-92 and Fe/Mn from 23-30, and like the olivines, there is a compositional gap between Mg-rich and diagenitic pyroxenes (Tables 2.2 and 2.2A; Figure 2.4). The restricted major-element composition is a consequence of the compositional range in diagenitic pyroxenes. Concentrations of minor elements in Mg-rich pyroxene grains are somewhat variable. For instance, Cr_2O_3 concentrations vary by an order of magnitude and Al_2O_3 concentrations vary by two orders of magnitude, whereas TiO_2 concentrations only vary by a factor of four (Table 2.2 and 2.2A). Pyroxene grains are homogenous with no observable evidence for prior zonation. Similar to diagenite pyroxenes, minor elements are decoupled from major elements owing to extensive metamorphism experienced on the HED parent body (Figure 2.5). Figure 2.6a compares the major element compositions of Mg-rich pyroxenes to other HED pyroxenes. An elemental plot of Al-Cr-2Ti (Figure 2.6b) shows a nearly constant trend of decreasing Cr/Al with slightly increasing Ti in Mg-rich pyroxenes, however, no Ti-rich branch as seen in diagenite pyroxenes. Figure 2.6c shows a positive correlation between Yb and Al.

Symplectites

The symplectites (Figure 2.7) in lithic clasts are composed of chromite and orthopyroxene, sometimes with minor clinopyroxene and FeNi metal. Representative mineral compositions for symplectite-forming phases are shown in Table 2.3. Electron microprobe analysis of individual chromite lamellae suggest they are homogeneous in composition (Table 2.3), although the EMP excitation volume is comparable to the width of chromite lamellae and therefore compositional zonation may not be apparent. In contrast, Cr x-ray maps of symplectites (Figures 2.7b, 2.7f) suggest the chromite lamellae are zoned; however, due to the edge effects produced by x-ray mapping, we suggest the apparent zonation may not be real. Chromite lamellae exhibit variations in Cr_2O_3 concentrations, which can vary from 52-65 wt.% between different symplectite inclusions, suggesting compositional variability of the bulk symplectites.

Table 2.1. Representative mineral chemistry of Mg-rich olivines.

n	DOM 10100,8				DOM 10105,6								DOM 10120,6				DOM 10837,7					
	3		4		4		2		3		4		6		2		3		3		3	
SiO ₂	40.4	(1)	39.7	(<1)	40.2	(1)	40.0	(<1)	40.3	(2)	40.3	(2)	40.8	(1)	40.3	(<1)	40.1	(2)	41.1	(1)	40.2	(<1)
Al ₂ O ₃	0.03	(1)	b.d.		b.d.		0.05	(4)	0.02	(1)	0.04	(4)	b.d.		b.d.		b.d.		b.d.		b.d.	
Cr ₂ O ₃	0.07	(1)	0.05	(1)	0.10	(2)	0.12	(1)	0.05	(1)	0.05	(2)	0.06	(1)	0.10	(<1)	0.04	(2)	0.05	(2)	b.d.	
MgO	47.1	(<1)	44.6	(2)	45.7	(<1)	45.7	(<1)	47.1	(2)	46.7	(3)	47.8	(1)	50.3	(<1)	47.6	(1)	51.0	(1)	47.0	(2)
CaO	0.05	(1)	0.04	(1)	0.06	(2)	0.05	(<1)	0.04	(1)	0.05	(1)	0.07	(1)	0.07	(2)	0.06	(<1)	0.05	(1)	0.06	(1)
MnO	0.29	(1)	0.37	(2)	0.33	(<1)	0.34	(1)	0.31	(1)	0.30	(2)	0.29	(1)	0.21	(<1)	0.28	(<1)	0.22	(1)	0.32	(1)
FeO	12.6	(<1)	15.8	(1)	14.6	(<1)	14.7	(1)	12.7	(1)	12.8	(5)	12.0	(1)	7.9	(<1)	12.1	(1)	8.0	(<1)	13.2	(<1)
Total	100.6		100.6		101.0		101.0		100.5		100.3		101.1		98.9		100.3		100.5		100.8	
Fe/Mn	42.2	(15)	42.5	(23)	43.1	(5)	42.3	(6)	40.9	(10)	42.9	(27)	40.9	(16)	36.9	(5)	41.8	(5)	36.1	(14)	41.1	(7)
Fe/Mg	0.15	(<1)	0.20	(<1)	0.18	(<1)	0.18	(<1)	0.15	(<1)	0.15	(<1)	0.14	(<1)	0.09	(<1)	0.14	(<1)	0.09	(<1)	0.16	(<1)
Mn/Mg	0.0036	(<1)	0.0047	(<1)	0.0042	(<1)	0.0043	(1)	0.0037	(1)	0.0036	(2)	0.0035	(1)	0.0024	(<1)	0.0034	(<1)	0.0024	(1)	0.0039	(1)
Mg#	87.0	(<1)	83.4	(1)	84.8	(<1)	84.7	(<1)	86.9	(1)	86.7	(1)	87.6	(1)	92.0	(<1)	87.6	(1)	91.9	(<1)	86.3	(<1)

* Fe/Mn, Fe/Mg, and Mn/Mg calculated from molar values.

*Values in parentheses represent 1 standard deviation, in terms of the last decimal place.

Table 2.1. Continued.

Table 2.1. Continued.

	DOM 10838,6									DOM 10839,6						
n	3		3		3		1		4		2		2		3	
SiO ₂	40.6	(<1)	38.5	(2)	38.4	(1)	41.3	39.4	(3)	39.7	(2)	39.3	(1)	38.8	(1)	
Al ₂ O ₃	b.d.		b.d.		b.d.		b.d.	b.d.		0.04	(1)	b.d.		b.d.		
Cr ₂ O ₃	0.06	(1)	b.d.		0.04	(1)	0.07	0.03	(2)	0.07	(1)	0.08	(<1)	0.13	(1)	
MgO	47.8	(<1)	39.4	(3)	38.5	(2)	51.6	47.5	(1)	47.2	(<1)	45.8	(3)	44.1	(<1)	
CaO	0.06	(1)	0.03	(<1)	0.13	(<1)	0.07	0.04	(1)	0.05	(<1)	0.06	(1)	0.11	(1)	
MnO	0.29	(2)	0.49	(2)	0.52	(1)	0.22	0.31	(2)	0.30	(1)	0.33	(1)	0.37	(1)	
FeO	11.7	(1)	22.0	(2)	23.2	(<1)	7.8	12.3	(1)	12.0	(<1)	13.4	(2)	15.6	(1)	
Total	100.6		100.4		100.9		101.1	99.5		99.4		99.0		99.1		
Fe/Mn	40.2	(25)	44.5	(14)	44.0	(5)	34.7	38.6	(23)	39.3	(14)	39.6	(3)	41.4	(13)	
Fe/Mg	0.14	(<1)	0.31	(<1)	0.34	(<1)	0.09	0.15	(<1)	0.14	(<1)	0.16	(<1)	0.20	(<1)	
Mn/Mg	0.0034	(2)	0.0070	(2)	0.0077	(1)	0.0025	0.0038	(2)	0.0036	(1)	0.0041	(1)	0.0048	(1)	
Mg#	87.9	(1)	76.2	(<1)	74.8	(1)	92.2	87.3	(1)	87.5	(<1)	85.9	(1)	83.4	(1)	

* Fe/Mn, Fe/Mg, and Mn/Mg calculated from molar values.

* Olivine with Mg# <80 represents diogenite olivine.

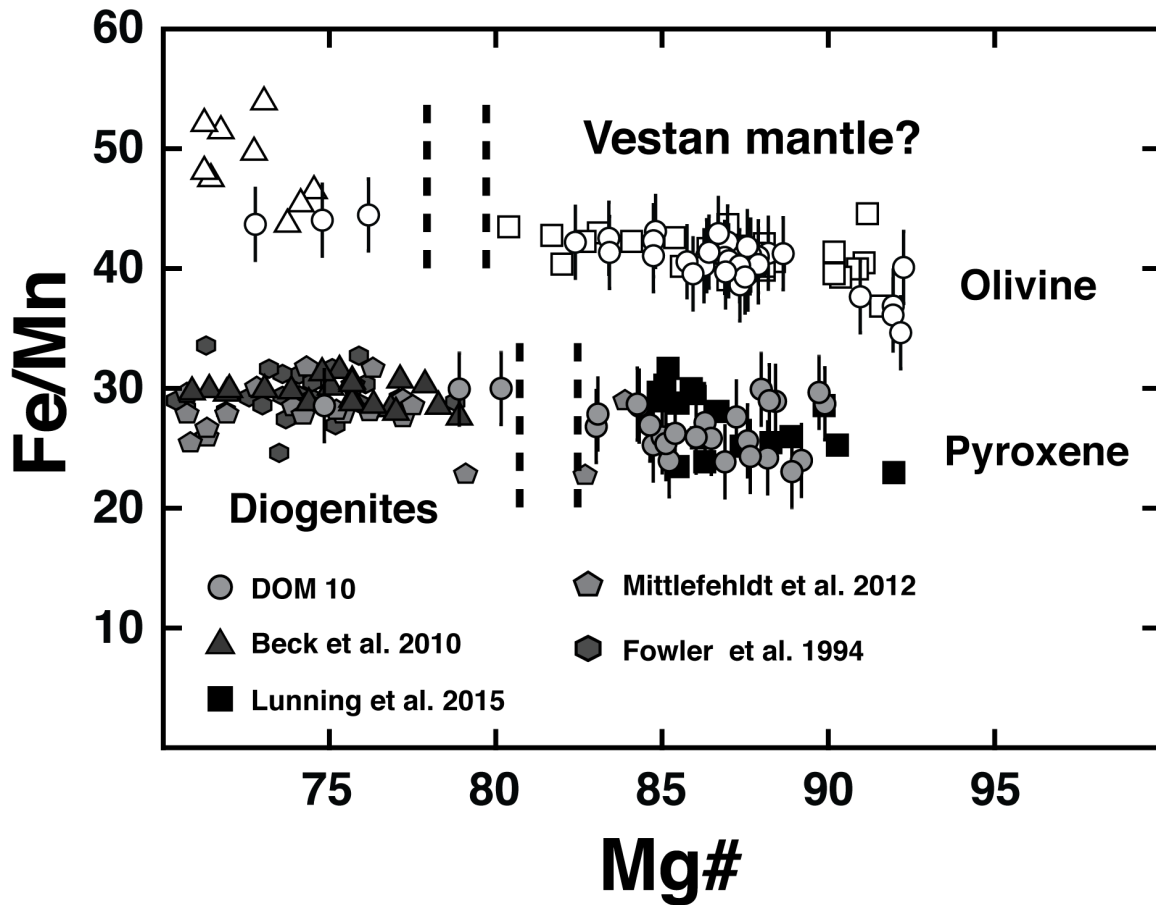


Figure 2.4 Fe/Mn Ratio Vs. Mg# Vestan Olivine and Pyroxene

Plot of Fe/Mn vs. Mg# in olivines and pyroxenes from DOM 10 (unfilled and filled circles, respectively). Diogenite data are shown as unfilled and filled triangles, respectively (Beck et al. 2010). Data for similar Mg-rich monomineralic olivine and pyroxene clasts in GRO 95 howardites are represented by unfilled and filled squares, respectively (Lunning et al. 2015). The vertical dashed lines mark compositional gaps between diogenites and Mg-rich harzburgite clasts. Additional diogenite data from Mittlefehldt et al. 2012 (filled pentagons) and Fowler et al 1994 (filled hexagons) are shown to help emphasize the compositional gap.

Table 2.2. Representative mineral Chemistry for Mg-rich pyroxene grains.

	DOM 10100,8				DOM 10105,6				DOM 10120,6				DOM 10837,7									
n	4		2		5		2		2		3		4		4		3		3		2	
SiO ₂	55.3	(2)	56.2	(1)	56.9	(1)	57.5	(<1)	57.7	(1)	55.3	(<1)	57.1	(2)	55.4	(1)	57.3	(3)	55.0	(3)	56.8	(3)
TiO ₂	0.05	(1)	0.04	(2)	0.04	(1)	b.d.		b.d.		0.09	(2)	0.03	(1)	0.05	(2)	b.d.		0.10	(1)	0.04	(<1)
Al ₂ O ₃	0.49	(2)	0.68	(2)	0.39	(3)	0.08	(4)	0.10	(1)	1.44	(2)	0.32	(8)	0.67	(4)	0.07	(1)	1.47	(13)	0.29	(1)
Cr ₂ O ₃	0.80	(6)	0.64	(1)	0.79	(3)	0.69	(2)	0.53	(2)	0.91	(3)	0.43	(3)	0.41	(1)	0.34	(16)	1.10	(4)	0.57	(1)
MgO	29.3	(2)	31.8	(<1)	32.5	(1)	34.2	(1)	34.5	(4)	29.9	(<1)	32.7	(3)	29.0	(1)	34.0	(5)	30.6	(3)	32.9	(2)
CaO	0.68	(3)	0.93	(1)	0.53	(1)	0.72	(13)	0.15	(1)	1.30	(3)	0.64	(3)	0.89	(4)	0.18	(2)	1.43	(19)	0.65	(2)
MnO	0.43	(2)	0.41	(<1)	0.34	(<1)	0.31	(3)	0.24	(<1)	0.39	(1)	0.35	(1)	0.46	(1)	0.27	(2)	0.37	(1)	0.37	(1)
FeO	12.9	(<1)	9.8	(1)	9.2	(1)	7.4	(2)	6.9	(1)	10.9	(1)	9.1	(1)	13.8	(<1)	7.9	(6)	9.6	(1)	8.9	(<1)
Na ₂ O	b.d.		b.d.		b.d.		b.d.		b.d.		b.d.		b.d.		b.d.		b.d.		b.d.		b.d.	
Total	100.0		100.5		100.7		100.9		100.1		100.2		100.6		100.7		100.1		99.7		100.4	
Fe/Mn	30.0	(11)	24.0	(6)	27.1	(1)	24.0	(23)	28.7	(1)	27.9	(8)	25.8	(11)	29.9	(3)	28.9	(4)	26.0	(8)	23.9	(6)
Fe/Mg	0.25	(<1)	0.17	(<1)	0.16	(<1)	0.12	(<1)	0.11	(<1)	0.20	(<1)	0.16	(<1)	0.27	(<1)	0.13	(1)	0.18	(<1)	0.15	(<1)
Mn/Mg	0.0083	(<1)	0.0072	(<1)	0.0059	(<1)	0.0051	(6)	0.0039	(<1)	0.0073	(2)	0.0061	(2)	0.0089	(1)	0.0045	(4)	0.0068	(3)	0.0063	(1)
Mg#	80.2	(1)	85.2	(2)	86.3	(1)	89.2	(2)	89.9	(<1)	83.1	(1)	86.5	(1)	78.9	(1)	88.4	(9)	85.0	(2)	86.9	(<1)
En	79.1	(1)	83.7	(2)	85.4	(1)	88.0	(1)	89.6	(1)	81.0	(2)	85.4	(1)	77.6	(1)	88.1	(9)	82.6	(5)	85.8	(<1)
Wo	1.3	(1)	1.8	(<1)	1.0	(<1)	1.3	(3)	0.3	(<1)	2.5	(1)	1.2	(1)	1.7	(1)	0.3	(<1)	2.8	(4)	1.2	(<1)

*Analyses with Mg# <85 correspond to diogenite material, although the boundaries may not be well defined.

Table 2.2. Continued.

n	DOM 10838,6						DOM 10839,6							
	3		4		3		3		2		2		5	
SiO ₂	56.3	(3)	55.5	(1)	56.6	(1)	55.6	(1)	57.2	(2)	56.8	(2)	54.0	(2)
TiO ₂	0.03	(3)	0.14	(1)	b.d.		0.06	(1)	b.d.		0.03	(1)	0.07	(1)
Al ₂ O ₃	0.16	(4)	1.60	(6)	0.23	(1)	0.99	(2)	0.12	(4)	0.38	(1)	0.54	(2)
Cr ₂ O ₃	0.28	(4)	1.08	(6)	0.63	(3)	0.85	(1)	0.61	(1)	0.69	(3)	0.60	(2)
MgO	34.3	(<1)	30.6	(1)	31.9	(2)	31.1	(1)	34.2	(<1)	32.6	(1)	26.3	(1)
CaO	0.28	(3)	1.71	(<1)	0.42	(1)	1.05	(1)	0.15	(3)	0.62	(2)	1.13	(1)
MnO	0.33	(1)	0.37	(1)	0.38	(1)	0.36	(<1)	0.23	(1)	0.30	(2)	0.55	(1)
FeO	7.6	(1)	9.5	(1)	10.3	(1)	9.5	(1)	7.0	(2)	8.5	(1)	15.8	(1)
Na ₂ O	b.d.		b.d.		b.d.		b.d.		b.d.		b.d.		b.d.	
Total	99.3		100.5		100.5		99.5		99.5		99.9		99.0	
Fe/Mn	23.1	(6)	25.4	(6)	27.0	(6)	26.3	(2)	29.7	(7)	27.6	(14)	28.6	(5)
Fe/Mg	0.12	(<1)	0.17	(<1)	0.18	(<1)	0.17	(<1)	0.11	(<1)	0.15	(<1)	0.34	(<1)
Mn/Mg	0.0054	(2)	0.0069	(2)	0.0067	(1)	0.0065	(1)	0.0039	(2)	0.0053	(3)	0.0118	(2)
Mg#	88.9	(1)	85.1	(1)	84.6	(1)	85.4	(<1)	89.7	(3)	87.2	(1)	74.8	(1)
En	88.4	(1)	82.3	(2)	84.0	(2)	83.7	(<1)	89.5	(3)	86.2	(1)	73.1	(1)
Wo	0.5	(1)	3.3	(1)	0.8	(<1)	2.0	(<1)	0.3	(<1)	1.2	(<1)	2.3	(<1)

*Analyses with Mg# <85 correspond to diogenite material, although the boundaries may not be well defined.

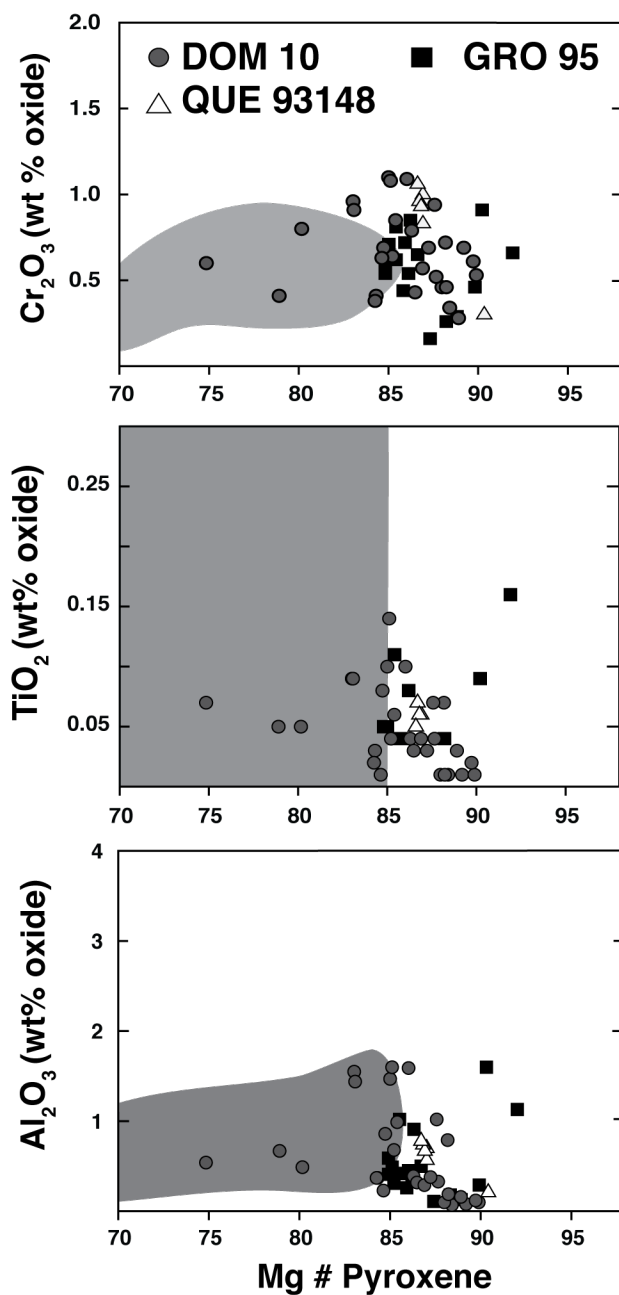


Figure 2.5 Minor-element Variation in Mg-rich Pyroxenes

Minor elements vs. Mg# in orthopyroxenes. No correlation exists between major and minor element compositions. Diogenite data (gray areas) are from Mittlefehldt et al. (2012). Data for GRO 95 howardites and QUE 93148 are from Lunning et al. (2015b) and Floss (2002), respectively.

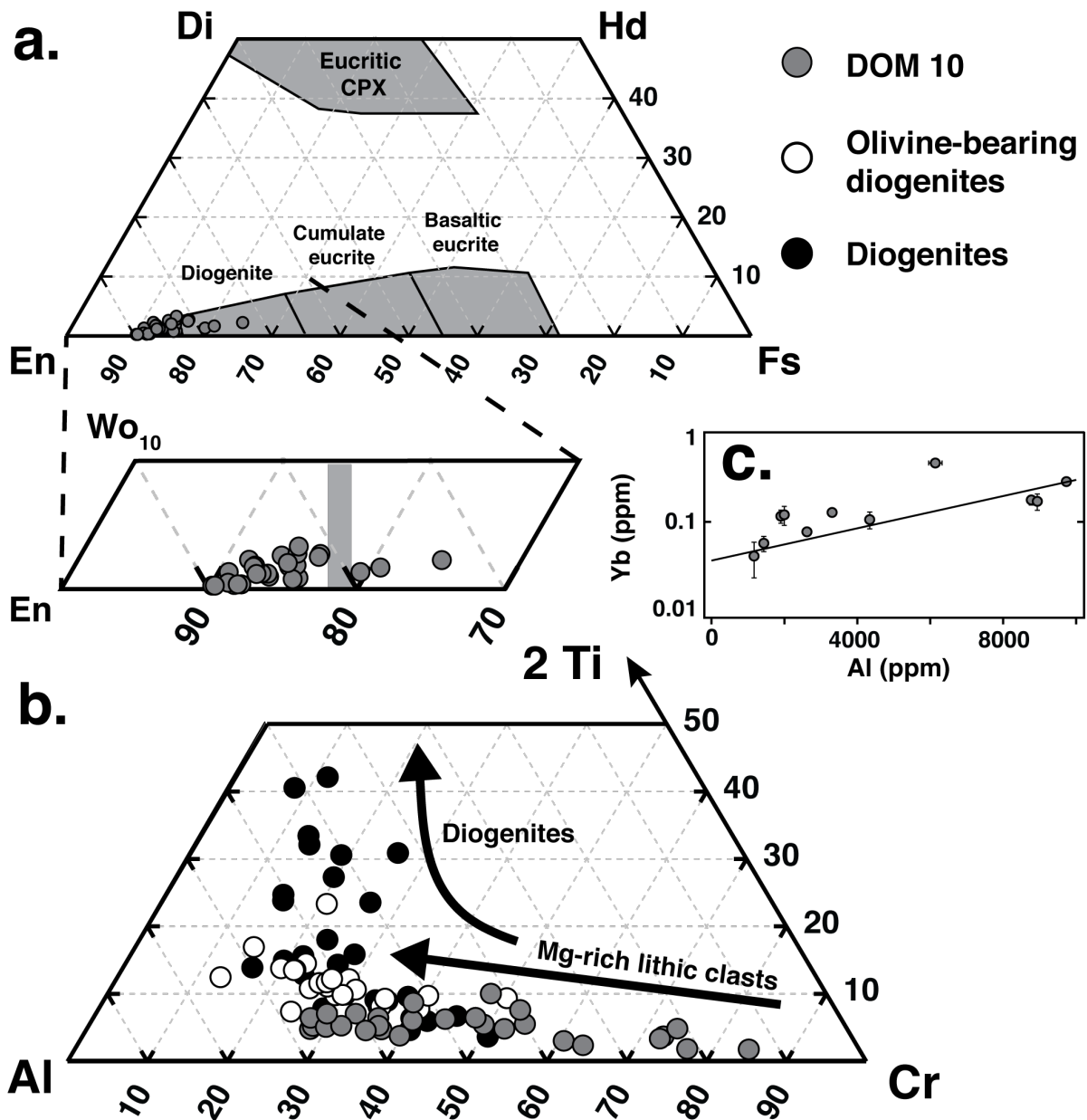


Figure 2.6 Chemistry of Diogenite and Mg-rich Pyroxenes

a) Pyroxene quadrilateral with Mg-rich pyroxene from this study shown as filled circles. Fields for other HED lithologies are from Beck et al. (2010). For clarity, an exploded view of the Mg-rich pyroxene and diogenite region is shown; although small, the compositional gap is still apparent. b) Ternary plot of Cr-Al-2Ti cations in Mg-rich pyroxene. The Mg-rich pyroxenes from DOM 10 show a continuous trend distinct from diogenites. Data for diogenites from Mittlefehldt et al. (2012) and Fowler et al. (1995). c) Variation of Yb with Al. in DOM 10 Mg-rich pyroxenes.

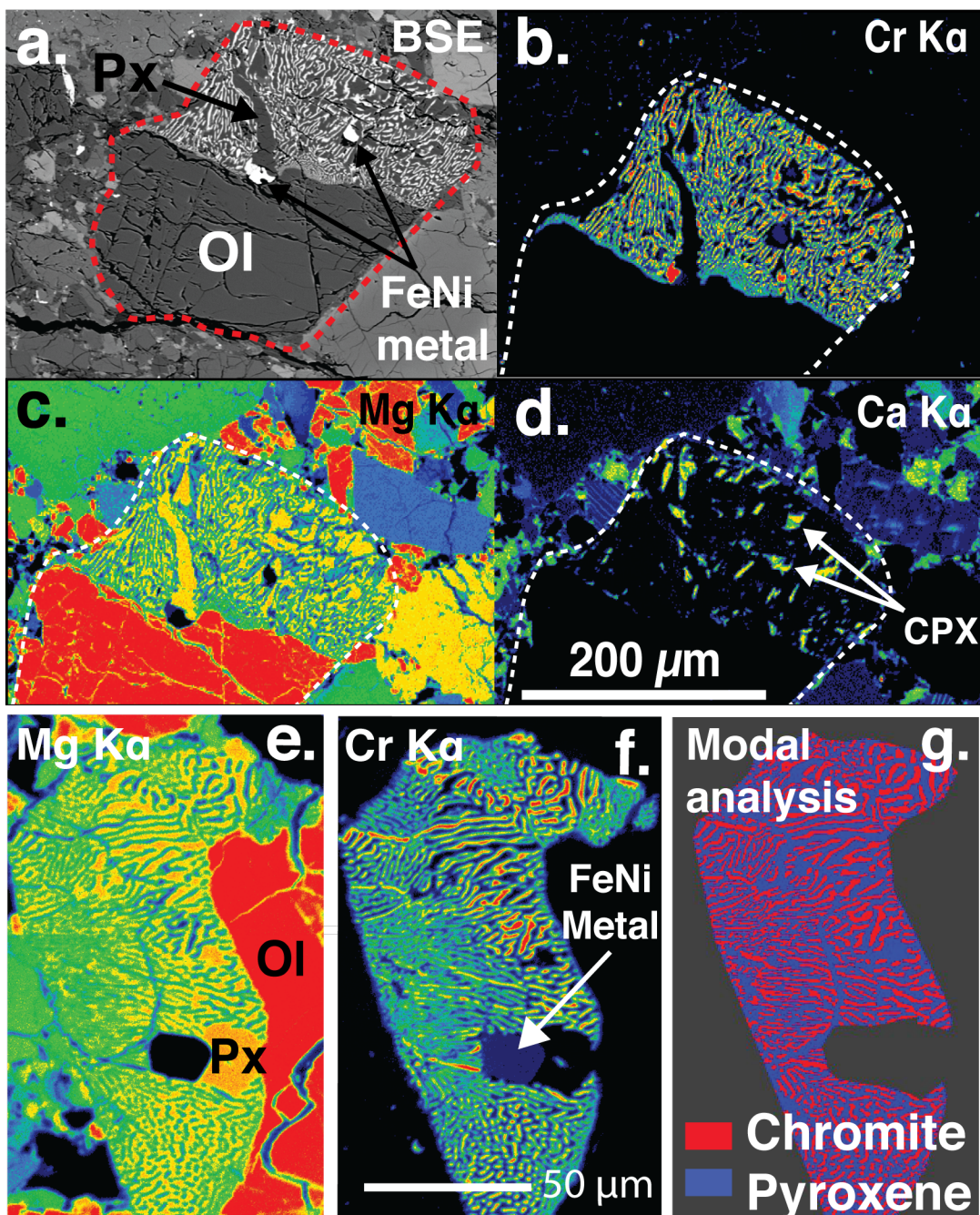


Figure 2.7 Symplectites in Mg-rich Harzburgites

Chromite-orthopyroxene symplectites containing other phases. (a) Bright grains are FeNi metal. (b-d) Elemental x-ray maps of Cr, Mg, and Ca, respectively, showing the distribution of elements within the symplectite. The Cr x-ray map does not illustrate the diffusion of Cr in the adjacent olivine, which is due to saturation of the image by chromite within the symplectite (see text). FeNi metal contains measurable Cr and can be seen in the Cr x-ray map. Clinopyroxene is indicated by brighter spots within the Ca x-ray map. (e-g) Mg and Cr elemental x-ray maps used to produce modal analysis map of symplectites (g). This technique allows for accurate modal abundance determinations using ENVI, which aids in reconstructing bulk chemistry.

Table 2.3. Mineral chemistry of phases associated with symplectite intergrowth (wt.% oxide).

Oxide	OI	OI	OI	OI	OI	OI	Oxide	Px	Px	Px	Px	Px
P ₂ O ₅	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	SiO ₂	56.6	55.7	56.2	53.7	56.8
SiO ₂	40.2	39.7	39.8	40.0	40.5	40.6	TiO ₂	b.d.	0.11	0.10	0.06	0.04
TiO ₂	b.d.	b.d.	b.d.	0.03	b.d.	b.d.	Al ₂ O ₃	0.24	2.91	2.43	0.49	0.22
Al ₂ O ₃	0.03	0.03	0.03	b.d.	b.d.	b.d.	Cr ₂ O ₃	0.82	1.41	1.23	1.73	0.91
Cr ₂ O ₃	0.20	0.08	0.08	0.04	0.1	0.1	MgO	33.6	33.7	34.0	18.2	34.0
MgO	48.1	47.6	47.5	47.2	50.9	50.9	CaO	0.90	1.11	1.13	22.4	0.82
CaO	0.03	0.05	0.05	0.05	0.05	b.d.	MnO	0.36	0.21	0.20	0.20	0.33
MnO	0.27	0.32	0.30	0.31	0.22	0.22	FeO	8.20	5.08	5.01	3.28	7.62
FeO	12.0	12.6	12.6	12.6	7.76	7.78	Na ₂ O	b.d.	b.d.	b.d.	0.28	b.d.
NiO	b.d.	b.d.	b.d.	0.03	b.d.	b.d.	Total	100.8	100.2	100.3	100.3	100.8
Total	100.9	100.5	100.4	100.2	99.5	99.6						

Cation formula based on 4 oxygen							Cation formula based on 6 oxygen					
P							Si	1.887	1.918	1.931	1.965	1.967
Si	0.984	0.986	0.989	0.991	0.990	0.991	Ti		0.003	0.003		
Ti				0.001			Al	0.018	0.118	0.099	0.010	0.009
Al	0.001	0.001	0.001				Cr	0.114	0.038	0.033	0.023	0.025
Cr	0.002	0.002	0.004	0.001	0.001	0.002	Mg	1.721	1.730	1.744	1.738	1.753
Mg	1.758	1.755	1.762	1.745	1.854	1.851	Ca	0.026	0.041	0.042	0.033	0.030
Ca	0.001	0.001	0.001	0.001	0.001		Mn	0.011	0.006	0.006	0.011	0.009
Mn	0.007	0.006	0.006	0.006	0.005	0.005	Fe	0.269	0.146	0.144	0.238	0.220
Fe	0.261	0.261	0.247	0.262	0.158	0.159	Na					
Ni				0.001			Total	4.047	4.001	4.001	4.018	4.016
Total	3.015	3.013	3.009	3.008	3.009	3.008						

Fe/Mn	44.4	38.7	41.2	40.4	34.5	35.2	Fe/Mn	22.4	23.4	25.0	16.5	23.7
Fe/Mg	0.14	0.15	0.15	0.15	0.09	0.09	Fe/Mg	0.14	0.08	0.08	0.10	0.13
Mn/Mg	0.0032	0.0038	0.0036	0.0037	0.0025	0.0024	Mn/Mg	0.0061	0.0036	0.0033	0.0061	0.0053
Mg#	87.7	87.1	87.1	86.9	92.1	92.1	Mg#	88.0	92.2	92.4	90.8	88.8
							En	86.5	90.2	90.4	50.3	87.5
							Wo	1.6	2.1	2.2	44.6	1.5

Table 2.3. Continued.

Spinel oxide weight %				FeNi metal elemental weight %		
	lamellae	lamellae	lamellae			
SiO ₂	0.09	0.14	0.10	n	2	2
TiO ₂	0.13	0.13	0.16	Si	0.04 (1)	0.05 (1)
Al ₂ O ₃	3.47	3.53	3.30	S	b.d.	b.d.
V ₂ O ₃	0.64	0.68	0.66	Fe	92.9 (5)	93.8 (5)
Cr ₂ O ₃	65.5	64.7	65.1	Co	1.20 (1)	1.39 (1)
MgO	6.30	6.19	6.15	Ni	3.60 (10)	2.71 (1)
CaO	0.03	0.05	0.04	P	b.d.	b.d.
MnO	0.55	0.59	0.59	Mg	b.d.	b.d.
FeO	22.8	23.0	23.0	Al	b.d.	b.d.
Total	99.5	99.0	99.1	Ti	b.d.	b.d.
				Ca	0.05 (1)	b.d.
				Cr	1.60 (4)	1.27 (61)
				Total	99.4	99.2

Pyroxenes in symplectites occur as both ortho- and clinopyroxene, although clinopyroxene is not ubiquitous, further suggesting compositional variability (e.g. Figures 2.7c, 2.7d). The composition of orthopyroxene within the symplectites is similar to the host orthopyroxene. Minor-element concentrations within symplectite pyroxenes are variable with Cr_2O_3 concentrations ranging from 0.8 to 1.7 wt.% (Table 2.3). Some of the Cr in the pyroxene analysis may be attributed to adjacent chromite; however, cation totals suggest only minor contamination, if any, and indicate that contamination cannot be used to explain the >1 wt.% Cr concentrations in the pyroxenes. Locally, FeNi metal is observed within the symplectites (Figures 2.1a, 2.7a) and contains Cr concentrations up to 2 wt. % (Table 2.3).

Olivines near symplectites are enriched in Cr_2O_3 , relative to core compositions, by an order of magnitude. As an example, the symplectite shown in Figure 2.2 (Table 2.4) contains ~0.4 wt.% Cr_2O_3 near symplectite boundaries, while EMP analyses conducted more than 100 mm away from symplectites show Cr_2O_3 concentrations of ~0.06 wt.% (Figure 2.8). The apparent Cr_2O_3 diffusion into adjacent olivine is not evident in Figures 2.7b or 2.7f due to the saturation of the detector caused by the chromite in the symplectites; however, Figure 2.8 illustrates strong evidence for Cr diffusion into olivine adjacent to symplectites. Further supporting the argument of Cr diffusion is the morphology of the symplectites, which suggests that the olivine grains are being replaced (e.g. Figure 2.2).

