

Interpreting Lunar Geochemistry Through Impact Events and Terrestrial Analogues

**A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville**

**Sarah Roberts
December 2019**

Copyright © 2019 by Sarah Roberts
All rights reserved.

DEDICATION

To Andy Barth and all the butterflies

ACKNOWLEDGEMENTS

I would like to thank Allan Patchen, Dawn Taylor, Angie Staley, Melody Branch, and Diane Pealor.

ABSTRACT

Impact cratering is the prevalent form of weathering in the solar system. Impacts can also eject samples off of planetary surfaces which can eventually fall to Earth. Lunar meteorite NWA 10986 is a consequence of impacts occurring on the surface of the Moon. Multiple impact events are recorded by the impact melt glass found in NWA 10986, however this meteorite still provides powerful petrogenetic information that can help us determine the origin and evolution of the Moon. The impact melt glass in NWA 10986, and other glasses found on the Moon, record the conditions during their formation including oxygen fugacity conditions. Oxygen fugacity is equally as important as temperature and pressure in terms of petrologic variables that control the crystallization of minerals and the formation of magmas from planetary interiors. Other glasses occur on the surface of the Moon, either as a result of volcanic eruptions generated from the lunar interior, or of impacts that produce impact melt glass and agglutinates. Investigating the oxygen fugacity conditions present during the formation of these glasses allows us to understand the equilibrium oxygen fugacity conditions of the lunar interior or during impact processes. Multivalent elements such as Fe and Cr are capable of recording oxygen fugacities through their oxidation states. On Earth, Fe can be used to determine the changes in oxidation state experienced during impacts using terrestrial analogs such as fulgurites and Trinitite. Beyond the Earth, Fe is not capable of measuring lower oxygen fugacities such as those found on the Moon. This work demonstrates the use of a new Fe and Cr oxybarometer to perform in situ measurements of oxygen fugacity using x-ray absorption spectroscopy. Iron oxidation states measured in fulgurites and Trinitite demonstrates how impacts are not always reducing and spatial variability in oxidation states can occur within microns. This chrome oxybarometer can measure the lower oxygen fugacities in lunar materials and again demonstrates the variable nature of impacts on primary oxygen fugacity signatures.

TABLE OF CONTENTS

INTRODUCTION.....	1
Lunar Meteorite NWA 10986.....	1
Oxygen fugacity.....	1
Fe and Cr Oxybarometry.....	2
Effects of impacts.....	4
Fulgurites.....	4
Agglutinates.....	5
References.....	6
CHAPTER I New lunar meteorite NWA 10986: A mingled impact melt breccia from the highlands; a complete cross section of the lunar crust.....	10
Abstract.....	11
Introduction.....	11
Analytical Methods.....	13
Bulk Rock Preparation.....	13
Major and Minor Element Geochemistry.....	13
Trace Element Geochemistry.....	13
Results.....	15
Evidence for Lunar Origin.....	15
Petrography and Clast Inventory.....	18
Whole Rock and Impact Melt Composition.....	24
Highland Clasts.....	24
Basalt Clasts.....	26
Symplectites and Matrix Minerals.....	29
Discussion.....	32
Impact melts vs pristine endogenous melts.....	32
Basalt Clasts-Pyroxferroite.....	33
Basalt Clasts-Mesostasis.....	34
Comparison to Apollo lithologies.....	35
Implications for source location and lunar evolution.....	36
Summary.....	37
Acknowledgements.....	37
References.....	39
Appendix.....	46
CHAPTER II Oxidation state of iron in fulgurites and trinitite: Implications for redox changes during abrupt high-temperature and pressure events.....	100
Abstract.....	101
Introduction.....	102
Samples Studied.....	104
Analytical Methods.....	110
Scanning electron microscope and electron probe microanalysis.....	110
Mössbauer analysis.....	111
X-ray absorption spectroscopy analysis.....	112

Results.....	112
Fulgurite and Trinitite petrography	112
Mössbauer results	119
XAS results	128
Discussion	128
Redox differences in the Mössbauer results	128
Spatial Variation in Redox	129
Mechanism of Oxidation change.....	130
Summary	132
References	134
CHAPTER III Redox character of lunar volcanic and impact glass: application of a new cr oxybarometer	139
Abstract.....	140
Introduction.....	141
Previous work.....	144
Methods	144
Experimental.....	144
Analytical.....	145
Results.....	146
Glass Calibrations.....	146
Samples	150
Discussion	156
Cr oxybarometer	156
fO ₂ of glass beads	162
fO ₂ of agglutinates and impact melt glass.....	162
Controls on redox changes	163
Implications.....	164
References	166
CONCLUSION	172
VITA.....	173

LIST OF TABLES

Table 1.1. Clasts investigated and EMP analyses of feldspar, pyroxene, and olivine along with associated lunar lithologies.	19
Table 2.1. Samples Studied and Mössbauer Results.....	105
Table 2.1 continued	106
Table 2.2. Glass Compositions.....	114
Table 2.2 Continued.....	115
Table 2.3a. Mössbauer Parameters.....	120
Table 2.3b. Mössbauer Parameters.....	121
Table 2.3c. Mössbauer Parameters	122
Table 3.1a. Composition of calibration glasses synthesized at QFM	147
Table 3.1b. Composition of calibration glasses synthesized at IW	147
Table 3.1c. Composition of calibration glasses synthesized at IW-2	148
Table 3.2. Average compositions of glass beads and agglutinates from 10084, 14148, and 15427.....	152
Table 3.3. Predicted oxygen fugacity relative to IW by Fe and Cr XAS for the glass beads, agglutinates, and impact melt.....	154
Table 3.4. Impact melt glass composition of NWA 10986. Data is from Roberts et al., in print.	160

LIST OF FIGURES

Figure I.1. Log fO_2 versus temperature for mineral buffer assemblages, from Frost 1991.....	3
Figure I.2. Range of fO_2 for sampled planetary bodies relative to the Iron-Wüstite (IW) buffer, from Wadhwa, 2008.	3
Figure 1.1. XPL and PPL photomosaics of thin sections 2-5 (a) and 2-2 (b) of NWA 10986. c) Detail of area shown in (a) of a large pyroxene in a glassy matrix with veins of clay. d) Detail of area shown in (b) of glassy impact melt area with two generations impact melt. Upper portion of glass features “haystack” textured plagioclase while the glass in the center of the image has preserved flow texture with preserved vesicles now infilled with secondary precipitated minerals. Abbreviations: Gl = glass, Vsc = vesicle, Cly = clay, Cl = clast, Pyx = pyroxene.	14
Figure 1.2. Mg # [Mg/(Mg+Fe)] of pyroxenes or olivines and An # [Ca/(Ca+Na)] of plagioclase from clasts compared to Apollo lithologies. Mg # of pyroxene grains found in the matrix without accompanying An # are shown on the right ordinate. Fields are from Lindstrom and Lindstrom (1986) and James et al. (1987).....	16
Figure 1.3. Fe and Mn ratios in NWA 10986 indicate a lunar origin. Fe and Mn trend lines are from Papike et al. (2003).....	17
Figure 1.4. Ca $K\alpha$, Fe $K\alpha$, and Si $K\alpha$ maps of the three sections of NWA 10986 with clasts and glass areas outlined. Red = Ca, Green = Fe, and blue = Si.	20
Figure 1.5. Glass areas (a-c, e) and a loose pyroxene grain (d). a) Photomicrograph of glass area A5 in plane polarized light and (b) in cross polarized light. Transparent glass has a wavy undulose extinction in cross polarized light. c) Glass area A3. d) Large exsolved pyroxene grain cut by clay-filled vein. e) Glass area A1. Abbreviations: Gl = glass, Vsc = vesicle, Cly = clay, pyx = pyroxene.	21
Figure 1.6. Highland clasts. a) Troctolite clast H1. b) Gabbronorite clast H3. c) Troctolite clast H2. d) Gabbronorite clast H4. e) Anorthositic norite clast H5. f) Troctolitic anorthosite clast H6. Abbreviations: Fo = fosterite, An = anorthite, Aug = augite, Pgt = pigeonite, En = enstatite.....	22
Figure 1.7. Basalt clasts. a) Clast B1. b) Clast B2. c) Clast B3. d) clast B4. Abbreviations: An = anorthite, Si = Silica, Pgt = pigeonite, Aug = augite, Ilm = ilmenite, Pxf = pyroxferroite, Fo = fosterite, Sp = spinel.	23
Figure 1.8. Comparative whole rock and glass compositions with Apollo samples and average lunar meteorites. a) Whole rock Al_2O_3 and FeO composition of NWA 10986 is similar to that of other feldspathic lunar meteorites yet also has a basaltic component as well. White square = average of some feldspathic lunar meteorites, white circle = average composition of VLT and LT mare basalts, black circle = average Apollo 14 soil composition. b) Sc and Sm whole rock and glass compositions compared to Apollo samples and lunar meteorites. Graphs and fields are after Korotev et al. 2005.	25

Figure 1.9. Pyroxene compositions and olivine Fo histogram of clasts and matrix material.	27
Figure 1.10. REE profiles of plagioclase, pyroxene, glass and whole rock compositions. Comparative pyroxene and plagioclase data of Apollo FAN, HMS, HAS, and KREEP lithologies are from Floss et al. (1998), Papike et al. (1996), Shervais and McGee (1998), Shervais and McGee (1999), Papike et al. (1997), Cronberger and Neal (2017).....	28
Figure 1.11. a) Elemental map of detail of mesostasis in clast B1. Red = K, Green = Fe, and blue = Si. b) Detail of area outlined in image a. c) Large masses of symplectite material. d) Detail of area outlined in image c. Abbreviations: Abbreviations: An = anorthite, Si = silica, Pgt = pigeonite, Aug = augite, Ilm = ilmenite, Pxf = pyroxferroite, Fo = fosterite, Sp = spinel, Ba = barite, Cly = clay.	30
Figure 1.12. Ti # [Ti/(Ti + Cr)] and Fe# [Fe/(Fe+Cr)] of pyroxenes from evolved basaltic clasts. Shaded fields representing VLT and LT mare basalts are from Nielsen and Drake (1978).	31
Figure 1.13. Representative cross section of the lunar crust and the source location of NWA 10986. Cryptomare depiction is after Antonenko et al. (1995) and crust depth data are from Wieczorek et al. (2013).	38
Figure 2.1. Examples of non-impacted target lithologies. A) Basalt rock from Mount Ararat B) Quartz sand from Sugarland, Texas.	107
Figure 2.2. Photos of hand samples used in this study. The metal cube represents 1cm ³ . A) Black Rock, Utah, B) Monahans, Texas, C) Pecos Plains, Texas, D) Starke, Florida, E) Sugarland, Texas, F) Cline Butte, Oregon, G) Algeria, H) Mount Ararat, I) West Virginia, and J) Trinitite.....	109
Figure 2.3. Backscattered electron (BSE) images of fulgurites investigated for this study. A) Black Rock, Utah, B) Monahans, Texas, C) Pecos Plain, Texas, and D) Sugarland, Texas	113
Figure 2.4. XAS spot locations with predicted Fe ³⁺ and spectra for Starke, Florida and Cline Butte, Oregon fulgurites.....	117
Figure 2.5. Backscattered electron (BSE) images of fulgurites and Trinitite investigated for this study. A) Algeria, B) Mount Ararat, C) West Virginia, and D) Trinitite.	118
Figure 2.6. Mössbauer spectra for fulgurites and country rock. A) Black Rock, Utah, B) Monahans, Texas, C) Pecos Plains, Texas, and D) Starke, Florida	124
Figure 2.7. Mössbauer spectra for fulgurites and country rock. A) Sugarland, Texas, B) Cline Butte, Oregon C) Algeria, and D) Mount Ararat.	125
Figure 2.8. Figure 8. XAS spot locations with predicted Fe ³⁺ and spectra for Starke, Florida and Cline Butte, Oregon fulgurites.....	126
Figure 3.1. Log fO ₂ versus temperature for mineral buffer assemblages, from Frost 1991.	143
Figure 3.2. Log fO ₂ versus the transition of Cr ²⁺ /Cr ²⁺⁺ Cr ³⁺ and Fe ²⁺ /Fe ²⁺⁺ Fe ³⁺ . Blue field represents the fO ₂ of MORB from Christie et	

al., 1986. Gray fields represent the fO_2 of lunar agglutinates and impact melt from NWA 10986. Cr and Fe data are from Berry and O'Neill, 2004 and Berry et al., 2003.	143
Figure 3.3. Fe(a) and Cr(b) XAS spectra of the calibration glasses.....	149
Figure 3.4. a) Lunar agglutinates and beads from 10084, b) Lunar agglutinates and beads from 14148, c) Lunar agglutinates and beads from 15427, d) NWA 10986.....	151
Figure 3.5. Agglutinate compositions compared to agglutinates from other Apollo sites.....	153
Figure 3.6. Element map of agglutinates and a glass bead from 10084 (left). Numbers represent predicted oxygen fugacity based on Cr oxidation state relative to the IW buffer. Cr XAS spectra of the agglutinates and glass bead (right).....	155
Figure 3.7. Element maps of agglutinates (a, c-d) from 14148. Numbers represent predicted oxygen fugacity relative to the IW buffer. (b) Cr XAS spectra of the agglutinate in (a).....	157
Figure 3.8. Element maps of agglutinates and volcanic glass beads from 15427 (a, c-f). Numbers represent predicted oxygen fugacity relative to the IW buffer. (b) Cr XAS spectra of the agglutinate and glass bead in (a).	158
Figure 3.9. (a) Element map of impact melt in NWA 10986. Numbers represent predicted oxygen fugacity relative to the IW buffer. (b) Cr XAS spectra of the impact melt in NWA 10986.....	159

INTRODUCTION

Impacts are a part of life in our solar system. Planetary samples returned from other bodies from past, current, and future exploration missions are invaluable for the information that they can provide about their body of origin, however, they will also undoubtedly be affected by impacts. The quest to understand the origin and evolution of other planets, including our own, hinges on the effects that impacts have on planetary samples. Impacts can destroy and irreversibly erase valuable petrologic information on planetary surfaces. The 6 Apollo missions returned a combined 842 pounds of rocks; however, all of these rocks are the direct result of prolonged exposure to impact events on the surface of the Moon (Lucey et al., 2006). Even before we begin to investigate lunar samples, the effects of impacts are already evident by their formation. The ability to read through the effects of impacts to investigate the thermal and magmatic history of a body is a skill that will be necessary with our continued efforts into planetary exploration.

Lunar Meteorite NWA 10986

Lunar meteorite NWA 10986 is a direct consequence of impacts occurring on the lunar surface. The impacts responsible for the formation of the meteorite itself and its eventual delivery to Earth are recorded through the extensive brecciation and impact melt glass within the meteorite. Even for the obvious effects of impacts, lunar meteorites including NWA 10986 are providing us with new samples from the lunar surface. Clasts in NWA 10986 represent both highland and basalt lithologies including troctolites, gabbro-norites, anorthositic norites, and troctolitic anorthosites. Some of these clasts represent “Gap” lithologies, or magnesian anorthosites, which are not found in Apollo samples. The magnesian anorthosites along with basalts without incompatible trace elements indicate that this meteorite is likely sourced from outside the Procellarum KREEP terrane, or even the farside of the Moon. This unique meteorite and others like it are questioning the lunar magma ocean theory for the formation of the Moon, however we still need to understand the effects of impacts on primary petrologic information.

Oxygen fugacity

Oxygen is the most abundant element in all rocks, meteorites, asteroids, and all of the terrestrial planets, samples from which consequentially provide us with a preserved record of oxygen present during the chemical reactions that formed those rocky bodies (Davis et al., 2008; Wadhwa, 2008). The presence of oxygen can be recorded in the oxidation state of an element by the number of electrons in the outer shell. Once a terrestrial body is formed from precursor materials, the differentiation of that body to form a core and mantle is dependent on the internal oxidation state of that body (Macpherson, 2008). This internal oxidation state then influences the composition of magmas and volatiles that are generated from

the interiors of these bodies to form subsequent crustal materials (Wadhwa, 2008).

Measuring oxidation states in planetary materials is made possible through multivalent elements such as Fe and Cr, whose valencies in melts are controlled by the prevailing redox conditions, temperature, pressure, and the structure (i.e., composition) of the silicate liquid (Kilinc et al., 1983). Oxidation states are the direct result of the activity of oxygen, or oxygen fugacity (fO_2) (Frost, 1991). Oxidation state is related to the equilibration fO_2 of a system and measuring the oxidation states of planetary materials allows determination of the oxygen fugacity present during formation (Frost, 1991). fO_2 is the chemical potential for an element to occur in a more oxidized or reduced state (Frost, 1991). By measuring the free energy change between the oxidized and reduced portions of a mineral assemblage in a rock, the fO_2 of the environment during which it was formed can be determined (Frost, 1991).

fO_2 exhibits the largest variation of any physical parameter (e.g., T, P, etc.) in terrestrial rocks, with terrestrial fO_2 ranging over eight orders of magnitude (Carmichael and Ghiorso, 1990; Carmichael, 1991). Analyzed planetary materials record fO_2 of nine orders of magnitude fO_2 from extremely reducing, to extremely oxidizing (Wadhwa, 2008). The ability to accurately measure oxidation state and identify possible alterations to intrinsic oxidation state is crucial in the investigation of planetary materials. Measuring oxidation states allows us to investigate the formation and evolution of planetary interiors, magmas and volatiles generated by these interiors, and the past influence of water on terrestrial bodies, including Mars (Herd et al., 2002).

Fe and Cr Oxybarometry

To define fO_2 in terms of the change of oxidation states, Fe is often used as it is the fourth most abundant element in the Earth's crust and is the most common rock-forming element that can occur in multiple oxidation states (Herd, 2008; Frost, 1991; Berry et al., 2003). Iron can exist in three oxidation states: in its native state (Fe_0), as a divalent ion (Fe_{2+}) in a silicate, or as a divalent or trivalent ion (Fe_{3+}) in an oxide or silicate (Frost, 1991). The change of iron's oxidation state in response to oxygen fugacity is represented by a series of mineral reactions (Frost, 1991) such as the transition of Fe_0 into oxidized wüstite ($Fe_{2+}O$). This transition is referred to as the IW (iron-wüstite) buffer (Figure 1). Terrestrial fO_2 varies from IW+2 to IW +6 while Mars fO_2 varies from IW to IW +2 and the Moon is lower in fO_2 at IW-2 to IW (Figure 2). Lower values of fO_2 are recorded in meteorites down to IW-5 which is close to the fO_2 estimation of the original bulk solar composition (Wadhwa, 2008). For terrestrial fO_2 , the ratio of ferrous to ferric iron is sufficient to measure fO_2 , however this reaction is not applicable for all planetary bodies with lower fO_2 at or below IW (Sutton et al., 2005). At low fO_2 , lunar rocks have been shown to contain no Fe_{3+} and may actually crystallize Fe_0 metal (Karner et al., 2006a). To extend the application of oxidation states to

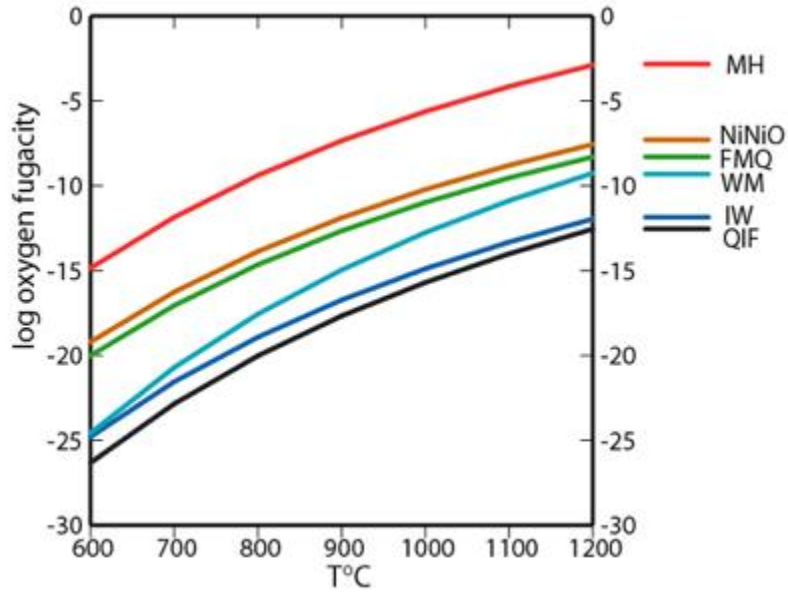


Figure I.1. Log fO_2 versus temperature for mineral buffer assemblages, from Frost 1991

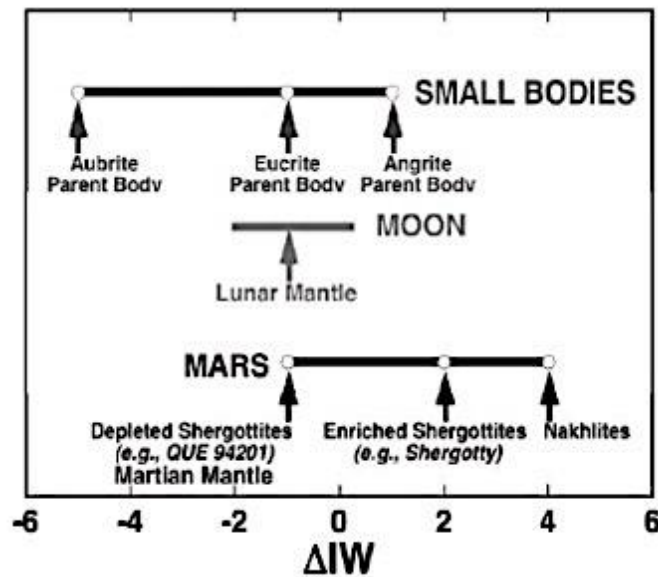


Figure I.2. Range of fO_2 for sampled planetary bodies relative to the Iron-Wüstite (IW) buffer, from Wadhwa, 2008.

lower values of fO_2 , other multivalent elements such as Cr are employed (Papike et al., 2005).

This work has directly aided efforts to determine the oxidation state of planetary materials by filling a void in analytical techniques, specifically the ability to measure Cr in-situ with well-defined accuracy through the creation of glass calibration standards. Synthetic glasses representing geologically relevant samples with added Cr were synthesized and equilibrated under a range of oxygen fugacity conditions. The oxidation state of Fe was determined first by Mössbauer spectroscopy as a ground-truth measurement and to calibrate Fe and Cr oxidation states measured by X-ray Absorption Spectroscopy (XAS). The Mössbauer and XAS were then used to build a multivariate prediction model using Python Analysis for XAS (PAXAS) software package that was written for this project. This multivariate analysis uses partial least squares analysis that considers every channel of data followed by lasso regression to remove the channels that are deemed to be less informative (Dyar et al., 2016). The end result is a freely available software for processing XAS data with a single command that directly predicts the oxygen fugacity for Fe and Cr in planetary melts. This technique can accurately predict oxygen fugacity with an RMS error of 1.28. XAS is a non-destructive technique that can perform in-situ measurements without destroying small and rare samples planetary samples that are returned to Earth.

Effects of impacts

In order for the fO_2 of a system to be determined, it is assumed that nothing has happened to overprint the oxidation state since crystallization (Carmichael, 1991; McCanta and Dyar, 2017). A possible mechanism for overprinting oxidation state is found in a common planetary occurrence: shock metamorphism (French, 1966; Grieve, 1991; French, 1988). Shock metamorphism occurs as a result of impacts on planetary surfaces. The shock produced by impacts has the ability to metamorphose material through intense pressure and temperature, potentially altering the oxidation state of the impacted materials (Stöffler, 1971). The ability to differentiate between intrinsic (those related to planetary origin and evolution) and extrinsic (those changed through outside processes) oxidation states is necessary for planetary exploration.

Fulgurites

Lightning is common on Earth and Venus (Rinnert, 1985) and was possibly present on early Mars (Segura and Navarro-González, 2005). Lightning strikes on Earth are potentially analogous to impacts and are capable of mimicking the pressure and temperature conditions experienced during impacts, even resulting in similar alterations to target materials such as shocked quartz (Sheffer et al., 2006; Pasek et al., 2012; Ende et al., 2012; Chen et al., 2017). Nuclear explosions can also provide pressures and temperatures that can simulate those of an impact. The intense heat and pressure provided by a lightning strike occurs

within tens of microseconds and may melt the target creating a fulgurite (Pasek et al., 2012). Nuclear explosions such as the atomic bomb test at the Trinity site in 1945 also produced glass referred to as Trinitite (Eby et al., 2015). Lightning strikes can also alter the oxidation state of target material similar to impact events, leading to an overprinting of intrinsic oxidation state as recorded in the resulting fulgurite. The terrestrial availability of fulgurites as analogs for impacts offers a unique opportunity to study more recent impacts and the effects of impacts on intrinsic oxidation state. More importantly, lightning is not discriminating when striking the surface and fulgurites can be created from a variety of target materials from loose sand to rock (Jones et al., 2005; Grapes and Müller-Sigmund, 2010; Pasek et al., 2012). Fulgurites and Trinitite investigated for this study have allowed for the consideration of other controls on oxidation state changes during impacts such as target composition, compaction, and density.

Agglutinates

Investigating materials on planetary surfaces that have experienced significant impact cratering, such as the Moon, necessitates the ability to identify the original oxidation state of the planetary material versus the inherited oxidation state from the impactor or the impact process. The Lunar regolith provides records of the impact process and of volcanism that have occurred on the lunar surface. Lunar agglutinates are the result of micrometeorite impacts into the lunar regolith (Basu 1977) causing localized melting of the regolith. Agglutinates are small (<1mm) aggregates of glass, mineral grains and older agglutinates fused together by vesicular glass (McKay et al., 1991). Volcanic glass beads found in the regolith are the result of fire-fountaining volcanic eruptions fueled by CO or H₂O gas (Rutherford et al., 2017). The volcanic glass beads represent a direct, unfractionated melt of the lunar material (Delano and Livi, 1981) and can provide us insight into the petrologic conditions of the lunar interior including fO_2 . By comparing the oxidation states of Cr in volcanic glass beads, agglutinates, and impact melt found in lunar meteorite NWA 10986, the alteration to primary fO_2 signatures can be measured. Chrome is capable of not only measuring the lower fO_2 of the Moon but is also sensitive enough to measure variations with fO_2 signatures.

References

Bassu A. ,1977, Steady state, exposure age, and growth of agglutinates in lunar soils: *Proceedings of the Lunar Science Conference*, v. 8, p. 3617-3632.

Berry, A.J., O'Neill, H. St.C., Jayasuriya, K.D., Campbell, S.J., and Foran, G.J., 2003, XANES calibrations for the oxidation state of iron in a silicate glass: *American Mineralogist*, v. 88, p. 967-977.

Carmichael, I.S.E, and Ghiorso, M.S., 1990, Controls on oxidation-reduction relations in magma, *in* Nicholls, J., and Russell, J.K, eds., *Modern Methods of Igneous Petrology: Understanding Magmatic Processes*, Volume 24: Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C., p. 191-212.

Carmichael, I.S.E., 1991, The redox state of basic and silicic magmas: a reflection of their source regions?: *Contributions to Mineralogy and Petrology*, v. 106, p. 129-141.

Chen, J., Elmi, C., Goldsby, D., and Gieré, R., 2017, Generation of shock lamellae and melting in rocks by lightning-induced shock waves and electrical heating: *Geophysical Research Letters*, v. 44, p. 8757-8768.

Davis, A.M., Hashizume, K. Chaussidon, M., Ireland, T.R., Prieto, C.A., and Lamberts, D.L., 2008, Oxygen in the Sun, *in* Macpherson, G.J., Mittlefehldt, D.W., and Jones, J.H., eds, *Oxygen in the Solar System*, Volume 68: Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Washington, D.C., p. 73- 92.

Delano J.W., and Livi K., 1981, Lunar volcanic glasses and their constraints on mare petrogenesis: *Geochimica et Cosmochimica Acta*, v. 45, p. 2137-2149.

Dyar, M.D., McCanta, M., Breves, E., Carey, C.J., and Lanzirotti, A., 2016, Accurate predictions of iron redox state in silicate glasses: a multivariate approach using X-ray absorption spectroscopy: *American Mineralogist*, v. 101, p. 744-747.

Eby, G.N., Charnley, N., Pirrie, D., Hermes, R., Smoliga, J. and Rollinson, G., 2015, Trinitite redux: Mineralogy and petrology: *American Mineralogist*, v. 100, p. 427-441.

Ende, M., Schorr, S., Kloess, G., Franz, A., and Tovar, M., 2012, Shocked quartz in Sahara fulgurite: *European Journal of Mineralogy*, v. 24, p. 499-507.

French, B.M., 1966, Shock metamorphism in natural materials: *Science*, v. 153, no. 3738, p. 903-906.

French, B.M., 1998, Traces of catastrophe: A Handbook of Shock-Metamorphic Effects in Terrestrial Meteorite Impact Structures: LPI Contribution No. 954, Lunar and Planetary Institute, Houston, 120 p.

Frost, B.R., 1991, Introduction to oxygen fugacity and its petrologic importance, in Lindsley, D.H., ed., *Oxide Minerals: Petrologic and Magnetic Significance*, Volume 25: Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C., p. 1-9.

Grapes, R.H., Müller-Sigmund, H., 2010, Lightning-strike fusion of gabbro and formation of magnetite-bearing fulgurite, Cornon di Blumone, Adamello, Western Alps, Italy: *Journal of Mineralogy and Petrology*, v. 99, p. 67-74.

Grieve, R.A.F., 1991, Terrestrial impact: The record in the rocks: *Meteoritics*, v. 26, p. 175-194.

Herd, C.D.K., Borg, L.E., Jones, J.H., and Papike, J.J., 2002, Oxygen fugacity and geochemical variations in the martian basalts: Implications for martian basalt petrogenesis and the oxidation state of the upper mantle of Mars: *Geochimica et Cosmochimica Acta*, v. 66, no. 11, p. 2025-2036.

Herd, C.D.K., 2008, Basalts as probes of planetary interior redox state, in Macpherson, G.J., Mittlefehldt, D.W., and Jones, J.H., eds, *Oxygen in the Solar System*, Volume 68: Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Washington, D.C., p. 527-554.

Jones, B.E., Jones, K.S., Rambo, K.J., Rakov, V.A., Jerald, J. and Uman, M.A., 2005, Oxide reduction during triggered-lightning fulgurite formation: *Journal of Atmospheric and Solar-Terrestrial Physics*, v. 67, p. 423-428.

Karner, J.M., Sutton, S.R., Papike, J.J., Shearer, C.K., Jones, J.H., and Newville, M., 2006a, Application of a new vanadium valence oxybarometer to basaltic glasses from the Earth, Moon, and Mars: *American Mineralogist*, v. 91, p. 270-277.

Kilinc, A., Carmichael, I.S.E., Rivers, M.L., and Sack, R.O., 1983, The ferric-ferrous ratio of natural silicate liquids equilibrated in Air: *Contributions to Mineralogy and Petrology*, v. 83, p. 136-140.

Lucey, P., Korotev, R.L., Gillis, J.J., Taylor, L.A., Lawrence, D., Campbell, B.A., Elphic, R., Feldman, B., Hood, L.L., Hunten, D., Mendillo, M., Noble, S., Papike,

J.J., Reedy, R.C., Lawson, S., Prettyman, T., Gasnault, O., and Maurice, S., 2006, Understanding the lunar surface and space-Moon interactions, *in*, Joliff, B.L., Wieczorek, M.A., Shearer, C.K. and Neal, C.R., eds. Volume 60: Reviews in mineralogy and geochemistry, Mineralogical Society of America, Chantilly, Virginia, p. 83-219.

Macpherson, G.J., 2008, Introduction, *in* Macpherson, G.J., Mittlefehldt, D.W., and Jones, J.H., eds, Oxygen in the Solar System, Volume 68: Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Washington, D.C., p. 1-3.

McCanta, M.C., and Dyar, M.D., 2017, Impact-related thermal effects on the redox state of Ca-pyroxene: *Meteoritics and Planetary Science*, v. 52, no. 2, p. 320-332.

McKay, D.S., Heiken, G., Basu, A., Blanford, G., Simon, S., Reedy, R., French, B.M., and Papike, J., 1991, The Lunar Regolith, *in* Heiken, G.H., Vaniman, D.T., and French, B.M., eds, Lunar Sourcebook: A User's Guide to the Moon. Lunar and Planetary Institute, Cambridge University Press, New York, New York. p. 285-356.

Papike, J.J., Karner, J.M., and Shearer, C.K., 2005, Comparative planetary mineralogy: valence state partitioning of Cr, Fe, Ti, and V among crystallographic sites in olivine, pyroxene, and spinel from planetary basalts: *American Mineralogist*, v. 90, p. 277-290.

Pasek, M.A., Block, K., and Pasek, V., 2012, Fulgurite morphology: a classification scheme and clues to formation: *Contributions to Mineralogy and Petrology*, v. 164, p. 477-492.

Rinnert, K., 1985, Lightning on other planets: *Journal of Geophysical Research*, v. 90, no. D4, p. 6225-6237.

Rutherford, M.J., Head, J.W., Saal, A.E., Hauri, E., and Wilson, L., 2017, Model for the origin, ascent, and eruption of lunar picritic magmas: *American Mineralogist*, v. 102, p. 2045-2053.

Segura, A., and Navarro-González, R., 2005, Nitrogen fixation on early Mars by volcanic lightning and other sources: *Geophysical Research Letters*: v. 32, p. 1-4.

Sheffer, A.A., Dyar, M.D., and Sklute, E.C., 2006, Lightning strike glasses as an analog for impact glasses: ^{57}Fe Mössbauer spectroscopy of fulgurites: Proceedings of the 37th Lunar and Planetary Science Conference, abstract no. 2009.

Stöffler, D., 1971, Progressive metamorphism and classification of shocked and brecciated crystalline rocks at impact craters: *Journal of Geophysical Research*, v. 67, no. 23, p. 5541-5551.

Wadhwa, M., 2008, Redox conditions on small bodies, the Moon and Mars, *in* Macpherson, G.J., Mittlefehldt, D.W., and Jones, J.H., eds, *Oxygen in the Solar System*, Volume 68: Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Washington, D.C., p. 31-54.

CHAPTER I
NEW LUNAR METEORITE NWA 10986: A MINGLED IMPACT
MELT BRECCIA FROM THE HIGHLANDS; A COMPLETE CROSS
SECTION OF THE LUNAR CRUST

A version of this chapter has been published by Sarah E. Roberts, Molly C. McCanta, Marlon M. Jean, and Larry A. Taylor:

Roberts S.E., McCanta M.C., Jean M.M., and Taylor L.A. *in print*. "New lunar meteorite NWA 10986: A mingled impact melt breccia from the highlands; a complete cross section of the lunar crust." *Meteoritics and Planetary Science*

I collected all data including petrography, images, and geochemical analyses, compiled previous research and wrote this manuscript. Molly McCanta reviewed and provided edits to the manuscript. Marlon Jean assisted with some data collection. Larry Taylor provided the meteorite along with verbal communication about the meteorite and the collected data. This manuscript was submitted to *Meteoritics and Planetary Science*, reviewed by two peer reviewers, and has undergone one major revision and two minor revisions.

Abstract

Northwest Africa (NWA) 10986 is a new mingled lunar meteorite found in 2015 in Western Sahara. This impact melt breccia contains abundant impact melt glass and clasts as large as 0.75mm. Clasts are predominantly plagioclase and pyroxene-rich and represent both highland and basalt lithologies. Highland lithologies include troctolites, gabbro-norites, anorthositic norites, and troctolitic anorthosites. Basalt lithologies include crystalline clasts with large zoned pyroxenes representing very low titanium to low titanium basalts. In situ geochemical analysis of minerals within clasts indicates they represent ferroan anorthosite, Mg-suite, and gabbro-norite lithologies as defined by the Apollo sample collection. Clasts representing magnesian anorthosite, or "Gap" lithologies, are prevalent in this meteorite. Whole rock and in situ impact glass measurements indicate low incompatible trace element concentrations. Basalt clasts also have low incompatible trace element concentrations and lack evolved KREEP mineralogy although pyroxferroite grains are present. The juxtaposition of evolved, basaltic clasts without KREEP signatures and highland lithologies suggests that these basaltic clasts may represent cryptomare. The lithologies found in NWA 10986 offer a unique and possibly a complete cross section view of the Moon sourced outside of the Procellarum KREEP Terrane.

Introduction

During the last century, six manned Apollo missions returned 381.7 kg of lunar materials from the central nearside of the Moon (Hiesinger and Head 2006). Geochemical and radioisotopic data from returned Apollo samples were used to construct the lunar magma ocean (LMO) theory for the origin and evolution of the Moon (e.g., Wood et al. 1970; Smith et al. 1970, Taylor and Jakes 1974; Shirley

and Wasson 1981; Warren 1985). The lunar magma ocean (LMO) theory postulates the state of the Moon as a molten body shortly after its formation (Wood et al. 1970; Smith et al. 1970; Taylor and Jakes 1974; Shirley and Wasson 1981; Warren 1985). Subsequent crystallization and magmatism produced lithologies identified in the Apollo samples including ferroan anorthosite (FAN) and Mg-suite lithologies. However, following the termination of the Apollo program, the Clementine and Lunar Prospector Missions discovered the existence of a unique KREEP-rich terrain, the Procellarum KREEP Terrane (PKT) located on the nearside of the Moon (Lawrence et al. 1999; Spudis 2000; Joliff et al. 2000; McCallum 2001). All Apollo missions landed near to or within the PKT and the samples used to construct the LMO theory were therefore derived from this unique nearside terrain.

With the discovery and identification of the first lunar meteorite in 1983 (Bogard 1983), lunar meteorites have provided additional samples to continue investigating the origin and evolution of the Moon. Apollo samples are invaluable for their petrologic data combined with known sampling locations, however lunar meteorites offer the ability to randomly sample the surface of the Moon, potentially including the farside, although the exact source locations for the meteorites are unknown. Indeed, half of all lunar meteorites may be sourced from the farside of the Moon as the current cratering rates for both sides of the Moon are about the same (Gallant et al., 2009). Lunar meteorites, therefore, provide a means to study lunar crustal rocks and planetary evolution outside of the influence of the PKT.

The lithologies of the returned Apollo samples are evident in many lunar meteorites (e.g., Koeberl et al. 1991; Joy et al. 2011; Day et al. 2006; Anand et al. 2003b), however additional lithologies have also been observed that suggest Apollo samples may not represent the entirety of lunar materials (Yamaguchi et al. 2010). Lunar meteorites present lithologies that do not fall in the Apollo-generated classification scheme of FAN and Mg-Suite rocks (Cahill et al. 2004; Yamaguchi et al. 2010; Takeda et al. 2006; Mercer et al. 2013; Nyquist et al. 2006) resulting in new lunar rock types including magnesium anorthosite (Takeda et al. 2006, Treiman et al. 2010) and mixed impactites (Cahill et al. 2004). Mg-suite lithologies are not as well represented in many lunar meteorites implying that the distribution of Mg-suite rocks and, consequently, the LMO, may not be global (Gross et al. 2014; Korotev 2005).

Northwest Africa (NWA) 10986 is a new lunar meteorite found in 2015 in Grarat Zawi, Western Sahara (Bouvier et al. 2017). This impact-melt breccia has a complicated breccia-in-breccia composition and abundant impact-melt glass indicating multiple generations of impacts. The anorthite-rich composition of this meteorite suggests this meteorite was sourced from the lunar highlands, an area of the Moon that has low Apollo sample coverage and occurs predominantly outside of the PKT (Hiesinger and Head 2006; Lucey et al. 2006). Clasts found within NWA 10986 represent large petrologic diversity, including highland lithologies and basalt lithologies. The combination of both highland and basalt

clasts offers a unique opportunity to investigate the lunar surface and may represent a cross-sectional view of the lunar crust. Here we present a petrological and geochemical study of NWA 10986, including in situ geochemical analysis of major, minor, and trace element abundances, and discuss how its components fit into prevailing lunar evolution theories.

Analytical Methods

Two thin sections (sections 2-2 and 2-5, Figure 1) and one thick section (section 2-1) of NWA 10986 were investigated using an Olympus BH-2 optical microscope with transmitted and reflected light.

Bulk Rock Preparation

Fused beads of powdered chips were created for whole rock analyses from detached portions of the meteorite. Two portions of the meteorite, each approximately 1cm³, were broken, mixed, and crushed by hand using a mortar and pestle and ground under acetone to make a fine, homogeneous powder. Once dry, 10 mg of powder were placed on a strip of molybdenum foil that was then heated by an electrical current causing the powder to melt. Six fused beads were created in this manner and mounted in epoxy for analysis.

Major and Minor Element Geochemistry

Backscattered electron (BSE) images, element maps, and major and minor element mineral compositions were collected by Wavelength Dispersive Spectroscopy (WDS) using a Cameca SX-100 electron microprobe (EMP) at the University of Tennessee. Minerals were analyzed using a 1 µm spot size with a probe current of 30 nA and an accelerating voltage of 15 KeV for all minerals with the exception of plagioclase when a 5 µm spot size and a probe current of 10 nA was used. In situ impact-glass and fused glass beads were analyzed using a 15 µm spot size and 20 nA probe current. Well-characterized natural and synthetic standards were used during all analytical sessions to calibrate and ensure precision of the data. Additional BSE images and Energy-Dispersive Spectrometry (EDS) analyses were collected on a Phenom Pro XL scanning electron microscope at the University of Tennessee.

Trace Element Geochemistry

Trace element analyses of minerals, glass, and fused beads were performed by Laser Ablation Inductively Coupled Plasma Mass Spectrometry at the University of Houston with a Varian 810 quadrupole ICP-MS. Fused beads and in situ mineral and glass analyses were performed using a CETAC LSX-213 laser and a Photon Machines Analyte.193 ArF excimer laser with He as a carrier gas at a flow of 0.5 lpm. A 100 µm spot size and a laser frequency of 20 Hz was used for

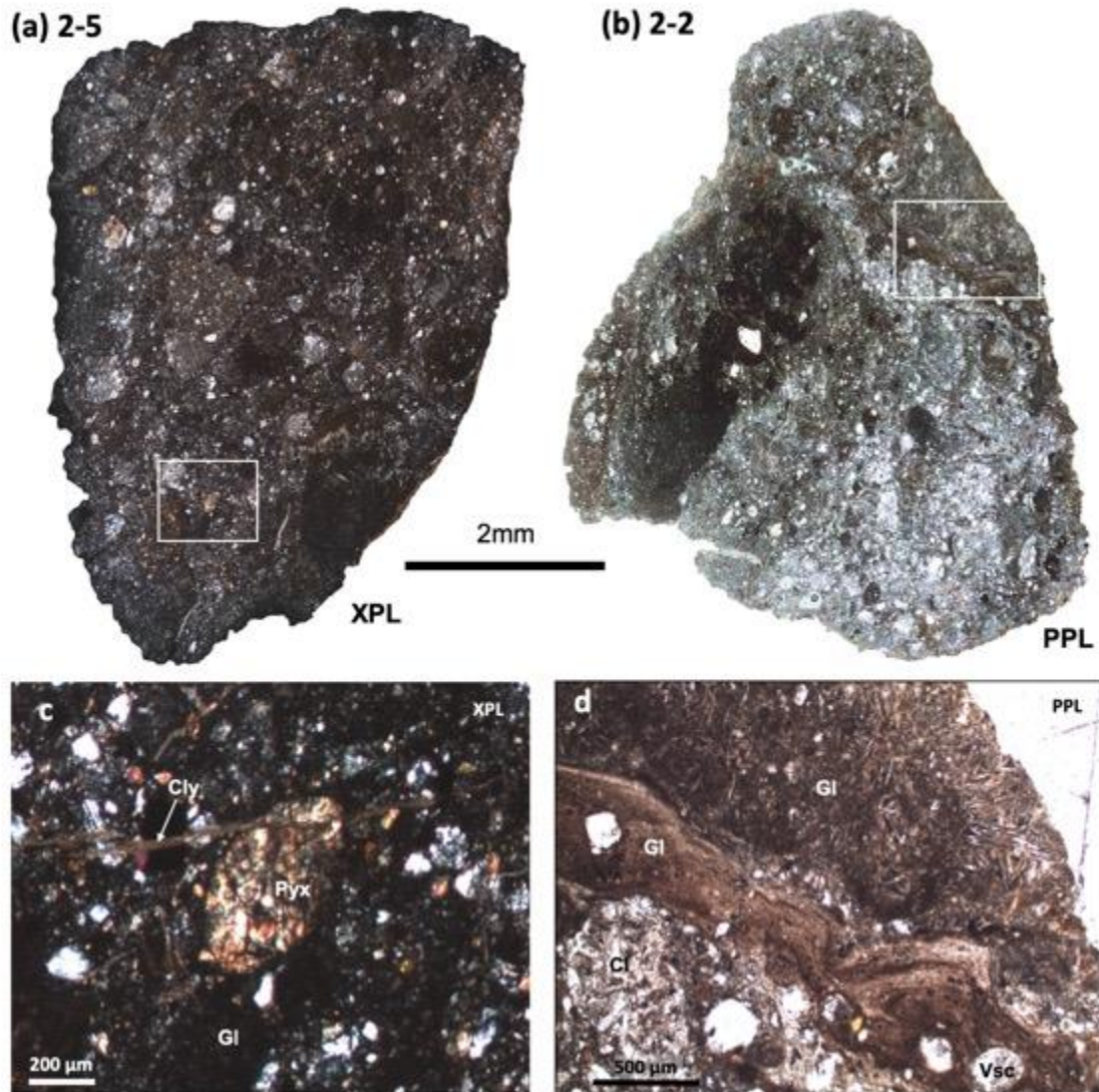


Figure 1.1. XPL and PPL photomosaics of thin sections 2-5 (a) and 2-2 (b) of NWA 10986. c) Detail of area shown in (a) of a large pyroxene in a glassy matrix with veins of clay. d) Detail of area shown in (b) of glassy impact melt area with two generations impact melt. Upper portion of glass features “haystack” textured plagioclase while the glass in the center of the image has preserved flow texture with preserved vesicles now infilled with secondary precipitated minerals. Abbreviations: Gl = glass, Vsc = vesicle, Cly = clay, Pl = clast, Pyx = pyroxene.

fused bead analysis and either a 50 or 30 μm spot size with a laser frequency of 10 Hz was used for in situ mineral and glass analyses. Background signal was collected for 18 seconds and the data signal was acquired for 30 seconds. Calcium measured by EMP was used as an internal standard for each spot analyses. The United States Geological Survey (USGS) Standard Reference Material (SRM) BHVO-2G was used as an external standard to correct for instrumental fractionation and drift using the software package Glitter (<http://www.glitter-gemoc.com/>). USGS SRM BIR-1G glass was also used as an external standard for external reproducibility and to assure accuracy. All background and data signals were visually selected to ensure data was free of any inclusions and the best signals were collected. Data reduction was performed by the Glitter software program.

Results

Evidence for Lunar Origin

NWA 10986 lacks a fusion crust, however this meteorite is a desert find and the fusion crust could have been eroded away during terrestrial weathering (Joy et al. 2008; Korotev 2005). Several lines of evidence indicate a lunar origin for NWA 10986. First, plagioclase grains found within this meteorite, both within clasts and as loose fragments, are An-rich (An₉₄ average, Figure 2). Second, pyroxene and olivine Fe and Mn abundances both follow lunar trends (Figure 3; Papike et al. 2003). Third, the primary mineralogy of NWA 10986 is anhydrous similar to lunar samples (Joy et al. 2008). Finally, grains of pyroxferroite are present in clasts in NWA 10986; this metastable mineral was initially found in returned Apollo 11 samples and is very rare terrestrially (Lindsley and Burnham 1970).

Minerals, both from clasts and isolated in the matrix, were used to determine potential Apollo lithologies represented in this meteorite. Olivine and pyroxene Mg# [molar $\text{Mg}/(\text{Mg}+\text{Fe})$] and plagioclase An# [molar $\text{Ca}/(\text{Ca}+\text{Na})$] were utilized for this comparison (Figure 2). Pyroxene grains found loose in the matrix were also included in this comparison even though they do not have corresponding plagioclase grains for An# (Figure 1c). Including these loose pyroxenes in the Mg# and An# comparison allows for lithologies that are not represented by the polymineralic clasts to be represented and expand on the diversity of the lunar crust that was not sampled by the clasts (Mercer et al. 2013; Yamaguchi et al. 2010). The clasts and matrix pyroxenes are not very Mg-rich trending to almost no Mg with a Mg# of 4. The clasts with the lowest Mg# are basaltic with pyroxene compositions that reach pyroxferroite. Many clasts plot within the “gap” between the FAN and Mg-suite lithologies as is common for many lunar meteorites (Mercer et al. 2013; Gross et al. 2014; Yamaguchi et al. 2010; Takeda et al. 2006; Nyquist et al. 2006; Cahill et al. 2004). The potential identity of these gap compositions will be discussed in the following sections.

