Chemical Effects of Metamorphism on Enstatite Chondrites

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Abstract

Chondrites are the most primitive and most unaltered form for any group of meteorites. The relative abundance of rock forming elements that are found in chondrites are similar to those of the Sun. Chondrites make up about 90% of all meteorite falls, so this group of meteorites are relatively common. I will be investigating the process of metamorphism in a specific subgroup of chondrites called enstatite chondrites. Enstatite chondrites make up only 2% of all meteorites that fall to the Earth and they are unique in their reduced mineralogy and their isotopic similarity to the Earth. Enstatite chondrites are assigned a metamorphic grade based on textural properties. Currently, there is no reliable quantitative method to determine the metamorphic grade for enstatite chondrites. Therefore, the overarching goal of this project is to build a more reliable, quantitative method to determine the metamorphic grade of enstatite chondrites. To do this, trace element concentrations will be measured, and this will be supported by a calculation of relative standard deviation (RSD) to estimate their variation. Major elements cannot be used because enstatite chondrites are rich in magnesium, so comparisons between major elements becomes difficult when there is one dominant major element. Typically, as meteorites are metamorphosed, elements diffuse and trend toward equilibration (homogenize). Therefore, as the grade of metamorphism increases, the expectation is that trace elements will homogenize for all enstatite grains. By utilizing petrography and the Electron Probe Microanalyzer (EPMA) to locate enstatite grains, trace elements present in enstatite chondrites were measured by way of Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). From LA-ICP-MS, it was found from the data collection process that the abundance of yttrium, titanium, and heavy rare earth elements (HREE), had an RSD that would decrease for higher metamorphic grades. The results from these analyses are in line with our expectations and there is evidence that the overall trend in the data supports the hypothesis.

Introduction

Meteorites are survivors from the first few million years of the evolution of the Solar System. As a result, they can inform us about the early stages of the Solar System and how it has evolved over time. Of all the different types of meteorites that fall to the Earth, chondrites are the most common, this includes ordinary chondrites, carbonaceous chondrites, and enstatite chondrites (Figure 1). Chondritic meteorites are primitive and have been largely unaltered since their formation as nebular sediments, therefore they can provide information about the early Solar System and the building blocks of the terrestrial planets. They can also provide information about the environmental conditions in which they formed and provide clues to a timeline of how the Solar System went from dust and gas to consolidated planetary materials. Because some of these primitive meteorites have been metamorphosed, it is important to understand how they have changed over time. If scientists can decipher the temperature and duration of meteorite parent body metamorphism, this can improve our understanding of the evolution of early planetesimals. Therefore, the greater understanding scientists have regarding chondrites, the better the understanding will be of the initial conditions of the Solar System.

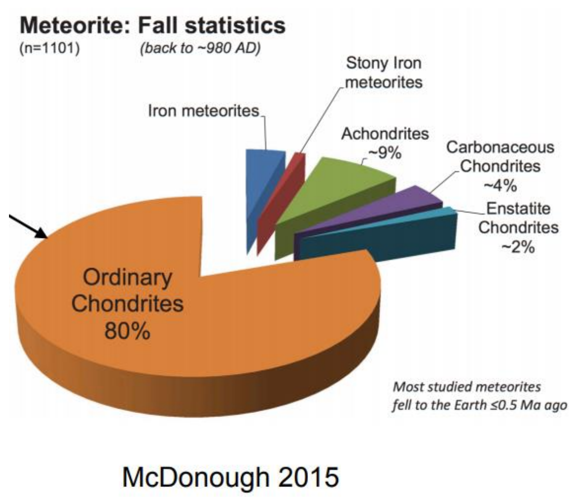


Figure 1: Of all the meteorites that fall to the Earth, about 80% of these meteorites are ordinary chondrites, while only 2% are enstatite chondrites. (McDonough 2015).

Meteorites are classified based on their chemical composition, mainly whether they are made up of silicate (stony meteorites) or metallic material (iron meteorites). Chondrites fall under the category of stony meteorites. Chondrites are distinguished from other meteorites by being chemically primitive (unaltered) and the relative (bulk) composition of rock forming elements in chondrites are similar to that of the Sun. The similarity of these rock forming element abundances allows us to appropriately draw comparisons between these meteorites and the Solar System, in general.

Chondrites are further sub-divided into carbonaceous, ordinary, and enstatite chondrites based on their mineralogy and petrography. Chondrites have not undergone any significant geochemical alteration since accretion but have been isochemically metamorphosed (Sears et al., 1984). The metamorphism process of chondrites is unique and will be discussed in more detail below. First, I will discuss chondrites, using ordinary chondrites as a template, and then I will apply that template to discuss enstatite chondrites and what makes these chondrites so unique and unordinary.

All chondrites consist of a variable mixture of chondrules, refractory inclusions and a fine-grained matrix. Ordinary chondrites can contain a wide variety of minerals but are dominated by olivine, pyroxene, and feldspar. Figure 2 below is a photomicrograph of an ordinary chondrite. The photograph does not easily show the location of minerals, analyses on an Electron Probe Micro-analyzer would be needed to differentiate minerals. However, the photomicrograph provides information about the characteristics of the chondrules and the matrix of this meteorite. Chondrules are crystallized pieces of molten solar nebula, and they are usually spherical in shape. The gold colored line in the image below roughly outlines one example of a chondrule for this photomicrograph. There are additional outlines that can be made in the image below that would detail more chondrules. The black, opaque portion of this image is called matrix and is made up of pre-solar, fine-grained materials (including pre-solar grains) that cements the chondrules together (Huss et al. 2006).

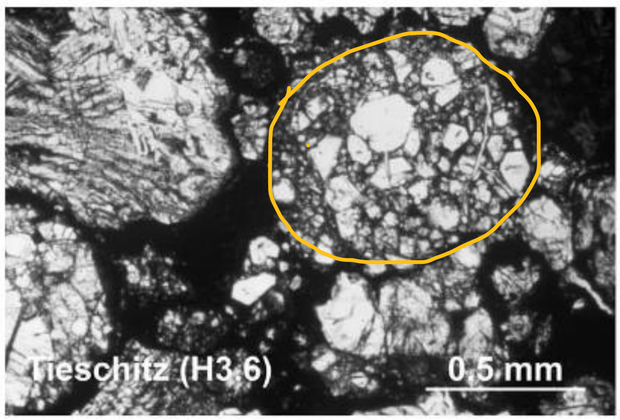


Figure 2: Photomicrograph of the Tieschitz, type 3 ordinary chondrite (Huss et al. 2006). The gold colored circle is an example of a chondrule while the surrounding black area is the matrix.

Metamorphism of Chondrites: Ordinary chondrites have been thermally metamorphosed. There is textural and mineral chemical evidence for metamorphism. There is a deterministic scale of metamorphic grade for ordinary chondrites, beginning with type 3 (low grade metamorphism) and goes through type 6 (high grade metamorphism), (type 1 and type 2 metamorphic grades involve hydrous alteration, these grades are only found in carbonaceous chondrites). If we were to go a type 7 grade, the highest grade, the meteorite would be considered as melt, or perhaps an igneous rock. As a result, this metamorphic grade may not accurately represent that of a chondritic meteorite (there are type 7 ordinary chondrites, but these are most likely impact melts).

The process of metamorphism on chondrites is very different to that experienced on Earth. The pressure is always low, being on such small parent bodies, and without any geologically significant variation. Chondrites are also very dry and there is no evidence for significant fluid flow and thus, no geochemical alteration. Therefore, the metamorphism of chondrites is said to be isochemical. This is because there is only local diffusion of elements and recrystallization occurs only due to an increase in temperature, the most likely heat source of which is the decay of elements. Because of these conditions/restraints on these metamorphism conditions, there are no apparent bulk chemical changes during metamorphism for chondritic meteorites. Instead, the changes are physical, and dominated by solid state diffusion. For instance, the minerals in the meteorite can recrystallize into new minerals. There is also localized equilibration (homogenization) of major and trace elements between minerals. The degree of recrystallization and equilibration is determined by the time-temperature regime of the metamorphism. If a chondrite undergoes metamorphism for a long time at high temperatures, there is a greater likelihood for complete equilibration of elements as well as further recrystallization of minerals (Weisberg et al., 2012).

Metamorphic Grade Scale: Chondrite metamorphism can be best described by the "Onion Shell Model," as shown in Figure 3. In this figure, assume that this image is a cross-section of the parent body of a meteorite that is kilometers to tens of kilometers in diameter. Heating of the parent body is internal, probably from the decay of short-lived radionuclides, such as ^{26}Al, that were live in the early Solar System, but are now long extinct. Heat is produced throughout the parent body and is lost to space from the surface. This diffusion of heat and surface loss results in a gradient from higher temperatures in the core (estimates up to 950°C [Dodd, 1981]) to lower temperature at the surface (260°C [Alexander et al., 1989]). Specifically note that the heating duration in the parent body is much longer on the inside relative to the surface. This results in high grade chondrites (type 6) in the core and low (type 3) at the surface. Furthermore, there is a range in size of parent bodies: small parent bodies naturally have less metamorphism that the larger parent bodies. The largest parent bodies could possibly result in possible melt phases and the formation of achondrites (meteorites without chondrules, that may be geologically differentiated).