Our reconstructed bulk compositions show variability between symplectites. Table 2.3A shows the average composition of symplectite phases used in bulk composition reconstructions. Modal analysis and bulk composition reconstructions are presented in Tables 2.4A and 2.5A, respectively. Additionally, we collected broad-beam analyses to compare with bulk composition calculations (Table 2.6A). Our modal analysis of symplectites indicates varying proportions of orthopyroxene and chromite. This observation is further substantiated by the variation in bulk composition (Table 2.5A), which show that SiO_2 concentrations vary by a factor of almost two.

Trace Element Chemistry

Minor- and trace-element concentrations determined using LA ICP-MS for representative Mg-rich olivine and pyroxene minerals are reported in Tables 2.5 and 2.6, respectively. In addition to Mg-rich grains, diogenite orthopyroxene was analyzed for comparison and is indicated by Mg# <85. Unabridged tables of trace element concentrations in olivine and pyroxene can be found in the appendix (Tables 2.7A and 2.8A, respectively).

Concentrations of Ni and Co in Mg-rich olivines range from 2 to 115 ppm and 9 to 43 ppm, respectively. Incompatible elements are depleted relative to CI chondrites, with Y concentrations ranging from 0.02 to 1.5 ppm (Table 2.5). Mg-rich olivines are depleted in REE relative to CI chondrites and either do not have concentrations above detection limits or have strong Ce anomalies (Ce/Ce^* values >1.5 or <0.5), indicating that trace-element concentrations have been compromised (Floss and Crozaz 1991).

Rare earth element concentrations (REE) in Mg-rich pyroxenes (Mg# ≥85) are depleted relative to CI chondrites and show LREE enrichments relative to typical low-Ca pyroxene REE patterns observed in diogenites: CI-normalized La/Tm = 0.2 to 1.2 with

Table 2.4. Mineral chemistry for symplectite-bearing Mg-rich clast (wt.% oxide).

Oxide	Ol	Ol	Ol	Ol	Ol	Ol	Ol	Oxide	Px	Px	Px	Px	Px	Px
P ₂ O ₅	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	SiO ₂	55.0	55.0	55.4	52.5	52.7	52.6
SiO ₂	39.8	39.8	39.7	39.7	39.7	39.7	39.9	TiO ₂	0.29	0.29	0.25	0.49	0.46	0.41
TiO ₂	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	Al ₂ O ₃	1.08	1.16	0.95	1.95	1.60	1.56
Al ₂ O ₃	b.d.	b.d.	0.03	b.d.	b.d.	0.03	b.d.	Cr ₂ O ₃	1.01	1.05	0.89	1.40	1.31	1.30
Cr ₂ O ₃	0.21	0.24	0.16	0.17	0.11	0.09	0.05	MgO	30.6	30.3	30.9	18.0	18.0	18.1
MgO	45.0	45.0	45.1	44.9	44.5	44.5	44.5	CaO	1.85	1.90	1.61	20.6	20.7	20.5
CaO	0.06	0.05	0.06	0.06	0.07	0.07	0.07	MnO	0.39	0.38	0.38	0.27	0.26	0.28
MnO	0.35	0.35	0.37	0.36	0.39	0.40	0.38	FeO	10.0	10.0	10.1	4.9	4.8	4.8
FeO	15.9	15.7	15.9	15.7	16.2	16.2	16.1	Na ₂ O	0.03	b.d.	b.d.	0.21	0.20	0.20
NiO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	Total	100.2	100.1	100.6	100.3	100.0	99.7
Total	101.3	101.2	101.4	100.8	101.0	101.1	101.0	Cation formula based on 6 oxygen						
Cation formula based on 4 oxygen								Si	1.942	1.946	1.949	1.918	1.928	1.930
P								Ti	0.008	0.008	0.007	0.013	0.013	0.011
Si	0.991	0.992	0.990	0.992	0.993	0.993	0.997	Al	0.045	0.048	0.040	0.084	0.069	0.068
Ti								Cr	0.028	0.029	0.025	0.040	0.038	0.038
Al			0.001					Mg	1.613	1.599	1.622	0.980	0.985	0.993
Cr	0.004	0.005	0.003	0.003	0.002	0.002	0.001	Ca	0.070	0.072	0.061	0.806	0.812	0.805
Mg	1.671	1.671	1.673	1.673	1.661	1.661	1.657	Mn	0.012	0.011	0.011	0.008	0.008	0.009
Ca	0.002	0.001	0.002	0.002	0.002	0.002	0.002	Fe	0.295	0.295	0.297	0.149	0.146	0.146
Mn	0.007	0.007	0.008	0.008	0.008	0.008	0.008	Na	0.002			0.015	0.014	0.014
Fe	0.331	0.328	0.331	0.328	0.339	0.338	0.337	Total	4.015	4.008	4.013	4.013	4.013	4.013
Ni								Fe/Mn	25.1	25.9	26.6	17.8	17.9	17.1
Total	3.007	3.005	3.008	3.006	3.006	3.005	3.002	Fe/Mg	0.18	0.18	0.18	0.15	0.15	0.15
Fe/Mn	44.9	43.8	42.9	43.2	41.0	39.8	41.3	Mn/Mg	0.0073	0.0071	0.0069	0.0085	0.0083	0.0086
Fe/Mg	0.198	0.196	0.198	0.196	0.204	0.204	0.203	Mg#	84.5	84.4	84.5	86.8	87.1	87.2
Mn/Mg	0.0044	0.0045	0.0046	0.0045	0.0050	0.0051	0.0049	En	81.5	81.3	81.9	50.6	50.7	51.1
Mg#	83.5	83.6	83.5	83.6	83.1	83.1	83.1	Wo	3.5	3.7	3.1	41.7	41.8	41.4

* Analyses for olivine correspond to distance from symplectite boundary, increasing from left to right in the table.

* Analyses reported here are for the lithic clast shown in Figure 2.1f.

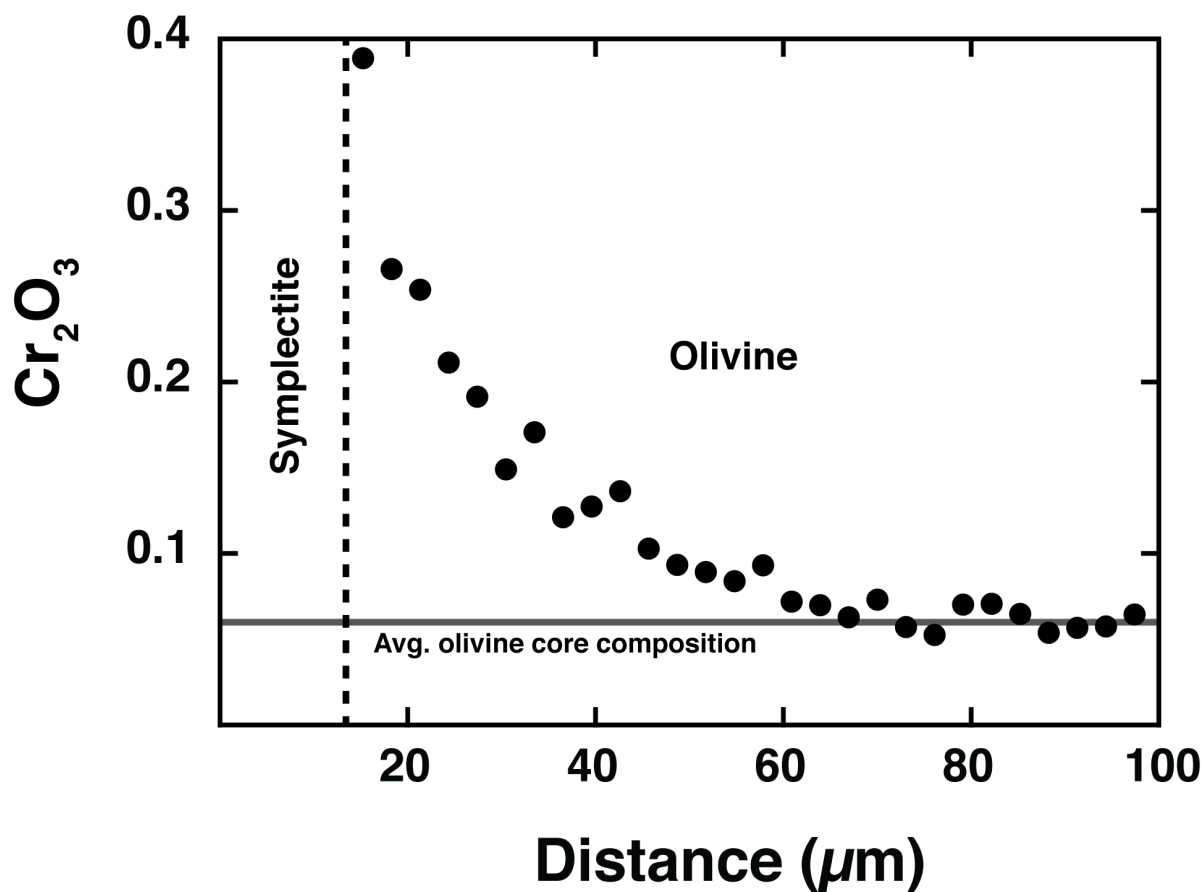


Figure 2.8 Diffusion Profile into Olivine

Diffusion profile of Cr_2O_3 away from symplectite boundary into the core of Mg-rich olivine. The diffusion profile is for the symplectite shown in Figure 1e. Concentration of Cr_2O_3 decreases from ~0.4 wt.% near symplectite boundary to less than ~0.06 wt.%. Average core composition of Mg-rich olivine is 0.06 wt.%.

Table 2.5. Representative trace element chemistry for Mg-rich olivines.

Mg#	DOM 10100,8		DOM 10105,6		DOM 10837,7									
	87	1σ	88.2	1σ	86.9	1σ	87.6	1σ	91.9	1σ	83.4	1σ	83.5	1σ
	μg/g		μg/g		μg/g		μg/g		μg/g		μg/g		μg/g	
Sc ^a	53.7	(4)	51.5	(21)	50.9	(7)	58.0	(8)	55.7	(9)	58.3	(38)	59.3	(37)
Ti	20.9	(5)	25.2	(21)	24.8	(16)	24.4	(10)	78.4	(15)	75.0	(73)	90.7	(52)
V	37.7	(2)	44.1	(10)	26.9	(4)	30.0	(3)	23.3	(3)	24.4	(12)	26.0	(9)
Cr	506	(3)	361	(10)	282	(7)	300	(2)	315	(3)	349	(15)	315	(7)
Co	18.2	(2)	25.4	(13)	23.9	(4)	18.0	(3)	9.9	(3)	29.6	(22)	25.4	(18)
Ni	15.5	(7)	63.9	(66)	32.8	(18)	12.3	(15)			37.0	(83)		
Zn	3.89	(22)			2.73	(36)								
Sr														
Y	0.024	(5)	1.40	(13)	0.884	(44)	0.066	(11)	0.138	(13)				
Ba					0.017	(5)								
Pb	0.137	(21)	0.299	(84)	0.186	(24)	0.063	(17)						
U					0.009	(2)								

^aMeasured values are consistently 1.5 to 2 times greater than real values.

*1σ error given in terms of the last decimal place.

Table 2.5 Continued.

Mg#	DOM 10838,6								DOM 10839,6							
	87.3		92.2		85.7		87		85.9		86.7		92.1			
	μg/g	1σ	μg/g	1σ	μg/g	1σ	μg/g	1σ	μg/g	1σ	μg/g	1σ	μg/g	1σ		
Sc	52.4	(5)	54.6	(8)	52.6	(4)	51.9	(12)	64.6	(30)	58.5	(13)	67.7	(42)		
Ti	10.2	(3)	26.3	(9)	68.9	(11)	58.0	(18)	30.4	(29)	31.3	(12)	26.9	(33)		
V	28.9	(2)	30.3	(4)	27.3	(2)	32.0	(6)	28.6	(10)	46.2	(8)	32.3	(10)		
Cr	205	(2)	431	(6)	266	(2)	353	(5)	454	(13)	489	(8)	483	(16)		
Co	17.8	(2)	8.2	(2)	11.3	(2)	42.7	(27)	15.9	(14)	15.1	(4)	9.5	(17)		
Ni	28.4	(13)	36.5	(19)	12.2	(8)	112	(10)	20.4	(48)	10.1	(15)	57.8	(87)		
Zn	2.62	(18)	2.31	(24)	1.67	(16)										
Sr	0.060	(6)	0.064	(9)	0.041	(5)	0.480	(39)								
Y	1.10	(4)	0.214	(16)	0.066	(6)	0.197	(24)	0.159	(47)	0.073	(15)	1.55	(16)		
Ba	0.031	(3)	0.026	(5)	0.023	(2)	0.160	(15)	0.036	(11)	0.034	(8)				
Pb	0.021	(4)									0.526	(139)				
U	0.010	(1)	0.007	(2)												

Table 2.6. Representative trace element chemistry for pyroxene.

Mg #	DOM 10105,6				DOM 10120,6				DOM 10837,7			
	86.3		85.4		86.4		86.0		85.0			
	µg/g	1σ	µg/g	1σ	µg/g	1σ	µg/g	1σ	µg/g	1σ		
Sc	85.2	(6)	82.3	(5)	77.7	(11)	86.3	(11)	77.1	(14)		
Ti	202	(2)	465	(3)	209	(4)	467	(6)	538	(9)		
V	82.4	(5)	134.0	(8)	89.6	(10)	147.9	(15)	141.0	(22)		
Cr	6181	(32)	2941	(16)	3039	(29)	7154	(69)	6676	(103)		
Mn	3210	(17)	4775	(27)	3104	(33)	2981	(27)	2900	(42)		
Co	19.6	(2)	11.5	(2)	10.5	(3)	10.6	(3)	9.3	(3)		
Ni	21.8	(11)	14.3	(12)	13.7	(17)	6.5	(12)				
Ga	0.112	(16)	0.101	(19)			0.242	(37)	0.259	(41)		
Sr	1.52	(2)	0.166	(9)	0.081	(13)	0.174	(14)	0.155	(17)		
Y	0.676	(23)	0.770	(22)	0.741	(33)	1.40	(4)	1.42	(5)		
Zr	0.845	(28)	0.236	(14)			3.32	(11)	1.01	(6)		
Nb	0.120	(14)										
Ba	0.008	(2)	0.013	(2)					0.062	(10)		
La	0.079	(5)	0.046	(6)	0.108	(14)	0.048	(8)	0.117	(15)		
Ce	0.446	(13)	0.126	(6)	0.133	(13)	0.208	(12)	0.301	(25)		
Pr	0.050	(4)	0.027	(3)	0.046	(6)	0.048	(6)	0.053	(9)		
Nd	0.229	(27)	0.125	(23)	0.268	(57)	0.347	(54)	0.288	(61)		
Sm	0.077	(16)	0.059	(10)								
Eu							0.025	(4)				
Gd	0.075	(16)	0.092	(18)	0.143	(40)	0.206	(43)	0.155	(35)		
Tb	0.017	(3)	0.016	(3)			0.024	(6)	0.031	(6)		
Dy	0.108	(15)	0.111	(14)	0.098	(26)	0.257	(29)	0.189	(38)		
Ho	0.022	(3)	0.031	(3)	0.018	(4)	0.046	(6)	0.056	(9)		
Er	0.075	(9)	0.095	(10)	0.083	(20)	0.156	(20)	0.194	(24)		
Tm			0.012	(3)			0.025	(6)	0.029	(7)		
Yb	0.078	(8)	0.128	(12)	0.116	(19)	0.176	(22)	0.170	(35)		
Lu			0.024	(4)								
Hf	0.030	(7)					0.121	(20)				
Pb	0.040	(8)			0.058	(16)						
Th									0.018	(5)		
U	0.004	(1)	0.004	(1)	0.012	(3)						

* Diogenite pyroxene is indicated by Mg# <85.

* Values in parentheses represent 1 standard deviation in terms of the last decimal place.

* Missing values are below detection limit or give bad statistics (i.e. 100σ/concentration >30)

Table 2.6. Continued

Mg #	DOM 10838,6						DOM 10839,6					
	88.9		87.6		85.1		85.4		77.0		84.0	
	µg/g	1σ	µg/g	1σ	µg/g	1σ	µg/g	1σ	µg/g	1σ	µg/g	1σ
Sc	53.3	(13)	86.3	(14)	79.5	(6)	47.6	(15)	106.2	(10)	85.5	(12)
Ti	153	(3)	197	(4)	799	(5)	549	(21)	698	(5)	124	(2)
V	91.0	(11)	93.8	(13)	154.6	(11)	62.8	(29)	91.0	(7)	69.2	(8)
Cr	1554	(16)	3696	(42)	7041	(60)	3117	(179)	4147	(30)	3645	(39)
Mn	1662	(30)	3101	(37)	2985	(19)	2076	(51)	3708	(25)	2889	(39)
Co	5.5	(4)	8.8	(4)	9.7	(2)	4.0	(3)	9.6	(3)	10.9	(3)
Ni	10.6	(16)			7.3	(8)	8.1	(7)	9.8	(8)	16.5	(14)
Ga					0.251	(23)	0.244	(24)	0.117	(27)		
Sr	0.437	(31)	1.46	(17)	1.16	(6)	4.64	(15)	0.376	(16)	0.202	(19)
Y	0.927	(50)	0.723	(46)	2.11	(4)	2.89	(7)	1.28	(3)	0.328	(31)
Zr	0.257	(42)	0.278	(48)	3.31	(8)	2.29	(10)	1.45	(5)		
Nb					0.123	(15)	0.120	(16)				
Ba	0.024	(6)			0.073	(10)	1.81	(7)	0.022	(4)	0.022	(5)
La	0.148	(18)			0.116	(16)	0.156	(10)	0.029	(7)	0.041	(9)
Ce	0.121	(15)	0.062	(12)	0.323	(34)	0.325	(12)	0.065	(6)	0.061	(8)
Pr	0.064	(11)			0.060	(6)	0.056	(4)	0.014	(3)		
Nd	0.285	(69)			0.362	(40)	0.299	(38)				
Sm					0.110	(21)	0.135	(20)				
Eu					0.014	(3)	0.039	(4)				
Gd	0.178	(41)			0.213	(21)	0.241	(27)	0.106	(26)		
Tb	0.039	(9)			0.045	(4)	0.050	(4)	0.021	(4)		
Dy	0.151	(37)	0.153	(33)	0.340	(25)	0.435	(28)	0.166	(26)		
Ho	0.037	(8)			0.075	(5)	0.111	(7)	0.052	(5)		
Er	0.089	(23)	0.157	(35)	0.254	(18)	0.383	(21)	0.179	(15)		
Tm					0.038	(4)	0.059	(5)	0.028	(4)		
Yb			0.120	(29)	0.282	(19)	0.455	(27)	0.216	(18)		
Lu					0.036	(6)	0.079	(6)	0.035	(6)		
Hf					0.091	(14)	0.078	(12)	0.067	(12)		
Pb					0.024	(7)	0.082	(9)			0.061	(16)
Th					0.021	(4)	0.033	(4)				
U					0.008	(2)	0.009	(2)				

* Diogenite pyroxene is indicated by Mg# <85.

* Values in parentheses represent 1 standard deviation in terms of the last decimal place.

* Missing values are below detection limit or give bad statistics (i.e. $100\sigma/\text{concentration} > 30$)

Table 2.6. Continued

DOM 10839,6				
Mg #	87.2		74.8	
	µg/g	1σ	µg/g	1σ
Sc	108	(4)	99.8	(9)
Ti	211	(8)	438	(4)
V	102	(3)	150	(1)
Cr	4909	(119)	4930	(35)
Mn	2913	(67)	5066	(34)
Co	12.8	(14)	13.5	(3)
Ni			2.6	(7)
Ga			0.094	(26)
Sr	0.658	(68)	0.321	(16)
Y	0.490	(79)	0.813	(18)
Zr	0.334	(92)	0.548	(33)
Nb				
Ba			0.011	(2)
La			0.033	(7)
Ce			0.061	(6)
Pr			0.017	(3)
Nd				
Sm			0.065	(11)
Eu			0.011	(2)
Gd				
Tb				
Dy			0.118	(24)
Ho			0.034	(5)
Er			0.086	(13)
Tm			0.015	(4)
Yb			0.114	(18)
Lu				
Hf				
Pb				
Th				
U				

* Diogenite pyroxene is indicated by Mg# <85.

* Values in parentheses represent 1 standard deviation in terms of the last decimal place.

* Missing values are below detection limit or give bad statistics (i.e. $100\sigma/\text{concentration} > 30$)

no appreciable Ce anomaly (Figures 2.9 and 2.10). We did not observe increased concentrations of Na, K, or P, which could indicate contamination of analyses by LREE-enriched phases (e.g. plagioclase or phosphate). Furthermore, plagioclase and phosphates are not observed within the lithic clasts, although they are observed within the matrix of the DOM 10 howardites. For all Mg-rich pyroxene grains, we calculated the CI-normalized Ce/Ce* in order to assess whether or not trace element results were adequate for interpretation, using the limits suggested by (Floss and Crozaz 1991): $2 \times \text{Ce}/(\text{La}+\text{Pr})$. Only REE data with Ce/Ce* values that fall between 1.5 and 0.75 are used for interpretation. We observe both positive and negative Ce anomalies, with Ce/Ce* ranging from 0.30 to 4.11. These anomalies indicate that REE elements for some Mg-rich pyroxenes have likely been redistributed due to terrestrial weathering. All pyroxenes with Mg# ≥ 85 exhibit variable CI-normalized Eu anomalies [$\text{Eu}/\text{Eu}^* = 2 \times \text{Eu}/(\text{Sm}+\text{Gd})$]: 0.02 to 0.76 (Figure 2.9). When calculating values for Eu/Eu* and Ce/Ce*, we use values for detection limits, only if two of the three values needed are above detection limit.

DISCUSSION

Similarities to Other Samples

Grosvenor Mountain Howardites

Lunning et al. (2015b) identified similar Mg-rich components in the GRO 95 howardite pairing group. The grains occur only as small (<600 μm) monomineralic fragments and therefore lack petrologic context. Moreover, the scarcity of Mg-rich pyroxene (only four grains of which were identified and two of which exhibited trace-element compositions that suggested re-mobilization of trace elements) further complicated interpretation. Consequently, only two pyroxene grains were used to interpret formation mechanisms. Contributing to the problem was the small and heavily fractured nature of the mineral grains, which allowed only a few LA ICP-MS spots to be analyzed per grain, thereby increasing the uncertainties. The harzburgite rock clasts in the current study provide a more robust data set from which we can evaluate the hypotheses set forth by Lunning et al. (2015b).

The major-element compositions of olivine and pyroxene fragments identified by Lunning et al. (2015b) overlap those in the harzburgite clasts from the DOM 10 howardites. Substantial overlap in minor-element concentrations also occurs (Figure 2.5). Although the major- and minor-element compositions are similar, the GRO 95 fragments lack the symplectite inclusions. We interpret the lack of symplectites as a sampling effect; although they are common in the DOM 10 fragments, they are not ubiquitous.

Trace-element compositions are also similar to those reported by Lunning et al. (2015b); however, the Mg-rich pyroxenes in this study exhibit a wider range in Sc (47-107 ppm), Ti (80-1739 ppm), and V (37-220 ppm) (Table 2.6). Concentrations of REE exhibit a more pronounced depletion in LREE relative to HREE in the GRO 95 Mg-rich pyroxenes (Figure 2.11a). We note, however, that the reported error for the GRO 95 Mg-rich pyroxenes overlaps the range in the DOM 10 pyroxenes. Additionally, we

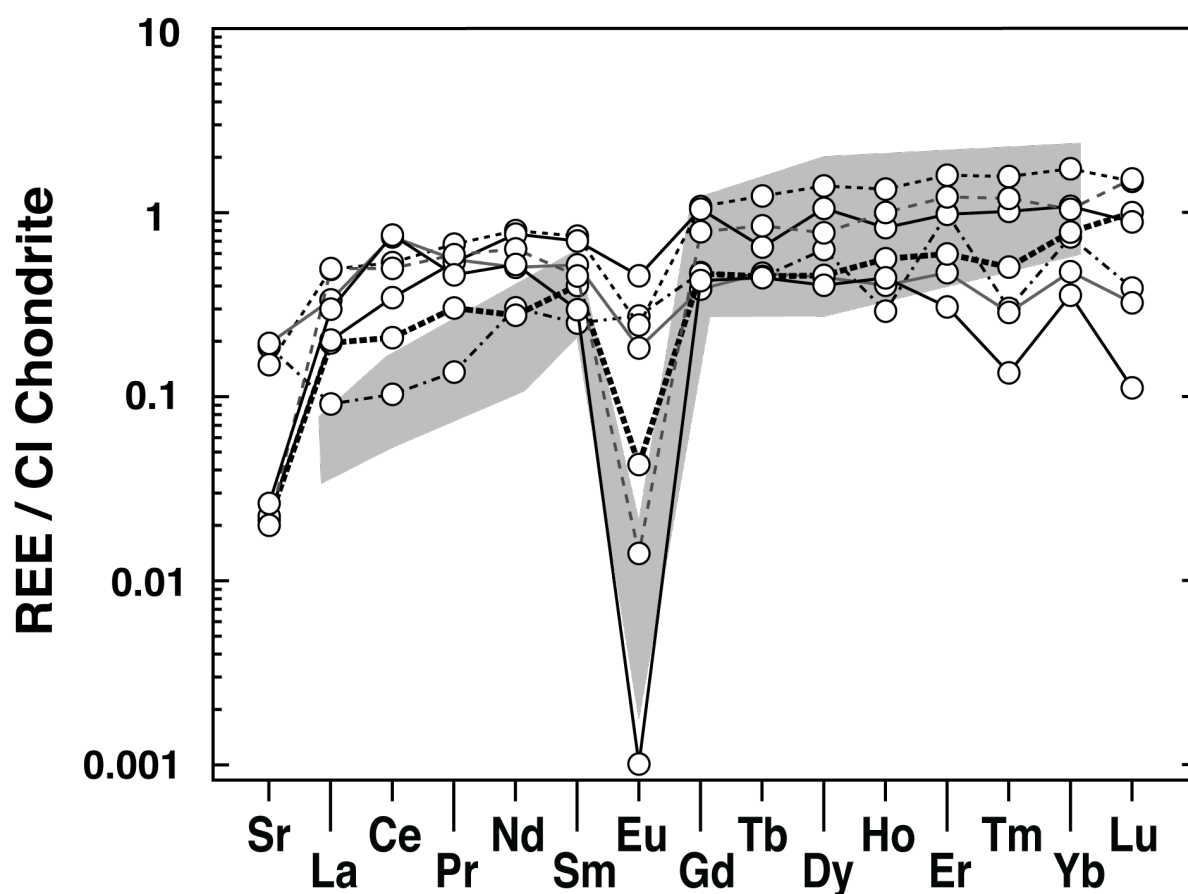


Figure 2.9 Rare Earth-Element Patterns of Mg-rich Pyroxenes

Rare-earth element patterns for Mg-rich pyroxenes compared to REE range for diogenites (Fowler et al. 1995). These data are used to define a range of REE concentrations in the DOM 10 Mg-rich pyroxenes in subsequent figures.

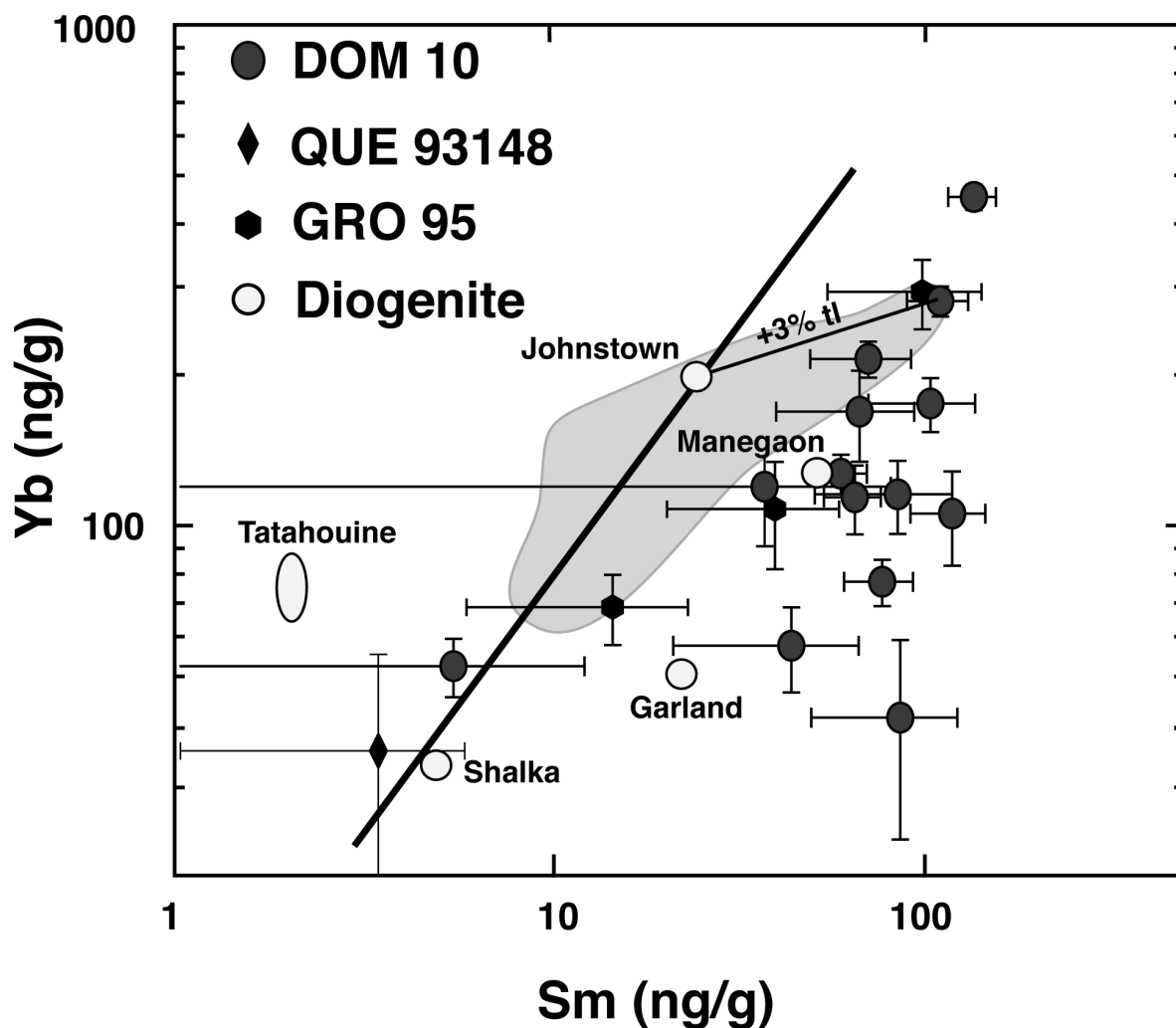


Figure 2.10 Trace-element Chemistry of Mg-rich Pyroxenes

Plot of Yb vs. Sm for Mg-rich pyroxenes in DOM 10 (filled circles; Lunning et al. 2015b), GRO 95 (filled hexagons; Floss 2002), and QUE 93148 (filled diamond; Floss 2002). The gray field defines the region occupied by orthopyroxenes in diogenites (Mittlefehldt 1994). Data for specific diogenites are shown as open circles and labeled accordingly (Mittlefehldt 1994). The plot indicates the Mg-rich pyroxenes could have formed from a melt enriched in LREE. Conversely, an addition of 3 % trapped melt (see figure) could produce the same enrichment (Mittlefehldt 1994). Trend line from Shalka to Johnstown defines chondritic ratios and could represent a fractionation sequence.

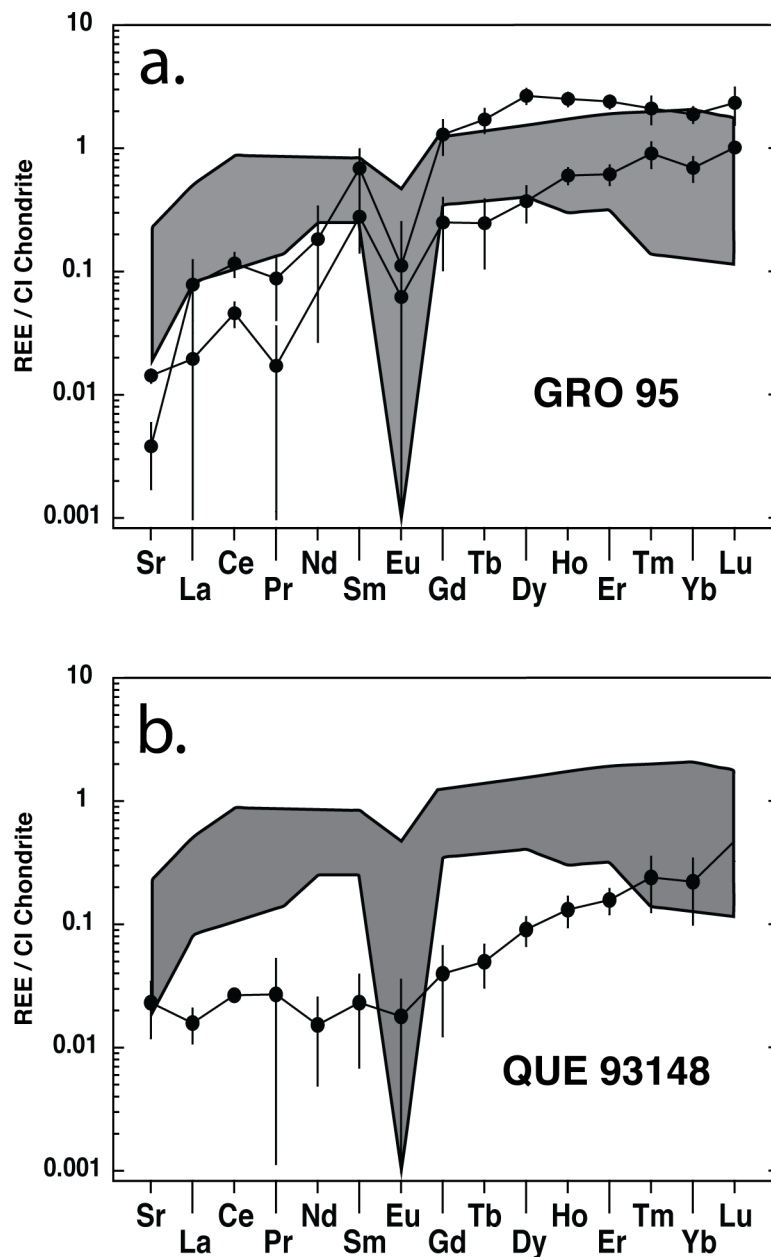


Figure 2.11 Comparison of Trace-element Chemistry in Mg-rich Pyroxenes

a) REE range for Mg-rich pyroxenes in DOM 10 (gray field), defined using Figure 9, compared to GRO 95 (black circles). b) Range of REE in DOM 10 Mg-rich pyroxenes compared to average orthopyroxene in QUE 93148 (Floss 2002).

observed variable Eu and Sr anomalies similar to those in the GRO 95 Mg-rich pyroxenes, although our data indicates these are not due to co-crystallization with plagioclase as proposed by Lunning et al. (2015b). Although small, the Ce anomalies in the GRO 95 Mg-rich pyroxenes can have profound implications for redistribution of REE (Floss and Crozaz 1991). Based on major-, minor-, and trace-element chemistry, we propose that the Mg-rich fragments of the GRO 95 and DOM 10 howardites share a common origin; however, we offer an alternative formation mechanism and differing explanations for chemical characteristics.

Queen Alexandra Range 93148

QUE 93148 is a 1.1 g ungrouped achondrite that shares some similarities in major-, minor-, and trace-element chemistry to the Mg-rich lithic clasts in DOM 10 howardites. Righter and Delaney (1997) showed that Cr_2O_3 and CaO concentrations in olivines differ from those of lodranites, ureilites, acapulcoites, and winonaites, suggesting that QUE 93148 is not a lodranite as originally classified. Additionally, Floss (2002) found that pyroxene in QUE 93148 exhibits a REE pattern distinct from typical low-Ca pyroxene, with a significant enrichment in LREEs (Figure 2.11b). Goodrich and Delaney (2000) concluded that the Fe/Mn and Fe/Mg systematics of QUE 93148 indicated a possible origin as a mantle residue from high degrees of melting, perhaps related to the HED parent body.