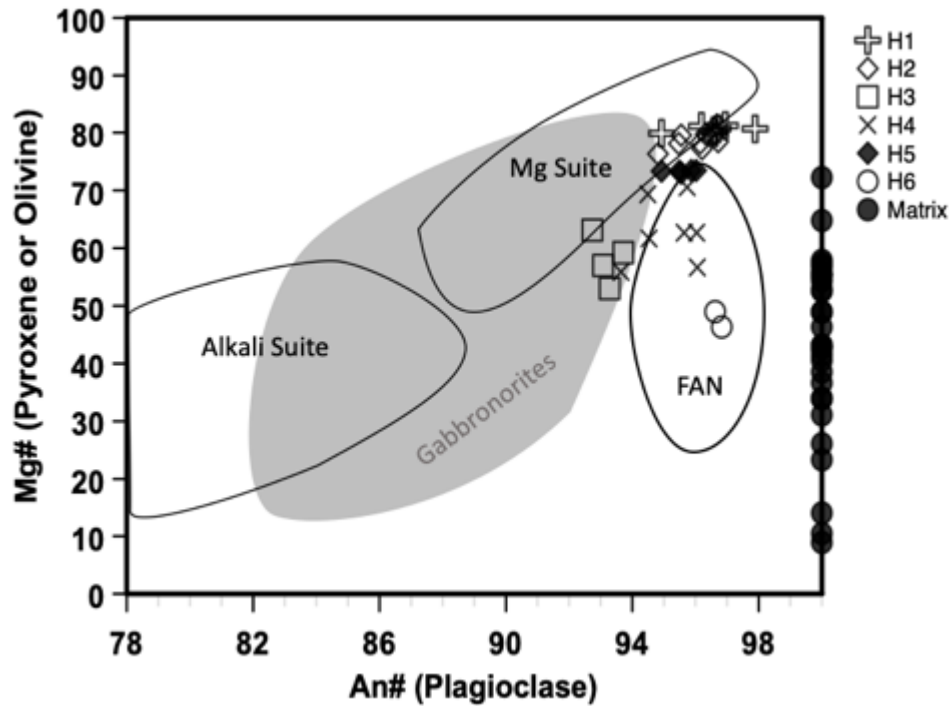


Figure 1.2. Mg # $[Mg/(Mg+Fe)]$ of pyroxenes or olivines and An # $[Ca/(Ca+Na)]$ of plagioclase from clasts compared to Apollo lithologies. Mg # of pyroxene grains found in the matrix without accompanying An # are shown on the right ordinate. Fields are from Lindstrom and Lindstrom (1986) and James et al. (1987).

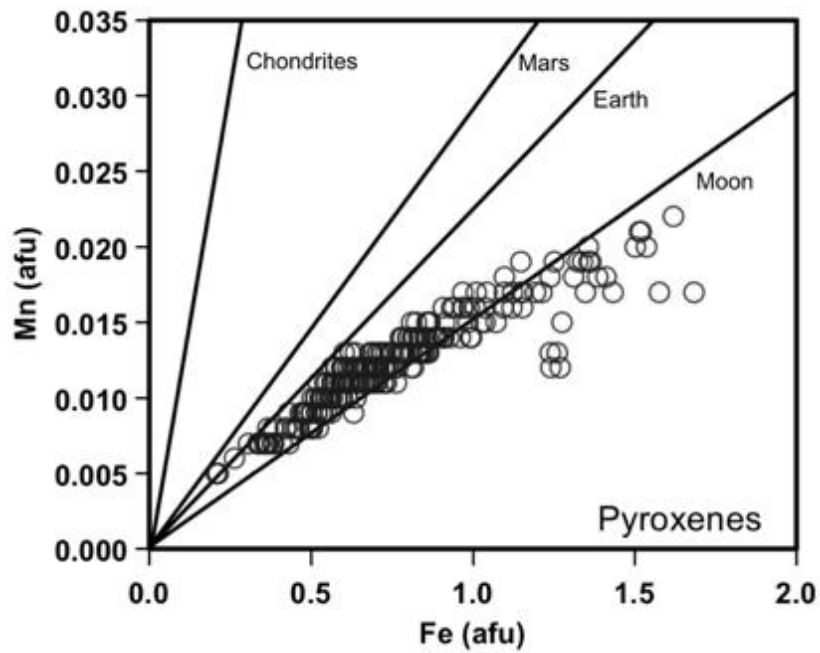


Figure 1.3. Fe and Mn ratios in NWA 10986 indicate a lunar origin. Fe and Mn trend lines are from Papike et al. (2003).

Petrography and Clast Inventory

NWA 10986 was found in the Western Sahara desert as several pieces with a total weight of 108.2 grams (Bouvier et al. 2017). The exterior, where a fusion crust would be present, has been subjected to substantial hot desert weathering and long cross-cutting veins of barite and calcite are present in all sections investigated (Figure 4). Clay is also present, both as an alteration product and as the infilling of vesicles that were preserved in impact melt glass (Figure 5a, b). Abundant impact melt glass shows variations in color and texture indicating multiple generations of impact events during the formation of this complex breccia-in-breccia (Figure 1, 5). Large sections of brown swirly schlieren contain mineral fragments and vesicles while other large areas of impact melt glass show a quenched “haystack” texture of plagioclase grains in a glassy matrix (Snyder and Taylor 1996; Fig. 1d).

The two thin sections (2-2 and 2-5, Figure 1) and one thick section (2-1, Figure 1) of NWA 10986 investigated are differed based on clast type population and abundance of impact melt glass (Figures 1, 4). Each section yielded abundant clast types that are unevenly distributed throughout the meteorite (Figure 4). Clasts representing highland and basalt lithologies were identified in the three sections (Figures 4, 6, 7; Table 1). Basalt clasts are concentrated in section 2-2 while highland clasts are more abundance in section 2-5 (Figure 4). Section 2-1 only contained two highland clasts (Figure 4). Individual clasts demonstrating the diversity of the groups were chosen to represent the clast types and are discussed below.

The clasts that are found throughout this meteorite vary in size (500-1000 μm) and composition (Figures 6-7; Table 1). We are interpreting the following clasts as being pristine representatives of the lunar crust (see discussion below for details of this classification) even though there is substantial debate regarding the pristinity and classification of clasts in lunar breccias such as NWA 10986. (Warren and Wasson, 1977; Warren 2012). Clasts are predominately plagioclase and pyroxene-rich and the matrix contains large mineral fragments of plagioclase (up to 1.5 mm long) and exsolved pyroxene (up to 675 μm long with exsolution lamellae 5-25 μm wide, Figure 1c, 4d)). Olivine is a minor phase in some clasts; ilmenite and chromite are rare. Grains of a SiO_2 polymorph are found in basalt clast B4 (Figure 7d).

A highland source region of this meteorite is inferred by the abundant plagioclase found within clasts and loose in the matrix. No obvious glass spherules or agglutinates were observed, however as agglutinates are also more fragile, any present may have succumbed to digestion by impact-melt glass. Regolith breccias from the Apollo missions with crystalline lithic clasts and large relict mineral grains may also lack glass spherules (Joy et al. 2010) so the absence of glass spherules does not preclude a lunar regolith source.

Evidence of shock alteration is optically negligible; no plagioclase was observed to have been converted to maskelynite. The only indicators of possible shock alteration are found in the symplectite material (possibly a result from the

Table 1.1. Clasts investigated and EMP analyses of feldspar, pyroxene, and olivine along with associated lunar lithologies.

Highland clasts	Type	Feldspar An range	An ave	Pyroxene En range	Fs range	Wo range	Mg# ave	Olivine Fo range	Fo ave	Lunar lithology
H1	Troctolite	96.2-97.9	96.6	-	-	-	-	79.9-81.5	80.7	Mg-suite
H2	Troctolite	94.8-96.7	96.0	49.8-74.5	10.9-19.7	5.9-39.2	80.2	76.1-78.5	77.9	Mg-suite
H3	Gabbro-norite	92.7-93.7	93.2	39.2-50.7	22.8-39.8	9.4-37.9	55.8	-	-	MAN
H4	Gabbro-norite	93.6-96.7	95.5	41.9-59.1	28.0-68.2	4.9-23.8	66.1	55.9-56.7	56.3	FAN
H5	Anorthositic norite	94.9-96.0	95.6	69.5-70.1	25.3-25.6	4.5-4.8	73.3	-	-	MAN
H6	Troctolitic Anorthosite	96.6-96.8	96.7	-	-	-	-	53.5-54.2	53.9	FAN

Basalt clasts	Type	Feldspar An range	An ave	Pyroxene En range	Fs range	Wo range	Mg# ave	Olivine Fo range	Fo ave	Lunar lithology
B1	Basalt	92.6-96.2	93.9	2.6-58.1	26.6-81.2	6.9-31.4	40.4	32.1-74.9	61.6	Basalt
B2	Basalt	96.1-97.6	96.8	9.7-58.9	29.9-54.5	9.8-25.4	54.9	-	-	Basalt
B3	Basalt	89.6-94.8	91.9	15.9-63.8	22.1-56.4	7.2-24.5	58.9	60.5-64.1	62.3	Basalt
B4	Basalt	83.9-96.3	90.3	7.6-39.8	29.5-60.2	28.4-40.4	37.5	-	-	Basalt

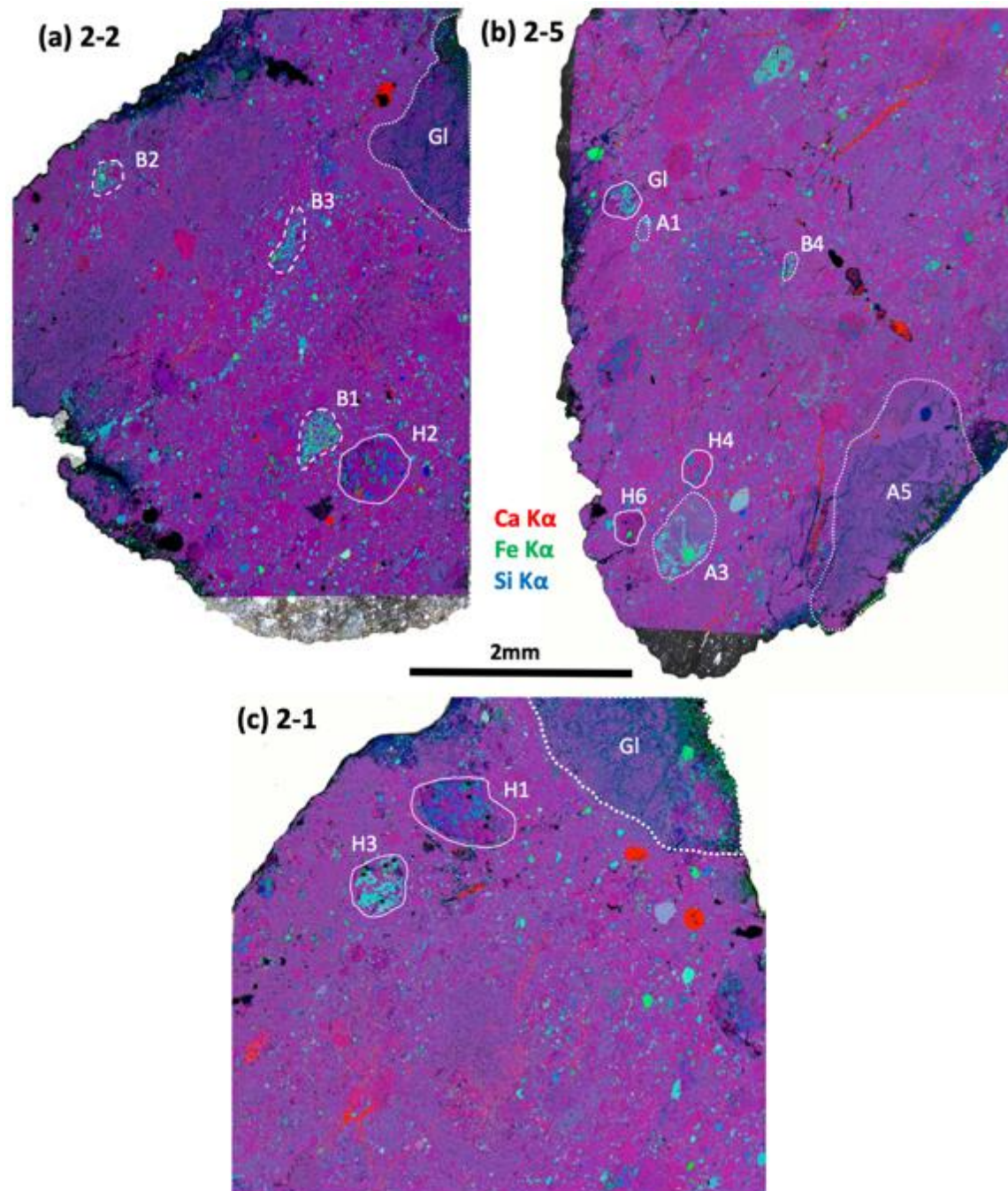


Figure 1.4. Ca K α , Fe K α , and Si K α maps of the three sections of NWA 10986 with clasts and glass areas outlined. Red = Ca, Green = Fe, and blue = Si.

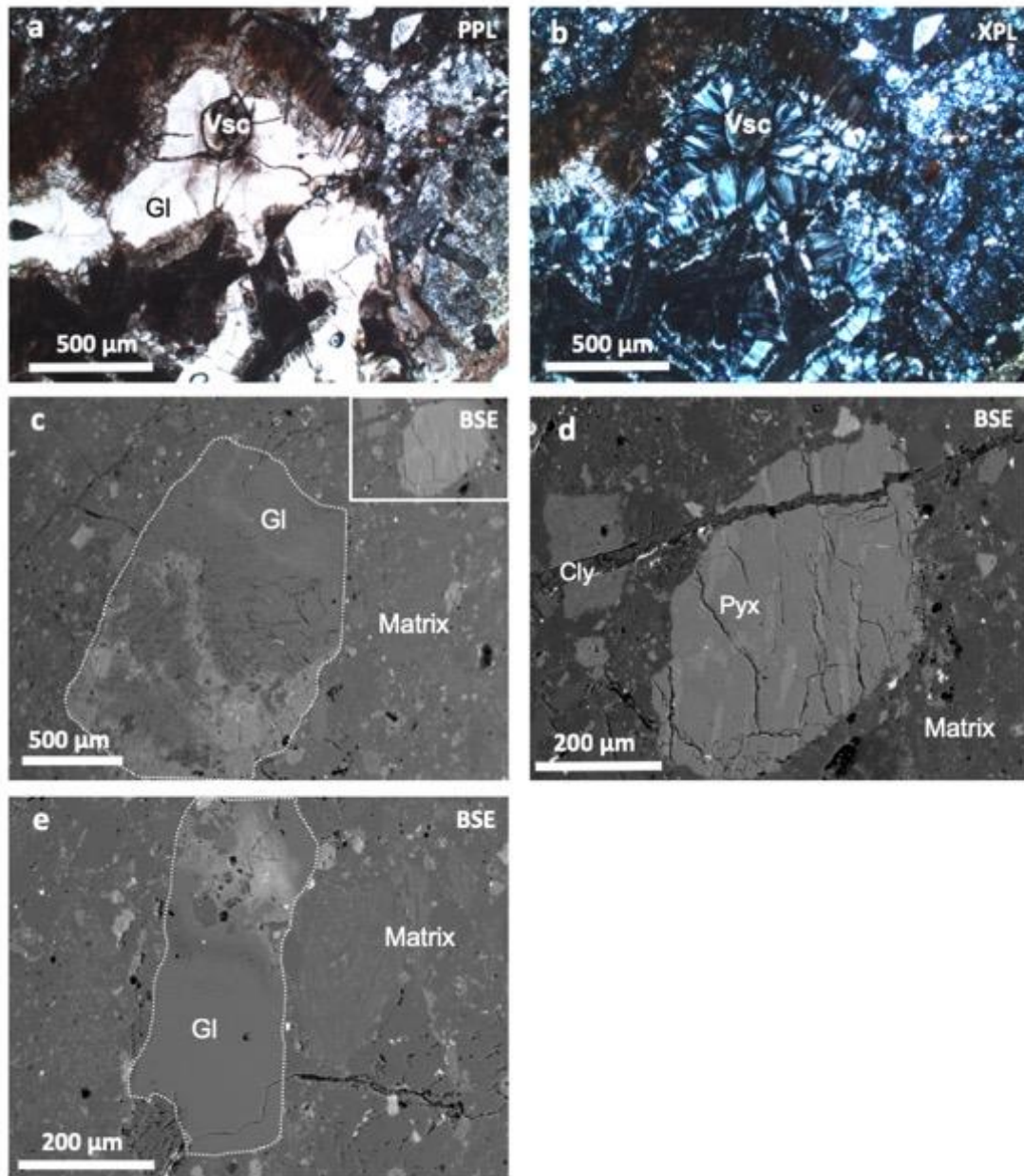


Figure 1.5. Glass areas (a-c, e) and a loose pyroxene grain (d). a) Photomicrograph of glass area A5 in plane polarized light and (b) in cross polarized light. Transparent glass has a wavy undulose extinction in cross polarized light. c) Glass area A3. d) Large exsolved pyroxene grain cut by clay-filled vein. e) Glass area A1. Abbreviations: Gl = glass, Vsc = vesicle, Cly = clay, pyx = pyroxene.

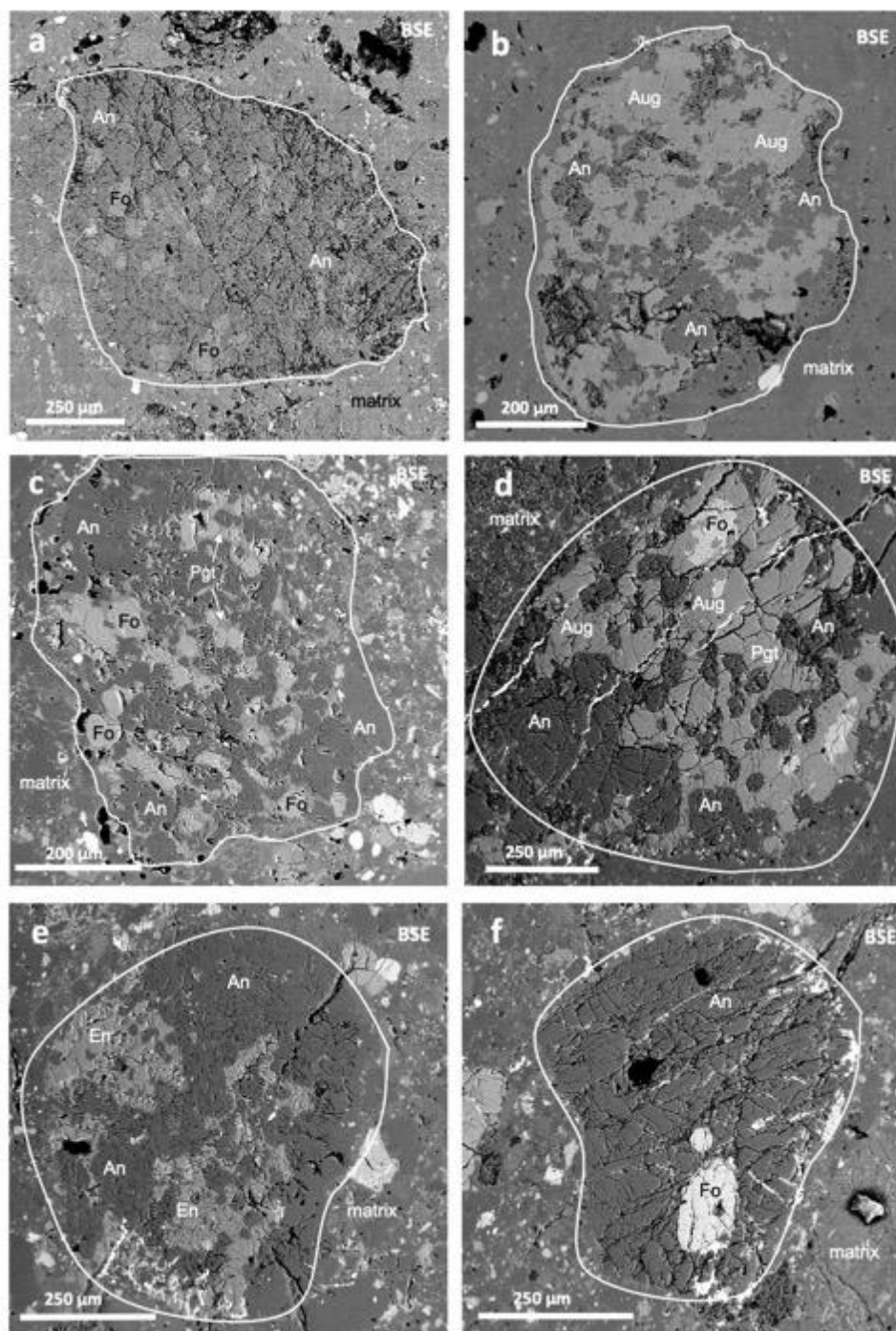


Figure 1.6. Highland clasts. a) Troctolite clast H1. b) Gabbronorite clast H3. c) Troctolite clast H2. d) Gabbronorite clast H4. e) Anorthositic norite clast H5. f) Troctolitic anorthosite clast H6. Abbreviations: Fo = fosterite, An = anorthite, Aug = augite, Pgt = pigeonite, En = enstatite.

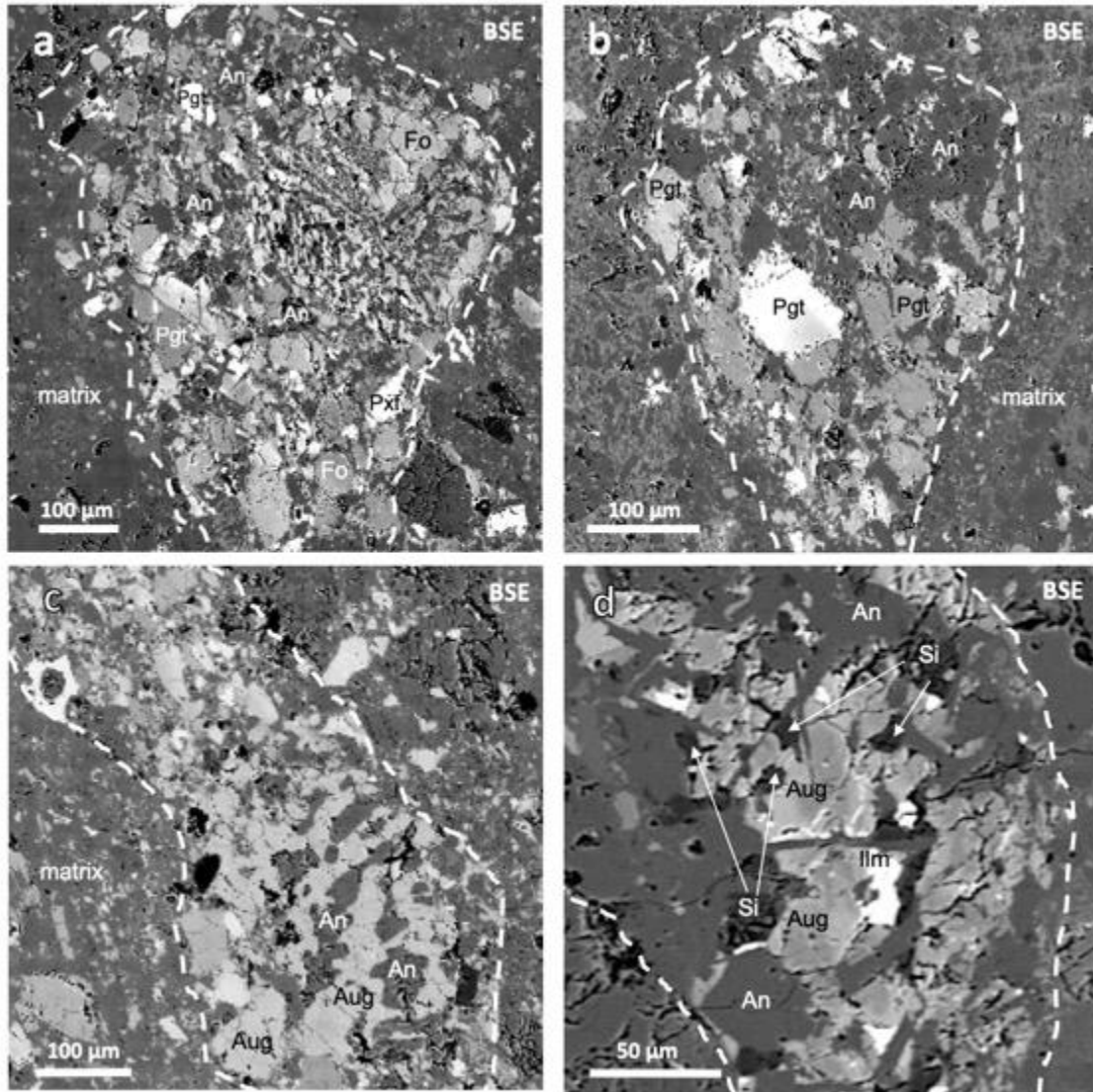


Figure 1.7. Basalt clasts. a) Clast B1. b) Clast B2. c) Clast B3. d) clast B4. Abbreviations: An = anorthite, Si = Silica, Pgt = pigeonite, Aug = augite, Ilm = ilmenite, Pxf = pyroxferroite, Fo = forsterite, Sp = spinel.

shock-induced breakdown of pyroxferroite) which is unevenly distributed throughout the meteorite although this may have a magmatic origin (see discussion of pyroxferroite below).

Whole Rock and Impact Melt Composition

The brecciated nature of NWA 10986 necessitates whole rock analysis to capture the extent of lunar lithologies sourced during the formation of this meteorite. Considering the clasts found within this meteorite are small and unevenly distributed throughout this meteorite, two large portions (~1cm³ each) of the meteorite were crushed and powdered to ensure a representative analysis of the bulk composition. The small size of the clasts and the glassy impact melt matrix precluded the possible removal of individual clasts for bulk clast analysis. Areas of homogeneous, crystallite-free impact melt (Figures 4, 5a-c, e,) were also utilized to compare the whole rock analysis against as these impact melt pockets represent whole rock compositions sampled during meteorite formation. All geochemical data can be found in the supplementary data set.

Comparing Al₂O₃ wt.% versus FeO wt.%, NWA 10986 has a predominantly anorthite-rich highland composition similar to other feldspathic meteorites (Figure 8a). The whole rock composition is close to the average feldspathic lunar meteorite composition but also falls on the mixing line with average Apollo low and very-low Ti basalts. The individual impact melt areas (A1, A3, and A5) show more enrichment in FeO (Figure 8a). Whole rock analysis indicates a mafic component reflecting the basaltic clast population, yet the whole rock composition is still more feldspathic-rich than the impact melt glass analyzed.

Sc and Sm abundances are also indicative of the mixed composition of NWA 10986 (Figure 8b). Again, the impact melt areas are more Sc-rich reflecting increasing mixture with Apollo low and very-low Ti basalt components. Both the whole rock and impact-melt glass compositions plot along a mixing line between feldspathic and basaltic compositions, but do not show enrichment in Sm which would be indicative of a KREEP component (Figure 8b).

Highland Clasts

Six clasts were selected from the sections as representatives of the highland lithologies observed in NWA 10986 (Table 1; Figure 6). Lithologies represented include troctolites (clasts H1 and H2), Gabbronorites (clasts H3 and H4), anorthositic norite (clast H5), and troctolitic anorthosite (clast H6).

Troctolite clast H1 (Figure 6a) is composed of anorthite and olivine in a poikilitic texture. Round olivines 50µm wide with the largest being 200µm long, are enclosed in shattered anorthite grains. Troctolite clast H2 (Figure 6c) also has a poikilitic texture with pigeonite rimmed olivines (75-100 µm wide) enclosed in anorthite. Gabbronorite clast H3 (Figure 6b) is subophitic with augite masses enclosed by euhedral anorthite. Clast H4 (Figure 6d) is another gabbronorite clast with an ophitic texture of anorthite surrounded by pigeonite and augite.

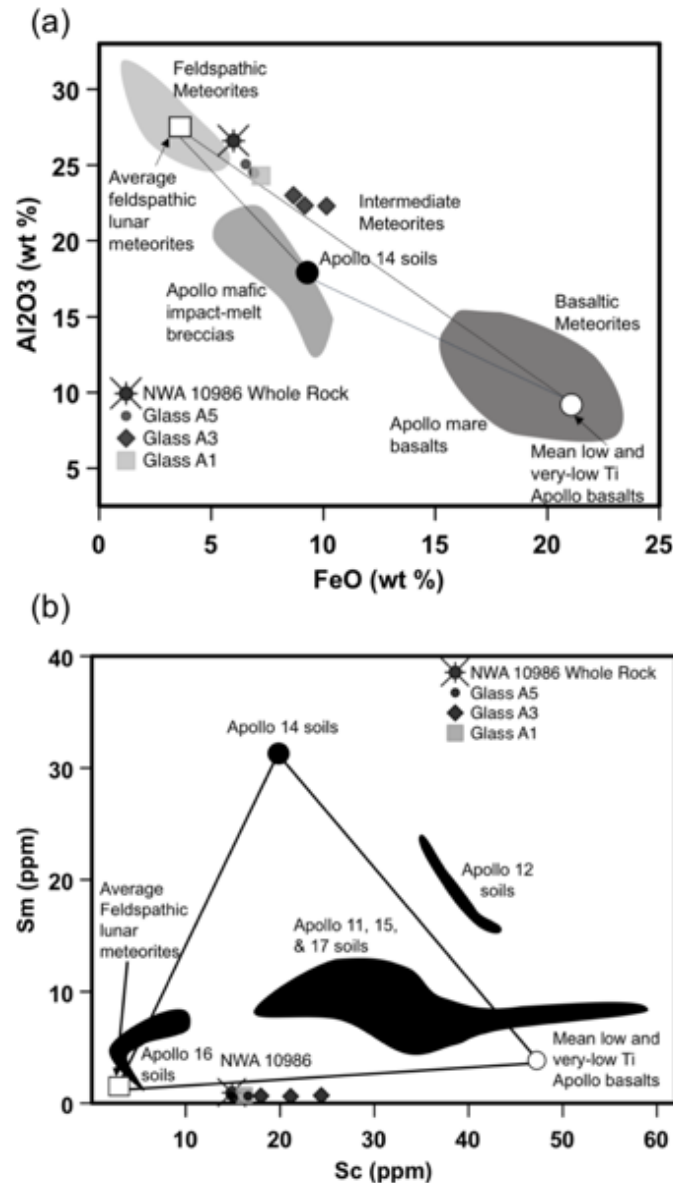


Figure 1.8. Comparative whole rock and glass compositions with Apollo samples and average lunar meteorites. a) Whole rock Al_2O_3 and FeO composition of NWA 10986 is similar to that of other feldspathic lunar meteorites yet also has a basaltic component as well. White square = average of some feldspathic lunar meteorites, white circle = average composition of VLT and LT mare basalts, black circle = average Apollo 14 soil composition. b) Sc and Sm whole rock and glass compositions compared to Apollo samples and lunar meteorites. Graphs and fields are after Korotev et al. 2005.

Fosterite (30 to 125 μm) is found in the cores of four pyroxene masses. Anorthositic norite clast H5 (Figure 6e) is composed of anorthite with pockets of enstatite poikilolitically enclosing anorthite. Troctolitic anorthosite clast H6 (Figure 6f) is a large rounded anorthite grain with two enclosed granular olivines 150 and 50 μm wide.

Pyroxenes are only found in four of the highland clasts. Analysis of these pyroxenes by EMP indicate that pyroxene compositions are Mg-rich with some Ca-rich pyroxenes (Figure 9a). Pyroxenes in clast H2 range in composition from $\text{En}_{75-50} \text{Fs}_{20-11} \text{Wo}_{39-6}$ (Figure 9a). Clast H3 has pyroxenes that range in composition from $\text{En}_{48-39} \text{Fs}_{39-23} \text{Wo}_{38-9}$. Pyroxenes in clast H4 (Figure 9a) are either pigeonites with pyroxene compositions of $\text{En}_{59-58} \text{Fs}_{36-35} \text{Wo}_6$ or augites with pyroxene compositions of $\text{En}_{42-44} \text{Fs}_{18-20} \text{Wo}_{37-41}$. Pyroxene analyses for clast H5 are all the same at $\text{En}_{70} \text{Fs}_{25} \text{Wo}_5$ indicating that these pyroxenes are one continuous grain.

Trace element analyses of low- and high-Ca pyroxenes show rare Earth element (REE) profiles with a negative Eu anomaly and a slight positive to an almost flat slope (Figure 10a, b). When compared to Apollo highland suites, the low-Ca pyroxene compositions of anorthositic norite clast H5 are similar to Apollo high-Mg suite pyroxenes, however substantial overlap with the high alkali suite rocks is observed (Figure 10b). Gabbronorite clast H3 is enriched in light REEs and could be assigned to either high-alkali or Mg-suite lithologies. High-Ca pyroxenes from gabbronorite clast H4 show little REE enrichment with compositions falling between FAN and high-Mg suite lithologies (Figure 10a).

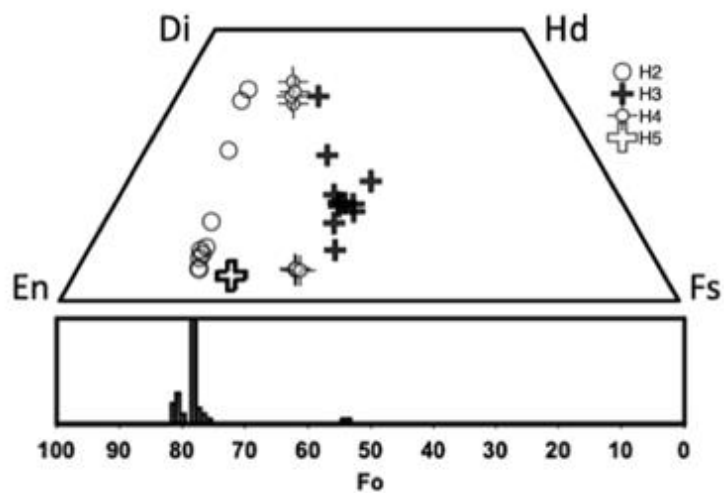
Feldspar compositions are restricted to An_{93-98} (Table 1). The two troctolite clasts, H1 and H2, have the highest anorthite compositions at An_{95-98} ; gabbronorite clasts have the lowest anorthite compositions at An_{93-97} . REE profiles of anorthite in troctolite clasts have flat slopes while gabbronorites, anorthositic norite, and noritic anorthosites have slight negative slopes (Figure 10c). All profiles display a positive Eu anomaly. Compositionally, the REEs in anorthites from the highland clasts are not very enriched in comparison to Apollo high Mg-suite anorthites however are enriched compared to FAN anorthites.

Olivine compositions for troctolite clasts H2 and H1 range from Fo_{76-78} to Fo_{80-82} respectively (Figure 9a). The granular olivines in troctolitic anorthosite clast H6 are not zoned with a composition of Fo_{54} for both.

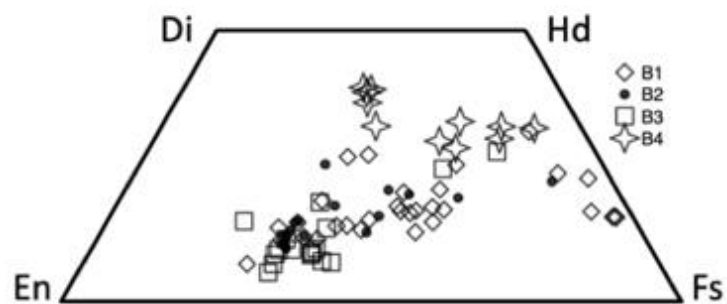
Basalt Clasts

Basalt clasts are found in every section of NWA 10986 (Table 1; Figure 7). Four of these were selected as representatives of the basalt clast population: B1, B2, B3, and B4 (Figures 4, 7). Basalt clast B1 is subophitic (Figure 7a) with largely unzoned pyroxenes and a fine-grained area in the center of this clast that could represent late-stage mesostasis (Figure 11a). This ophitic fine-grained mesostasis area has pigeonite and anorthite with minor spinel and small interstitial glass pockets that are slightly enriched in potassium, however no late stage minerals such as apatite and K feldspar are found in this area, in this clast,

(a) Highland Clasts



(b) Basalt Clasts



(c) Matrix

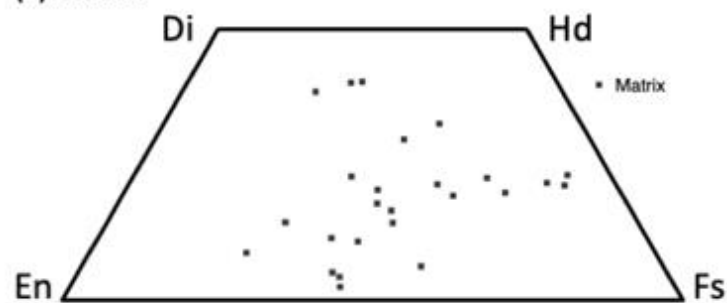


Figure 1.9. Pyroxene compositions and olivine Fo histogram of clasts and matrix material.

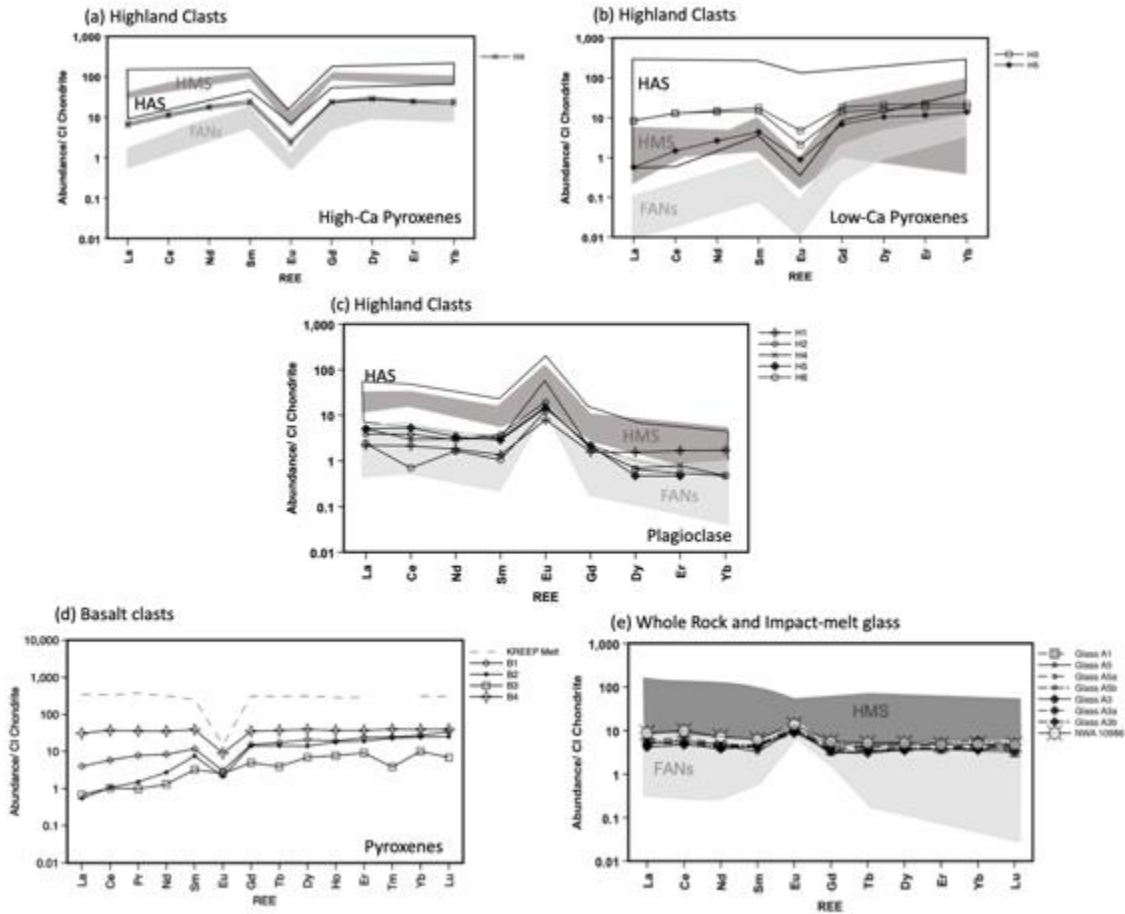


Figure 1.10. REE profiles of plagioclase, pyroxene, glass and whole rock compositions. Comparative pyroxene and plagioclase data of Apollo FAN, HMS, HAS, and KREEP lithologies are from Floss et al. (1998), Papike et al. (1996), Shervais and McGee (1998), Shervais and McGee (1999), Papike et al. (1997), Cronberger and Neal (2017).

nor in any clast within this meteorite. Basalt clast B2 is also subophitic with anorthite enclosed by pigeonite (Figure 7b). Basalt clast B3 has a subophitic texture with jagged augites surrounding anorthite grains (Figure 7c). Clast B4 is also composed of augite and anorthite but includes small grains of ilmenite (10-30 μm) and a silica phase (10-25 μm) as well (Figure 7d).

Pyroxene compositions in the basalt clasts range from augites to pigeonites (Figure 9b). Pyroxene compositions for clasts B1 range from $\text{En}_{67}\text{Fs}_{26}\text{Wo}_7$ to pyroxferroite at $\text{En}_{3}\text{Fs}_{82}\text{Wo}_{15}$. Pyroxferroite is observed as whole grains in several basalt clasts including B1 (Figure 7a, 11a). The pyroxferroite grain found in clast B1 is adjacent to the central mesostasis area (figures 7a, 11a). Clast B2 has augites ranging from $\text{En}_{59}\text{Fs}_{31}\text{Wo}_{10}$ to $\text{En}_{10}\text{Fs}_{68}\text{Wo}_{22}$, almost pyroxferroite composition (Figure 9b). Clast B3 has pyroxenes starting with pigeonite compositions at $\text{En}_{62}\text{Fs}_{31}\text{Wo}_7$ to augites at $\text{En}_{16}\text{Fs}_{56}\text{Wo}_{28}$ (Figure 9b). Clast B4 has augites only in a limited range from $\text{En}_{30}\text{Fs}_{30}\text{Wo}_{40}$ to $\text{En}_8\text{Fs}_{60}\text{Wo}_{32}$ (Figure 9b).

REE profiles of pyroxenes in the 4 basalt clasts show a flat to slightly positive slope with negative Eu anomalies. Pyroxenes in clasts B4 and B1 have the most enriched REEs in comparison to other analyzed clasts. To compare these pyroxenes to Apollo basalts, equilibrium liquids of pyroxenes from Apollo 15 KREEP basalt 15434,181 (Cronberger and Neal 2017) were calculated following the method of Yao et al (2012) and Sun and Liang (2013). Pyroxenes from the basalt clasts show less enrichment in REEs compared to KREEP pyroxene equilibrium liquids (Figure 10d).

Pyroxene Ti# ($\text{Ti}/(\text{Ti}+\text{Cr})$) can be used to estimate the whole rock TiO_2 content for basalts when bulk rock analyses are not possible (Nielsen and Drake 1978; Arai et al. 1996; Arai and Warren 1999; Anand et al. 2003a). Plotted against the Fe# ($\text{Fe}/(\text{Fe}+\text{Mg})$), Ti# indicates that these basalt clasts are representative of very low titanium (VLT) and low titanium (LT) basalts (Figure 12). Ilmenite is a very rare phase in the basaltic clasts supporting the low titanium to very low titanium interpretation.

Feldspar compositions range from An_{88-97} . Basalt clasts B3 and B4 have the most sodic anorthite at An_{88-95} and An_{87-96} , respectively. The basalt clasts generally have no olivine present with the exception of clast B1 which has a few grains ranging from Fo_{32-75} with an average of Fo_{62} .

Symplectites and Matrix Minerals

Matrix minerals are as diverse as the clast population of NWA 10986. Large grains of exsolved pyroxene (Figures 1c, 5d), feldspar, olivine, and chromite were observed in the glassy matrix and in areas of impact melt glass. Large mineral grains were selected for individual analysis to compliment the mineral analyses of the individual clasts (Figure 2, 9c).

Symplectites were found as large masses scattered throughout the meteorite (Figures 11c, d). The fine-grained nature of these symplectites made

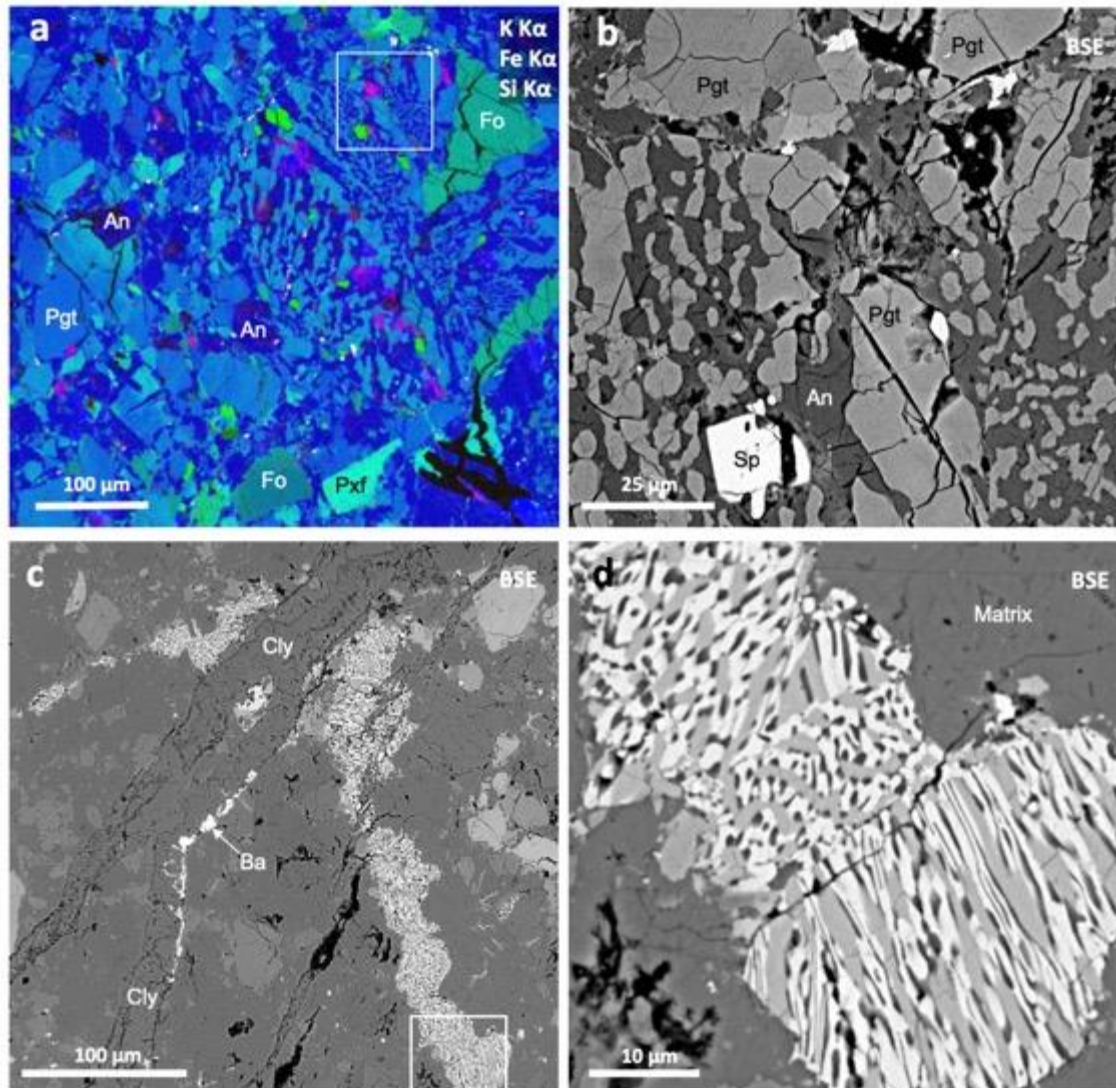


Figure 1.11. a) Elemental map of detail of mesostasis in clast B1. Red = K, Green = Fe, and blue = Si. b) Detail of area outlined in image a. c) Large masses of symplectite material. d) Detail of area outlined in image c. Abbreviations: Abbreviations: An = anorthite, Si = silica, Pgt = pigeonite, Aug = augite, Ilm = ilmenite, Pxf = pyroxferroite, Fo = fosterite, Sp = spinel, Ba = barite, Cly = clay.