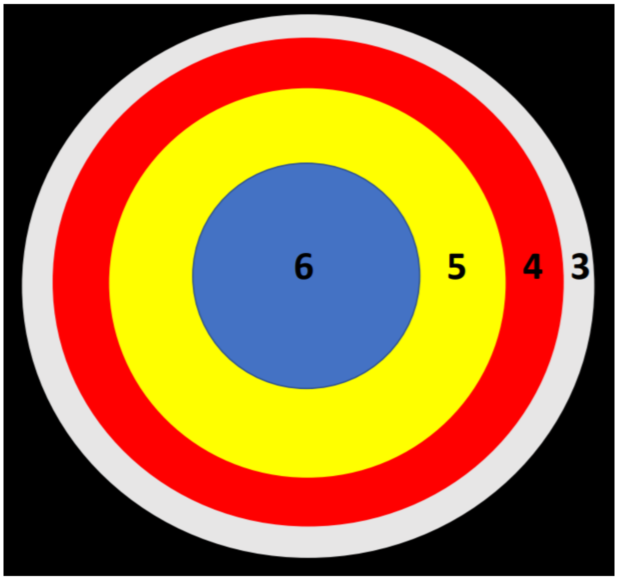


Figure 3: Onion Shell Model. The numbers in the figure indicate the metamorphic grade for this parent body. Also notice how the section thickness for each grade increases toward the center of the image.

Determining the metamorphic grade for any meteorite is difficult and requires a combination of qualitative and quantitative analyses. These analyses typically include textural properties and elemental abundance ratios, which will now be described in more detail. The meteorite in the photomicrograph in Figure 2 is a type 3 ordinary chondrite. This is evidenced in part by the ability to clearly and easily identify chondrules in the photo. The ability to identify chondrules is a textural property that can be used to classify any chondritic meteorite to a certain grade. As the metamorphic grade increases, the ability to clearly identify chondrules becomes difficult. The meteorite in Figure 4 below is an ordinary chondrite that is classified as a type 6 because there are no clear circular constituents that would be considered a chondrule. However, by only using qualitative (textural) properties, there is subjective judgement in assigning a grade to a meteorite. These subjective assignments are most concerning for deciding whether a meteorite is a type 3 or 4, a type 4 or 5, or a type 5 or 6. Textural properties are best used to identify the extremes of the most primitive unmetamorphosed type 3s and the most metamorphosed completely recrystallized type 6.

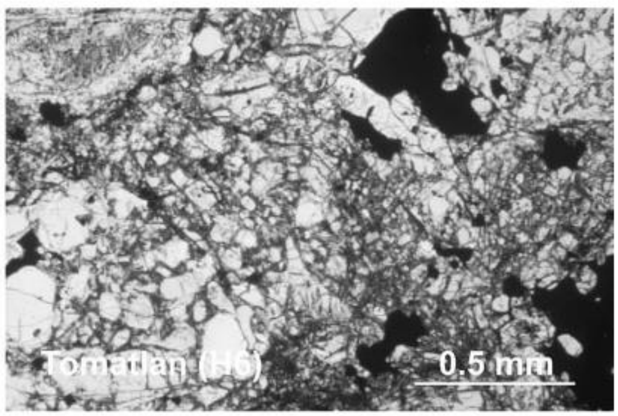


Figure 4: This is a photomicrograph of an ordinary chondrite, named Tomatlan (Huss et al. 2006). Note how there are no chondrules that can be clearly identified at this scale. If this photo was at lower magnification, we might be able to identify chondrules because the chondrules would be larger.

In addition to assigning metamorphic grade by textural properties, chemical methods can also be used to assign metamorphic grades for ordinary chondrites. The chemical method for ordinary chondrites involves analyzing major element distributions, particularly the distribution between Fe and Mg. As metamorphic grade increases, the variation between the amount of Fe and Mg at a location in the ordinary chondrite will narrow. In other words, the range of Fe/Mg that are found in silicate minerals of low-grade ordinary chondrites is large. As the metamorphic grade increases, this range decreases because the Fe and Mg homogenize (diffuse) rapidly. Although metamorphic grades of type 3 can be further subdivided by the degree of homogenization (i.e. type 3.0-type 3.9). By the time the chondrites have reached type 4, the elements are largely homogenized. Beyond type 3.9, the subjective petrographic method is relied on (Huss et al. 2006).

Enstatite Chondrites: Enstatite chondrites are a group of chondritic meteorites characterized by their mineralogy (dominated by the mineral enstatite), their highly reduced composition (there is typically less than 1% Fe in the silicates with the dominant form of Fe being present in metal or sulfides), and their oxygen isotopic composition which, uniquely amongst chondrites, is indistinguishable from that of the Earth. In addition, enstatite chondrites contain very low concentrations of water, and this is in support of the fact that they undergo isochemical metamorphism. Because enstatite chondrites have such a low oxygen fugacity, there is a very small amount of oxidized iron in the silicate minerals of these meteorites. As a result, most of these minerals are composed of primarily magnesium end-members including enstatite ($Mg_2Si_2O_6$) and forsterite (Mg_2SiO_4). Given that these are near end member compositions, the lack of Fe in the silicates means that the elemental Fe and Mg distributions cannot be used to assess the metamorphic grade. The amount of oxidized Fe is so small in enstatite chondrites that there is no feasible way to quantitatively asses the variation, or any change in the variation, because the uncertainties would be too large. Therefore, because using major elements are clearly not an option for enstatite chondrites, we will attempt to use trace element distributions between minerals instead. Particularly, the variation of trace elements will be determined by analyzing the ubiquitous grains of enstatite and perform a relative standard deviation calculation. There has been some evidence to show that there is an order of magnitude variation in concentrations of some trace elements (Jacquet et al, 2018), and diffuse more slowly than Fe-Mg, therefore it should offer a more sensitive method of assessment for assigning metamorphic grade.

Subgroups of Enstatite Chondrites: Within the enstatite chondrite group of meteorites, there are two significant subgroups; EL- and EH-type chondrites where each type is distinguished by containing a low concentration of total iron or a high concentration of total iron, respectively. Both subgroups contain a very small amount of oxidized iron, but the EH chondrites carry slightly more oxidized iron than EL chondrites, so they need to be distinguished as such. Given the scope of our project, in that we are most concerned about metamorphic grade, I do not expect these subgroups to behave differently from each other. Nevertheless, it is still important to be aware of these two subgroups and to see if there is any correlation in their behavior during the data collection process.

Applicable Research for Enstatite Chondrites: Studying enstatite chondrites will allow us to investigate a uniquely reduced region of the Solar System that seems to have isotopic links to the Earth. Understanding the formation and evolution of chondrites will allow us to clarify the range of processes occurring in the early solar system. This will enable us to compare and contrast the behavior of chondritic materials under differing oxidation conditions. It may also help us understand the evolution of the terrestrial building blocks for the solar system. Because enstatite chondrites are isotopically similar to the Earth, they may be able to provide information about the early planet forming constituents that have evolved into the Earth. By understanding the metamorphic grade scale for enstatite chondrites, we can track the history of how enstatite chondrites have metamorphosed. To achieve this goal, we want to be able to determine if there is a relationship between trace element distributions and texturally determined metamorphic grades for enstatite chondrites.

Hypothesis

Given that the major elements in ordinary chondrites homogenize for higher metamorphic grades, similar predictions can be made specific to enstatite chondrites. Knowing that it is too difficult to compare major element concentrations in enstatite chondrites, another option would be to rely on trace elements to determine metamorphic grade instead. Therefore, my hypothesis is that **the variation in select trace element concentrations in enstatite grains observed in enstatite chondrites will decrease with increasing metamorphic grade**. It is known that major and trace elements diffuse in ordinary chondrites with increasing metamorphic grade. Therefore, this hypothesis is a credible prediction for how trace elements could consequentially homogenize in enstatite chondrites. Not all trace elements will diffuse or homogenize at the same rate or at all, but elements of similar properties should behave similarly. These elements could possibly be the rare earth elements (REE).

Prior Study: The reason for selecting REE to be prime candidates to answer this hypothesis comes from a previous study by (Jacquet et al. 2018), see Figure A below. The lines of most interest on this plot are the two red enstatite lines. This graph is plotting the approximate concentration (abundance) of rare earth elements for a type 3 enstatite chondrite. The biggest takeaway from this graph is the large range in the REE abundances, this indicates a lot of variation of abundance between two grains of enstatite. Also notice that light REE are not nearly as abundant as heavy REE, this is because of the enrichment of heavy rare earths in enstatite. Our hypothesis predicts that this variation will narrow with increasing metamorphic grade. For instance, if this plot were of a higher graded enstatite chondrite, the expectation is that the two red enstatite lines would be closer together. In addition, Sc and Y may also be useful as they behave like REE but have much higher abundance in enstatite chondrites overall.