Olivine in QUE 9314 has an average Mg# of 85.7 and Fe/Mn of 39.4, well within the range of the DOM 10 olivines. Pyroxene in QUE 93148 also shows similar overlap. One noticeable difference in olivine composition between the two samples is the concentration of Cr_2O_3 , where QUE 93148 is enriched by a factor of 2 to 3 relative to DOM 10 olivines. Although the major- and minor-element geochemistry of olivine and pyroxene in QUE 93148 are comparable to the harzburgite clasts in the DOM 10 howardites (Figure 2.5), the CI-normalized trace-element concentrations are enriched in the latter (Figure 2.11b).

Figure 2.11b shows the CI-normalized REE range for Mg-rich pyroxene in DOM 10, compared to average orthopyroxene in QUE 93148. Although the overall trend and slope of DOM 10 and QUE 93148 orthopyroxenes appear to be similar, DOM 10 Mg-rich pyroxenes are enriched in LREE: $\text{La/Tm} = 0.2$ to 1.2 (DOM 10) and 0.02 to 0.11 (QUE 93148). In addition to LREE enrichments, the CI-normalized values for all REE are an order of magnitude greater in DOM 10 pyroxenes (Figure 2.11b).

The low trace-element concentrations and primitive chemical signature of QUE 93148 support the interpretations of Floss (2002) and Goodrich and Righter (2000) that QUE 93148 is a residue from a high degree of melting, possibly from the HED parent body mantle (Floss 2002). Although depleted relative to CI chondrites, such depletions as observed in QUE 93148 are not present in the GRO 95 or DOM 10 Mg-rich pyroxenes. At first glance, this seems to suggest that the Mg-rich pyroxenes in howardites identified by Lunning et al. (2015b) are not mantle in origin. However, we advocate for secondary processes to explain the elevated trace-element concentrations in DOM 10 Mg-rich pyroxenes.

Lunar Mg-suite

Both the lunar Mg-suite and the DOM 10 harzburgites are ultramafic, Mg-rich lithologies, with enriched REE concentrations; therefore, a comparison is warranted. The formation of the lunar Mg-suite evokes re-melting of magma ocean cumulates and assimilation or metasomatism by a KREEP-rich melt (e.g. Shearer and Papike 2005); however, Ni and Co concentrations within the GRO 95 and DOM 10 Mg-rich olivines are likely too low to be reconciled with a mechanism similar to the lunar Mg-suite (Table 2.5). Conversely, the low Ni, Co, and Cr concentrations in the DOM 10 harzburgite clasts could be the consequence of FeNi metal fractionation and low fO_2 . Moreover, DOM 10 and GRO 95 Mg-rich olivines do not record crustal contamination, which further rules out a mechanism analogous to the lunar Mg-suite (Table 2.5).

If the age of the Mg-rich components within the howardites were known, and if the ages determined were younger than any HEDs, we might be able to show evidence for a mechanism similar to the lunar Mg-suite. However, Vesta melted, differentiated, and fully solidified within a short time period (<150 m.y.; McSween et al. 2013 and references therein) and therefore, it is hard to reconcile processes applicable to the lunar Mg-suite operating on such a short time scale. Furthermore, the removal of the dominant heat source (^{26}Al) from the source region would preclude the re-melting of magma ocean cumulates.

Origin of Symplectites

The origin of symplectites in other rocks has prompted a long and ongoing debate (e.g. Albee et al. 1975; Bell et al. 1975; Elardo et al. 2012; Gooley et al. 1974). Numerous hypotheses have been proposed to explain formation of spinel-orthopyroxene symplectite assemblages: plagioclase-olivine reaction (Gooley et al. 1974), exsolution from olivine (Gooley et al. 1974), crystallization of trapped melt (Albee et al. 1975), and metasomatism (Elardo et al. 2012). Although formation involving the breakdown of Cr-rich garnet was suggested by Bell and Mao (1975), the pressures needed for garnet formation are not attainable on a small planetesimal, like Vesta. The absence of plagioclase in the harzburgite clast suggests that plagioclase-olivine reaction is not a viable explanation; therefore, we only discuss an origin as exsolution from olivine, trapped melt, and metasomatism.

Chromite-orthopyroxene symplectites occur in both QUE 93148 and the lunar Mg-suite rocks; thus, a comparison can provide constraints on the origin of the symplectites. Several types of symplectites occur in QUE 93148; however, the type 3 inclusions identified by Goodrich and Delaney (2000) are most similar to those in the DOM 10 harzburgite clasts. Type 3 symplectites in QUE 93148 occur as small (<20 μm), irregularly shaped intergrowths of chromite, orthopyroxene, and clinopyroxene in varying proportions. Goodrich and Delaney (2000) concluded that type 3 inclusions in QUE 93148 formed by exsolution from olivine. Their conclusion was anchored to the observation that the symplectites were volumetrically insignificant, and therefore could be recombined with the olivine, while only slightly increasing the Cr and Ca content of the olivine. The spatial correlation of symplectites along grain boundaries was attributed to the opportunity of a nucleation site and not an indication of trapped melt. An origin involving a trapped melt was further ruled out due to the high Cr_2O_3

concentration (~25 wt.%) of the reconstructed composition, which cannot be accommodated in a silicate melt.

Although the symplectites in QUE 93148 resemble those in the harzburgite clasts, specifically in mineralogy, composition, and morphology, we do not agree with the formation mechanism favored by Goodrich and Delaney (2000); although, we argue for a common origin for symplectites in QUE 93148 and DOM 10 harzburgite clasts. First, olivines abutting symplectites in QUE 93148 show higher Cr_2O_3 than the cores, which seems to indicate a diffusion of Cr into the olivine; a similar diffusion profile is observed in the DOM 10 harzburgites. Second, the small size of the symplectites could prohibit the identification of FeNi metal and sulfides within the symplectites, which could be the source of Cr in a trapped silicate-metallic melt, since metallic melts can accommodate large amounts of Cr at low $f\text{O}_2$.

The symplectites in the DOM 10 harzburgites are as much as an order of magnitude larger (e.g., 400 μm ; Figure 2.2); thus, recombination of their bulk composition into adjacent olivine would yield unsatisfactory stoichiometry. A cogent argument against exsolution from olivine is the presence of a Cr diffusion profile suggesting diffusion into the olivine rather than out. Based on these observations and the spatial correlation along olivine-olivine and olivine-orthopyroxene grain boundaries, we conclude that the symplectites in the DOM 10 harzburgites did not form by exsolution from olivine.

The lunar Mg-suite contains symplectites that are also similar in mineralogy and morphology to those in the DOM 10 howardites; however, the Cr_2O_3 in chromite lamellae differs slightly (~50 wt.%; Elardo et al. 2012). Elardo et al. (2012) argued against the accepted formation model (olivine-plagioclase reaction), instead proposing the symplectites formed via the infiltration of an exogenic melt. They reasoned that the stoichiometry of the olivine-plagioclase reaction was deficient in Cr and Fe, and therefore, addition of these elements was required. Moreover, textural (spatial correlation to grain boundaries and relict grain boundaries) and geochemical (Cr diffusion into olivine) evidence suggested they were produced by interaction of a melt with the host rock; however, no evidence of this melt was documented.

The symplectites in the DOM 10 harzburgite clast (e.g. Figure 2.2) share many similarities to those in QUE 93148 and the lunar Mg-suite. We posit, based on textural and geochemical information, the symplectites in the DOM 10 harzburgite clasts formed from the crystallization and reaction of a melt with olivine. Our hypothesis stems from (1) the spatial correlation of symplectites along grains boundaries (e.g. Figures 1b and 1f), (2) diffusion of Cr into adjacent olivine (Figure 2.8), (3) presence of FeNi metal in the assemblage, which could be the source of Cr (Figures 2.7b and 2.7f), and (4) preservation of a potential trapped melt (Figure 2.12b).

The preservation of a probable trapped melt provides strong support for the crystallization of a melt to produce the symplectites. The stoichiometry of this phase does not match a known mineral, and therefore suggests this phase could be a glass (Table 2.7), although the small size prevents us from identifying this phase as glass. The melt composition does not match our reconstructed bulk composition of the symplectites (Table 2.6A): 44.5 wt.% SiO_2 , 10.4 wt.% Cr_2O_3 , 17.4 wt.% MgO , 21.0 wt.% CaO , 1.56 wt.% Al_2O_3 , and 3.26 wt.% FeO . The difference between our reconstructed symplectite composition, broad beam analyses, and point analyses of the

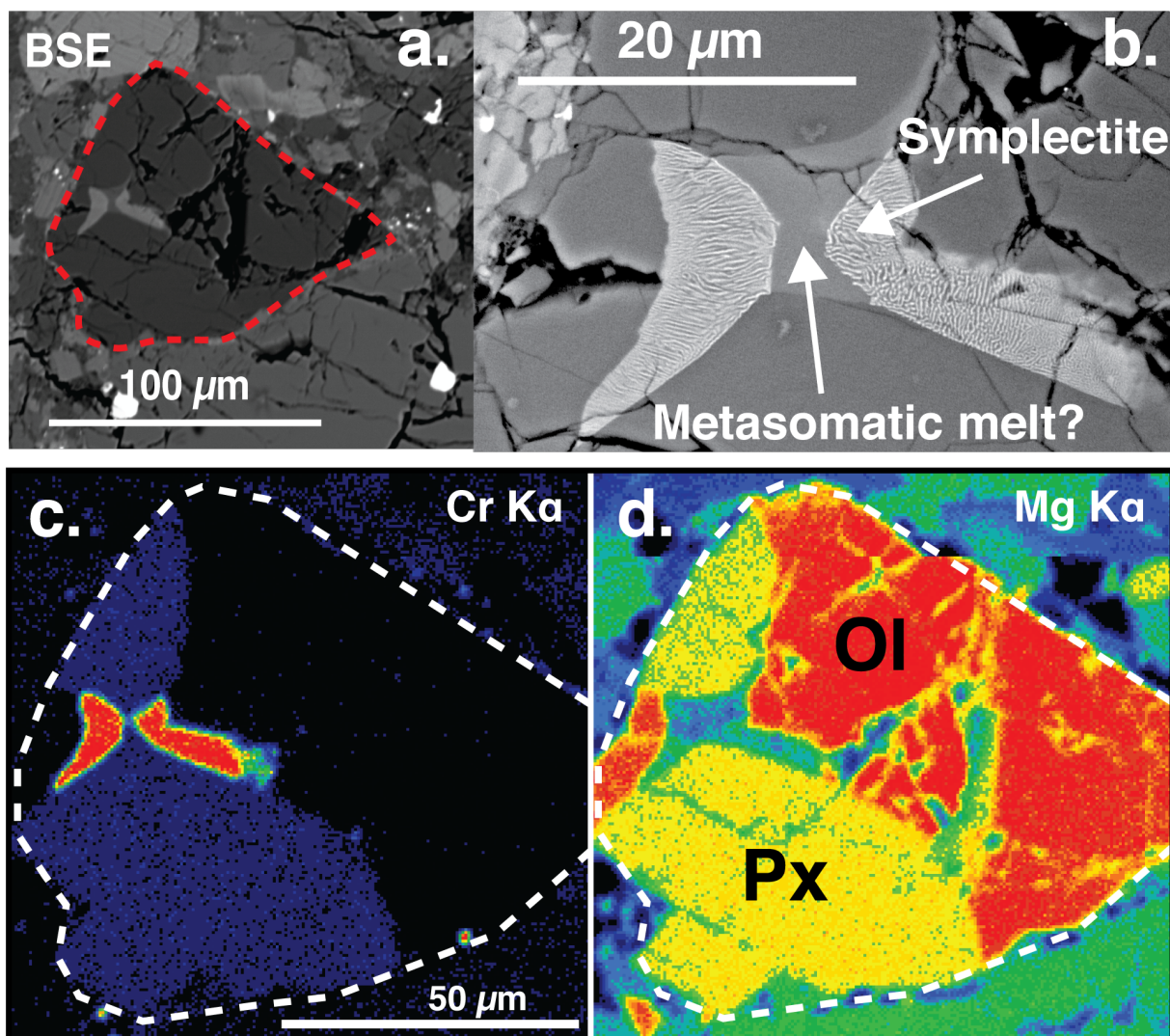


Figure 2.12 Harzburgite Clast with Trapped Melt

a) Lithic clast of Mg-rich olivine and pyroxene grains containing a chromite-orthopyroxene symplectite. b) The symplectite occurs at the boundary between grains and resembles a residual melt pocket or trapped infiltrating melt. Note there appears to be a chromite front migrating into the residual phases, which could be representative of a trapped metasomatic melt composition (see text; Table 2.7). c-d) Cr and Mg x-ray maps, which help delineate grain boundaries and phases shows the symplectite occurs at the boundary between four separate grains of olivine and pyroxene. We believe the phase between the symplectites in (b) could be a quenched melt, although the optical properties of this phase prohibit any conclusive evidence due to its small size.

Table 2.7. Composition of phases associated with the Mg-rich clast in Figure 2.12 (wt.% oxide).

Oxide	Px	Px	Oxide	OI	OI	Oxide	Symplectite*			Melt?*
SiO ₂	55.7	56.2	SiO ₂	40.5	40.6	SiO ₂	38.0	37.4	37.9	44.5
TiO ₂	0.11	0.10	TiO ₂	b.d.	b.d.	TiO ₂	0.12	0.11	0.10	0.13
Al ₂ O ₃	2.91	2.43	Al ₂ O ₃	b.d.	b.d.	Al ₂ O ₃	1.53	1.60	1.38	1.56
Cr ₂ O ₃	1.41	1.23	Cr ₂ O ₃	0.1	0.1	Cr ₂ O ₃	22.2	21.6	22.0	10.4
MgO	33.7	34.0	MgO	50.9	50.9	MgO	21.3	18.7	21.0	17.4
CaO	1.11	1.13	CaO	0.05	b.d.	CaO	6.72	9.95	7.35	21.0
MnO	0.21	0.20	MnO	0.22	0.22	MnO	0.30	0.29	0.31	0.19
FeO	5.08	5.01	FeO	7.76	7.78	FeO	9.68	8.75	9.69	3.26
Na ₂ O	b.d.	b.d.	NiO	b.d.	b.d.	Na ₂ O	0.06	0.08	0.06	0.11
Total	100.2	100.3	Total	99.5	99.6	Total	99.9	98.4	99.7	98.4
Cation formula based of 6 oxygen						Cation formula based on 6 oxygen				
Si	1.918	1.931	Si	0.990	0.991	Si				1.715
Ti	0.003	0.003	Ti			Ti				0.004
Al	0.118	0.099	Al			Al				0.071
Cr	0.038	0.033	Cr	0.001	0.002	Cr				0.316
Mg	1.730	1.744	Mg	1.854	1.851	Mg				1.000
Ca	0.041	0.042	Ca	0.001		Ca				0.866
Mn	0.006	0.006	Mn	0.005	0.005	Mn				0.006
Fe	0.146	0.144	Fe	0.158	0.159	Fe				0.105
Na			Ni			Na				0.008
Total	4.001	4.001	Total	3.009	3.008	Total				4.091
Fe/Mn	23.4	25.0	Fe/Mn	34.5	35.2	Fe/Mn	31.6	30.1	31.1	16.6
Fe/Mg	0.08	0.08	Fe/Mg	0.09	0.09	Fe/Mg	0.26	0.26	0.26	0.11
Mn/Mg	0.0036	0.0033	Mn/Mg	0.0025	0.0024	Mn/Mg	0.0081	0.0087	0.0083	0.0063
Mg#	92.2	92.4	Mg#	92.1	92.1	Mg#	79.7	79.2	79.4	90.5

* Point analysis of symplectite with 1 µm beam.

+ Analysis of possible metasomatic melt.

possible melt composition is likely due to error associated with broad beam analysis and the reconstruction process. If this phase is representative of a melt composition, it must contain both a silicate and metallic melt component because even at low fO_2 (IW-1) a silicate melt can only accommodate small amounts of Cr_2O_3 (<1 wt.%) (Elardo et al. 2012). The metallic melt component could be associated with descending FeS-FeNi melts during core formation.

We attempted to model the crystallization and reaction of the inferred melt composition with olivine using the MELTS numerical model (Ghiorso and Sack 1995; Smith and Asimow 2005); however, our efforts were unsuccessful in producing the symplectite assemblage. The failure to reproduce our observations likely results from the sensitivity of MELTS to the crystallization of spinel, the large uncertainties in the original melt composition, and the inability of MELTS to perform calculations below the IW buffer. Even with these shortcomings, some basic conclusions can be drawn about the origin of the symplectites. Reaction textures of the melt with olivine suggest that the melt composition was not in equilibrium with olivine, and the presence of a chromite front migrating into the melt phase indicates that chromite was a primary phase precipitating from the melt, conceivably with minor FeNi metal. Therefore, we hypothesize that reaction of the melt with the olivine yields the remaining phases – orthopyroxene and clinopyroxene. Although we favor crystallization of trapped melt and reaction with surrounding olivine as the symplectite-producing mechanism, we cannot discern an exogenic (melt infiltration) or endogenic (*in situ* melt generation) origin for the melt, although the disequilibrium between olivine and the melt argues for melt infiltration.

Evidence in Favor of and in Contradiction of a Mantle Origin

In Favor of

Multiple lines of evidence support a mantle origin for Mg-rich harzburgite clasts in howardites. The primitive composition of the Mg-rich lithic clasts in DOM 10 and GRO 95 howardites (Figures 2.4 and 2.6; Lunning et al. 2015b), as well as rare occurrences in other howardites (Mittlefehldt et al. 1998 and references therein), suggest that these fragments formed in the mantle of their parent body. In addition to their primitive major-element composition, the harzburgite clasts also have low Ni contents, consistent with the formation in a mantle residue that is in equilibrium with FeNi metal descending to the core (Lunning et al. 2015b). Further support for a mantle origin can be argued due to the presence of Cr in FeNi metal grains (e.g. Figure 2.1a). Chabot and Agee (2003) have shown that at low fO_2 ($\Delta IW-2$) and high temperature, conditions during core formation in a magma ocean, Cr becomes increasingly siderophile and will partition into the metallic phase. These chemical attributes of the harzburgites clasts support the conclusion that they originated in the mantle of their parent body (Vesta).

In Contradiction of

Although major- and minor-element chemistry suggests formation in the vestan mantle, the trace elements show a more evolved composition similar to that of the diogenites (Figure 2.9), which could indicate that the Mg-rich clasts are cumulates from shallow crustal magma chambers. Indeed, this could be used to support a fractional

crystallization trend between diogenites and the Mg-rich clasts; however, we offer an alternative explanation. The gaps in composition in both olivine and pyroxene (Figure 2.4) suggest different origins for diogenites and the Mg-rich harzburgites. The high Ni/Co ratios of Mg-rich olivines appear to be distinct from that of olivine within olivine diogenites (Figure 2.13), which also suggests no genetic relationship between the two (Shearer et al. 2010). We attribute the REE composition of the Mg-rich pyroxene to the symplectite-forming metasomatic event.

The infiltration of a silicate melt that is enriched in LREE during partial melting could have altered the original trace-element composition of the Mg-rich pyroxenes in DOM 10 (Barrat 2004). Further, this could explain the large variations in Sr and Eu anomalies, which Lunning et al. (2015b) suggested could be due to co-crystallization of plagioclase. The effect of an infiltrating melt can be evaluated in a manner similar to that used to evaluate a trapped interstitial melt. Barrat (2004) showed that increasing the trapped melt component will enhance the Eu/Eu* anomaly. Indeed, we do see very large and variable Eu anomalies, consistent with the effect of an infiltrating melt. Additionally, Barrat (2004) showed that LREE are extremely sensitive to the fraction of trapped melt and just 3 % trapped melt can cause a factor of ten enrichment in LREE. Large Eu anomalies could also be enhanced by the presumed low oxygen fugacity of the system (~IW-1.7 for QUE 93148; Goodrich and Delaney 2000).

An observation that is inconsistent with the hypothesis of co-genetic crystallization of plagioclase, put forth by Lunning et al. (2015b), is the trend exhibited by pyroxene on a plot of Al-Cr-2Ti (Figure 2.6b). If this trend represents the interaction of plagioclase with Mg-rich pyroxene, then we would expect the trend to move away from Al once plagioclase began to crystallize. Instead, we see only a slight increase in Ti as the Cr/Al decreases. Therefore, the variability in Eu anomalies could be proxies for the extent of melt interaction. Further arguing against plagioclase crystallization are the melting models of Shearer et al. (1997), which show that plagioclase is exhausted after only ~15 % melting.

If the LREE enrichment in Mg-rich pyroxenes is a primary feature of the parental magma, then we would expect to see LREE enrichments in olivine as well (Floss 2002); however, trace-element concentrations for Mg-rich olivine are depleted relative to CI chondrites and no LREE enrichments are observed. This supports an interpretation that the LREE enrichments and possibly the overall enrichments are a secondary feature, which could be attributed to the infiltration of a metasomatic melt.

Interpretation

All of the geochemical evidence suggests that these samples are indeed from the vestan mantle. The primitive composition and high Ni/Co are consistent with the modeled composition of the vestan mantle (Floss 2002). Additionally, the harzburgite clasts contain FeNi metal grains with >1 wt.% Cr, consistent with the formation in a high-temperature and low fO_2 environment, which would be expected during core formation in a magma ocean. Although the REE concentrations are not what are expected for a mantle assemblage; we conclude this is a geochemical fingerprint from the symplectite forming metasomatic event.

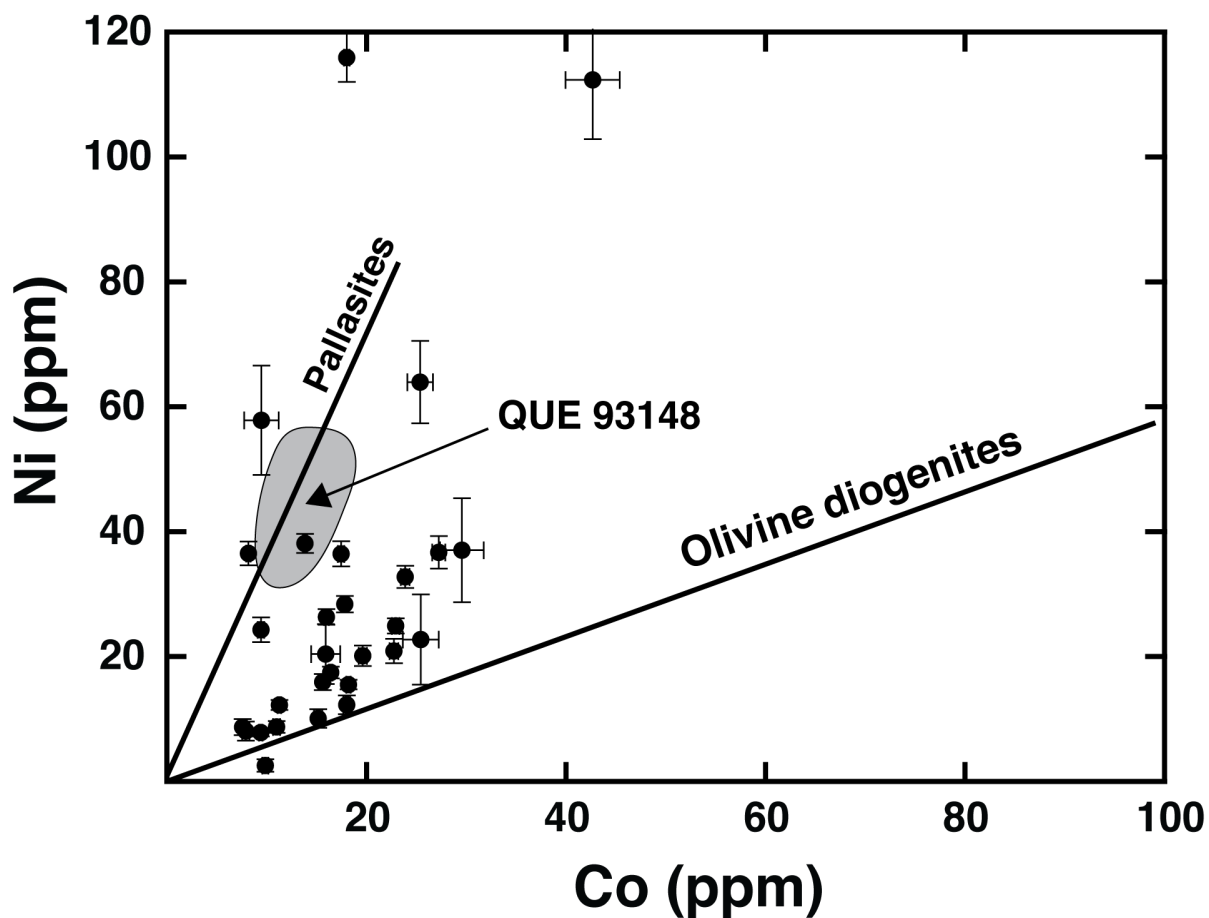


Figure 2.13 Ni vs. Co Concentration in Mg-rich Olivine

Ni/Co in Mg-rich olivine compared to best-fit lines defined by diogenites and pallasites (Shearer et al. 2010). The range of Ni/Co for QUE 93148 is indicated by the gray field (Shearer et al. 2010). The Ni/Co systematics are distinct from the olivine diogenites and likely do not share a common origin. Instead, the Ni/Co are consistent with the formation in a mantle residuum in equilibrium with FeNi metal.

Cumulates or Residua?

Goodrich and Delaney (2000) used Fe/Mn and Fe/Mg relationships (Figure 2.14) to show the trend exhibited by igneous rocks (melts and cumulates) versus residues produced by crystallization and partial melting. The olivine and pyroxene composition in residues produced during partial melting will show higher Fe/Mn and lower Fe/Mg, whereas cumulate compositions become smeared out along a line of constant Fe/Mn with variable Fe/Mg. Further, in a reducing environment, like that in the vestan mantle, these trends would be enhanced. Goodrich and Delaney (2000) used these relationships to show that QUE 93148 was a residue from a high degree of melting. Figure 2.14 suggests the Mg-rich clasts are residues related to HED meteorites.

Melting of an ordinary chondritic starting composition that contains some carbonaceous chondrite component can satisfy the oxygen isotope and Fe/Mn requirements of HED meteorites (e.g. Bosesenberg et al. 2000; Clayton and Mayeda 1996), as well as produce melts that are negatively to marginally buoyant (Fu and Elkins-Tanton 2014). As a preliminary assessment, we have modeled the residuum composition over a range of partial melting of a chondritic mixture of 75 % H-chondrite and 25 % CM-chondrite (Toplis et al. 2013). Figure 2.15 illustrates the changing composition of the residuum with increasing degrees of melting. Our preliminary model indicates that pyroxene is exhausted at 50 % partial melting; therefore, a Mg-rich harzburgite assemblage is not obtainable (Toplis et al. 2013). We note, however, that our observation of FeNi metal in the residuum and the presumably low fO_2 can increase the Mg# of olivine and pyroxene in the residuum (Shearer et al. 1997); however, we cannot currently assess this effect with present MELTS models due to the limitations of operating below the IW buffer. General conclusions from our modeling indicate it is likely necessary for >50 % melting of a 0.75 H-0.25 CM chondritic mixture to occur, at redox conditions below the IW buffer, in order to allow the formation of Mg-rich (Mg# >88) harzburgite-dunite residuum.

Differentiation Models

In the ensuing section, we examine the various differentiation models proposed for Vesta including a global magma ocean (e.g. Mandler and Elkins-Tanton 2013; Ruzicka et al. 1997), a shallow magma ocean (Neumann et al. 2014), and continuous extraction of melts precluding a magma ocean (Wilson and Keil 2012), and partial melting (Stolper 1977) in order to assess the origin of Mg-rich harzburgites (Figure 2.16). The main distinction among competing models is the degree of melting; this variation changes the chemical and physical properties of the vestan mantle.

Magma Ocean Models

Melting and crystallization models that evoke complete melting, followed by either fractional or equilibrium crystallization, have been suggested to explain the differentiation of Vesta (Richter and Drake 1997; Ruzicka et al. 1997). The mantles in these models are dunite-harzburgite cumulates (Figures 2.16a); we have already shown that a cumulate origin for the Mg-rich harzburgites is not supported by Fe/Mn and Fe/Mg systematics.

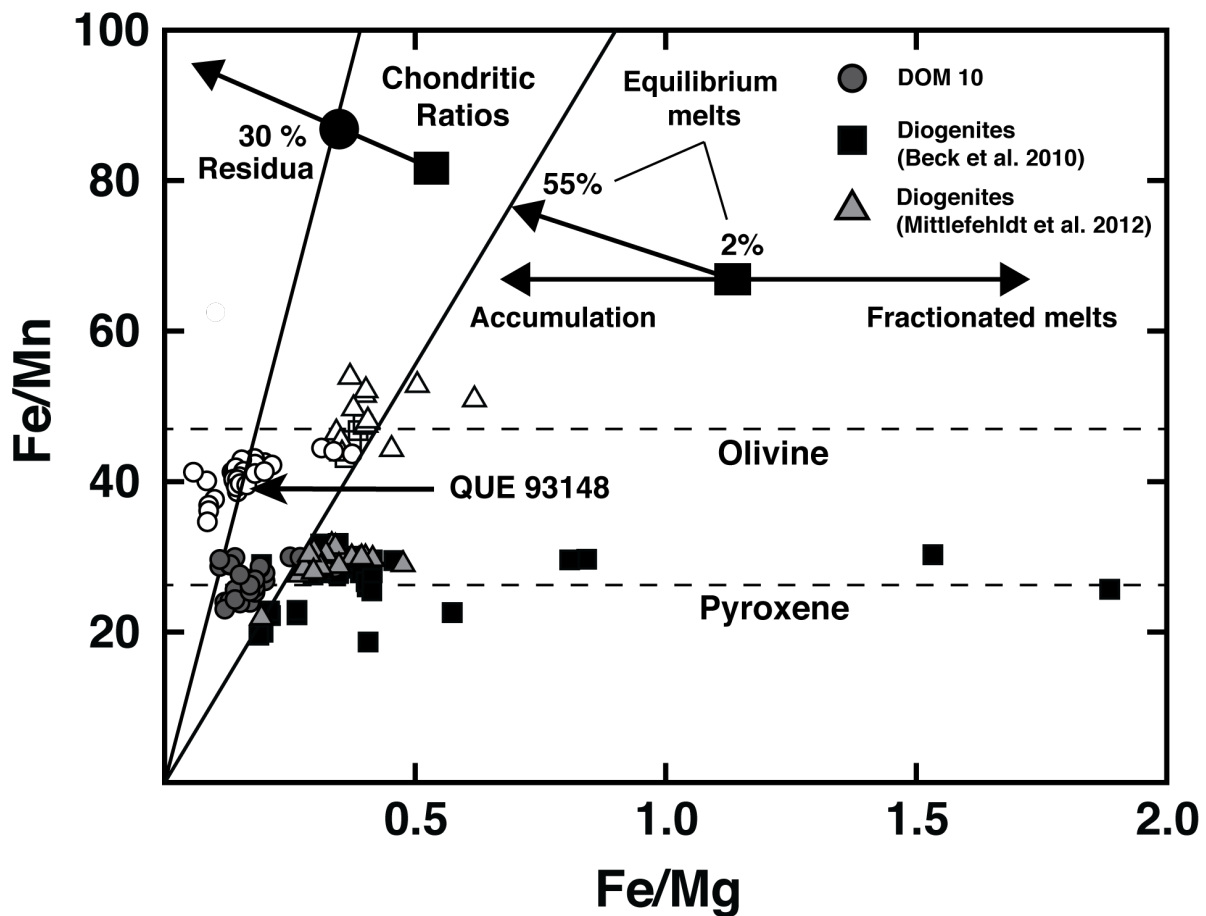


Figure 2.14 Fe/Mn and Fe/Mg Systematics

Fe/Mn and Fe/Mg systematics in olivine (open symbols) and pyroxene (closed symbols) from Mg-rich lithic clasts in howardites (circles). Goodrich and Delaney (2000) discussed the consequences of various geological processes that affect the Fe/Mn and Fe/Mg systematics. A graphical illustration of these processes is shown in the upper portion of the plot. Chondritic meteorites will produce equilibrium melt with lower Fe/Mn and higher Fe/Mg than the starting chondritic ratios, which will become less exaggerated with higher degrees of melting. Accumulation and fractionation of these melts will smear the compositions along a line of constant Fe/Mn and variable Fe/Mg. The residues produced during melting will show an opposite trend from melting and have increased Fe/Mn and lower Fe/Mg. The data for diogenites (squares and triangles) appears to show a trend more consistent with accumulation and fractionation, while the DOM 10 Mg-rich lithic clasts (circles) and QUE 93148 show ranges consistent with the formation as a residue (Beck et al. 2010; Mittlefehldt et al. 2010; and Floss 2002).

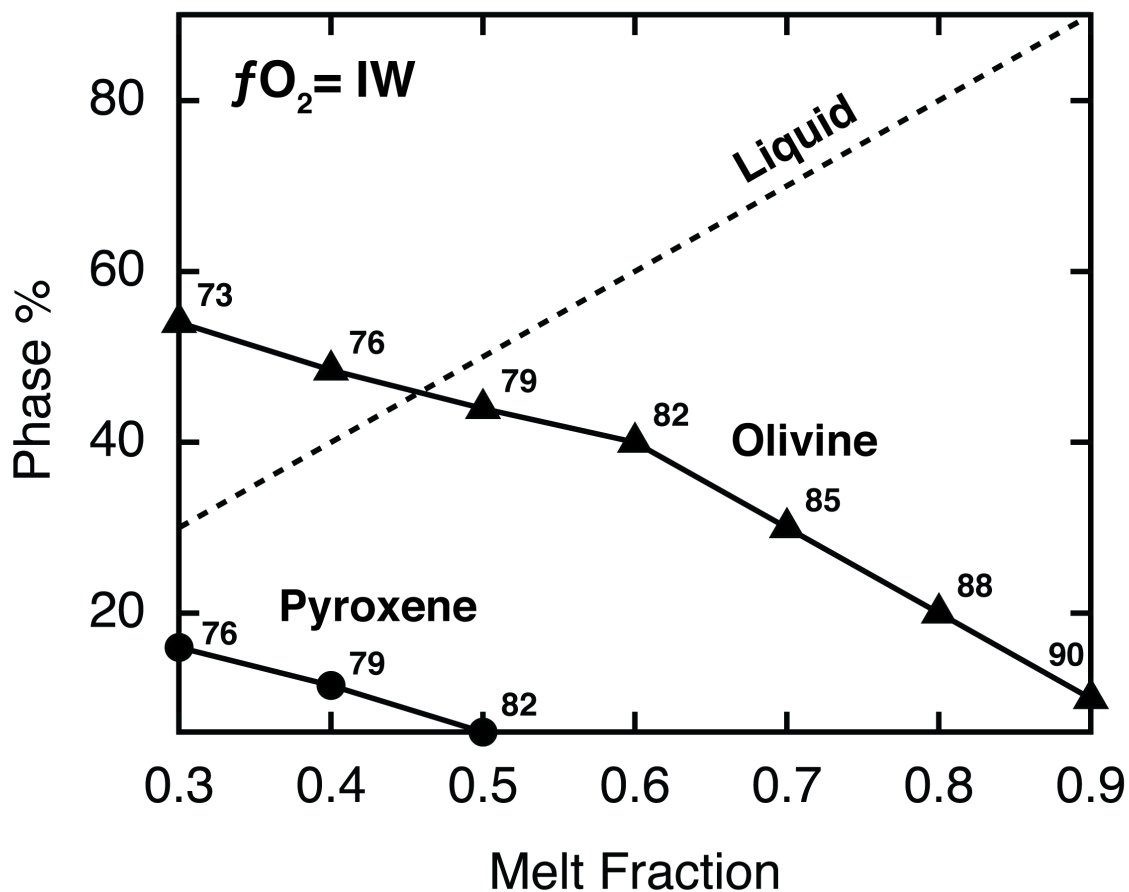


Figure 2.15 Residua Composition During Partial Melting

Results of MELTS modeling showing the phase proportions and composition of olivine, pyroxene, and liquid in the solid residuum as a function of the degree of melting. For modeling purposes, we used the bulk-silicate composition of Vesta with a chondritic mixture of 0.75 H chondrite and 0.25 CM chondrite component, as determined by Toplis et al. (2013). As a first order approximation, the bulk-silicate composition suggested by Toplis et al. (2013) cannot produce the Mg-rich lithic clasts observed in the DOM 10 howardites. For instance, pyroxene is exhausted in the residuum at 50 % melting and the composition of co-existing olivine and pyroxene before exhaustion is too Fe-rich. We, however, believe this is a consequence of the limitations imposed by the MELTS modeling program and the presence of FeNi metal in the residuum (see text).