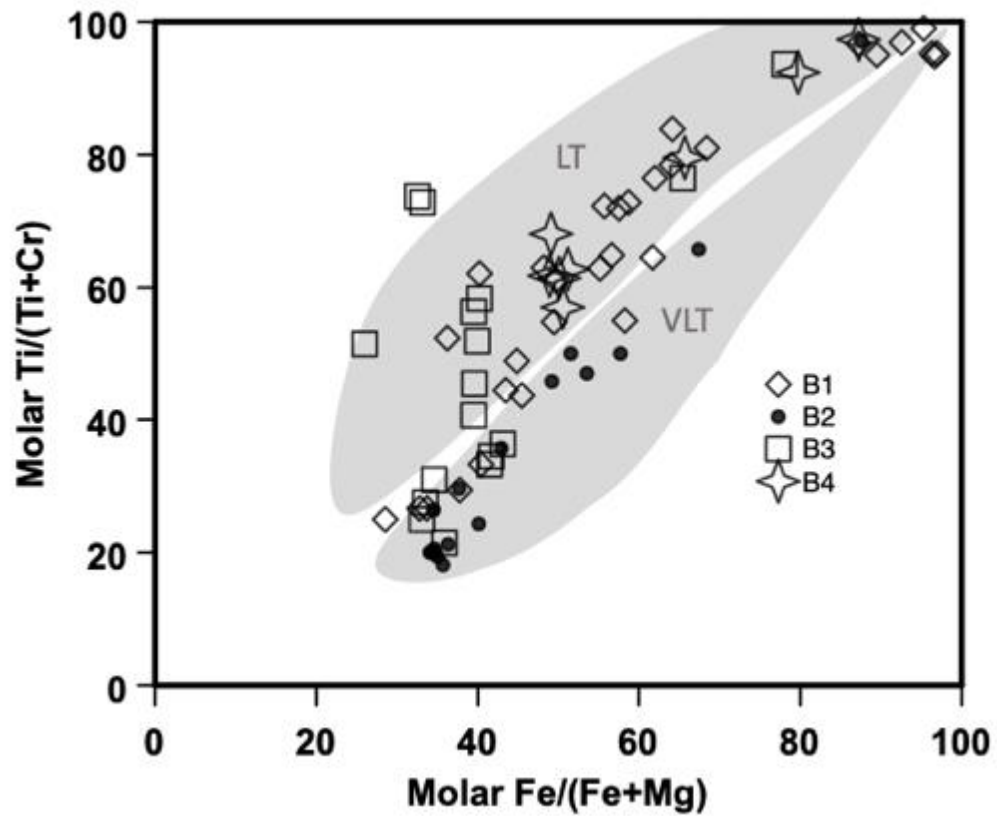


Figure 1.12. Ti # $[Ti/(Ti + Cr)]$ and Fe# $[Fe/(Fe+Cr)]$ of pyroxenes from evolved basaltic clasts. Shaded fields representing VLT and LT mare basalts are from Nielsen and Drake (1978).

EMP analysis by WDS not possible. The large isolated masses of symplectites have a composition of silica, fayalite, and ferroan augite.

Discussion

Impact melts vs pristine endogenous melts

All lunar samples have undoubtedly been affected by impacts in some way. At the very least, all lunar rocks have been displaced by impacts from the locations where they were originally formed (Lucey et al., 2006). With the evidence of impacts on the lunar surface, we continue to search for lunar rocks that we can describe as being pristine (igneous) rocks compared to impact derived melts (Warren and Wasson, 1977; Papike, 1998). Using petrographic, major and trace element, and isotopic data, a definition of pristine rocks as “rocks with primary compositions (albeit not necessarily textures) produced by lunar endogenous igneous processes” along with criteria to establish the pristine nature of lunar samples was established by Warren and Wasson (1977). These criteria are, in order of increasing weight: low concentration of siderophile elements, very low incompatible element concentrations, coarse grain sizes over 3mm, homogeneity in mineral compositions, antiquity (low $^{87}\text{Sr}/^{86}\text{Sr}$), and a “cumulate” character. With this criteria, Warren and Wasson compiled a list of 260 “possibly pristine” rocks with only 89 of those being confidently pristine (Warren and Wasson, 1977). Of those 89, less than half are over 1 gram in mass, most of them being small clasts from breccias (Lucey et al., 2006).

With the determination that only 89 rocks from the mass of 382 kg of lunar rocks returned by the Apollo missions are confidently pristine, frustration develops when trying to research the petrologic evolution of the Moon with the few pristine samples that we have. Using Apollo lunar samples as representatives of lunar geology is already restrictive since we have only collected samples from six locations, with only one collection site being truly highlands (Hiesinger and Head, 2006; Wieczorek et al., 2006). Some additional samples are provided by the Luna regolith samples, however again, only one mission (Luna 20) was to a highlands site (Wieczorek et al., 2006). Lunar meteorites have also been supplementing our lunar sample collection, but we will never know their source locations. Using only samples from one of these suites of rocks by themselves will never be able to address the stratigraphic sequence of lithologies nor relative abundances other than at a local scale (Papike, 1998). As we are limited to only three sources of lunar samples, the criteria used to designate lunar rocks as pristine is challenged as it severely limits the number of rocks available for study. This is creating the need for other criteria and methods to be developed to designate the pristine nature of lunar rocks including the use of quantitative petrography with crystal size distributions (Neal et al., 2015).

The pristine nature of clasts found within lunar meteorites is difficult to assess due to the large variety of different clast types and their varied petrogenetic and metamorphic histories (e.g., Lindstrom and Lindstrom, 1986).

Although not considered pristine by the criteria set by Warren (2012), their presence in lunar meteorites and the implications for their distribution across the lunar surface cannot be discounted. Gross et al. (2014) argued against the criteria for the pristine nature of clasts as established by Warren (2012) with the conclusion that based on these criteria, no clasts within any feldspathic meteorites would be considered pristine.

It is clear that evaluating the nature of impact-driven changes in lunar material is not straightforward, however we attempted identification within the framework laid out by Warren (2012) to distinguish between pristine and impact-derived material. The small nature of these clasts and their enclosure in a glassy matrix makes bulk rock analysis of individual clasts impossible. Raster analysis by EMP is another possibility to estimate the bulk composition of these clasts however this technique is fraught with potential errors and avoided for this reason (Joy et al., 2010).

We were able to identify clasts as either pristine or as impact derived within this meteorite. To identify clasts as pristine, we considered textural, mineralogical, and geochemical evidence. Large (0.75-1 mm) clasts with defined and distinct boundaries against the glassy matrix and large fractured mineral grains were considered to be pristine and not the product of quenched cooling as in impact melts (Figure 4). Where plagioclase and pyroxene are present as large continuous grains in these clasts, the minerals are cracked and fractured, indicative of a battered past and reinforcing the interpretation of these as pristine clasts of the lunar regolith (Figures 6, 7). Even though all clasts immediately fail the coarse grain size of 3mm set by Warren and Wasson (1977), some clasts, especially clast H5, were especially homogenous in mineral compositions satisfying the criteria of homogeneity in mineral compositions.

Basalt clasts with intact pyroxferroite grains were also considered to be pristine (Figure 7a, 11a). Pyroxferroite is a metastable mineral that requires formation at depth followed by quick eruption to preserve the phase without it decomposing into breakdown products (Lindsley and Burnham 1970). Additionally, exsolved pyroxenes are abundant throughout NWA 10986 both within clasts and as mineral fragments in the matrix. Pyroxene exsolution suggests slow cooling, which is unlikely in impact melts (Koeberal et al. 1991; Anand et al. 2003a).

Basalt Clasts-Pyroxferroite

Pyroxferroite is found as whole grains in basalt clast, B1 (Figures 7a, 11a). The initial discovery of pyroxferroite in returned Apollo 11 samples and its continued identification in returned Apollo basalts prompted experimental studies into the stability of this pyroxenoid (Chao et al. 1970; Ware and Lovering 1970; Lindsley and Burnham 1970; Lindsley et al. 1972; Grove and Lindsley 1979). Initial experimental work by Lindsley and Burnham (1970) with synthetic pyroxferroite suggested that it was only stable at pressures greater than 10 kbars and temperatures greater than 1030°C. Subsequent experimental work on

pyroxferroite by Lindsley et al. (1972) indicated that lunar basalts that contained pyroxferroite must have cooled rapidly to temperatures below 990°C in less than 3 days. Despite these early experimental constraints on the crystallization conditions of pyroxferroite, more recent work has synthesized pyroxferroite at higher pressures (1.3×10^{-6} kbars; Ried and Korekawa 1980). In addition, the phase has been identified in lunar basalts that would have been formed at lower pressures, such as in lava flows (Warren et al. 2004). The formation and preservation of pyroxferroite under these lower pressure conditions necessitates rapid nucleation and cooling (Warren et al. 2004).

Although the conditions for the formation of pyroxferroite are still in contention, the decomposition of pyroxferroite undergoing slow cooling is not. This process results in a symplectitic intergrowth of fayalite, SiO_2 , and ferroan augite, referred to as Pyroxferroite Breakdown Material (PBM) (Ware and Lovering 1970; Rubin et al. 2000). NWA 10986 contains symplectite assemblages of fayalite, SiO_2 , and ferroan augite as isolated areas within the matrix (Figure 11c, d).

An alternative method of pyroxferroite decomposition into PBM has been attributed to rapid reheating from shock (Anand et al. 2003b; Warren et al. 2004), however despite being extremely brecciated with abundant impact melt glass, there are no signs of shock metamorphism such as maskelynite detected in this meteorite. The only evidence of possible shock metamorphism is undulatory extinction observed in impact melt glass (Figures 5a, b). Therefore, it is unlikely that shock was responsible for the formation of PBM in NWA 10986. Additionally, grains of pyroxferroite are found intact near PBM masses. The juxtaposition of both whole pyroxferroite grains and PBM suggest that clasts derive from more than one source, possibly basalt flows of different thicknesses.

Basalt Clasts-Mesostasis

Basaltic clast B1 features an ophitic, fine-grained area ($300 \times 300 \mu\text{m}$) included within the center of the clast that could represent late-stage melt mesostasis products (Figures 7a, 11a, b). This area could also represent PBM however that is unlikely. The location of this area near an intact grain of pyroxferroite suggests that this area does not represent PBM since the pyroxferroite grain should have decomposed to PBM as well. When investigated using EDS and element maps, the mineralogy of this area is composed of pigeonite, anorthite, occasional spinel (chromite), and glassy areas that are mildly enriched in potassium (Figure 11a, b). Besides some potassium, there are no other elements that would indicate the extreme chemical evolution of a late-stage melt, such as phosphorous. The lack of evolved mineralogy would be supportive of a PBM interpretation, as was determined for an area of similar texture found in lunar meteorite EET 96008, however a PBM interpretation is still unlikely for the aforementioned reason (Anand et al. 2003a). Mesostasis is commonly found in lunar basalts and was also found in lunar mare basaltic meteorite Dhofar 287A (Anand et al. 2003b). The mesostasis found in Dhofar 287A was adjacent to pyroxferroite grains and

had a KREEPy composition with evolved mineralogy such as apatite (Anand et al. 2003b). Given that NWA 10986 in its entirety shows no incompatible trace element enrichment, it could still be this area does represent mesostasis, although with no late-stage KREEP mineralogy. If the lava from which this basalt crystallized did contain KREEP elements it is likely they would be observed in this area of highly evolved late-stage melt. This KREEP-free basaltic clast could represent the existence of basalt on the Moon that is independent of KREEP in its petrogenetic history.

Comparison to Apollo lithologies

The An# and Mg# of the clasts and matrix materials from NWA 10986 can be used to identify lithology types similar to those observed in the Apollo sample suite (Figure 2). Matrix materials were included although without accompanying An#. Inclusion of these minerals expands the diversity of lithologic types not represented by the clasts, but found in this meteorite. The diversity observed in the mineral fragments indicates the existence of lunar lithologies that have not been sampled previously (Yamaguchi et al. 2010; Mercer et al. 2013). Troctolitic clasts H1 and H2 are similar to the Mg-suite (Figure 2). Gabbronorite clast H4 and troctolitic anorthosite clast H6 are most similar to FAN suite rocks. However, gabbonorite clast H3 and anorthositic norite clast H5 plot in the “gap” between FAN and Mg-suite lithologies. Several clasts, including H1 and H2, could belong to this compositional gap.

The lithologies represented by these gap compositions may be prominent components of the lunar crust as they are increasingly well represented in lunar meteorites (Figure 2; Yamaguchi et al. 2010; Cahill et al. 2004; Nyquist et al. 2006; Takeda et al. 2006; Gross et al. 2014; Mercer et al. 2013). Cahill et al. (2004) classified gap lithologies as “mixed impactites,” i.e., a mixture of FAN and Mg-suite components. This implies that gap lithologies are mixtures of FAN and Mg-suite lithologies that were metamorphosed by impact melting, however clasts within NWA 10986 that plot within this gap do not show signs of recrystallization and are interpreted as pristine. Takeda et al (2006) proposed a new rock type, magnesian anorthosite, to represent gap lithologies that do not indicate recrystallization with the suggestion that this lithology was dominate on the far side of the Moon. Additionally, lithologies that fall within this compositional gap, such as granulites, were found in Apollo samples from highland sites (Apollo 15, 16, and 17). Granulites were determined to be ancient metamorphic rocks consisting of parent materials free of KREEP signatures (Lindstrom and Lindstrom 1986). Granulites have been observed in lunar meteorites as well (Treiman et al. 2010; Cahill et al. 2004) however the clasts in NWA 10986 that plot in this compositional gap do not have granulite textures. Regardless of formation mechanism of gap lithologies, if lunar meteorites do provide a random sampling of the lunar surface, then our conceptions as to the distribution of Apollo suite lithologies outside the PKT may be misleading (Gross et al. 2014).

Implications for source location and lunar evolution

Compositions of the impact glass areas in NWA 10986 can provide insight into the source location of this meteorite. When compared to the whole rock compositions for average feldspathic lunar meteorites, Apollo mare basalts, and Apollo mafic impact melt breccias, the compositions of the NWA 10986 impact glass areas are similar to feldspathic lunar meteorites, although the FeO trends toward average Apollo mare basalt composition (Figure 8a). The heterogeneity of the impact melt glass areas reflect the composition of the area impacted during the formation of this meteorite. The areas sampled were not composed entirely of highland materials, but also had a mafic basalt component as well, with some areas more mafic than others. The predominantly anorthositic composition of this meteorite, with an added mafic component, indicates that this meteorite was sourced at a location where lunar highlands coexist with basalts.

Impact glass and whole rock compositions also have very low values of Sm (Figure 8b). Incompatible trace elements and Apollo KREEP signatures are absent in the impact glass and in every part of NWA 10986 including Mg-suite and basalt lithologies. Since basalt clast B1 has features of chemically evolved late stage melt such as pyroxferroite and mesostasis then this clast should also be the most chemically enriched and contain increased incompatible trace element signatures however this is not the case. Clast B1 has no signs of enrichment in incompatible trace elements in pyroxenes and does not contain KREEP indicative mineralogy such as apatite. The absence of KREEP indicators in this and other lunar meteorites (e.g., Kalahari 009: Terado et al., 2007; Dhofar 489: Takeda et al. 2006; Yamato-86032: Nyquist et al. 2006; Yamaguchi et al. 2010; Yamato-793169, Asuka-881757, MIL 05035, and MET 01210: Arai et al. 2010; Joy et al. 2008; Liu et al. 2009), suggests that these meteorites are not only sampling an area of the lunar surface outside of the PKT, but also that KREEP may not be a global occurrence.

NWA 10986 provides us with a sampling of the lunar crust away from the PKT. Compared to Apollo sample suite lithologies, this meteorite contains samples of FANs, Mg-suite, magnesian anorthosites, and basalts. The magnesian anorthosites appearing in NWA 10986, as well as other lunar meteorites, implies this may be the dominate surface lithology outside of the PKT rather than FANs (Arai et al. 2008; Yamaguchi et al. 2010; Cahill et al. 2004; Nyquist et al. 2006; Takeda et al. 2006; Gross et al. 2014; Mercer et al. 2013; Gross et al. 2014). This meteorite was sourced at a location where highlands and basalt were both available for mixing outside of the PKT. With the basalts in NWA 10986 identified as VLT and LT with no enrichment in incompatible trace elements, these basalts could potentially represent cryptomare (Arai et al. 1996; Terada et al. 2007; Arai et al. 2010; Joy et al. 2010).

Summary

NWA 10986 contains primitive and evolved clasts representing FAN, Mg-suite, magnesian anorthosites, and basalts. The anorthositic-rich nature of NWA 10986 indicates that it was sourced from the highlands, however the presence of basaltic clasts suggests it was sourced from a location where highlands and basalts coexist. Mineralogically and geochemically, no enriched incompatible trace element nor KREEP signatures were found in any component of NWA 10986, including basalts and Mg-suite clasts, despite evidence for late-stage crystallization, including pyroxferroite and mesostasis. Intact pyroxferroite and associated symplectite assemblages document a mixed eruptive and cooling histories for the basalts sampled by this meteorite. NWA 10986 was likely sourced from unsampled terrains located outside of the PKT and offers a unique cross-sectional view of the Moon (Figure 13).

The presence of gap lithologies (e.g., magnesian anorthosite) and the lack of KREEP signatures in NWA 10986, as well as other lunar meteorites, suggests a reevaluation of lunar evolution theories may be required. The global distribution of a FAN crust is often presented as evidence for the LMO, however the dominant crustal lithology outside of the PKT, as suggested by lunar meteorites, may be magnesian anorthosite (Arai et al. 2008; Gross et al. 2014). The lack of KREEP signatures in NWA 10986 Mg-suite, basalt, and magnesian anorthosite clasts indicates a global KREEP layer, another tenet of LMO theory, is also questionable. Considering that the LMO model was built on returned samples from the Apollo missions, all located within the PKT, suggest this terrane may play an outsized role in the current understanding of lunar evolution. Lunar meteorites expand the geologic record outside of the PKT. Lunar sample return missions from known locations outside of the PKT are needed to provide further input into the origin and evolution of the Moon.

Acknowledgements

We would like to thank Allen Patchen for his assistance with EMP analysis, Chris Wetteland for his help with SEM analysis, and Dawn Taylor. We would like to acknowledge support from NASA grant NNX15AL98G and Vanderbilt University grant 3800-019687 for University of Tennessee Space Outreach: Activities in Eastern Tennessee, both awarded to L.A.T. We would also like to thank Minako Righter, Yongjun Gao, and Tom Lapen at the University of Houston for their assistance with LA-ICP-MS.

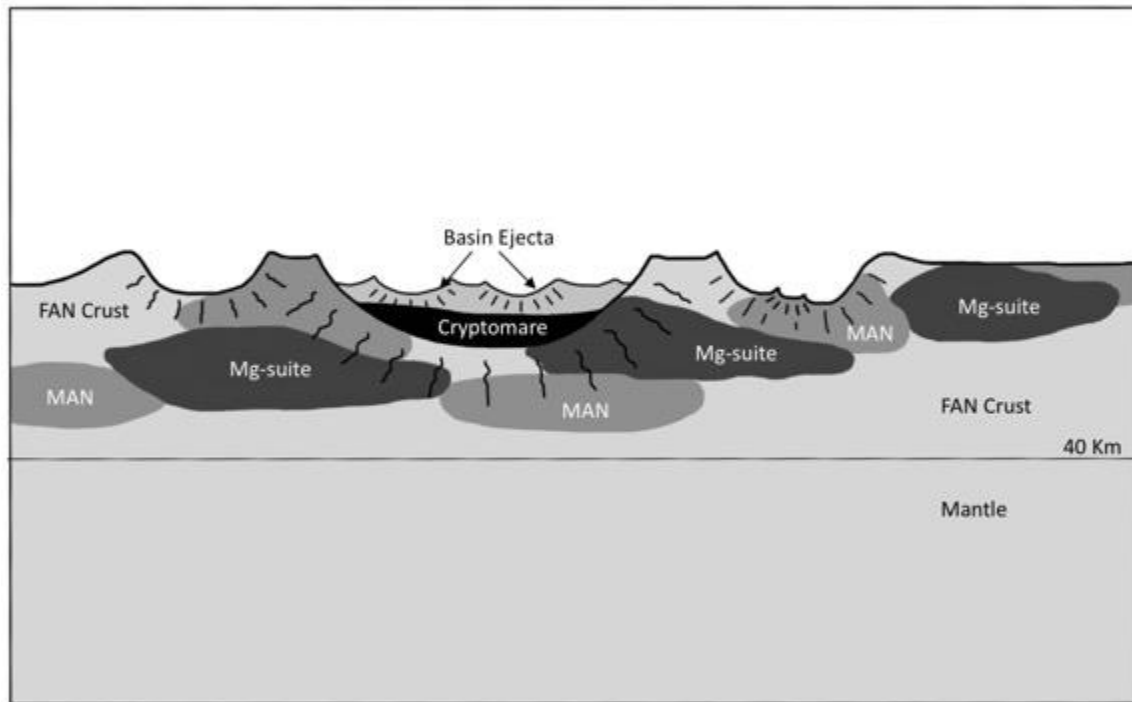


Figure 1.13. Representative cross section of the lunar crust and the source location of NWA 10986. Cryptomare depiction is after Antonenko et al. (1995) and crust depth data are from Wieczorek et al. (2013).

References

- Anand M., Taylor L. A., Neal C. R., Snyder G. A., Patchen A., Sano Y., and Terado K. 2003a. Petrogenesis of lunar meteorite EET 96008. *Geochimica et Cosmochimica Acta* 67:3499-3518.
- Anand M., Taylor L. A., Misra K. C., Demidova S. I., and Nazarov M. A. 2003b. KREEPy lunar meteorite Dhofar 287A: A new lunar mare basalt. *Meteoritics & Planetary Science* 38:485-499.
- Antonenko I., Head J. W., Mustard J. F., and Hawke B. R. 1995. Criteria for the detection of lunar cryptomaria. *Earth, Moon and Planets* 69:141-172.
- Arai T., Takeda H., and Warren P. H. 1996. Four lunar mare meteorites: Crystallization trends of pyroxenes and spinels. *Meteoritics & Planetary Science* 31:877-892.
- Arai T., Takeda H., Yamaguchi A., and Ohtake M. 2008. A new model of lunar crust: asymmetry in crustal composition and evolution. *Earth Planets Space* 60:433-444.
- Arai T., and Warren P. H. 1999. Lunar meteorite Queen Alexandra Range 94281: Glas compositions and other evidence for launch pairing with Yamato 793274. *Meteoritics & Planetary Science* 34:209-234.
- Arai T., Hawke B. R., Giguere T. A., Misawa K., Miyamoto M., and Kojima H. 2010. Antarctic lunar meteorites Yamato-793169, Asuka-881757, MIL 05035, and MET 01210 (YAMM): Launch pairing and possible cryptomare origin. *Geochimica et Cosmochimica Acta* 74:2231-2248.
- Bogard D. D. 1983. A meteorite from the Moon. *Geophysical Research Letters* 10:773.
- Bouvier A., Gattacceca J., Grossman J., and Metzler, K. 2017. The Meteoritical Bulletin, No. 105. 2017 September. *Meteoritics and Planetary Science* 52:1-250.
- Cahill J. T., Floss C., Anand M., Taylor L. A., Nazarov M. A., and Cohen B. A. 2004. Petrogenesis of lunar highlands meteorites: Dhofar 025, Dhofar 081, Dar al Gani 262, and Dar al Gani 400. *Meteoritics & Planetary Science* 39:503-529.
- Chao E. C. T., Minkin J. A., Frondel C., Klein Jr C., Drake J. C., Fuchs L., Tani B., Smith J. V., Anderson A. T., Moore P. B., Zechman Jr G. R., Traill R. J., Plant A. G., Douglas J. A. V., and Dence M. R. 1970. Pyroxferroite, a new calcium-

bearing iron silicate from Tranquility Base. Proceedings, Apollo 11 Lunar Science Conference 1:65-79.

Cronberger K., and Neal C. R. 2017. KREEP basalt petrogenesis: Insights from 15434,181. *Meteoritics & Planetary Science* 52: 827-841

Day J. M. D, Taylor L. A., Floss C., Patchen A. D., Schnare D. W., Pearson D. G. 2006. Comparative petrology, geochemistry, and petrogenesis of evolved, low-Ti lunar mare basalt meteorites from the LaPaz Icefield, Antarctica. *Geochimica et Cosmochimica Acta* 70:1581-1600.

Floss C., James O. B., McGee J. J., and Crozaz G. 1998. Lunar ferroan anorthosite petrogenesis: Clues from trace element distributions in FAN subgroups. *Geochimica et Cosmochimica Acta* 62:1255-1283.

Gallant J., Gladman B., and Cuk M. 2009. Current bombardment of the Earth-Moon system: Emphasis on cratering asymmetries. *Icarus* 202: 371-382.

Gross J., Treiman A. H., and Mercer C. N. 2014. Lunar feldspathic meteorites: Constraints on the geology of the lunar highlands, and the origin of the lunar crust. *Earth and Planetary Science Letters* 388: 318-328.

Grove T. L., and Lindsley D. H. 1979. An experimental study on the crystallization of pyroxferroite. Proceedings, 10th Lunar and Planetary Science Conference 470-472.

Hiesinger H., and Head III J. W. 2006. New views of lunar geoscience. In *New views of the Moon*, edited by Joliff B. L., Wieczorek M. A., Shearer C. K. and Neal C. R. Reviews in mineralogy and geochemistry, 60. Chantilly, VA: Mineralogical Society of America. pp. 1-81.

James O. B., Lindstrom M. M., and Flohr M. F. 1987. Petrology and Geochemistry of Alkali Gabbroanorites from Lunar Breccia 67975. Proceedings, 17th Lunar and Planetary Science Conference 92:E314-E330.

Joliff B. L., Gillis J. J., Haskin L. A., Korotev R. L., and Wieczorek M. A. 2000. Major lunar crustal terranes: Surface expressions and crust-mantle origins. *Journal of Geophysical Research* 105:4197-4216.

Joy K. H., Crawford I. A., Anand M., Greenwood R. C., Franchi I. A., and Russell S. S. 2008. The petrology and geochemistry of Miller Range 05035: A new lunar gabbroic meteorite. *Geochimica et Cosmochimica Acta* 72:3822-3844.

Joy K. H., Crawford I. A., Russell S. S., and Kearsley A. T. 2010. Lunar meteorite regolith breccias: An in situ study of impact melt composition using LA-ICP-MS with implications for the composition of the lunar crust. *Meteoritics & Planetary Science* 45:917-946.

Joy K. H., Burgess R., Hinton R., Fernandes V. A., Crawford I. A., Kearsley A. T., and Irving A. J. 2011. Petrogenesis and chronology of lunar meteorite Northwest Africa 4472: a KREEPy regolith breccia from the Moon. *Geochimica et Cosmochimica Acta* 75:2420-2452.

Koeberl C., Kurat G., and Brandstätter F. 1991. Lunar meteorite Yamato-793274: Mixture of mare and highland components, and barringerite from the Moon. Proceedings, NIPR Symposim Antarctic Meteorites

Korotev R. L. 2005. Lunar geochemistry as told by lunar meteorites. *Chemie der Erde-Geochemistry* 65:297-346.

Lawrence D. J., Feldman W. C., Barraclough B. L., Binder A. B., Elphie R. C., Maurice S., Miller M. C., and Prettyman T. H. 1999. High resolution measurements of absolute thorium abundances on the lunar surface. *Geophysical Research Letters* 26:2681-2684.

Lindsley D. H., and Burnham C. W. 1970. Pyroxferroite: Stability and X-ray crystallography of synthetic $\text{Ca}_{0.15}\text{Fe}_{0.85}\text{SiO}_3$ pyroxenoid. *Science* 168:364-367.

Lindsley D. H., Papike J. J., and Bence A. E. 1972. Pyroxferroite: Breakdown at low pressure and high temperature. Proceedings, Lunar and Planetary Science Conference 3:483-485

Lindstrom M. M., and Lindstrom D. J. 1986. Lunar granulites and their precursor anorthositic norites of the early lunar crust. Proceedings, 16th Lunar and Planetary Science Conference 91:D263-D276.

Liu Y., Floss C., Day J. M. D., Hill E., and Taylor L. A. 2009. Petrogenesis of lunar mare basalt meteorite Miller Range 05035. *Meteoritics & Planetary Science* 44:261-284.

Lucey P., Korotev R. L., Gillis J. J., Taylor L. A., Lawrence D., Campbell B. A., Elphic R., Feldman B., Hood L. L., Hunten D., Mendillo M., Noble S., Papike J. J., Reedy R. C., Lawson S., Prettyman T., Gasnault O., and Maurice S. 2006. Understanding the lunar surface and space-Moon interactions. In *New views of the Moon*, edited by Joliff B. L., Wieczorek M. A., Shearer C. K. and Neal C. R. Reviews in mineralogy and geochemistry, 60. Chantilly, VA: Mineralogical Society of America. pp. 83-219.

- McCallum I. S. 2001. A new view of the Moon in light of data from Clementine and Prospector missions. *Earth Moon and Planets*. 85-86:253-269.
- Mercer C. N., Treiman A. H., and Joy K. H. 2013. New lunar meteorite Northwest Africa 2996: A window into farside lithologies and petrogenesis. *Meteoritics & Planetary Science* 48: 289-315.
- Neal C. R., Donohue P., Fagan A. L., O'Sullivan K., Oshrin J., and Roberts S. 2015. Distinguishing between basalts produced by endogenic volcanism and impact processes: A non-destructive method using quantitative petrography of lunar basaltic samples. *Geochimica et Cosmochimica Acta* 148: 62-80.
- Nielsen R. L., and Drake M. J. 1978. The case for at least three mare basalt magmas at the Luna 24 landing site. *Proceedings, Mare Crisium: The View from Luna 24* pp. 419-428
- Nyquist L., Bogard D., Yamaguchi A., Shih C. -Y., Karouji Y., Ebihara M., Reese Y., Garrison D., McKay G., and Takeda H. 2006. Feldspathic clasts in Yamato-86032: Remnants of the lunar crust with implications for its formation and impact history. *Geochimica et Cosmochimica Acta* 70:5990-6015.
- Papike J. J., Fowler G. W., Shearer C. K., and Layne G. D. 1996. Ion microprobe investigation of plagioclase and orthopyroxene from lunar Mg-suite norites: Implications for calculating parental melt REE concentrations and for assessing postcrystallization REE redistribution. *Geochimica et Cosmochimica Acta* 60:3967-3978.
- Papike J. J., Fowler G. W., and Shearer C. K. 1997. Evolution of the lunar crust: SIMS study of plagioclase from ferroan anorthosites. *Geochimica et Cosmochimica Acta* 61:2343-2350.
- Papike J. J., Ryder G., and Shearer C. K. 1998. Lunar Samples. In *Planetary Materials*, edited by Papike J. J. Reviews in mineralogy, 36. Chantilly, VA: Mineralogical Society of America. pp. 5-001-5-234.
- Papike J. J., Karner J. M., and Shearer C. K. 2003. Determination of planetary basalt parentage: A simple technique using the electron microprobe. *American Mineralogist* 88:469-472.
- Ried H., and Korekawa M. 1980. Transmission electron microscopy of synthetic and natural fünferketten and siebernerketten pyroxenoids. *Physics and Chemistry of Minerals* 5:352-365.

Rubin A. E., Warren P. H., Greenwood J. P., Verish R. S., Leshin L. A., Hervig R. L., Clayton R. N., and Mayeda T. K. 2000. Petrology of Los Angeles: A new basaltic shergottite find. *Geology* 28:1011-1014.

Shervais J. W., and McGee J. J. 1998. Ion and electron microprobe study of troctolites, norite, and anorthosites from Apollo 14: evidence for urKREEP assimilation during petrogenesis of Apollo 14 Mg-suite rocks. *Geochimica et Cosmochimica Acta* 62:3009-3023.

Shervais J. W., and McGee J. J. 1999. KREEP cumulates in the western lunar highlands: Ion and electron microprobe study of alkali-suite anorthosites and norites from Apollo 12 and 14. *American Mineralogist* 84:806-820.

Shirley D. N., and Wasson J. T. 1981. Mechanism for the extrusion of KREEP. Proceedings, 12th Lunar and Planetary Science Conference. pp. 965-978.

Smith J. V., Anderson A. T., Newton R. C., Olsen E. J., and Wyllie P. J. 1970. Petrologic history of the Moon inferred from petrography, mineralogy, and petrogenesis of Apollo 11 rocks. Proceedings, 11th Lunar Science Conference. pp. 897-925.

Snyder G. A., and Taylor L. A. 1996. Apollo 14 high-Al basalts may not represent earliest volcanism on the Moon: the enigma of disturbed Sm-Nd and undisturbed Rb-Sr isotopic systems. Proceedings, 27th Lunar and Planetary Science Conference. pp. 1233-1234.

Spudis P. D. 2000. Petrologic mapping of the Moon from Clementine and Lunar Prospector data: Incorporation of new thorium data (abstract #1414). 31st Lunar and Planetary Science Conference.

Sun C. and Liang Y. 2013. Distribution of REE and HFSE between low-Ca pyroxene and lunar picritic melts around multiple-saturation points. *Geochimica et Cosmochimica Acta* 119:340-358.

Takeda H., Yamaguchi A., Bogard D. D., Karouji Y., Ebihara M., Ohtake M., Saiki K., and Arai T. 2006. Magnesian anorthosites and a deep crustal rock from the farside crust of the Moon. *Earth and Planetary Science Letters* 247:171-184.

Terada K., Anand M., Sokol A. K., Bischoff A., and Sano Y. 2007. Cryptomare magmatism 4.35 Gyr ago recorded in lunar meteorite Kalahari 009. *Nature* 450:849-852.

Taylor S. R., and Jakes P. 1974,. The geochemical evolution of the Moon. Proceedings of the 5th Lunar Science Conference. pp. 1287-1305.

- Treiman A. H., Maloy A. K., Shearer C. K., and Gross J. 2010. Magnesian anorthositic granulites in lunar meteorites Allan Hills A81005 and Dhofar 309: Geochemistry and global significance. *Meteoritics & Planetary Science* 45:163-180.
- Ware N. G. and Lovering J. F. 1970. Electron-microprobe analyses of phases in lunar samples. *Science* 167:517-520.
- Warren P. H. 1985. The magma ocean concept and lunar evolution. *Annual Review of Earth and Planetary Science* 13:201-240.
- Warren P. H., and Wasson J. T. 1977. Pristine nonmare rocks and the nature of the lunar crust. Proceedings, 18th Lunar Science Conference, pp. 2215-2235.
- Warren P. H., Greenwood J. P., and Rubin A. E. 2004. Los Angeles: A tale of two stones. *Meteoritics and Planetary Science* 39:137-156.
- Warren P. H. 2012. Let's get real: Not every lunar rock sample is big enough to be representative for every purpose (abstract #9034). Second Conference on the Lunar Highlands Crust.
- Wieczorek M. A., Jolliff B. A., Khan A., Pritchard M. E., Weiss B. P., Williams J. G., Hood L. L., Richter K., Neal C. R., Shearer C. K., McCallum I. S., Tompkins S., Hawke B. R., Peterson C., Gillis J. J., and Bussey B. 2006. The Constitution and structure of the lunar interior. In *New views of the Moon*, edited by Jolliff B. L., Wieczorek M. A., Shearer C. K., and Neal C. R. *Reviews in mineralogy and geochemistry*, vol. 60. Chantilly, VA: Mineralogical Society of America. pp. 221-364.
- Wieczorek M. A., Neumann G. A., Nimmo F., Kiefer W. S., Taylor G. J., Melosh H. J., Phillips R. J., Solomon S. C., Andrews-Hanna J. C., Asmar S. W., Konopliv A. S., Lemoine F. G., Smith D. E., Watkins M. M., Williams J. G., and Zuber M. T. 2013. The crust of the Moon as seen by GRAIL. *Science* 339:671-674.
- Wood J. A., Dickey Jr, J. S., Marvin, U. B., and Powell, B. N. 1970. Lunar anorthosites and a geophysical model of the Moon. Proceedings, 11th Lunar Science Conference. pp. 965-988.
- Yamaguchi A., Karouji Y., Takeda H., Nyquist L., Bogard D., Ebihara M., Shih C.-Y., Reese Y., Garrison D., Park J., and McKay G. 2010. The variety of lithologies in the Yamato-86032 lunar meteorite: Implications for formation processes of the lunar crust. *Geochimica et Cosmochimica Acta* 74:4507-4530.

Yao L., Sun C., and Liang Y. 2012. A parameterized model for REE distribution between low-Ca pyroxene and basaltic melts with applications to REE partitioning in low-Ca pyroxene along a mantle adiabat and during pyroxenite-derived melt and peridotite interaction. *Contributions to Mineralogy and Petrology* 164:261-280.

Appendix

Whole Rock
wt. %

Point#	MoO3	P2O5	SiO2	SO2	TiO2
FB_1_B	0.0212	0.0672	44.527	0.1588	0.263
FB_1_B	0.0333	0.074	44.4802	0.122	0.2213
FB_1_B	0.0624	0.0345	44.7863	0.1205	0.3069
FB_2_A	0.1763	0.071	45.1935	0.1318	0.2996
FB_2_A	0.0394	0.0124	45.1451	0.1915	0.2535
FB_2_A	0.1067	0.0649	44.726	0.0933	0.2713
FB_2_B	0.0255	0.0159	43.4894	0.0129	0.1261
FB_2_B	0.0735	0.0361	44.9784	0.1433	0.3012
FB_2_B	0.0921	0.0437	44.3144	0.0707	0.1764
FB_3_A	0	0.0643	44.5768	0.0869	0.2806
FB_3_A	0.077	0.0401	44.8328	0.0402	0.2412
FB_3_A	0.0255	0.0484	44.5535	0.0805	0.2104
FB_3_B	0.0349	0.0394	44.8106	0.1007	0.2779
FB_3_B	0	0.0348	44.6828	0.0752	0.2646
FB_4_A	0.0903	0.0761	45.0708	0.1431	0.3182
FB_4_A	0.0176	0.0375	44.5689	0.1398	0.2584
FB_4_A	0.1067	0.0417	45.3511	0.1335	0.2924
FB_4_B	0.1918	0.018	45.2803	0.1176	0.2759
FB_4_B	0.2168	0.0428	45.4504	0.1337	0.2791
FB_4_B	0.0438	0.031	45.0271	0.1726	0.2615
FB_5_A	0.0752	0.0237	44.8042	0.1094	0.2726
FB_5_B	0.1057	0.0485	44.7074	0.1063	0.3035
FB_5_B	0.0613	0.0459	44.6962	0.1546	0.2793
FB_5_B	0	0.0274	45.0338	0.1128	0.2971
FB_6_A	0.0036	0.066	45.0673	0.1419	0.2981
FB_6_A	0	0.0129	45.1275	0.1225	0.3519
FB_6_A	0	0.0356	44.7906	0.1224	0.6098
FB_6_B	0	0	44.9168	0.0822	0.2411
FB_6_B	0	0.0314	45.1035	0.1383	0.2979

Whole Rock
wt. %

Point#	Al ₂ O ₃	Cr ₂ O ₃	MgO	CaO	MnO
FB_1_B	26.8008	0.1398	5.9998	14.4093	0.1329
FB_1_B	27.2497	0.1283	5.849	14.3649	0.107
FB_1_B	26.7075	0.1247	6.0704	13.7892	0.1099
FB_2_A	26.3189	0.1544	5.8521	14.476	0.1007
FB_2_A	26.5918	0.1499	6.0528	14.0124	0.1325
FB_2_A	26.4837	0.1289	6.0787	14.1019	0.1256
FB_2_B	30.5431	0.0771	3.4469	16.5956	0.0765
FB_2_B	26.354	0.1676	6.0194	14.4957	0.1006
FB_2_B	29.5672	0.0529	3.1545	16.5882	0.046
FB_3_A	26.0305	0.1309	6.4138	14.8446	0.0915
FB_3_A	26.8866	0.1122	5.2912	16.0055	0.0902
FB_3_A	27.6582	0.1193	5.3383	15.3691	0.101
FB_3_B	25.7599	0.1455	6.2343	14.4	0.0862
FB_3_B	25.6128	0.1418	6.501	14.0407	0.1023
FB_4_A	26.2158	0.1449	6.1658	14.097	0.127
FB_4_A	26.6181	0.1375	5.7837	14.5993	0.0852
FB_4_A	26.6759	0.1601	5.88	14.1783	0.1231
FB_4_B	25.843	0.1575	6.2567	13.9515	0.1283
FB_4_B	25.7074	0.1338	6.3484	13.7777	0.1268
FB_4_B	26.901	0.1489	5.8073	13.8586	0.1154
FB_5_A	26.2212	0.1531	5.7873	14.4262	0.0899
FB_5_B	26.1687	0.1395	6.0073	14.2151	0.1139
FB_5_B	26.2227	0.1448	5.9153	14.2735	0.1233
FB_5_B	26.2966	0.1533	5.9539	14.0795	0.1038
FB_6_A	26.5005	0.1445	5.7636	14.4459	0.1122
FB_6_A	25.656	0.143	6.2485	14.1888	0.1317
FB_6_A	25.5446	0.1451	6.1553	14.0336	0.1334
FB_6_B	26.775	0.1066	5.574	14.5541	0.0945
FB_6_B	25.2448	0.1358	6.1046	14.8078	0.1131

Whole Rock
wt.%

Point#	FeO	NiO	Na2O	K2O	Total
FB_1_B	6.1194	0.0051	0.3297	0.153	99.1269
FB_1_B	5.915	0.0153	0.3149	0.1553	99.0302
FB_1_B	5.9962	0.0212	0.3461	0.19	98.6657
FB_2_A	6.1229	0.0063	0.3591	0.1785	99.4411
FB_2_A	6.2642	0.0106	0.2804	0.1858	99.3224
FB_2_A	6.2123	0.0039	0.3022	0.1709	98.8704
FB_2_B	4.4129	0	0.3224	0.0457	99.1899
FB_2_B	5.9401	0.0126	0.3313	0.1683	99.1221
FB_2_B	4.499	0.0083	0.3694	0.0767	99.0596
FB_3_A	6.3037	0	0.3039	0.1352	99.2626
FB_3_A	5.3561	0	0.3709	0.0651	99.4089
FB_3_A	5.3805	0.0028	0.3378	0.123	99.3481
FB_3_B	6.0564	0	0.3009	0.1458	98.3925
FB_3_B	6.356	0	0.3192	0.1556	98.2868
FB_4_A	6.0848	0	0.29	0.1926	99.0165
FB_4_A	5.7992	0.037	0.3281	0.1409	98.5512
FB_4_A	6.0684	0.0118	0.3095	0.1964	99.5288
FB_4_B	6.4998	0.0055	0.2808	0.1786	99.1854
FB_4_B	6.7222	0.017	0.2956	0.1726	99.4243
FB_4_B	6.0009	0.0036	0.3127	0.2053	98.8896
FB_5_A	5.9855	0.0181	0.3058	0.1498	98.422
FB_5_B	6.0648	0	0.3299	0.1839	98.4946
FB_5_B	6.1382	0.0114	0.3053	0.1768	98.5488
FB_5_B	6.0965	0.0288	0.327	0.1715	98.6819
FB_6_A	6.0879	0	0.3279	0.1665	99.126
FB_6_A	6.545	0.0055	0.322	0.168	99.0234
FB_6_A	6.8035	0	0.3439	0.1574	98.8751
FB_6_B	5.8274	0.0233	0.3146	0.1862	98.6959
FB_6_B	6.4343	0.017	0.3338	0.1421	98.9044

Whole Rock
ppm

Ca43	FB1-A	FB1-B	FB1-C	FB2-A	FB2-B
Sc45	101400.37	101400.37	101400.37	107526.05	107526.05
Ti49	15.33	15.63	15.66	16.32	15.97
V51	1685.19	1688.73	1732.4	1807.63	1783.32
Cr52	7.21	5	4.43	7.64	1.248
Mn55	975.42	998.8	1008.38	1079.59	1034.73
Co59	953.08	952.63	983	1039.97	975.32
Ni61	16.53	15.81	15.84	20.39	19.81
Cu65	46.7	46.35	51.64	74.5	67.25
Zn66	5.54	7.82	7.94	6.87	6.2
Ga69	4.55	5.35	5.17	5.74	5.86
Rb85	96.73	97.11	97.43	104.82	97.89
Sr88	1.58	1.56	1.62	1.643	1.561
Y89	234.76	236.98	243.29	250.57	241.69
Zr91	7.81	8.11	8.11	8.15	7.94
Nb93	23.32	23.59	23.75	24.96	27.84
Ba137	1.78	1.85	1.81	1.865	1.837
La139	3755.16	3866.26	3996.12	3822.35	3710
Ce140	2.28	2.2	2.27	2.5	2.35
Pr141	6.67	6.44	6.76	7.11	6.8
Nd146	0.783	0.775	0.785	0.848	0.827
Sm147	3.43	3.43	3.54	3.61	3.66
Eu151	0.933	0.975	1.005	1.041	1.006
Gd157	0.789	0.765	0.767	0.852	0.817
Tb159	1.185	1.152	1.213	1.24	1.201
Dy163	0.1958	0.2016	0.2003	0.2071	0.1998
Ho165	1.322	1.372	1.339	1.393	1.371
Er166	0.28	0.285	0.279	0.29	0.291
Tm169	0.779	0.829	0.8	0.827	0.834
Yb172	0.1239	0.1243	0.1237	0.1303	0.1248
Lu175	0.811	0.854	0.851	0.886	0.868
Hf178	0.122	0.1246	0.1224	0.1275	0.1235
Pb208	0.635	0.653	0.665	0.697	0.74
Th232	0.199	0.26	0.239	0.608	0.314
U238	0.382	0.45	0.404	0.412	0.4

Whole Rock
ppm

Ca43	FB2-C	FB3-A	FB3-B	FB3-C	FB4-A
Sc45	107526.05	106719.01	106719.02	106719.02	100608.47
Ti49	15.29	15.01	11.66	15.63	13.01
V51	1716.3	1646.12	1263.27	1915.08	1367.1
Cr52	3.81	3.58	0.938	5.14	5.47
Mn55	1080.85	979.31	758.8	992.86	865.77
Co59	942.6	897.55	668.05	960.05	717.69
Ni61	18.33	17.36	18.09	18.41	14.71
Cu65	59.71	52.55	60.75	57.16	54.17
Zn66	7.03	4.99	4.17	5.11	7.27
Ga69	7.41	6	5.61	5.63	8.85
Rb85	99.67	113.25	28.03	85.72	94.81
Sr88	1.482	1.36	0.499	1.521	0.967
Y89	240.56	236.33	165.32	236.66	221.44
Zr91	7.67	7.77	4.93	7.82	6.41
Nb93	27.24	21.04	11.55	22.96	16.47
Ba137	1.674	1.681	0.933	1.925	1.297
La139	3543.44	4144.9	972.93	3238.61	3559.04
Ce140	2.3	2.25	1.293	2.29	1.744
Pr141	6.58	6.48	3.58	6.56	4.74
Nd146	0.806	0.794	0.474	0.793	0.625
Sm147	3.5	3.55	2.174	3.48	2.71
Eu151	0.979	1.006	0.658	0.979	0.759
Gd157	0.824	0.795	0.735	0.829	0.774
Tb159	1.157	1.192	0.765	1.151	0.902
Dy163	0.1943	0.196	0.1326	0.1988	0.1551
Ho165	1.296	1.347	0.879	1.351	1.088
Er166	0.28	0.285	0.1883	0.282	0.2274
Tm169	0.811	0.818	0.533	0.819	0.659
Yb172	0.1215	0.127	0.085	0.1285	0.1016
Lu175	0.847	0.835	0.586	0.869	0.71
Hf178	0.124	0.1203	0.0801	0.1302	0.0974
Pb208	0.941	0.645	0.341	0.633	0.475
Th232	0.451	0.324	0.294	0.458	0.466
U238	0.369	0.385	0.1623	0.402	0.25

Whole Rock
ppm

Ca43	FB4-B	FB4-C	FB5-A	FB5-B	FB5-C
Sc45	100608.47	100608.47	101834.17	101834.19	101834.18
Ti49	15.18	15.72	14.73	14.73	14.67
V51	1616.99	1651.7	1610.24	1536.62	1580.23
Cr52	2.63	3.43	7.31	4.11	2.18
Mn55	897.48	996.52	941.48	962.35	934.3
Co59	787.63	978.03	888.14	856.16	865.59
Ni61	15.28	19.44	16.84	16.5	16.69
Cu65	55.32	60.42	58.11	60.9	62.57
Zn66	5.36	6.19	5.51	4.72	4.22
Ga69	8.42	5.25	5.16	4.3	4.22
Rb85	78.62	98.78	76.23	71.64	75.46
Sr88	0.874	1.585	1.345	1.268	1.298
Y89	209.89	238.09	222.24	215.05	225.99
Zr91	6.92	7.81	7.34	7.38	7.98
Nb93	18.94	22.45	22.38	20.79	23.54
Ba137	1.486	1.698	1.589	1.57	1.727
La139	3068.11	3717.32	3001.35	2750.96	2900.26
Ce140	1.754	2.29	2.11	2.26	2.32
Pr141	4.86	6.63	6.02	6.29	6.45
Nd146	0.633	0.797	0.732	0.788	0.8
Sm147	2.82	3.51	3.19	3.47	3.42
Eu151	0.85	0.982	0.947	0.969	0.977
Gd157	0.764	0.777	0.763	0.752	0.781
Tb159	0.984	1.192	1.059	1.129	1.17
Dy163	0.1754	0.1979	0.1894	0.1897	0.1973
Ho165	1.214	1.319	1.282	1.293	1.334
Er166	0.257	0.28	0.268	0.276	0.282
Tm169	0.728	0.803	0.757	0.783	0.819
Yb172	0.1174	0.1257	0.112	0.1223	0.1245
Lu175	0.771	0.818	0.794	0.79	0.835
Hf178	0.1141	0.1235	0.1158	0.1187	0.1226
Pb208	0.536	0.619	0.619	0.57	0.637
Th232	0.502	0.299	0.224	0.231	0.209
U238	0.27	0.372	0.338	0.349	0.374