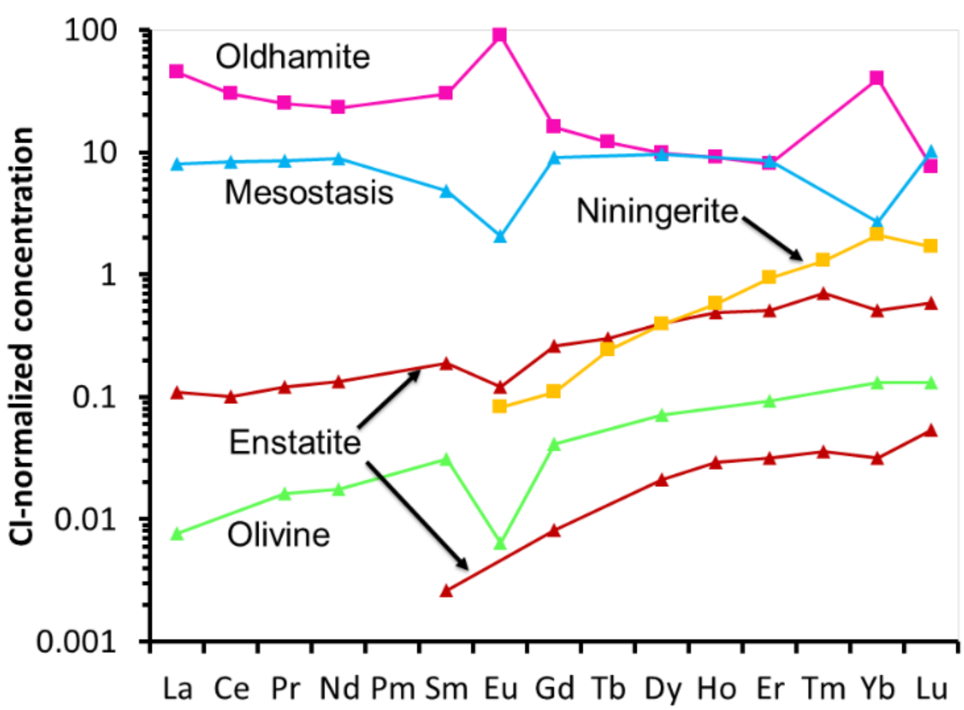


Figure A: This figure estimates the abundance of REE in Sarah 97072, an EH3 enstatite chondrite. Note the two red enstatite lines and how they are initially far apart for a type 3 enstatite chondrite, this is unsurprising (Jacquet et al. 2018).

Methods

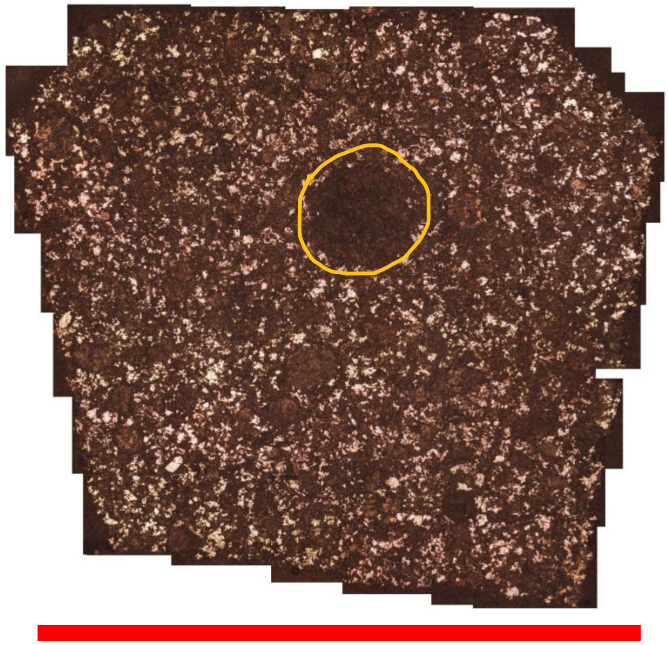
A series of analytical methods including petrographic context, mineralogy, and mineral chemistry were used to test the hypothesis. A total of 12 polished enstatite chondrite samples were analyzed (Table 1). The main analyses utilized non-destructive, and minimally destructive, geochemical methods such as an optical microscope (petrography), an Electron Probe Microanalyzer (EPMA), and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). An analytical protocol was developed starting with examination using an optical microscope for the preliminary identification of enstatite grains suitable for analysis, followed by electron microprobe measurements to confirm our initial identification, then laser ablation analysis of identified areas for trace element determination.

Table 1: Progress of Analyses					
Meteorite Name	**Meteorite Type**	**Full Mosaic?**	**Analyses completed on probe?**	**Analyses completed on laser?**	**Comments**
Sahara 97072	EH3	No	Yes (Lehner et al. 2014)	Yes (Lehner et al. 2014)	(Lehner et al. 2014)
ALH 84170	EH3	No	Yes (Lehner et al. 2014)	Yes (Lehner et al. 2014)	(Lehner et al. 2014)
LAR 06252	EH3	No	Yes (Lehner et al. 2014)	Yes (Lehner et al. 2014)	(Lehner et al. 2014)
Abee	EH4	Yes	Yes	Yes	Completed
Indarch	EH4	Yes	Yes	Yes	Completed
Adhi Kot	EH4	No	No	Yes	Completed
NWA 1222	EL5	Partial	Yes	Yes	Completed
Saint Sauveur	EH5	Yes	Yes	Yes	Completed
St. Mark's	EH5	Yes	Yes	Yes	Completed
Eagle	EL6	Partial	Yes	Yes	Completed
Blithfield	EL6	No	No	No	Incomplete
Daniel's Kuil	EL6	Yes	No	Yes	Completed
Hvittis	EL6	Partial	No	No	Incomplete
Atlanta	EL6	Yes	No	Yes	Completed
Jajh deh Kot Lalu	EL6	Yes	No	Yes	Completed
Pillistfer	EL6	Yes	Yes	No	Incomplete
Khairpur	EL6	Yes	No	No	Incomplete

Table 1: Meteorite samples that are considered complete have been analyzed well. Meteorite samples that are incomplete must be analyzed further, either on the probe, the laser, or both.

Optical Microscopy

Firstly, an optical microscope was used to examine meteorite textures, identify potential target enstatite grains, and take photomicrographs of potential minerals for further analysis (Figure 5). For reference, an example chondrule from the St. Mark’s meteorite is outlined in yellow on the figure.



Scale: 1 cm

Figure 5: A sample photomicrograph of one of our samples, St. Mark's, an EH5 enstatite chondrite. The irregular white specks indicate a reflective material, most commonly sulfides or iron-nickel metal. Brown or tan phases are silicate, namely enstatite, olivine, or diopside.

The photomicrograph can provide information about meteorite texture and the abundance of metallic content (metal is reflective when viewed using a reflected light microscope). Photomicrographs will also serve as a map when these samples are hosted in other data collection instruments, including EPMA and LA-ICP-MS. Locations of interest can be quickly identified on the photomicrograph by presence of chondrules, and these are the prime locations where I will choose to make further analyses.

Electron Probe Microanalyzer (EPMA)

Following the basic optical characterization of samples, the electron probe was used to gather chemical data. EPMA is a non-destructive, geochemical instrument that steers a stream of electrons toward a solid sample (in this case, meteorites) to determine major and trace element abundances.

Before analyses can begin on these meteorites, the surface of the samples needed to be polished flat in a thin or thick section, or as a probe mount. The samples were then carbon coated so that charge would not build up on as electrons interact with the sample. The carbon conducts these electrons away and prevents charge build-up.

The electron beam from the probe excites electrons in a small volume (typically about 1-5 micron diameter) on the mineral or phase of interest. These excited electrons then lose energy and drop back down to their ground state, emitting an x-ray of characteristic energy when doing so. The composition of the mineral can be determined by measuring the energy and wavelength of the emitted x-rays and comparing them with standard minerals. The tabulated data produced by EPMA and the standard data will be detailed in Appendix B. Please note that we did not complete quantitative data analyses for all the samples on the probe. In most cases, we utilized the probe to ensure that the minerals identified for analysis by optical mineralogy were enstatite targets, and therefore, we did not take quantitative measurements for most samples. We simply looked at the EDS spectrum and confirmed whether the mineral grain was enstatite.

There are two methods of determining the concentration of major and minor elements using the EPMA: energy dispersive (EDS) and wavelength dispersive (WDS) spectroscopy. EDS measures the number of x-rays over a given energy range, whereas WDS counts the number of x-rays of a specific wavelength diffracted by a crystal. EDS is quicker, but less accurate than WDS and is useful for rapid identification of minerals (Figure 6). Generally, for accurate determination of element concentration by WDS, several points for analysis are set-up for overnight measurement. These overnight measurements for a few samples are summarized in Appendix C.