Figure 2.16 Differentiation Models

Schematic showing four variations of differentiation models for Vesta. a) Global magma ocean model proposed by Ruzika et al. (1997) and Righter and Drake (1997). These models assume complete melting of the chondritic precursor, followed by equilibrium or fractional crystallization to produce a layered internal structure for Vesta. The mantles of global magma ocean models are dunite cumulates. b) A shallow magma ocean model, proposed by Neumann et al. (2014), as a consequence of buoyant melts produced during the melting of a chondritic precursor. This model assumes that no whole magma ocean forms because the melt retained in the mantle never reaches more than a few percent; therefore, the heat source (^{26}Al) is partitioned into the melt and the degree of melting is minimized. The mantle in this body is a harzburgite-dunite residuum, the composition of which depends on the degree of melting. c) Partial melting-Continuous extraction model proposed by Stolper (1977) and Wilson and Keil (2014). This model assumes that eucrites are primary melts and diogenite melts are from higher degrees of melting of sources from which eucrites have already been extracted. The mantle of this model is similar to shallow ocean models; however, partial melting and continuous extraction models predict lower degrees of melting, and therefore their mantles are harzburgite. d) Magma ocean model proposed by Mandler and Elkins-Tanton (2013). This model envisions complete melting, followed by 60-70 % equilibrium crystallization to produce a harzburgite mantle. Extraction and fractionation of residual melts produces the various other HED lithologies. No one model can accommodate the presence of a Mg-rich ($\text{Mg\#} > 85$) harzburgite-dunite residuum because the degree of melting in partial melting and shallow magma ocean models are too low to produce sufficiently Mg-rich compositions (see text). We favor a hybrid model between a shallow magma ocean model (Neumann et al. 2014) and the magma ocean model of Mandler and Elkins-Tanton (2013). This model could be considered a multiple magma ocean reservoir model, where the degree of melting is variable and sufficient to produce Mg-rich mantle residuum; multiple smaller magma reservoirs that are not in geochemical communication can produce the chemical variations of diogenites and eucrites.

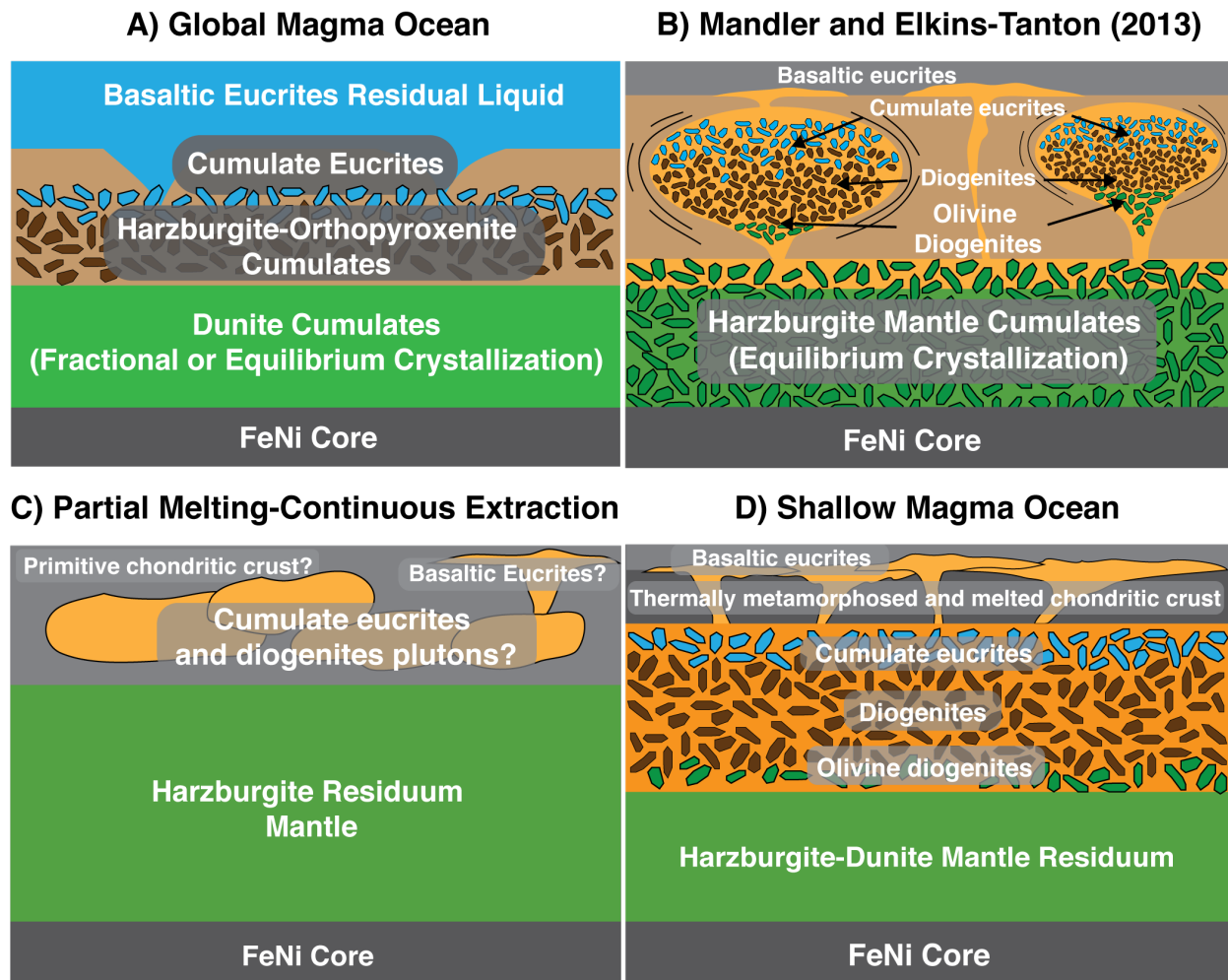


Figure 2.16 Continued.

Mandler and Elkins-Tanton (2013) proposed a model involving the differentiation of Vesta via a magma ocean, followed by serial magmatism. They suggested that 70 to 80 % melting must have occurred in order to facilitate oxygen isotope homogenization and efficient core separation. A two-step model was proposed, whereby Vesta melted and then experienced 60 to 70 % equilibrium crystallization to produce a cumulate harzburgite mantle, after which convective lockup and extraction of the residual melt into crustal magma chambers occurred. Fractional crystallization in these chambers produced plutonic diogenite and eucrite cumulates. The Mandler and Elkins-Tanton (2013) model allows two possible explanations for the petrogenesis of Mg-rich components in howardites: harzburgite mantle or Mg-rich cumulates from shallow crustal magma chambers (Figure 2.16b).

Although an origin for the Mg-rich lithic clasts as cumulates from crustal chambers would be supported by a fractional crystallization trend in Mg-rich and diogenitic pyroxenes (Figure 2.6b), the major-element compositions of olivines and pyroxenes do not support this conclusion. First, Mandler and Elkins-Tanton (2013) showed that although Mg-rich olivine and pyroxene would crystallize in shallow magma chambers, perfect fractional crystallization is unlikely and therefore the Mg# of the first cumulates (dunites and harzburgites) would be similar to that of diogenites (Mg# <85). Additionally, the compositional gap between diogenites and Mg-rich lithic clasts is hard to reconcile with a fractional crystallization sequence (Figure 2.4). The Mg-rich lithic clasts from GRO 95 and DOM 10 could have formed during equilibrium crystallization in the mantle of the magma ocean, although re-equilibration would cause the Mg# of olivine and pyroxene to be similar to diogenites. Because global magma ocean models require that the mantle of Vesta be cumulate in origin, we conclude they are not applicable to the differentiation of Vesta.

Partial Melting and Continuous Extraction

Stolper (1977) used a partial melting model to explain the clustering of eucrite compositions around the olivine-plagioclase-pyroxene peritectic; however, the origin of diogenites in this model is less clear. It was suggested that diogenites might form by re-melting of depleted mantle residue. This seems unlikely since the heat source required to further melt the mantle would have been partitioned into the first melts (Taylor et al. 1993; Wilson and Keil 2012), even at low degrees of melting (<15 %). Moreover, Shearer et al. (1997) showed that plagioclase is exhausted early, which is the dominant source of ^{26}Al . Wilson and Keil (2012) offered physical support for partial melting models, proposing that magma oceans do not form in asteroidal bodies because no more than a few percent of melts can exist in the mantle before being extracted into crust reservoirs or erupting. In a partial melting model, an origin of harzburgite as a mantle residue is the only possible explanation (Figure 2.16c).

Due to removal of ^{26}Al from the mantle (Taylor et al. 1993), only low degrees of melting are likely to have occurred; however, the high Mg# of olivine in Mg-rich harzburgite clasts would require larger degrees of melting (>50 %). This argues against a partial melting model involving small degrees of partial melting to explain the Mg-rich harzburgites clasts. Further, a partial melting model does not seem applicable in light of the petrologic and remote sensing constraints from HED meteorites and the DAWN mission, respectively. First, the occurrence of abundant, relatively coarse-grained,

cumulates seems to suggest that large magma reservoirs were common, and capable of producing a range of incompatible-element compositions (Fowler et al. 1994, 1995). Second, it is difficult to explain the presence of a massive FeNi core (Russell et al. 2012) and the homogenous oxygen isotopes of HEDs (Clayton and Mayeda 1996; Greenwood et al. 2014 and references therein) with the low degree of melting inferred

Shallow Magma Ocean Models

Neumann et al. (2014) proposed a model that requiring the formation of a shallow magma ocean based on the partitioning of ^{26}Al into early-formed melts (Figure 2.16d). Additionally, the buoyant nature of the melts removes ^{26}Al from the source region and inhibits further melting (<50 %); therefore, no global magma ocean forms (Fu and Elkins-Tanton 2014; Taylor et al. 1993). Although the model of Neumann et al. (2014) was purely a physical and thermal model, we can infer some useful conclusions about the structure and composition of the vestan mantle based on the MELTS modeling by Shearer et al. (1997): Cumulate eucrites and diogenites represent fractional crystallization products of the shallow magma ocean (upper mantle), and the lower mantle of Vesta would be dominated by a harzburgite-dunite residuum with the olivine:pyroxene dependent upon the degree of melting.

A cumulate origin for the Mg-rich harzburgites, preceding diogenite cumulates in the shallow magma ocean, is unlikely because the first phases to crystallize are not Mg-rich enough. Greater than 50 % melting would be required to explain the major-element composition of the Mg-rich lithic clasts, which is not consistent with the model proposed by Neumann et al. (2014). Further, a cumulate origin is not supported by Fe/Mn and Fe/Mg systematics in Mg-rich harzburgites (Figure 2.14).

An alternative explanation for the harzburgite mantle clasts, in the context of a shallow magma ocean, is a formation in the mantle residuum. Shearer et al. (1997) determined that plagioclase is exhausted early regardless of the starting bulk composition, and therefore the residuum will be a mixture of olivine and orthopyroxene $\pm$ spinel depending on the degree of melting. Moreover, at melting >50 % for specific starting compositions, the residuum overlaps the major-element chemistry of the Mg-rich harzburgite clasts (Mg# 83-89), although some chondritic precursors would require >60 % melting (Shearer et al. 1997); such high degrees of melting are, again, not consistent with a shallow magma ocean model.

Constraints on an Acceptable Model?

Our study indicates that the characteristics of the vestan mantle require survival of a Mg-rich mantle residuum. We envision a model that involves a hybrid of the shallow magma ocean model proposed by Neumann et al. (2014) and the two-stage model of Mandler and Elkins-Tanton (2013). Such a model would possibly involve multiple, possibly separated magma seas and serial magmatism.

SUMMARY

Mg-rich olivine and orthopyroxene in the DOM 10 howardite pairing group occur as harzburgite clasts containing pyroxene-chromite symplectites. The coexisting olivines and pyroxenes are in chemical and textural equilibrium, and their measured Fe/Mn are consistent with formation on the HED parent body (Vesta). Similar Mg-rich monomineralic fragments in the GRO 95 howardites were further shown to have HED-like oxygen three-isotope compositions (Lunning et al. 2015b). The Mg-rich mineral compositions and the gaps between these compositions and those in diogenites, as well as high Ni/Co in olivine and the presence of Cr in FeNi metal, support a mantle origin for the Mg-rich clasts. The Fe/Mg and Fe/Mn systematics in these harzburgite clasts are consistent with their formation as melting residua, rather than cumulates. The observed compositional gap between diogenites and the vestan mantle residuum may be explained by the presence of FeNi metal in the mantle and the effect of lower fO_2 on the major-element composition of melts produced during partial melting. Rare earth element concentrations in Mg-rich orthopyroxene are likely secondary features and not representative of the original composition of the vestan mantle. Correlations and trends exhibited by minor elements suggest that the degree of melting was variable. The formation of pyroxene-chromite symplectites can be attributed to interaction of mantle rocks with metasomatic melts, possibly a combination of metallic and silicates melts, both descending to the core and ascending towards the surface, respectively. This melt interaction could also have enriched pyroxenes in LREE and produced the observed Cr diffusion profile in olivines. Our study suggests that Vesta did not experience complete melting early in its history, and that >50 % partial melting below the IW buffer was sufficient to produce Mg-rich (Mg# ~88) harzburgite and possibly dunite residuum in the mantle.

Chapter 3: Dacite Formation on Vesta During Late-stage Eucrite Crystallization

Disclosure: The following chapter was submitted to the journal of *Meteoritics and Planetary Science* in April 2016, as a result of the primary author's graduate research. Co-authorship is shared with Nicole G. Lunning (National Museum of Natural History, Smithsonian Institution), Harry Y. McSween (UTK), Robert Bodnar (Virginia Tech, and Lawrence A. Taylor (UTK). Timothy M. Hahn Jr. prepared the manuscript. The content of the chapter contains the original submission materials in a form that has undergone only minor revisions.

ABSTRACT

The Dominion Range 10 howardite pairing group contains an evolved lithic clast of dacite composition. We describe textural and geochemical characteristics of the clast based on petrographic, electron microprobe, laser ablation ICP-MS, Raman spectroscopy, and secondary ion mass spectrometry analyses to elucidate key features that provide insight into the petrogenesis of this lithology. The dacite clast is an assemblage of plagioclase, quartz, and augite, with minor pigeonite, troilite, ilmenite, FeNi metal, K-feldspar, and phosphates. Primary augite occurs as >1 mm oikocrysts enclosing plagioclase. Quartz is abundant, comprising approximately 30 % of the clast. Numerical modeling (MELTS) suggests 80 to 90 % equilibrium crystallization of a liquid composition similar to Sioux County, followed by late-stage melt segregation could have produced the dacite lithology. The dacite likely formed as evolved-melt pockets, and thus, represents a volumetrically minor lithology in the vestan crust, although its formation may explain the conundrum of phosphorous depletion in eucrites.

INTRODUCTION

Eucrites are meteoritic basalts, which together with diogenites (orthopyroxenites, harzburgites, and dunites) and howardites (brecciated mixtures of eucrite and diogenite) comprise the largest suite of achondrites – the howardite-eucrite-diogenite (HED) clan, associated with asteroid 4 Vesta (McSween et al. 2013 and references therein). The HED meteorite clan is commonly considered to be representative of the lithologic diversity on Vesta due to the large number of HEDs discovered and characterized (Mittlefehldt 2014 and references therein). However, differentiation models (e.g. Mandler and Elkins-Tanton 2013), along with melting and crystallization experiments on basaltic eucrites (Stolper 1977), predict the possible existence of more evolved lithologies on Vesta. Indeed, petrologic investigations of howardites have revealed clasts distinct from typical HED meteorites, suggesting other minor lithologies are present on Vesta that are not represented in meteorite collections (e.g. Barrat et al. 2012; Hahn et al. 2015a; Hahn et al. 2015b). Investigation of these components has the potential to reveal significant insight into petrologic processes on Vesta. Additionally, a sufficient number of impacts are needed to adequately sample the vestan surface; Barrat et al. (2012) argue that the estimated half a dozen impacts supposed to have delivered HEDs to Earth (Eugster and Michel 1995; Welten et al. 1997) are inadequate to sample its lithologic diversity.

Basaltic eucrites are subdivided into the Main-Group-Nuevo-Laredo (MGNL) and Stannern trends. MGNL eucrites show increasing incompatible element concentrations

with decreasing Mg#, whereas Stannern trend eucrites show a relatively constant Mg# with respect to increasing incompatible element concentrations. The correlation between major- and minor-element composition in the MGNL eucrites is likely a result of fractional crystallization (Stolper 1977); thus, it is plausible that evolved lithologies identified in HED meteorites could have formed through a similar process.

Unbrecciated MGNL basaltic eucrites are dominated by pyroxene and plagioclase, with minor amounts of silica, ilmenite, chromite, troilite, and metal (Mayne et al. 2009). Additionally, rare accessory phases, such as phosphates, olivine, and K-feldspar have been documented (Mayne et al. 2009). Primary pyroxene in eucrites occurs as pigeonite, often with an exsolved augite component. In this paper, we describe the geochemistry and textural characteristics of a large, evolved eucritic lithic clast within the Dominion Range 10 howardite pairing group (DOM 10), with augite as the primary pyroxene, abundant silica (30 %), rare phases (i.e. K-feldspar), and unique textures. Using the IUGS classification scheme for volcanic rocks (Streckeisen 1979), we classify this rock as a dacite (volcanic equivalent of tonalite). We discuss the geochemical implications of this clast in the context of eucrite petrogenesis, and evaluate the hypothesis that this clast represents the most evolved lithology identified on Vesta thus far. We also evaluate its possible origin as a late-stage differentiate of basaltic eucrite magma.

MATERIALS AND METHODS

Samples

We analyzed thin-sections from a proposed howardite pairing group consisting of six stones (DOM 10105,6; 10100,8; 10120,6; 10837,7; 10838,6; 10839,6). These meteorites were collected from the Dominion Range, Antarctica and were initially paired based on close proximity during collection and similarities in petrologic characteristics (Corrigan et al. 2011). The howardites contain an array of diagenetic and eucritic lithic clasts, secondary impact-derived clasts such as impact breccia clasts within overall howardite breccia, in addition to non-typical HED material, set in a fine-grained matrix consisting of comminuted plagioclase and pyroxene. One of the thin-sections (DOM 10100,8) contains a large (4 mm X 4 mm) lithic clast comprised of a unique assemblage of plagioclase and pyroxene (augite), rich in quartz. Additionally, two sections (DOM 10105,6 and 10839,6) contain smaller lithic clasts (>1 mm) with textures and mineralogy resembling the clast in DOM 10100,8.

Electron Microprobe (EMP)

Major- and minor-element chemistry was determined for mineral phases using a Cameca SX-100 electron microprobe (EMP) at the University of Tennessee. Mineral analyses were conducted with a potential of 15 kV, a beam current of 30 nA, and a 1 μm beam for pyroxene, olivine, spinel, and ilmenite. Feldspar and merrillite analyses were conducted at 15 kV and 10 nA, using a 7 μm spot size. Analyses of FeNi metal were performed at 15 kV and 20 nA. Count times for individual elements varied from 20-60s. Standard PAP corrections were applied. For calibration purposes, a combination of natural and synthetic standards was utilized; analysis of standards deviate <1 % from known values.

Laser Ablation ICP-MS

An Agilent 7500ce inductively coupled plasma mass spectrometer (ICP-MS) at Virginia Tech was used to determine trace-element concentrations *in-situ* for individual mineral phases. Sample material was ablated using an Excimer 193 nm ArF GeoLasPro laser. Spot sizes for analysis ranged from 16 to 60 μm , with the laser spot size determined by the availability of fracture- and inclusion-free areas. The NIST SRM610 reference glass was used as an external standard. The reference standard was analyzed before and after each data collection period (~2 hours) to allow for drift correction. Prior to each analysis, approximately 60s of He gas background signal was collected. Mineral ablation times varied from 20 to 60s; however, during the data-reduction process we only used signal with minimal evidence of noise or contamination from inclusions. The LA ICP-MS lab at Virginia Tech has previously established analytical precision for elements analyzed during the course of this study. The 3σ precision, relative to NIST 612, provides results typically in the range of 5 to 10 %; however, certain elements can be as high as 10 to 20 % (i.e. REE and Sc). For a detailed description of analytical precision and protocols, see www.geochem.geos.vt.edu. All ICP-MS data were reduced using the SILLS software program (Guillong et al. 2008).

Raman Spectroscopy

Raman analyses were performed using a JY Horiba LabRam High Resolution (HR 800 mm) spectrometer with 600 grooves/mm gratings. The slit width was set to 150 μm , and the confocal aperture at 400 μm . Excitation was provided by a 514.57 nm (green) Laser Physics 100S-514 Ar⁺ laser. The laser output was 50 mW at the source and ~10 mW at the sample. The detector used is an electronically cooled open electrode 1024 pixel CCD. The laser was focused through a 100x objective (NA = 0.90) with an analytical area (spot size) of ~1 μm diameter. The various silica polymorphs all show characteristic bands in the range from ~100-600 cm^{-1} , and the spectrometer was centered on 360 cm^{-1} to provide a spectral window from 74-633 cm^{-1} . Spectra for the silica phase in both areas analyzed show the characteristic intense peaks for quartz located at ~464 and 127 cm^{-1} .

Procedures for Apatite Analysis

Electron Microprobe

The chemical and structural complexity of apatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{Cl},\text{OH})_2]$, along with the potential for F migration, make electron microprobe analysis (EMPA) problematic (e.g. Henderson 2011; McCubbin et al. 2011; Pan and Fleet 2002; Stormer et al. 1993). To minimize these problems, we utilized a two-step EMP procedure similar to that of Patiño Douce et al. (2011). First, elemental concentrations of F, Na, and Cl are determined using a 5 μm beam with a potential of 10 kV and 4 nA; this low beam current condition and short peak counting time (30s) act to minimize F migration. As a consequence, detection limits are increased (0.18 and 0.09 wt. % for F and Cl, respectively). Following this procedure, P, Mg, Si, Ca, Fe, Mn, La, and Ce were analyzed using a 5 μm beam with a potential of 15 kV and 10 nA. Pseudo-crystal 1

(PC1; $2d = 59.302$) was used to analyze F, and Cl was analyzed using a PET crystal. Wilberforce apatite was used as a standard for F, P, and Ca; HgCl₂, assumed stoichiometric, was used as a standard for Cl. Amelia albite was used as a standard for Na; Mg and Si were standardized using diopside. Hematite and spessartine garnet were used as a standard for Fe and Mn, respectively. Standard LaB₆ was used for La, and Ce was standardized using CeO₂.

The calculation of apatite structural formula can be a problematic process due to the presence of a missing structural component in the monovalent anion site (Pan and Fleet 2002). It is often assumed that this missing component is hydroxyl, though other species have been recognized in lunar apatites (i.e. S²⁻, Boyce et al. 2010). The inability of the EMP to directly measure hydroxyl leads to a number of assumptions in the calculation of the mineral formula; however, OH concentrations can be estimated based on stoichiometry if F and Cl concentrations are measured accurately (Ketcham 2015). Two normalization procedures are commonly employed for apatites, which assume either a fixed number of anions or cations, though no prior knowledge exists to prefer one method to the other (McCubbin et al. 2011). Recently, Ketcham (2015) developed a procedure that adapts the anion normalization factor based on an estimate of the OH concentration. The method is valid for apatites with any combination of F, Cl, and OH mixing occupying the anion X-site, and allows for quantification of uncertainty for apatites with multiple analyses. In order to calculate the structural formula for apatite, we used approach one in the supplemental data file supplied by Ketcham (2015).

Secondary Ion Mass Spectrometry

Water concentrations in apatites were determined with a Cameca ims 7f –GEO secondary ion mass spectrometer (SIMS) at Caltech. The analytical procedure is similar to that in (Mosenfelder et al. 2011). Specifically, a rastered +10 keV Cs⁺ primary beam of ~4-5 nA was used to sputter C-coated samples across areas of ~40x40 μm. Secondary ions (¹²C⁻, ¹⁶O¹H⁻, ¹⁸O⁻, ¹⁹F⁻, ³⁰Si⁻, ³²S⁻, and ³⁵Cl⁻) of -9 keV from the center areas of ~10 μm in diameter were collected sequentially under high mass resolution conditions. The mass-resolving power (MRP) was set at ~5500, which is sufficient for resolving all the interferences to the ions of interests (such as ¹⁷O⁻ to ¹⁶O¹H⁻). Positive charge build-up from the Cs⁺ bombardment was neutralized using a normal-incidence electron gun (NEG) of -9 keV.

Ion-image maps created by the SIMS (C, OH, HOH, Si) were examined to test for possible contamination of OH from cracks and grain boundaries. Initially, it is possible to see the inherent OH along with the C-coat. Then, as the C-coat is ablated away, the C content, as seen with the C- and OH-maps, is reduced drastically until the ablated surface is low in C and OH. It is possible to see OH/HOH in cracks, and to avoid potential OH contamination by staying clear of these areas. A Si-map was used to confirm the spot of analysis relative to the mineral. Therefore, with a C-map, with an ablated-spot diameter of 40 μm, indicating a C signal of zero, the OH is measured over a 5-10 μm spot in the center, by effectively rastering the 2 μm beam to cover this small area.

Mineral Mapping

We constructed a mineral distribution map, using a modified method developed by Beck et al. (2012), to determine modal abundances and locate mineral grains of interest (i.e. phosphates). Specifically, we used a combination of 4 elemental X-ray maps collected using wave-dispersive spectrometers (WDS; Fe, Si, K, and P); this combination of elements provides adequate compositional resolution. All maps were collected at a potential of 15 kV and a beam current of 30 nA using a 1 μm beam and a 4 μm step-size. Dwell times were 50 ms for all elements. After data collection, the elemental maps were combined into a “geochemical information cube”, analogous to a multispectral image cube, using ENVI 4.2. Phases with known mineral compositions, determined from point analyses, were used to define regions of interest (ROIs) for each phase present in the assemblage. A minimum distance classification was then applied, where all pixels in the image are assigned to a class according to their distance from the ROI mean. Pixels that lie outside the standard deviation set for each class are deemed unclassified. Before classification, we used a minimum value protocol to mask out cracks and the surrounding background in order to create a more accurate modal classification. Classification trials were run and ROIs adjusted until the unclassified pixels were less than 10 %. For our study, we achieved <7 % unclassified pixels, which we interpreted to indicate a reliable classification. Additionally, we conducted “ground-truth” analyses to assess the validity of the classification. The essentially 4 μm X 4 μm pixel size (determined from the step-size) results in larger uncertainties for small and minor phases because their classification is based only on a few pixels, while the entire image consists of ~700,00 pixels.

Bulk Composition Reconstruction

To reconstruct the bulk composition of the large clast, we combined average mineral analyses with modal abundances determined from the mineral map. The bulk composition was determined using Equation 3.1 (Appendix), which incorporates the phase density, and allows for a more accurate bulk composition to be determined (Berlin et al. 2008). Furthermore, we calculated both the bulk composition using all mineral phases in the assemblage (BULK), in addition to a composition in which only the silicate-oxide component is considered (FeNi metal and sulfide removed; SILICATE-OXIDE), and the bulk composition with only the FeS component removed (BULK-FeS). This approach has two purposes: (1) to calculate a bulk composition in which the state of Fe (i.e. Fe^0 or Fe^{2+}) is not considered (BULK) and considered (SILICATE-OXIDE); and (2) to calculate a composition that considers textural evidence suggesting the FeS component of the clast is exogenous.

Geochemical Modeling

To evaluate our hypothesis on the petrogenesis of the evolved clast as a late-stage differentiate of a eucritic magma, we conducted crystallization calculations on basaltic eucrite bulk compositions (Sioux County, Nuevo Laredo, Juvinas, and Stannern; Kitts and Lodders 1998) using the MELTS modeling software (Asimow 1998; Ghiorso and Sack 1995). Our crystallization models were performed at the IW buffer and at pressures of 1 and 200 bars, which are appropriate for Vesta, and correspond to eruptions on the surface (Stolper 1977) and crystallization at depth (25 km) in the crust

(Mandler and Elkins-Tanton 2013), respectively. Fractional crystallization and equilibrium crystallization followed by late-stage melt segregation processes were modeled in order to evaluate the evolution of the melt, mineral crystallization, and the ability to produce melt compositions similar to the dacite clast in this study.

RESULTS

Petrography

The large (4 mm X 4 mm), heavily fractured, polymineralic clast is composed of plagioclase, augite, and quartz, along with minor amounts of pigeonite, troilite, FeNi metal, ilmenite, phosphates, and K-feldspar. The majority of the clast exhibits equigranular textures, though subophitic to ophitic textures are observed locally. Specifically, augite occurs as oikocrysts, >1 mm in length, enclosing tabular grains of plagioclase (Figure 3.1a).

Plagioclase occurs as euhedral lath-shaped grains that range in size from 100 to 500 μm . The textural nature of quartz is complex; both discrete and elongated tabular grains occur interstitially, although a few quartz grains are included in pyroxene and plagioclase (Figures 3.1b and 3.2c). Optical anisotropy distinguishes quartz as a crystalline phase, rather than a glass. Further, Raman spectra of silica polymorphs are readily distinguishable, and confirm the identification of quartz in the sample (Figure 3.3). There appears to be a distinctive textural difference between the two occurrences of silica; discrete grains are inclusion-free, whereas elongated tabular grains are rich in sulfide globules (Figure 3.1b and 3.1c). The tabular silica grains, in some places, resemble the “hackle” fracture pattern observed by (Seddio et al. 2015) in the Apollo 12 lunar granites (Figure 3.4c), suggesting that they originally crystallized as tridymite or cristobalite that were subsequently inverted to quartz.

Primary augite, containing pigeonite exsolution lamellae, occurs within the clast; pigeonite lamellae are <1 μm in width, and therefore are unresolved by the EMP (Figures 3.1a, 3.1d, 3.4d and 3.5). Pigeonite also occurs as small (<200 μm) isolated grains within the matrix. Troilite, FeNi metal, and ilmenite are observed as irregular grains, ranging in size from 10s to 100s of microns. Additionally, troilite forms veins that traverse the section (Figures 3.1b-c and 3.2a). Microtextures suggest troilite veins are a result of secondary processes (Figures 3.4a and 3.4b). Phosphates appear to be spatially associated with sulfide-rich quartz, are irregular in shape, and can be up to 100 μm in longest dimension (Figure 3.2d). All major phases (i.e. augite, plagioclase, and quartz) contain abundant opaque inclusions. Using the modal abundances of mineral phases, we classify this clast as a dacite (volcanic equivalent of tonalite) using the IUGS classification (Q, 40%; A, 1%; P, 60%; Streckeisen 1979).

Major-, Minor- and Trace-Element Geochemistry

Pyroxenes

Major- and minor-element composition of pyroxenes (pigeonite and augite) are displayed in Tables 3.1A and 3.1, respectively; end-member compositions are plotted in Figure 3.6. Pyroxenes in the dacite clast are similar in major-element composition to

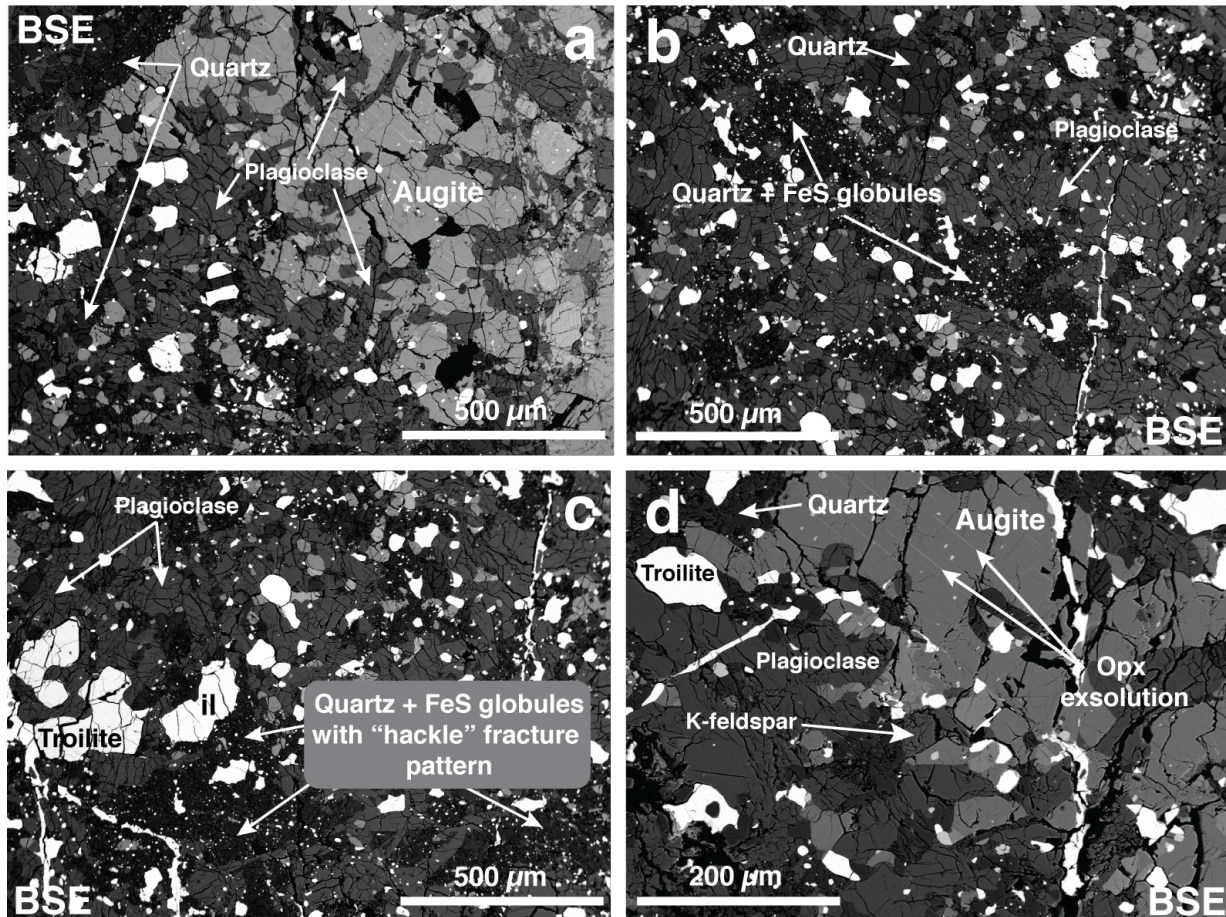


Figure 3.1 Dacite Clast Mineralogy and Textures

Backscattered electron (BSE) images of dacite clast. a) Augite occurs as >1 mm oikocrysts with submicron exsolution lamellae of pigeonite. b) Silica occurs as both discrete grains and tabular interstitial areas, which contain abundant FeS globule inclusions. c) FeS veins (lower left) and grains, as well as disseminated ilmenite and FeNi metal (bright grains). d) The “large” grain size of K-feldspar. Also, note the pigeonite lamellae in augite oikocrysts.