Whole Rock
ppm

Ca43	FB6-A	FB6-B	FB6-C
Sc45	102242.28	102242.28	102242.28
Ti49	15.2	12.99	16.21
V51	1642.37	1271.62	1774.47
Cr52	5.98	3.2	7.78
Mn55	969.76	761.02	1043.93
Co59	948.94	754.9	1025.75
Ni61	17.16	14.04	18.29
Cu65	42.83	37.22	44.04
Zn66	4.76	6.92	3.68
Ga69	4.18	4.84	3.48
Rb85	77.86	34.63	88.7
Sr88	1.535	0.727	1.601
Y89	227.9	171.77	237.34
Zr91	7.49	5.73	8.02
Nb93	20.65	17.27	22.15
Ba137	1.531	1.085	1.727
La139	3087.32	1342.57	3728
Ce140	2.14	1.324	2.38
Pr141	6.15	3.82	7.01
Nd146	0.75	0.481	0.818
Sm147	3.3	2.15	3.61
Eu151	0.921	0.635	0.995
Gd157	0.76	0.689	0.799
Tb159	1.124	0.811	1.271
Dy163	0.1898	0.1396	0.2015
Ho165	1.273	0.976	1.363
Er166	0.271	0.2092	0.287
Tm169	0.748	0.606	0.827
Yb172	0.1198	0.0936	0.1298
Lu175	0.796	0.656	0.825
Hf178	0.116	0.0982	0.126
Pb208	0.573	0.439	0.627
Th232	0.174	0.138	0.09
U238	0.347	0.185	0.425

Impact Melt wt.%

Point#	P2O5	SiO2	SO2	TiO2	Al2O3
A1_18	0.0319	44.7994	0.1109	0.2942	24.2995
A3_1	0.0393	42.6328	0.1084	0.3291	22.2819
A3_2	0.0477	45.6914	0.0898	0.3291	23.0071
A3_3	0.0455	46.1478	0.1423	0.3976	22.3202
A5	0.0391	45.8859	0.0868	0.2904	24.5557
A5b	0	45.3075	0.1061	0.2576	25.0517
A5c	0.0216	45.6401	0.0916	0.3218	24.4497

Impact Melt wt.%

Point#	Cr2O3	MgO	CaO	MnO	FeO
A1_18	0.1454	6.6451	15.1558	0.1229	7.2222
A3_1	0.1936	6.0828	14.0088	0.1453	10.1368
A3_2	0.1988	6.6961	14.6028	0.1451	8.6749
A3_3	0.1985	6.2687	14.6862	0.1246	9.1807
A5	0.169	6.936	15.2717	0.0845	6.8844
A5b	0.1398	7.0313	15.236	0.1034	6.5438
A5c	0.1689	6.9048	15.058	0.1192	6.9233

Impact Melt wt.%

Point#	NiO	Na2O	K2O	Total
A1_18	0.0028	0.3408	0.0296	99.2003
A3_1	0	0.2796	0.0115	96.2714
A3_2	0	0.3067	0.0376	99.8271
A3_3	0.011	0.3122	0.0184	99.8596
A5	0.0213	0.3139	0.0348	100.5736
A5b	0.0174	0.3355	0.0266	100.1567
A5c	0.0028	0.3319	0.037	100.0707

Impact Melt ppm

Element	A118	A31	A32	A34	A5
Mg25	37262.76	35727.3	41069.57	38971.76	41283.16
Mg26	39632.48	36163.51	42096.18	38473.89	43355.14
Si29	209410	199282.48	213579.59	215712.98	214488.77
Si30	270658.06	189744.86	227103.34	200774.03	212052.2
Ca43	95925.2	88912.98	106294.13	95853.2	101009.59
Sc45	16.25	17.95	21.14	24.39	15.07
Ti49	1735.03	1594.65	1804.47	1933.96	1560.37
V51	21.02	18.96	34.75	27.2	13.59
Cr52	1098.42	1130.43	1310.93	1281.67	1016.47
Mn55	838.23	938.6	1026.64	1081.04	760.47
Co59	18.3	15.98	17.44	16.51	15.65
Ni61	120.7	46.43	93.93	<34.79	55.4
Cu65	3.64	4.94	4.41	5.18	4.72
Zn66	4.12	3.61	4.85	3.85	3.79
Ga69	3.06	3.31	5	3.08	3.6
Rb85	0.82	<0.72	<0.78	<0.72	<0.67
Sr88	114.22	98.32	116.83	100.3	124.14
Y89	5.46	5.42	6.06	7.56	5.2
Zr91	16.55	14.1	15.38	14.79	13.38
Nb93	1.35	1.1	1.17	1.2	1.24
Ba137	21.93	28.44	51.63	19.51	22.66
La139	1.25	0.99	1.22	1.02	1.23
Ce140	3.54	3.05	3.18	2.85	3.48
Pr141	0.492	0.433	0.453	0.402	0.488
Nd146	2	1.73	1.9	1.86	2.17
Sm147	0.678	0.664	0.614	0.67	0.474
Eu151	0.588	0.54	0.596	0.49	0.608
Gd157	0.68	0.65	0.78	1	0.6
Tb159	0.159	0.108	0.131	0.161	0.125
Dy163	0.994	0.9	0.84	1.2	0.888
Ho165	0.237	0.192	0.197	0.268	0.194
Er166	0.603	0.603	0.677	0.84	0.598
Tm169	0.108	0.07	0.099	0.141	0.1
Yb172	0.721	0.56	0.639	0.97	0.587
Lu175	0.078	0.08	0.117	0.125	0.107
Hf178	0.48	0.38	0.427	0.539	0.43
Pb208	0.088	0.26	0.62	0.092	0.099
Th232	0.178	0.164	0.174	0.118	0.182
U238	0.0554	0.062	0.107	0.0356	0.063

Impact Melt ppm

Element	A5b	A5c
Mg25	39619.89	40165.2
Mg26	40045.16	42039.92
Si29	213339.8	211785.09
Si30	225837.08	196819.98
Ca43	95915.54	97582.21
Sc45	16.59	14.79
Ti49	1910.92	1542.67
V51	21.06	18.18
Cr52	1114.82	1027.41
Mn55	768.48	746.47
Co59	13.89	13.68
Ni61	48.78	36.37
Cu65	4.44	3.84
Zn66	4.05	4.01
Ga69	3.44	3.29
Rb85	<0.65	<0.67
Sr88	120.68	120.25
Y89	6.65	5.43
Zr91	20.89	17.21
Nb93	1.59	1.34
Ba137	24.97	22.74
La139	1.5	1.29
Ce140	4.13	3.59
Pr141	0.581	0.469
Nd146	2.31	2.17
Sm147	0.645	0.688
Eu151	0.708	0.68
Gd157	0.87	0.68
Tb159	0.158	0.118
Dy163	1.24	1.05
Ho165	0.276	0.187
Er166	0.651	0.589
Tm169	0.101	0.1
Yb172	0.755	0.654
Lu175	0.112	0.095
Hf178	0.491	0.349
Pb208	0.123	0.084
Th232	0.199	0.185
U238	0.064	0.059

Clast H1 wt.
%

Feldspar

Point#	SiO2	Al2O3	MgO	CaO	FeO
16	41.8529	20.9486	18.5258	10.168	8.4907
17	43.6506	35.1835	0.1456	19.5791	0.1634
18	43.6777	35.5552	0.0945	19.4902	0.2917
19	43.8265	35.0984	0.1381	19.1965	0.396
20	43.6737	35.1312	0.1331	19.4677	0.2259
21	43.2597	35.4469	0.1027	19.4388	0.2144
23	43.9377	35.0177	0.1584	19.2528	0.2253

Clast H1
Olivine wt.
%

Point#	P2O5	SiO2	TiO2	Al2O3	Cr2O3
2	0.006	38.8264	0.0379	0.4077	0.1163
4	0	39.3312	0.0194	0.0117	0.1085
5	0.01	38.4753	0.0323	0.2951	0.1097
7	0	38.7008	0.0582	0.0202	0.1325
8	0.0184	38.7689	0.0672	0.1295	0.0911
9	0	39.6171	0.0365	0.1103	0.0993
10	0	38.8462	0.0473	0.4298	0.0897
11	0.0106	39.0254	0.0541	0.4115	0.1007
12	0	38.8488	0.0611	0.0425	0.1008
13	0	39.0048	0.05	0.0137	0.1258
14	0	39.0065	0.0301	0.0192	0.1119
15	0.0029	39.1223	0.0541	0.2666	0.1303

Clast H1
Feldspar
wt. %

Point#	Na2O	K2O	Total
16	0.2748	0.0322	100.2929
17	0.3292	0.0103	99.0616
18	0.3718	0.0075	99.4886
19	0.4049	0.014	99.0745
20	0.3547	0.0226	99.0089
21	0.2174	0.0093	98.689
23	0.3545	0.032	98.9783

Clast H1
Olivine wt.
%

Point#	MgO	CaO	MnO	FeO	NiO
2	41.0058	0.209	0.1897	18.1985	0
4	42.8013	0.1136	0.1797	17.4437	0.0294
5	41.4114	0.2003	0.1919	18.1893	0.006
7	42.7477	0.108	0.1888	17.5256	0.0229
8	41.9338	0.1772	0.1786	17.713	0
9	42.1733	0.1589	0.2	17.7179	0.0171
10	41.0726	0.1752	0.1687	17.6667	0.01
11	41.704	0.1878	0.1753	17.7325	0.0152
12	42.1976	0.1654	0.1846	17.7117	0.0257
13	42.7898	0.1234	0.2025	17.4861	0.0089
14	42.9631	0.1157	0.1748	17.1686	0.0018
15	41.7404	0.1786	0.1949	18.0868	0

Clast H1
Olivine wt.
%

Point#	Total
2	98.9971
4	100.0386
5	98.9212
7	99.5047
8	99.0776
9	100.1302
10	98.5063
11	99.4171
12	99.3381
13	99.805
14	99.5917
15	99.7769

Clast H1 Feldspar ppm

Element	23	17
Mg25	61837.11	66625.08
Mg26	57305.34	62129.93
Si29	205382.13	204040.13
Si30	199921.63	200512.92
Ca43	59457.23	73099.48
Sc45	10.6	9.89
Ti49	820.14	810.74
V51	<0.15	<0.15
Cr52	1334.43	1375.29
Mn55	563.38	559.32
Co59	14.6	13.21
Ni61	94.03	54.4
Cu65	5.06	2.95
Zn66	5.43	6.04
Ga69	24.25	12.34
Rb85	0.1	0.07
Sr88	123.49	112.7
Y89	2.2	2.22
Zr91	5.77	6.71
Nb93	0.25	0.34
Ba137	676.49	341.9
La139	0.42	0.52
Ce140	0.93	1.31
Pr141	0.12	0.17
Nd146	0.59	0.82
Sm147	0.17	0.2
Eu151	0.36	0.45
Gd157	0.24	0.31
Tb159	0.044	0.052
Dy163	0.36	0.38
Ho165	0.086	0.082
Er166	0.286	0.267
Tm169	0.0347	0.0417
Yb172	0.345	0.274
Lu175	0.0545	0.0534
Hf178	0.17	0.18
Pb208	1.14	0.77
Th232	0.03	0.04
U238	0.019	0.016
Cr53	1372.55	1410.94

Clast H2 Pyroxene wt. %

Point#	SiO2	TiO2	Al2O3	Cr2O3	MgO
12	52.2278	1.9766	2.5371	0.7157	17.0576
18	52.8043	1.2186	1.4803	0.5508	21.1032
30	52.0649	0.9111	2.0258	0.6527	18.2894
32	54.2367	0.7004	0.6709	0.3952	27.2602
33	54.6547	0.5462	1.288	0.3552	26.9448
34	53.8962	0.9091	1.2148	0.4641	25.99
35	53.9394	0.8401	1.033	0.4448	26.413
36	54.4254	0.5243	1.2576	0.3698	26.5929
37	53.8343	0.752	1.2651	0.5302	24.7369
38	53.9918	0.9164	0.9695	0.4825	25.9187

Clast H2 Feldspar wt. %

Point#	SiO2	Al2O3	MgO	CaO	FeO
39	44.1066	35.1939	0.1251	19.3456	0.3254
40	43.9638	35.3521	0.1418	19.3782	0.259
42	43.7983	35.3446	0.1562	19.4498	0.1997
43	44.0481	35.5618	0.1628	19.5861	0.1805
44	44.3203	34.7762	0.1599	19.3866	0.2042
45	44.1393	35.1681	0.1397	19.5095	0.2847
46	44.1845	35.2082	0.116	19.1198	0.3446
47	43.8676	34.8606	0.1668	19.09	0.3752
48	44.1173	35.0896	0.1653	19.5193	0.1814
49	43.971	34.765	0.4377	19.2999	0.4745
50	44.0533	34.9763	0.159	19.0186	0.4084

Clast H2 Pyroxene wt. %

Point#	CaO	MnO	FeO	Na2O	K2O
12	18.6846	0.1551	6.6943	0.0038	
18	13.9444	0.1795	8.6167	0	
30	18.1624	0.1497	6.8134	0.0102	
32	3.0379	0.2441	12.7025	0.0106	0.0052
33	2.9764	0.2274	12.6992	0.0164	0.022
34	4.3003	0.2512	12.0308	0.025	0.0096
35	4.7475	0.2128	11.8305	0.0218	0.0006
36	3.9967	0.2167	12.128	0.0187	0.0134
37	7.4131	0.2134	11.1466	0.0154	0.0063
38	5.0452	0.2291	12.1733	0.0125	0.0037

Clast H2 Feldspar wt. %

Point#	Na2O	K2O	Total
39	0.3456	0.0338	99.4759
40	0.4066	0.0226	99.524
42	0.3642	0.0076	99.3205
43	0.3507	0.0273	99.9172
44	0.4871	0.0215	99.3559
45	0.3956	0.0164	99.6531
46	0.5483	0.0576	99.5791
47	0.4425	0.0565	98.8592
48	0.4269	0.0076	99.5074
49	0.4055	0.0211	99.3746
50	0.4698	0.0297	99.115

Clast H2 Pyroxene wt. %

Point#	Total
12	100.0663
18	99.9103
30	99.0888
32	99.2638
33	99.7303
34	99.0912
35	99.4834
36	99.5435
37	99.9133
38	99.7427

Clast H2 Olivine wt. %

Point#	P2O5	SiO2	TiO2	Al2O3	Cr2O3
1	0.0115	37.6596	0.1474	0.0728	0.0688
2	0.0009	38.7871	0.0778	0.0713	0.0779
3	0.0023	38.3482	0.0546	0.1257	0.044
4	0.0062	38.7122	0.0589	0.018	0.0654
5	0	38.7044	0.0647	0.0127	0.0841
6	0.0348	39.0447	0.0582	0.2847	0.0597
7	0.0013	38.511	0.0433	0.0147	0.0565
8	0	38.7925	0.0366	0.0331	0.0567
9	0.0146	38.37	0.0817	0.1083	0.053
10	0.0122	38.6804	0.0628	0.0229	0.062
11	0.0185	38.4169	0.0791	0.0244	0.0436
13	0.0026	38.7501	0.031	0.0368	0.0767
14	0.0165	38.5396	0.0915	0.0452	0.1236
15	0	38.6976	0.0565	0.049	0.0924
16	0	38.7112	0.0548	0.0589	0.0571
19	0.0082	38.4728	0.1042	0.4016	0.0728
20	0	38.6958	0.0375	0.1371	0.0939
21	0.0004	38.7126	0.0315	0.0361	0.0781
22	0.0213	38.7079	0.0468	0.0473	0.0805
23	0.0053	38.3192	0.0415	0.3239	0.123
25	0.0012	38.8126	0.0511	0.0208	0.0482
26	0.0021	38.8793	0.0606	0.081	0.0621
27	0.0031	38.5238	0.0248	0.0441	0.0358
28	0.015	38.5561	0.0785	0.0255	0.0713
29	0	38.5761	0.0516	0.2509	0.06
31	0.0036	38.2531	0.0947	0.3436	0.0721

Clast H2 Olivine wt. %

Point#	MgO	CaO	MnO	FeO	NiO
1	40.0481	1.3144	0.2019	19.5675	0.0088
2	40.7232	0.1639	0.1922	19.959	0.0056
3	39.8891	0.1854	0.2245	20.7087	0.0212
4	40.7676	0.4173	0.19	19.7011	0.0016
5	41.0072	0.1625	0.1874	20.0265	0.0224
6	39.9274	0.2667	0.1948	19.594	0.0069
7	40.4853	0.1566	0.2034	19.9812	0.0122
8	40.8449	0.1474	0.1982	19.9305	0
9	40.2452	0.2214	0.1973	20.2733	0.008
10	40.6284	0.1679	0.2083	20.0835	0
11	40.4301	0.2593	0.2248	19.8181	0
13	40.8244	0.1974	0.1946	19.7503	0.0285
14	40.7156	0.166	0.1825	20.0923	0
15	40.9556	0.1504	0.181	19.8672	0
16	40.4804	0.1554	0.209	20.1571	0.0225
19	38.5401	0.3113	0.2324	21.3164	0.0196
20	40.2319	0.1913	0.2072	20.1783	0.0003
21	40.8188	0.1864	0.2073	19.8818	0.0157
22	40.7577	0.2077	0.2046	19.7187	0
23	38.8673	0.3047	0.199	21.2352	0.0029
25	40.9015	0.1414	0.2004	19.9955	0.0064
26	40.7716	0.1776	0.1906	19.9464	0
27	40.2192	0.208	0.2025	20.1778	0
28	40.6263	0.1529	0.2042	20.0901	0
29	39.5748	0.2685	0.1982	20.4472	0.0053
31	38.6255	0.296	0.2145	21.1002	0.0271

Clast H2 Olivine wt. %

Point#	Total
1	99.1008
2	100.0589
3	99.6036
4	99.9382
5	100.2719
6	99.472
7	99.4655
8	100.0399
9	99.5728
10	99.9285
11	99.3147
13	99.8923
14	99.9727
15	100.0497
16	99.9063
19	99.4794
20	99.7733
21	99.9687
22	99.7923
23	99.422
25	100.1792
26	100.1712
27	99.439
28	99.8199
29	99.4325
31	99.0303

Clast H2 Element	Plagioclase ppm		Pyroxene	
	43	48	42	12
Mg25	932.77	1272.83	1073.38	319383.22
Mg26	1072.09	1285.54	1029.02	89239.5
Si29	205898.14	206221.59	204730.48	244133.27
Si30	222504.75	211594.02	202162.33	248220.34
Ca43	168176.08	149693.02	138445.97	9501.7
Sc45	5.68	<4.84	4.02	14.52
Ti49	136.73	97.63	147.89	780.01
V51	<7.66	<9.12	<7.10	<6.64
Cr52	<17.47	<20.71	<16.10	1096.69
Mn55	34.13	36.68	28.58	2376.75
Co59	<3.57	9.24	<3.27	74.03
Ni61	292.66	<277.51	<213.90	<194.80
Cu65	<9.79	<11.40	<8.97	10.39
Zn66	<4.39	<4.88	<3.68	29.68
Ga69	8.28	8.79	9.35	2.87
Rb85	<3.56	<4.23	<3.35	<3.01
Sr88	201.54	197.91	193.92	10.18
Y89	0.94	<0.66	<0.51	2.28
Zr91	<7.11	<9.02	<6.69	7.08
Nb93	<0.236	<0.31	<0.221	<0.26
Ba137	137.27	218.61	157.38	69.51
La139	0.91	0.378	0.817	0.137
Ce140	2.36	1.15	2.37	0.527
Pr141	0.24	0.169	0.196	0.082
Nd146	1.3	<0.56	0.99	<0.47
Sm147	0.56	<0.68	<0.49	<0.46
Eu151	1.1	0.92	1	<0.183
Gd157	<1.02	1.32	<0.95	<1.01
Tb159	<0.091	<0.125	<0.085	<0.077
Dy163	<0.31	<0.39	<0.33	0.53
Ho165	<0.080	0.116	<0.078	<0.100
Er166	<0.25	<0.39	<0.207	0.21
Tm169	<0.104	<0.105	<0.088	<0.062
Yb172	<0.33	<0.44	<0.43	<0.31
Lu175	<0.074	<0.117	<0.087	<0.071
Hf178	<0.30	<0.43	<0.27	<0.31
Pb208	0.27	<0.33	<0.28	0.83
Th232	<0.107	<0.116	<0.075	<0.096
U238	<0.061	<0.068	<0.048	<0.047

Clast H3 Pyroxene wt.%

Point#	SiO2	TiO2	Al2O3	Cr2O3	MgO
24	49.8443	0.5017	1.426	0.4863	14.5684
25	50.3058	0.6696	2.0013	0.6728	13.3326
26	50.235	0.4237	1.7339	0.5388	15.5568
27	50.1829	0.5857	1.7929	0.5865	14.688
28	50.904	0.2385	0.897	0.4377	17.519
29	50.4202	0.4704	1.1378	0.418	15.671
30	50.7447	0.4418	1.4547	0.5507	16.538
31	49.8366	0.4449	1.7301	0.6581	15.1094
32	49.5965	0.6931	1.763	0.4296	12.8242
33	50.1694	0.4617	1.277	0.5191	14.9717
34	50.2617	0.4513	1.4525	0.6519	15.5167

Clast H3 Feldspar wt.%

Point#	SiO2	Al2O3	MgO	CaO	FeO
35	45.2772	34.5964	0.125	18.5081	0.5683
36	43.2079	33.2899	0.1329	17.2839	3.8377
37	44.112	33.8266	0.071	18.1118	1.9784
38	45.3402	34.6667	0.1014	18.7279	0.6437

Clast H3 Pyroxene wt.%

Point#	CaO	MnO	FeO	Na2O	K2O
24	8.3287	0.4082	23.0636	0.029	0
25	17.9378	0.2508	13.8399	0.0487	0.0085
26	9.2708	0.3552	20.9182	0.0156	0.0068
27	12.7266	0.3136	18.0235	0.0237	0
28	4.5347	0.4055	24.5166	0.0163	0.0046
29	8.3116	0.3881	22.152	0.0067	0.0035
30	6.8623	0.3788	22.7075	0.0184	0.0006
31	8.4711	0.3621	22.287	0.008	0.0084
32	10.2399	0.3611	23.1811	0.0401	0.01
33	7.8086	0.3929	23.7546	0.0123	0.001
34	8.6137	0.3502	21.7652	0.0233	0.013

Clast H3 Feldspar wt.%

Point#	Na2O	K2O	Total
35	0.7163	0.0364	99.8277
36	0.6809	0.0961	98.5294
37	0.7241	0.0396	98.8635
38	0.6684	0.0328	100.1811

Clast H3 Pyroxene wt. %

Point#	Total
24	98.6562
25	99.0679
26	99.0547
27	98.9233
28	99.474
29	98.9791
30	99.6974
31	98.9158
32	99.1384
33	99.3681
34	99.0994

Clast H3 Pyroxene ppm

Element	26	33	31
Mg25	80058.2	74387.68	76564.58
Mg26	84306.88	74663.25	80128.66
Si29	234818.22	234511.59	232955.94
Si30	234030.19	238380.3	233016.63
Ca43	58714.21	59659.86	49086.19
Sc45	61.68	56.99	50.86
Ti49	2331.61	3621.47	2381.87
V51	4.17	9.59	5.14
Cr52	3538.76	2610.47	2845.04
Mn55	2936.23	3025.98	2982.67
Co59	32.35	29.64	29.49
Ni61	35.55	29.1	29.48
Cu65	8.47	7.14	7.6
Zn66	13.03	14.53	14.21
Ga69	4.54	4.76	6.12
Rb85	<****	<****	<****
Sr88	23.38	38.52	37.12
Y89	24.2	30.15	22.21
Zr91	17.25	40.09	33.17
Nb93	0.16	0.94	0.4
Ba137	147.07	132.28	218.4
La139	2.01	2.01	1.82
Ce140	8.02	7.92	6.55
Pr141	1.31	1.38	1.09
Nd146	6.45	6.97	5.58
Sm147	2.18	2.65	1.93
Eu151	0.12	0.27	0.2
Gd157	2.81	3.68	2.84
Tb159	0.6	0.71	0.51
Dy163	4.05	5.25	3.73
Ho165	0.93	1.18	0.86
Er166	2.94	3.62	2.7
Tm169	0.43	0.54	0.4
Yb172	2.93	3.57	2.7
Lu175	0.415	0.517	0.4
Hf178	0.44	0.94	0.85
Pb208	0.44	0.43	0.48
Th232	0.29	0.18	0.33
U238	0.06	0.05	0.07

Clast H4 Pyroxene wt. %

Point#	SiO2	TiO2	Al2O3	Cr2O3	MgO
5	52.6485	0.4444	0.6021	0.199	20.931
6	52.3107	0.4668	0.8257	0.2112	20.6676
7	52.5237	0.5382	0.7046	0.2508	20.6462
8	51.1613	1.0829	1.7477	0.5042	15.2407
9	51.4042	1.0846	1.7499	0.5353	15.0759
10	52.0761	0.5414	0.6422	0.2701	20.5667
11	50.6483	1.1178	2.2117	0.5019	14.4614
12	50.0776	1.0699	2.5096	0.5209	14.5832

Clast H4 Feldspar wt. %

Point#	SiO2	Al2O3	MgO	CaO	FeO
13	44.9294	34.8071	0.579	18.1051	0.3194
14	44.397	35.344	0.0871	19.6583	0.2053
15	43.775	35.1397	0.0749	19.3438	0.1986
16	39.4582	31.5801	0.0869	23.4044	0.3239
17	44.1111	35.1117	0.0627	19.3947	0.4073
18	43.9483	34.959	0.1394	19.3544	0.5454
19	44.0341	35.1418	0.1442	19.357	0.352
20	44.8728	34.9683	0.0911	19.0165	0.2583

Clast H4 Olivine wt. %

Point#	P2O5	SiO2	TiO2	Al2O3	Cr2O3
1	0.0135	35.0558	0.0768	0.1251	0.0195
2	0.008	35.1872	0.0459	0.0437	0.0144

Clast H4 Pyroxene wt. %

Point#	CaO	MnO	FeO	Na2O	K2O
5	2.7998	0.3662	22.2612	0.0175	0.0045
6	2.7676	0.3895	22.2725	0.0127	0.0132
7	2.937	0.3646	21.9403	0.0092	0.002
8	17.6554	0.2349	12.126	0.0387	0
9	18.2329	0.2187	11.4358	0.0537	0.0143
10	2.7565	0.3933	22.8252	0.0097	0
11	19.492	0.2113	10.7487	0.062	0.011
12	18.4934	0.2185	11.4444	0.0699	0.0498

Clast H4 Feldspar wt. %

Point#	Na2O	K2O	Total
13	0.6166	0.0997	99.4564
14	0.4231	0.0287	100.1435
15	0.4181	0.034	98.9841
16	0.4077	0.0495	95.3107
17	0.48	0.0104	99.5778
18	0.5901	0.053	99.5896
19	0.4414	0.0501	99.5206
20	0.6041	0.0242	99.8352

Clast H4 Olivine wt. %

Point#	MgO	CaO	MnO	FeO	NiO
1	26.4031	0.1438	0.357	36.7286	0.0202
2	27.3972	0.1057	0.349	36.9901	0

Clast H4 Pyroxene wt. %

Point#	Total
5	100.2742
6	99.9376
7	99.9164
8	99.7918
9	99.8054
10	100.0812
11	99.4662
12	99.0371

Clast H4 Olivine wt. %

Point#	Total
1	98.9435
2	100.1412

Clast H4	Pyroxene ppm			Felspar	
Element	C712	C711	C75	C715	C714
Mg25	84934.75	84789.19	137711.09	3018.07	1489.47
Mg26	1474.2	1533.16	2717.11	3209	1623.41
Si29	234082.41	236750.08	246099.8	204621.55	207529.05
Si30	157596.56	187921.53	258777.11	176703.14	60835.7
Ca43	109342.59	120406.83	17711.43	122490.96	125159.93
Sc45	73.55	75.23	29.73	4.04	3.31
Ti49	4944.72	4951.32	1404.17	150.28	144.26
V51	31.57	25.46	56.78	<2.28	<2.44
Cr52	3593.32	3612.37	1191.82	<4.48	<4.81
Mn55	1960.73	1892.38	3226.29	57.93	48.44
Co59	24.8	24.44	56.02	2.4	1.13
Ni61	<18.99	24.27	110	<28.43	<29.68
Cu65	14.16	8.63	8.15	3.27	<1.66
Zn66	12.72	13.69	20.14	4.1	1.98
Ga69	9.5	193.78	4.3	81.03	22.72
Rb85	1.24	0.46	0.75	1.58	<0.67
Sr88	13.99	80.05	6.87	206.04	191.73
Y89	36.46	38.65	10.24	1.79	0.863
Zr91	80.05	91.99	12.39	1.46	<1.21
Nb93	0.302	0.24	0.222	<0.056	<0.061
Ba137	144.31	3039.45	67.12	1317.27	364.24
La139	1.45	1.67	0.474	1.183	1.039
Ce140	6.46	7.4	0.968	1.82	2.12
Pr141	1.367	1.44	0.149	0.316	0.313
Nd146	7.55	8.52	0.94	1.39	1.04
Sm147	3.23	3.8	0.516	0.454	0.299
Eu151	0.125	0.149	0.035	0.884	0.926
Gd157	4.53	4.84	0.7	0.38	0.277
Tb159	0.979	1.015	0.154	0.039	0.0443
Dy163	6.72	7.12	1.5	0.17	0.082
Ho165	1.372	1.49	0.365	0.0252	0.0311
Er166	3.76	4.1	1.21	0.126	0.065
Tm169	0.588	0.66	0.197	<0.0125	<0.0116
Yb172	3.45	4.12	1.72	0.076	<0.063
Lu175	0.497	0.517	0.221	<0.0143	<0.0142
Hf178	2.46	2.93	0.311	0.051	<0.064
Pb208	3.26	2.98	3.08	1.04	<0.10
Th232	0.0625	0.112	0.156	0.0181	0.0229
U238	0.101	0.099	0.101	0.0528	<0.0087
Cr53	3705.9	3750.4	1154.27	<-NaN	<-NaN
Yb173	3.5	4.13	1.45	<-NaN	<-NaN

Clast H5 Pyroxene wt. %

Point#	SiO2	TiO2	Al2O3	Cr2O3	MgO
30	53.6859	0.7376	0.8736	0.3521	25.6
31	53.2178	0.8277	1.0691	0.3885	25.3558
32	53.0608	0.7924	1.1195	0.3572	25.2891
33	52.7622	1.0893	1.3828	0.4935	24.9989
34	53.1806	0.9553	1.2239	0.4055	25.2236
35	53.0329	0.9679	1.2298	0.4606	25.1726

Clast H5 Feldspar wt. %

Point#	SiO2	Al2O3	MgO	CaO	FeO
25	44.7815	35.1345	0.1974	19.3064	0.2335
26	44.3499	35.1632	0.1056	19.4307	0.2841
27	44.0885	35.0387	0.1119	19.5944	0.3014
28	44.3739	34.9499	0.1447	19.3947	0.1606
29	44.1263	34.7142	0.1491	19.0397	0.5148

Clast H5 Pyroxene wt. %

Point#	CaO	MnO	FeO	Na2O	K2O
30	2.261	0.2594	16.4984	0.0054	0.0115
31	2.3082	0.2685	16.3291	0.0149	0.1505
32	2.344	0.2886	16.2668	0.0137	0.0324
33	2.4215	0.257	16.4599	0.0071	0.0065
34	2.404	0.2553	16.3708	0	0.0009
35	2.415	0.2809	16.4034	0.0112	0.0013

Clast H5 Feldspar wt. %

Point#	Na2O	K2O	Total
25	0.4416	0.181	100.2757
26	0.4219	0.0369	99.7921
27	0.4438	0.0299	99.6086
28	0.4708	0.0433	99.5378
29	0.4213	0.1207	99.0861

Clast H5 Pyroxene wt. %

Point#	Total
30	100.2848
31	99.9302
32	99.5646
33	99.8787
34	100.0199
35	99.9755

Clast H5	Feldspar ppm			Pyroxene	
Element	C228	C226	C225	C235	C232
Mg25	1215.26	3268.8	1777.54	113097.26	129981.18
Mg26	1247.83	3389.51	1781.69	2482.32	2271.2
Si29	207449.14	207308.89	209326.38	247896.64	248027.05
Si30	202804.34	231102.66	202121.06	242640.64	249732.45
Ca43	151915.45	129747.35	159613.41	40385.14	33827.31
Sc45	4.03	3.81	4.23	36.98	34.16
Ti49	213.07	276.68	224.71	4525.9	4082.03
V51	<2.72	2.62	<2.67	<1.79	36.32
Cr52	<5.47	53.72	9.41	2764.23	2770.11
Mn55	34.39	66.36	40.05	1901.1	2164.2
Co59	<0.86	1.07	<0.85	27.66	39.52
Ni61	<42.75	<37.58	48.68	33.27	130.09
Cu65	2.93	1.98	<2.08	8.28	11.71
Zn66	1.3	2.28	<0.96	19.39	20.62
Ga69	5.24	145.47	8.49	3.1	111.93
Rb85	1.46	0.81	1.02	0.91	1.07
Sr88	220.07	197.64	238.2	45.74	69.12
Y89	0.748	1.09	0.769	15.99	17
Zr91	<1.76	<1.55	<1.78	44.18	36.55
Nb93	<0.064	0.106	<0.082	0.503	0.223
Ba137	43.37	2411.05	109.8	42.36	2119.62
La139	1.21	1.25	1.19	0.269	0.135
Ce140	3.32	3.22	3.24	0.97	0.91
Pr141	0.397	0.37	0.388	0.156	0.181
Nd146	1.54	1.52	1.54	0.83	1.22
Sm147	0.449	0.264	0.423	0.405	0.654
Eu151	0.9	0.849	0.804	0.158	0.05
Gd157	0.47	0.32	0.43	0.96	1.37
Tb159	0.049	0.0266	0.032	0.278	0.3
Dy163	0.186	0.176	0.116	2.25	2.58
Ho165	0.0222	0.0292	0.0229	0.598	0.64
Er166	0.195	<0.050	0.075	1.75	1.86
Tm169	<0.0152	<0.0184	<0.0210	0.382	0.357
Yb172	<0.079	0.195	<0.080	2.38	2.24
Lu175	<0.0165	0.0125	<0.0186	0.405	0.353
Hf178	<0.073	<0.062	0.059	1.28	1.16
Pb208	0.39	0.34	0.51	1.41	1.23
Th232	<0.0193	0.0266	0.023	0.077	0.054
U238	0.081	0.0384	0.143	0.15	0.15
Cr53	8.26	53.28	7.48	<-NaN	<-NaN

Clast H5 Pyroxene ppm	
Element	C230
Mg25	119981.9
Mg26	2094.4
Si29	250949.02
Si30	254204.8
Ca43	31961.35
Sc45	33.37
Ti49	4024.77
V51	40.59
Cr52	2657.67
Mn55	2104.12
Co59	31.35
Ni61	<24.87
Cu65	5.75
Zn66	19.1
Ga69	87.95
Rb85	0.58
Sr88	65.95
Y89	13.56
Zr91	27.05
Nb93	0.185
Ba137	1652.2
La139	0.14
Ce140	0.496
Pr141	0.084
Nd146	0.556
Sm147	0.312
Eu151	0.113
Gd157	0.88
Tb159	0.19
Dy163	1.78
Ho165	0.543
Er166	1.53
Tm169	0.281
Yb172	2.09
Lu175	0.33
Hf178	0.749
Pb208	0.48
Th232	0.053
U238	0.094

Clast H6 Pyroxene wt.%

Point#	SiO2	TiO2	Al2O3	Cr2O3	MgO
40	49.7655	0.3224	1.77	0.147	13.2813
41	50.4654	0.2956	0.7082	0.1581	13.193
42	29.6377	0.1217	0.0195	0.0094	1.5626

Clast H6 Feldspar wt.%

Point#	SiO2	Al2O3	MgO	CaO	FeO
38	44.2257	35.6455	0.084	19.6188	0.2088
39	44.0616	35.5361	0.1207	19.719	0.1453

Clast H6 Olivine wt.%

Point#	P2O5	SiO2	TiO2	Al2O3	Cr2O3
36	0	35.1318	0.0164	0.0367	0.0146
37	0	35.2312	0.0296	0.0272	0.0171

Clast H6 Pyroxene wt.%

Point#	CaO	MnO	FeO	Na2O	K2O
40	8.2163	0.3664	24.6231	0.0374	0.0917
41	7.8688	0.4344	27.1855	0.0042	0.018
42	0.9898	0.7276	66.7179	0	0

Clast H6 Feldspar wt.%

Point#	Na2O	K2O	Total
38	0.3608	0.0363	100.1799
39	0.3458	0.0221	99.9506

Clast H6 Olivine wt.%

Point#	MgO	CaO	MnO	FeO	NiO
36	26.0351	0.0739	0.3779	38.7361	0.026
37	25.6029	0.0991	0.4097	39.1735	0.0152

Clast H6 Pyroxene wt.%

Point#	Total
40	98.6211
41	100.3311
42	99.7861

Clast H6 Olivine wt.%

Point#	Total
36	100.4483
37	100.6054

Clast H6	Pyroxene ppm		Feldspar	
Element	40	41	39	38
Mg25	68759.69	72512.3	7453.06	2550.54
Mg26	880.64	906.64	7912.5	2555.42
Si29	232623.53	235895.14	205961.27	206728.34
Si30	243545.86	250721.16	204730.56	179073.36
Ca43	77555.8	63386.94	104002.05	117137.2
Sc45	83.37	74.47	3.4	3.6
Ti49	3583.37	3783.82	49.98	45.8
V51	4.68	<1.36	3.79	3.46
Cr52	2259.5	2614.97	12.9	10.77
Mn55	3069.45	3350.9	89.71	142.54
Co59	30.72	32.91	<0.84	1.7
Ni61	51.26	51.84	<42.97	<47.96
Cu65	9.34	8.2	12.59	6.89
Zn66	17.74	16.56	9.02	7
Ga69	3.64	2.46	6.53	27.13
Rb85	0.8	<0.48	1.18	2.24
Sr88	8.78	5.67	157.85	169.24
Y89	35.21	29.73	0.485	1.12
Zr91	44.37	30.67	8.87	<2.03
Nb93	0.711	0.682	<0.079	<0.085
Ba137	52.74	29.03	94.81	422.86
La139	2.64	2.21	0.581	0.565
Ce140	11.44	7.88	1.11	0.427
Pr141	1.92	1.38	0.169	0.156
Nd146	9.71	6.97	0.468	0.75
Sm147	3.49	2.49	0.163	0.158
Eu151	0.082	0.075	0.5	0.704
Gd157	4.5	3.5	<0.25	<0.26
Tb159	0.784	0.642	0.028	<0.0197
Dy163	5.9	4.91	<0.088	0.159
Ho165	1.28	1.1	<0.030	0.03
Er166	3.67	3.13	0.411	0.085
Tm169	0.59	0.503	0.018	<0.0193
Yb172	3.8	3.21	<0.075	0.077
Lu175	0.52	0.49	0.02	<0.022
Hf178	1.51	1.06	0.202	0.089
Pb208	1.39	1.01	1.47	2.13
Th232	0.147	0.16	0.056	<0.0195
U238	0.106	0.098	0.058	0.0251
Cr53	2267.73	2731.85	<-NaN	<-NaN

Clast B1 Pyroxene wt. %

Point#	SiO2	TiO2	Al2O3	Cr2O3	MgO
13	47.016	1.1206	2.3753	0.2408	7.5449
21	50.0724	0.7499	0.9849	0.4399	14.461
22	45.6452	0.6232	0.4856	0.0223	0.9645
23	51.8844	0.2987	2.2985	0.7645	20.453
24	48.4117	1.014	1.3514	0.1863	9.5904
26	49.239	0.8804	1.2323	0.3347	12.3146
27	49.601	0.7367	1.0798	0.4344	12.3153
28	50.6141	0.5418	1.622	0.6561	16.5479
29	50.4188	0.8112	2.3481	0.712	18.8568
30	50.9951	0.6153	2.0703	0.3608	18.0405
31	50.1529	0.5897	1.5481	0.3205	15.237
32	50.6988	0.4943	1.1488	0.6008	16.0673
33	51.2577	0.351	1.7904	0.7972	18.8973
34	52.0833	0.327	2.2475	0.9214	23.5668
35	45.7556	1.8929	1.5977	0.0525	2.7112
36	49.7204	0.7935	1.939	0.7741	13.6212
37	49.7143	0.8013	1.6735	0.634	12.3358
38	48.5503	0.9738	1.0834	0.2448	9.3262
39	52.0239	0.2731	1.8508	0.756	20.2832
41	48.6591	0.6754	0.9251	0.3512	10.8079
42	50.5636	0.4209	2.1239	0.8105	16.4867
50	45.4137	0.555	0.3836	0.0371	0.8761
51	45.3918	0.6005	0.3964	0.0169	0.806
52	45.9406	1.2128	1.3492	0.0599	2.4735
54	44.7949	0.9579	2.081	0.0384	1.9086
56	42.6997	3.0102	2.2506	0.0285	1.1095
57	49.3456	0.3595	0.6749	0.2888	12.1873
58	48.5665	0.813	0.8506	0.2761	11.4385
60	48.3758	0.8515	0.8743	0.247	10.3512
61	49.6841	0.8026	2.1598	0.4109	11.2301
63	49.0803	0.7756	1.026	0.2979	11.7561

Clast B1 Pyroxene wt. %

Point#	CaO	MnO	FeO	Na2O	K2O
13	11.2404	0.4294	29.1224	0	
21	7.1557	0.402	25.5029	0.0174	0.001
22	6.6033	0.7945	43.9414	0	0.0058
23	5.5604	0.3383	18.5119	0.0024	0.0032
24	7.5967	0.4265	30.5475	0.014	0.0018
26	7.7759	0.4146	27.6262	0.0212	0.0033
27	8.1479	0.42	26.9813	0.0109	0.0057
28	6.6019	0.3707	22.6982	0.0028	0.0017
29	6.9959	0.3525	19.071	0.0118	0.0052
30	5.5201	0.3934	21.6347	0.0101	0.0093
31	6.2555	0.4247	25.2237	0.005	0.004
32	6.6544	0.3769	23.8375	0.005	0.004
33	5.721	0.3662	20.4436	0.0063	0.001
34	3.4274	0.2991	16.7788	0.0021	0
35	13.5723	0.464	33.0686	0.0171	0
36	12.5233	0.3221	19.7235	0.0322	0
37	12.663	0.3403	21.5369	0.0191	0
38	9.443	0.4273	29.6011	0.0319	0.0001
39	6.6462	0.3425	17.6046	0.0171	0
41	6.7167	0.4557	31.0064	0.0232	0
42	8.7826	0.3633	19.9195	0.0283	0.0082
50	6.7099	0.7653	44.4421	0.0212	0.0126
51	6.5958	0.7646	44.5268	0.0109	0.0008
52	10.209	0.5243	37.6812	0.0224	0.0006
54	7.1837	0.5856	42.7698	0.0788	0.0299
56	9.635	0.4584	39.908	0.015	0.0329
57	5.9771	0.4707	30.2944	0.0097	0
58	7.7685	0.4884	28.9714	0	0.001
60	7.9872	0.4869	30.0762	0.0107	0
61	9.1424		26.1359	0.014	0.0333
63	7.5176	0.4672	28.3427	0.0174	0.0067

Clast B1 Pyroxene wt. %

Point#	Total
13	99.1424
21	99.7872
22	99.0857
23	100.1154
24	99.1403
26	99.8422
27	99.733
28	99.6571
29	99.5833
30	99.6496
31	99.761
32	99.8878
33	99.6316
34	99.6533
35	99.1319
36	99.4493
37	99.7183
38	99.6819
39	99.7974
41	99.6207
42	99.5075
50	99.2165
51	99.1104
52	99.4733
54	100.4286
56	99.1479
57	99.6081
58	99.174
60	99.2609
61	100.0444
63	99.2875

Clast B1 Feldspar wt.%

Point#	SiO2	Al2O3	MgO	CaO	FeO
43	46.7688	33.2072	0.1195	18.2583	1.3071
44	45.0393	34.6106	0.1301	19.0142	0.8968
45	44.1096	35.4555	0.1089	19.3482	0.7665
46	47.3625	31.8392	0.5995	17.1208	1.551
47	45.0272	32.333	0.4727	18.4703	1.9506
48	44.8392	34.9698	0.1231	18.7467	0.5958
49	44.1563	35.3044	0.1195	19.1293	0.6163
50	46.9656	32.9866	0.1678	18.2579	1.3097

Clast B1 Olivine wt.%

Point#	P2O5	SiO2	TiO2	Al2O3	Cr2O3
2	0.0006	36.4626	0.046	0.0038	0.0453
3	0.0051	36.451	0.0652	0.0483	0.0746
4	0.0016	35.9978	0.0582	0.3894	0.056
5	0.003	35.7234	0.0408	0.4143	0.0821
6	0.0218	36.5147	0.0532	0.0142	0.0451
7	0	36.861	0.0561	0.172	0.0357
8	0.0035	36.3353	0.0363	0.0049	0.0265
9	0.0382	36.368	0.0479	0.0707	0.0395
10	0	36.3384	0.0506	0.0803	0.0239
11	0.0036	35.7104	0.0577	0.0215	0.0646
12	0.0123	32.3338	0.0998	0.0287	0.0768
15	0	38.012	0.0375	0.3355	0.3911
16	0.0033	37.7598	0	0.0823	0.3495
17	0.0177	36.0874	0.0461	0.0479	0.0262

Clast B1 Feldspar wt. %

Point#	Na2O	K2O	Total
43	0.81	0.0318	100.5026
44	0.6607	0.0236	100.3753
45	0.4005	0.0294	100.2187
46	0.7077	0.0689	99.2495
47	0.5635	0.0524	98.8697
48	0.6482	0.0979	100.0207
49	0.4675	0.0115	99.8046
50	0.7235	0.0745	100.4856

Clast B1 Olivine wt. %

Point#	MgO	CaO	MnO	FeO	NiO
2	31.041	0.2018	0.3424	32.3979	0.0121
3	31.0643	0.19	0.3112	31.874	0
4	29.5159	0.3047	0.3096	33.2032	0.0089
5	29.7362	0.2869	0.3245	32.3762	0
6	31.6991	0.2195	0.3436	31.6168	0.0211
7	31.0434	0.1883	0.3434	32.0929	0
8	30.4219	0.2253	0.3298	32.9776	0.0087
9	29.9531	0.2455	0.3439	33.5169	0
10	31.2686	0.289	0.3064	31.8857	0
11	28.8884	0.2761	0.3645	34.8921	0.005
12	14.0754	0.5265	0.5218	52.4589	0.0039
15	36.5563	0.4097	0.2381	23.6998	0.0074
16	38.2638	0.3064	0.2732	22.6511	0.0063
17	29.9945	0.2263	0.3279	33.5012	0

Clast B1 Olivine wt.%

Point#	Total
2	100.5536
3	100.0839
4	99.8453
5	98.9874
6	100.5491
7	100.7928
8	100.3697
9	100.6237
10	100.2429
11	100.2838
12	100.1377
15	99.6874
16	99.6957
17	100.2751

Clast B1 Pyroxene ppm

Element	SA-50	SA-38	SA-36	SA-52	SA-39	SA-39
Mg25	35392.45	62552.08	80198.77	15912.25	114939.46	114939.46
Mg26	34679.2	63299.56	81017.15	16034.12	104154	104154
Si29	212281.48	226943.19	232412.72	214744.42	243180.17	243180.17
Si30	200518.8	229205.03	224547.81	232643	274985	274985
Ca43	41641	113147.76	71380.55	73663.35	37798.07	37798.07
Sc45	78.98	107.75	99.53	102.28	81.54	81.54
Ti49	3190.27	5342.4	3456.67	6774.74	1486.27	1486.27
V51	79.91	62.98	48.31	8.57	296.43	296.43
Cr52	1838.51	2891.96	4932.37	605.02	5982	5982
Mn55	4088.61	3114.76	2717.2	3880.66	2760.58	2760.58
Co59	28.03	29.31	31.73	33.79	38.85	38.85
Ni61	<130.68	<130.42	<134.55	<135.53	<141.18	<141.18
Cu65	9.11	<5.73	<5.91	<5.77	<6.04	<6.04
Zn66	8.07	5.19	5.12	<2.58	5.24	5.24
Ga69	6.09	3.16	3.37	2.95	2.87	2.87
Rb85	1.94	<1.96	<2.02	<2.04	<2.16	<2.16
Sr88	26.94	35.74	11.77	19.67	10.32	10.32
Y89	83.38	29.68	12.21	30.49	4.33	4.33
Zr91	32.79	21.81	14.85	29.93	<4.53	<4.53
Nb93	0.621	<0.172	0.399	0.416	<0.161	<0.161
Ba137	153.92	50.66	71.33	37.26	77.69	77.69
La139	0.908	0.699	0.201	0.947	<0.074	<0.074
Ce140	3.49	3.33	0.957	3.55	0.184	0.184
Pr141	0.752	0.621	0.191	0.718	0.049	0.049
Nd146	4.57	3.89	0.8	3.76	<0.31	<0.31
Sm147	2.71	2.14	0.37	1.74	<0.32	<0.32
Eu151	0.203	0.172	<0.145	0.171	<0.128	<0.128
Gd157	5.55	2.93	<0.68	3	<0.67	<0.67
Tb159	1.27	0.555	0.276	0.62	0.066	0.066
Dy163	10.64	4.26	2.18	5.13	0.52	0.52
Ho165	3.06	1.07	0.427	1.04	0.15	0.15
Er166	9.84	2.98	1.54	3.74	0.47	0.47
Tm169	1.62	0.55	0.198	0.6	0.069	0.069
Yb172	13.66	3.94	1.58	4.35	0.63	0.63
Lu175	2.37	0.469	0.218	0.83	0.137	0.137
Hf178	1.06	0.7	0.61	1.08	0.225	0.225
Pb208	0.55	0.359	0.333	0.372	0.406	0.406
Th232	0.079	0.08	<0.053	0.092	<0.066	<0.066
U238	0.035	0.047	<0.024	<0.033	0.026	0.026
Cr53	1820.41	2924.51	4884.64	586.86	5904.77	5904.77