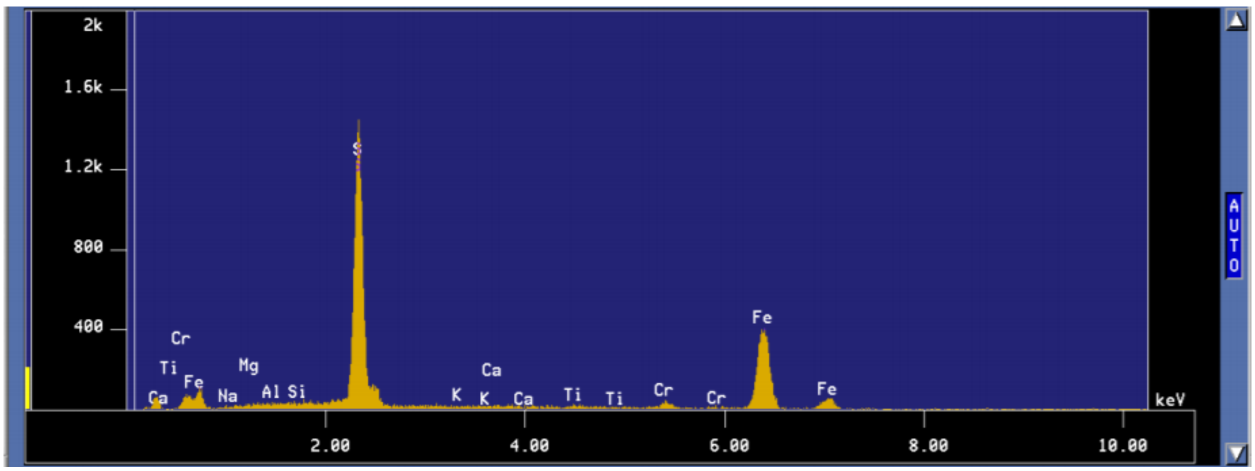


Figure 6: EDS Spectrum from one of the samples that we tested. This reveals a sulfide composition of troilite (FeS), an additional mineral beside enstatite that we knew we may encounter.

The electron probe quantified the abundance of major and minor elements at each location of interest, ultimately showing what mineral is present at a specific location. The elements measured on the probe were, in order of atomic number Na, Mg, Al, Si, Ca, Cr, Mn, Fe, and Co. In some locations, precise measurements were made for the minerals of interest. The relative peak heights (by EDS) of Mg and Si were sufficient to distinguish between enstatite and forsterite, with the Mg/Si of enstatite being 1, that of forsterite being 2. Diopside is easily distinguished by containing Ca.

<u>Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)</u>

The laser ablation technique was focused on producing high quality trace element data, which has been the most helpful in answering our hypothesis. LA-ICP-MS will produce concentrations for a variety of trace elements of enstatite. The trace elements that we are interested in collecting data for are listed in order of atomic number: Sc, Ti, V, Ni, Ga, Ga, Ge, Ge, Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm, Eu, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Th, and U. Note that I had to use multiple isotopes for some of these elements to monitor interference from other elements or molecules. These include ^{69}Ga, ^{71}Ga, ^{73}Ge, ^{74}Ge, ^{151}Eu and ^{153}Eu. If the measured ratios for these elements differed from the natural ratio it was clear that there was an interference so the isotope that appeared to be not over-abundant was used.

LA-ICP-MS involves firing a UV laser (New Wave UP213) at the mineral of interest, thereby removing a small (typically an 80-micron diameter spot) amount of material. The removed material is then swept into the plasma by a stream of He gas where it is atomized and ionized. The positive ionized sample is drawn into the mass spectrometer by a -2000 V electrical potential then, after shaping and steering, enters a magnetic and electric field that separates ions based on their mass/charge ratio. An electron multiplier amplifies the signal and records the numbers of ions located for each mass/charge station. The relative ion abundances in the standard (with a known concentration) are compared to those measured in the sample and, using the major element abundance determined by the electron probe as an internal standard, the concentration of the trace elements can be calculated using the data processing package LAMTRACE (Achterberg et al., 2001). Where the major elements had not been determined accurately on the electron probe, it was assumed that the enstatite was the stoichiometric end-member (a reasonable assumption from our data and literature data) and that the SiO_2 content was 57 wt% (the presence of small amounts of FeO substituting for MgO will not affect the SiO_2 abundance significantly for these analyses).

LA-ICP-MS was the main instrument in providing the data that used to test the proposed hypothesis. Laser ablation was performed for various grades of metamorphosed enstatite chondrites (type 3 to type 6), such that we can compare the collected data for each type. The data collected so far by LA-ICP-MS is summarized in multiple tables in Appendix C. The operations conditions utilized for this instrument will also be detailed in Appendix C. Specific subsections of these data tables will be explained in detail in the Results section.

Accuracy and Precision of LA-ICP-MS

When performing analyses using the method of LA-ICP-MS, two standards were used to estimate the uncertainty in the measurements. These serve two purposes. Firstly, as outlined above, to use in the calculation of concentration, and secondly, to help constrain our accuracy and precision. The two standards we used for our data collection process for the laser were the National Bureau of Standards (NBS) sodium-calcium aluminosilicate glass NIST 610 (National Institutes Standards and Technology) and the USGS vitrified Hawaiian basalt BHVO2g. These two standards also allowed us to assess the precision and accuracy of our measurements.

Assessing the accuracy and precision of laser ablation analyses is challenging and there are a variety of ways to do so. Poisson counting statistics can be used as the absolute limit as to how precisely a measurement can be made. We can also use the standard (NIST 610) and reference material (BHVO2g) to assess the precision and accuracy. Each of these materials is uniform in composition, and the concentrations are known and accepted in the microanalysis community.

NIST 610 is a common standard that has high (~440 ppm) concentrations of all the lithophile trace elements, allowing for a strong signal for all the analyzed elements when using

LA-ICP-MS. BHVO2g is a vitrified rock that has only the level of trace elements found in an ocean island basalt, so many elements are in low concentration. This means the latter is not the best standard as the precision of measurement of the standard is comparable to that of the samples. However, it is useful to determine the accuracy and precision of the concentration determinations as it is more similar to the samples analyzed. The LAMTRACE data reduction software package requires two analyses of the standard at the beginning of a block of analyses and two at the end (a block consists of 20 analyses, including standards and samples).

Results

To begin the Results section, I would like to recall my hypothesis: **the variation in select trace element concentrations in enstatite grains observed in enstatite chondrites will decrease with increasing metamorphic grade.** To appropriately evaluate this hypothesis, we must be able to quantify the term, variation. Measuring the variation and how it changes is important to determine whether our results can falsify this hypothesis.

Due to time constraints, all the meteorite samples could not be analyzed by EPMA and LA-ICP-MS. However, the few type 4 and type 5 meteorites were each analyzed fully on both instruments. Because we had many type 6's, it was acceptable to not analyze each of them. Also note that some of the samples were not analyzed with the electron probe and were only analyzed on the laser, mostly for meteorite samples that were a type 6. This is because it was easier to locate enstatite grains on the photomicrograph for higher grades than it was for lower grades. Table 2 below indicates the number of enstatite grains analyzed on each sample when using the laser.

Table 2: Enstatite Grains Analyzed using LA-ICP-MS

Sample Name	**Number of Grains Analyzed**
*Sahara 97096 (EH3)**	11
Type 3, <u>Partial</u> of Total*:	11
Abee (EH4)	6
Indarch (EH4)	7
Adhi Kot (EH4)	20
Type 4, Total:	33
NWA 1222 (EL5)	7
St. Sauveur (EH5)	8
St. Mark's (EH5)	12
Type 5, Total:	27
Eagle (EL6)	18

Daniel's Kuil (EL6)	3
Atlanta (EL6)	10
Jaih deh Kot Lalu (EL6)	7
Type 6, Total:	38

(Lehner et al. 2014)* – ***Note: All the original data from Lehner was not immediately available.

Table 2: The number of analyses per sample varied due to mineral abundance and grain size. The goal for each sample that was analyzed was to collect a representative data set from the entire meteorite. The statistic we used to compare data analyses was relative standard deviation, which considers the difference in the number of analyses per sample and makes the data comparable, relatively.

Because we are completing many analyses on the laser at many different locations on each sample, we decided that the best way to quantify the variation between enstatite grains is to utilize a statistical calculation called relative standard deviation (RSD). At each location on the sample, we were able to compute the concentration of various trace elements. Using these concentrations for each sample, we then produced the average value and the standard deviation for each data set. To calculate the RSD, we computed the quotient of the average and the standard deviation and then multiplied that by 100. RSD tells us how far away, in terms of a percent, the standard deviation is from the mean. Using RSD as a percent makes more sense because the concentration for individual trace elements can vary widely.

Electron Probe Microanalysis

Before analyses were performed by EPMA, there was some preparation. Using the mosaics and photomicrographs that were produced earlier, we created potential areas of interest that we wanted to investigate further. These locations would then be marked on our photomicrograph using yellow boxes, see Figure 7 below. Then, we would use the probe and travel to these boxed locations and see if we could find some enstatite. A purple, circular mark would indicate that enstatite is present in that location, while an 'x' would indicate no enstatite. As a result, we developed a full inventory for the locations of enstatite grains to analyze on the laser for many different samples.