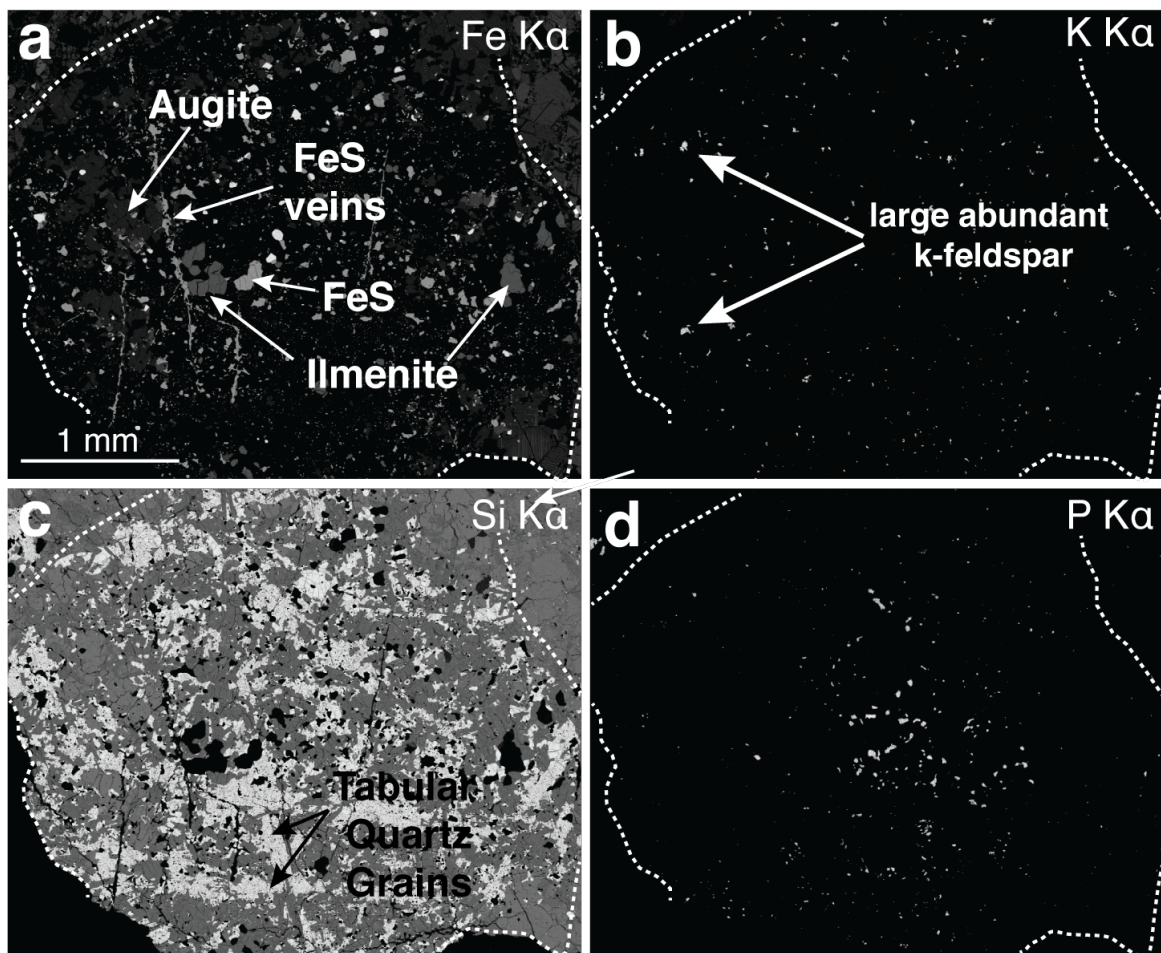


Figure 3.2 Elemental Maps of Dacite Clast

Elemental x-ray maps, illustrating the distribution and abundance of phases. a) Fe K α ; notice the FeS vein that cuts across the clast. b) K K α ; shows the distribution of K-feldspar grains, which are large, by HED standards, and abundant. c) Si K α ; silica appears to form large tabular crystals (veins?) that cut across the section; however, these silica grains are not optically continuous. d) P K α ; illustrates the distribution of phosphates that appear to be concentrated near the center, which may be a secondary effect.

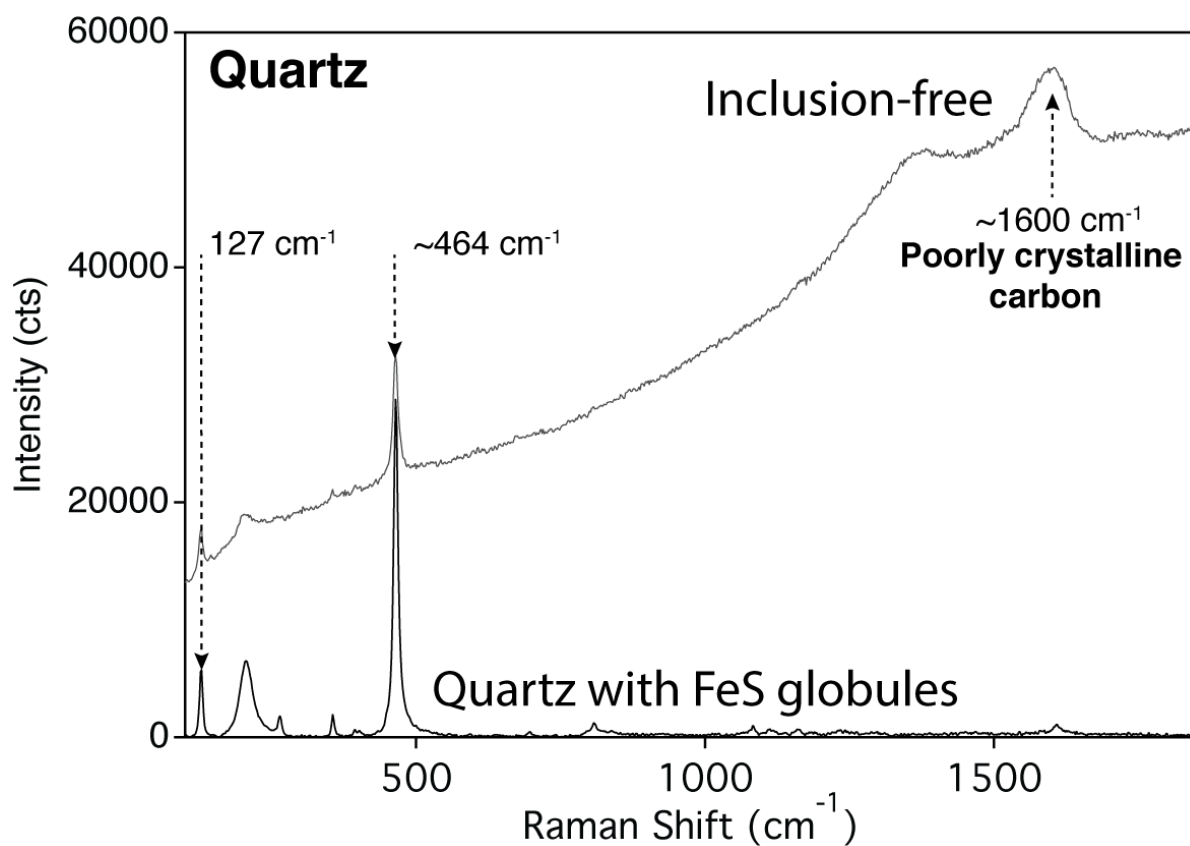


Figure 3.3 Raman Spectra on Silica Grains

Raman spectra of silica grains in the dacite clast. Analyses were performed on an FeS-rich tabular silica grain, and inclusion-free silica. Both spectra show a strong peak at ~464 and 127 cm⁻¹ that is characteristic of quartz. The higher background for the inclusion-free silica is due to some carbon-coating on the surface. The broad peak at ~1600 cm⁻¹ is characteristic of poorly-crystallized carbon. Other analyses gave similar results.

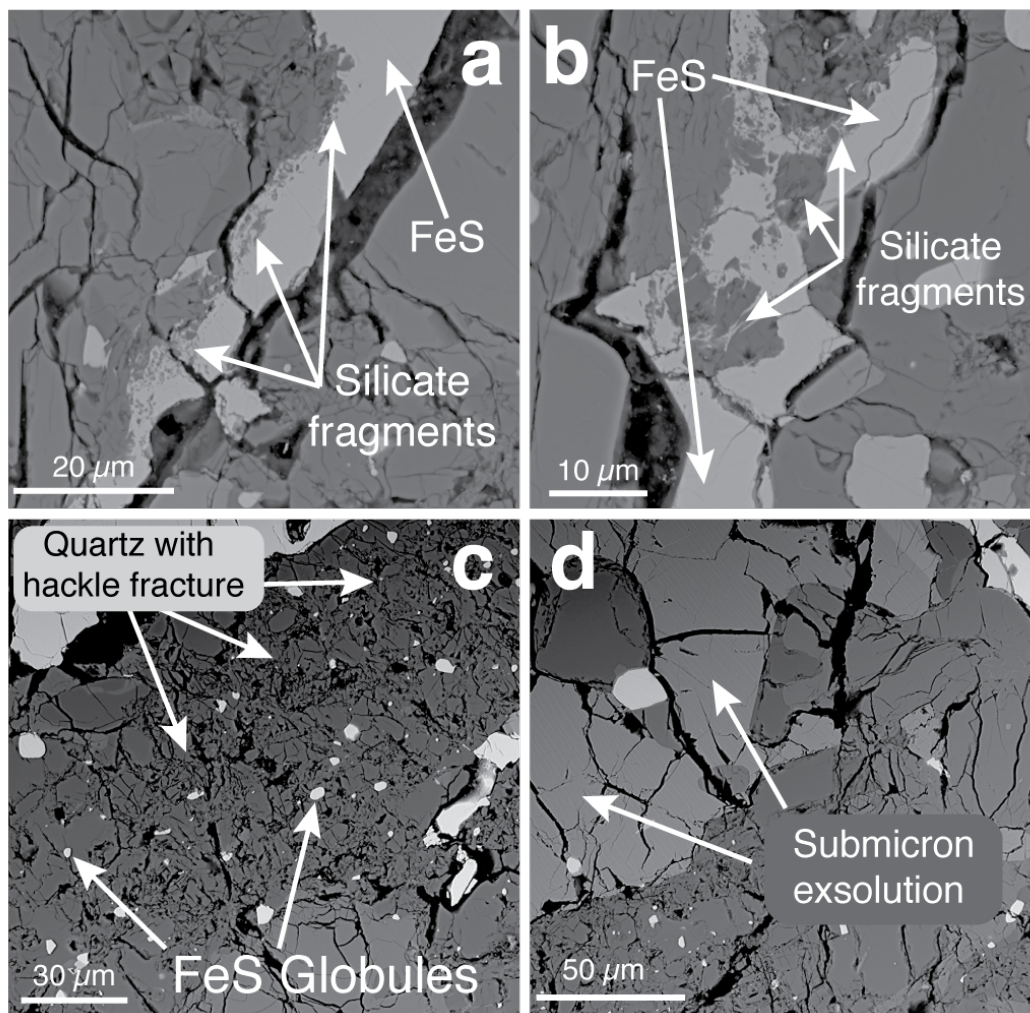


Figure 3.4 Microtextures in Dacite Clast

SEM images of the dacite clast showing microtextures. a-b) FeS appears to have been injected into the clast, as indicated by the incorporation of surrounding crystal material. c) Microstructure of FeS-rich silica is similar to the “hackle” pattern observed by Seddio et al. (2015) in silica phases from lunar granites and felsites. d) Submicron exsolution lamellae of pigeonite from augite.

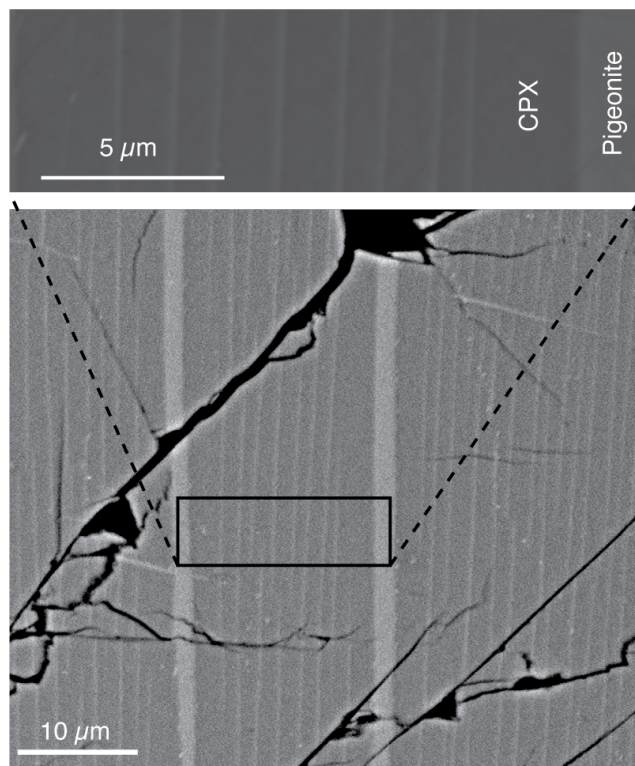
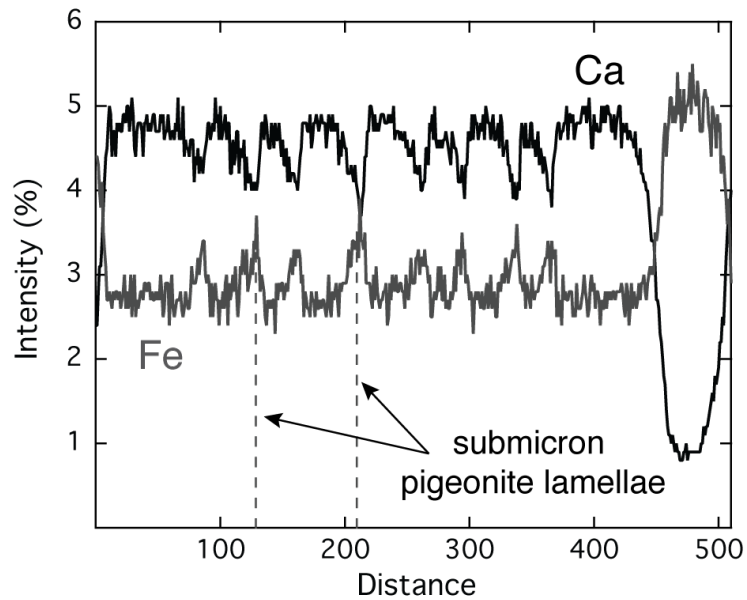


Figure 3.5 Submicron Exsolution in Dacite Pyroxenes

SEM image of submicron exsolution lamellae of pigeonite in augite, along with Fe and Ca x-ray intensity line maps across the grain. Ca peaks correspond to augite, while Fe peaks correspond to pigeonite.

Table 3.1. Representative major- and minor-element composition of augite (wt.% oxide).

Oxide	Augite	Augite	Augite	Augite	Augite	Augite	Augite	Augite	Augite	Augite
SiO ₂	50.3	50.5	50.3	50.5	50.6	50.1	50.6	50.0	50.4	50.1
TiO ₂	0.53	0.49	0.43	0.44	0.38	0.40	0.43	0.36	0.41	0.38
Al ₂ O ₃	0.54	0.66	0.65	0.64	0.53	0.62	0.57	0.59	0.60	0.55
Cr ₂ O ₃	0.48	n.d.	n.d.	n.d.	0.31	0.37	n.d.	n.d.	n.d.	n.d.
MgO	9.92	9.98	9.63	9.67	9.80	9.62	9.85	9.81	9.83	9.65
CaO	18.7	18.2	19.6	19.4	19.4	19.3	19.4	19.2	19.0	18.7
MnO	0.59	0.62	0.55	0.62	0.52	0.58	0.57	0.59	0.57	0.58
FeO	19.2	19.5	18.1	18.1	17.9	18.4	18.6	18.7	18.6	19.3
Total	100.2	100.3	99.5	99.7	99.5	99.4	100.4	99.7	99.8	99.6
Cation formula based on 6 oxygen										
Si	1.957	1.961	1.964	1.967	1.972	1.962	1.961	1.956	1.964	1.963
Ti	0.015	0.014	0.013	0.013	0.011	0.012	0.013	0.011	0.012	0.011
Al	0.025	0.030	0.030	0.029	0.024	0.029	0.026	0.027	0.027	0.025
Cr	0.015				0.010	0.012				
Mg	0.575	0.578	0.560	0.561	0.570	0.561	0.569	0.572	0.571	0.563
Ca	0.777	0.757	0.819	0.810	0.810	0.807	0.806	0.805	0.793	0.786
Mn	0.019	0.020	0.018	0.020	0.017	0.019	0.019	0.019	0.019	0.019
Fe	0.623	0.634	0.590	0.589	0.583	0.601	0.604	0.613	0.607	0.631
Total	4.010	4.009	4.007	4.004	4.002	4.009	4.012	4.019	4.008	4.011
En	29.1	29.4	28.4	28.6	29.0	28.5	28.8	28.7	29.0	28.4
Fs	31.5	32.2	30.0	30.1	29.7	30.5	30.5	30.8	30.8	31.9
Wo	39.3	38.4	41.6	41.3	41.3	41.0	40.7	40.5	40.2	39.7
Fe/Mg	1.08	1.10	1.05	1.05	1.02	1.07	1.06	1.07	1.06	1.12
Fe/Mn	32.8	31.7	32.8	29.5	34.3	31.6	31.8	32.3	31.9	33.2

basaltic eucrites ($\text{En}_{36}\text{Fs}_{62}\text{Wo}_2$; $\text{En}_{29}\text{Fs}_{31}\text{Wo}_{40}$; Figure 3.6); however, the textural setting differs from typical eucrites. For example, augite characteristically occurs as exsolution lamellae in pigeonite hosts within eucrites, whereas augite within the dacite clast occurs as primary pyroxene oikocrysts. Pyroxenes show only small variations in minor-element composition (inset in Figure 3.6). For instance, Al_2O_3 concentrations in augite range from 0.53 to 0.66 wt.%, and TiO_2 concentrations vary from 0.36 to 0.53 wt.% (Table 3.1). Pigeonites show similar limited variation in minor-element concentrations, though their absolute values are a factor of three less than augite (i.e. $\text{TiO}_2 = 0.1$ wt.%; Table 3.1A).

Trace-element concentrations in augite are reported in Table 3.2, and their rare earth element (REE) patterns are displayed in Figure 3.7. Augite is enriched in REEs relative to CI chondrites, and shows LREE depletions typical of pyroxene. Although the augite contains pigeonite exsolution lamellae, their small size (~ 1 μm) is easily re-incorporated during the LA ICP-MS analysis; therefore, we interpret these to represent the trace-element chemistry of the original pyroxenes. This conclusion is supported by the similarities in REE patterns obtained from multiple augite grains. Unfortunately, the differences in augite and pigeonite partition coefficients preclude a direct comparison to primary pyroxenes (pigeonite) in eucrites. However, Barrat et al. (2012) recently identified a unique low-Mg lithology in howardites, which they interpret to represent an evolved lithology associated with Vesta; augite from the dacite clast display comparable REE patterns to augite within their low-Mg lithology (Figure 3.7), although the former exhibits greater LREE depletions. Undesirably, the small size of pigeonite grains (< 200 μm) and inclusion-rich nature prevented reliable LA ICP-MS analyses.

Feldspars

Plagioclase and K-feldspar major- and minor-element compositions are listed in Table 3.3. The composition of plagioclase falls within the range defined by unequilibrated eucrites (Mayne et al. 2009). For instance, end-member compositions of basaltic eucrite plagioclase range from An_{95} to An_{73} , and plagioclase analyses within the dacite clast define a narrow range from An_{85} to An_{87} . Plagioclase grains show homogenous compositions with no evidence of primary or relict zonation. Additionally, we observed no compositional difference between plagioclase grains within the matrix and those included in augite oikocrysts. K-feldspar has only been identified within a handful of HED meteorites (Barrat et al. 2012; Mayne et al. 2009), and usually occurs as small (10s of μm) grains within the mesostasis. We identified K-feldspar grains an order of magnitude larger (~ 150 μm ; Figure 3.1d), and optical anisotropy, along with EMP analysis, indicates a crystalline structure and stoichiometric consistency with K-feldspar (Table 3.3); these are not K-rich glasses. Concentrations of BaO within K-feldspar are low (< 2 %), and the average end-member composition reflects this characteristic ($\text{An}_{0.3}\text{Ab}_1\text{Or}_{96.7}\text{Cn}_2$; Celsian [Cn] is the Ba-feldspar end-member).

Trace-element concentrations in plagioclase are enriched relative to typical eucritic plagioclase (i.e. Sr and La; Figure 3.8; Table 3.4). The REE patterns for plagioclase also show similar enrichments (Figure 3.9); however, our LA ICP-MS analyses appear to suffer from contamination. For instance, REE patterns of plagioclase show a large range in HREE concentrations, which can be explained

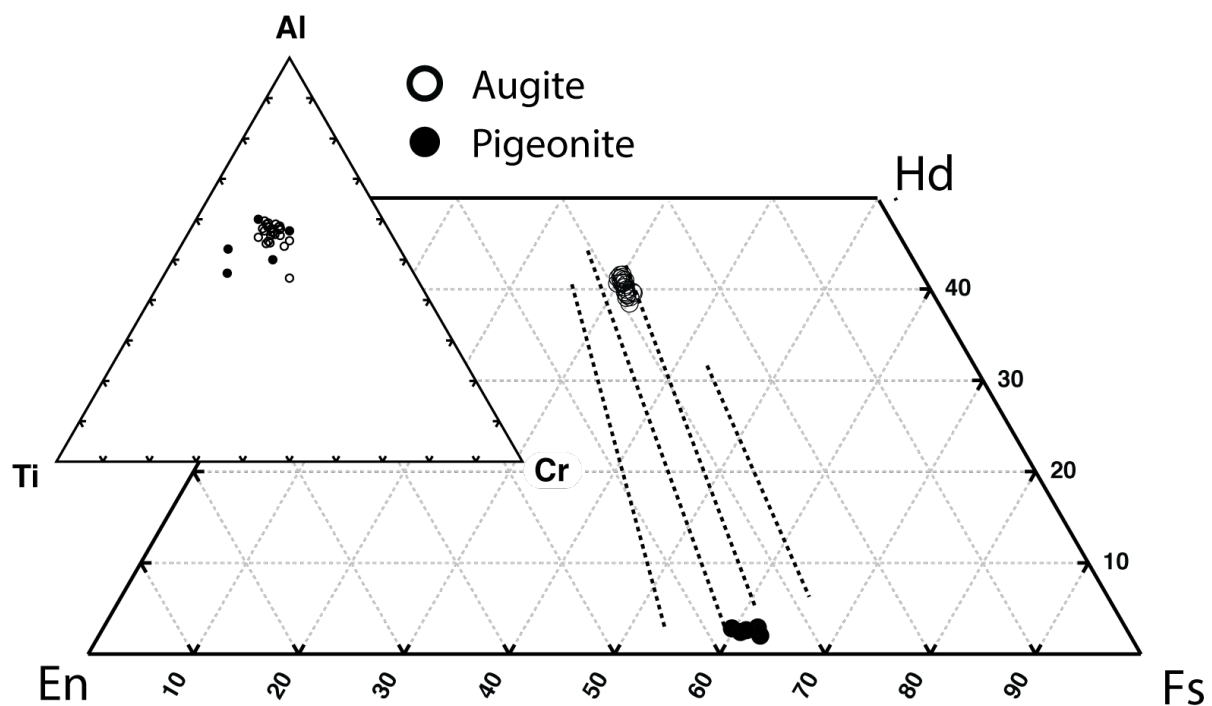


Figure 3.6 Dacite Pyroxene Chemistry

Pyroxene quadrilateral displaying end-member compositions of pyroxene in the dacite clast. A Ti-Cr-Al ternary (cations) inset shows the minor element variation of the pyroxenes. Pigeonite compositions correspond to discrete intergranular grains, rather than analyses of pigeonite lamellae. Dashed lines are representative tie-lines between high- and low-Ca pyroxene in basaltic eucrites (Mittlefehldt 2014).

Table 3.2. Representative trace element chemistry for augite.

	Px1		Px2		Px3	
	µg/g	1 σ	µg/g	1 σ	µg/g	1 σ
Sc	169	(2)	163	(2)	167	(2)
Ti	2703	(27)	2636	(49)	3265	(28)
V	77	(1)	80	(1)	85	(1)
Cr	2280	(42)	2016	(57)	2997	(34)
Mn	5208	(43)	4915	(70)	4890	(42)
Co	2.88	(21)	4.14	(24)	2.91	(19)
Ni	10.1	(15)	16.9	(25)	15.4	(15)
Ga	0.318	(40)	0.573	(50)	0.309	(36)
Sr	6.45	(11)	13.3	(45)	6.67	(10)
Y	53.7	(5)	49.0	(7)	54.4	(5)
Zr	48.1	(5)	44.1	(7)	49.3	(5)
Nb					0.088	(22)
Ba	0.068	(10)	2.67	(19)	0.104	(12)
La	0.572	(31)	0.629	(29)	0.590	(25)
Ce	3.22	(6)	3.19	(8)	3.36	(7)
Pr	0.870	(31)	0.796	(27)	0.798	(24)
Nd	6.02	(20)	6.01	(19)	5.82	(21)
Sm	3.61	(13)	3.15	(17)	3.40	(12)
Eu	0.122	(12)	0.125	(15)	0.079	(10)
Gd	6.41	(20)	5.34	(21)	5.70	(19)
Tb	1.29	(4)	1.13	(4)	1.29	(4)
Dy	10.2	(2)	9.62	(25)	10.1	(2)
Ho	2.19	(5)	2.00	(5)	2.29	(5)
Er	7.15	(15)	6.10	(15)	6.99	(13)
Tm	1.04	(3)	0.93	(4)	1.03	(3)
Yb	6.92	(16)	6.15	(17)	6.94	(18)
Lu	1.16	(4)	1.06	(4)	1.09	(3)
Hf	3.06	(11)	2.70	(13)	2.93	(10)
Ta						
Pb	0.082	(20)	0.116	(27)	0.143	(31)
Th	0.017	(4)				
U	0.019	(4)	0.012	(3)	0.013	(3)

* Values in parentheses represent 1 standard deviation.

* Error given in terms of the last decimal place.

* Missin values are either below detection limits or give bad statistics (i.e 100σ/concentration >30)

Table 3.2. Continued.

	Px4		Px5		Px6	
	µg/g	1 σ	µg/g	1 σ	µg/g	1 σ
Sc	191	(3)	156	(5)	155	(2)
Ti	3155	(140)	4115	(268)	2372	(49)
V	57	(1)	151	(9)	118	(5)
Cr	2132	(24)	5744	(490)	2402	(306)
Mn	4813	(54)	4732	(144)	4972	(60)
Co	5.66	(59)	7.09	(68)	6.50	(37)
Ni	24.2	(34)	43.7	(5)	10.7	(22)
Ga	0.343	(95)	0.552	(80)	0.304	(76)
Sr	6.77	(15)	9.01	(29)	6.38	(16)
Y	56.7	(7)	48.8	(15)	52.1	(8)
Zr	52.6	(9)	41.8	(13)	36.3	(7)
Nb	1.32	(20)				
Ba	0.214	(25)	1.15	(13)	0.102	(24)
La	0.532	(38)	0.446	(35)	0.459	(37)
Ce	2.86	(8)	2.75	(11)	2.72	(10)
Pr	0.754	(31)	0.744	(41)	0.716	(333)
Nd	5.60	(27)	4.97	(27)	5.26	(35)
Sm	3.47	(19)	3.30	(24)	3.50	(21)
Eu	0.101	(24)	0.091	(22)	0.081	(23)
Gd	5.90	(25)	4.93	(31)	5.92	(32)
Tb	1.32	(5)	1.14	(6)	1.14	(5)
Dy	10.4	(3)	9.33	(43)	9.53	(49)
Ho	2.45	(7)	1.98	(8)	2.07	(8)
Er	7.45	(20)	6.11	(27)	7.18	(21)
Tm	1.20	(4)	0.93	(5)	1.11	(7)
Yb	6.99	(22)	6.43	(24)	6.54	(34)
Lu	1.21	(5)	1.00	(6)	1.06	(6)
Hf	3.06	(13)	2.57	(16)	2.29	(14)
Ta	0.081	(21)				
Pb					0.134	(40)
Th						
U						

* Values in parentheses represent 1 standard deviation.

* Error given in terms of the last decimal place.

* Missin values are either below detection limits or give bad statistics (i.e $100\sigma/\text{concentration} > 30$)

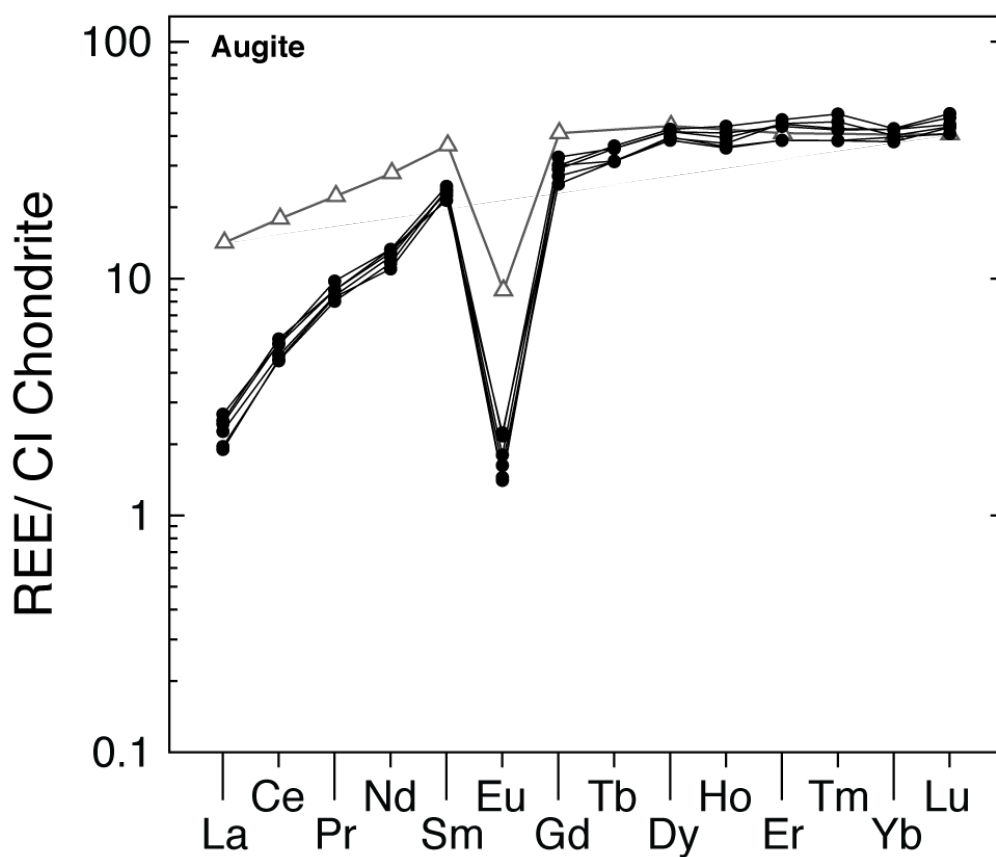


Figure 3.7 Rare Earth-Element Patterns of Dacite Pyroxene

Rare-earth element patterns for augite in the dacite clast. We interpret these to reflect the composition of the original pyroxene before submicron exsolution. For comparison, data are shown from high-Ca pyroxene in KREEPy lithologies on Vesta, described by Barrat et al. (2012) (gray triangles). Data are normalized to CI chondrites (Anders and Grevesse 1989).

Table 3.3. Representative mineral composition of feldspars (wt.% oxide).

	Kfs	Kfs	Kfs	Kfs	Kfs	Kfs	Pl	Pl	Pl	Pl	Pl	Pl
SiO ₂	64.3	64.2	63.9	63.5	63.2	63.2	47.6	47.1	46.7	46.6	46.5	46.4
Al ₂ O ₃	18.0	17.5	18.2	17.7	18.0	18.1	33.0	32.6	33.3	33.1	33.0	32.9
Fe ₂ O ₃	0.27	0.49	0.25	0.50	0.39	0.35	0.32	0.27	0.16	0.32	0.25	0.44
CaO	0.07	0.05	0.04	0.06	0.09	0.04	17.5	17.4	17.8	18.0	17.8	17.8
BaO	0.78	0.50	0.83	0.97	1.41	1.51	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Na ₂ O	0.09	0.12	0.15	0.13	0.12	0.15	1.71	1.54	1.40	1.49	1.48	1.50
K ₂ O	16.6	16.3	16.5	16.4	16.0	16.3	0.15	0.14	0.10	0.15	0.10	0.13
Total	100.1	99.1	99.9	99.3	99.2	99.6	100.2	99.1	99.6	99.6	99.1	99.1
Cation formula based on 6 oxygen												
Si	2.995	3.008	2.984	2.990	2.982	2.975	2.184	2.186	2.159	2.156	2.161	2.159
Al	0.987	0.970	1.002	0.983	0.998	1.003	1.782	1.784	1.816	1.806	1.806	1.802
Fe	0.009	0.017	0.009	0.018	0.014	0.013	0.011	0.009	0.006	0.011	0.009	0.015
Ca	0.003	0.003	0.002	0.003	0.004	0.002	0.862	0.865	0.882	0.891	0.887	0.885
Ba	0.014	0.009	0.015	0.018	0.026	0.028						
Na	0.008	0.011	0.013	0.012	0.011	0.014	0.152	0.139	0.125	0.134	0.133	0.136
K	0.985	0.974	0.982	0.986	0.965	0.980	0.009	0.008	0.006	0.009	0.006	0.008
Total	5.003	4.991	5.008	5.009	5.000	5.014	5.000	4.991	4.995	5.007	5.002	5.004
An	0.30	0.30	0.20	0.29	0.40	0.20	84.3	85.5	87.1	86.2	86.5	86.0
Or	97.5	97.7	97.0	96.8	95.9	95.7	0.9	0.8	0.6	0.9	0.6	0.8
Ab	0.79	1.10	1.28	1.18	1.09	1.37	14.9	13.7	12.3	13.0	13.0	13.2
Cn	1.39	0.90	1.48	1.77	2.58	2.73						

*Pl; Plagioclase

*Kfs; K-feldspar

by ablation of pyroxene during the analysis. Indeed, plagioclase grains within the dacite clast are riddled with inclusions (Figure 3.1a), including pyroxene grains. We attribute the variability in HREE concentrations to be a consequence of contamination, and therefore use these data cautiously for interpretation of petrogenesis.

FeNi Metal

The occurrence of FeNi metal as an accessory phase in eucrites is ubiquitous, and generally occurs as kamacite (Mayne et al. 2009). Grains of FeNi metal are observed within the dacite lithology, and exhibit a wide range in Ni concentrations (3.5 to 12.1 wt.%; Table 3.2A). An apparent zonation of Ni was observed within one grain; Ni concentrations increase near the rim. In fact, the uppermost limit of Ni concentrations (12.1 wt.%) was observed near the rim of one FeNi metal grain. The concentration of Co is less variable, with values of 0.4 to 0.7 wt.%. All other elements remained below detection limits (0.03 wt.%) during analysis.

Phosphates

The dacite clast contains a roughly equal mixture of apatite and merrillite; Table 3.3A displays the major- and minor-element compositional data for these minerals, and trace-element concentrations are shown in Table 3.4A. Apatite occurs as nearly pure fluorapatite with F and Cl concentrations ranging from 3.29 to 3.57 wt.% and 0.11 to 0.17 wt.%, respectively. The OH concentrations of apatites within the clasts fall within the range of typical basaltic eucrite apatites (Table 3.8; Sarafian et al. 2013). Figure 3.10 illustrates the composition of these apatites within F-Cl-OH compositional space. Apatite displays a relative flat REE pattern, and is enriched approximately 200 X Cl chondrites with large Eu anomalies (Figure 3.11).