Clast B2 Pyroxene wt. %

Point#	SiO2	TiO2	Al2O3	Cr2O3	MgO
60	49.9372	0.3387	2.3463	1.0039	15.0105
61	51.0155	0.2091	1.8328	0.9034	18.9888
62	50.9337	0.2422	1.8146	0.8771	18.6922
63	51.3914	0.2006	1.6249	0.7994	20.4788
64	51.248	0.2463	2.106	0.905	20.2424
65	48.9552	0.5363	1.5109	0.5777	12.3186
66	48.715	0.5514	1.304	0.5178	11.2863
67	47.3112	0.7644	1.2863	0.3786	8.5105
68	45.6952	1.0273	0.9159	0.0357	3.0436
69	51.3664	0.2271	1.823	0.8352	19.5533
70	52.0728	0.2045	2.0362	0.8257	20.1742
71	51.6627	0.2021	1.57	0.7936	20.4105
72	51.2447	0.3116	1.7765	0.8302	20.0897
73	50.9364	0.2808	1.9497	0.6474	18.8208
74	49.0365	0.5129	2.1931	0.4932	13.4001
75	49.9755	0.3811	1.0502	0.4192	15.1251
76	50.1797	0.3485	1.5286	0.6017	16.0342

Clast B2 Feldspar wt. %

Point#	SiO2	Al2O3	MgO	CaO	FeO
52	44.2164	34.2193	0.3691	19.2367	0.7628
53	43.6299	35.046	0.2504	19.3242	0.8402
54	44.467	34.4199	0.3894	19.2586	0.4563
55	44.4919	31.8704	1.7286	18.3972	2.2615
56	43.5048	35.0645	0.2324	19.5835	0.7166
57	43.704	34.0904	0.5015	17.909	1.7588
58	46.8543	23.5164	6.6504	14.0973	7.2394
59	43.9364	34.5035	0.3737	19.3024	0.7699

Clast B2 Pyroxene wt. %

Point#	CaO	MnO	FeO	Na2O	K2O
60	11.8677	0.3746	17.9321	0.0035	0.0036
61	7.0556	0.3439	18.7799	0	0
62	7.144	0.3377	18.9852	0.0127	0.0022
63	4.7238	0.3617	19.426	0.0119	0.0015
64	4.9543	0.3616	19.102	0.009	0
65	9.61	0.4073	25.2566	0.0012	0.0122
66	9.1665	0.4228	27.4333	0	0
67	8.6223	0.4462	31.4117	0.022	0.0052
68	9.697	0.4826	38.0483	0.0013	0
69	6.2815	0.3437	18.8052	0.0088	0.015
70	5.7111	0.366	18.5881	0.0129	0.007
71	5.1734	0.361	18.9505	0.0055	0.0077
72	5.8535	0.3728	18.8692	0.0031	0.0009
73	5.7792	0.3534	20.3127	0.0254	0.0045
74	7.2112	0.39	25.3622	0.0345	0.0223
75	6.0879	0.3924	26.0783	0.0161	0.0039
76	8.3877	0.3614	21.4766	0.0114	0.0088

Clast B2 Feldspar wt. %

Point#	Na2O	K2O	Total
52	0.3318	0.0006	99.1367
53	0.3236	0.0193	99.4337
54	0.416	0.0082	99.4154
55	0.3441	0.0093	99.103
56	0.2892	0	99.391
57	0.3199	0.127	98.4107
58	0.2681	0.0222	98.648
59	0.2614	0.0052	99.1526

Clast B2 Pyroxene wt. %

Point#	Total
60	98.818
61	99.129
62	99.0416
63	99.02
64	99.1746
65	99.186
66	99.3971
67	98.7585
68	98.9468
69	99.2594
70	99.9982
71	99.1369
72	99.3522
73	99.1104
74	98.656
75	99.5296
76	98.9387

Clast B2	Pyroxenes ppm				
Element	68	66	75	62	61
Mg25	23260.17	64691.36	77354.75	67892.3	82850.13
Mg26	22706.77	64138.65	73608.76	69001.47	73573.46
Si29	213597.36	227713.06	233605.11	238084.14	238466.5
Si30	233396.78	220028.84	231970.73	225757.53	211885.5
Ca43	66030.07	68418.77	55264.02	88275.63	68413.16
Sc45	110.43	114.64	79.11	46.95	54.46
Ti49	5652.54	2881.14	3764.98	770.63	881.51
V51	18.55	93.69	124.02	161.94	198.61
Cr52	645.51	3920.22	3413.37	3719.37	4418.52
Mn55	3529.46	3116.73	3100.5	1698.4	2096
Co59	37.54	37.41	31.68	35.85	32.01
Ni61	<120.46	<131.19	<135.09	<175.67	<181.68
Cu65	<4.96	<5.55	<5.47	7.99	10.99
Zn66	4.21	3.12	9.64	7.9	6.88
Ga69	0.68	1.39	4.57	7.63	7.76
Rb85	<1.85	<2.08	<2.13	<2.90	2.92
Sr88	5.63	3.07	13.32	54.51	45.99
Y89	25.32	9.23	14.09	1.3	2.4
Zr91	7.72	<4.23	11.07	<5.59	<6.02
Nb93	<0.110	<0.117	0.257	<0.193	<0.213
Ba137	8.33	7.49	104.47	167.45	195.94
La139	0.13	<0.063	0.253	<0.089	<0.085
Ce140	0.658	0.111	0.913	0.202	<0.073
Pr141	0.14	<0.050	0.168	<0.056	<0.079
Nd146	1.25	0.42	0.62	<0.28	0.63
Sm147	1.11	0.37	0.65	<0.44	<0.43
Eu151	<0.119	<0.143	0.138	0.191	<0.180
Gd157	2.8	<0.61	0.78	<0.81	0.71
Tb159	0.509	0.163	0.276	<0.079	<0.083
Dy163	3.41	1.35	1.9	0.3	0.33
Ho165	0.98	0.4	0.467	0.121	0.098
Er166	3.01	1.04	1.33	<0.20	0.34
Tm169	0.57	0.172	0.27	<0.071	<0.082
Yb172	3.93	1.42	1.87	0.4	<0.37
Lu175	0.62	0.247	0.341	<0.066	<0.082
Hf178	0.248	0.218	0.37	<0.24	0.31
Pb208	<0.153	<0.168	0.227	0.38	0.27
Th232	<0.054	<0.041	0.064	<0.076	<0.062
U238	<0.028	<0.033	<0.025	<0.038	<0.037
Cr53	632.05	3847.44	3320.52	3682.33	4355.08
Yb173	3.99	1.38	2.25	<0.32	<0.37

Clast B3 Pyroxene wt. %

Point#	SiO2	TiO2	Al2O3	Cr2O3	MgO
19	52.6315	0.6317	1.7235	0.5932	22.2381
20	51.9513	0.2129	0.9165	0.7477	20.2785
21	51.4118	0.361	1.0664	0.6393	17.4405
22	48.1051	0.8714	1.3136	0.255	8.4621
23	46.4535	1.4072	1.7582	0.0952	5.0199
24	51.5958	0.517	0.8989	0.5875	19.0183
25	51.7218	0.3957	1.7285	0.5401	18.7232
27	50.9852	0.3994	1.5437	0.7214	18.4746
28	50.7893	0.4258	1.2277	0.6913	18.061
A	51.7995	0.6269	1.5817	0.4619	18.8701
B	52.5048	0.263	1.2547	0.6995	21.4862
C	52.45	0.3018	1.1515	0.7149	21.1793
D	52.2305	0.3252	1.2167	0.6926	20.2256
E	52.9462	0.5185	0.5083	0.1778	23.0518
F	52.488	0.5588	0.681	0.2126	22.2798
G	51.3084	0.4997	0.8647	0.4365	18.9356
H	51.5883	0.7341	0.7976	0.4948	18.5853

Clast B3 Olivine wt. %

Point#	P2O5	SiO2	TiO2	Al2O3	Cr2O3
18	0.0092	36.0338	0.0522	0.1156	0.0087
26	0	36.4463	0.0634	0.0211	0.0401

Clast B3 Feldspar wt. %

Point#	SiO2	Al2O3	MgO	CaO	FeO
31	46.1006	32.9781	0.2594	18.2032	1.0133
32	45.0171	34.0912	0.1349	18.3658	0.6879
33	46.1461	33.466	0.2822	16.623	0.9386
34	44.3296	35.0348	0.1325	18.7865	0.6421
I	45.9814	33.485	0.1462	17.9286	0.8225
J	45.8941	34.0874	0.2599	16.7848	0.7666
K	46.3374	32.7302	0.1657	17.4836	0.9507
L	45.5634	33.0401	0.1049	17.8474	0.7663
M	44.7328	34.4555	0.1099	19.076	0.2794
Q	45.9496	33.1444	0.0906	17.9217	0.7829

Clast B3 Pyroxene wt. %

Point#	CaO	MnO	FeO	Na2O	K2O
19	7.2816	0.273	13.9139	0.0334	0.0081
20	4.6804	0.3237	20.247	0.0058	0.0013
21	6.5259	0.382	22.2217	0.0196	0
22	11.0569	0.4028	28.5025	0.0449	0.0043
23	12.1781	0.4491	31.7632	0.0148	0.0081
24	4.4494	0.3745	22.2529	0.0119	0.0013
25	4.0387	0.3531	21.7593	0.0192	0.0149
27	3.521	0.4146	23.3468	0.0107	0.0039
28	3.437	0.4271	24.4295	0	0
A	4.252	0.3398	21.9446	0.0265	0.0111
B	4.321	0.3255	18.9464	0.0133	0.002
C	4.7066	0.3232	19.079	0.0039	0.0093
D	5.5998	0.3128	19.0754	0.0108	0.0068
E	2.6875	0.3627	19.8205	0.0094	0.0031
F	3.4367	0.3525	19.6473	0.0189	0
G	9.8791	0.3391	22.4374	0.0133	0
H	4.6931	0.3697	22.3396	0.0265	0.004

Clast B3 Olivine wt. %

Point#	MgO	CaO	MnO	FeO	NiO
18	29.5139	0.0778	0.3583	33.9411	0.0407
26	31.4537	0.3039	0.3301	31.1018	0.0126

Clast B3 Feldspar wt. %

Point#	Na2O	K2O	Total
31	0.1337	0.136	99.4172
32	0.0766	0.1344	99.2303
33	0.0891	0.3806	98.7341
34	0.0268	0.0972	99.5538
I	1.02	0.1325	99.5162
J	0.7189	0.2751	98.7867
K	1.238	0.1059	99.0114
L	0.9637	0.1194	98.4053
M	0.5359	0.0678	99.2573
Q	1.033	0.1185	99.0408

Clast B3 Pyroxene wt. %

Point#	Total
19	99.328
20	99.3651
21	100.0682
22	99.0185
23	99.1473
24	99.7074
25	99.2944
27	99.4214
28	99.4887
A	99.9141
B	99.8165
C	99.9196
D	99.6961
E	100.0859
F	99.6756
G	104.7136
H	99.6331

Clast B3 Olivine wt. %

Point#	Total
18	100.1513
26	99.773

Clast B3	Pyroxenes ppm			
Element	18	19	21	22
Mg25	163597.44	133188.78	81878.1	61149.61
Mg26	83732.42	111407.15	81861.13	60623.48
Si29	168436.14	246020.33	240318.97	224862.14
Si30	170592.78	247261.95	226424.63	216866.97
Ca43	<1177.77	48974.49	59388.73	74412.8
Sc45	8.74	55.77	60.98	54.8
Ti49	250.55	3176.6	2217.41	3994.44
V51	<4.63	91.77	136.34	61.68
Cr52	42.85	4272.3	4554.77	2366.13
Mn55	2983.5	2142.72	2397.05	1953.15
Co59	86.83	8.72	28.44	19.21
Ni61	<142.80	<144.38	<155.84	<171.87
Cu65	5.75	7.64	<6.48	<6.96
Zn66	18.57	8.67	7.05	5.18
Ga69	1.84	3.66	9.05	9.94
Rb85	<2.25	<2.38	<2.56	<2.82
Sr88	5.02	11.21	50.12	79.59
Y89	0.64	10.69	6.51	10.45
Zr91	<4.20	5.7	8.01	16.12
Nb93	<0.144	<0.154	0.357	1.53
Ba137	50.87	69.31	208.18	196.39
La139	<0.089	0.162	0.41	1.35
Ce140	0.083	0.634	1.37	3.97
Pr141	<0.074	0.092	0.144	0.598
Nd146	<0.22	0.6	0.9	2.23
Sm147	<0.39	<0.48	<0.37	1.01
Eu151	<0.166	<0.144	0.268	0.36
Gd157	<0.68	0.99	<0.71	<0.83
Tb159	<0.081	0.141	0.107	0.184
Dy163	<0.233	1.7	1.16	1.64
Ho165	<0.072	0.416	0.232	0.427
Er166	<0.253	1.46	1.04	1.29
Tm169	<0.058	<0.094	0.118	0.184
Yb172	<0.23	1.61	0.95	1.46
Lu175	<0.058	0.169	0.126	0.139
Hf178	<0.207	<0.30	0.23	0.31
Pb208	0.57	0.312	0.41	0.48
Th232	<0.059	<0.087	0.064	<0.070
U238	<0.037	<0.033	<0.034	<0.043
Cr53	46.88	4280.27	4539.63	2380.04
Yb173	<0.37	1.61	0.81	<0.73

Clast B4	Plagioclase ppm		
Element	C47	C48	C49
Mg25	35826.66	33615.96	24516.2
Mg26	38055.53	31897.03	25318.95
Si29	209417.48	216204.69	205343.31
Si30	256105.58	263400.69	209993.41
Ca43	90758.91	110272.82	97051.73
Sc45	85.39	61.47	28.76
Ti49	6905.85	8068.24	2579.66
V51	46.25	35.6	6.32
Cr52	2247.18	2364.77	943.78
Mn55	2454.44	1856.14	1239.03
Co59	27.25	19.64	11.63
Ni61	<29.03	<28.40	<28.18
Cu65	22.96	10.44	5.7
Zn66	12.59	8.94	4.98
Ga69	564.4	37.14	40.57
Rb85	<0.60	<0.58	<0.61
Sr88	468.66	144.81	189.41
Y89	35.04	101.32	14.51
Zr91	48.76	163.98	27.35
Nb93	1.82	12.99	0.678
Ba137	10225.82	650.29	642.26
La139	3.24	36.49	1.9
Ce140	10.04	98.4	5.43
Pr141	1.53	11.99	0.835
Nd146	7.86	54.6	3.97
Sm147	3.02	14.06	1.49
Eu151	0.766	1.158	1.27
Gd157	4.57	15.54	1.86
Tb159	0.844	2.48	0.339
Dy163	5.67	16.98	2.48
Ho165	1.25	3.64	0.552
Er166	3.75	10.05	1.6
Tm169	0.565	1.51	0.261
Yb172	3.65	8.68	1.78
Lu175	0.66	1.28	0.266
Hf178	1.85	4	0.84
Pb208	0.195	0.67	0.26
Th232	0.299	2.29	0.259
U238	0.16	0.462	0.119
Cr53	<-NaN	<-NaN	<-NaN
Yb173	<-NaN	<-NaN	<-NaN

CHAPTER II
OXIDATION STATE OF IRON IN FULGURITES AND TRINITITE:
IMPLICATIONS FOR REDOX CHANGES DURING ABRUPT HIGH-
TEMPERATURE AND PRESSURE EVENTS

A version of this chapter has been published by Sarah E. Roberts, Abigail A. Sheffer, Molly C. McCanta, M. Darby Dyar, and Elizabeth C. Sklute:

Sarah E. Roberts, Abby A. Sheffer, Molly C. McCanta, M. Darby Dyar, and Elizabeth C. Sklute "Oxidation State of Iron in Fulgurites and Trinitite: Implications for Redox Changes During Abrupt High-Temperature and Pressure Events." *Geochimica et Cosmochimica Acta*. 266 (2019): 332-350.

I was responsible for sample petrography and geochemical analysis. I did an extensive overview of previous research, compiled data, and wrote this manuscript. This research was based on research originally done by Abigail Sheffer, however we collected and used new and different data for this manuscript. Molly McCanta collected data and provided edits. M. Darby Dyar provided data and edits. Elizabeth Sklute also helped in data collection and processing. This article was reviewed by anonymous peer reviewers and revised 3 times.

Abstract

Understanding the geochemical effects of shock metamorphism that occur on planetary surfaces is critical when using potentially shocked planetary samples. Fulgurites, formed by lightning strikes on Earth's surface, could provide an analog for understanding shock metamorphism, because the intense heat and pressure of impact events are similar to those experienced during lightning strikes. The oxidation state generated during impact is the result of temperature (above 2000 K) and pressure (above 10 GPa) conditions, though the composition and physical nature of the country rock are also important. Atomic explosions such as the Trinity nuclear test and the resulting melted surface material Trinitite can also serve as proxies of shock metamorphism. This study compares samples of fulgurite and Trinitite glasses with the associated country rock using petrography, backscattered electron images, and Mössbauer spectroscopy, with a focus on evaluating redox changes associated with lightning-induced and atomic explosion metamorphism as a function of target material. Two fulgurite melts were also subjected to additional analysis using x-ray absorption spectroscopy to assess potential spatial variations in redox state via in-situ microscale measurements. Results indicate lightning-induced redox variations are heterogeneous at micron scales, although the net effect is overall target reduction with an average reduction of Fe₃₊ by 66%. Moreover, the data show that the physical state of the country rock (i.e., particulate vs. solid rock) has an effect on the magnitude of how the lightning-induced metamorphism effects are observed.

Introduction

Oxygen is the most abundant element in the terrestrial planets and meteorite parent bodies, samples from which provide a record of oxygen present throughout Solar System history (Davis et al., 2008; Wadhwa, 2008). The presence of oxygen is recorded in the redox state of multivalent elements, which is controlled by the activity of oxygen, or oxygen fugacity (fO_2) (Frost, 1991). Redox conditions govern many geochemical reactions in planetary interiors including the differentiation of a rocky body to form a core and mantle (Macpherson, 2008), magmatic composition and volatile concentration, and the evolution of planetary atmospheres (Wadhwa, 2008).

Igneous rocks from planetary bodies provide a record of the intrinsic oxidation state prevalent during their formation (e.g., Carmichael, 1991). Extraterrestrial materials record fO_2 variations of nine orders of magnitude from reducing (i.e., aubrite meteorites at iron-wüstite (IW)-5) to oxidizing (i.e., nakhlites at IW+4) (Wadhwa, 2008). In terrestrial rocks, fO_2 exhibits the largest variation of any physical parameter, including temperature and pressure, and shows nine orders of magnitude change in fO_2 (Carmichael, 1991; Frost, 1991). Therefore, constraining the equilibration fO_2 of a magmatic system is imperative for understanding planetary evolution, magmatic generation, and the past influence of water on terrestrial bodies (Herd et al., 2002).

Investigations of redox state often rely on iron, which is the fourth most abundant element in the Earth's crust and the most common rock-forming multivalent element in planetary samples: Fe^0 , Fe^{2+} , and Fe^{3+} (Frost, 1991; Berry et al., 2003; Herd, 2008). Concentrations of Fe species can be used to determine the redox state of the environment where they equilibrated. However, primary melt redox ratios may be altered through processes such as mineral fractionation and metasomatism (e.g., Ague, 1998; McCammon, 2005; Papike et al., 2005). For example, in subduction zones, oxygen liberated from a subducting slab can metasomatize the overlying mantle wedge (Brandon and Draper, 1996; Frost and Ballhaus 1998; Parkinson and Arculus, 1999), while lavas at mid-ocean ridges are subjected to degassing and hydrogen loss (Christie et al., 1986). Both processes increase fO_2 . Alternatively, Fe^{3+} is incompatible in some mantle minerals due to crystallographic constraints and may not be reflective of equilibrium redox conditions (McCammon, 2005; Papike et al., 2005).

Shock metamorphism (French, 1966, 1988; Grieve, 1991) is a prevalent form of alteration on terrestrial bodies resulting from hypervelocity impact. With intense temperatures (100°C up to 10,000°C) and pressures (from less than 2 up to 400 GPa) possible, shock metamorphic changes are often greater in scale than those observed during typical terrestrial metamorphism (French, 1998; Stöffler et al., 2018). Results of shock metamorphism range from mineral, textural, or chemical alteration to complete vaporization of target materials. There are also profound effects on the radiometric ages recorded in shocked rocks, which may be reset to the time of impact (Nyquist et al., 1997; Shearer et al.,

2006; Stöffler et al., 2018). In addition, shock metamorphism may also alter the oxidation state of the target material, which poses a substantial obstacle when interpreting the geochemical equilibration conditions recorded in igneous rocks (Stöffler et al., 2018). Changes to fO_2 occur on a much greater order of magnitude during shock metamorphism compared to pressure and temperature changes. An increase in temperature from 200° to 600°C has the ability to change fO_2 by 30 orders of magnitude (Frost 1991). To accurately measure the intrinsic oxidation state of samples that may have experienced shock metamorphism, it is necessary to identify potential redox state changes that may have occurred within the context of the original rock's chemistry and texture. This issue forms the core motivation for this paper.

Shocked samples are not common in the rock record on Earth as many have been subsequently altered through additional geologic processing (Grieve, 1991; French, 1998). Meteorite samples have many unknowns related to body of origin and target material (McSween, 2000). Therefore, to better constrain the effects of shock conditions and target material properties on the resulting melt redox state, alternate materials must be considered. Lightning strikes can be good analogues for impact processes because they have P and T effects and durations that can be comparable to planetary impacts. The intense heat and pressure (temperatures above 2000 K and pressures above 10 GPa) generated during a lightning strike occur within tens of microseconds and may melt the target material, resulting in a fulgurite, a glassy material fused by lightning (Grapes and Müller-Sigmund, 2010; Gieré et al., 2015; Chen et al., 2017). Similar to the glass created during lightning strikes, nuclear explosions such as the atomic bomb test at the Trinity site in 1945 also produced glass referred to as Trinitite as a result of high temperatures (~1600°C) and pressures (> 8 GPa) experienced during the explosion (Eby et al., 2015).

Features associated with traditional impact materials, such as shocked quartz (pressures from 10-34 GPa), have been identified in fulgurites and Trinitite (Sheffer et al., 2006; Carter et al., 2010; Pasek et al., 2012; Ende et al., 2012; Eby et al., 2015; Gieré et al., 2015; Chen et al., 2017; Stöffler et al., 2018) suggesting conditions may correlate with shock metamorphism. Even though lightning strikes produce alterations similar to those of impacts, the changes that occur during a lightning strike will be distinguished from those occurring during impacts by the term lightning-induced metamorphism. The terrestrial availability of fulgurites offers a unique opportunity to study the effects of target composition, physical properties, and volatile content on the redox conditions generated during lightning impact, allowing for comparisons between pre and post-impact redox state to be made.

Previous studies on fulgurites have explored the possible mechanisms for changes in redox state. Extreme reduction has been seen in fulgurites (Weeks et al., 1980; Essene and Fisher, 1986; Pasek et al., 2012; Plyashkevich et al., 2016). The availability of carbon in the target material has been suggested to lead to reduction (Essene and Fisher, 1986; Pasek and Block, 2009; Elmi et al.,

2017) but it has also been shown that reduction can occur without carbon present (Jones et al., 2005). An alternative method of shock reduction was proposed by Jones et al. (2005) to arise from shock wave propagation through the target material however shocked minerals were not observed in early fulgurite studies (i.e., Essene and Fisher, 1986) making this theory difficult to substantiate. The identification of shocked minerals in fulgurites indicates that this method of reduction may be viable. Shocked quartz in Trinitite along with native metals indicate that Trinitite is also formed in a reducing environment, possibly reduced by the same methods as fulgurites (Eby et al., 2015).

Although common, reduction is not always seen in fulgurites (Grapes and Müller-Sigmund, 2010). In an attempt to constrain the conditions under which reduced or oxidized fulgurites are produced, Pasek et al. (2012) studied 57 fulgurites formed in sand, clay, caliche, and rock and divided the fulgurites morphologically into four types dependent on the country rock they were formed in. They found that morphology varied with several factors including country rock composition, country rock water content, and the energy of the lightning strike. They suggested that the composition and physical characteristics (i.e., particulate vs. solid) of the country rock could provide different heating rates that may or may not allow volatilization of alkalis and changes in oxidation state.

This project uses a suite of nine natural fulgurite samples along with Trinitite that were collected along with the country rock (i.e., pristine unmelted material) in which they were formed (Sheffer, 2007). We present geochemical analyses of the fulgurite-country rock pairs and Mössbauer data to evaluate the redox effects of lightning-induced and atomic explosion metamorphism as a function of the chemical and physical state of the target material. In addition, x-ray absorption spectroscopic (XAS) analyses of iron redox were undertaken on two of the fulgurite samples to determine potential spatial variations in oxidation state at microscale.

Samples Studied

Samples for this study were obtained from mineral dealers and museums and were selected to include both target material and glass (Table 1). Four samples (Algeria, Mount Ararat, Oregon, and West Virginia) occurred in rock targets (Figure 1A), while the other 6 formed in unconsolidated material (Figure 1B). We have grouped the fulgurites according to the types based on target material as designated by Pasek et al., 2012: 1) quartz sand, 2) unconsolidated soil and/or rock and 4) consolidated rock (type 3 fulgurites are not used in this study). In each case, samples of the country rock were carefully removed by handpicking under a binocular microscope and crushed for subsequent Mössbauer analyses. In some cases, this was difficult because the different phases (i.e., country rock and unmelted material) were all the same color; this resulted in some cross-contamination that is evident in some of the Mössbauer data.

Table 2.1. Samples Studied and Mössbauer Results

Sample Name	Provenance	Country Rock Type	Fulgurite Type (Pasek et al., 2012)
Black Rock	Black Rock, UT	Quartz sand	1
Monahans	Monahans Sandhills, TX	Quartz sand	1
Pecos Plain	Pecos Plain, TX	Quartz sand	1
Starke	Starke, FL	Quartz sand	1
Sugarland	Sugarland, TX	Quartz sand	1
Oregon	Cline Butte, OR	Unconsolidated basalt talus	2
Algeria	Algeria	Granite	4
Mount Ararat	Mount Ararat, Turkey	Basalt rock	4
West Virginia	Cacapon River District, West Virginia	Sandstone rock	4
Trinite	Trinity Site, NM, now White Sands Missile Range	Arkose	-

Table 2.1 continued

Grain Size (mm)	% Fe₃₊ Country Rock	%Fe₃₊ Glass
~0.5	48	37
~0.2	100	58
0.1-1.2	100	46
~0.2	57	58
0.2-0.4	58	47
0.2-0.4	18	30
0.15-0.2	40	19
0.05-0.5	24	30
~1.0	12	33
0.1-0.3	76	27

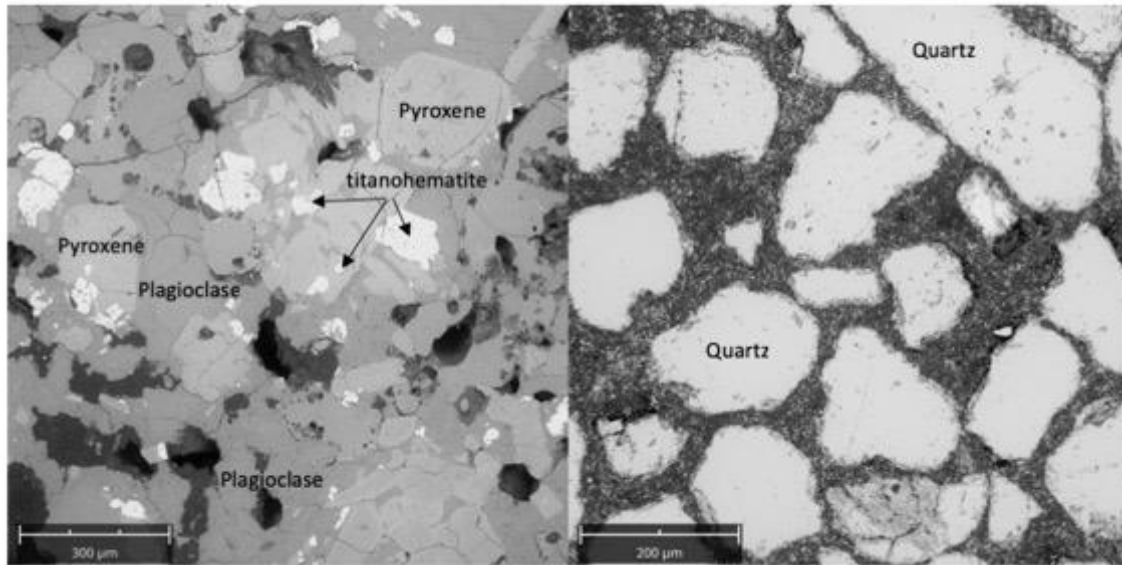


Figure 2.1. Examples of non-impacted target lithologies. A) Basalt rock from Mount Ararat B) Quartz sand from Sugarland, Texas.

The Black Rock, Utah sample (Figure 2A) is a quartz sand fulgurite. It is a thin, flattened tube with a central void present in some portions, but absent in others. The fulgurite glass color ranges from white to black to orange. Grains of unmelted sand adhere to the outside of the tube. The glassy body of the fulgurite is vesicular, and the vesicles appear to be elongated radially away from the center.

The fulgurite from Monahans, Texas was collected in the Monahans Sandhills by co-author Sheffer. The fulgurite is a narrow, hollow tube of white to gray glass with many adhered external sand grains (Figure 2B). The tube exhibits a slight spiraling of irregular ridges down the length of the sample, similar to those noted by Fenner (1949).

The Pecos Plains, Texas fulgurite (Figure 2C) formed from quartz sand with traces of Fe-rich clay. It is a hollow, uneven tube with one end partially blocked by a 1 cm diameter pebble. The tube consists of a thin layer of glass inside and cemented sand grains outside. The fulgurite glass color ranges from white to gray or tan. The sample was obtained from the Mineralogical Research Company.

The Starke, Florida sample is a quartz sand fulgurite (Figure 2D). It has a delicate, hollow tubular shape consisting of a thin layer of glass inside the tube with partially melted and unmelted sand grains adhered to the outside. The fulgurite glass color ranges from white to orange to dark gray. The sample was obtained from the Nature Source Collection.

The Sugarland, Texas fulgurite formed in primarily quartz sand (Figure 2E). It has an open tube lined with gray glass. The tube exterior is white to pink in color, and many sand grains are cemented to the outside. Parts of the fulgurite tube are ringed or spiraled in appearance.

The Cline Butte, Oregon fulgurite (Figure 2F) formed in unconsolidated basalt talus. The glassy, tubular interior is black, and the external partially melted material is dark gray. Several 0.5 cm rock chips are embedded in the glassy matrix. The sample was obtained from the Mineralogical Research Company.

The Algeria fulgurite (Figure 2G) is a rock fulgurite that formed in a quartz-rich igneous rock (granite). Unlike a typical fulgurite, it has no central void yet has a radial symmetry with ridges running down the length of the fulgurite. The white to gray fulgurite glass is highly vesicular with vesicles elongated and radiating out from the center of the fulgurite (Figure 2G). Partially melted grains are adhered to the outside edges. The sample was obtained from Michael Farmer Meteorites.

The Mount Ararat, Turkey fulgurite formed in solid basalt (Figure 2H). The sample has no central void, but the roughly circular glassy interior surrounded by partially melted material is shaped similarly to more typical fulgurites. The glass is dark green to black, and the external material is dark gray. This sample was provided by the Smithsonian Institution (NMNH #52093).

The West Virginia fulgurite formed in sandstone rock. It has an off-center tube with a surrounding area of vesicular, friable glass (Figure 2I). The interior of

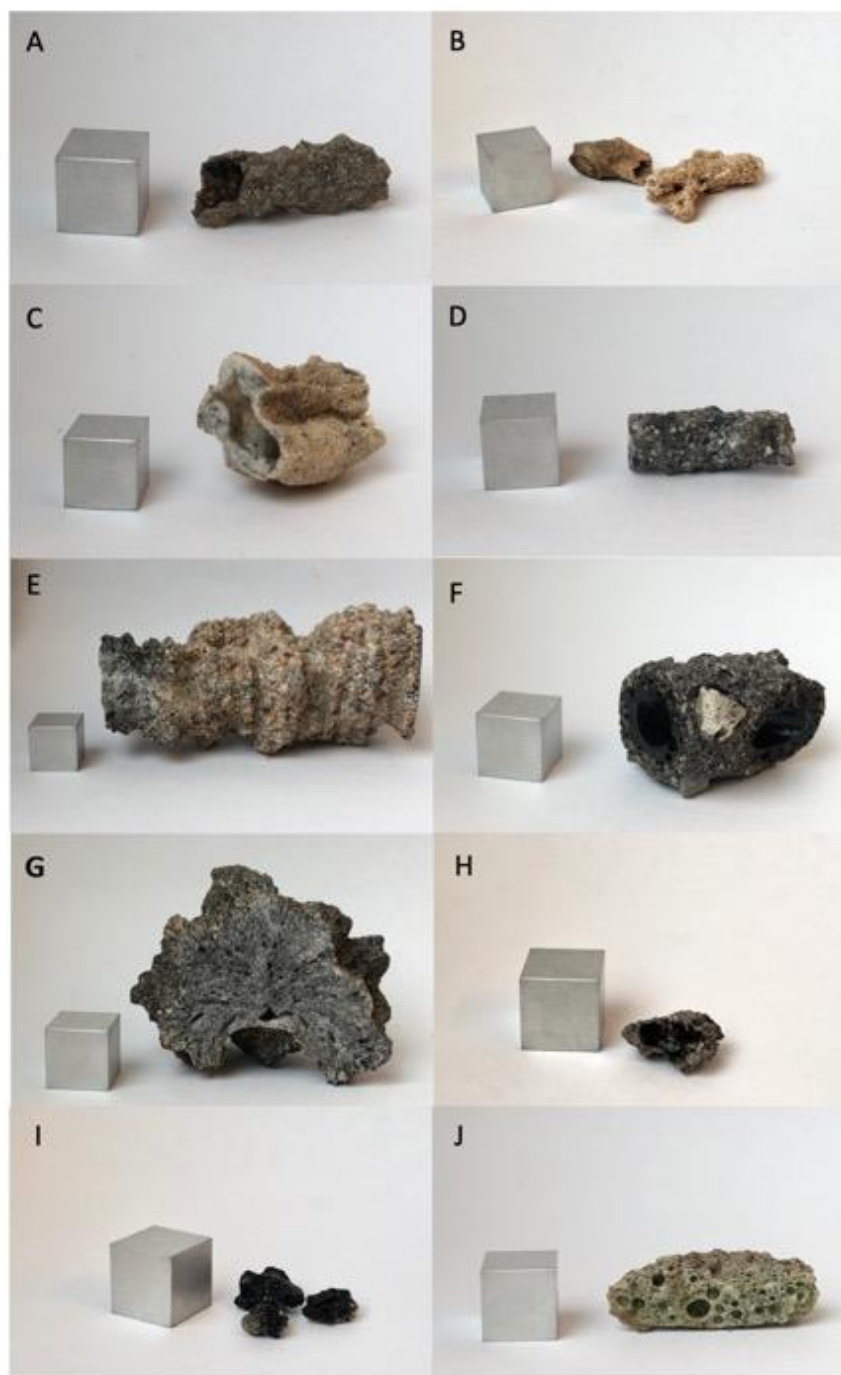


Figure 2.2. Photos of hand samples used in this study. The metal cube represents 1cm³. A) Black Rock, Utah, B) Monahans, Texas, C) Pecos Plains, Texas, D) Starke, Florida, E) Sugarland, Texas, F) Cline Butte, Oregon, G) Algeria, H) Mount Ararat, I) West Virginia, and J) Trinitite.

the tube is white, but the majority of the glass is black or dark gray. The dusty outer surface is white to gray in color. Melted but unmixed grains of quartz glass are present throughout the fulgurite. The sample was obtained from the Mineralogical Research Company.

Trinitite is green glass (Figure 2J) named for the Trinity Site, New Mexico (now White Sands Missile Range), where the first nuclear bomb test on July 16, 1945 melted the desert arkosic sand in a roughly circular radius of ~340 m (Eby et al., 2015). The glass formed an irregular, thin crust on the ground of ~1 cm thickness. Traditionally, it has been assumed that the glass formed in place simply from heating of the desert surface; however, a more recent study suggests that some of the glass may have rained down from the explosion cloud as droplets (Hermes and Strickfaden, 2005). The original location where this sample formed relative to the detonation tower is not known as this sample was collected by someone who worked at the site. Based on the appearance of this sample, it probably formed within 30 to 210 m from the detonation tower (Eby et al., 2015). The analyzed sample has a smooth, glassy surface with a few vesicles on one side and a rough surface with embedded, partially melted rocks on the other side. The smooth side is interpreted to be the upper surface that experienced the highest heat, while the rough side is interpreted to be the lower surface in contact with the unmelted ground. The sample was obtained from the Mineralogical Research Company.

Analytical Methods

Scanning electron microscope and electron probe microanalysis

Images and chemical analyses were collected from polished sections made from each fulgurite sample to provide textural and geochemical data for the melts. Back Scattered Electron (BSE) images were collected on a Phenom Pro XL scanning electron microscope (SEM) at the University of Tennessee with an accelerating voltage of 10 kV under low vacuum. Major and minor element analyses were collected on polished thick sections with electron probe microanalysis (EPMA) using a Cameca SX-100 electron probe at the University of Tennessee. An accelerating voltage of 15 kV, current of 10 nA, and a defocused beam of 10 μm was used for the analyses. Peak counting times were 20 seconds for Si, Al, Ca, Na, and K and 30 seconds for Fe, Mn, Cr, P, Ti, and S. To minimize volatile loss effects in the glass analyses, Na and K were measured first and second respectively, for a count time of 5 seconds, repeated four times to determine the zero intercept. Well-characterized synthetic and natural standards were used for calibration.

Mössbauer analysis

For Mössbauer analyses, 300 mg of sample were used for low Fe samples (i.e. sands) while 20-40 mg was used for high Fe samples including basalts. Samples were gently crushed under acetone, diluted with sugar to provide a thin absorber, and gently heaped in a sample holder confined by kapton tape. Mössbauer spectra were acquired at 295K using a source of 100-60 mCi ^{57}Co in Rh on a WEB Research Co. model WT302 spectrometer at Mount Holyoke College. For each spectrum, the fraction of the baseline due to the Compton scattering of 122 keV gammas was subtracted. Run times were 1-7 days, and baseline counts ranged from ~1-40 million after the Compton correction, as needed to obtain reasonable counting statistics. Several samples were so low in Fe that they required more than a week of run time to obtain sufficient signal to noise ratios. Spectra were collected in 2048 channels and corrected for nonlinearity via interpolation to a linear velocity scale defined by the spectrum of the 25 μm Fe foil used for calibration.

To model the Mössbauer data, two in-house programs generously made available to us by Eddy DeGrave and Toon VanAlboom at the University of Ghent, Belgium, were used. For all spectra except those noted below, the Dist3e program was used. It models spectra using model-independent quadrupole splitting or hyperfine field distributions for which the subspectra are constituted by Lorentzian shaped lines; it uses velocity approximations rather than solving the full Hamiltonian. This program does not presume any particular shape of the distribution (hence, model-independent).

For both the Monahans fulgurite and the Black Rock country rock, the Mexfieldd program was used because the spectra contained heavily overlapped distributions; satisfactory fits could not be obtained with Dist3e. The Mexfieldd program was developed for magnetic Fe_{2+} spectra in which the quadrupole interaction cannot be regarded as a first-order perturbation on the magnetic interaction. As a consequence, the magnetic Fe_{2+} spectrum is not a simple sextet with approximately 3:2:1:1:2:3 area ratios; in fact, up to eight absorption lines may be observed. To fit such spectra, the full hyperfine-interaction Hamiltonian must be set up (including not only the common hyperfine interaction parameters but also the asymmetry parameter and direction of the electric field gradient). It is then necessary to diagonalize this Hamiltonian to calculate the transition energies (and hence the velocities of the absorption lines) and the transition probabilities for the different nuclear energy levels in order to obtain the line intensities of the eight Lorentzian absorption lines. The Mexfieldd program executes this procedure for a superposition of a discrete number of subspectra. Although these spectra did not contain magnetic components, they did contain four overlapped Fe_{3+} distributions that could not be modeled with Dist3e due to its model-independent nature. Mexfieldd was thus used to provide Lorentzian line shapes and the capability of solving the full Hamiltonian.

A variety of parameter constraints and models for varying numbers of doublets and sextets were used to model the spectra. In general, widths of peaks

in pairs or sextets were held constant. Values of quadrupole splitting, hyperfine field, and peak area were generally allowed to vary freely, though constraints were used rarely to keep isomer shift values realistic.

Errors on isomer shifts are estimated at ± 0.04 mm/s because of high peak overlap and low signal-to-noise ratios. Quadrupole splitting values are ± 0.05 mm/s. The distribution of area among multiple Fe^{2+} doublets/sextets or among multiple Fe^{3+} doublets/sextets is probably ± 10 -30% absolute, but the summed areas of all Fe^{3+} components relative to the total area are accurate to within ± 1 -3% absolute. Areas of Fe^{3+} components were not corrected for differential recoil-free fractions because the appropriate correction factors are unknown.

X-ray absorption spectroscopy analysis

To investigate the localized effects of redox state, two select fulgurite samples (Cline Butte and Starke) were also subjected to x-ray absorption spectroscopic (XAS) analysis. X-ray absorption spectroscopy spectra were collected at the GeoSoilEnviroCARS beamline at Advanced Photon Source, Argonne National Lab using a spot size of $1 \times 1 \mu\text{m}$. To quantify the redox state of Fe in silicate melts, a suite of calibration glasses representing geologically relevant compositions from komatiite to rhyolite were synthesized under a range of $f\text{O}_2$ (McCanta et al., 2015; Dyar et al., 2016). A multivariate prediction model was built from the data using an in-house Python software package that relies on partial least squares analysis that considers every channel of data followed by lasso regression to remove the channels that are deemed to be less informative (Dyar et al., 2016). More detailed information about the modeling and software package can be found in Dyar et al. (2016).

Results

Fulgurite and Trinitite petrography

Lightning strikes into soil results in fused material that can be separated from the loose soil while lightning strikes into rock is the entire assemblage of fused material along with surrounding rock (Pasek et al., 2012). Fulgurites are generally cylindrical shape and single or multiple voids in the center from escaping volatiles during fulgurization. The morphology of the fulgurite is the result of the temperature and pressure gradients experienced in the soil from the lightning strike. The soil in direct contact with the lightning strike is vaporized, creating a central void, while the area around it is boiled producing vesicles and voids (Pasek et al., 2012). The central void represents the direction that the current traveled and smaller voids may extend radially from this void. The central void is usually glassy while the exterior of the fulgurite will contain partially melted or even adhered unaltered material. Rock fulgurites can result in heterogeneous glass as the minerals in the target rock melt congruently.