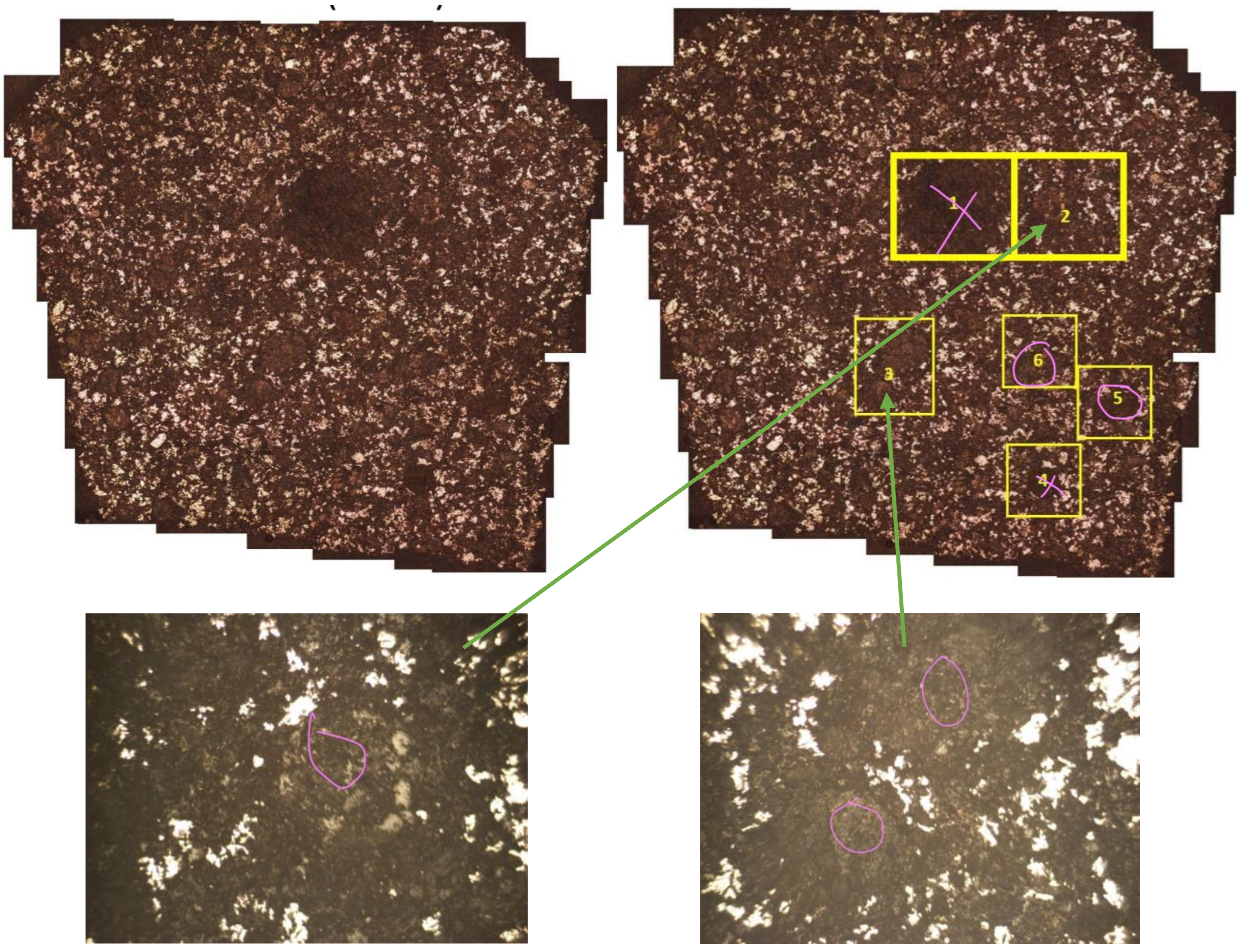


Figure 7: The original and inked image of St. Mark's (EH5). The yellow boxes indicate the areas of interest and the violet color indicates presence (circle) or absence (x mark) of enstatite. The markings for locations 2 and 3 are on another image that is zoomed in much further.

The elements that were analyzed and present on the EDS spectrum were Na, Mg Al, Si, Ca, Cr, Mn, Fe, and Co. If the abundances of these elements matched our expectations for enstatite, we would then use the values of major element abundances for the internal standardization in LA-ICP-MS. If you look in Appendix B at the second data table titled "Concentration of Elements for Abee, NWA1222, Eagle, and Saint-Sauveur," it is clear that the relative abundance of Si and Mg is a 1 : 1 ratio. In other words, there are two Si atoms for every two Mg atoms, as in the mineral formula for enstatite: $Mg_2Si_2O_6$. From this data table, notice that Mg is consistently less than two, meaning that the enstatite we located in these samples are not completely filled with magnesium – this is expected. We expect that there would be some other trace element substitutions with the magnesium end member, but only in very small amounts.

*Note: The third table in Appendix B gives the uncertainty in the measurement of the standard, which was calculated for big peaks for N number of counts by the equation $\sigma = (\text{sqrt}(N) / N) * 100\%$.

Laser Ablation

After performing probe measurements, we would repeat the procedure of finding the locations of the yellow boxes with enstatite on the data collection instrument. Because the laser focuses on a spot that is very precise, a zoomed-in image of a photomicrograph would need to be utilized. By using these photomicrographs, we were able to travel across the meteorite and find the specific locations we wanted to test. We would then mark the location accordingly with a letter and number, see Figure 8 below. The full comprehensive quantitative data set can be found in the Appendix.

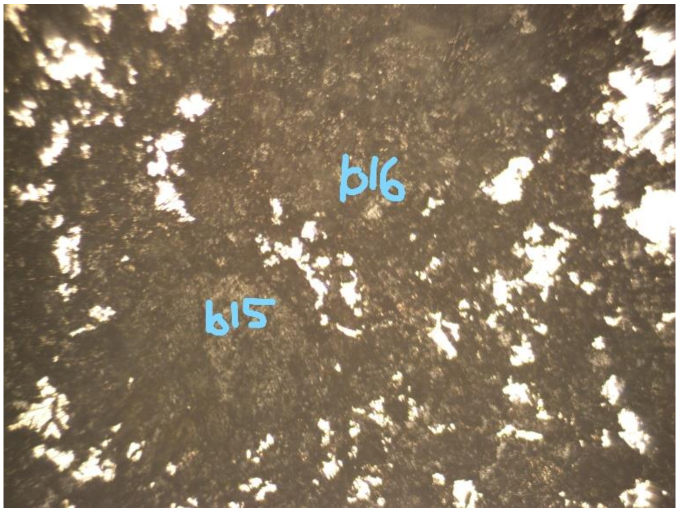


Figure 8: A photomicrograph from yellow box #3 in Figure 7 (St. Mark's (EH5)). The labels b15 and b16 mark the locations that were analyzed with the laser. Notice that these locations are roughly similar to the locations of the purple circles in Figure 7.

Laser ablation has been used to determine trace element abundances accurately and precisely for each analyzed location. Some elements have proven to be more useful than others in testing my hypothesis. Some have been in an abundance that is too low for consistent measurement and others have not varied between metamorphic grades, probably due to slow diffusion rates. Specifically, we have focused on Sc and Y, as well as heavy REE. These elements tend to trend toward equilibrium for higher metamorphic grades, thus supporting our hypothesis. There may be other select trace elements that support our hypothesis, but Sc, Y, and HREE, show a consistent a trend and are likely the most useful for future analyses and for future statistical calculations.

For our purposes, the variation observed is much larger than the error associated with the analyses. While there is an uncertainty attached to the RSD, the uncertainty is so small that it will not be able to noticeably change any trend we see in the data. In Figures 9 thru 12 are graphs of RSD vs Metamorphic Grade for specific elements including Sc, Y, and HREE. The HREE were split into two groups because 6 elements on one graph produced a crowded figure.

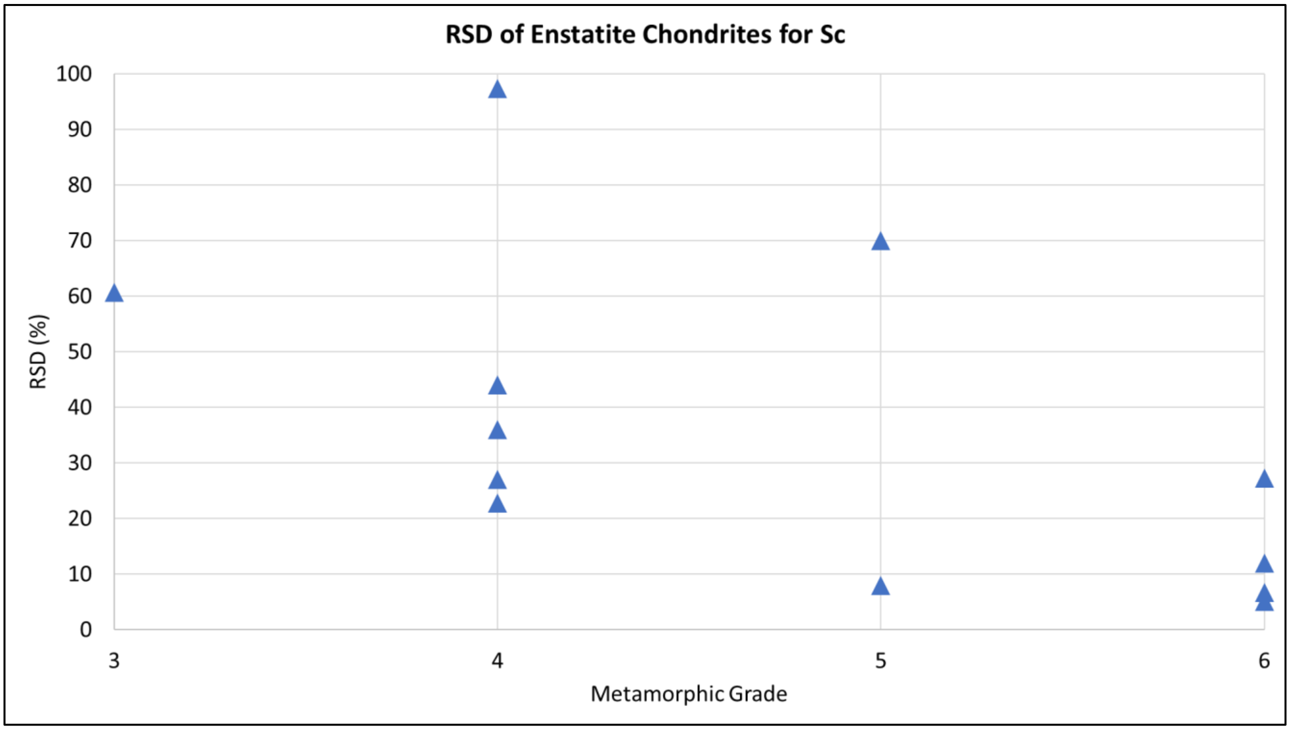


Figure 9: RSD for scandium for various metamorphic grades of enstatite chondrites. Notice that the overall trend is decreasing, which is what our hypothesis predicted.