Electron microprobe analyses of merrillite grains are listed alongside apatite compositions in Table 3.3A. Merrillite contains significant quantities of minor oxides such as FeO, MgO, and Na₂O (~2.1, 2.5, and 1.1 wt.%, respectively). Additionally, EMPA indicate merrillite contains several weight percent of REE oxides. Consequently, EMPA totals for merrillite are always below acceptable limits because the whole range of REEs was not analyzed. Laser ablation ICP-MS data indicates that merrillite is enriched in REE, with values 10,000 X Cl chondrites and accompanied by deep Eu anomalies (Figure 3.11). Unsurprisingly, merrillite also exhibits enrichments in Y, Zr (20 ppm), Th (~400 ppm), and U (~10 ppm) (Table 3.4A).

Bulk Composition

Modal recombination analysis was utilized to estimate the bulk composition of the dacite clast. The modal analysis determination is shown in Table 3.5, and the calculated bulk major- and minor-element composition of the clast is listed in Table 3.6; selected eucrite compositions described by (Mayne et al. 2009) are shown for comparison. Additionally, Figure 3.12 displays the mineral map used to determine mineral phase modal abundances. Relative to analogous non-cumulate eucrites, the clast is enriched in SiO₂, TiO₂, Al₂O₃, Na₂O, K₂O, P₂O₅, and CaO; depletions in MgO and FeO are also evident. Figure 3.13 shows the various calculated bulk compositions of the dacite clast, illustrating the enrichment in CaO relative to MgO and FeO in relation to eucrites.

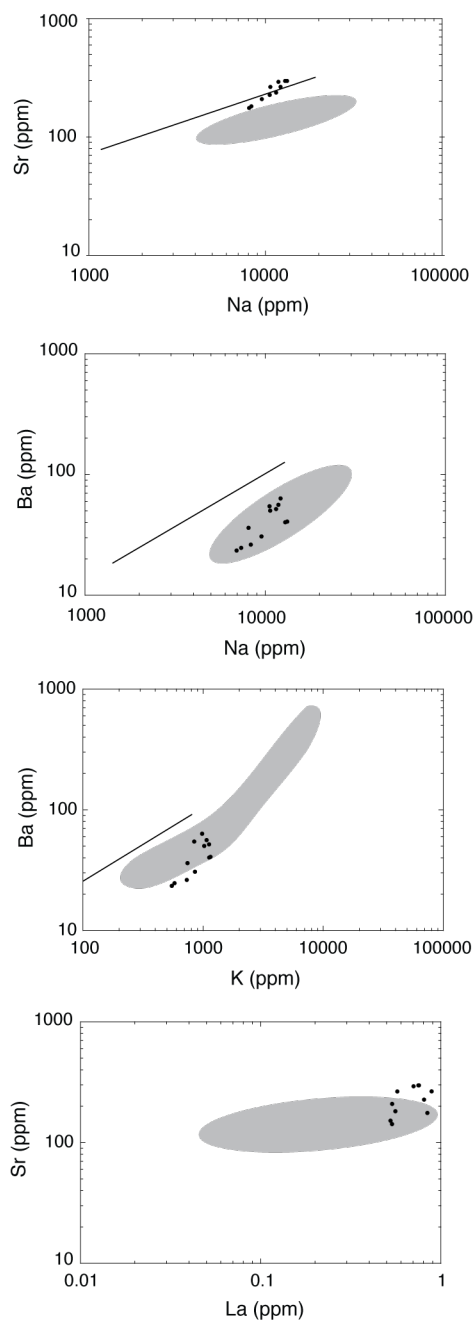


Figure 3.8 Variation Diagram for Dacite Feldspars

Variation diagrams of minor- and trace-element concentrations in plagioclase. Solid trend lines represent concentrations in Ibitira and the gray ellipse is the compositional range for basaltic eucrites (Hsu and Crozaz 1996). Plagioclase in the dacite clast is enriched in Sr and La. All external data from Hsu and Crozaz (1996).

Table 3.4. Representative trace element chemistry for plagioclase.

	Plag1		Plag2		Plag3		Plag4		Plag5		Plag6	
	µg/g	1 σ	µg/g	1 σ	µg/g	1 σ	µg/g	1 σ	µg/g	1 σ	µg/g	1 σ
K	982	(27)	856	(31)	578	(16)	741	(11)	1070	(16)	1125	(31)
Sc	74	(4)	82	(4)	101	(4)	98	(1)	53	(5)	59	(5)
Ti	309	(39)	689	(54)	1073	(46)	1415	(97)	56	(9)	64	(7)
Sr	265	(6)	209	(7)	152	(3)	176	(2)	292	(3)	298	(5)
Y	4.28	(66)	11.6	(10)	16.9	(7)	16.8	(3)	0.898	(214)		
Zr	2.78	(56)	10.8	(11)	17.6	(9)	12.9	(4)				
Ba	63.4	(16)	30.7	(12)	24.7	(9)	36.2	(5)	56.1	(13)	40.2	(11)
La	0.888	(79)	0.536	(99)	0.525	(80)	0.841	(61)	0.705	(153)	0.755	(139)
Ce	1.61	(10)	1.75	(13)	1.96	(21)	2.69	(14)	0.872	(168)	1.23	(17)
Pr	0.253	(41)	0.340	(69)	0.507	(60)	0.380	(29)				
Nd	1.16	(29)			3.01	(46)	3.25	(26)				
Sm	0.370	(105)			1.53	(26)	1.38	(15)				
Eu	2.33	(16)	2.19	(22)	1.37	(16)	1.65	(8)	2.89	(32)	2.94	(27)
Gd	0.680	(196)			1.67	(34)	2.03	(18)				
Tb			0.291	(55)	0.471	(71)	0.368	(33)				
Dy			2.90	(41)	3.71	(42)	2.92	(18)				
Ho			0.429	(91)	0.770	(78)	0.643	(43)				
Er	0.603	(123)	1.49	(28)	2.13	(24)	2.01	(12)				
Tm			0.271	(58)	0.343	(52)	0.306	(30)				
Yb	0.570	(157)	1.64	(32)	1.87	(27)	1.77	(14)				
Lu			0.271	(68)	0.470	(78)	0.351	(33)				

* Values in parentheses represent 1 standard deviation.

* Error given in terms of the last decimal place.

* Missin values are either below detection limits or give bad statistics (i.e 100 σ /concentration >30)

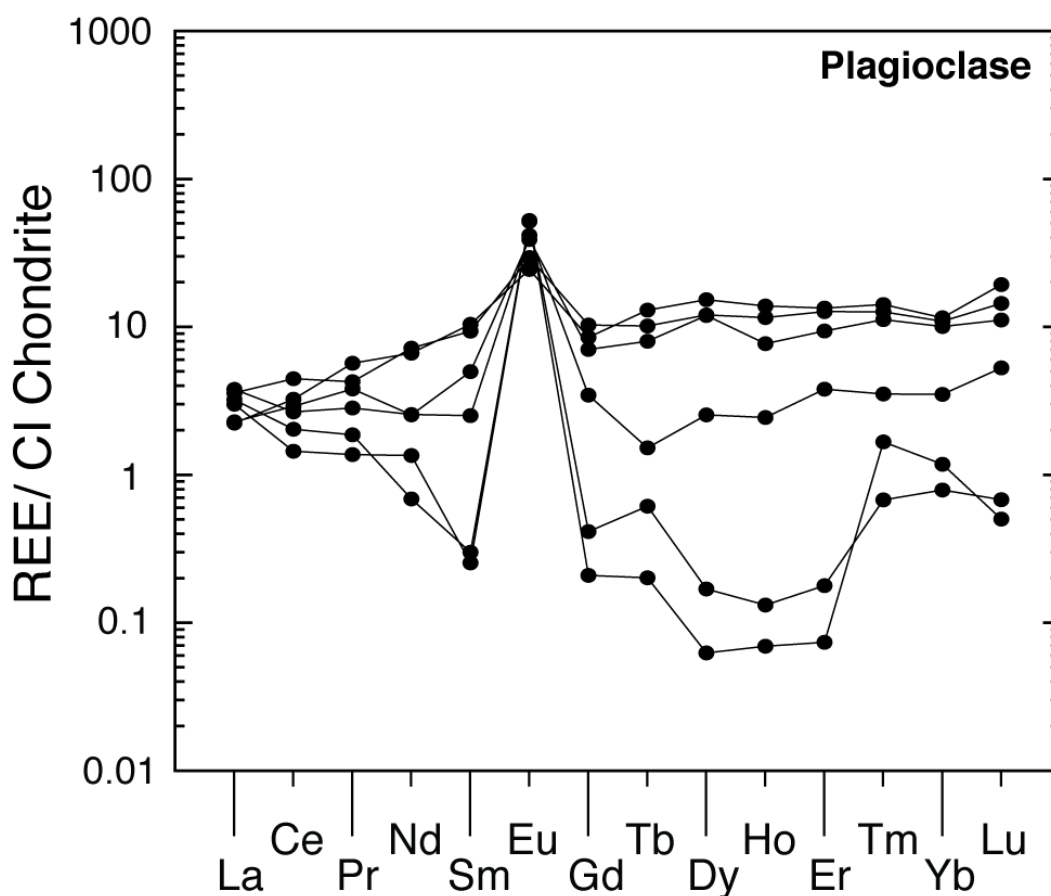


Figure 3.9 Rare Earth-Element Composition of Dacite Plagioclase

Rare-earth element patterns for plagioclase analyses in the dacite clast. The large variations in HREE concentrations are interpreted to reflect contamination from pyroxene inclusions. Data are normalized to CI chondrites (Anders and Grevesse 1989).

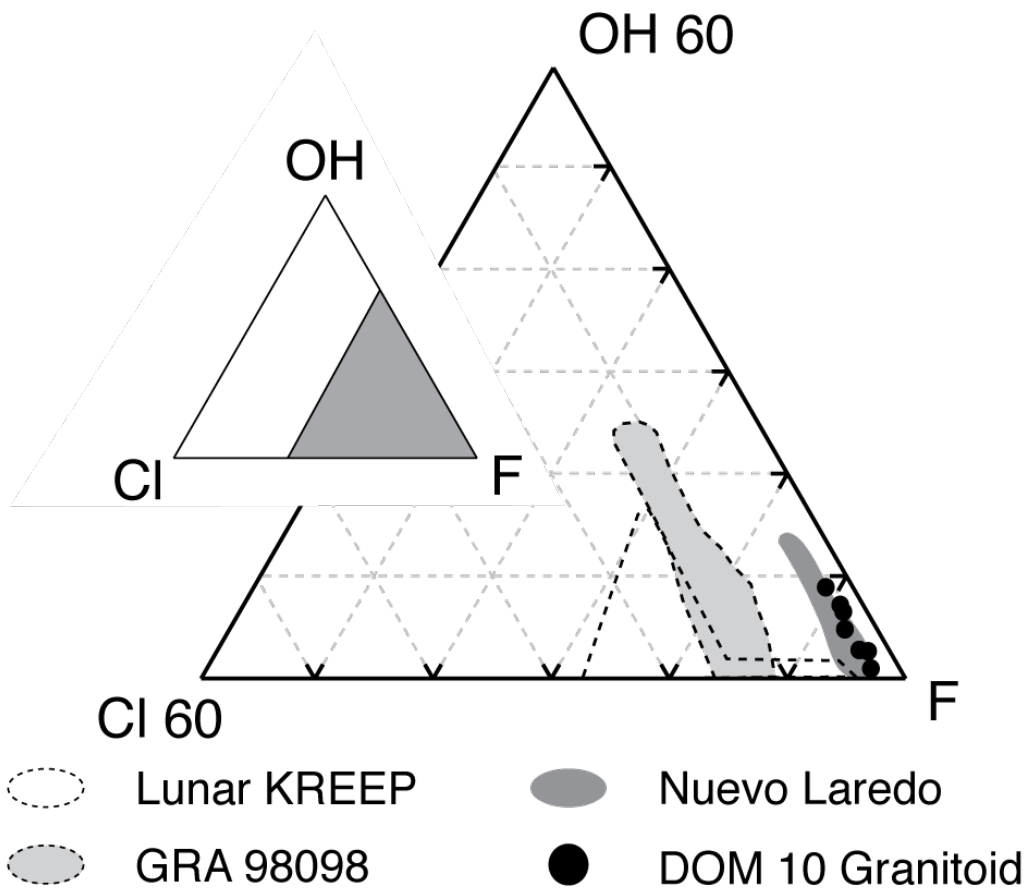


Figure 3.10 Apatite Volatile Composition in Dacite

F-Cl-OH (molar) ternary displaying the composition of apatites in the dacite clasts. Data points are plotted from EMP data, with OH calculated by difference using the method of Ketcham (2015). Apatites from the dacite clast plot within the range of non-cumulate eucrites. External data fields are from Sarafian et al. (2013).

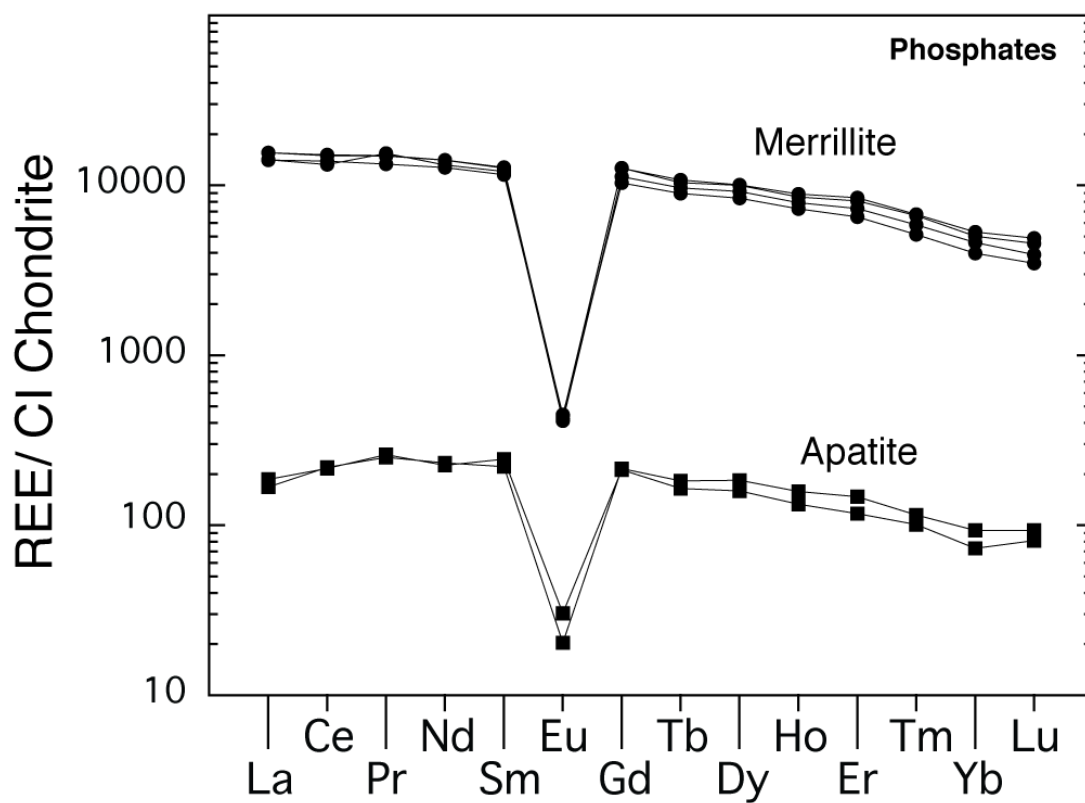


Figure 3.11 Trace-element Chemistry of Phosphates

Rare-earth element patterns for phosphates in the dacite clast. Data are normalized to CI chondrites (Anders and Grevesse 1989).

DISCUSSION

The identification of a distinctive dacite lithology associated with Vesta, containing primary augite oikocrysts and abundant rare phases (i.e. K-feldspar, silica, and phosphates), is a testament to the diversity of vestan lithologies. Such a lithology has, to our knowledge, not been previously described, and can therefore provide insight into differentiation and melt production mechanisms that operated on Vesta. Furthermore, the differences in petrography between the large (4 mm X 4 mm) dacite clast and other evolved lithologies, i.e. the low-Mg rock debris described by Barrat et al. (2012), suggest the complete lithologic diversity of Vesta remains elusive. In the following sections, we discuss possible origins for the dacite lithology.

Comparison with Basaltic Eucrites

The evolved clast shares textural and chemical similarities to basaltic eucrites; however, various petrographic and chemical features indicate a distinctive origin. Mayne et al. (2009) reported on the chemistry and textural variations of 29 unbrecciated eucrites; they showed the common eucrite mineral assemblage to consist of plagioclase, pigeonite, and silica in varying proportions. Minor minerals often include augite, FeNi metal, sulfide, and oxides. We observe that compositions of pyroxenes and plagioclase in the dacite clast resemble those reported by Mayne et al. (2009) and Hsu and Crozaz (1996). Additionally, most coarser-grained basaltic eucrites exhibit subophitic to ophitic textures (Mayne et al. 2009), similar to that observed in the dacite clast. However, the mineral modes are dissimilar. The most obvious distinction is the presence of primary augite within the clast; pigeonite is the primary pyroxene in eucrites, and the occurrence of augite is associated with exsolution caused by metamorphism (Duke and Silver 1967; Takeda and Graham 1991). Primary augite has only been observed in Kapoeta howardite (Dymek et al. 1976), though its identification has been disputed by Stolper (1977). Pigeonite only comprises ~5% of the dacite clast, and is therefore a relatively minor phase. In addition to primary augite, the dacite clast also exhibits an increased abundance of FeNi metal, oxides, and sulfides (~6%), a factor of 3 to 5 more than the unbrecciated eucrites studied by Mayne et al. (2009). Moreover, phosphates, quartz, and K-feldspars, rare phases associated with eucrite mesostasis areas are abundant and disseminated throughout the sample. These observations further support the evolved nature of this clast.

Mayne et al. (2009) found that most unbrecciated eucrites are of types 4-6, in reference to their degree of metamorphic equilibration. These metamorphic indices (Takeda and Graham 1991) indicate that most eucrites have experienced homogenization of major elements within pyroxenes, as well as the exsolution of augite lamellae from the pigeonite host, which is resolvable by EMPA. Further, type 4-6 eucrites either lack mesostasis areas, or such regions have been recrystallized. Unlike most eucrites, submicron pyroxene exsolution in the dacite clast is unresolvable by EMPA (Figure 3.5). Moreover, the preservation of possible mesostasis suggests the clast has experienced lower degrees of metamorphism (types 2 to 3?).

Table 3.5. Modal analysis of mineral phases associated with dacite clast.

Phase (modal %)	Raw data	Bulk	Silicate-oxide	Bulk-FeS	Phase density
Unclassified	7				
Clinopyroxene	12.2	14.4	15.1	15.1	3.40
FeNi metal	0.4	0.5		0.5	7.90
Ilmenite	1.4	1.7	1.8	1.8	4.72
Pigeonite	3.9	4.6	4.8	4.8	3.38
Phosphates	0.4	0.5	0.5	0.5	3.19
Plagioclase	40.0	47.1	49.5	49.3	2.75
Silica	22.4	26.4	27.7	27.6	2.65
Troilite	3.6	4.3			4.61
K-felspar	0.4	0.5	0.5	0.5	2.57

Table 3.6. Reconstructed bulk composition of dacite clast.

Wt.% oxide	Bulk ^a	Silicate-Oxide ^b	Bulk-FeS ^c	Juvinas	Sioux County	Stannern	Nuevo Laredo
SiO ₂	54.5	59.2	58.4	49.1	49.4	49.2	49.5
TiO ₂	1.5	1.6	1.6	0.6	0.6	1.0	0.9
Al ₂ O ₃	14.5	15.8	15.6	13.1	13.4	12.2	12.0
Cr ₂ O ₃	0.1	0.1	0.1	0.3	0.3	0.3	0.3
MgO	2.2	2.4	2.4	7.0	7.3	7.0	5.5
CaO	11.2	12.2	12.0	10.7	10.3	10.6	10.3
MnO	0.2	0.2	0.2	0.5	0.6	0.5	0.6
FeO ^T	13.2	6.9	8.5	17.9	18.1	18.1	19.4
Na ₂ O	0.7	0.7	0.7	0.4	0.4	0.5	0.5
P ₂ O ₅	0.2	0.2	0.2	0.1	0.1	0.1	0.1
K ₂ O	0.1	0.2	0.2			0.1	0.1
S	5.9			0.2	0.1	0.2	
Fe# (molar)	77	61	67	59	58	59	66
Total	104.5	99.6	100.0	99.9	100.6	99.8	99.1

* FeO^T assuming all Fe as FeO.

^aBulk composition includes all phases within the dacite clast.

^bBulk composition excludes FeNi metal and FeS.

^cBulk composition excludes FeS component.

Table 3.6 Continued.

Wt.% Element	Bulk ^a	Silicate-Oxide ^b	Bulk-FeS ^c
Si	25.5	27.7	27.3
Ti	0.9	1.0	1.0
Al	7.7	8.4	
Cr	0.1	0.1	0.1
Mg	1.4	1.5	1.4
Ca	8.0	8.7	8.6
Mn	0.1	0.1	0.1
Fe ⁰	5.4	0.0	1.3
Fe ²⁺	4.8	5.2	5.2
Fe ³⁺	0.1	0.1	0.1
Na	0.5	0.5	0.5
K	0.1	0.1	0.1
P	0.1	0.1	0.1
S	2.4		

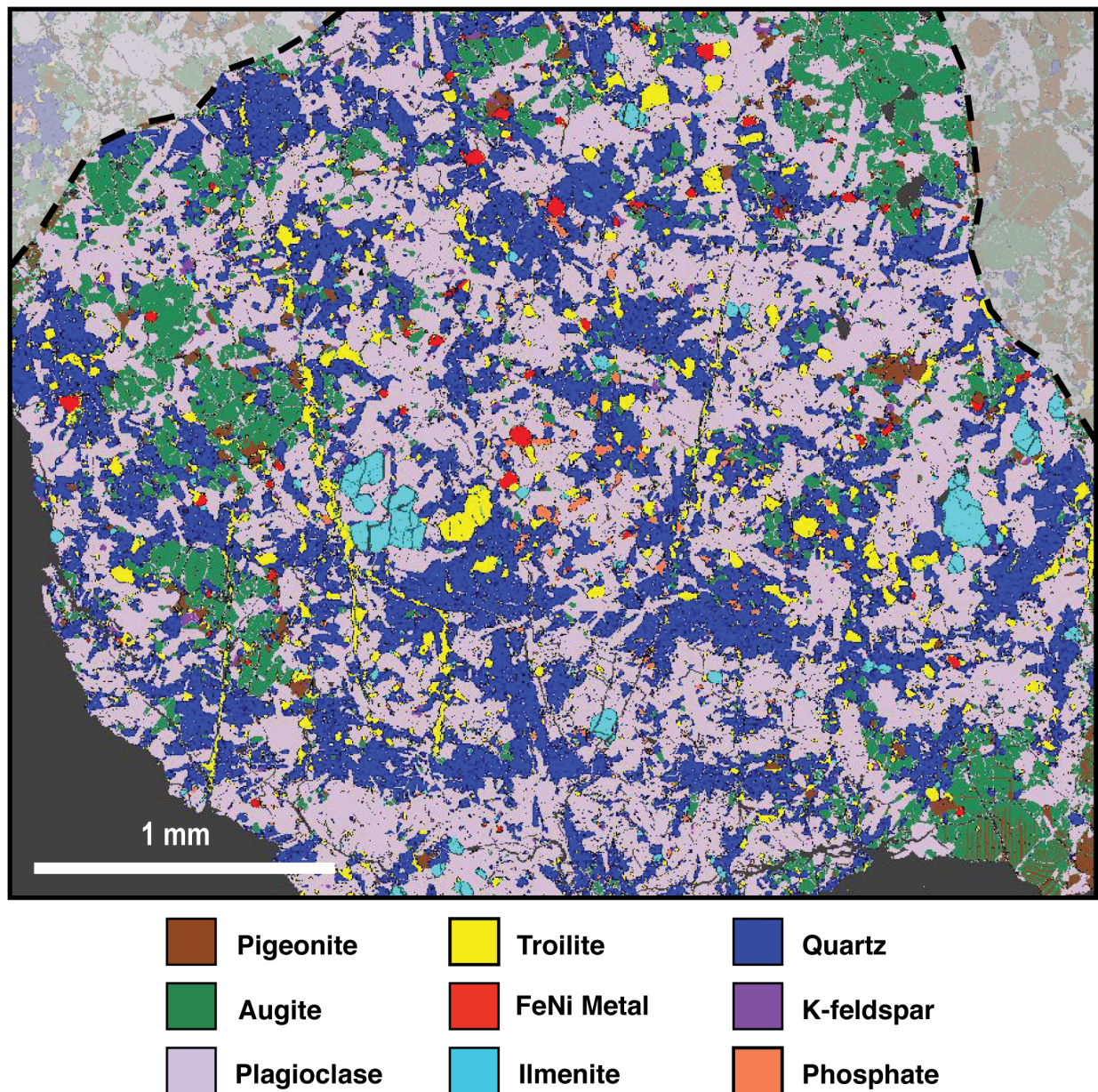


Figure 3.12 Mineral Map of Dacite Clast

Mineral distribution map displays the abundance of mineral phases in the dacite clast. The map was used to determine precise modal abundances in order to better calculate the bulk composition of the clast. Note the FeS veins which cut across the clast.

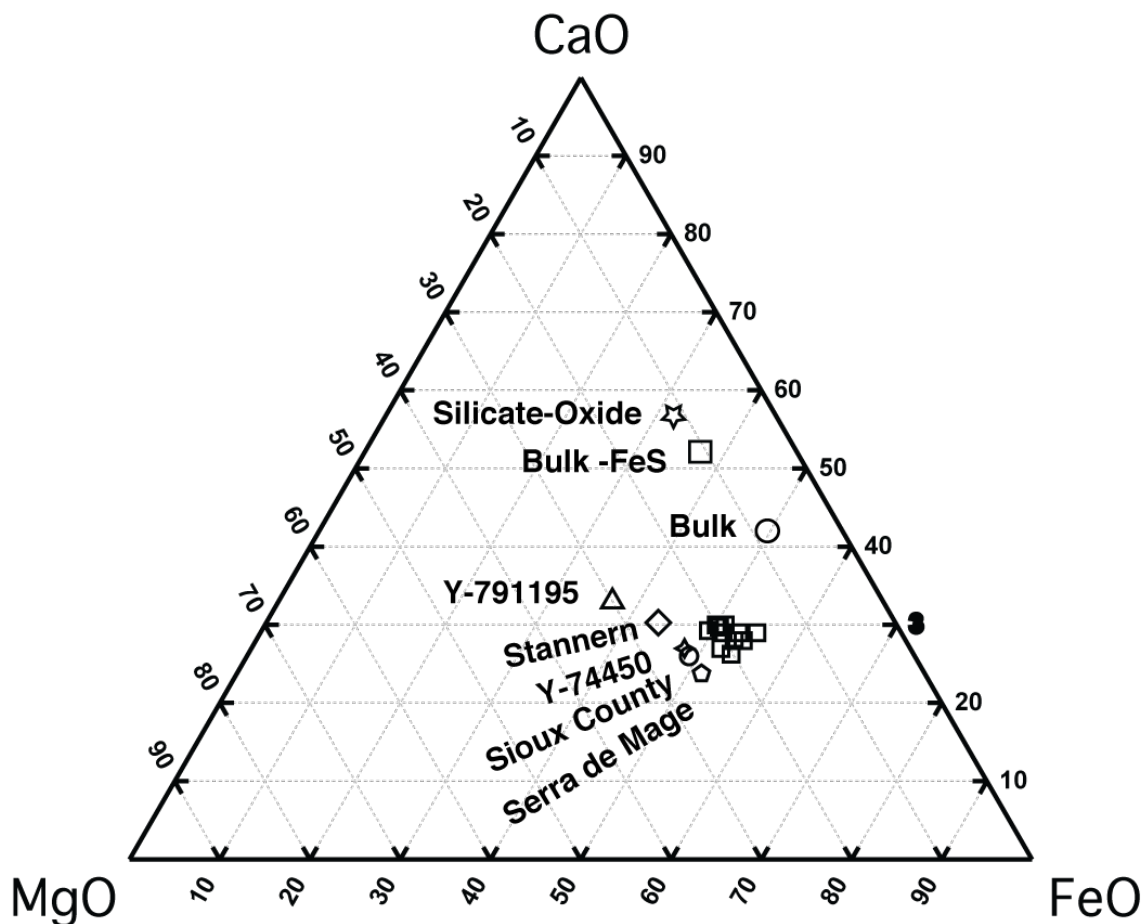


Figure 3.13 MgO-FeO-CaO Ternary

Calculated bulk compositions plotted on a CaO-MgO-FeO (wt. %) ternary plot. Small squares are representative compositions of typical eucrites. Additional symbols, labeled on figure, show outliers. Although the three calculated bulk compositions show a large range in composition, mainly due to the assumptions of the state of Fe in the reconstruction calculations, they are distinctly different from known HED eucrite compositions. External data from Kitts and Lodders (1998).

The textural setting of quartz within the clast resembles the silica veins in GRA 98098, which appear to have a distinctive tabular shape (Figure 3.2c). This feature has been suggested to result from partial melting, mobilization, and recrystallization of a melt (Yamaguchi et al. 2009). While some might argue this indicates that the dacite clast has experienced a higher degree of metamorphism, and thus partial melting, other evidence does not support this. Mainly, the lack of coarse exsolution lamellae suggests metamorphism was limited, and likely not capable of producing the large volume of tabular silica grains. Conversely, such veins could have originated as the result of an infiltrating melt; this mechanism has been suggested for some eucrites (Yamaguchi et al. 2009), although (Mittlefehldt and Galindo Jr 2002) suggested this was not the case for GRA 98098. Interestingly, the quartz in the dacite clast, in some places, resembles the “hackle” fracture pattern observed by Seddio et al. (2015) in quartz from lunar granites; they use these fracture patterns to infer the genesis of lunar granite and felsite. Specifically, this unique fracture pattern forms as a result of a decrease in volume during transformation of tridymite or cristobalite to quartz, and is interpreted by Seddio et al. (2015) to indicate that some silicic magmas on the Moon occurred as eruptions, rather than crystallization at depth. Although speculative, this could support the interpretation that the dacite clast formed during a volcanic eruption.

Volatile Composition

The volatile inventory of Vesta was investigated by Sarafian et al. (2013) by examination of apatite compositions in eucrites. They showed that apatites in most basaltic eucrites are F-rich, exhibit magmatic textures, and are spatially associated with mesostasis pockets. Unfortunately, these observations indicate they were relatively late-crystallizing phases, and therefore are inadequate as a tool for investigating the volatile composition of magmas, as most magmas on Vesta were likely degassed due to the low overburden pressure. Regrettably, the apatites in the dacite clast share all of the same textural and chemical properties (Figure 3.10; Table 3.3A), and thus only indicate that the magma was relatively rich in P_2O_5 (abundant apatite and merrillite); their composition provides no information regarding the volatile content of the original magma.

The observed enrichment of P_2O_5 in the dacite clast, relative to basaltic eucrites, may be the missing reservoir for which incompatible elements were concentrated (e.g. P_2O_5 , K_2O , and Na_2O) during differentiation. A depletion of such elements has long been recognized in eucrites, for which several explanations have been proposed (e.g. Drake et al. 1989; Mittlefehldt 1987; Newsom 1985). For instance, Mittlefehldt (1987) suggested that volatile degassing during late-stage interstitial liquid crystallization or during post-brecciation thermal metamorphism could explain such depletions. However, P and Mn are comparably volatile, and therefore parent-body-scale depletion for P cannot be reconciled with the chondritic abundances of Mn (Drake et al. 1989; Righter and Drake 1997). Alternatively, the incompatibility of P relative to Mn during crystallization could produce the observed fractionation. Crystallization processes can thus explain the P-depleted nature of eucrites; the dacite lithology may address the long-standing conundrum of the missing reservoir of P, which resulted during the differentiation of Vesta.

Evolved Lithologies on Vesta

The suggestion that evolved lithologies should exist within the eucrite parent body was first predicted by Stolper (1977), and was later supported by the identification of K-rich impact melt spherules (Barrat et al. 2009a; Barrat et al. 2009b) and low-Mg rock fragments (Barrat et al. 2012) in howardites. Two hypotheses have been proposed to explain the production of evolved lithologies: fractional crystallization (i.e. Barrat et al. 2012; Stolper 1977) and crustal partial melting (e.g. Yamaguchi et al. 2009). Barrat et al. (2012) considered that low-Mg lithic clasts in the Northwest Africa (NWA) 1664 and 1769 howardites could have formed by fractional crystallization of eucrites; however, the inability to determine reliable bulk compositions prevented evaluation of their hypothesis. Partial melting of the vestan crust has also been evoked to explain the origin of the Stannern trend eucrites, which are enriched in incompatible elements (Barrat et al. 2007). Such a mechanism is certainly possible, and supported by highly metamorphosed eucrites (Yamaguchi et al. 2009). Additionally, heating experiments carried out on basaltic eucrites indicate melt production occurs at temperatures just above the solidus ($\sim 1060^{\circ}\text{C}$); melts produced are enriched in K_2O , TiO_2 , and P_2O_5 relative to typical basaltic eucrites. Fractional crystallization and partial melting of the eucritic crust provide a means of generating felsic melt capable of producing the dacite clast identified in this study; therefore, we evaluate both mechanisms, and consider geochemical evidence that would allow us to distinguish between them.

Geochemical Modeling

Melting and crystallization experiments were carried out by Stolper (1977) on basaltic eucrites to evaluate the hypothesis that non-cumulate eucrites originated from partial melting and fractionation of the bulk eucrite parent body, and that these meteorites represent quenched liquids. As suggested by eucrite textures, these magmas would have erupted onto the surface or solidified in the crust as dikes (Duke and Silver 1967); this view is commonly incorporated into differentiation models, and supported by physical constraints (e.g. Mandler and Elkins-Tanton 2013; Neumann et al. 2014). Stolper (1977) concluded that small amounts of pigeonite and plagioclase fractionation of eucrite liquids with compositions similar to Juvinas and Sioux County could produce the range of eucrite compositions, with larger amounts of fractionation (40 %) needed to produce compositions similar to Nuevo Lardeo and Lakangaon. It is thus plausible to consider that increasing degrees of crystallization may be responsible for producing even more evolved magmas.

Fractional Crystallization

Fractionation of Juvinas and Sioux County liquid compositions, at pressures corresponding to the mid-crust on Vesta (200 bars) will initially produce an assemblage of pigeonite, plagioclase, and spinel. With increasing fractionation, pigeonite compositions become enriched in Fe and Ca (Figure 3.14), while feldspar compositions show little variation ($\sim \text{An}_{88-91}$). After 55 to 65 % crystallization augite joins the liquidus (Figure 3.14); olivine shortly follows. Fractional crystallization of Sioux County is not capable of producing augite compositions similar to those observed in this study; however, after 55 % crystallization Juvinas will begin to crystallize augite that approaches the average composition in the dacite clast ($\text{En}_{31}\text{Fs}_{35}\text{Wo}_{34}$ and

En₂₉Fs₃₁Wo₄₀, respectively; Figure 3.14b). Though similar clinopyroxene compositions are produced, modeled pigeonite compositions are much higher in CaO (~7 wt.%), compared to the 1.5 wt.% measured by the EMP. Therefore, pure fractional crystallization of a liquid with a basaltic eucrite composition (Juvinas and Sioux County) is unlikely to have produced the observed assemblage. Moreover, if the dacite clast is representative of a liquid composition, Figure 3.15 illustrates that fractional crystallization is unable to produce such a liquid composition; an eruption of the last gasp of residual magma resulting from fractional crystallization is therefore not supported.