The quartz sand fulgurite from Black Rock, Utah (Figure 3A) is vesicular and homogenous with an almost pure SiO_2 composition (Table 2). Small metal

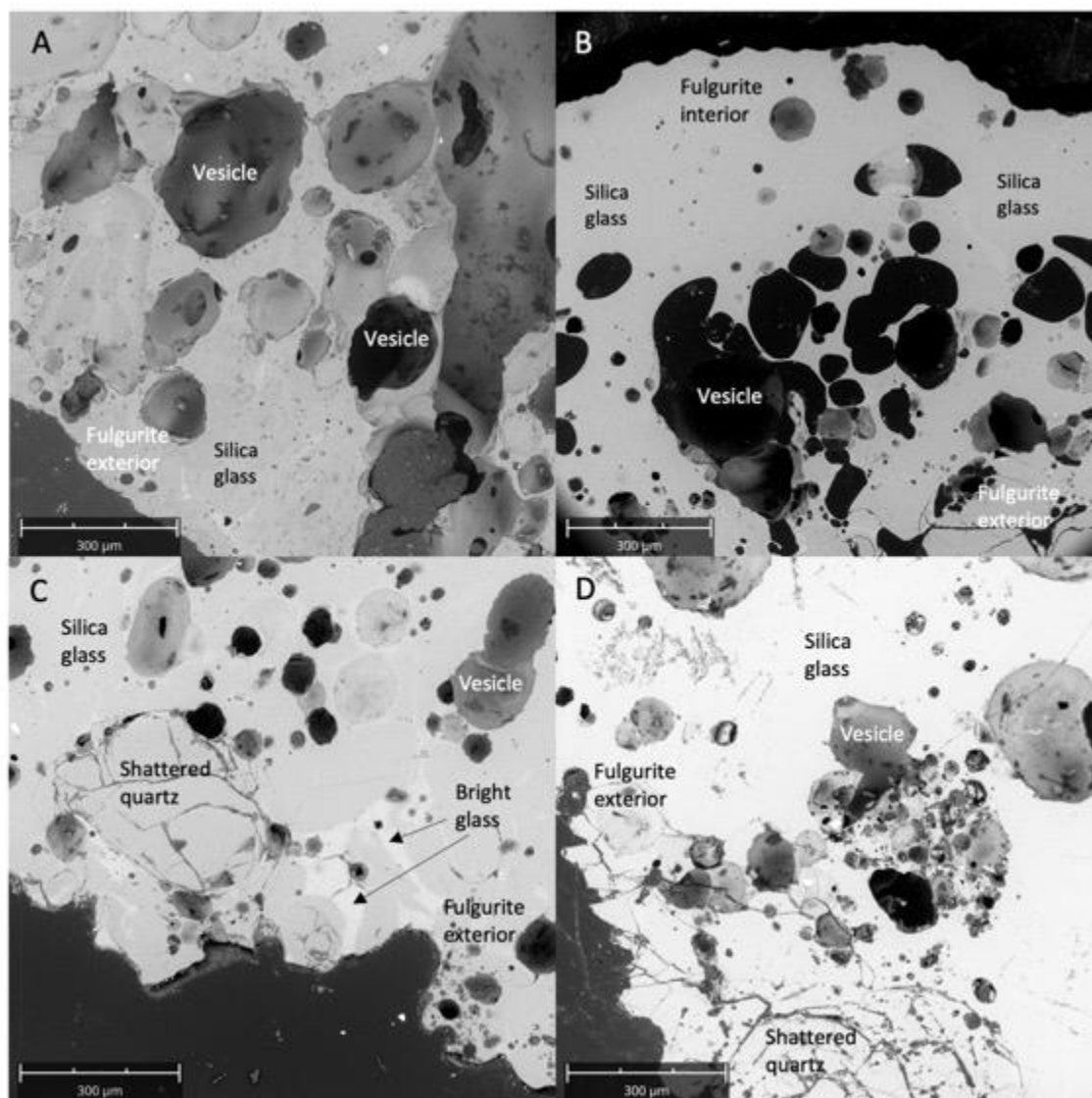


Figure 2.3. Backscattered electron (BSE) images of fulgurites investigated for this study. A) Black Rock, Utah, B) Monahans, Texas, C) Pecos Plain, Texas, and D) Sugarland, Texas

Table 2.2. Glass Compositions

Fulgurite		<i>SiO₂</i>	<i>TiO₂</i>	<i>Al₂O₃</i>	<i>Cr₂O₃</i>	<i>MgO</i>	<i>CaO</i>
Algeria	Glass	95.7±2.75	0.01±0.01	0.01±0.01	0.00±0.01	0.00±0.00	0.00±0.01
	Bright glass	70.7±2.22	5.89±1.42	10.4±1.82	0.01±0.01	0.78±0.13	0.28±0.05
Black Rock	Glass	99.3±0.58	0.02±0.01	0.14±0.24	0.00±0.00	0.00±0.00	0.01±0.00
Monahans	Glass	98.6±0.78	0.02±0.02	0.24±0.38	0.01±0.02	0.02±0.01	0.01±0.01
	Bright glass	64.4±3.25	0.64±0.83	18.8±1.72	0.01±0.02	0.74±0.64	0.55±0.46
Mount Ararat	Glass	58.6±2.74	1.26±0.40	19.7±2.97	0.00±0.01	2.80±1.28	6.57±1.61
	Bright glass	51.9±0.00	4.10±0.00	14.9±0.00	0.02±0.00	5.25±0.00	5.62±0.00
Oregon	Glass	58.5±2.74	1.17±0.40	18.5±2.97	0.02±0.01	3.26±1.28	5.72±1.61
	Bright glass	52.3±0.00	2.02±0.00	15.8±0.00	0.02±0.00	5.91±0.00	6.11±0.00
	Dark glass	72.5±0.82	0.14±0.00	13.8±0.96	0.01±0.01	0.22±0.09	1.36±0.09
Pecos Plains	Glass	97.9±2.11	0.02±0.04	0.51±0.80	0.00±0.00	0.03±0.04	0.02±0.03
	Bright glass	69.0±2.70	0.00±0.00	18.1±2.66	0.01±0.01	0.12±0.10	0.11±0.11
Starke	Glass	98.9±0.78	0.01±0.01	0.04±0.01	0.00±0.00	0.00±0.00	0.01±0.01
	Bright glass	65.1±8.34	0.15±0.06	9.63±4.98	0.00±0.00	0.11±0.05	1.29±2.03
Sugarland	Glass	99.3±0.05	0.02±0.03	0.02±0.02	0.02±0.02	0.84±0.00	0.01±0.01
	Bright glass	73.6±7.82	7.84±10.9	6.87±5.41	0.04±0.03	0.00±0.32	4.84±2.86
West Virginia	Dark glass	99.3±4.08	0.02±0.07	0.24±1.61	0.00±0.01	0.01±0.06	0.01±0.06
	Bright glass	90.9±0.91	0.27±0.02	5.95±0.38	0.01±0.00	0.20±0.02	0.10±0.01
Trinite	Dark glass	99.5±2.95	0.02±0.68	0.00±1.93	0.00±0.00	0.00±0.18	0.02±5.37
	Bright glass	64.0±0.47	0.75±0.02	13.2±0.00	0.00±0.00	1.19±0.00	0.07±0.02

Table 2.2 Continued

Fulgurite		<i>MnO</i>	<i>FeO</i>	<i>Na₂O</i>	<i>K₂O</i>	<i>Total</i>
Algeria	Glass	0.00±0.01	0.01±0.01	0.01±0.00	0.04±0.03	95.9±2.72
	Bright glass	0.08±0.03	3.67±0.77	0.18±0.12	2.37±0.62	94.5±1.77
Black Rock	Glass	0.00±0.00	0.04±0.04	0.02±0.03	0.06±0.1	99.6±0.27
Monahans	Glass	0.00±0.00	0.04±0.05	0.01±0.02	0.09±0.17	99.0±0.38
	Bright glass	0.02±0.1	2.82±1.43	0.31±0.27	7.50±7.09	95.9±1.29
Mount Ararat	Glass	0.09±0.05	5.34±2.37	4.82±0.55	0.94±0.36	100.3±1.80
	Bright glass	0.14±0.00	11.6±0.00	4.62±0.00	1.01±0.00	99.6±0.00
Oregon	Glass	0.13±0.05	6.96±2.36	3.99±0.55	1.26±0.36	99.7±1.80
	Bright glass	0.21±0.00	11.7±0.00	2.86±0.00	0.80±0.00	97.9±0.00
	Dark glass	0.04±0.02	1.67±0.72	4.51±0.08	3.07±0.10	97.3±1.11
Pecos Plains	Glass	0.00±0.00	0.09±0.10	0.05±0.08	0.17±0.23	98.8±1.04
	Bright glass	0.00±0.00	0.55±0.46	1.11±0.32	10.3±0.75	99.4±0.19
Starke	Glass	0.00±0.00	0.05±0.05	0.01±0.01	0.01±0.02	99.0±0.73
	Bright glass	0.08±0.03	19.0±9.75	1.18±1.42	1.88±0.77	98.7±0.86
Sugarland	Glass	0.00±0.00	0.01±0.01	0.01±0.02	0.01±0.02	99.4±0.47
	Bright glass	0.03±0.02	1.96±0.89	0.4±0.23	1.92±0.89	98.5±1.20
West Virginia	Dark glass	0.01±0.06	0.05±0.57	0.02±0.06	0.09±0.34	99.7±3.35
	Bright glass	0.12±0.02	0.90±0.05	0.08±0.03	0.99±0.17	99.8±0.36
Trinite	Dark glass	0.00±0.03	0.02±0.53	0.04±0.37	0.05±0.82	99.7±0.52
	Bright glass	0.07±0.01	2.72±0.02	1.98±0.03	2.60±0.05	99.4±0.42

inclusions were observed in some regions. Larger vesicles in the fulgurite are slightly elongated and are oriented radially away from the center of the fulgurite (Figure 3A).

Back scattered electron images of the Monahans, Texas, fulgurite indicate very homogenous, vesicular glass with no metal inclusions (Figure 3B). The quartz sand country rock resulted in a Si-rich fulgurite glass composition (Table 2). Cracked quartz grains are adhered to the outside of the fulgurite. Isolated pockets of frothy glass (~300 μm) are found included in the outer edges of the fulgurite. Small areas of BSE bright glass occur around cracked quartz grains on one side of the fulgurite (Figure 3B). The brighter glass contains decreased SiO_2 and increased Al_2O_3 and K_2O compared to the primary quartz glass (Table 2).

Back scattered electron images of the Pecos Plains, Texas, quartz sand fulgurite, show a very vesicular, compositionally homogenous glass of almost pure SiO_2 (Figure 3C; Table 2). Occasional faint traces of BSE brighter glass, possibly bordering former minerals grains that were melted during fulgurization are observed in the outer edges of the fulgurite. This brighter glass has a lower SiO_2 and higher Al_2O_3 and K_2O , approximately a feldspar composition (Table 2). Shattered quartz grains (200 μm) are included in the glass near the outer edge of the fulgurite.

The glass in the Starke, Florida quartz sand fulgurite is homogenous and SiO_2 -rich (Figure 4A, Table 2). Few vesicles and no original or shattered grains were noted. Pockets of brighter glass containing less SiO_2 and more Al_2O_3 and FeO are found in the outer margins of the glass (Table 2).

The composition of the Sugarland, Texas fulgurite reflects the quartz sand country rock that was fused to form the fulgurite. Back scattered electron images show that the fulgurite is primarily vesicular, homogenous SiO_2 glass (Figure 3D; Table 2). Pockets of BSE brighter glass are found around quartz grains along the outer edges of the fulgurite. The BSE brighter glass contains less SiO_2 and more TiO_2 , Al_2O_3 , CaO , and FeO (Table 2). Incompletely melted mineral grains and large shattered grains (up to 700 μm) are included in the outer edges of the fulgurite.

The Cline Butte, Oregon, fulgurite was formed in basalt talus. Back scattered electron images show radial variation in the texture of the fulgurite; the area around the central void is mostly glass and grades into unaltered basalt (Figure 4B). The glass is predominantly basaltic, however streaks of brighter glass, of basaltic andesitic composition, are present (Table 2). Small pockets (200-500 μm) of darker, more vesicular glass with higher SiO_2 and K_2O , and lower MgO , FeO , and CaO are included in the glass. Minerals from the target material, including pyroxene, plagioclase, quartz, and ulvöspinel are observed in the glassy matrix.

Back scattered electron images of the Algeria fulgurite preserve some of the original granitic texture of the target (Figure 5A). Large areas of homogenous silica glass with shattered and melted mineral grains are observed throughout the fulgurite. Veins and pockets of brighter glass delineate the borders of minerals

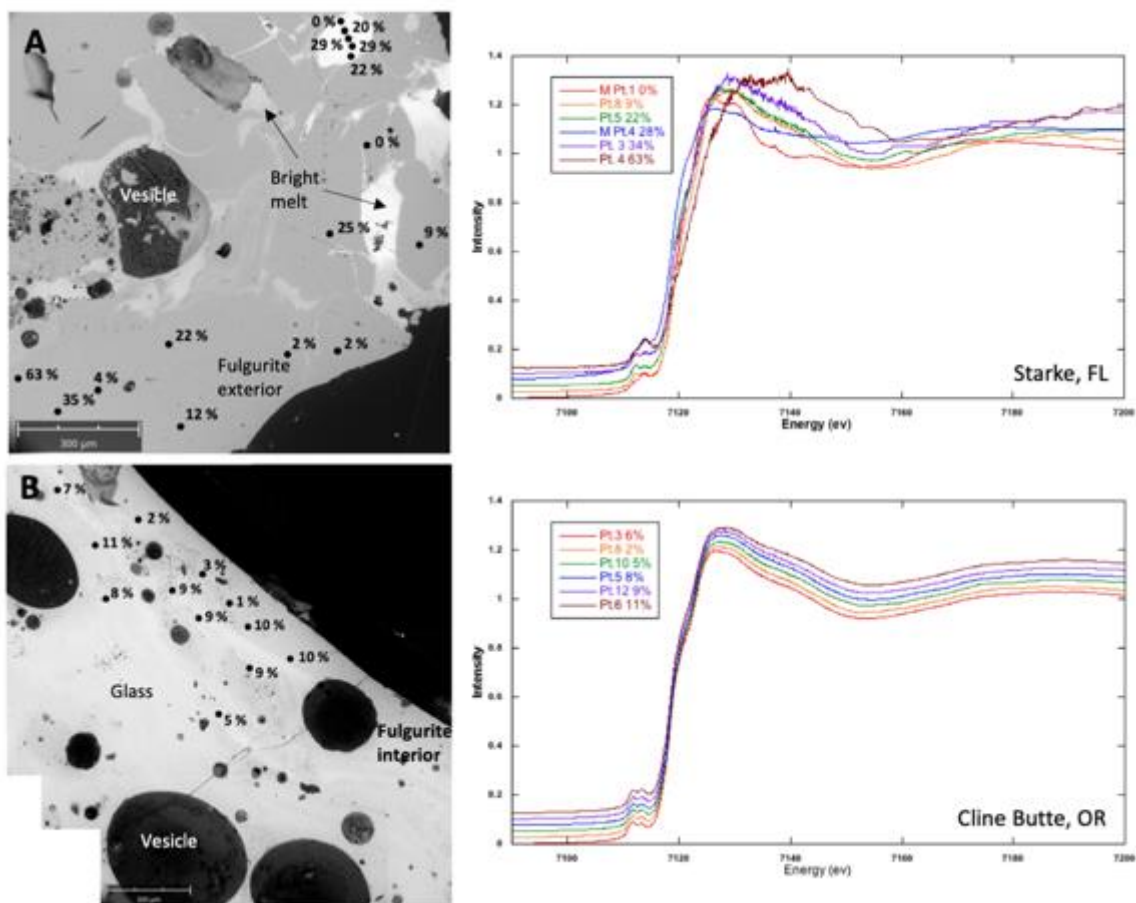


Figure 2.4. XAS spot locations with predicted Fe³⁺ and spectra for Starke, Florida and Cline Butte, Oregon fulgurites.

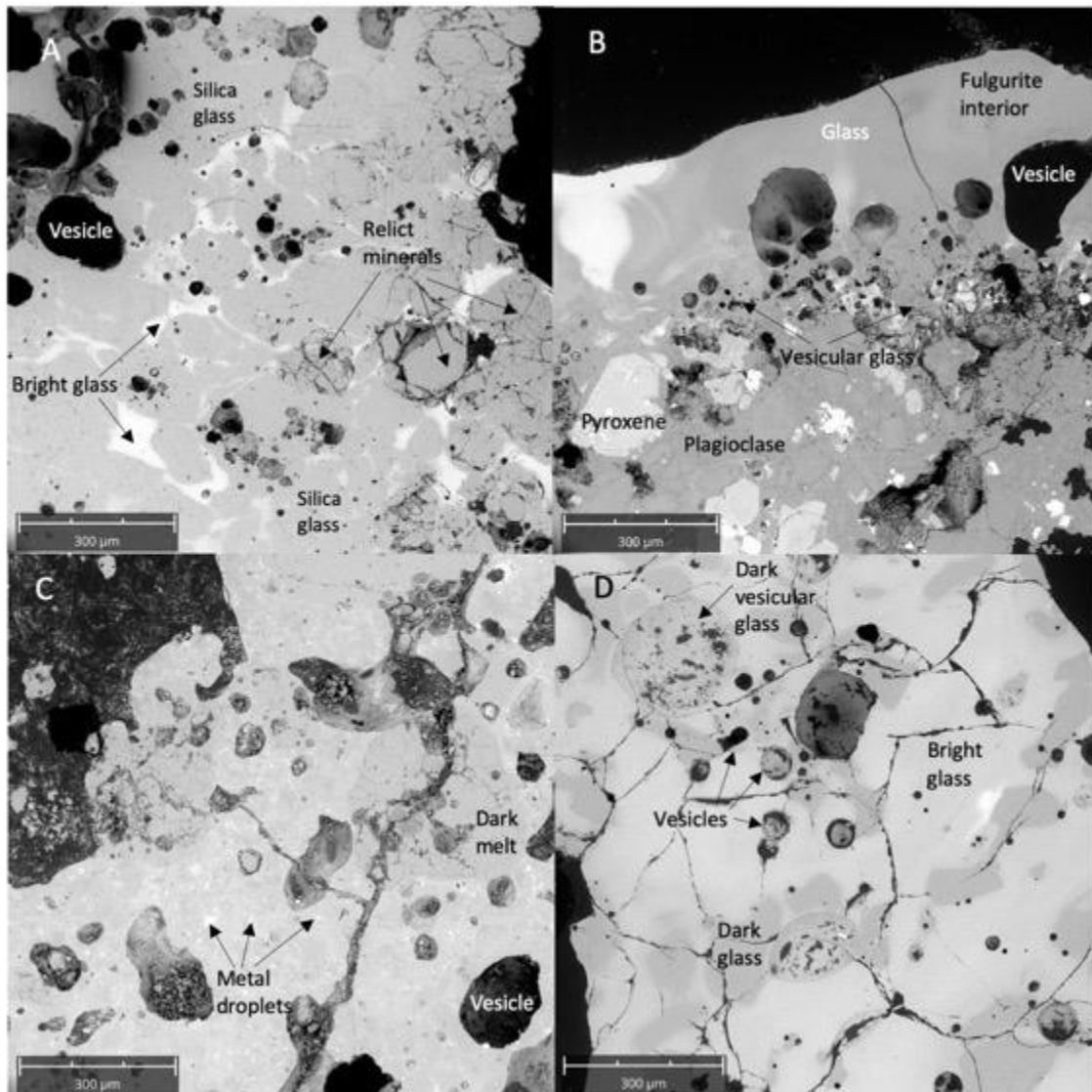


Figure 2.5. Backscattered electron (BSE) images of fulgurites and Trinitite investigated for this study. A) Algeria, B) Mount Ararat, C) West Virginia, and D) Trinitite.

that were melted during fulgurization. The composition of the glass is almost entirely SiO_2 ; brighter glass (Figure 5A) has less SiO_2 with increased TiO_2 and Al_2O_3 (Table 2). Small droplets of Fe metal are visible in some portions of the fulgurite in BSE. Textural variations are observed in the melt with larger areas of glass and elongated vesicles near the central cavity transitioning to glass with unmelted, shattered mineral grains towards the outer edges of the fulgurite (Figure 5A). Unmelted grains are adhered on the outside.

The Mount Ararat fulgurite is primarily original, unmelted basalt country rock with only a small area of inhomogeneous glass in the interior of the fulgurite (Figure 5B). The outer portion of the fulgurite contains large (200-250 μm) intact phenocrysts of plagioclase and zoned pyroxene with small phenocrysts (up to 200 μm) of titanohematite. A highly vesicular glass borders the contact between the fulgurite glass and the target basalt that is reflective of the original basalt composition (Figure 5B; Table 2). Brighter melt pockets within the fulgurite glass is basaltic-trachyandesitic in composition (Table 2).

The West Virginia fulgurite formed in sandstone country rock (Figure 5C). The glass is heterogenous with abundant metal droplets (1 to 10 μm , up to 100 μm across) scattered throughout. Both BSE dark (pure SiO_2) and light (less SiO_2 , more Al_2O_3) melts are observed (Table 2). In some areas, the glass is streaky or isolated in pockets. Shattered quartz grains (50-100 μm) are observed throughout. The interiors of the larger metal droplets (>50 μm) contain 99% pure metallic Si and several different iron silicides – fersilicite (FeSi), ferdissilicite (FeSi_2), and FeTiSi_2 . The smaller droplets (~5 μm) also contain hapkeite (Fe_2Si) and an unnamed FeSi. These metal phases are fairly unique in the shock metamorphic literature. The only other report of FeTiSi_2 is from a soil and glacial till fulgurite from Winans Lake, Michigan, identified by Essene and Fisher (1986). Similarly, the only previous occurrences of hapkeite is in a fulgurite studied by Pasek et al., 2012 and the lunar meteorite Dhofar 280 inside maskelynite glass (Anand et al., 2004).

The Trinitite glass differs from the other samples having been formed by an atomic explosion at the Trinity site. The country rock at the site is arkosic sand with quartz, feldspar including plagioclase (Eby et al., 2015). The resulting glass is heterogeneous and contains two different glass compositions. Because they delineate the shape of former mineral grains that were melted and fused during the explosion (Figure 5D), these may represent melted quartz and feldspar grains. The dark glass is representative of a quartz composition, and the BSE bright glass is approximately feldspathic in composition (Table 2). Cracks run throughout this sample, some along former mineral boundaries.

Mössbauer results

The Mössbauer spectra in this project presented considerable challenges to the technique due to the low Fe contents of most samples, the fact that glass has no crystal structure (resulting in a broad variety of Fe valence states and sites), and the fact that many of these samples are multiphase. However, by

Table 2.3a. Mössbauer Parameters

Assignment	Mössbauer Parameter	Algeria		Black Rock		Monahans		Mount Ararat	
		rock	glass	rock	glass	rock	glass	rock	glass
octahedral Fe ₂₊	□ (mm/s)	0.65	0.77	0.62	0.60		0.53		0.70
	□ (mm/s)	1.78	1.58	1.64	1.63		1.85		1.72
	□ (mm/s)	1.00	1.00	0.87	1.00		1.12		1.01
	Area	0.25	0.30	0.10	0.13		0.30		0.36
octahedral Fe ₂₊	□ (mm/s)	0.40	0.30					0.45	0.27
	□ (mm/s)	2.25	2.18					2.08	2.08
	□ (mm/s)	1.11	1.10					1.11	1.13
	Area	0.16	0.08					0.34	0.18
octahedral Fe ₂₊	□ (mm/s)			0.41	0.60		0.62		
	□ (mm/s)			2.53	2.62		2.60		
	□ (mm/s)			1.23	1.35		1.12		
	Area			0.07	0.02		0.12		
octahedral Fe ₂₊	□ (mm/s)								
	□ (mm/s)								
	□ (mm/s)								
	Area								
(IV) Fe ₃₊	□ (mm/s)						0.59		
	□ (mm/s)						1.39		
	□ (mm/s)						0.90		
	Area						0.16		
octahedral Fe ₃₊	□ (mm/s)	0.69					0.26	0.48	0.77
	□ (mm/s)	0.63					1.31	0.63	0.99
	□ (mm/s)	0.43					0.43	0.44	0.34
	Area	0.16					0.06	0.24	0.30
octahedral Fe ₃₊	□ (mm/s)			0.32	0.30	0.52	0.21		
	□ (mm/s)			0.98	0.80	0.88	0.94		
	□ (mm/s)			0.29	0.37	0.31	0.27		
	Area			0.06	0.04	0.25	0.05		
tetrahedral Fe ₃₊	□ (mm/s)	0.26	0.26	0.77	0.47	0.40	0.36		
	□ (mm/s)	0.56	0.54	0.58	0.54	0.43	0.53		
	□ (mm/s)	0.12	0.13	0.25	0.16	0.29	0.15		
	Area	0.24	0.19	0.42	0.33	0.75	0.31		
sextet Fe oxide	□ (mm/s)			0.53					
	□ (mm/s)			0.00					
	□ (mm/s)			-0.05					
	B _{Hf} (kOe)			340.0					
sextet Fe oxide	area			0.16					
	□ (mm/s)	0.40	0.40	0.80	0.50			0.34	0.40
	□ (mm/s)	-0.02	-0.01	-0.07	0.04			-0.18	-0.22
	□ (mm/s)	0.01	0.01	0.45	0.02			0.36	0.38
	B _{Hf} (kOe)	329.1	331.4	520.0	318.6			515.10	509.5
	area	0.19	0.43	0.19	0.48			0.42	0.15
□ ₂		7.17	12.14	0.88	9.89	4.39	1.71	1.83	1.20
% Ferric		40	19	48	37	100	58	24	30

Table 2.3b. Mössbauer Parameters

Assignment	Mössbauer Parameter	Oregon		Pecos Peak		Starke		Sugarland	
		rock	glass	rock	glass	rock	glass	rock	glass
octahedral Fe ₂₊	□ (mm/s)	0.48	0.41		0.40	0.70	0.70	0.30	0.87
	□ (mm/s)	1.60	1.67		1.72	1.65	1.73	1.62	1.68
	□ (mm/s)	1.01	1.04		1.09	1.10	1.17	1.00	1.00
	Area	0.28	0.26		0.21	0.31	0.34	0.07	0.36
octahedral Fe ₂₊	□ (mm/s)	0.24	0.30						0.30
	□ (mm/s)	2.01	2.09						2.02
	□ (mm/s)	1.11	1.07						1.14
	Area	0.23	0.13						0.08
octahedral Fe ₂₊	□ (mm/s)	0.30			0.40	0.50	0.50	0.30	
	□ (mm/s)	2.52			2.44	2.33	2.48	2.46	
	□ (mm/s)	1.11			1.07	1.21	1.31	1.22	
	Area	0.18			0.15	0.12	0.08	0.11	
octahedral Fe ₂₊	□ (mm/s)	0.24	0.53						
	□ (mm/s)	3.02	2.58						
	□ (mm/s)	1.15	1.07						
	Area	0.13	0.31						
(IV) Fe ₃₊	□ (mm/s)	0.30	0.44		0.91				
	□ (mm/s)	1.05	1.17		1.20				
	□ (mm/s)	0.91	0.99		0.90				
	Area	0.07	0.10		0.36				
octahedral Fe ₃₊	□ (mm/s)	0.54	0.73						
	□ (mm/s)	0.96	0.99						
	□ (mm/s)	0.33	0.48						
	Area	0.12	0.21						
octahedral Fe ₃₊	□ (mm/s)			0.30		0.30	0.30		
	□ (mm/s)			1.16		1.23	1.23		
	□ (mm/s)			0.43		0.48	0.48		
	Area			0.12		0.04	0.05		
tetrahedral Fe ₃₊	□ (mm/s)			0.30		0.30	0.30		
	□ (mm/s)			0.84		0.87	0.87		0.30
	□ (mm/s)			0.29		0.31	0.30		1.02
	Area			0.45		0.21	0.15		0.36
sextet Fe oxide	□ (mm/s)								0.36
	□ (mm/s)							0.30	0.30
	□ (mm/s)							0.79	0.57
	B _{Hf} (kOe)							0.31	0.15
sextet Fe oxide	Area							0.13	0.11
	□ (mm/s)			0.51	2.98	4.75	4.77	0.30	0.30
	□ (mm/s)			100	46	57	58	-0.29	0.06
	□ (mm/s)							0.28	0.52
sextet Fe oxide	B _{Hf} (kOe)							506.50	515.80
	Area							0.24	0.09
	□ ₂	1.77	1.45	0.51	2.98	4.75	4.77	2.14	3.81
	% Ferric	18	30	100	46	57	58	58	47

Table 2.3c. Mössbauer Parameters

Assignment	Mössbauer Parameter	Trinite		W. Virginia	
		rock	glass	rock	glass
octahedral Fe ₂₊	□ (mm/s)	0.70	0.26	0.65	0.30
	□ (mm/s)	1.65	1.64	1.60	1.62
	□ (mm/s)	1.01	1.04	1.06	0.87
	Area	0.14	0.20	0.44	0.09
octahedral Fe ₂₊	□ (mm/s)				
	□ (mm/s)				
	□ (mm/s)				
	Area				
octahedral Fe ₂₊	□ (mm/s)		0.30	0.26	0.70
	□ (mm/s)		2.23	2.37	2.33
	□ (mm/s)		1.06	1.07	1.28
	Area		0.28	0.26	0.10
octahedral Fe ₂₊	□ (mm/s)	0.26	0.32	0.22	
	□ (mm/s)	3.17	2.50	2.75	
	□ (mm/s)	0.88	1.10	1.14	
	Area	0.09	0.16	0.18	
(IV) Fe ₃₊	□ (mm/s)		0.30		
	□ (mm/s)		1.20		
	□ (mm/s)		1.10		
	Area		0.18		
octahedral Fe ₃₊	□ (mm/s)	0.26	0.70		
	□ (mm/s)	1.14	1.06		
	□ (mm/s)	0.77	0.70		
	Area	0.03	0.18		
octahedral Fe ₃₊	□ (mm/s)	0.35			
	□ (mm/s)	0.84			
	□ (mm/s)	0.35			
	Area	0.26			
tetrahedral Fe ₃₊	□ (mm/s)	0.30			0.32
	□ (mm/s)	0.51			0.44
	□ (mm/s)	0.39			0.30
	Area	0.28			0.33
sextet Fe oxide	□ (mm/s)				0.40
	□ (mm/s)				1.35
	□ (mm/s)				0.62
	B _{Hf} (kOe)				82.90
	area				0.49
	□ ₂	0.76	0.66	9.71	1.19
	% Ferric	76	27	12	33

employing long run times and highly sophisticated fitting strategies, we were able to obtain fairly robust fits to all spectra, as given in Table 3a,b,c. It is important to note that doublet parameters that represent Fe in glass are expected to be highly variable because the number of sites in a glass is a function of its bulk composition and cooling history. Therefore, there is no a priori reason to expect similar parameters among different samples. However, the characteristics of Fe oxides, where present, are fairly distinctive, though they vary with grain size and subtle compositional variations. Thus the plots of Mössbauer data for different samples are not expected to look alike; only the difference between the country rock and the fulgurite for each sample is important.

The Black Rock Utah sample was shocked in quartz sand. This sample contains blebs of Fe metal with more metal in the fulgurite (48% of the total Fe) than in the country rock separate (19%). Iron metal is shown as being present in the country rock due to fulgurite glass inadvertently contaminating the country rock sample. This is clearly seen in Figure 6A, because the sextets are prominent, and they conspicuously become larger in the shocked samples. For this Utah sample, there is also a small sextet arising from hematite that is present only in the unshocked sample.

The quartz sand target material of the Monahans, Texas fulgurite was initially completely oxidized to the Fe_{3+} state (Figure 6B), consistent with the Fe oxides observed in BSE. After shock, the fulgurite glass is considerably more reduced, with only 60% of the Fe as Fe_{3+} . The new Fe_{2+} doublet is evident in the spectra (Figure 6B) by its prominent doublet at ca. 0.3 and 2.1 mm/s.

The Pecos Plains quartz sand is completely oxidized (100% Fe_{3+}), possibly due to the presence of hematite impurities or a small amount of clay in the source sand. The latter is the favored explanation because there is no sign of a hematite sextet in the Mössbauer data (Figure 6C). The shocked fulgurite in this case is significantly more reduced (46% Fe_{3+}).

The precursor rock for the Starke, FL fulgurite is a quartz sand. Here the Mössbauer data (Figure 6D) for the target sand and the glass show that they are identical within experimental error. Perhaps the handpicking here was again quite imperfect. Neither sample contains Fe metal nor any sign of Fe oxide such as hematite.

In contrast, the Sugarland sample does contain minor amounts of hematite: 58% of the total Fe in the precursor quartz sand and 47% of the total Fe in the fulgurite. The resultant sextet is evident in Figure 7A, though it is poorly resolved due to the overall low Fe content of this sample. The oxide must be present at extremely fine scales because it is not seen in the BSE or EMPA data.

For the Cline Butte Oregon sample, the host rock is the same as for Mount Ararat (basalt), but here the physical form of the sample is as loose, heterogeneous talus. Here it is again the case that no Fe metal is observed. However, this sample differs from that of Mount Ararat because the fulgurite appears to be slightly more oxidized (30% of the total Fe is Fe_{3+}) than the host rock (18% Fe_{3+}), such that the spectra appear quite similar (Figure 7B). However,

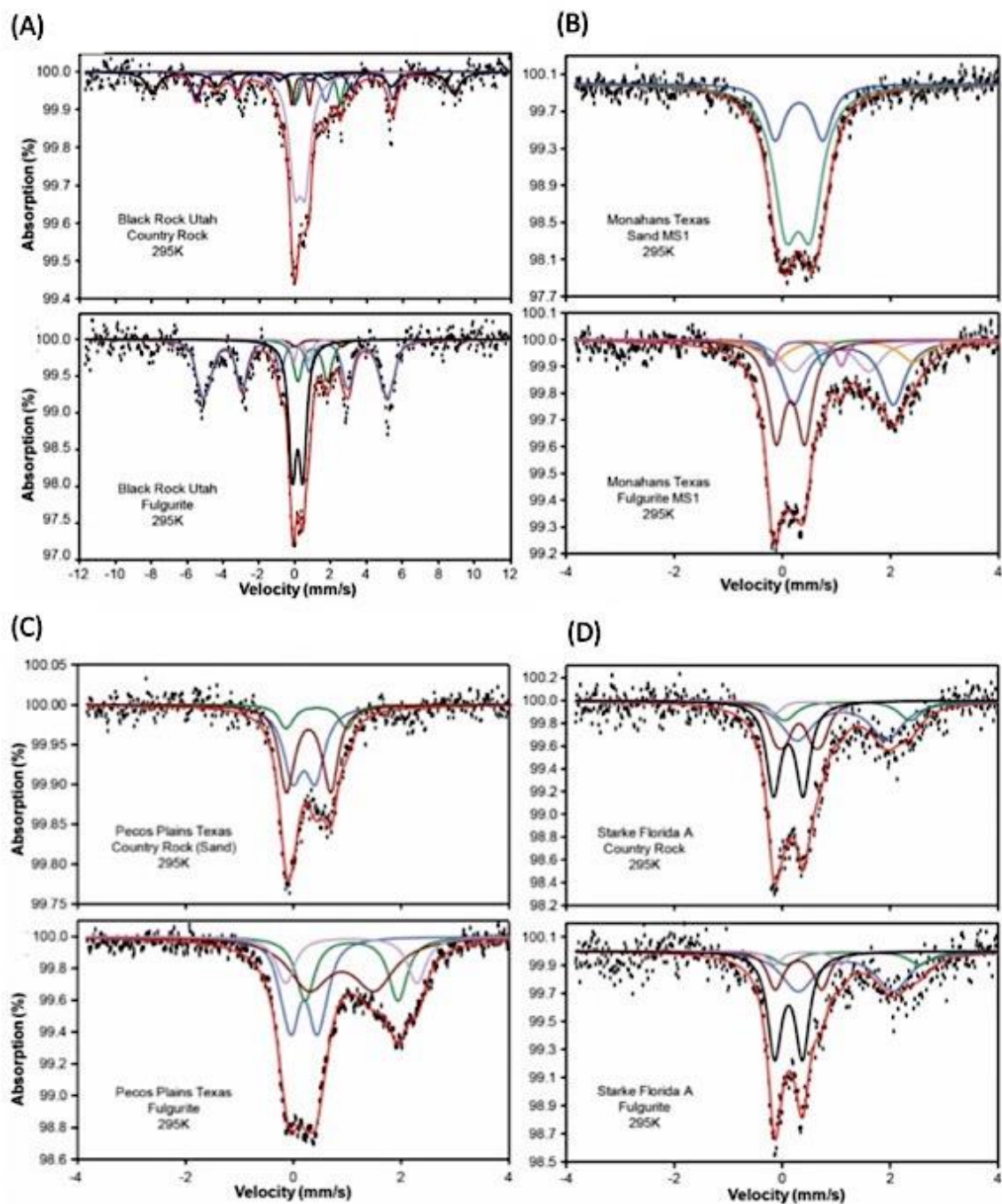


Figure 2.6. Mössbauer spectra for fulgurites and country rock. A) Black Rock, Utah, B) Monahans, Texas, C) Pecos Plains, Texas, and D) Starke, Florida

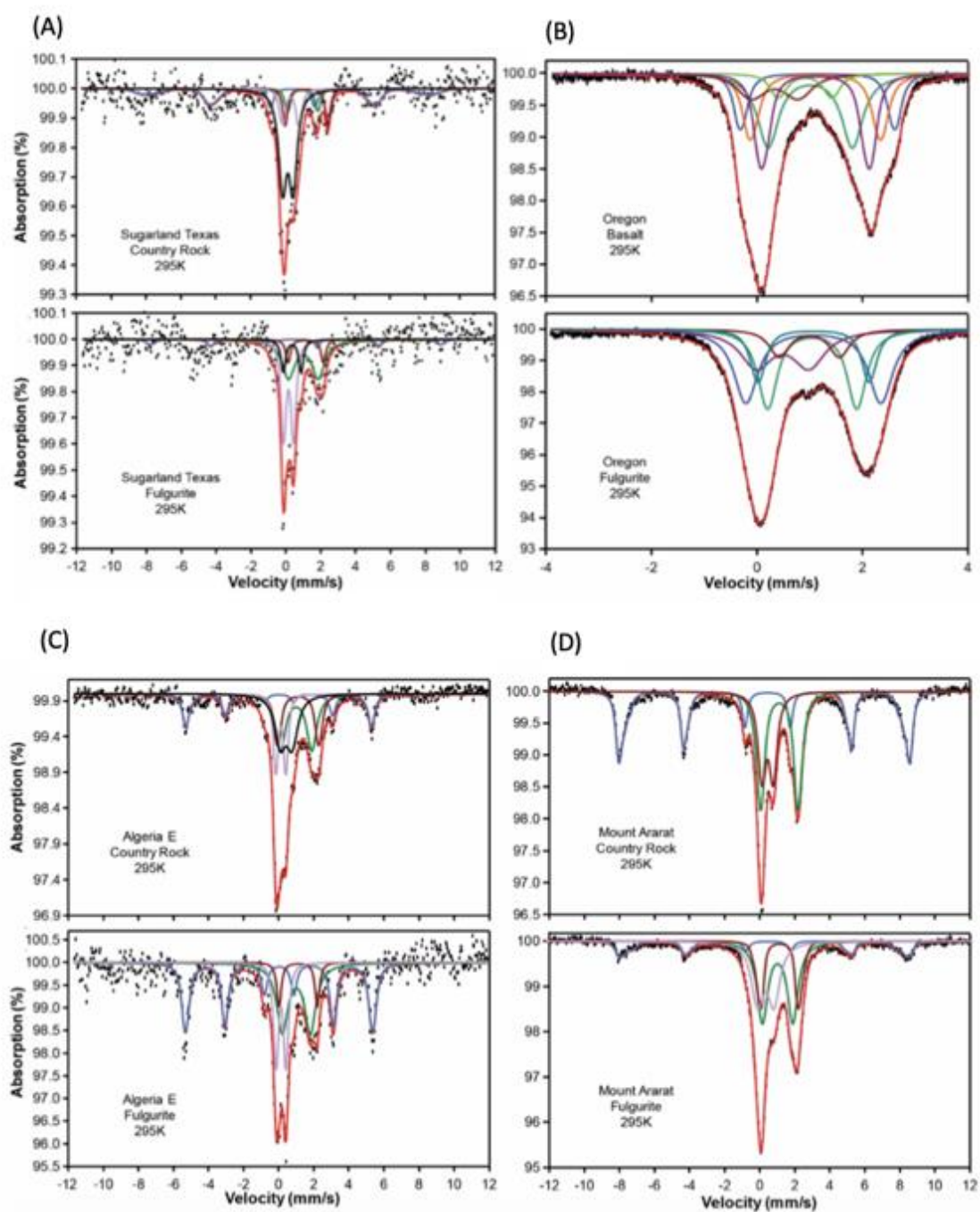


Figure 2.7. Mössbauer spectra for fulgurites and country rock. A) Sugarland, Texas, B) Cline Butte, Oregon C) Algeria, and D) Mount Ararat.

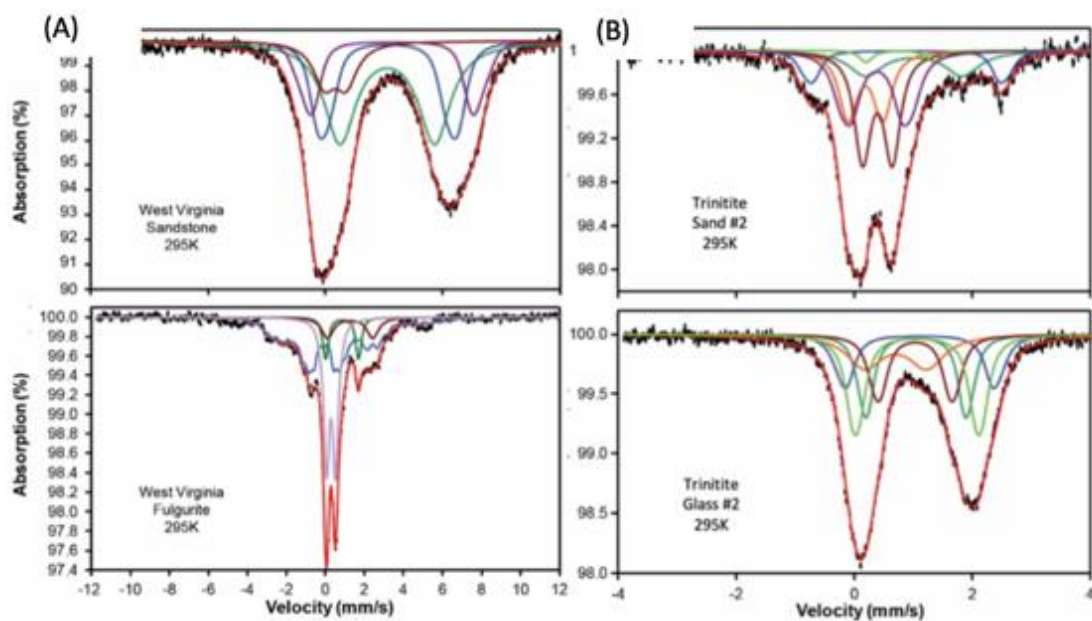


Figure 2.8. Figure 8. XAS spot locations with predicted Fe^{3+} and spectra for Starke, Florida and Cline Butte, Oregon fulgurites.

this sample is very heterogeneous, and the Fe-Ti oxide crystals are not easily distinguished in the hand sample. It is likely that in the process of hand picking the fulgurite glass pieces for analysis, ulvöspinel crystals at the edge of the glassy area were included. Because the oxide crystals tend to appear in the middle of the sample, it is possible that few or none were included with the country rock pieces taken from as close to the edge of the sample as possible. In other words, for this sample the “country rock” and “fulgurite” samples were indistinct.

Because the country rock for the Algerian sample was a quartz-rich igneous rock, it was difficult to separate the country rock from the actual fulgurite. As a result, the Mössbauer data (Figure 7C) show the presence of Fe metal in both the fulgurite and the country rock, though there is significantly more (43% of the total Fe) metal in the fulgurite than in the country rock that likely contained some fulgurite (19%). Otherwise, the data show a distribution of Fe^{3+} and Fe^{2+} in both the unshocked and shocked sample, with a bulk % Fe^{3+} of 40% in the starting rock and 19% in the fulgurite.

The Mount Ararat sample is the only one in this study that was impacted into coherent basalt – the best analog for most extraterrestrial planetary surfaces. In this case, it was easier to separate the fulgurite glass from the host basalt because the latter remained intact very close to the fulgurite. Here both shocked and unshocked samples contain hematite, as evidenced by its characteristic sextet (Figure 7D). Unlike the prior samples discussed above, the Mössbauer data show that the fulgurite glass is slightly oxidized (30% Fe^{3+}) compared to the country rock (21% Fe^{3+}), but this result could easily be a function of sampling. A very small heterogeneity in the distribution of hematite could result in a big change in the bulk Fe^{3+} contents because hematite contains so much more Fe than the basalt. Interestingly, in this sample, there was no creation of Fe metal. Perhaps this lightning strike was lower in temperature or the basalt conducted the heat away more efficiently, such that Fe metal did not form.

Finally, the West Virginia sample is somewhat anomalous in that the shocked sample is more oxidized (33% Fe^{3+}) than the precursor sandstone (12% Fe^{3+}). However, the Mössbauer fit to the fulgurite is complicated by an unresolved Fe oxide that appears to be in the intermediate state between a superparamagnetic doublet and a sextet (Figure 8A). At this temperature, it is impossible to speculate on the identity of the oxide, but its presence makes the fit difficult to interpret properly. So for this sample, the apparent oxidation with shock is likely caused by our inability to properly interpret the fulgurite spectrum.

The Trinitite sample began as highly oxidized sand at 74% Fe^{3+} , but its glass equivalent was considerably more reduced down to 27% Fe^{3+} . As seen in Figure 8B, the spectra were complicated by the presence of multiple Fe-bearing phases in this sample, and the sample itself contains populations that were likely quartz-rich (99.5 wt% SiO_2) and more feldspathic, with some more mafic minerals as well based on the microprobe compositions. No Fe metal is observed (Figure 8B), perhaps because the total amount of Fe is very low.

In summary, the Mössbauer data largely show the expected result of reduction from the lightning strikes and atomic explosions (Table 1). The few exceptions to this result can be explained away by poor separation of the country rock from the starting material or difficult-to-interpret spectra. Consistent with the idea that shock should be an inherently reducing process, Fe metal was identified in several but by no means in all the samples. This variation may have multiple indistinguishable causes: distribution of Fe in the country rock, the pressure and temperature extent of the lightning strike or explosion, and the magnitude of Fe in the bulk rock overall. The overall imprecision in our bulk analyses thus led us to pursue an alternative approach by using XAS to study redox at microscales.

XAS results

As a test to understand the extent of heterogeneity of oxidation at micro-scales, two fulgurite glasses were studied using XAS. In-situ spot analysis of the Starke, Florida fulgurite reveals significant variation in Fe³⁺ within the fulgurite glass (Figure 4). Fe³⁺ ranges from 0-63% (average = 17%). The darker, primary fulgurite glass shows the widest Fe³⁺ variation from 0 to 63%, with a change from 4 to 63% Fe³⁺ occurring within 200 μm. BSE brighter melt ranges from 0 to 29% Fe³⁺ (average = 20%). Location within the fulgurite (exterior versus interior) does not appear to influence Fe³⁺ concentration (Figure 4). The transition from Fe³⁺ to Fe²⁺ is seen in the XAS spectra as a shift in the pre-edge feature from a single peak (mainly Fe²⁺) to a double peak (increasing Fe³⁺) (Figure 4). Reduction is observed in most of the fulgurite compared to the country rock, however some areas have remained unchanged in Fe³⁺.

XAS analysis of the Cline Butte, Oregon fulgurite also reveals spatial variation in Fe³⁺ with a range in Fe³⁺ concentration from 1 to 11% (average = 7%) (Figure 4). Similar to the Starke fulgurite, Fe³⁺ concentration does not appear to be correlated with location in the fulgurite. The streaks of BSE brighter melt also do not appear to be more reduced or oxidized compared to the BSE darker melt (Figure 4B). The limited Fe³⁺ range in the Cline Butte fulgurite results in XAS spectra that are very similar with only slight changes in the pre-edge feature (Figure 4). All XAS measurements indicate that the fulgurite has been reduced compared to the 18% Fe³⁺ measured by Mössbauer in the target rock.

Discussion

Redox differences in the Mössbauer results

Mössbauer spectroscopy of the Fe³⁺ in fulgurite glass suggests that, of the ten fulgurites studied, six have been reduced, three have been oxidized, and one is unchanged. All the sand fulgurites were reduced with the exception of Starke, which is unchanged or slightly oxidized from the original Fe³⁺. Of the rock fulgurites investigated, Mount Ararat and Oregon, formed in basalt, appear

oxidized while the Algeria fulgurite, formed in granite, appears reduced. The potential oxidation of mafic material during a lightning strike is consistent with the results of Grapes and Müller-Sigmund (2010), who observed similar oxidation in a gabbro fulgurite. Pasek et al. (2012) suggested that type 4, rock, fulgurites should show less variation in Fe_{3+} from the country rock since the volatilized material can only escape through the central void of the fulgurite, and often that void is blocked by glass. Of the three rock fulgurites studied here (Algeria, Mount Ararat, and West Virginia), Algeria has experienced 52% reduction in Fe_{3+} compared to the starting Fe_{3+} while the other two are oxidized with the West Virginia fulgurite experiencing the most oxidation at almost three times more than the starting Fe_{3+} .

Back scattered electron images and EPMA analysis reveal the composition of the fulgurite glass is heterogenous at microscales with respect to major and minor elements (Table 2; Figures 3-5) and often contains a mixture of different relict phases that have been fused. Shattered and incompletely melted grains from the target material are also often embedded in the fulgurite glass. Mössbauer spectroscopy is a bulk measurement tool that requires milligrams of material to be ground and mixed. Therefore if Fe_{3+} variations are present, Mössbauer measurements represent an average redox value. This same problem applies to appearances of Fe metal in Mössbauer spectra while it may be absent from the investigated fulgurite section. The large sample amount needed to complete Mössbauer measurements leads to the possibility that unevenly distributed phases which are not present in the section of the fulgurite will be included in the bulk sample. This has the potential to be obscuring the true nature of reduction or oxidation during lightning induced metamorphism.

Spatial Variation in Redox

Fulgurites, Trinitite, and impact melts are glassy in composition without crystallites, implying a rapid quenching after formation (Arndt et al., 1984; Arndt and Engelhardt, 1987; French 1998) and resulting in geochemical heterogeneities in the melt as described above. The bulk Fe_{3+} analytical results of Mössbauer spectroscopy are therefore unlikely to capture spatial variations in redox state. X-ray absorption spectroscopy data from the Starke and Oregon fulgurite glasses show significant variations in the Fe_{3+} concentrations across the samples studied. The Starke fulgurite shows the largest variation in oxidation states, with a range in Fe_{3+} from 0-63% (average = 17%) (Figure 4). The bulk Mössbauer Fe_{3+} measurements of this fulgurite indicated (Table 1) no change to the redox state during lightning strike. The XAS measurements reveal, within error, that the majority of the glass has been reduced to some degree, with a wide range in reduction values present. They also explain why the Mossbauer results are somewhat inconclusive – likely bulk results will vary more as a function of sampling, failing to capture the subtleties of heterogeneous glass formation in the fulgurites.

X-ray absorption spectroscopic analysis of the Oregon fulgurite also shows a range of Fe^{3+} from 1 to 11% (average = 7%)(Figure 4). The original Mössbauer analysis of Oregon indicated oxidation to 30% Fe^{3+} from a target rock Fe^{3+} value of 18% (Table 2). XAS analysis indicates reduction for all analyzed material. The higher average Fe^{3+} reported by Mossbauer is likely due to difficulties in obtaining a pure glass sample. The reduced nature of Oregon, originally regarded as one of the most oxidized fulgurites in this study, suggests that other fulgurites that appear oxidized should be reexamined at micro-scales.

Mechanism of Oxidation change

Fulgurites can be either reduced, oxidized, or unchanged from the starting composition. Two theories remain to explain the reduction of fulgurites: the thermodynamic breakdown of oxides at superheated temperatures or shock wave propagation. If these theories could potentially explain the reduction of fulgurites, could either of them explain the oxidation or lack of change seen in fulgurites? Pasek et al., (2012) suggested that different country rocks could provide different heating rates and could control whether alkalis were volatilized or changes in oxidation state occurred. There is no doubt that fulgurites experience high temperatures as seen in the melting and fusion of mineral grains in the fulgurite glass. Some fulgurites, especially the rock fulgurites, do not have as much glass in them, with more unaltered minerals left behind in the outer edges of the fulgurite. It could be questioned if these fulgurites experienced the same high temperatures as the sand fulgurites that are primarily glass, but it could also be a function of the grains themselves and how closely packed (or interlocking for rock fulgurites) they are with other grains in the country rock. Of the three rock fulgurites investigated here, two have been oxidized and one reduced. Mount Ararat and Algeria fulgurites both had relict minerals in the fulgurites; however the Algeria fulgurite is reduced and the Mount Ararat fulgurite is oxidized. The Starke, Florida fulgurite is composed of homogenous glass with no original minerals remaining, which is the result of extreme and thorough heating by a lightning strike. However, that fulgurite has remained unchanged in oxidation state compared to the country rock.

Some contribution to the reduction by a process similar to electrolysis cannot be ruled out by these samples. If this process were active, it would suggest that the degree of reduction would correlate with the duration of the strike and the volume of melted glass. The longer that the lightning strike channel is in contact with the surface, the more reduced the sample would become. A longer heating period should also produce a larger volume of glass, and the interior of the glassy tube should be more reduced than the exterior. Because source materials respond differently to lightning strikes, this comparison can only be made within source material groups. The sand fulgurites are the only group with enough samples to compare glass thicknesses; however, these fulgurites have very thin tubes of glass with little variation in thickness between samples.