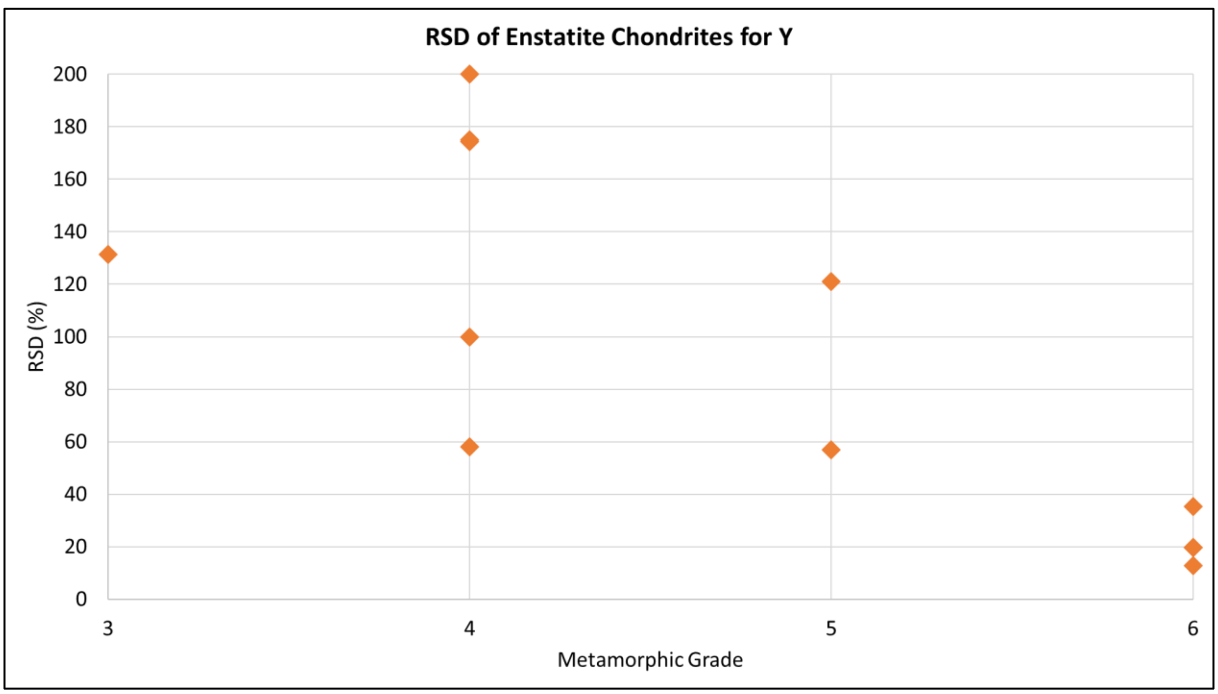


Figure 10: RSD for yttrium for various metamorphic grades of enstatite chondrites. Notice that the overall trend is decreasing, which is what our hypothesis predicted. However, the data points for grade 4 vary widely between each other.

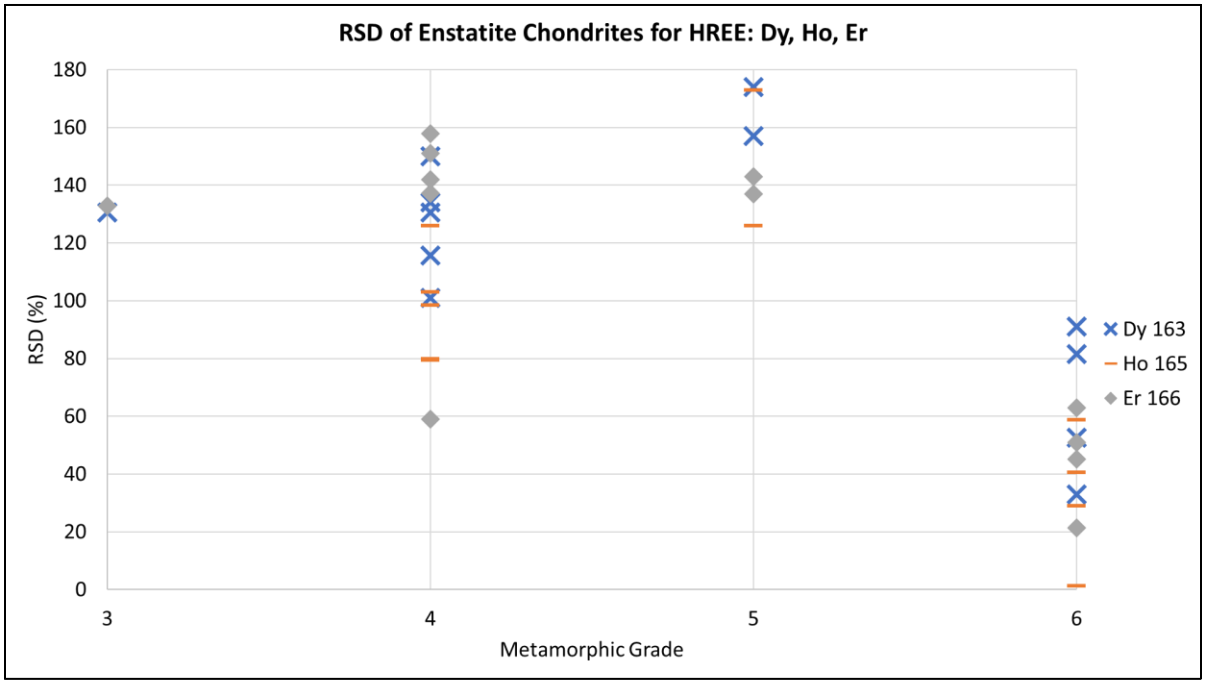


Figure 11: RSD for the first three (the lightest) HREE for various metamorphic grades of enstatite chondrites. There appears to be a slight increase from type 4 to type 5, but once we reach type 6, there is significant decrease, just like with Sc and Y.

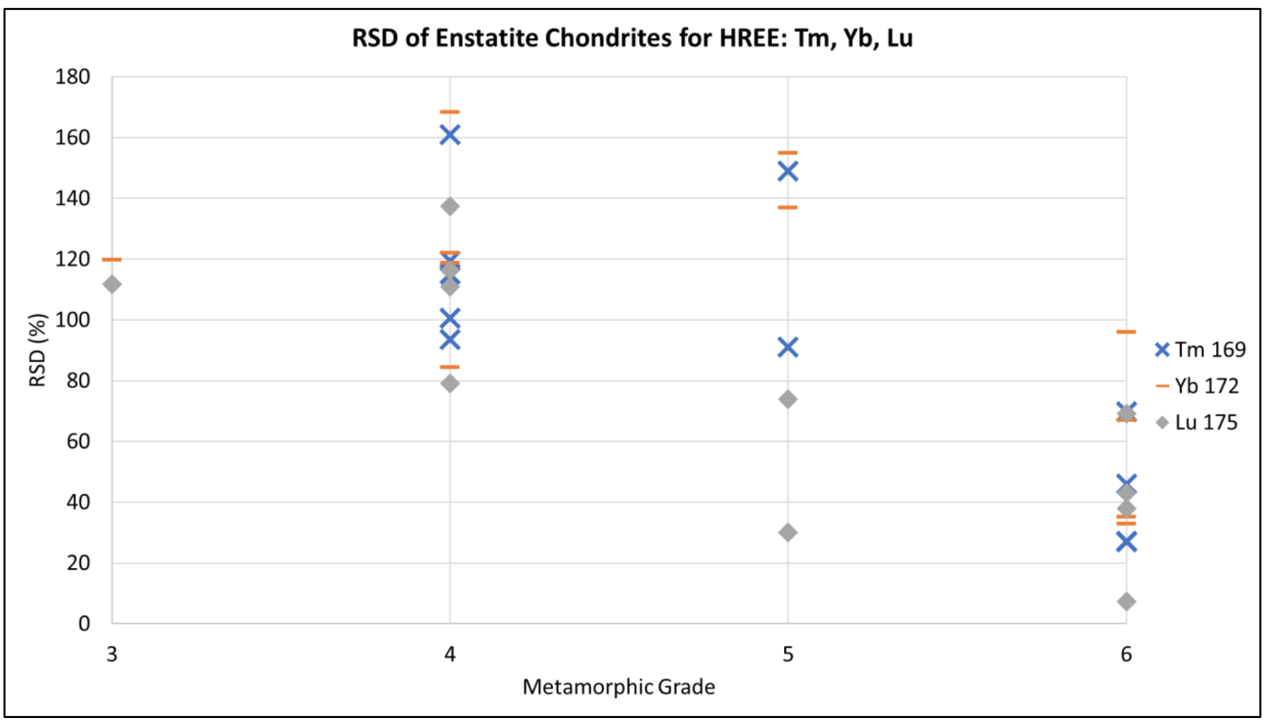


Figure 12: RSD for the last three (the heaviest) HREE for various metamorphic grades of enstatite chondrites. There appears to be an overall decrease in RSD, supporting our hypothesis.