Late-Stage Melt Segregation

Models involving the crystallization of basaltic eucrite liquid compositions under equilibrium conditions at 200 bars originally crystallize pigeonite (En₆₃Fs₂₉Wo₈; Figure 3.14) and spinel, followed shortly by plagioclase (~An₈₉). The equilibrium phase assemblage remains constant throughout most of the crystallization sequence, while the compositions of the phases equilibrate with the liquid producing variations in end-member compositions (i.e. pigeonite; Figure 3.14). The chemical evolution of pigeonite closely resembles the fractional crystallization sequence; however, at 85 and 90 % crystallization (Juvinas and Sioux County, respectively) augite joins the equilibrium phase assemblage (Figure 3.14); the appearance of augite closely coincides with a decrease in the Ca concentrations of pigeonite. This sequestration of Ca from pigeonite drives the liquid composition towards that observed in the dacite clast. Figure 3.15b displays the liquid line of descent (LLD) for equilibrium crystallization of magmas with initial compositions of Juvinas, Sioux County, Stannern, and Nuevo Laredo. Additionally, Figure 3.16 displays the effect of decreased pressure on the LLD and pyroxene compositions during equilibrium crystallization. There is very little pressure dependence during equilibrium crystallization, although we note that higher pressures tend to favor the formation of augite earlier in the crystallization sequence, and ultimately produce pigeonite compositions closer to those observed in the dacite clast.

If the dacite clast formed under equilibrium conditions and is representative of a melt composition, between 80 and 90 % crystallization must have occurred (Figures 3.15b and 3.16a). The extensive amount of crystallization needed to produce liquid compositions and the observed phase assemblage similar to the dacite clast, offers additional support that this is a highly evolved lithology. We therefore conclude that equilibrium crystallization, followed by segregation of the final 10-20% melt, accounts for the genesis of the dacite clast. Below we offer a conceptual model for the genesis of this lithology.

Limitations of Crystallization Models

We consider our MELTS crystallization models to represent a first-order approximation of likely liquid evolution paths and phase assemblages produced during the advanced crystallization of eucritic melts, which can serve as a means of evaluating possible petrogenetic hypotheses. However, we note that caution must be taken when evaluating these models due to several sources of error and conditions, which, if not considered properly, would drastically affect the system. First, the reconstructed bulk

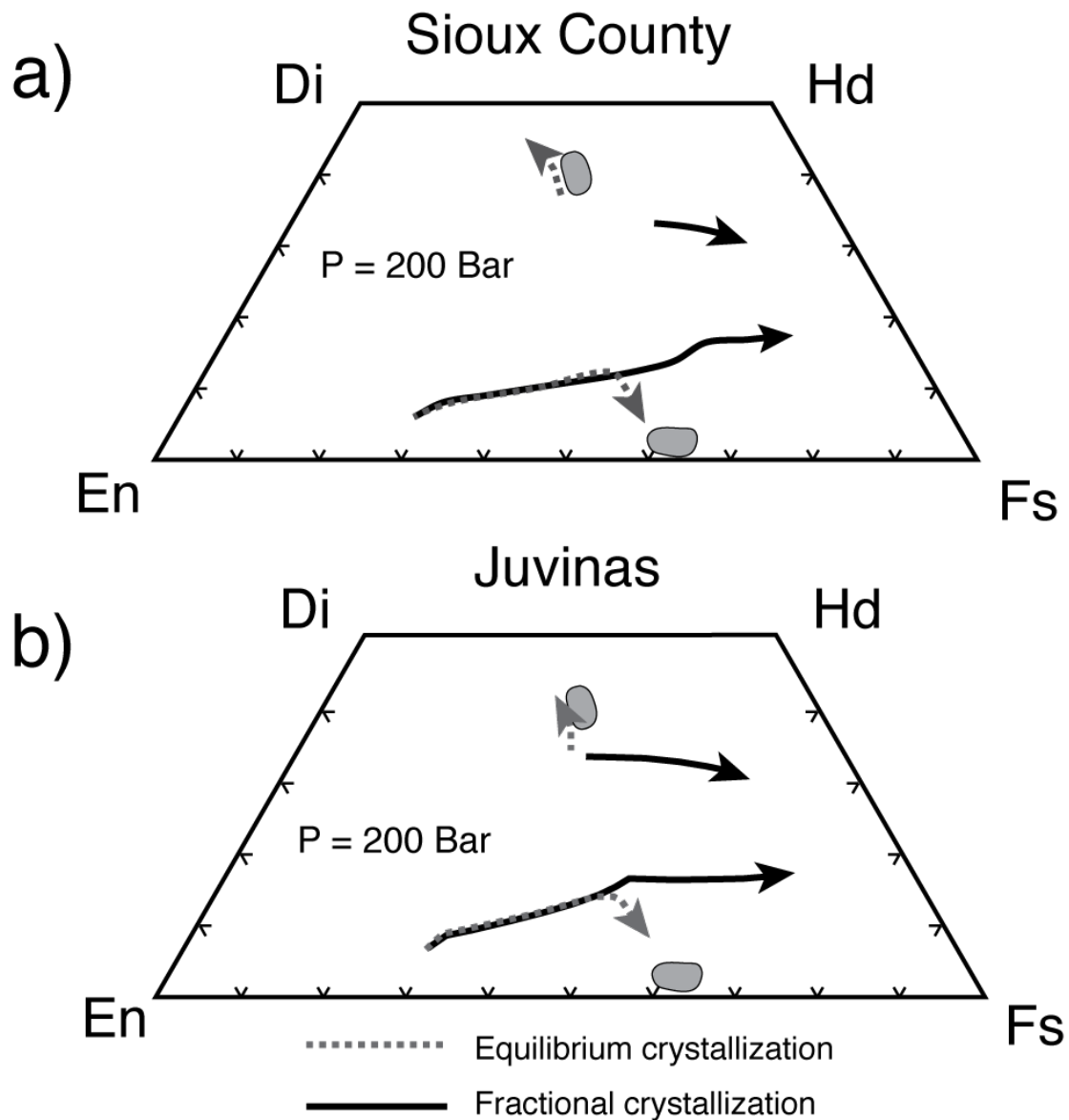
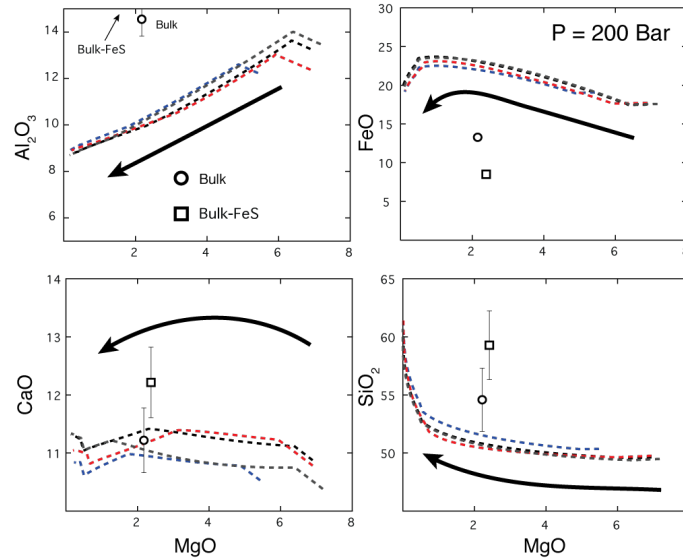


Figure 3.14 Modeled Pyroxene Compositions at 200 Bars

MELTS-modeled pyroxene compositions for equilibrium and fractional crystallization at 200 bars. Gray fields define the range of end-member compositions identified in the dacite clast. Compositions produced from (a) Sioux County liquid compositions and (b) compositions Juvinas liquid compositions (Kitts and Lodders 1998).

a) Fractional Crystallization



b) Equilibrium crystallization

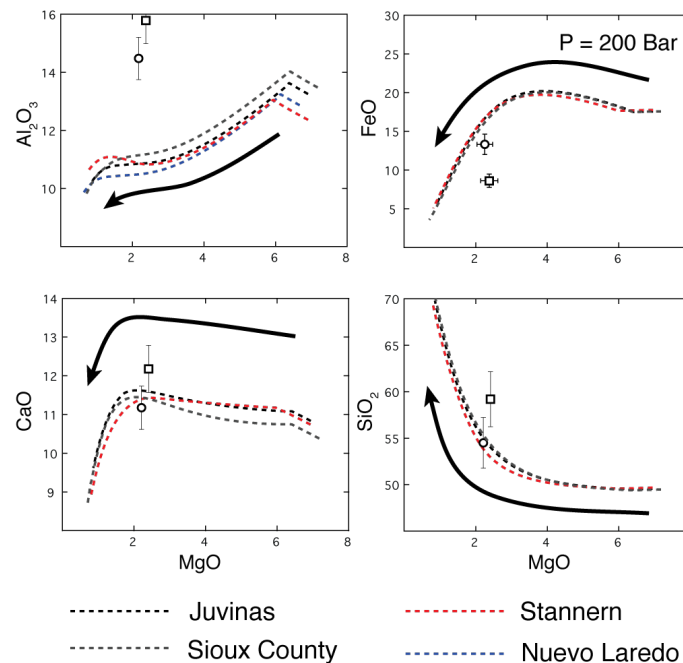


Figure 3.15 Liquid Composition During Crystallization

Variation diagrams showing the liquid line of descent (LLD) during (a) fractional and (b) equilibrium crystallization at 200 bars for various starting liquid compositions (Sioux County, Juvinas, Stannern, and Nuevo Laredo). Where error bars are shown, they represent an overall 10% error in the calculated values, and are only used to qualitatively illustrate how reasonable error affects the interpretation.

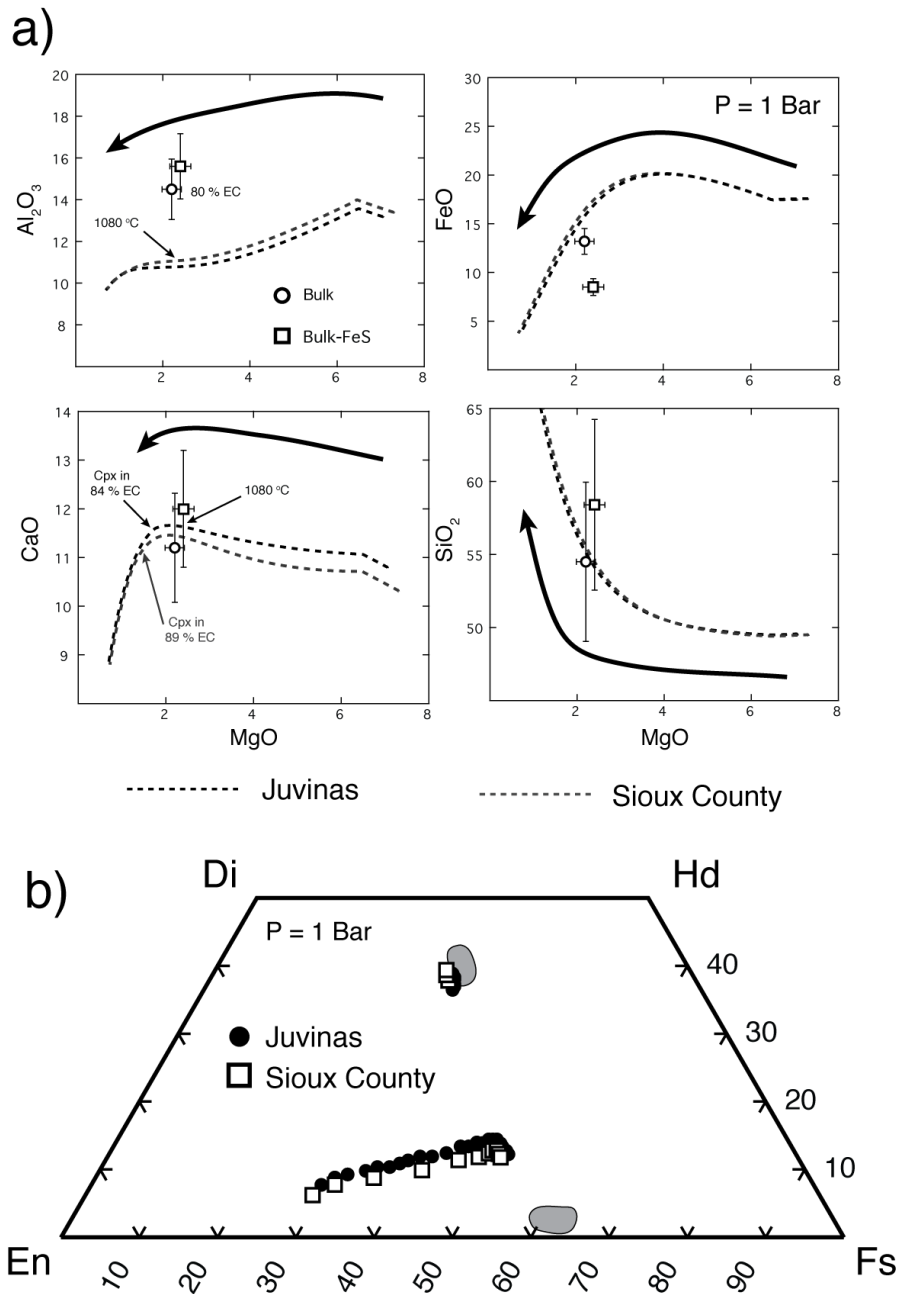


Figure 3.16 Modeled Pyroxene Composition at 1 Bar

a) Liquid line of descent during equilibrium crystallization of Juvinas and Sioux County liquid compositions at 1 bar. The LLDs show little dependence on pressure between 1 bar and 200 bars. b) Modeled pyroxene compositions from liquids in (a) at 1 bar. Again, we observe little dependence on pyroxene compositions, though we note that higher-pressure produces pyroxenes with higher Ca concentrations.

composition contains potential sources of error which cannot accurately be quantified; sources of error include unrepresentative assemblage and variations in major- and minor- element compositions within the minerals. Additionally, the errors relative to concentrations are much larger for minor elements, which could cause large uncertainties in the calculated concentrations; these can have a large effect on phase stability and composition. The presence of various states of Fe within the clast (i.e. Fe⁰, Fe²⁺, and Fe³⁺) also has implications on the modeled phase assemblage, especially given MELTS inability to operate below the IW buffer; the crystallization of FeNi metal from the melt will have a dramatic effect on the composition of the melt and mineral phases (i.e. pyroxene; Shearer et al. 1997). This is an important concern because FeNi metal is observed within the clast. Our last concern is the accuracy of phase stabilities modeled by MELTS during the last stages of crystallization (i.e. <10%). Many of the phases within the dacite clast are late-stage minerals, and therefore cannot be accurately modeled by MELTS, which ultimately hampers our ability to evaluate our hypothesis. Specifically, silica, K-feldspar, and phosphates only reach the liquidus after >90 % crystallization. Therefore, we note that our conclusions are based largely on textural and compositional considerations, and our MELTS models only serve as support for these conclusions.

Petrogenesis of Dacite

Textural and geochemical evidence indicates the dacite clast from the DOM 10 howardite pairing group represents the most evolved lithology identified from Vesta. The occurrence of primary augite oikocrysts enclosing plagioclase grains supports this interpretation. The fine exsolution lamellae (<1 µm) and lack of zonation in augite could indicate that this assemblage was in chemical equilibrium. Conversely, this could also indicate that small degrees of metamorphism caused the exsolution of pigeonite from augite, while erasing any primary zoning. However, with such low degrees of metamorphism, we would expect to see the original zonation preserved in the minor-element concentrations; the latter is not observed as minor-element concentrations show very little variation within augite. High trace-element concentrations in augite also support an evolved origin for the dacite clast (Y, ~50 ppm; HREE, ~40 to 50 X CI-chondrite). Additionally, merrillite and apatite grains exhibit REE enrichments 11,000 and 200 X CI-chondrites, respectively. Rare accessory phases (i.e. K-feldspar) add increasing support for an evolved origin. The enrichment in P₂O₅ within the dacite clast also suggests the dacite clast is a product of extensive crystallization.

We considered that such an evolved assemblage likely formed during equilibrium crystallization of basaltic eucrite liquid compositions similar to Juvinas and Sioux County, followed by late-stage melt separation. Our calculated bulk composition plots near the ternary eutectic for liquids with Fe# 65 (Figure 3.17), which would be saturated with pyroxene, plagioclase, and silica. Therefore, we conclude that 80 to 90 % equilibrium crystallization of a basaltic liquid composition is the mechanism that produced the melt composition of the dacite clast. Rather than large plutonic bodies of evolved residual melt, we envision the dacite lithology as a localized melt pocket. The possible occurrence of a hackle fracture pattern in quartz grains may indicate a volcanic origin for the dacite lithology.

Alternative formation mechanisms for the dacite clast include a partial melting or impact origin. Partial melting models have been used to explain the origin of the Stannern trend eucrites (Barrat et al. 2007), and extensively metamorphosed eucrites support this as a possible formation mechanism (Yamaguchi et al. 2009). However, without bulk trace-element data, this hypothesis is difficult to test. Additionally, an impact origin is difficult to evaluate, though support for such an origin could be argued given that FeNi metal grains in the dacite clast contain unusually high amount of Ni (3 to 12 wt.%). However, we dismiss an impact origin as a likely formation mechanism. First, the texture of the clast is not consistent with an impact origin (i.e. the absence of heavily shocked clasts). Second, if the target rock were completely melted, it would still have to be of dacite composition. We interpret the Ni contents of the FeNi metal grains as suggesting a contamination event may have been involved.

CONCLUSIONS AND SUMMARY

We have identified an evolved dacite lithology within the DOM 10 howardite pairing group, which has undergone minimal metamorphism. The clast contains the first unambiguous identification of primary augite in a eucrite-associated lithology. This clast contains abundant phases that are rare in typical HED meteorites: phosphates, quartz, and K-feldspar. Enriched trace-element concentrations in augite reflect the original evolved characteristics of the magma from which this lithology formed. Additionally, calculated P_2O_5 concentrations in the dacite offer an explanation for the phosphorous-depleted nature of typical eucrites. Geochemical modeling supports an origin as late-stage differentiates from a magma with a composition similar to Sioux County or Juvinas. Specifically, we conclude that 80 to 90 % equilibrium crystallization of a basaltic eucrite liquid is responsible for producing a residual liquid with the composition of this dacite clast. The dacite clast may, therefore, have a direct relationship to non-cumulate eucrites. The magmatism of Vesta was apparently capable of producing compositionally evolved melts, although possibly only within pockets in solidifying chambers, which may not have erupted to the surface.

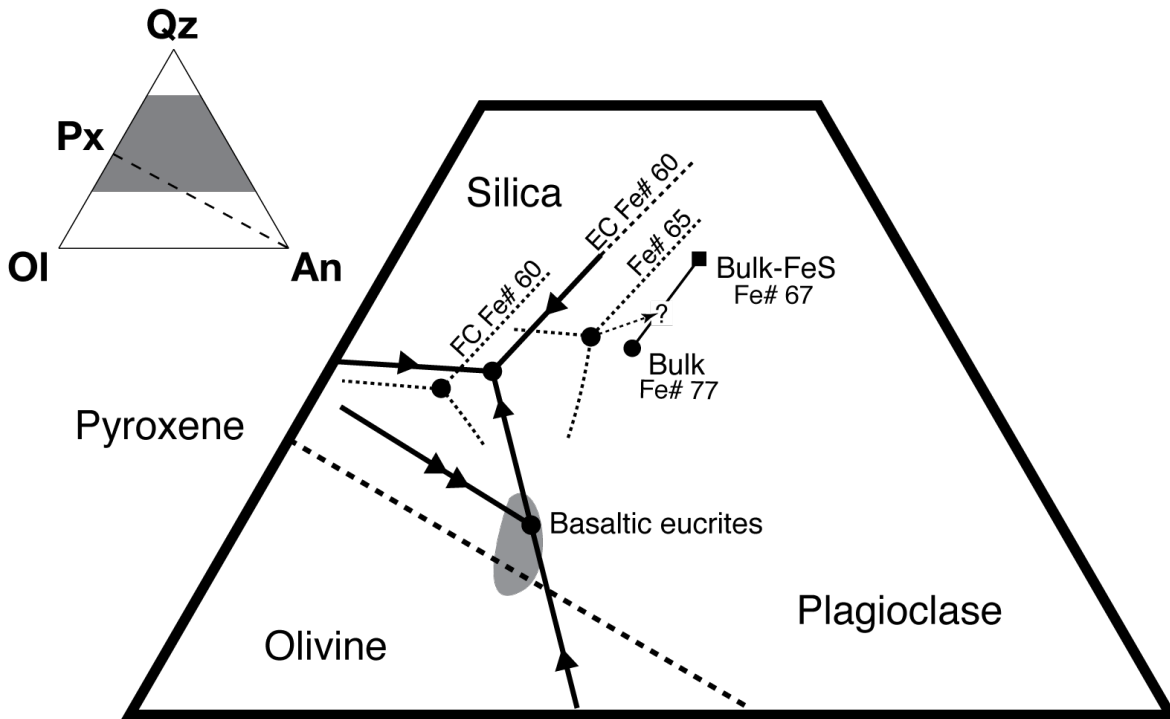


Figure 3.17 Pseudo-liquidus Diagram of Ol-An-Qz System

Pseudo-liquidus diagram modified from Stolper (1977) with calculated bulk compositions (BULK and BULK-FeS) of the dacite clast plotted. Phase boundaries shown are for liquids with Fe# 60 to 65. Reconstructed bulk compositions for the clast (molar units) were projected by recalculating into Ol-An-Qz coordinates. Residual liquids produced during fractional crystallization of a basaltic eucrite liquid (Fe# ~60) will evolve along a path towards the ternary eutectic at FC, while equilibrium crystallization of pigeonite and plagioclase will evolve towards the ternary eutectic at EC. The ternary eutectic during equilibrium crystallization will move progressively to the upper right with increasing Fe#. The true composition of the dacite clast likely lies along a mixing line between the two compositions, with Fe# 67 to 77, given that all FeS in the dacite does not occur as veins. Projection of the ternary eutectic towards the dacite composition mixing line gives an approximation of the eutectic location with a Fe# similar to the dacite clast. The reconstructed bulk compositions plot close, likely within error, to the ternary pyroxene-plagioclase-silica eutectic, and indicate advanced crystallization is responsible for the origin of the dacite.

SUMMARY

The Dominion Range 10 howardite pairing group is comprised of six individual stones with a combined mass of approximately ~1.1 kg; petrographic and geochemical indicators suggest these meteorites originated in the megaregolith on Vesta. Petrologic investigations of the samples have enabled the recognition of 21 individual lithologies, each with its own unique petrogenesis, represented as lithic fragments. Moreover, additional lithologies may be represented in comminuted mineral fragments. Of the lithologies recognized there are 7 diogenites, 4 cumulate eucrites, 8 basaltic eucrites, a Mg-rich harzburgite, and a dacite. The characteristics of these howardites indicate that they are among the most heterogeneous howardites yet characterized. Additionally, a comprehensive examination of their mineralogy revealed diogenite:eucrite and cumulate eucrite:basaltic eucrite ratios that are potentially important for interpreting remote-sensing observations. Furthermore, these distinctive ratios are likely inherited from their source terrains, suggesting that the DOM 10 howardites record an extensive period of impact excavation and gardening, as represented by the distinct breccia clasts and large inter- and intrasample variations.

Two unique lithologies have not been previously recognized in HED studies, and provide important new insights into the magmatic evolution of Vesta. The Mg-rich harzburgite clasts, interpreted to have originated from the vestan mantle, suggest that Vesta did not completely melt, and that the vestan mantle is residua in origin. Additionally, the presence of FeNi metal with ~2 wt. % Cr indicates the conditions in vestan mantle were more reducing than previously thought. The trace-element concentrations in mantle pyroxenes appear to have been affected by secondary processes, and are therefore not pristine. The secondary alteration may have originated from a metasomatic event, during which the chromite-orthopyroxene symplectite was produced; this is hypothesized to be a consequence of silicate and metallic melt interactions during early differentiation. The observed range of minor-element concentrations implies the amount of partial melting was variable. The implications of a harzburgite mantle profoundly affect those current differentiation models that invoke the formation of a complete magma ocean. Our findings support more recent developments in geochemical models that involve partial melting and serial magmatism.

A dacite lithology was also identified, which is proposed to be the product of extensive crystallization, followed by melt extraction. The identification of an evolved lithology is important in itself; however, the specific geochemical characteristics have more profound implications. Specifically, the dacite clast contains the first unambiguous identification of primary augite, which supports the evolved origin of this lithology. Moreover, bulk composition reconstructions indicate the lithology is enriched in P_2O_5 relative to typical basaltic eucrites; this may be evidence of the “phosphorus sink”, which appears to be missing in the HED meteorite collection. Magmatic processes on Vesta were apparently complex enough to produce highly evolved pockets of melt that may not have erupted onto the surface.

The Dominion Range 10 howardites reveal the complexity of the vestan geological record, and shed light on some important questions. Particularly, investigation of the howardites leads to the conclusion that Vesta, although only ~525 km in diameter, was an incredibly complex world in terms of its magmatic evolution. It appears that Vesta has undergone differentiation via partial melting and serial magmatism. Further, differentiation in crustal plutons and isolated melt pockets created the range of HED lithologies. Additionally, Vesta has experienced an intense impact history, which excavated deep lithologies and distributed them within the vestan megaregolith.

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Appendix

Table 2.1A. Mineral chemistry of Mg-rich olivine (Unabridged).

n	DOM 10100,8				DOM 10105,6						DOM 10120,6	
	3	3	4	5	4	2	3	3	4	4	6	1
P ₂ O ₅	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
SiO ₂	40.9	40.4	39.7	37.4	40.2	40.0	40.6	41.3	40.3	40.3	40.8	40.7
TiO ₂	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Al ₂ O ₃	b.d.	0.03	b.d.	b.d.	b.d.	0.05	b.d.	0.15	b.d.	0.04	b.d.	b.d.
Cr ₂ O ₃	b.d.	0.07	0.05	b.d.	0.10	0.12	0.09	0.25	0.05	0.05	0.06	0.08
MgO	50.3	47.1	44.6	37.0	45.7	45.7	47.5	47.3	47.1	46.7	47.8	50.7
CaO	b.d.	0.05	0.04	b.d.	0.06	0.05	0.11	0.03	0.04	0.05	0.07	0.07
MnO	0.14	0.29	0.37	0.56	0.33	0.34	0.30	0.27	0.31	0.30	0.29	0.19
FeO	9.1	12.6	15.8	24.6	14.6	14.7	12.0	11.3	12.7	12.8	12.0	7.6
NiO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Total	100.6	100.6	100.6	99.6	101.0	101.0	100.7	100.6	100.5	100.3	101.1	99.4
Fe/Mn	62.5	42.2	42.5	43.7	43.1	42.3	39.5	41.3	40.9	42.9	40.9	40.1
Fe/Mg	0.10	0.15	0.20	0.37	0.18	0.18	0.14	0.13	0.15	0.15	0.14	0.08
Mn/Mg	0.0016	0.0036	0.0047	0.0086	0.0042	0.0043	0.0036	0.0032	0.0037	0.0036	0.0035	0.0021
Mg#	90.8	87.0	83.4	72.8	84.8	84.7	87.6	88.2	86.9	86.7	87.6	92.3

*Fe/Mn, Fe/Mg, and Mn/Mg calculated from molar values.

*Olivine with Mg# <80 represents diogenite olivine

Table 2.1A. Continued.

n	DOM 10120,6				DOM 10837,7						DOM 10838,6	
	1	1	2	3	3	3	3	3	2	3	3	3
P ₂ O ₅	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
SiO ₂	40.2	39.7	40.3	39.3	40.1	41.1	40.2	39.6	39.6	38.9	40.6	38.5
TiO ₂	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Al ₂ O ₃	0.03	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Cr ₂ O ₃	0.10	0.09	0.10	0.08	0.04	0.05	b.d.	0.10	0.11	0.07	0.06	b.d.
MgO	49.5	47.4	50.3	47.0	47.6	51.0	47.0	46.7	46.7	43.8	47.8	39.4
CaO	0.08	0.08	0.07	0.07	0.06	0.05	0.06	0.07	0.10	0.08	0.06	0.03
MnO	0.23	0.28	0.21	0.28	0.28	0.22	0.32	0.33	0.31	0.39	0.29	0.49
FeO	8.8	11.6	7.9	11.8	12.1	8.0	13.2	13.3	13.1	16.7	11.7	22.0
NiO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Total	99.0	99.2	98.9	98.6	100.3	100.5	100.8	100.1	99.9	100.0	100.6	100.4
Fe/Mn	37.6	41.0	36.9	41.1	41.8	36.1	41.1	40.2	41.4	42.2	40.2	44.5
Fe/Mg	0.10	0.14	0.09	0.14	0.14	0.09	0.16	0.16	0.16	0.21	0.14	0.31
Mn/Mg	0.0026	0.0034	0.0024	0.0034	0.0034	0.0024	0.0039	0.0040	0.0038	0.0051	0.0034	0.0070
Mg#	91.0	87.9	92.0	87.7	87.6	91.9	86.3	86.3	86.4	82.4	87.9	76.2

*Fe/Mn, Fe/Mg, and Mn/Mg calculated from molar values.

*Olivine with Mg# <80 represents diogenite olivine

Table 2.1A. Continued

n	DOM 10838,6							DOM 10839,6				
	3	1	4	4	2	3	3	2	2	2	3	3
P ₂ O ₅	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
SiO ₂	38.4	41.3	39.7	39.4	40.4	40.9	40.0	39.7	39.7	39.3	39.2	38.8
TiO ₂	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Al ₂ O ₃	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.04	b.d.	b.d.	b.d.	b.d.
Cr ₂ O ₃	0.04	0.07	0.05	0.03	b.d.	0.08	0.07	0.07	0.04	0.08	0.10	0.13
MgO	38.5	51.6	47.9	47.5	46.5	48.5	47.5	47.2	46.7	45.8	45.2	44.1
CaO	0.13	0.07	0.04	0.04	0.05	0.05	0.04	0.05	0.09	0.06	0.09	0.11
MnO	0.52	0.22	0.29	0.31	0.34	0.27	0.30	0.30	0.31	0.33	0.35	0.37
FeO	23.2	7.8	11.8	12.3	13.8	11.1	12.3	12.0	12.5	13.4	14.5	15.6
NiO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Total	100.9	101.1	99.8	99.5	101.1	100.9	100.2	99.4	99.4	99.0	99.4	99.1
Fe/Mn	44.0	34.7	40.3	38.6	40.6	41.3	40.2	39.3	39.7	39.6	41.1	41.4
Fe/Mg	0.34	0.09	0.14	0.15	0.17	0.06	0.15	0.14	0.15	0.16	0.18	0.20
Mn/Mg	0.0077	0.0025	0.0034	0.0038	0.0041	0.0027	0.0036	0.0036	0.0038	0.0041	0.0044	0.0048
Mg#	74.8	92.2	87.9	87.3	85.7	88.6	87.3	87.5	86.9	85.9	84.7	83.4

*Fe/Mn, Fe/Mg, and Mn/Mg calculated from molar values.

*Olivine with Mg# <80 represents diogenite olivine

Table 2.2A. Mineral Chemistry for Mg-rich pyroxene grains (Unabridged).

	DOM 10100,8		DOM 10105,6			DOM 10120,6					DOM 10837,7	
n	4	2	5	2	4	2	3	4	4	3	3	2
SiO ₂	55.3	56.2	56.9	57.5	55.1	57.7	55.3	57.1	55.4	56.2	57.3	57.1
TiO ₂	0.05	0.04	0.04	b.d.	0.09	b.d.	0.09	0.03	0.05	0.07	b.d.	b.d.
Al ₂ O ₃	0.49	0.68	0.39	0.08	1.55	0.10	1.44	0.32	0.67	0.79	0.07	0.10
Cr ₂ O ₃	0.80	0.64	0.79	0.69	0.96	0.53	0.91	0.43	0.41	0.72	0.34	0.46
MgO	29.3	31.8	32.5	34.2	29.8	34.5	29.9	32.7	29.0	32.4	34.0	33.6
CaO	0.68	0.93	0.53	0.72	1.41	0.15	1.30	0.64	0.89	1.20	0.18	0.20
MnO	0.43	0.41	0.34	0.31	0.40	0.24	0.39	0.35	0.46	0.32	0.27	0.27
FeO	12.9	9.8	9.2	7.4	10.9	6.9	10.9	9.1	13.8	7.8	7.9	8.2
Na ₂ O	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Total	100.0	100.5	100.7	100.9	100.2	100.1	100.2	100.6	100.7	99.5	100.1	100.0
Fe/Mn	30.0	24.0	27.1	24.0	26.8	28.7	27.9	25.8	29.9	24.2	28.9	29.9
Fe/Mg	0.25	0.17	0.16	0.12	0.20	0.11	0.20	0.16	0.27	0.13	0.13	0.14
Mn/Mg	0.0083	0.0072	0.0059	0.0051	0.0076	0.0039	0.0073	0.0061	0.0089	0.0056	0.0045	0.0046
Mg#	80.2	85.2	86.3	89.2	83.0	89.9	83.1	86.5	78.9	88.2	88.4	88.0
En	79.1	83.7	85.4	88.0	80.7	89.6	81.0	85.4	77.6	86.2	88.1	87.6
Wo	1.3	1.8	1.0	1.3	2.7	0.3	2.5	1.2	1.7	2.3	0.3	0.4

*Analyses with Mg# <85 correspond to diogenite material, although the boundaries may not be well defined.

Table 2.2A. Continued.

n	DOM 10837,7							DOM 10838,6			
	2	2	2	3	3	2	2	3	4	4	3
SiO ₂	56.2	56.0	55.3	55.2	55.0	56.8	56.0	56.3	57.2	55.5	57.3
TiO ₂	0.03	b.d.	0.08	0.10	0.10	0.04	0.07	0.03	0.04	0.14	b.d.
Al ₂ O ₃	0.37	0.37	0.86	1.59	1.47	0.29	1.02	0.16	0.33	1.60	0.19
Cr ₂ O ₃	0.41	0.38	0.69	1.09	1.10	0.57	0.94	0.28	0.52	1.08	0.46
MgO	31.7	31.7	31.3	31.4	30.6	32.9	32.6	34.3	33.0	30.6	34.0
CaO	0.45	0.46	0.98	1.36	1.43	0.65	0.97	0.28	0.92	1.71	0.21
MnO	0.36	0.36	0.39	0.35	0.37	0.37	0.32	0.33	0.34	0.37	0.28
FeO	10.5	10.6	10.1	9.1	9.6	8.9	8.2	7.6	8.3	9.5	8.1
Na ₂ O	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Total	100.1	99.9	99.7	100.2	99.7	100.4	100.2	99.3	100.6	100.5	100.5
Fe/Mn	28.5	28.7	25.3	25.9	26.0	23.9	25.6	23.1	24.3	25.4	29.0
Fe/Mg	0.19	0.19	0.18	0.16	0.18	0.15	0.14	0.12	0.14	0.17	0.13
Mn/Mg	0.0065	0.0065	0.0071	0.0063	0.0068	0.0063	0.0055	0.0054	0.0058	0.0069	0.0046
Mg#	84.3	84.3	84.7	86.0	85.0	86.9	87.6	88.9	87.6	85.1	88.2
En	83.6	83.5	83.2	83.8	82.6	85.8	86.0	88.4	86.1	82.3	87.9
Wo	0.9	0.9	1.9	2.6	2.8	1.2	1.9	0.5	1.7	3.3	0.4

*Analyses with Mg# <85 correspond to diogenite material, although the boundaries may not be well defined.