Because the glass tubes are thin, it is impossible to separate the inside from the outside of the tube when hand picking glass for Mössbauer analysis. The best sample set to evaluate the contribution from electrolysis would be several large fulgurites of the same rock type (e.g., basalts).

As discussed earlier, composition of the country rock controls reduction, and rock fulgurites may be more likely to be oxidized compared to sand fulgurites. Grain size of the country rock may also control reduction. The fulgurites studied here represent a range in grain sizes, with the Pecos Plains fulgurite formed in some of the smallest grains and the Black Rock fulgurite formed in some of the largest. When comparing changes in oxidation states in the fulgurites to grain sizes of the country rock (Table 1), fulgurites formed from larger grains such as West Virginia with grains of 1 mm may be more likely to be oxidized compared to fulgurites formed from smaller grains. The different grain sizes could control reduction or oxidation if the mechanism for reduction is by shock wave propagation. Pasek et al. (2012) did divide fulgurites based on different target rock composition and suggested that differing target rock could provide different heating rates that may or may not allow volatilization of alkalis and changes in oxidation state. Type 1 (sand) fulgurites should experience reduction, and most of the sand fulgurites studied here did, however our type 4 (rock) fulgurites showed both reduction and oxidation. Beyond the composition of the country rock, grain size may have an equal control on heating rates and shock wave propagation.

The formation of a fulgurite is not unlike that of an impact melt during an impact event. Temperatures can easily exceed 2000K during impact events with a shock wave that results in the spontaneous and complete melting of the target rock (French, 1998). The shocked quartz observed in fulgurites indicates that a pressure component is involved during a lightning strike (Carter et al., 2010; Ende et al., 2012; Gieré et al., 2015; Chen et al., 2017). Based on shocked quartz found in a granite fulgurite, Chen et al. (2017) modeled the amount of pressure experienced during a lightning strike into granite at greater than 7 GPa. Pasek and Hurst (2016) determined that the energy dissipated by a lightning strike was a function of the density of the target material through which it travels. Density could also be considered in terms of grain size and how closely the grains are packed. The reduction seen in a fulgurite could be the result of shock wave propagation based on grain size and packing.

A shock wave traveling through a fulgurite would affect grains differently depending on their density and location to the lightning strike. Variation is observed within fulgurite glass with completely melted glassy centers and shattered or incompletely melted grains adhered to the outside of the fulgurite. A textural difference exists radially within fulgurites as shown in BSE images demonstrating the incomplete effect of melting during a lightning strike. As previously mentioned, Mössbauer spectroscopy is a bulk analytical method that averages the Fe^{3+} within the entire fulgurite glass and fails to capture the spatial

variation in Fe_{3+} within the fulgurite glass and employing an in-situ method would help show the variation in Fe_{3+} .

Based on the results of this study, the effects of target physical properties on lightning-induced redox changes cannot be fully constrained. It is not as simple as concluding that all rock fulgurites should experience oxidation while all sand fulgurites should experience reduction. Outliers are observed even in the small sample suite studied here. The Starke sand fulgurite should be reduced, however the Mössbauer results indicate that no reduction has occurred (Table 1). Could this be caused by sampling bias in the Mössbauer mounts? Conversely, the Algeria rock fulgurite should be oxidized, however bulk Fe_{3+} data suggest reduction (Table 1). Some contribution to reduction by carbon oxidation cannot be ruled out, although the reduced dune sand fulgurites are relatively free from organic materials, supporting the conclusions of Jones et al. (2005) that carbon is not necessary for reduction in fulgurites.

The composition of the target material may also be a factor in redox changes during lightning-induced metamorphism, but again, the bulk redox results are inconclusive. The Algeria granite and quartz sand fulgurite target materials all have high SiO_2 contents and all appear reduced in the Mössbauer results. Alternatively, the West Virginia quartz sandstone fulgurite should therefore be reduced as well, but it appears oxidized in the Mössbauer results.

Although formed by a different method and at a much larger scale than the fulgurites, the 65% reduction of Fe_{3+} seen in the Trinitite supports the idea that reduction occurs by a shockwave propagating through the target material. The Trinity detonation had a pressure component of at least 8 GPa as indicated by the shocked quartz found in Trinitite glass. The grain size of the arkosic grains of the target material are also similar to the type 1, sand fulgurites that experienced reduction.

Summary

Glasses created from lightning strikes or atomic explosions serve as effective proxies to investigate impact processes. The terrestrial availability of fulgurites, Trinitite, and non-impacted target material provides an ideal situation to determine the changes in oxidation states during lightning strikes, atomic explosions, and impacts. Mössbauer spectroscopy is a robust method to measure Fe oxidation states and this technique reveals that Fe in fulgurites can be reduced from 100 to 46% Fe_{3+} , oxidized from 12 to 33% Fe_{3+} , or Fe_{3+} can remain unchanged from the starting Fe_{3+} in the target material. The change in Fe_{3+} in the most reduced fulgurites represents a change in recorded $f\text{O}_2$ by 15 orders of magnitude while oxidized fulgurites record changes by 2 orders of magnitude (Kress and Carmichael, 1991). The degree of reduction or oxidation may be attributed to compositional and density controls provided by the target material. Even for the strengths of Mössbauer spectroscopy in determining the

oxidation state of Fe, it is still a bulk method that averages any variations that exist in oxidation states. In-situ XAS analysis indicates that abrupt high-temperature and pressure alteration is generally reducing, however the amount and degree is highly variable among samples and locations within the fulgurite. Large scale spatial variation in Fe_{3+} can occur within microns in the fulgurite glass. In some cases, the $\text{Fe}_{3+}/(\text{Fe}_{2+}+\text{Fe}_{3+})$ ratios remained unchanged or even increased during lightning strikes.

X-ray absorption spectroscopy provides a spatial resolution in measuring Fe oxidation states previously not attainable by Mössbauer spectroscopy. This technique has enabled us to see that lightning strikes and ultimately impact alteration is a highly disequilibrium process that cannot be simply modeled. Considering that impacts are the prevalent and continuous form of surface alteration on planetary surfaces, this study demonstrates the need to understand the potential alteration that could occur to planetary samples. For terrestrial $f\text{O}_2$, the ratio of ferrous (Fe_{2+}) to ferric (Fe_{3+}) iron is sufficient to measure $f\text{O}_2$, however this reaction is not applicable for all planetary bodies with lower $f\text{O}_2$ (Sutton et al., 2005). At low $f\text{O}_2$, lunar rocks have been shown to contain little to no Fe_{3+} and may actually crystallize Fe_0 metal (Papike et al., 2005). To accurately measure oxidation states to lower values of $f\text{O}_2$, such as found on the Moon, multivalent elements such as Cr, V, Mn and Ti are much more suitable as they undergo valence state changes at lower $f\text{O}_2$ (Papike et al., 2005; Lanzirotti et al., 2018). This same method of comparing pre and post impacted material using XAS can be applied to other planetary samples such as lunar glass beads and agglutinates to quantify the change in $f\text{O}_2$.

Acknowledgements. Research supported by NASA Solar System Workings grant NNX16AR18G (M.C.M., M.D.D.), NASA grant NNA14AB04A (M.D.D.), and NASA RIS4E SSERVI. We would like to thank our reviewers and James Day for their thoughtful comments. We are grateful to H. Jay Melosh for early support of this project.

References

- Ague J. J. (1998) Simple models of coupled fluid infiltration and redox reactions in the crust. *Contrib. Mineral. Petrol.* **132**, 180-197.
- Anand M., Taylor L.A., Nazrov M.A., Shu J. and Mao H.-K (2004) Space weathering on airless planetary bodies: Clues from the lunar mineral hapkeite. *Proc. Nat. Ac. Sci.* **101**, 6847-6861.
- Arndt J. Engelhardt W. v., Gonzalez-Cabez J. and Meier B. (1984) Formation of Apollo 15 green glass beads. *Proc. Lunar Sci. Conf.* **5**, 225-232.
- Arndt J. and Engelhardt W. v. (1987) Formation of Apollo 17 orange and black glass beads. *Proc. Lunar Sci. Conf.* **7**, 372-376.
- Berry A. J., O'Neill H. St.C., Jayasuriya K. D., Campbell S. J. and Foran G. J. (2003) XANES calibrations for the oxidation state of iron in a silicate glass. *Am. Mineral.* **88**, 967-977.
- Brandon A. D. and Draper D. S. (1996) Constraints on the origin of the oxidation state of mantle overlying subduction zones: An example from Simcoe, Washington, USA. *Geochim. Cosmochim. Acta* **60**, 1739-1749.
- Carmichael I. S. E. (1991) The redox state of basic and silicic magmas: a reflection of their source regions? *Contrib. Mineral. Petrol.* **106**, 129-141.
- Carter E.A., Pasek M.A., Smith T., Kee T.P., Hines P. and Edwards H.G.M (2010) Rapid Raman mapping of a fulgurite. *Anal. Bioanal. Chem.* **397**, 2647-2658.
- Chen J., Elmi C., Goldsby D. and Gieré R. (2017) Generation of shock lamellae and melting in rocks by lightning-induced shock waves and electrical heating. *Geophys. Res. Lett.* **44**, 8757-8768.
- Christie D. M., Carmichael I. S. E. and Langmuir C. H. (1986) Oxidation states of mid-ocean ridge basalt glasses. *Earth Planet. Sci. Lett.* **79**, 397-411.
- Davis A. M., Hashizume K., Chaussidon M., Ireland T. R., Prieto C. A. and Lamberts D. L. (2008) Oxygen in the Sun. In *Oxygen in the Solar System* (eds. G. J. Macpherson, D. W. Mittlefehldt, and J. H. Jones), *Rev. Min. Geochem.* Mineralogical Society of America, vol. **68**. pp. 73- 92.

- Dyar M. D., McCanta M., Breves E., Carey C. J. and Lanzirotti A. (2016) Accurate predictions of iron redox state in silicate glasses: a multivariate approach using X-ray absorption spectroscopy. *Am. Min.* **101**, 744-747.
- Eby G. N., Charnley N., Pirrie D., Hermes R., Smoliga J. and Rollinson G. (2015). Trinitite redux: Mineralogy and petrology. *Am. Min.* **100**, 427-441.
- Elmi C., Chen J., Goldsby D. and Gieré R. (2017) Mineralogical and compositional features of rock fulgurites: A record of lightning effects on granite. *Am. Min.* **102**, 1470-1481.
- Ende M., Schorr S., Kloess G., Franz A. and Tovar M. (2012) Shocked quartz in Sahara fulgurite. *Eur. J. Min.* **24**, 499-507.
- Essene E.J. and Fisher D.C. (1986) Lightning strike fusion: Extreme reduction and metal-silicate liquid immiscibility. *Science* **234**, 189-193.
- Fenner C. (1949) Sandtube fulgurites and their bearing on the tektite problem. *Rec. S. Aus. Mus.* **9**, 127-142.
- French B. M. (1966) Shock metamorphism in natural materials. *Science* **153**, 903-906.
- French B. M. (1998) *Traces of catastrophe: A Handbook of Shock-Metamorphic Effects in Terrestrial Meteorite Impact Structures*. LPI Contribution No. 954, Lunar Planet. Inst., Houston, TX, USA, pp. 120.
- Frost B. R. (1991) Introduction to oxygen fugacity and its petrologic importance. In *Oxide Minerals: Petrologic and Magnetic Significance* (ed. D. H. Lindsley) *Rev. Min.* Mineralogical Society of America, vol. **25**, pp. 1-9.
- Frost B. R. and Ballhaus C. (1998) Comment on "Constraints on the origin of the oxidation state of mantle overlying subduction zones: An example from Simcoe, Washington, USA" by A. D. Brandon and D. S. Draper. *Geochim. Cosmochim. Acta*. **62**, 329-331.
- Gieré R., Wimmenauer W., Müller-Sigmund H., Wirth R., Lumpkin G. R. and Smith K. L. (2015) Lightning-induced shock lamellae in quartz. *Am. Min.* **100**, 1645-1648.
- Grapes R. H. and Müller-Sigmund H. (2010) Lightning-strike fusion of gabbro and formation of magnetite-bearing fulgurite, Cornon di Blumone, Adamello, Western Alps, Italy. *J. Min. Pet.* **99**, 67-74.

- Grieve R. A. F. (1991) Terrestrial impact: The record in the rocks. *Meteoritics* **26**, 175-194.
- Herd C. D. K., Borg L. E., Jones J. H. and Papike J. J. (2002) Oxygen fugacity and geochemical variations in the martian basalts: Implications for martian basalt petrogenesis and the oxidation state of the upper mantle of Mars. *Geochim. Cosmochim. Acta*. **66**, 2025-2036.
- Herd C. D.D. (2008) Basalts as probes of planetary interior redox state. In *Oxygen in the Solar System* (eds. G. J. Macpherson, D. W. Mittlefehldt, and J. H. Jones), *Rev. Min. Geochem.* Mineralogical Society of America, vol. **68**. pp. 527-554.
- Hermes R.E. and Strickfaden W.B. (2005) A new look at Trinitite. *Nuc. Weap. J.* **2**, 2-7.
- Jones B.E., Jones K.S., Rambo K.J., Rakov V.A., Jerald J. and Uman M.A. (2005) Oxide reduction during triggered-lightning fulgurite formation. *J. Atmos. Solar-Terrest. Phys.* **67**, 423-428.
- Kress V. C. and Carmichael I. S. E. (1991) The compressibility of silicate liquids containing Fe₂O₃ and the effect of composition, temperature, oxygen fugacity and pressure on their redox state. *Contrib. Mineral. Petrol.* **108**, 82-92.
- Lanzirotti A., Dyar M. D., Sutton S., Newville M., Head E., Carey C. J., McCanta M., Lee Lopeka, King P. L. and Jones J. (2018) Accurate predictions of microscale oxygen barometry in basaltic glasses using V K-edge X-ray absorption spectroscopy: A multivariate approach. *Am. Min.* **103**, 1282-1297.
- Macpherson G. J. (2008) Introduction. In *Oxygen in the Solar System* (eds. G. J. Macpherson, D. W. Mittlefehldt, and J. H. Jones), *Rev. Min. Geochem.* Mineralogical Society of America, vol. **68**. pp. 1-3.
- McCammon C. (2005) The paradox of mantle redox. *Science* **308**, 807-808.
- McSween, H. Y. Jr. (2000) *Meteorites and Their Parent Planets*. Cambridge University Press, Cambridge, United Kingdom, 310 pp.
- Nyquist L., Bogard D., Takeda H., Bansal B., Wiesmann H. and Shih C.-Y. (1997) Crystallization, recrystallization, and impact-metamorphic ages of eucrites Y792510 and Y791186. *Geochim. Cosmochim. Acta*. **61**, 2119-2138.
- Papike J. J., Karner J. M. and Shearer C. K. (2005) Comparative planetary mineralogy: valence state partitioning of Cr, Fe, Ti, and V among crystallographic

sites in olivine, pyroxene, and spinel from planetary basalts. *Am. Min.* **90**, 277-290.

Parkinson I. J. and Arculus R. J. (1999) The redox state of subduction zones: insights from arc-peridotites. *Chem. Geol.* **160**, 409-423.

Pasek M. and Block K. (2009) Lightning induced reduction of phosphorus oxidation state. *Nat. GeoSci.* **2**, 553-556.

Pasek M. A., Block K. and Pasek V. (2012) Fulgurite morphology: a classification scheme and clues to formation. *Contrib. Mineral. Petrol.* **164**, 477-492.

Pasek M.A. and Hurst M. (2016) A fossilized energy distribution of lightning. *Sci. Rep.* **6**, 30586.

Plyashkevich A.A., Minyuk P.S., Subbotnikova T.V. and Alshevskiy A.V. (2016) Newly formed minerals of the Fe-P-S system in Kolyma fulgurite. *Doklady Earth Sci.* **467**, 380-383.

Shearer, C. K., Hess, P. C., Wiczorek, M. A., Pritchard, M. E., Parmentier, E. M., Borg, L. E., Longhi, J., Elkins-Tanton, L. T., Neal, C. R., Antonenko, I., Canup, R. M., Halliday, A. N., Grove, T. L., Hager, B. H., Lee, D.-C. and Wiechert, U., 2006. Thermal and magmatic evolution of the Moon. In *New Views of the Moon* (eds. B. L. Jolliff, M. A. Wiczorek, C. K. Shearer and C.R. Neal), *Rev. Mineral. Geochem. Mineralogy Society of America* **60**. pp. 365–518.

Sheffer A. (2007) Chemical reduction of silicates by meteorite impacts and lightning strikes. Dissertation, University of Arizona.

Sheffer A. A., Dyar M. D. and Sklute E. C. (2006) Lightning strike glasses as an analog for impact glasses: ^{57}Fe Mössbauer spectroscopy of fulgurites. *Lunar Planet. Sci. Conf. XXXVII #2009* (abstr.)

Stöffler D., Hamann C. and Metzler K. (2018) Shock metamorphism of planetary silicate rocks and sediments: Proposal for an updated classification system. *Meteorit. Planet. Sci.* **53**, 5-49.

Sutton S. R., Karner J., Papike J., Delaney J.S., Shearer C., Newville M., Eng P., Rivers M. and Dyar M.D. (2005) Vanadium K edge XANES of synthetic and natural basaltic glasses and application to microscale oxygen barometry. *Geochim. Cosmochim. Acta.* **69**, 2333-2348.

Wadhwa M. (2008) Redox conditions on small bodies. In *Oxygen in the Solar System* (eds. G. J. Macpherson, D. W. Mittlefehldt, and J. H. Jones), *Rev. Min. Geochem.* Mineralogical Society of America, vol. **68**. pp. 31-54.

Weeks R.A., Nasrallah M., Arafa S. and Bishay A. (1980) Studies of fusion processes of natural glasses by electron magnetic resonance spectroscopy. *J. Non-Cryst. Sol.* **38 & 39**, 129-134.

CHAPTER III
REDOX CHARACTER OF LUNAR VOLCANIC AND IMPACT
GLASS: APPLICATION OF A NEW CR OXYBAROMETER

A version of this chapter is being prepared to be submitted to be published by Sarah E. Roberts, Molly C. McCanta, M. Darby Dyar, and Cai Ytsma:

Sarah E. Roberts, Molly C. McCanta, M. Darby Dyar, and Cai Ytsma.
“Redox character of lunar volcanic and impact glass: Application of a new Cr oxybarometer.” *American Mineralogist*.

I was responsible for petrography, photomicrographs, BSE imaging, EPMA analysis and element mapping of the samples. I performed background research, created figures, combined data and wrote this manuscript. Molly McCanta provided data and edits. Darby Dyar provided data and edits. Cai Ytsma synthesized data.

Abstract

Lunar materials are valuable for their petrologic information which can reveal information about the evolution and composition of the Moon. Among this information is the oxygen fugacity (fO_2) conditions of the lunar interior which influences mineral compositions and magma and volatile generation. Volcanic glass beads record fO_2 conditions of the lunar mantle where they are formed, as well as changes during their ascent through the crust, and eruption. Measuring the fO_2 in volcanic beads can therefore provide information otherwise not available on the fO_2 conditions of the lunar interior. Glasses produced by impacts and micrometeorite impacts on the lunar surface record the equilibrium fO_2 conditions present during the intense heat, pressure, and volatile loss during impact. Impact events on the lunar surface form impact melt glass while micrometeorite impacts into the lunar regolith form agglutinates.

Multivalent elements such as Fe and Cr are capable of recording the prevailing fO_2 conditions of a melt. Terrestrially, the ratio of Fe^{2+} to Fe^{3+} in a melt allows for fO_2 to be measured, however the transition of Fe^{2+} to Fe^{3+} occurs at higher fO_2 which is not ideal for the reduced conditions of the lunar interior and surface as little Fe^{3+} remains available to measure. The transition of Cr^{3+} to Cr^{2+} occurs at lower fO_2 making it a more suitable oxybarometer for lunar melts.

We have developed a calibration set by which to measure Cr oxidation states in glasses with X-ray Absorption Spectroscopy (XAS). XAS provides an in situ, non-destructive method to measure fO_2 in small volume planetary materials. Synthetic glasses representing basalts to basaltic andesites from Mars, the Moon, and Earth (SiO_2 wt.% 38.5-57.9, FeO wt.% 22.9-5.82) were synthesized and equilibrated under oxygen fugacities of IW-2, IW, and QFM. To demonstrate the use of this method, we have measured Cr redox in situ within volcanic, agglutinic, and impact melt glasses in lunar samples. Variation in fO_2 is seen within the samples with the volcanic beads ranging from IW to IW-1 while the impact melt and agglutinic glass record lower fO_2 (i.e., ~IW-2). This method of

measuring fO_2 in situ reveals the inhomogeneous nature of impacts on oxidation states.

Introduction

The 842 pounds of lunar samples returned by the 6 Apollo missions were all collected from the lunar regolith (Lucey et al., 2006). The lunar regolith is composed of mineral fragments, lithic and breccia fragments, glasses, and agglutinates (Papike and Simon, 1982; McKay et al., 1991). The entire petrologic history of the Moon is preserved within this regolith, from the original primary crust, to volcanism, and subsequent impact bombardment that has gradually broken, pulverized, and melted the surface for more than 4 billion years (Lucey et al., 2006). The regolith has served as the direct source of almost all of our information about the Moon with even smallest lithic fragments providing crucial information into the formation and development of the Moon (e.g., Wood, 1970; Lucey et al., 2006; Liu et al., 2012; Gross et al., 2014; Barboni et al., 2017).

A common constituent of the lunar regolith is glassy material originating from both impact and volcanic processes (Lucey et al., 2006). Impact glass is formed via melting of surface materials during shock events (Delano et al., 1981; Stöffler 1984; McKay et al., 1991). Impact-melt glass has also been identified in samples derived from the regolith such as lunar meteorites, which are formed and ejected from the surface of the Moon through impact events (Delano 1991).

Agglutinate glass is also formed via shock, but through micrometeorite impacts (Basu 1977; McKay et al., 1991; Papike and Simon, 1982). Agglutinates form on terrestrial planets with fine-grained regolith and without an atmosphere, as an atmosphere would prevent micrometeorites from reaching the surface. (Basu 1977; McKay and Basu, 1983; McKay et al., 1991). When formed, agglutinates are small (<1mm) aggregates of smaller particles of mineral grains, glasses, and older agglutinates, that are fused together by vesicular glass. Minute droplets of Fe metal (as single domain Fe_0 and troilite FeS) are found in agglutinates, the result of H and He from solar wind trapped in lunar soil being liberated during melted and reducing FeO in the glass (Pieters et al., 2000; McKay et al., 1991).

In contrast to the impact glasses described above, spherical glass beads are the result of explosive, fire-fountaining volcanic eruptions fueled by CO or H_2O gas (Delano and Livi 1981; Delano 1986, Rutherford et al. 2017). These glasses are especially valuable when investigating the interior of the Moon as they represent a direct, unfractionated melt from the mantle and serve as the best representative of primary lunar mantle material (Delano and Livi, 1981).

All of the glasses present in the lunar regolith record the conditions present during their formation. In the case of the volcanic glass beads, this glass records equilibrium conditions of the mantle where it was formed and during ascent through the crust. Among this recorded information is the oxygen fugacity (fO_2) conditions of the mantle which controls the oxidation states of elements

within the glass. Different mineral buffer assemblages are used to describe the equilibrium fO_2 conditions such as the iron-wüstite (IW) buffer which describes iron in its native state (Fe_0) oxidizing to ferrous iron (wüstite, $Fe_{2+}O$; Figure 1). At higher fO_2 , the transition of Fe_{2+} in fayalite into Fe_{3+} in magnetite occurs at the fayalite-magnetite-quartz (FMQ) buffer (Figure 1). By measuring oxidation states in lunar glass beads, we can determine the fO_2 of the lunar mantle and trace the evolution of the lunar interior, magmas and volatiles generated by the lunar interior along with the past influence of water (Sato 1978; Herd et al., 2002; Herd 2008). Secondary events such as impacts can impart their own equilibrium fO_2 signatures allowing for the preservation of the volatile conditions during the intense heat and pressure of the impact event (Stöffler et al., 2018).

Measuring fO_2 in lunar glasses is made possible through multivalent elements such as Fe and Cr, whose valencies in melts are controlled by the prevailing fO_2 , temperature, pressure, and composition of the silicate liquid (Kilinc et al., 1983; Kress and Carmichael, 1990; Berry and O'Neill, 2004). The ratio of ferrous (Fe_{2+}) to ferric (Fe_{3+}) iron provides an accurate measure of fO_2 in many terrestrial systems as the oxidizing conditions prevalent occur where both Fe_{2+} and Fe_{3+} are present (Kilinc et al., 1983; Kress and Carmichael, 1990; Figure 2). The interior of the Moon has an fO_2 of IW-1 (Wadhwa 2008), under which little Fe_{3+} should be present; Fe_0 is the stable phase (Karner et al., 2006). The valence state change between Cr_{2+} and Cr_{3+} occurs at lower fO_2 values than that of iron suggesting Cr redox may provide more accurate fO_2 measurements under reducing lunar conditions found on the Moon (Papike et al., 2005).

We have developed an accurate method to measure the oxidation states of Cr with X-ray Absorption Spectroscopy (XAS) through the creation of glass standards. Synthetic glasses representing planetary samples with a range of oxides including Si and Fe concentrations along with added Cr were synthesized and equilibrated under a range of oxygen fugacity conditions. Using a combination of Mössbauer spectroscopy followed by XAS, a multivariate prediction model using Python Analysis for XAS (PAXAS) software package was written for this project. This multivariate analysis uses partial least squares analysis that considers every channel of data followed by lasso regression to remove the channels that are deemed to be less informative (Dyar et al., 2016). The end result is a freely available software for processing XAS data with a single command that directly predicts the oxygen fugacity for Fe and Cr in planetary melts.

To demonstrate the use of this new software in conjunction with XAS, we measured Cr_{2+}/Cr_{3+} in situ within lunar glass beads and agglutinates from Apollo 11, 14, and 15, and impact melt glass in lunar meteorite NWA 10986. We compared the fO_2 data to that recorded by Fe redox to illustrate the utility of the Cr-melt oxybarometer. With this new oxybarometer calibration we are able to quantify the prevailing redox conditions in the lunar interior and during impact processes and investigate any variations that may occur.

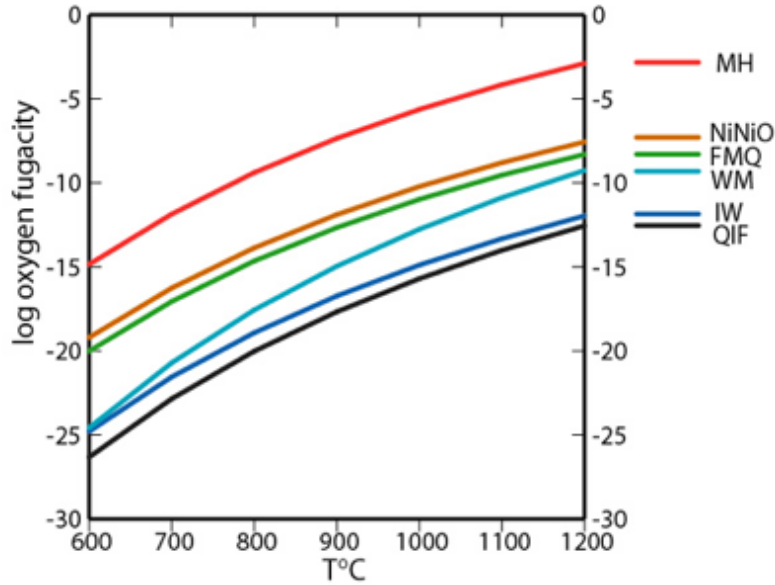


Figure 3.1. Log fO_2 versus temperature for mineral buffer assemblages, from Frost 1991.

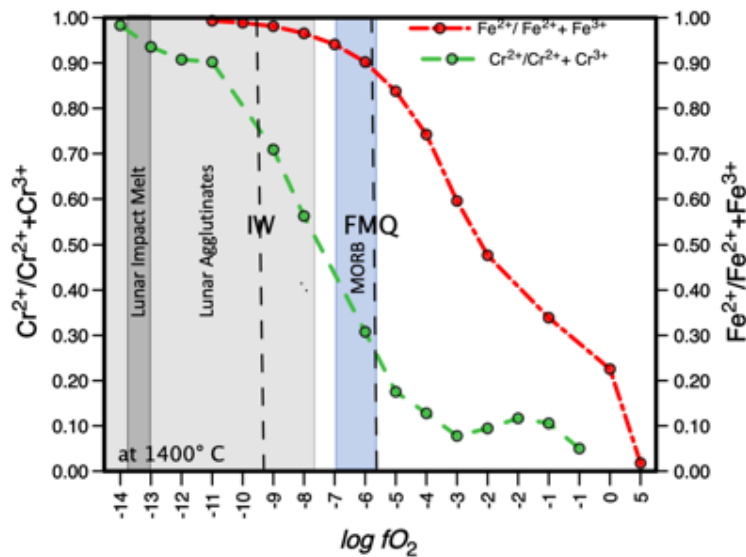


Figure 3.2. Log fO_2 versus the transition of $Cr^{2+}/Cr^{2+}+Cr^{3+}$ and $Fe^{2+}/Fe^{2+}+Fe^{3+}$. Blue field represents the fO_2 of MORB from Christie et al., 1986. Gray fields represent the fO_2 of lunar agglutinates and impact melt from NWA 10986. Cr and Fe data are from Berry and O'Neill, 2004 and Berry et al., 2003.

Previous work

Previous work in developing Cr oxybarometers have often exploited the ability of minerals to partition elements. Chromite grown from basaltic and ultramafic compositions at fugacities between IW, FMQ, and nickel-nickel oxide (NNO) were used by Murk and Campbell (1986) to determine the relationship between fO_2 , temperature, and bulk composition on the solubility of chromite in basic and ultrabasic magmas. Their results showed that Cr_{3+} is partitioned into the melt at higher temperatures because of the greater number of sites available (Murk and Campbell, 1986).

A similar investigation using pyroxene to record Cr_{3+} partitioning between pyroxene and melt found that the partitioning of Cr into pyroxene was not only controlled by fO_2 , but also by the availability of charge-balancing elements for coupled substitutions with Cr, such as Al and Na (Karner et al., 2007). Other studies involving mineral-melt partitioning have only focused on basalts, particularly martian compositions (Karner et al., 2007; Goodrich et al., 2013; Bell et al., 2014; Richter et al., 2006).

Berry and O'Neill (2004) avoided the constraints of crystallographic sites in minerals by using basaltic silicate glasses. This work also addressed the absence of Cr_{2+} in Fe-bearing systems as the result of an electron exchange reaction between Cr_{2+} and Fe_{3+} . This is especially problematic at higher fO_2 with an abundance of Fe_{3+} as this exchange completely removes Cr_{2+} from the melt (Berry and O'Neill, 2004). As a solution to identify small amounts of Cr_{2+} in Fe-bearing melts, Berry and O'Neill (2004) demonstrated the use of X-ray absorption near-edge structure (XANES) to measure and differentiate between oxidation states. The work completed by Berry and O'Neill (2004) showed the advantage of using XANES as an in situ measurement tool to develop Cr oxybarometers.

Methods

Experimental

Glass Calibrations

To calibrate the Cr XAS oxybarometer oxide and carbonate powders representing martian, lunar, and terrestrial lithologies were synthesized and doped with 0.1 wt. % of Cr_2O_3 . All samples were run in vertical 1-atm gas mixing furnaces at Washington University St. Louis and California Institute of Technology. A 100 mg sample of the powder was mixed with polyvinyl alcohol to adhere the sample to either Pt or Re wires. For fO_2 less than QFM, Re wires were used as Fe has lower solubility in Re (Borisov and Jones, 1999). Experiments at QFM used Pt wires that had been pre-doped with identical starting material and ran for 6 hours at the desired oxygen fugacity. The glassy material was then dissolved off the Pt loop using a mixture of HF and HNO_3 and the loop then reused for the actual run. fO_2 was fixed by flowing air or an H_2 - CO_2

gas mixture at IW-2, IW, and FMQ buffers for the duration of an experiment and during cooling. Samples were placed into the hot spot under the desired gas mixture at 1000°C with temperatures ramped up to the composition specific temperature at 500°C per hour. To ensure melt homogenization, the glass remained at peak temperatures for the duration of the run. Following the completion of the run, samples were drop quenched into deionized water. The glass beads created from these runs were split in half. The first portion was mounted in epoxy and polished into a 1" thick mount.

Analytical

Scanning electron microscope and electron probe microanalysis

Backscattered electron (BSE) images and major and minor element analysis of the calibration glasses were completed by electron probe microanalysis (EPMA) on the Cameca SX-100 electron microprobe at the University of Tennessee. An accelerating voltage of 15kV, current of 20 nA, and a defocused beam of 12 μm was used to analyze the calibration glasses. The agglutinates were analyzed using an accelerating voltage of 15 kV, a probe current of 20 nA, and 5 μm spot size. Impact melt glass from NWA 10986 was analyzed using a voltage of 15kV, a probe current of 20 nA, and a 15 μm spot size. Peak counting times were 20 seconds for Si, Al, Ca, Na, and K and 30 seconds for Fe, Mn, Cr, P, Ti, and S. To minimize volatile loss effects in the glass analyses, Na and K were measured first and second respectively, for a count time of 5 seconds, repeated four times to determine the zero intercept. Well-characterized synthetic and natural standards were used for calibrations.

Element maps of NWA 10986 and agglutinates from 10084, 14148, and 15427 were collected using an accelerating voltage of 15kV, probe current of 20 nA, and a dwell time of 50 to 100 milliseconds with an average of 2 μm step size.

Mössbauer Spectroscopy

Mössbauer spectroscopy was completed on the second portion of the synthesized glasses to determine the oxidation state of Fe as a ground-truth measurement. The glass beads were gently ground to powder under acetone to prevent oxidation from the heat of grinding. Sugar was added to dilute the sample and provide a thin absorber before being gently heaped in a sample holder confined by kapton tape. Mössbauer spectra of these powders were collected at Mount Holyoke College at 295K using a source of 100-60 MCi ^{57}Co in Rh on a WEB Research Co. model WT302 spectrometer. Mössbauer data was then used to calibrate the Fe XAS data.

XAS

The oxidation state of Cr and Fe were analyzed in the mounted polished glass beads by XAS at the GeoSoilEnviroCARS beamline at Advanced Photon Source,

Argonne National Lab using a spot size of $1 \times 1 \mu\text{m}$. Oxidation of Fe in hydrous glasses can occur during XAS analysis as a result of radiation dose conditions (Cottrell et al., 2018). All glasses analyzed for this study were anhydrous eliminating this concern, however beam current was minimized to limit any changes in oxidation. The reproducibility of XAS data has been tested between two separate facilities using the same samples and no appreciable differences in data have been found (Dyar et al., 2016)

The Mössbauer and XAS data were then used to build a multivariate prediction model using Python Analysis for XAS (PAXAS) software package (Dyar et al., 2016). Instead of only focusing on the pre-edge portion of the XAS spectra such is done with XANES, the entire spectral range including the extended x-ray absorption fine structure (EXAFS) region is used (Dyar et al., 2016). This multivariate analysis uses partial least squares analysis that considers every channel of data followed by lasso regression to remove the channels that are deemed to be less informative (Dyar et al., 2016). By including the entire spectra, more accurate predictions of redox states can be made when combined with multivariate regression techniques (Dyar et al., 2016; McCanta et al., 2017).

Results

Glass Calibrations

Scanning electron microscope and electron probe microanalysis

The calibration glasses are mostly homogenous however variation is seen in BSE of some of the glasses. Glasses synthesized at IW-2 and IW have precipitation of chromite and Re metal. Some crystallization of Mg-rich olivines is seen in glasses synthesized at QFM. Electron microprobe analysis of the calibration glasses confirms the variation seen in BSE based on the fO_2 at which the glasses were synthesized (Tables 1a,b,c). Glasses synthesized at IW-2 exhibit the largest variation in composition compared to glasses synthesized at IW and QFM (Table 1c).

XAS

Iron XAS of the calibration glasses show distinct variations in all portions of the spectra when compared to fO_2 (Figure 3a). A double pre-edge is present at all fO_2 however the intensity of the peaks changes to higher energy channels at higher fO_2 . The edge shifts from higher to lower intensity at higher fO_2 while the energy of the edge decreases at higher fO_2 . The EXAFS region of the spectra also shows significant variation as the fO_2 increases.

Chrome XAS of the calibration glasses shows substantial variation similar to that of the Fe XAS (Figure 3b). A double pre-edge is again present. At lower fO_2 (log fO_2 -11 to -12), a peak is seen half-way up the edge. This peak disappears at higher fO_2 (log fO_2 -10 and above). The energy and intensity of the

Table 3.1a. Composition of calibration glasses synthesized at QFM

	Gusev Basalt	Apollo 15 Green Glass	Apollo 17 VLT Basalt	MORB	BHVO	Mount Shasta Basaltic Andesite
SiO₂	48.21 ± 0.19	48.48 ± 0.16	39.90 ± 0.17	49.28 ± 1.03	51.18 ± 0.64	53.36 ± 0.39
TiO₂	0.02 ± 0.02	0.01 ± 0.01	9.63 ± 0.09	0.01 ± 0.01	0.00 ± 0.00	-
Al₂O₃	11.12 ± 0.08	8.16 ± 0.11	5.78 ± 0.05	16.62 ± 0.31	14.14 ± 0.30	18.06 ± 0.13
FeO	16.81 ± 0.14	14.60 ± 0.05	19.23 ± 0.10	7.86 ± 0.21	11.09 ± 0.20	5.99 ± 0.17
MgO	11.64 ± 0.05	18.36 ± 0.10	15.72 ± 0.09	110.48 ± 0.16	7.63 ± 0.04	8.77 ± 0.14
CaO	8.63 ± 0.07	9.06 ± 0.05	7.59 ± 0.06	12.54 ± 0.28	12.12 ± 0.11	10.16 ± 0.09
Na₂O	2.12 ± 0.05	0.18 ± 0.29	0.47 ± 0.02	1.84 ± 0.06	2.09 ± 0.08	2.39 ± 0.05
K₂O	0.21 ± 0.2	0.03 ± 0.02	0.03 ± 0.01	0.13 ± 0.02	0.52 ± 0.03	0.46 ± 0.02
Cr₂O₃	0.29 ± 0.02	0.38 ± 0.01	0.45 ± 0.02	0.44 ± 0.79	0.23 ± 0.22	0.20 ± 0.07
V₂O₃	0.29 ± 0.01	0.38 ± 0.02	0.59 ± 0.02	0.33 ± 0.05	0.29 ± 0.03	0.18 ± 0.01
Total	99.34	99.65	99.38	99.54	99.28	99.57

Table 3.1b. Composition of calibration glasses synthesized at IW

	Gusev Basalt	Apollo 15 Green Glass	Apollo 17 VLT Basalt	MORB	BHVO	Mount Shasta Basaltic Andesite
SiO₂	49.97 ± 1.62	48.09 ± 0.27	39.11 ± 0.21	49.87 ± 0.16	51.44 ± 2.00	50.42 ± 0.19
TiO₂	-	0.01 ± 0.01	9.46 ± 0.06	-	-	-
Al₂O₃	12.77 ± 0.51	8.04 ± 0.07	5.68 ± 0.07	16.43 ± 0.10	12.82 ± 0.87	19.30 ± 0.16
FeO	17.21 ± 1.41	15.81 ± 0.12	21.21 ± 0.14	8.44 ± 0.07	13.28 ± 0.65	7.30 ± 0.08
MgO	6.55 ± 0.18	17.56 ± 0.07	15.04 ± 0.08	10.04 ± 0.07	6.68 ± 0.53	9.46 ± 0.04
CaO	10.79 ± 0.61	8.83 ± 0.07	7.36 ± 0.05	12.49 ± 0.08	12.89 ± 0.69	10.73 ± 0.05
Na₂O	1.41 ± 0.16	0.40 ± 0.02	0.28 ± 0.02	1.47 ± 0.05	1.76 ± 0.23	2.03 ± 0.05
K₂O	0.06 ± 0.03	0.06 ± 0.01	0.04 ± 0.02	0.20 ± 0.02	0.21 ± 0.02	0.23 ± 0.01
Cr₂O₃	0.16 ± 0.02	0.36 ± 0.02	0.64 ± 0.01	0.34 ± 0.02	0.15 ± 0.02	0.26 ± 0.02
V₂O₃	0.17 ± 0.02	0.31 ± 0.01	0.50 ± 0.03	0.36 ± 0.02	0.17 ± 0.04	0.18 ± 0.11
Total	99.09	99.46	99.33	99.63	99.38	99.89

Table 3.1c. Composition of calibration glasses synthesized at IW-2

	Gusev Basalt	Apollo 15 Green Glass	Apollo 17 VLT Basalt	MORB	BHVO
SiO₂	55.24 ± 0.22	48.09 ± 0.27	45.45 ± 0.12	50.80 ± 0.14	55.58 ± 0.15
TiO₂	-	0.01 ± 0.01	11.36 ± 0.08	-	-
Al₂O₃	12.76 ± 0.13	8.04 ± 0.07	6.86 ± 0.08	17.56 ± 0.13	14.95 ± 0.18
FeO	7.13 ± 0.11	15.81 ± 0.12	8.25 ± 0.08	6.10 ± 0.10	5.79 ± 0.29
MgO	13.29 ± 0.09	17.56 ± 0.07	17.61 ± 0.12	10.95 ± 0.06	7.61 ± 0.10
CaO	9.88 ± 0.08	8.83 ± 0.07	8.53 ± 0.06	13.18 ± 0.09	12.36 ± 0.11
Na₂O	0.37 ± 0.02	0.40 ± 0.02	0.02 ± 0.01	0.12 ± 0.01	0.75 ± 0.04
K₂O	0.11 ± 0.02	0.06 ± 0.01	0.01 ± 0.01	0.04 ± 0.01	0.35 ± 0.03
Cr₂O₃	0.53 ± 0.02	0.36 ± 0.02	0.70 ± 0.01	0.42 ± 0.02	0.50 ± 0.02
V₂O₃	0.47 ± 0.02	0.31 ± 0.01	0.71 ± 0.03	0.35 ± 0.02	0.40 ± 0.02
Total	98.94	99.47	99.46	99.31	99.28

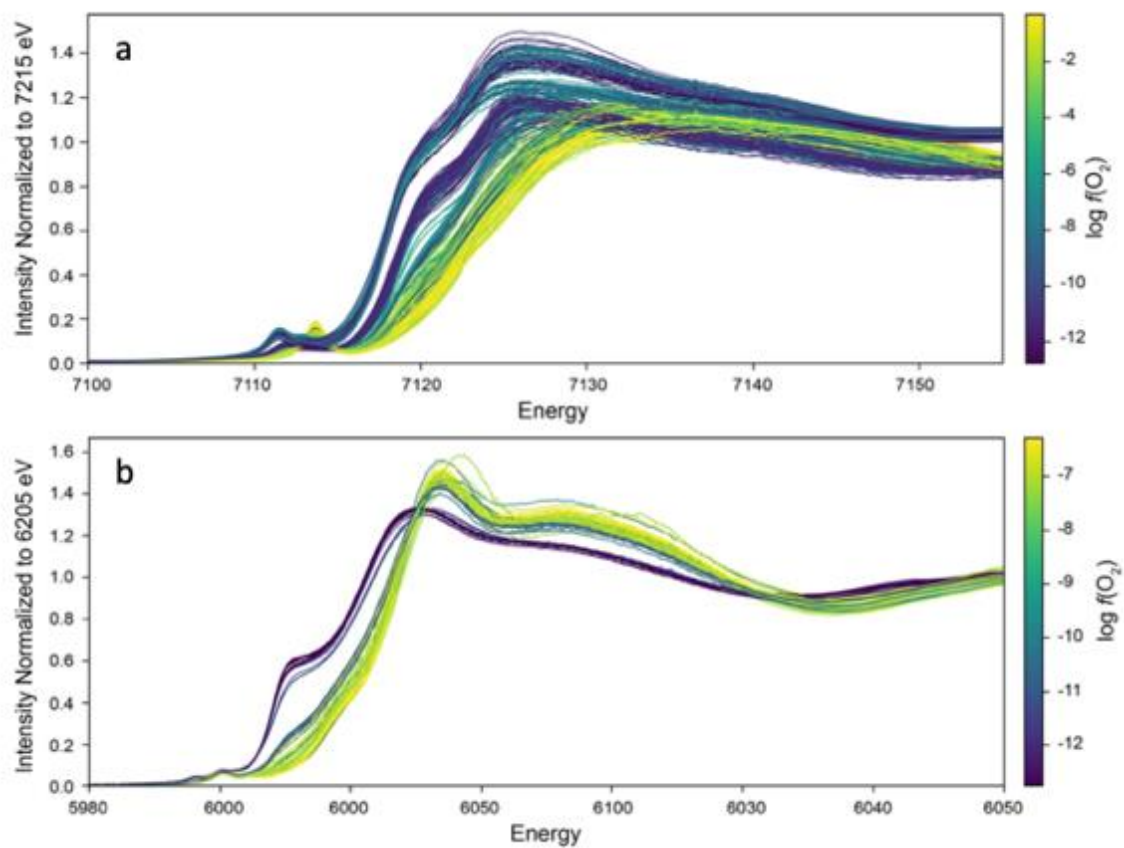


Figure 3.3. Fe(a) and Cr(b) XAS spectra of the calibration glasses.

edge shifts considerably at $\log fO_2$ -10. A large shift also occurs in the EXAFS region at this same fO_2 ($\log fO_2$ -10).

The predictive model built with the Cr XAS analysis of these glasses predicts equilibrium fO_2 conditions with a root mean square error of 1.28.

Samples

10084

Soil sample 10084 is the <1mm sieve fraction from a bulk sample collected by Apollo 11 in the southern part of Mare Tranquillitatis (Papike et al., 1982; Figure 4a). This soil contains mare basalt fragments, breccias, and mineral fragments along with anorthositic rock fragments, agglutinates, and orange, red, and green glass beads (Duke et al., 1970; Korotev and Gillis, 2001). Glass beads in 10084 have low SiO_2 but have high TiO_2 (Table 2). Agglutinates have high Al_2O_3 and CaO (Table 2). Agglutinates analyzed for this study are chemically distinct from other agglutinates in 10084 and are most similar to agglutinates from Apollo 15 (Figure 5).

The glass bead analyzed in sample 10084 by XAS has fO_2 that is higher compared to other samples (Table 3). The fO_2 of the bead ranges from IW+0.62 to IW+0.96. No zonation in fO_2 is observed within the glass beads (Table 3). Analyzed agglutinates in 10084 exhibit highly variable fO_2 (Figure 6) ranging from IW-4.10 to IW+1.84, the highest fO_2 value observed among all agglutinates analyzed.

14148

Sample 14148 represents the <1 mm sieve fraction of a larger sample that was collected from the top of a trench dug into the soil of the smooth plains unit by Apollo 14 (Simon et al., 1982; McKay et al., 1972). Half of this sample is agglutinitic material with breccias, brown glass beads, impact glass, and mineral fragments are also observed (McKay et al., 1972; Figure 4b). Glass beads in 14148 are similar in composition to those found in 10084 and 15427 with the exception of TiO_2 (Table 2). Agglutinates in 14148 have the highest amounts of MgO among the agglutinates analyzed for this study and are similar in composition to agglutinates from Apollo 14 and Apollo 15 (Table 2; Figure 5).