From each of the four graphs above, most of these data follow a trend that supports our hypothesis. Because RSD is a measurement that quantifies the variation of trace element concentrations, our hypothesis leads to the expectation of an overall decrease in RSD for an increase in metamorphic grade. Our hypothesis is supported from the data on the graphs above because there is indeed an overall decreasing trend for each of these graphs, especially at the type 6 grade relative to lower grades. In all cases and for all trace elements included in the graphs above, the type 6 grade has the lowest RSD value. This is because the trace elements between enstatite grains homogenized during metamorphism and thus, the distribution of these trace elements has the smallest amount of variation. However, while the overall decreasing trend is noteworthy, there are some outliers. In some cases, the RSD increases either from type 3 to type 4 or from type 4 to type 5. Therefore, this goes against our hypothesis because there is an increase in RSD, which is the opposite of our expectation. So, it is critical that we identify any possible clear and consistent trends for a progressively decreasing RSD value. For example, I would consider yttrium in Figure 10 to have a clear, progressive decrease in RSD for an increase in metamorphic grade.

Conclusions

The findings in this project have led to a conclusion that strongly supports that of the hypothesis. There is a clear trend that the **variation in select trace element concentrations in enstatite grains observed in enstatite chondrites will decrease with increasing metamorphic grade.** After analyzing multiple samples of texturally graded meteorite samples (type 4 to type 6) and using literature data for type 3, the collected data has been shown to support this hypothesis with the use of RSD calculations. Overall, RSD was used to estimate the variation of trace element concentrations in enstatite grains and the RSD at the type 6 grade was consistently the lowest of the grades. While the general trend was an overall decrease, there was considerable scatter for type 4 and type 5 grades. This reflects the natural variation of elements in each sample and the range of conditions experienced within a given grade. As has been stated previously, the boundaries between grades are not well defined and within a grade there is a range of metamorphic conditions (temperature and time). There was a significant amount of overlap between the RSDs between the type 4's and type 5's. However, considering all the data points, the overall trend of the data is clearly decreasing, which is in line with our prediction.

The data that is presented in the graphs above allows for us to clearly determine when a meteorite has a metamorphic grade of type 6 by identifying low RSD values. However, because there is a lot of separation between RSD values for type 4 grades and type 5 grades, it would be difficult to use this method to differentiate between a type 4 and a type 5. A crucial detail that must be considered is that these meteorite samples were assigned metamorphic grades mainly based on their textural properties. As stated in the introduction, textural properties are used in the assignment of metamorphic grades, but these properties are certainly not as precise as chemical properties because the classifications are somewhat subjective. Therefore, because there is currently no reliable major element chemical method to assign metamorphic grade for enstatite chondrites, there is going to be larger error in the metamorphic grade value. As a result, some enstatite chondrites that are perceived as type 5 from their textural properties might be type 4. The reverse may also be true. Currently, the assignment of metamorphic grades for enstatite chondrites is subjective and relies mostly on textural properties. By developing a more calculated approach to identifying a metamorphic grade scale for enstatite chondrites, it will be possible to make more conclusions from future data sets.

Discussion

The findings in this project have been quite promising. The data that was presented above allowed the hypothesis to be evaluated and the feasibility of this project gives reason for more research to be completed on enstatite chondrites. With more research and more data, more analyses will be able to be made and the conclusions can become more specific. One of the long-term goals for research on enstatite chondrites is to develop a standard quantitative metamorphic grade scale. While there are many quantitative statistics and analyses that could have been utilized, this project showed that this goal can be possibly achieved by using the variation in trace element abundances. The conclusion confirmed that there is an overall trend for the decrease in trace element abundance variation with increasing metamorphic grade. However, this trend is not perfect, it is only a correlation. The largest reason the conclusions can be stated above is that type 6 metamorphic grades continuously have the lowest RSD for the given trace elements. With more data collection, the conclusion may be reinforced or countered (adjusted in such a way that makes it more correct).

From the selected trace elements, the overall trend shows a clearly decreasing RSD. If you were to take the average of the RSD for a given metamorphic grade for a given element, this trend will become more noticeable. While this is our expectation, an additional question to ask now is, can we use this trend or is there another statistic that we can use in this data to confirm this hypothesis? The calculation of diffusion rates may possibly allow us to answer this question, but due to time constraints, this idea was never fully developed. Nevertheless, further research and more data will be necessary to have a sense of how effectively we can quantitatively use trace element abundances to reliably assign metamorphic grades. This project confirms that there is a significant overall trend for some trace elements that support our hypothesis, but these trends will need to hold for a much larger data set to be useful. The goal for this research was to be able to quantitatively determine and assign a metamorphic grade for enstatite chondrites. I believe we have just begun this process and it is just a matter if somebody sees the promise I have in this research and takes it one step further.

While it is possible to use the methods presented in this paper to differentiate a type 6 metamorphic grade from other grades, it still remains somewhat difficult to use the RSD calculation to quantitatively predict a metamorphic grade of type 3, 4, or 5. Recalling Table 1, it is clear that the amount of samples we had for type 3's, 4's, and 5's, are not as plentiful as that of type 6. Therefore, the argument that it is possible that there was a lack of diverse samples to analyze is valid. In addition, Table 2 does not show an equal number of enstatite grains being analyzed for each metamorphic grade. While these analyses do not need to be exactly equal, there is a large discrepancy between the total number of grains that cannot be ignored and must be considered. There were numerous factors that lead to some samples being analyzed more than others in terms of the total number of grains, including meteorite size and time. Larger meteorites naturally received more attention and more analyses were performed on those samples rather than smaller meteorites. In all cases, we attempted to analyze locations across the meteorite and not focus on any one location.

In addition to the lack of diversity in these samples, there was also noticeable differences in the characteristics of type 4's, 5's, and 6's. In type 4's and 5's, it was difficult to perform analyses on enstatite grains. We had to completely rely on the probe to find locations of enstatite and then find the same locations again on the laser. The more metamorphosed type 6 grade meteorites were easier to analyze as they were more metamorphosed and there was an absence of trace elements. The probe was not completely necessary to analyze the type 6 samples as enstatite grains would be encountered often. With more data analyses from a larger data set, a quantitative scale for metamorphic grade for enstatite chondrites could be developed.

With a metamorphic grade scale in place for enstatite chondrites, it will become easier to trace back the history for any enstatite chondrite. Each metamorphic grade is associated with a temperature and duration that represents some degree of how much the meteorite was isochemically metamorphosed. For higher metamorphic grades, the temperature and duration of metamorphism will clearly be hotter and longer. The opposite is true for lower metamorphic grades. Therefore, this metamorphic grade scale is important because if we can accurately identify the correct metamorphic grade, then we can predict the conditions under which a meteorite has been metamorphosed. The temperatures and durations that I mentioned are still being researched, there are no specific numbers that define certain boundaries for enstatite chondrites. These values are not needed to develop a metamorphic grade scale if a different method can be utilized. In fact, it might be easier if the metamorphic grade scale was developed first, and then using that information we can determine the conditions under which that enstatite chondrites have been metamorphosed.

Reflection and Future Steps

Given the sudden impact that COVID-19 has had on our research progress, I would like to take some time to detail how things could have gone better or what we would have done differently on this research project if we had more time. While a significant quantity of research was completed for this project, being absent from campus hindered the project in some respects. For example, while analyses were completed on a wide variety of samples, time constraints restricted us to completing fewer analyses per sample than desired. The original plan in place was to get a representative sample of data from as many of our samples as we could, then upon further analysis of the quantitative data, we would pick and choose the samples that we would want to make more analyses on. While significant data was collected and was sufficient to make some conclusions, more data could have been collected and it could have resulted in more conclusions.

In preparation for evaluating the hypothesis, the initial data collection did not focus on any specific trace element or any specific group of trace elements. However, based on other research that has been completed on enstatite chondrites and meteorites in general, we knew that rare earth elements would likely be prime candidates for evaluating our hypothesis. It was determined that heavy rare elements and Sc and Y were the most useful trace elements to use to support our hypothesis. Light rare elements had such low concentrations that the amount of error on those data values was very large, so these elements were not directly used to support our hypothesis. Now that there is certainty on what trace elements we want to investigate, our method for data collection can improve. By restricting our data collection to HREE and Sc and Y, we can dedicate more counting time to these trace elements, which will lead to an increase in the preciseness of measurements. This increase in counting time would be most noteworthy for some HREE elements that had a low, but still detectable, abundance. By constraining our focus to certain trace elements, we could have been more efficient with our data collection. However, this phase of data collection was never reached due to extenuating circumstances that prevented non-essential research to continue. If this phase of data collection was reached, data analyses and conclusions may have changed.