Table 2.2A. Continued.

n	DOM 10839,6			
	3	2	2	5
SiO ₂	55.6	57.2	56.8	54.0
TiO ₂	0.06	b.d.	0.03	0.07
Al ₂ O ₃	0.99	0.12	0.38	0.54
Cr ₂ O ₃	0.85	0.61	0.69	0.60
MgO	31.1	34.2	32.6	26.3
CaO	1.05	0.15	0.62	1.13
MnO	0.36	0.23	0.30	0.55
FeO	9.5	7.0	8.5	15.8
Na ₂ O	b.d.	b.d.	b.d.	b.d.
Total	99.5	99.5	99.9	99.0
Fe/Mn	26.3	29.7	27.6	28.6
Fe/Mg	0.17	0.11	0.15	0.34
Mn/Mg	0.0065	0.0039	0.0053	0.0118
Mg#	85.4	89.7	87.2	74.8
En	83.7	89.5	86.2	73.1
Wo	2.0	0.3	1.2	2.3

*Analyses with Mg# <85 correspond to diogenite material, although the boundaries may not be well defined.

Table 2.3A. Chemistry of symplectite phases.

	Chromite	(+/-)	OPX	(+/-)
SiO ₂	0.11	0.03	57.0	0.29
TiO ₂	0.14	0.02	0.02	0.02
Al ₂ O ₃	3.43	0.12	0.21	0.11
V ₂ O ₃	0.66	0.02	b.d	b.d
Cr ₂ O ₃	65.1	0.36	0.92	0.15
MgO	6.22	0.08	33.9	0.20
CaO	0.04	0.01	0.76	0.10
MnO	0.58	0.02	0.31	0.02
FeO	22.9	0.08	7.55	0.14
Na ₂ O	b.d	b.d	b.d	b.d
Total	99.2		100.6	

*Average for analyses taken from multiple symplectites.

Table 2.4A. Modal analysis for symplectites.

Phase	Symplectite 1	Symplectite 2				Symplectite 3			
	Whole	Whole				Whole			
Chromite	36.3%	60.2%	54.9%	47.8%	51.1%	50.9%	48.6%	46.6%	52.8%
Orthopyroxene	63.7%	39.8%	45.1%	52.2%	48.9%	49.1%	51.4%	53.4%	47.2%

*Ca-rich pyroxene was excluded from reconstructions because the phase is not ubiquitous in all symplectites

*Specific areas, along with entire symplectites, were measured to characterize heterogeneity.

Table 2.5A. Bulk chemistry reconstruction for symplectites.

Area	Symplectite 1		Symplectite 2							
	Whole	Whole	Whole	Whole						
Density (Opx/Chr)	3.3/5.09	3.3/4.5	3.3/5.09	3.3/4.5	3.3/5.09	3.3/4.5	3.3/5.09	3.3/4.5	3.3/5.09	3.3/4.5
Oxide Weight %										
SiO ₂	30.4	32.1	17.2	18.7	19.9	21.5	23.7	25.4	21.9	23.6
TiO ₂	0.08	0.07	0.10	0.10	0.10	0.09	0.09	0.09	0.09	0.09
Al ₂ O ₃	1.72	1.62	2.47	2.38	2.31	2.22	2.10	2.00	2.20	2.10
V ₂ O ₃	0.31	0.29	0.46	0.45	0.43	0.41	0.39	0.37	0.41	0.39
Cr ₂ O ₃	30.9	29.0	45.8	44.1	42.8	41.0	38.5	36.6	40.5	38.6
MgO	21.0	21.8	14.5	15.3	15.8	16.6	17.7	18.5	16.8	17.6
CaO	0.42	0.44	0.25	0.27	0.29	0.31	0.34	0.36	0.31	0.33
MnO	0.44	0.43	0.50	0.49	0.48	0.48	0.47	0.46	0.48	0.47
FeO	14.7	14.3	18.3	17.9	17.6	17.2	16.6	16.1	17.0	16.6
Total	100.0	100.0	99.6	99.7	99.7	99.7	99.8	99.8	99.8	99.8
Cations based on 24 Oxygen										
Si	5.816	6.000	4.047	4.289	4.472	4.709	5.011	5.233	4.765	4.995
Ti	0.011	0.010	0.018	0.017	0.017	0.016	0.014	0.013	0.015	0.014
Al	0.194	0.179	0.343	0.322	0.307	0.287	0.262	0.243	0.282	0.263
V	0.024	0.022	0.044	0.041	0.039	0.036	0.033	0.030	0.036	0.033
Cr	2.344	2.143	4.273	4.009	3.809	3.551	3.222	2.979	3.490	3.239
Mg	5.983	6.075	5.105	5.225	5.316	5.434	5.584	5.694	5.461	5.576
Ca	0.087	0.089	0.064	0.067	0.069	0.072	0.076	0.079	0.073	0.076
Mn	0.071	0.068	0.099	0.095	0.092	0.089	0.084	0.080	0.088	0.084
Fe	2.363	2.233	3.612	3.441	3.312	3.145	2.931	2.774	3.105	2.943
Total	16.892	16.818	17.605	17.508	17.434	17.338	17.217	17.127	17.316	17.223

*Density selected based on phase compositions due to the solid solution between Fe, Mg, and Al end-members for both phases.

Table 2.5A. Continued.

Area	Symplectite 3							
	Whole	Whole						
Density (Opx/Chr)	3.3/5.09	3.3/4.5	3.3/5.09	3.3/4.5	3.3/5.09	3.3/4.5	3.3/5.09	3.3/4.5
Oxide Weight %								
SiO ₂	22.0	23.7	23.2	24.9	24.3	26.1	21.0	22.6
TiO ₂	0.09	0.09	0.09	0.09	0.09	0.09	0.10	0.09
Al ₂ O ₃	2.19	2.10	2.12	2.03	2.06	1.96	2.25	2.16
V ₂ O ₃	0.41	0.39	0.39	0.37	0.38	0.36	0.42	0.40
Cr ₂ O ₃	40.4	38.5	39.0	37.1	37.7	35.8	41.6	39.7
MgO	16.9	17.7	17.5	18.3	18.0	18.9	16.4	17.2
CaO	0.31	0.34	0.33	0.35	0.34	0.37	0.30	0.32
MnO	0.47	0.47	0.47	0.46	0.46	0.46	0.48	0.47
FeO	17.0	16.6	16.7	16.2	16.4	15.9	17.3	16.8
Total	99.8	99.8	99.8	99.8	99.8	99.9	99.7	99.8
Cations based on 24 Oxygen								
Si	4.780	5.009	4.952	5.176	5.099	5.318	4.635	4.868
Ti	0.015	0.014	0.016	0.015	0.014	0.013	0.016	0.015
Al	0.281	0.262	0.295	0.274	0.254	0.236	0.293	0.274
V	0.035	0.033	0.037	0.034	0.032	0.029	0.037	0.034
Cr	3.474	3.223	3.635	3.366	3.126	2.887	3.632	3.377
Mg	5.469	5.583	6.144	6.271	5.627	5.736	5.397	5.513
Ca	0.073	0.076	0.084	0.087	0.077	0.080	0.072	0.074
Mn	0.087	0.084	0.094	0.090	0.082	0.079	0.090	0.086
Fe	3.095	2.932	3.288	3.115	2.869	2.715	3.197	3.032
Total	17.310	17.217	18.544	18.429	17.181	17.093	17.368	17.274

*Density selected based on phase compositions due to the solid solution between Fe, Mg, and Al end-members for both phases.

Table 2.6A. Bulk composition of symplectites determined by broad beam analysis (wt.% oxide).

Oxide	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO ₂	39.0	40.5	40.9	41.2	42.7	38.7	38.8	39.4	38.2	40.0	40.1	38.7	39.4
TiO ₂	0.03	0.02	0.01	0.04	0.03	0.05	0.03	0.02	0.03	0.04	0.03	0.04	0.07
Al ₂ O ₃	0.97	0.94	0.87	0.91	0.76	0.77	0.95	0.92	0.95	0.91	1.33	1.50	1.76
V ₂ O ₃	0.29	0.24	0.25	0.19	0.21	0.24	0.25	0.28	0.28	0.28	0.21	0.21	0.20
Cr ₂ O ₃	21.5	20.5	19.1	19.9	18.2	22.2	21.2	20.4	22.9	21.3	19.7	19.9	21.0
MgO	26.0	25.9	26.2	26.2	27.0	24.7	22.0	23.5	24.2	25.1	25.5	22.6	26.3
CaO	0.43	0.71	1.05	0.47	0.50	1.21	4.91	3.32	0.97	0.66	2.58	5.43	0.53
MnO	0.41	0.41	0.43	0.41	0.44	0.40	0.39	0.41	0.43	0.41	0.39	0.38	0.44
FeO	12.8	12.5	12.4	12.4	12.3	12.5	11.7	11.9	12.9	12.6	12.0	11.5	12.8
Na ₂ O	0.00	0.02	0.02	0.02	0.01	0.02	0.07	0.05	0.01	0.03	0.03	0.08	0.02
Total	101.5	101.8	101.1	101.7	102.2	100.8	100.3	100.2	100.9	101.3	101.9	100.4	102.4

Oxide	14	15	16	17	18	19	20	21	22	23	24	25	26
SiO ₂	40.9	39.7	38.6	38.9	41.7	38.5	39.9	39.9	38.1	39.6	39.4	38.4	38.2
TiO ₂	0.06	0.06	0.03	0.04	0.02	0.05	0.05	0.01	0.03	0.04	0.04	0.05	0.04
Al ₂ O ₃	1.57	1.58	1.61	1.83	1.53	2.02	1.76	0.92	1.01	0.95	0.92	0.71	0.96
V ₂ O ₃	0.23	0.24	0.21	0.23	0.18	0.24	0.24	0.25	0.24	0.25	0.23	0.22	0.24
Cr ₂ O ₃	20.2	21.0	20.8	21.5	17.2	21.8	20.4	21.2	22.6	21.4	21.1	24.0	23.0
MgO	26.6	25.5	24.0	25.1	27.0	26.5	26.6	25.6	24.2	26.0	23.5	24.3	23.4
CaO	0.49	0.89	2.35	0.91	0.48	0.36	0.47	0.85	1.46	0.38	3.07	0.87	2.58
MnO	0.43	0.44	0.41	0.42	0.42	0.44	0.43	0.42	0.42	0.44	0.39	0.41	0.43
FeO	12.6	12.6	12.3	12.7	11.7	13.1	12.8	12.8	13.0	13.0	12.1	12.5	12.7
Na ₂ O	0.01	0.04	0.02	0.01	0.00	0.01	0.03	0.03	0.02	0.03	0.03	0.02	0.03
Total	103.0	102.0	100.4	101.7	100.2	103.1	102.7	101.9	101.1	102.1	100.8	101.5	101.6

Table 2.6A. Continued.

	Average (n=26)	Std. Dev.	Cation based on 24 oxygen	
SiO ₂	39.6	1.2	6.081	Si
TiO ₂	0.04	0.01	0.004	Ti
Al ₂ O ₃	1.19	0.39	0.215	Al
V ₂ O ₃	0.24	0.03	0.029	V
Cr ₂ O ₃	20.9	1.5	2.539	Cr
MgO	25.1	1.4	5.754	Mg
CaO	1.46	1.40	0.240	Ca
MnO	0.42	0.02	0.054	Mn
FeO	12.5	0.4	1.602	Fe
Na ₂ O	0.03	0.02	0.008	Na
Total	101.5		16.527	Total Cations

Table 2.7A. Trace element chemistry of Mg-rich olivines.

Mg#	DOM 10100,8		DOM 10105,6								DOM 10120,6		DOM 10837,7	
	87		84.7		88.2		86.9		86.7		87.6		87.6	
	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ
Sc	53.7	(4)	53.0	(9)	51.5	(21)	50.9	(7)	50.7	(8)	56.6	(6)	58.0	(8)
Ti	20.9	(5)	33.5	(12)	25.2	(27)	24.8	(16)	22.7	(10)	18.8	(6)	24.4	(10)
V	37.7	(2)	49.9	(5)	44.1	(10)	26.9	(4)	32.3	(5)	33.5	(3)	30.0	(3)
Cr	506	(3)	568	(6)	361	(10)	282	(7)	405	(6)	412	(3)	300	(2)
Co	18.2	(2)	22.7	(4)	25.4	(13)	23.9	(4)	27.2	(6)	18.0	(3)	18.0	(3)
Ni	15.5	(7)	20.9	(19)	63.9	(66)	32.8	(18)	36.7	(26)	116	(4)	12.3	(15)
Zn	3.9	(2)	2.0	(4)			2.7	(4)	2.2	(4)	1.6	(4)		
Sr											0.102	(8)		
Y	0.024	(5)	0.116	(18)	1.40	(13)	0.884	(44)	0.776	(53)	0.273	(18)	0.066	(11)
Ba							0.017	(5)			0.062	(6)		
Pb	0.137	(21)	0.198	(52)	0.299	(84)	0.186	(24)	0.380	(56)	0.186	(16)	0.063	(17)
U							0.009	(2)	0.009	(2)	0.009	(2)		

Table 2.7A. Continued.

Mg#	DOM 10837,7												DOM 10838,6	
	91.9		86.3		83.4		83.5		86.0		86.3		87.9	
	$\mu\text{g/g}$	1σ	$\mu\text{g/g}$	1σ	$\mu\text{g/g}$	1σ	$\mu\text{g/g}$	1σ	$\mu\text{g/g}$	1σ	$\mu\text{g/g}$	1σ	$\mu\text{g/g}$	1σ
Sc	55.7	(9)	57.3	(9)	58.3	(38)	59.3	(37)	52.6	(7)	54.6	(9)	54.5	(4)
Ti	78.4	(15)	21.0	(8)	75.0	(73)	90.7	(52)	24.7	(9)	14.4	(8)	16.9	(5)
V	23.3	(3)	29.6	(4)	24.4	(12)	26.0	(9)	31.8	(3)	37.7	(5)	35.1	(3)
Cr	315	(3)	226	(4)	349	(15)	315	(7)	274	(3)	766	(10)	413	(3)
Co	9.9	(3)	11.0	(4)	29.6	(22)	25.4	(18)	7.6	(3)	19.6	(4)	16.4	(2)
Ni			8.8	(9)	37.0	(83)			8.7	(13)	20.2	(16)	17.5	(9)
Zn													1.9	(2)
Sr			0.054	(8)									0.030	(5)
Y	0.138	(13)	0.050	(10)					0.072	(14)	0.114	(17)	0.251	(18)
Ba			0.099	(9)					0.040	(9)	0.019	(6)	0.012	(2)
Pb			0.204	(18)									0.019	(5)
U			0.009	(2)									0.003	(1)

Table 2.7A. Continued.

Mg#	DOM 10838,6													
	87.3		92.2		85.7		87		88.6		86.8		87	
	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ
Sc	52.4	(5)	54.6	(8)	52.6	(4)	53.2	(4)	52.1	(8)	51.5	(8)	51.9	(12)
Ti	10.2	(3)	26.3	(9)	68.9	(11)	15.1	(5)	12.4	(8)	4.3	(11)	58.0	(18)
V	28.9	(2)	30.3	(4)	27.3	(2)	27.3	(2)	35.4	(4)	25.7	(3)	32.0	(6)
Cr	205	(2)	431	(6)	266	(2)	203	(2)	342	(5)	145	(2)	353	(5)
Co	17.8	(2)	8.2	(2)	11.3	(2)	9.4	(2)	17.4	(3)	9.4	(3)	42.7	(27)
Ni	28.4	(13)	36.5	(19)	12.2	(8)	7.8	(6)	36.5	(20)	24.3	(20)	112	(9)
Zn	2.6	(2)	2.3	(2)	1.7	(2)	1.0	(2)	1.5	(3)	1.4	(4)		
Sr	0.060	(6)	0.064	(9)	0.041	(5)	0.015	(3)	0.075	(9)	0.195	(23)	0.480	(39)
Y	1.10	(4)	0.214	(16)	0.066	(6)	0.108	(12)	1.99	(5)	0.948	(48)	0.197	(24)
Ba	0.031	(3)	0.026	(5)	0.023	(2)			0.033	(5)	0.012	(4)	0.160	(15)
Pb	0.021	(4)							0.050	(14)				
U	0.010	(1)	0.007	(2)					0.015	(3)				

Table 2.7A. Continued.

Mg#	DOM 10838,6						DOM 10839,6									
	87.3		85.1		85.4		85.9		84.7		86.4		86.7		92.1	
	μg/g	1σ	μg/g	1σ	μg/g	1σ	μg/g	1σ	μg/g	1σ	μg/g	1σ	μg/g	1σ	μg/g	1σ
Sc	53.6	(7)	51.6	(6)	53.8	(6)	64.6	(30)	70.6	(8)	58.8	(13)	58.5	(13)	67.7	(42)
Ti	30.4	(9)	25.0	(5)	28.9	(7)	30.4	(29)	33.7	(10)	16.6	(10)	31.3	(12)	26.9	(33)
V	30.9	(3)	30.8	(3)	36.9	(4)	28.6	(10)	37.4	(3)	32.3	(6)	46.2	(8)	32.3	(10)
Cr	491	(5)	449	(5)	562	(8)	454	(12)	619	(11)	579	(16)	489	(8)	483	(16)
Co	15.6	(3)	13.8	(2)	16.0	(2)	15.9	(14)	22.9	(4)	7.9	(4)	15.1	(4)	9.5	(17)
Ni	15.9	(13)	38.1	(15)	26.4	(13)	20.4	(48)	24.9	(12)	8.1	(15)	10.1	(15)	57.8	(87)
Zn			1.4	(2)	2.4	(2)			1.1	(3)						
Sr	0.030	(7)	0.109	(9)	0.049	(5)			0.057	(7)	0.039	(9)				
Y	0.244	(20)	0.060	(8)	0.106	(10)	0.159	(47)	0.069	(11)	0.144	(24)	0.073	(15)	1.55	(16)
Ba			0.049	(5)	0.028	(8)	0.036	(11)	0.053	(6)			0.034	(8)		
Pb									0.329	(30)	0.493	(96)	0.526	(139)		
U																

Table 2.8A. Trace element chemistry for pyroxene.

Mg#	DOM 10100,8		DOM 10105,6				DOM 10120,6				DOM 10837,7	
	80.1		86.3		85.4		86.4		78.9		86.0	
	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ
Sc	78.2	(5)	85.2	(6)	82.3	(5)	77.7	(11)	85.9	(11)	86.3	(11)
Ti	300	(2)	202	(2)	465	(3)	209	(4)	333	(4)	467	(6)
V	108	(1)	82.4	(5)	134	(1)	89.6	(10)	94.4	(8)	148	(2)
Cr	5448	(39)	6181	(32)	2941	(16)	3039	(29)	3337	(26)	7154	(69)
Mn	3768	(19)	3210	(17)	4775	(27)	3104	(33)	4298	(35)	2981	(27)
Co	12.9	(2)	19.6	(2)	11.5	(2)	10.5	(3)	25.3	(5)	10.6	(3)
Ni	3.7	(4)	21.8	(11)	14.3	(12)	13.7	(17)	32.4	(23)	6.53	(117)
Ga	0.106	(13)	0.112	(16)	0.101	(19)			0.180	(39)	0.242	(37)
Sr	0.101	(6)	1.52	(2)	0.166	(9)	0.081	(13)	0.174	(17)	0.174	(14)
Y	0.264	(9)	0.676	(23)	0.770	(22)	0.741	(33)	1.37	(5)	1.40	(4)
Zr	0.184	(12)	0.845	(28)	0.236	(14)			0.864	(61)	3.32	(11)
Nb			0.120	(14)					0.113	(23)		
Ba	0.014	(3)	0.008	(2)	0.013	(2)			0.031	(7)		
La			0.079	(5)	0.046	(6)	0.108	(14)	0.182	(16)	0.048	(8)
Ce	0.012	(2)	0.446	(13)	0.126	(6)	0.133	(13)	0.121	(11)	0.208	(12)
Pr			0.050	(4)	0.027	(3)	0.046	(6)	0.049	(7)	0.048	(6)
Nd			0.229	(27)	0.125	(23)	0.268	(57)	0.376	(65)	0.347	(54)
Sm			0.077	(16)	0.059	(10)			0.118	(27)		
Eu											0.025	(4)
Gd			0.075	(16)	0.092	(18)	0.143	(40)	0.169	(40)	0.206	(43)
Tb			0.017	(3)	0.016	(3)			0.034	(6)	0.024	(6)
Dy	0.043	(6)	0.108	(15)	0.111	(14)	0.098	(26)	0.193	(33)	0.257	(29)
Ho	0.010	(2)	0.022	(3)	0.031	(3)	0.018	(4)	0.042	(6)	0.046	(6)
Er	0.034	(5)	0.075	(9)	0.095	(10)	0.083	(20)	0.119	(20)	0.156	(20)
Tm	0.007	(2)			0.012	(3)					0.025	(6)
Yb	0.053	(7)	0.078	(8)	0.128	(12)	0.116	(19)	0.106	(23)	0.176	(22)
Lu	0.011	(3)			0.024	(4)						
Hf			0.030	(7)							0.121	(20)
Pb	0.033	(7)	0.040	(8)			0.058	(16)				
Th												
U	0.011	(1)	0.004	(1)	0.004	(1)	0.012	(3)				

* Diogenite pyroxene is indicated by Mg# <85.

Table 2.8A. Continued.

Mg#	DOM 10837,7								DOM 10838,6			
	85.0		87.5		86.8		84.5		88.9		87.6	
	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ
Sc	77.1	(14)	87.6	(13)	86.3	(17)	101	(5)	53.3	(13)	86.3	(14)
Ti	538	(9)	361	(6)	196	(6)	1739	(49)	153	(3)	197	(4)
V	141	(2)	164	(2)	82.9	(16)	221	(7)	91.0	(11)	93.8	(13)
Cr	6676	(103)	6734	(58)	3727	(55)	6726	(188)	1554	(16)	3696	(42)
Mn	2900	(42)	2896	(28)	3127	(42)	3343	(86)	1662	(30)	3101	(37)
Co	9.26	(34)	11.5	(7)	8.48	(60)	9.87	(191)	5.53	(37)	8.80	(38)
Ni									10.6	(16)		
Ga	0.259	(41)										
Sr	0.155	(17)	0.178	(29)	0.718	(85)			0.437	(31)	1.46	(17)
Y	1.42	(5)	1.32	(9)	0.590	(66)	8.39	(39)	0.927	(50)	0.723	(46)
Zr	1.01	(6)	0.760	(99)			30.8	(14)	0.257	(42)	0.278	(48)
Nb												
Ba	0.062	(10)							0.024	(6)		
La	0.117	(15)							0.148	(18)		
Ce	0.301	(25)	0.063	(16)	0.073	(20)			0.121	(15)	0.062	(12)
Pr	0.053	(9)							0.064	(11)		
Nd	0.288	(61)							0.285	(69)		
Sm												
Eu												
Gd	0.155	(35)							0.178	(41)		
Tb	0.031	(6)							0.039	(9)		
Dy	0.189	(38)	0.195	(54)					0.151	(37)	0.153	(22)
Ho	0.056	(9)	0.066	(13)			0.345	(65)	0.037	(8)		
Er	0.194	(24)					0.840	(180)	0.089	(23)	0.157	(35)
Tm	0.029	(7)										
Yb	0.170	(35)					1.22	(22)			0.120	(29)
Lu												
Hf							1.30	(20)				
Pb												
Th	0.018	(5)										
U												

* Diogenite pyroxene is indicated by Mg# <85.

Table 2.8A. Continued.

Mg#	DOM 10838,6				DOM 10839,6							
	85.1		88.2		85.4		77.0		84.0		89.7	
	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ	$\mu\text{g/g}$	1 σ
Sc	79.5	(6)	64.3	(7)	47.6	(15)	106	(1)	85.5	(12)	96.8	(33)
Ti	799	(5)	82.1	(21)	549	(21)	698	(5)	124	(2)	80.0	(48)
V	155	(1)	37.6	(5)	62.8	(29)	91.0	(7)	69.2	(8)	60.5	(16)
Cr	7041	(60)	3136	(38)	3117	(179)	4147	(30)	3645	(39)	4155	(80)
Mn	2985	(19)	2056	(15)	2076	(51)	3708	(25)	2889	(39)	2202	(42)
Co	9.66	(18)	13.3	(3)	3.98	(28)	9.61	(26)	10.9	(3)	12.2	(13)
Ni	7.34	(78)	13.5	(12)	8.06	(73)	9.82	(83)	16.5	(14)	49.0	(71)
Ga	0.251	(23)			0.244	(24)	0.117	(27)			1.12	(20)
Sr	1.16	(6)	0.204	(20)	4.64	(15)	0.376	(16)	0.202	(17)	0.179	(44)
Y	2.11	(4)	0.537	(27)	2.89	(7)	1.28	(3)	0.328	(26)	0.341	(74)
Zr	3.31	(8)			2.29	(10)	1.45	(5)				
Nb	0.123	(15)			0.120	(16)						
Ba	0.073	(10)	0.083	(9)	1.81	(7)	0.022	(4)	0.022	(5)	0.090	(26)
La	0.116	(16)	0.070	(9)	0.156	(10)	0.029	(7)	0.041	(9)		
Ce	0.323	(34)	0.457	(24)	0.325	(12)	0.065	(6)	0.061	(8)		
Pr	0.060	(6)	0.041	(5)	0.056	(4)	0.014	(3)				
Nd	0.362	(40)	0.237	(41)	0.299	(38)						
Sm	0.110	(21)			0.135	(20)						
Eu	0.014	(3)			0.039	(4)						
Gd	0.213	(21)	0.084	(22)	0.241	(27)	0.106	(26)				
Tb	0.045	(4)	0.016	(4)	0.050	(4)	0.021	(4)				
Dy	0.340	(25)	0.098	(21)	0.435	(28)	0.166	(26)				
Ho	0.075	(5)	0.025	(5)	0.111	(7)	0.052	(5)				
Er	0.254	(18)	0.049	(11)	0.383	(21)	0.179	(15)				
Tm	0.038	(4)			0.059	(5)	0.028	(4)				
Yb	0.282	(19)	0.058	(11)	0.455	(27)	0.216	(18)				
Lu	0.036	(6)			0.079	(6)	0.035	(6)				
Hf	0.091	(14)			0.078	(12)	0.067	(12)				
Pb	0.024	(7)	0.056	(14)	0.082	(9)			0.061	(16)		
Th	0.021	(4)			0.033	(4)						
U	0.008	(2)	0.007	(2)	0.009	(2)						

* Diogenite pyroxene is indicated by Mg# <85.

Table 2.8A. Continued.

Mg#	DOM 10839,6			
	87.2		74.8	
	$\mu\text{g/g}$	1σ	$\mu\text{g/g}$	1σ
Sc	108	(4)	99.8	(9)
Ti	211	(8)	438	(4)
V	102	(3)	150	(1)
Cr	4909	(119)	4930	(35)
Mn	2913	(67)	5066	(34)
Co	12.8	(14)	13.5	(3)
Ni			2.64	(74)
Ga			0.094	(26)
Sr	0.658	(75)	0.321	(16)
Y	0.490	(83)	0.813	(25)
Zr	0.334	(92)	0.548	(30)
Nb				
Ba			0.011	(2)
La			0.033	(7)
Ce			0.061	(6)
Pr			0.017	(3)
Nd				
Sm			0.065	(11)
Eu			0.011	(2)
Gd				
Tb				
Dy			0.118	(24)
Ho			0.034	(5)
Er			0.086	(13)
Tm			0.015	(4)
Yb			0.114	(18)
Lu				
Hf				
Pb				
Th				
U				

* Diogenite pyroxene is indicated by Mg# <85.

Table 3.1A. Representative major- and minor-element composition of pigeonite (wt.% oxide).

SiO ₂	49.5	49.5	49.5	49.6	49.0	49.1
TiO ₂	0.12	0.20	0.11	0.13	0.08	0.24
Al ₂ O ₃	0.15	0.16	0.18	0.19	0.12	0.20
Cr ₂ O ₃	0.08	0.08	0.10	0.07	0.08	0.08
MgO	12.4	11.5	12.0	12.2	11.7	11.6
CaO	1.31	1.36	1.22	1.12	1.10	0.93
MnO	0.98	1.15	1.01	1.08	1.03	1.18
FeO	35.2	36.5	36.2	35.9	37.0	36.9
Na ₂ O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	99.8	100.5	100.4	100.3	100.0	100.2

Cation formula based on 6 oxygen

Si	1.985	1.982	1.981	1.981	1.976	1.976
Ti	0.004	0.006	0.003	0.004	0.003	0.007
Al	0.007	0.007	0.008	0.009	0.006	0.01
Cr	0.003	0.002	0.003	0.002	0.002	0.002
Mg	0.739	0.688	0.716	0.728	0.701	0.694
Ca	0.056	0.058	0.052	0.048	0.048	0.04
Mn	0.033	0.039	0.034	0.036	0.035	0.04
Fe	1.179	1.224	1.211	1.201	1.247	1.24
Na						
Total	4.006	4.008	4.01	4.009	4.018	4.011
En	37.4	34.9	36.2	36.8	35.1	35.2
Fs	59.7	62.1	61.2	60.7	62.5	62.8
Wo	2.84	2.94	2.63	2.43	2.40	2.03
Fe/Mg	1.60	1.78	1.69	1.65	1.78	1.79
Fe/Mn	35.7	31.4	35.6	33.4	35.6	31.0

Table 3.2A. Major-, minor-, and trace-element chemistry of selected FeNi metal grains.

Element	FeNi 1	FeNi 2	FeNi 3	FeNi 4	FeNi 5	
Fe ^a	91.7	94.9	94.5	93.9	95.2	wt. %
Co ^a	0.4	0.7	0.6	0.7	0.4	wt. %
Ni ^a	6.7	3.7	3.7	4.1	3.5	wt. %
Si	265	1061	183	278	203	µg/g
Cu	107	23.7	17.2	20.6	21.7	µg/g
W	3.74	4.12	9.12	11.3	2.72	µg/g

^aValues measured by EMP.

^bValues measured by LA ICP-MS.

Table 3.3A. Electron microprobe analyses of phosphate.

Oxide wt. %									Oxide wt. %	Merrillite
	ap1	ap2	ap3	ap4	ap5	ap6	ap7	ap8		<i>n</i> =5
P ₂ O ₅	42.3	40.8	41.9	41.4	41.7	42.0	41.4	41.4	P ₂ O ₅	44.4
SiO ₂	0.07	0.16	0.11	0.13	0.10	0.16	0.19	0.28	La ₂ O ₃	0.46
La ₂ O ₃	0.05	0.04	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	Ce ₂ O ₃	1.19
Ce ₂ O ₃	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	0.04	Pr ₂ O ₃	0.17
MgO	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	0.07	0.14	Nd ₂ O ₃	0.81
CaO	55.2	53.9	55.2	54.9	55.4	54.9	54.8	54.8	Sm ₂ O ₃	0.26
MnO	n.d.	n.d.	n.d.	0.04	n.d.	0.04	n.d.	n.d.	MgO	2.47
FeO	0.21	1.68	0.18	0.36	0.30	0.48	0.25	0.31	CaO	43.4
H ₂ O ^a	0.04	0.09	n.d.	n.d.	0.05	n.d.	0.06	n.d.	MnO	0.08
Na ₂ O	n.d.	0.06	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	FeO	2.14
F	3.47	3.29	3.49	3.57	3.44	3.57	3.39	3.46	Na ₂ O	1.06
Cl	0.14	0.14	0.16	0.11	0.12	0.15	0.11	0.17		
Total	101.6	100.2	101.1	100.5	101.1	101.3	100.3	100.7	Total	96.5
O=F	1.46	1.39	1.47	1.50	1.45	1.50	1.43	1.46		
O=Cl	0.03	0.03	0.04	0.02	0.03	0.03	0.02	0.04		
Σ	1.49	1.42	1.50	1.53	1.48	1.54	1.45	1.49		
Total	100.1	98.8	99.6	99.0	99.6	99.8	98.9	99.2		
Est. OH wt. % ^a	0.21	0.29	0.16	0.09	0.21	0.09	0.24	0.16		
Net corrected total ^b	100.3	99.1	99.8	99.1	99.9	99.9	99.1	99.3		
H ₂ O (ppm) ^c	780	640	2010	980	780	980	1150	961		

Table 3.3A Continued.

Structural formulae based on 26 anions								
	ap1	ap2	ap3	ap4	ap5	ap6	ap7	ap8
P	6.004	5.920	5.985	5.962	5.961	5.986	5.967	5.949
Si	0.012	0.027	0.019	0.023	0.017	0.027	0.032	0.048
Σ B-site cations	6.016	5.947	6.004	5.985	5.977	6.013	5.999	5.997
La	0.003	0.002				0.003		
Ce	0.004						0.004	0.003
Mg								
Ca	9.919	9.889	9.963	9.993	10.018	9.903	9.977	9.977
Mn				0.005		0.005		
Fe	0.029	0.241	0.026	0.051	0.042	0.068	0.035	0.044
Na	0.008	0.019	0.015					
Σ A-site cations	9.963	10.15	10.00	10.05	10.06	9.979	10.02	10.02
F	1.84	1.78	1.86	1.92	1.84	1.90	1.82	1.86
Cl	0.04	0.04	0.05	0.03	0.03	0.04	0.03	0.05
OH	0.12	0.18	0.10	0.05	0.13	0.05	0.14	0.09
Σ X-site anions	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00

^aEstimation of OH wt. % from derivation of Ketcham 2015.^bNet corrected totals include estimation of OH wt. %.^cDetermined by secondary ion mass spectrometry.

Table 3.4A Trace element chemistry for phosphates (µg/g).

	Merrilite	Merrilite	Merrilite	Merrilite	Apatite	Apatite
Y	10983	12320	13151	13437	227	218
Zr	14.6	21.7	19.8	17.9	26.2	26.8
La	3307	3322	3654	3652	39	44
Ce	8378	8002	9015	9127	132	130
Pr	1189	1376	1325	1334	22	23
Nd	5753	5955	6363	6374	105	102
Sm	1700	1778	1857	1875	33	36
Eu	25.0	23.1	23.7	24.7	1.1	1.7
Gd	2029	2210	2485	2475	42	42
Tb	326	351	376	390	6.6	6.0
Dy	2040	2233	2428	2443	45	39
Ho	405	440	475	494	8.8	7.4
Er	1037	1161	1287	1343	23	19
Tm	124	142	161	163	2.8	2.4
Yb	648	749	815	863	15.2	11.9
Lu	84.5	95.1	111	119	2.3	2.0
Pb	167	181	179	181	11.8	15.3
Th	379	395	436	436	29.2	33.5
U	9.8	10.7	18.1	33.3	105	85.6

Equation 3.1. Bulk Compostion Reconstruction

$$\text{Element A} = \text{Conc.}_{\text{Phase 1}}^{\text{Element A}} \cdot \left[\frac{\text{Vol. \%}_{\text{Phase 1}} \cdot \rho_{\text{Phase 1}}}{\sum_1^n (\text{Vol. \%}_{\text{Phase}} \cdot \rho_{\text{Phase}})} \right] + \text{Conc.}_{\text{Phase 2}}^{\text{Element A}} \cdot \left[\frac{\text{Vol. \%}_{\text{Phase 2}} \cdot \rho_{\text{Phase 2}}}{\sum_1^n (\text{Vol. \%}_{\text{Phase}} \cdot \rho_{\text{Phase}})} \right] + \dots + \text{Conc.}_{\text{Phase n}}^{\text{Element A}} \cdot \left[\frac{\text{Vol. \%}_{\text{Phase n}} \cdot \rho_{\text{Phase n}}}{\sum_1^n (\text{Vol. \%}_{\text{Phase}} \cdot \rho_{\text{Phase}})} \right]$$

Vita

Timothy M. Hahn Jr. was born in St. Louis, Missouri, to the parents of Timothy and Sheila Hahn Sr., and is a husband and father to Erika and Owen Hahn, respectively. He attended Hillsboro High School in Hillsboro, Missouri. Following graduation, Timothy attended Missouri State University where he obtained a Bachelors of Science in Geology with a minor in Analytical Chemistry in August 2014. Timothy continued his education by pursuing a Masters of Science degree at the University of Tennessee with an anticipated graduation in August 2016, while serving as a graduate teaching and research assistant. Timothy has accepted a position as graduate research and teaching assistant at Washington University, St. Louis in order to pursue a Doctorate degree in Earth and Planetary Science.