Three glass beads in sample 14148 show a range of fO_2 from IW+1.63 to IW -2.90 when measured by XAS (Table 3). Bead 6 has the highest fO_2 with an average fO_2 of 0.51 while beads 2 and 4 have an average fO_2 of IW -2.56 and -

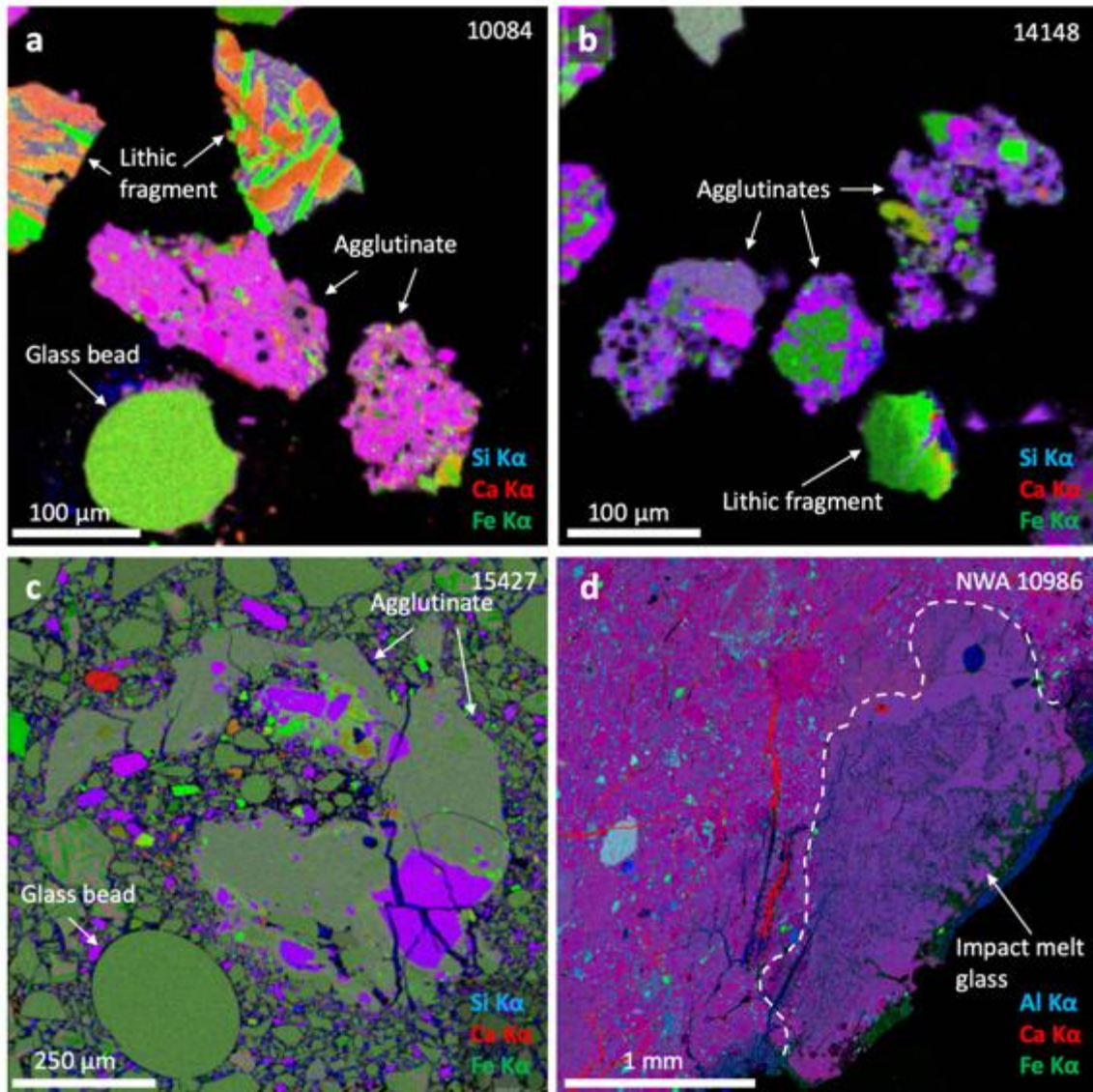


Figure 3.4. a) Lunar agglutinates and beads from 10084, b) Lunar agglutinates and beads from 14148, c) Lunar agglutinates and beads from 15427, d) NWA 10986

Table 3.2. Average compositions of glass beads and agglutinates from 10084, 14148, and 15427

	10084		14148		15427	
	Glass beads	Agglutinates	Glass beads	Agglutinates	Glass beads	Agglutinates
SiO₂	37.94 ± 0.33	46.48 ± 2.43	44.39 ± 0.31	47.99 ± 2.39	45.33 ± 0.32	45.10 ± 2.60
TiO₂	10.18 ± 0.12	1.65 ± 2.14	1.02 ± 0.15	0.98 ± 0.50	0.41 ± 0.02	4.29 ± 1.21
Al₂O₃	5.43 ± 0.11	21.27 ± 8.71	6.97 ± 0.13	17.73 ± 7.90	7.41 ± 0.18	10.81 ± 1.60
FeO	22.65 ± 0.58	7.40 ± 4.58	23.13 ± 0.25	9.93 ± 4.71	20.21 ± 0.34	18.53 ± 2.75
MgO	13.80 ± 0.28	7.83 ± 4.51	15.41 ± 0.24	10.06 ± 5.33	17.04 ± 0.15	8.58 ± 1.64
MnO	0.32 ± 0.03	0.11 ± 0.07	0.29 ± 0.03	0.14 ± 0.09	0.29 ± 0.01	0.23 ± 0.03
CaO	7.61 ± 0.14	13.89 ± 2.76	8.32 ± 0.14	11.41 ± 2.70	8.56 ± 0.12	9.85 ± 0.40
Na₂O	0.30 ± 0.05	0.55 ± 0.29	0.22 ± 0.07	0.60 ± 0.45	0.15 ± 0.02	0.56 ± 0.13
K₂O	0.05 ± 0.01	0.10 ± 0.06	0.07 ± 0.01	0.25 ± 0.17	0.02 ± 0.00	0.31 ± 0.27
Cr₂O₃	0.65 ± 0.10	0.18 ± 0.16	0.50 ± 0.11	0.21 ± 0.14	0.55 ± 0.02	0.29 ± 0.05
Total	98.94	99.47	100.32	99.31	99.97	98.57
Number analyzed	9	3	3	3	10	5

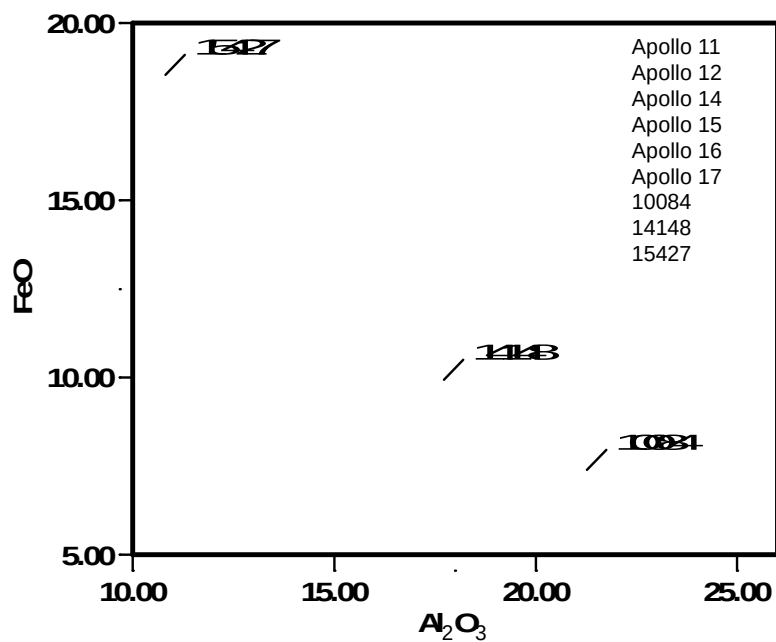


Figure 3.5. Agglutinate compositions compared to agglutinates from other Apollo sites.

Table 3.3. Predicted oxygen fugacity relative to IW by Fe and Cr XAS for the glass beads, agglutinates, and impact melt. B.D.L = below detection limit

	Size		Fe $fO_2 \Delta IW$	Number analyzed	Cr $fO_2 \Delta IW$	Number analyzed
Glass Beads						
10084		1	0.38 ± 0.34	11	0.79 ± 0.19	4
		10	0.61 ± 0.17	8	0.76 ± 0.18	3
14148		2	-0.23 ± 0.78	10	-2.56 ± 0.39	4
		4	-0.64 ± 0.19	3	-2.51 ± 0.28	3
		6	0.83 ± 0.30	3	0.51 ± 0.99	3
15427		1-5	-		0.11 ± 0.57	5
Agglutinates						
10084	<1mm	1-2	B.D.L.	36	-1.37 ± 3.00	3
14148	<1mm	1-3	B.D.L.	14	-1.70 ± 0.18	5
15427	<20 μm to >500 μm	1	B.D.L.	9	-1.59 ± 1.40	8
		4	B.D.L.	10	-0.88 ± 0.62	10
		5	B.D.L.	12	-2.24 ± 1.11	7
		6	B.D.L.	7	-2.13 ± 1.70	6
		7	B.D.L.	9	-0.82 ± 0.86	6
Impact melt						
NWA 10986	1 x 2 mm ₂		B.D.L.		-3.98 ± 0.24	3

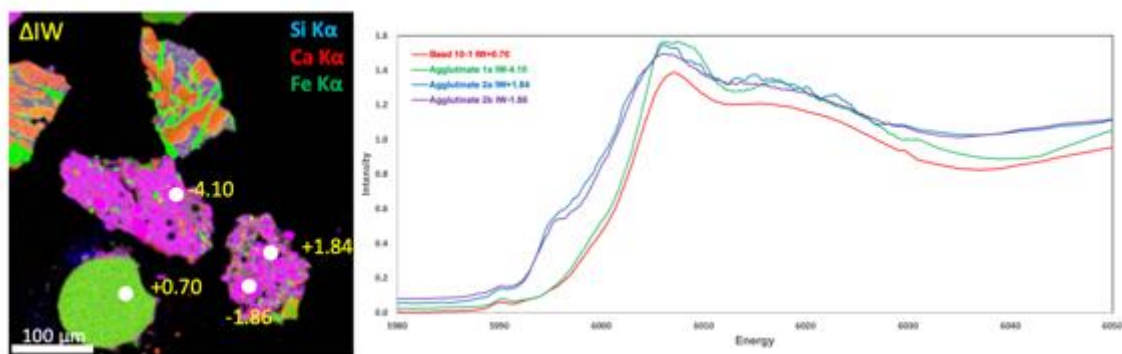


Figure 3.6. Element map of agglutinates and a glass bead from 10084 (left). Numbers represent predicted oxygen fugacity based on Cr oxidation state relative to the IW buffer. Cr XAS spectra of the agglutinates and glass bead (right).

2.51 respectively (Table 3). Bead 6 also shows zonation in fO_2 with the outer edge having a lower fO_2 at IW-0.24 with the interior having a higher fO_2 at IW+1.63. Beads 2 and 4 show no zonation in fO_2 . Agglutinates in 14148 have a narrower range of fO_2 with an average of IW-1.70 (Figure 7). Spatial variation in fO_2 is seen within the agglutinate glass (Figure 7).

15427

Regolith breccia 15427 was collected from Spur Crater on the Apennine Front during Apollo 15 (Ridley et al., 1973; McKay et al., 1989). This breccia contains a large amount of green glass beads along with orange/black glass beads, breccias, lithic fragments, impact glasses, and agglutinates (McKay et al., 1989; Figure 4c). Unlike the other regolith samples, this breccia was collected as a coherent “clod” and was not sieved (Ridley et al., 1973). The glass beads in 15427 have the highest SiO_2 , Al_2O_3 , MgO , and lowest TiO_2 and FeO among the analyzed beads (Table 2). Agglutinates have the highest TiO_2 , FeO , lowest Al_2O_3 and CaO and are the most compositionally distinct from other agglutinates from Apollo 15 and all other Apollo missions (Table 2; Figure 5).

XAS analysis of glass beads in 15427 have fO_2 from IW -0.67 to 0.75 (Table 3). The agglutinates have a wide range in fO_2 from IW -5.17 to 0.39 (Figure 8). Spatial variation is seen in the fO_2 of every agglutinate with the agglutinate in Figure 8b ranging from IW -4.58 to -0.74 and the agglutinate in Figure 8c ranging from IW -5.17 to -0.46 (Figure 8).

NWA 10986

Lunar meteorite NWA 10986 is an impact melt breccia containing clasts from both the lunar highlands and basalts (Roberts et al., 2019, a; Figure 4d). Abundant impact melt glass of varying colors and texture is found throughout the meteorite suggesting multiple generations of impact events. The largest area of impact melt was utilized for this study (Figure 4d). This impact melt is homogeneous with low concentrations of TiO_2 and high concentrations of CaO (Table 4).

The impact melt glass analyzed by XAS in NWA 10986 indicates fO_2 values of IW -4.18 to -3.72 (Figure 9).

Discussion

Cr oxybarometer

Iron is the fourth most abundant element in Earth’s crust and the most common rock-forming element that can exist in multiple oxidation states (Herd, 2008; Frost, 1991; Berry et al., 2003). The ability of Fe to react to fO_2 along with well-established techniques to measure Fe oxidation states such as Mössbauer spectroscopy makes Fe an excellent element to use for oxybarometer (Dyar et al., 2006). Terrestrial fO_2 can be easily measured using the ratio of ferrous to ferric iron, however this reaction is not applicable for all planetary bodies with

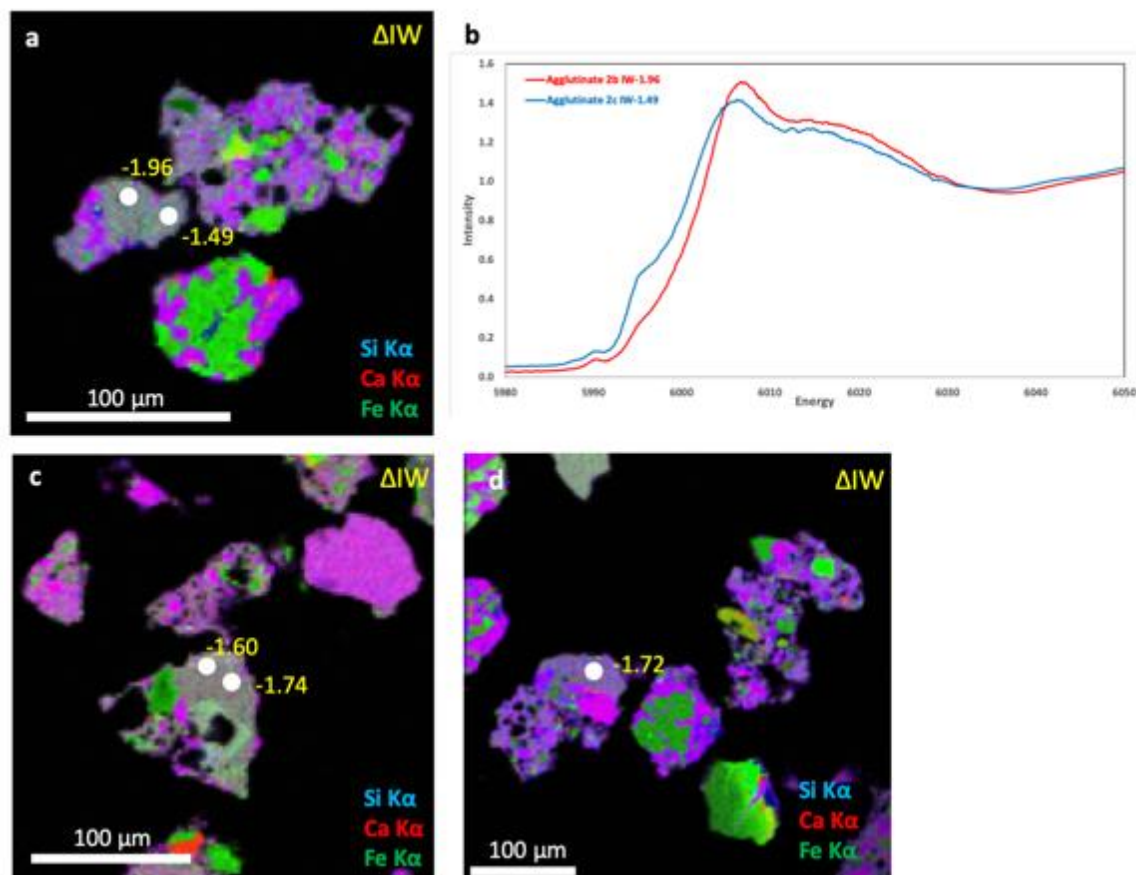


Figure 3.7. Element maps of agglutinates (a, c-d) from 14148. Numbers represent predicted oxygen fugacity relative to the IW buffer. (b) Cr XAS spectra of the agglutinate in (a).

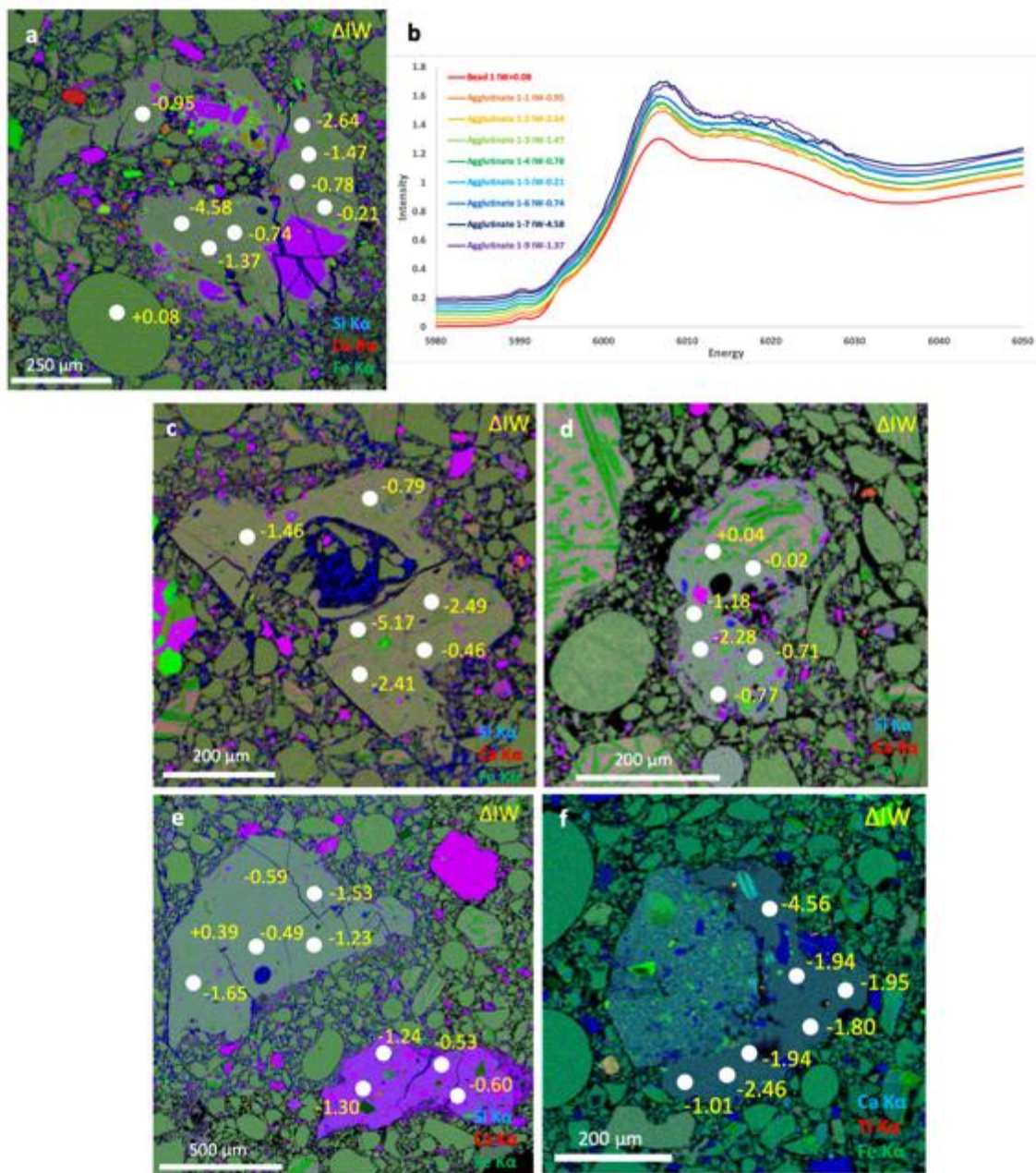


Figure 3.8. Element maps of agglutinates and volcanic glass beads from 15427 (a, c-f). Numbers represent predicted oxygen fugacity relative to the IW buffer. (b) Cr XAS spectra of the agglutinate and glass bead in (a).

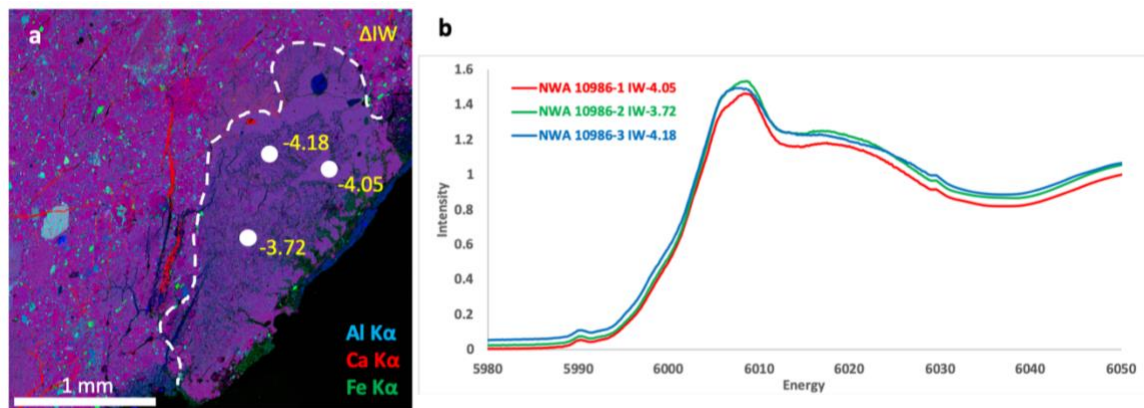


Figure 3.9. (a) Element map of impact melt in NWA 10986. Numbers represent predicted oxygen fugacity relative to the IW buffer. (b) Cr XAS spectra of the impact melt in NWA 10986.

Table 3.4. Impact melt glass composition of NWA 10986. Data is from Roberts et al., in print.

	A5-a	A5-b	A5-c
SiO₂	45.89	45.31	45.64
TiO₂	0.29	0.26	0.32
Al₂O₃	24.56	25.05	24.45
FeO	6.88	6.54	6.92
MgO	6.94	7.03	6.90
MnO	0.08	0.10	0.12
CaO	15.27	15.24	15.06
Na₂O	0.31	0.33	0.33
K₂O	0.25	0.02	0.31
Cr₂O₃	0.17	0.14	0.17
Total	100.57	100.16	100.22

lower fO_2 at or below IW (Figure 2; Sutton et al., 2005). At low fO_2 , lunar rocks have been shown to contain no Fe^{3+} and may actually crystallize Fe^0 metal (Karner et al., 2006).

To extend the application of oxidation states to lower values of fO_2 , elements such as Cr, which is found in two oxidation states, Cr^{2+} and Cr^{3+} are used (Papike et al., 2005). Cr is common in mantle melts and is a compatible element in pyroxenes, olivines, and spinels (chromite). The varying compositions of these minerals can reflect the chemical, physical, and fO_2 conditions of the melt from which they crystallized (Papike et al., 2005). These minerals are also common in basalts, and basaltic volcanism is dominant on the Earth, Moon, Mars, and asteroids (Papike et al., 2005; Herd 2008).

The oxidation states of Cr in minerals can be used to determine the fO_2 of a melt, however minerals contain crystallographic constraints that limit the ability of elements in different oxidation states to be incorporated into minerals (Murk and Campbell, 1986; Karner et al., 2007; Berry and O'Neill, 2004). Using glass instead of minerals allows for the effects that fO_2 has over valence-state partitioning of elements in crystallographic sites in minerals to be avoided (Papike et al., 2005). Because the crystallization sequence, element partitioning, nature of fractionation, and ultimately evolution of a magma can vary over fO_2 , eliminating the crystallographic constraints allows for more accurate measurements in the transition of valence states in minerals (Papike et al., 2005).

The Cr oxybarometer developed for this work is sensitive to oxygen fugacities below FMQ including those above and below IW (Figure 3). At IW ($\log fO_2$ -9.5), the transition of Cr from Cr^{3+} to Cr^{2+} has a change of 0.10 $Cr^{2+}/(Cr^{2+}+Cr^{3+})$ per log unit fO_2 while the transition of Fe from Fe^{3+} to Fe^{2+} only has a change of 0.01 $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ per log unit fO_2 which is an order of magnitude less (Figure 2). At such low fO_2 , the amount of Fe^{3+} available to determine fO_2 from Fe oxidation states decreases so much to where analytical techniques lose sensitivity and worse, the measured amounts are not greater than the error. The Cr spectra shows the transition at $\log fO_2$ -9.5 as a distinct separation of spectra below and above this fO_2 (Figure 3b) demonstrating why Cr is a much better element to use at fO_2 of IW or below.

Chrome XAS measurements of lunar glass beads show a larger range, especially in lower fO_2 , in predicted fO_2 than those predicted by Fe XAS (Table 3). When using Fe XAS to predict the fO_2 of lunar agglutinates, the predicted fO_2 drops considerably to IW-5 to -6, which is below the detection limit of Fe using this technique (Figure 2). This demonstrates the loss of sensitivity of Fe to measure such reduced fO_2 as there is no Fe^{3+} available to measure and again demonstrates how Cr has increased accuracy for fO_2 values below IW. Iron redox states are best applied to terrestrial materials which record higher fO_2 as demonstrated by measurements of MORB at FMQ -1 to -2 (Figure 2; Christie et al., 1986). Using Cr to measure lunar materials can provide us with a better understanding on fO_2 on the lunar surface.

fO₂ of glass beads

The fO_2 of the glass beads measured using Cr XAS shows a greater range of fO_2 between the beads than Fe XAS (Table 3). Again, this demonstrates the ability of Cr to measure reduced fO_2 with better sensitivity than Fe. Two beads from 14148, beads 2 and 4, record lower fO_2 (IW-2.5) than the other beads from 10084 and 15427 (Table 3). No appreciable differences in composition between these beads and the others can be made to attribute the lower fO_2 to composition (Tables 2,3). Differences in fO_2 seen within the beads must be the result of pre or post eruptive processes.

Transacts of in situ Cr XAS measurements were completed during analysis to reveal possible zoning of fO_2 within the beads. Only one bead from 14148 (bead 6) shows zoning in fO_2 with lower fO_2 (IW-0.24) at the outer edge grading into higher fO_2 (IW+1.63) in the interior of the bead. Zoning in fO_2 has been seen before in glass beads using Fe XAS (McCanta et al., 2017). Beads with lower fO_2 such as the very reduced beads 2 and 4 in 14148 could again be the result of a less volatile rich source region or could have undergone diffusive reduction when erupted into the lunar vacuum (McCanta et al., 2017).

fO₂ of agglutinates and impact melt glass

In order for the fO_2 of a system to be determined, it is assumed that nothing has happened to overprint the oxidation state since crystallization (Carmichael, 1991; McCanta and Dyar, 2017). A possible mechanism for overprinting oxidation state is found in a common planetary occurrence: shock metamorphism (French, 1966; Grieve, 1991; French, 1988). Shock metamorphism occurs as a result of impacts on planetary surfaces. The effects of intense pressure on intrinsic oxidation state has been shown to be oxidizing (McCanta and Dyar, 2017), however when considering the relationship between $\log fO_2$ and temperature as shown in figure 1, a sudden increase in temperature should result in a reduction of intrinsic fO_2 . Regardless, the shock produced by impacts has the ability to metamorphose material through intense pressure and temperature, potentially altering the oxidation state of the impacted materials (Stöffler, 1971). The ability to differentiate between intrinsic (those related to planetary origin and evolution) and extrinsic (those changed through outside processes) oxidation states is necessary for planetary exploration.

Impact cratering has been and continues to be a major process on planetary surfaces (French, 1988, Grieve, 1991). Investigating materials on planetary surfaces that have experienced significant impact cratering, such as the Moon, necessitates the ability to identify the original oxidation state of the planetary material versus the inherited oxidation state from the impactor or the impact process. Meteorites are also inevitably subjected to shock metamorphism by the impact processes that also eject them from planetary surfaces and allow them to eventually fall onto the Earth (e.g., Bischoff and Stöffler, 1982). Meteorites provide us with planetary samples that we are not yet capable of

retrieving ourselves, including asteroids and unsampled terrains of the Moon (e.g. Fritz et al., 2005; Gross and Treiman, 2011; Takeda et al., 2006; Binzel and Xu, 1993; Warren et al., 2004; Yamaguchi et al., 2010). These samples are therefore invaluable for the information they can provide for intrinsic oxidation states of the planetary bodies they are derived from, however shock metamorphism can again, overprint this intrinsic oxidation signature. Lunar meteorite NWA 10986 has suffered from repeated impacts as evidenced by the abundant impact melt glass that composes this meteorite. Geochemical analysis indicates that it represents a region of the Moon not sampled by the Apollo missions, and is possibly derived from the farside of the Moon (Roberts et al., 2019).

Use of Cr XAS analysis to measure in situ fO_2 reveals a wide variation and distribution of redox conditions within agglutinitic material and impact melt glass, suggesting that impact and shock metamorphism is actually a highly non-equilibrium process (Figures 6-9). Spatial variation in fO_2 occurs within microns in the agglutinitic glass (Figures 6-8). The large agglutinates in 15427 demonstrate the variation in fO_2 that occurs during impact with the agglutinate shown in Figure 8c recording fO_2 from IW-5.17 to IW-0.46. All agglutinates analyzed in this study record the heterogeneous effects and the disequilibrium nature of impacts on fO_2 . Impact melt glass in NWA 10986 also shows spatial variation in fO_2 although in a narrower range of fO_2 (Figure 9a).

Spatial variation in fO_2 has also been observed previously in terrestrial fulgurite glasses. Fulgurites are the glassy products of lightning strikes on Earth which experience pressures and temperatures that may be similar to those experienced during impact (Grapes and Müller-Sigmund, 2010; Gieré et al., 2015; Chen et al., 2017). Using Fe XAS, fO_2 was measured in situ in fulgurites formed in different target compositions ranging from quartz sand to basaltic rock (Roberts et al., 2019, b). The fO_2 values recorded in the fulgurite glasses were compared to pristine target material collected with the fulgurite to determine the changes in Fe during impact. Fulgurites were observed to be both oxidized and reduced from starting fO_2 with wide variation in fO_2 occurring within microns in the fulgurite glass. These results again emphasize the disequilibrium nature of impacts and abrupt high temperature and pressure events. The effects of impacts on fO_2 cannot and should not be simply modeled.

Controls on redox changes

Besides composition, the agglutinates and impact melts vary in size. Agglutinates in 10084 and 14148 represent the < 1mm fraction collected with those samples (Table 3; Figures 6-7). Regolith breccia 15427 has not been sorted for size as the sample was formed and collected on the lunar surface as a coherent “clod” (Table 3; Figure 8; Ridley et al., 1973; McKay et al., 1989). Impact melt in NWA 10986 is the largest sample analyzed with an area size of ~ 1 x 2 mm² (Table 3; Figure 9). When comparing these samples by fO_2 , agglutinates in samples 10084

and 14148 have higher fO_2 while agglutinates in 15427 which have not been sorted by size have the largest range of fO_2 (Table 3). Impact melt in NWA 10986 is the most reduced and also has the largest area (Table 3).

With the comparison of size versus fO_2 , there does appear to be influence on fO_2 by the size of the melt. During impacts, several processes occur including liberation of solar wind implanted H and He (McKay et al., 1991). Liberated H and He reacts with FeO, reducing it to metallic iron and producing H_2O and O (Pieters et al., 2000; McKay et al., 1991). This would produce available O to oxidize and raise the fO_2 of the resulting melt. Conversely, the liberated H could also result in reduction. With multiple processes occurring during impact, the controlling factor may be diffusion and sufficient time to re-equilibrate. Larger melts such as that found in NWA 10986 would not have sufficient time to re-equilibrate after impact before quenching while smaller melts such as agglutinates in 10084 and 14148 could efficiently re-equilibrate before quenching.

Implications

Oxygen fugacity exhibits the largest variation of any physical parameter (e.g., T, P, etc.) in terrestrial rocks, with terrestrial fO_2 ranging over eight orders of magnitude (Carmichael and Ghiorso, 1990; Carmichael, 1991). Analyzed planetary materials record fO_2 of nine orders of magnitude from extremely reducing (aubrites), to extremely oxidizing (nakhilites) (Wadhwa, 2008). Measuring oxidation states allows us to investigate the formation and evolution of planetary interiors, magmas and volatiles generated by these interiors, and the past influence of water on terrestrial bodies, including Mars (Herd et al., 2002).

The Cr oxybarometer demonstrated in this work is capable of measuring low fO_2 of IW and below, such as those found on the Moon and in more reduced sample such as aubrites (Wadhwa 2008) XAS offers an in situ, non-destructive method to determine oxidation state with a small spot size of $1 \times 1 \mu m$. Cr fO_2 in lunar glass beads, agglutinates, and impact melt from NWA 10986 reveals spatial variation in fO_2 within these glasses. With a better understanding of equilibrium fO_2 , more work can be completed to understand the petrogenetic conditions of lunar glass beads and the formation of agglutinates.

The ability to accurately measure oxidation state and identify possible alterations to intrinsic oxidation state is crucial in the investigation of planetary materials. The effects of impacts on fO_2 is a highly variable, disequilibrium process, however this work has reiterated that the effects of impact on fO_2 cannot be simply modeled. Mapping the spatial variation of fO_2 of agglutinates and impact melts using this technique will allow us to explore the other controls of redox during impact such as target material composition, density, and compaction. Understanding how impacts affect the primary fO_2 of planetary samples will allow us to fully utilize all samples returned from planetary surfaces regardless of impact history. XAS is especially relevant to future planetary

sample return missions as it is a non-destructive method that allows for the preservation of small and rare materials that cannot be replaced.

References

- Anders, E., and Grevesse, N. (1989) Abundances of the elements: Meteoritic and solar. *Geochimica et Cosmochimica Acta*, 53, 197-214.
- Barboni M., Boehnke P., Keller B., Kohl I.E., Schoene B., Young E.D., and Mckeegan K.D. (2017) Early formation of the Moon 4.51 billion years ago. *Science Advances*, 3, 1-8.
- Bassu A. (1977) Steady state, exposure age, and growth of agglutinates in lunar soils. *Proceedings of the Lunar Science Conference*, 8, 3617-3632.
- Bell, A.S., Burger, P.V., Le, L., Shearer, C.K., Papike, J.J., Sutton, S.R., Newville, M., and Jones, J. (2014) XANES measurements of Cr valence in olivine and their applications to planetary basalts. *American Mineralogist*, 99, 1404-1412.
- Berry, A.J., O'Neill, H.St.C, Jayasuriya, K.D., Campbell, S.J., and Foran, G.J. (2003) XANES calibrations for the oxidation state of iron in a silicate glass, *American Mineralogist*, 88, 967-977.
- Berry, A.J., and O'Neill, H. St.C. (2004) A XANES determination of the oxidation state of chromium in silicate glasses, *American Mineralogist*, 89, 790-798.
- Borisov, A., and Jones, J. H. (1999) An evaluation of Re, as an alternative to Pt, for the 1 bar loop technique: An experimental study at 1400 °C, *American Mineralogist*, 84, 1528-1534.
- Calas, G., Brown Jr., G.E., Waychunas, G.A., and Petiau, J. (1987) X-ray absorption spectroscopic studies of silicate glasses and minerals, *Physics and Chemistry of Minerals*, 15, 19-29.
- Carmichael, I.S.E., and Ghiorso, M.S. (1990) Controls on oxidation-reduction relations in magma. In J. Nicholls and J.K. Russell, Eds., *Modern Methods of Igneous Petrology: understanding Magmatic Processes*, 24, p. 190-212. *Reviews in Mineralogy*, Mineralogical Society of America, Chantilly, Virginia.
- Carmichael, I.S.E. (1991) The redox state of basic and silicic magmas: a reflection of their source regions?, *Contributions to Mineralogy and Petrology*, 106, 129-141.
- Chen, J., Elmi, C., Goldsby, D., and Gieré, R. (2017) Generation of shock lamellae and melting in rocks by lightning-induced shock waves and electrical heating, *Geophysical Research Letters*, 44, 8757-8768.

Cottrell E., Lanzirotti, A., Mysen, B., Birner S., Kelley K. A., Botcharnikov R., Davis F. A., and Newville, M. (2018) A Mössbauer-based XANES calibration for hydrous basalt glasses reveals radiation-induced oxidation of Fe, *American Mineralogist*, 103, 489-501.

Davis, A.M., Hashizume, K. Chaussidon, M., Ireland, T.R., Prieto, C.A., and Lamberts, D.L. (2008) Oxygen in the Sun. In G.J. Macpherson, D.W. Mittlefehldt, and J.H. Jones, Eds., *Oxygen in the Solar System*, 68, p. 73-92. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Chantilly, Virginia.

Delano, J.W., and Livi K. (1981) Lunar volcanic glasses and their constraints on mare petrogenesis, *Geochimica et Cosmochimica Acta*, 45, 2137-2149.

Delano, J.W., Lindsley D.H., and Rudowski R. (1981) Glasses of impact origin from Apollo 11, 12, 15, and 16: Evidence for fractional vaporization and mare/highland mixing. *Proceedings of the Lunar and Planetary Science Conference*, 12, 339-370.

Delano, J.W. (1986) Pristine Lunar Glasses: Criteria, Data, and Implications. *Proceedings of the 16th LPSC part 2, Journal of Geophysical Research*, vol. 91, p.D201-D213.

Delano, J.W. (1991) Geochemical comparison of impact glasses from lunar meteorites ALHA81005 and MAC88105 and Apollo 16 regolith 64001, *Geochimica et Cosmochimica Acta*, 55, 3019-3029.

Duke, M.B., Woo C.C., Sellers G.A., Bird M.L., and Finkelman R.B. (1970) Genesis of lunar soil at Tranquility Base. *Proceedings of the Apollo 11 Lunar Science Conference*, 1, 347-361.

Dyar, M.D., Agresti D. G., Schaefer M. W., Grant C.A., and Sklute E.C. (2006) Mossbauer Spectroscopy of Earth and planetary materials, *Annual Review in Earth and Planetary Sciences*, 34, 83-125.

Dyar, M.D., McCanta, M., Breves, E., Carey, C.J., and Lanzirotti, A. (2016) Accurate predictions of iron redox state in silicate glasses: a multivariate approach using X-ray absorption spectroscopy, *American Mineralogist*, 101, 744-747.

Frost, B.R. (1991) Introduction to oxygen fugacity and its petrologic importance. In D.H. Lindsley, Eds., *Oxide Minerals: Petrologic and Magnetic Significance*, 25,

p. 1-9. Reviews in Mineralogy, Mineralogical Society of America, Chantilly, Virginia.

Gieré, R., Wimmenauer, W., Müller-Sigmund, H., Wirth, R., Lumpkin, G. R., and Smith, K. L., (2015) Lightning-induced shock lamellae in quartz, *American Mineralogist*, 100, 1645-1648.

Goodrich, C.A., Sutton, S.R., Wirick, S., and Jercinovic, M.J. (2013) Chromium valences in ureilite olivine and implications for ureilite petrogenesis, *Geochimica et Cosmochimica Acta*, 122, 280-305.

Grapes, R. H., and Müller-Sigmund, H., (2010) Lightning-strike fusion of gabbro and formation of magnetite-bearing fulgurite, Cornon di Blumone, Adamello, Western Alps, Italy, *Journal of Mineralogy and Petrology*, 99, 67-74.

Gross, J., Treiman, A.H., and Mercer, C.N. (2014) Lunar feldspathic meteorites: Constrains on the geology of the lunar highlands, and the origin of the lunar crust, *Earth and Planetary Science Letters*, 388, 318-328.

Herd, C.D.K., Borg, L.E., Jones, J.H., and Papike, J.J. (2002) Oxygen fugacity and geochemical variations in the martian basalts: Implications for martian basalt petrogenesis and the oxidation state of the upper mantle of Mars, *Geochimica et Cosmochimica Acta*, 66, 2025-2036.

Herd, C.D.K. (2008) Basalts as probes of planetary interior redox state. In G.J. Macpherson, D.W. Mittlefehldt, and J.H. Jones, Eds., *Oxygen in the Solar System*, 68, p. 527-554. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Chantilly, Virginia.

Karner, J.M., Sutton, S.R., Papike, J.J., Shearer, C.K., Jones, J.H., and Newville, M. (2006) Application of a new vanadium valence oxybarometer to basaltic glasses from the Earth, Moon, and Mars, *American Mineralogist*, 91, 270-277.

Karner, J. M., Papike, J. J., Shearer, C. K., McKay, G., Le, L., and Burger, P. (2007) Valence State partitioning of Cr and V between pyroxene-melt: Estimates of oxygen fugacity for martian basalt QUE 94201, *American Mineralogist*, 92, 1238-1241.

Kilinc, A., Carmichael, I.S.E., Rivers, M.L., and Sack, R.O. (1983) The ferric-ferrous ratio of natural silicate liquids equilibrated in Air, *Contributions to Mineralogy and Petrology*, 83, 136-140.

Kress, V.C., and Carmichael, I.S.E. (1991) The compressibility of silicate liquids containing Fe₂O₃ and the effect of composition, temperature, oxygen fugacity and

pressure on their redox states, *Contributions to Mineralogy and Petrology*, 108, 82-92.

Korotev, R.L. and Gillis J.J. (2001) A new look at the Apollo 11 regolith and KREEP, *Journal of Geophysical Research*, 106, 12339-12353.

Liu, Y., Guan, Y., Zhang, Y., Rossman, G.R., Eiler, J.M., and Taylor, L.A. (2012) Direct measurement of hydroxyl in the lunar regolith and the origin of lunar surface water, *Nature Geoscience*, 5, 779-782

Lucey P., Korotev R. L., Gillis J. J., Taylor L. A., Lawrence D., Campbell B. A., Elphic R., Feldman B., Hood L. L., Hunten D., Mendillo M., Noble S., Papike J. J., Reedy R. C., Lawson S., Prettyman T., Gasnault O., and Maurice S. 2006. Understanding the lunar surface and space-Moon interactions. In *New views of the Moon*, edited by Joliff B. L., Wieczorek M. A., Shearer C. K. and Neal C. R. Reviews in mineralogy and geochemistry, 60. Chantilly, VA: Mineralogical Society of America. pp. 83-219.

Macpherson, G.J. (2008) Introduction. In G.J. Macpherson, D.W. Mittlefehldt, and J.H. Jones, Eds., *Oxygen in the Solar System*, 68, p. 1-3. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Chantilly, Virginia.

Mallmann, G., and O'Neill, H. St. C. (2009) The crystal/melt partitioning of V during mantle melting as a function of oxygen fugacity compared with some other elements (Al, P, Ca, Sc, Ti, Cr, Fe, Ga, Y, Zr and Nb, *Journal of Petrology*, 50, 1765-1794.

McCanta, M.C., Dyar, M.D., Rutherford, M.J., Lanzirotti, A., Sutton, S.R., and Thomson, B.J. (2017) In situ measurement of ferric iron in lunar glass beads using Fe-XAS. *Icarus*. 285, 95-102.

McKay, D.S., Heiken, G.H., Taylor, R.M., Clanton, U.S., Morrison, D.A., and Ladle G.H. (1972) Apollo 14 soils: Size distribution and particle types. *Proceedings of the 3rd Lunar Science Conference*, 1, 983-994.

McKay, D.S., and Bassu, A. (1983) The production curve for agglutinates in planetary regoliths. *Proceedings of the Lunar and Planetary Science Conference*, 19, B193-B199.

McKay, D.S., Bogard, D.D., Morris, R.V., and Korotev, R.L. (1989) Apollo 15 regolith breccias: Window to a KREEP Regolith. *Proceedings of the Lunar and Planetary Science Conference*, 19, 19-41.

McKay, D.S., Heiken, G., Basu, A., Blanford, G., Simon, S., Reedy, R., French, B.M., and Papike, J. (1991) The Lunar Regolith. In G. H. Heiken, D.T. Vaniman, and B.M. French, Eds, *Lunar Sourcebook: A User's Guide to the Moon*. p. 285-356. Lunar and Planetary Institute, Cambridge University Press, New York, New York.

Meyer, B.S., Nittler, L.R., Nguyen, A.N., and Messenger, S. (2008) Nucleosynthesis and chemical evolution of Oxygen. In G.J. Macpherson, D.W. Mittlefehldt, and J.H. Jones, Eds., *Oxygen in the Solar System*, 68, p. 31-54. *Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America, Chantilly, Virginia.

Murck, B.W., and Campbell, I.H. (1986) The effects of temperature, oxygen fugacity and melt composition on the behavior of chromium in basic and ultrabasic melts, *Geochimica et Cosmochimica Acta*, 50, 1871-1887.

Papike, J.J., and Simon, S.B. (1982) The lunar regolith: chemistry, mineralogy, and petrology. *Reviews of Geophysics and Space Physics*, 20, 761-826.

Papike, J.J., Karner, J.M., and Shearer, C.K. (2005) Comparative planetary mineralogy: valence state partitioning of Cr, Fe, Ti, and V among crystallographic sites in olivine, pyroxene, and spinel from planetary basalts, *American Mineralogist*, 90, 277-290.

Pieters, C. M., Taylor, L.A., Noble, S.K., Keller, L.P., Hapke, B., Morris, R.V., Allan, C.C., McKay, D.S., and Wentworth, S. (2000) Space weathering on airless bodies: resolving a mystery with lunar samples. *Meteoritics and Planetary Science*, 35, 1101-1107.

Ridley, W.J., Reid, A.M., Warner, J.L., and Brown R.W. (1973) Apollo 15 green glasses, *Physics of the Earth and Planetary Interiors*, 7, 133-136.

Righter, K., Sutton, S.R., Newville, M., Le, L., Schwandt, C.S., Uchida, H., Lavina, B., and Downs, R.T. (2006) An experimental study of the oxidation state of vanadium in spinel and basaltic melt with implications for the origin of planetary basalt, *American Mineralogist*, 91, 1643-1656.

Roberts, S.E., McCanta, M.C., Jean, M.M., and Taylor, L.A. (in print, a) New lunar meteorite NWA 10986: A mingled impact melt breccia from the highlands; a complete cross section of the lunar crust. *Meteoritics and Planetary Science*.

Roberts, S.E., Sheffer, A.A., McCanta, M.C., Dyar, M.D., and Sklute, E.C. (in print, b) Oxidation state of iron in fulgurites and Trinitite: Implications for redox

changes during ultra-high T-P metamorphism. *Geochimica et Cosmochimica Acta*.

Rutherford, M.J., Head, J.W., Saal, A.E., Hauri, E., and Wilson, L. (2017) Model for the origin, ascent, and eruption of lunar picritic magmas. *American Mineralogist*, 102, 2045-2053.

Sato, M. (1978) Oxygen fugacity of basaltic magmas and the role of gas-forming elements. *Geophysical Research Letters*, 5, 447-449.

Simon, S.B., Papike, J.J., and Laul J.C. (1981) The Apollo 14 regolith: Petrology of cores 14210/14211 and 14220 and soils 14141, 14148, and 14149, *Proceedings of the 13th Lunar and Planetary Science Conference*, 87, A232-A236.

Stöffler, D. (1984) Glasses formed by hypervelocity impact, *Journal of Non-crystalline Solids*, 67, 465-502.

Stöffler, D. Hamann, C., Metzler, K. (2018) Shock metamorphism of planetary silicate rocks and sediments: Proposal for an updated classification system. *Meteoritics and Planetary Science*, 53, 5-49.

Wadhwa, M. (2008) Redox conditions on small bodies, the Moon and Mars. In G.J. Macpherson, D.W. Mittlefehldt, and J.H. Jones, Eds., *Oxygen in the Solar System*, 68, p. 31-54. *Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America, Chantilly, Virginia.

CONCLUSION

The Fe and Cr oxybarometer developed for this work can accurately measure oxidation states and predict equilibrium oxygen fugacities of both terrestrial and lunar samples. XAS is an in situ, non-destructive technique capable of achieving small spot sizes of 1 micron. This technique will be especially valuable to accurately measure oxidation states of small and rare samples returned from future missions including Osiris Rex and Mars 2020. Understanding the equilibrium oxygen fugacity conditions present during the formation of these samples will help in our efforts to understand the role of oxygen in the early solar system and in the development of planetary samples.

Impacts are unavoidable in planetary exploration and their effects need to be understood before we can analyze returned planetary samples for their petrologic information. The fulgurites, lunar agglutinates, impact melts, and glass beads analyzed using this oxybarometer indicate that impacts are not always reducing as originally thought but can be oxidizing. Fulgurites formed in both unconsolidated and consolidated target materials of varying compositions indicate that the composition along with the compaction of the target material probably controls rather reduction or oxidation occur. Large spatial variation of oxidation states can occur within a small area. Oxidation states of Cr in lunar agglutinates also indicate that oxidation can occur during impacts on the lunar surface in addition to reduction, and spatial variation can exist similar to what is seen in the fulgurites. Impact alteration cannot be simply modeled, and there exists many controls on changes in oxidation states that have not been fully explored.

Although impacts can erase primary petrologic information in planetary samples, they can also provide us with new samples from planetary surfaces. Lunar meteorites such as NWA 10986 are providing us with new lunar samples that are potentially sourced from outside of the area on the near side of the Moon where the Apollo samples were collected. This meteorite records the effects of impacts responsible for its formation and ejection from the lunar surface by its extensive impact melt. This meteorite along with many like it are questioning our theory for the formation and evolution of the Moon by providing new lithologies not represented by the Apollo samples.

VITA

Sarah Roberts was born in Birmingham, Alabama. She graduated with a Bachelor of Fine Arts in painting from Birmingham-Southern College. She then completed a Masters of Art in painting at the University of Alabama. Sarah went back to school for geology and completed a Masters in Earth Sciences at Indiana University Purdue University Indianapolis followed by another Masters in Earth Sciences at the University of Notre Dame.