The data analyses that we performed for this project only included meteorites that were classified as types 4, 5, or 6. The data for type 3 grades were extracted from the literature, Lehner et al. (2014). If we had some in-hand type 3 samples, we would be able to make better comparisons among our analyses. Relying on a small number of literature values means that the starting material (type 3) is not well characterized. In addition to analyzing more type 3 samples, analyzing more samples and more grains in each sample can give us better statistics to analyze. Overall, a more representative data set could have led to more data analyses and conclusions. The conclusions that were made were limited to only the data that was available.

The trace element data that was collected using the laser provided valuable evidence to evaluate our conclusion. However, the other forms of data collection that could have been improved include the utilization of the petrographic microscope and the electron probe. For some meteorite samples, the petrographic microscope did not take the highest resolution image or there were locations on the meteorite that were mistakenly skipped and had no photo. Higher resolution pictures would have been helpful, in addition to making sure there were no fragmented mosaics. Havin full mosaics and better photographs would have produced a more detailed “map” to follow and make the data analysis process more efficient.

In addition, the electron probe was not used as often as desired. The main purpose of the electron probe was to identify grains of enstatite. However, an additional purpose was that the probe could give us an idea of the whole composition of the meteorite. The probe could indicate pockets of metal and matrix, detailing the specific major elements found in each. The probe could also indicate the presence of other minerals besides enstatite, most notably troilite (FeS) and forsterite ($Mg_2 Si O_4$). In addition to this information, the probe can produce precise quantitative measurements, as seen in Appendix B. The data table produced by the probe can show how much magnesium was found for some enstatite grains. While magnesium is the most abundant major element in enstatite chondrites, there are additional major elements, most notably iron (Fe). In summary, the quantitative values produced by the probe can show how much magnesium is in these enstatite grains, and therefore, the quantity that is not magnesium. Overall, it gives an idea of the abundance of impurities in the overall sample for each enstatite grain.

An additional feature of these meteorites that was not investigated further due to time constraints is the fact that some of these samples were clearly brecciated, such as Adhi Kot (see image below). Analyses were completed and compiled for this entire sample. Given more time, it would have been interesting if two data sets were collected for Adhi Kot. One data set would represent the top half of the sample and the other data set would represent the bottom half of the sample. How would these results compare? If, for example, the top half had a higher RSD than the bottom half, could we use that as evidence that the bottom half was metamorphosed more than the top half? Could we say the top half of this meteorite had a metamorphic grade that resembled a type 4, but the bottom half was instead a type 5? What about individually investigating the different brecciated fragments, could that show some sort of trend or correlation in the data? This sample is very interesting because it could indicate the difference between a type 4 and a type 5 if the datasets are completely different. However, if the data sets are not completely different, it shows how unreliable textural properties can be. The textural properties observed between the top and bottom of this sample are very different. Visual inspection clearly indicates that the top half is completely unlike the bottom half, however, this specimen was classified as a type 4. Therefore, if this sample is truly a type 4, what specific textural properties can differentiate a type 4 from a type 5? What are the visual indicators? Or is there an alternative explanation to why half of this sample is brecciated, and the other half is fine-grained. Further investigation into this sample could possibly answer some of these questions. This sample could possibly indicate how reliable or unreliable textural properties can be used to identify metamorphic grades for enstatite chondrites.

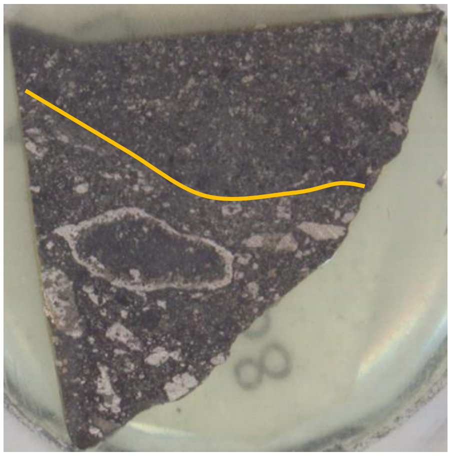


Figure 13: This is a scan of Adhi Kot (EH4). Notice how the lower half of sample is brecciated, but the upper half is not. This is very interesting because it could indicate that a part of this meteorite may have been metamorphosed differently.

Most of this project focused on quantifying the trace elements present in the mineral enstatite. However, there are other minerals in enstatite chondrites as well as metals that were not investigated. For future research purposes, it is not necessary to only focus on the enstatite grains in these samples. There can be correlations between mineral grains, metals and nonmetals, and chondrules and matrix. There are numerous options to select from. However, it was easiest to focus on the most abundant mineral (enstatite) and quantify the trace elements in each enstatite grain. We could have investigated all the trace elements in the metals (or something else) in the meteorite and see if there was a correlation, but the results likely would not have been consistent. Nevertheless, whatever method you choose, it is imperative that you are consistent, and the method has reasoning. For example, it would not make sense to compare trace elements in enstatite with the trace elements in an iron-nickel metal, the results would obviously be vastly different and unhelpful in answering anything.

Acknowledgements

The author would like to extend thanks to Dr. Philip Piccoli, for the assistance he provided during the use of the Electron Probe Microanalyzer. In addition, I would like to thank my advisor, Dr. Richard Ash, for being incredibly helpful, accessible, and supportive throughout the duration of this project.

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Honor Pledge

"I, Nicholas Emm, pledge on my honor that I have not given or received any unauthorized assistance on this assignment."

Appendices

Appendix A: Meteorite Sample Information

Appendix B: EPMA Standards and Data

Appendix C: LA-ICP-MS Parameters and Data Table

Appendix D: Method Specifications for Mass Spectrometer

Appendix E: Average, Standard Deviation, and RSD Calculations

**IMPORTANT NOTE: Due to the surprise cancellation of classes/closing of UMD on the Friday before Spring Break began, all the data from this project is not included in this report. Some data sets were left in the lab because I had all of the calculations I needed for the purpose of writing this report. Most of the data sets that were not included were the original LAMTRACE data tables from the Spring semester. The data sets from the Fall are still present in the Appendix. I apologize for the inconvenience.

Appendix A: Meteorite Sample Information

Table 1: Progress of Analyses					
Meteorite Name	**Meteorite Type**	**Full Mosaic?**	**Analyses completed on probe?**	**Analyses completed on laser?**	**Comments**
Sahara	EH3	No	Yes (Lehner et al. 2014)	Yes (Lehner et al. 2014)	(Lehner et al. 2014)
ALH	EH3	No	Yes (Lehner et al. 2014)	Yes (Lehner et al. 2014)	(Lehner et al. 2014)
LAR	EH3	No	Yes (Lehner et al. 2014)	Yes (Lehner et al. 2014)	(Lehner et al. 2014)
Abee	EH4	Yes	Yes	Yes	Completed
Indarch	EH4	Yes	Yes	Yes	Completed
Adhi Kot	EH4	No	No	Yes	Completed
NWA 1222	EL5	Partial	Yes	Yes	Completed
Saint Sauveur	EH5	Yes	Yes	Yes	Completed
St. Mark's	EH5	Yes	Yes	Yes	Completed
Eagle	EL6	Partial	Yes	Yes	Completed
Blithfield	EL6	No	No	No	Incomplete
Daniel's Kuil	EL6	Yes	No	Yes	Completed
Hvittis	EL6	Partial	No	No	Incomplete
Atlanta	EL6	Yes	No	Yes	Completed
Jajh deh Kot Lalu	EL6	Yes	No	Yes	Completed
Pillistfer	EL6	Yes	Yes	No	Incomplete
Khairpur	EL6	Yes	No	No	Incomplete

Appendix B: EPMA Standards and Data

Group: Analyses Sample: NE-18Oct19

*****   NEW CALIBRATION   *****

CITZAF

JEOL On-line type Implemented by Paul Carpenter Caltech 1993

JEOL License of CITZAF Version: 3.50

Standard Data

Element		Standard name	Wt.(%)
1	Na2O	Augite	1.2700
2	FeO	Augite	6.3400
3	Cr2O3	Chromite-Tieb	60.5000
4	CaO	Augite	15.8200
5	Al2O3	Augite	8.7300
6	MgO	Hypersthene	26.7900
7	MnO	Rhodonite	33.3400
8	SiO2	Hypersthene	54.0900
9	CoO	Co	127.1509

Standard Intensity of WDS

Element		Curr.(A)	Net(cps)	Bg-(cps)	Bg+(cps)	S.D.(%)	Date
1	Na	2.003E-08	114.5	9.9	6.2	1.15	Oct 18 10:36 2019
2	Fe	2.003E-08	611.6	22.4	18.0	0.66	Oct 18 10:36 2019
3	Cr	2.500E-08	5516.0	81.1	54.1	0.18	Sep 27 07:46 2019
4	Ca	2.003E-08	2144.5	15.2	15.4	0.34	Oct 18 10:36 2019
5	Al	2.003E-08	1379.9	22.4	15.6	0.43	Oct 18 10:36 2019
6	Mg	2.003E-08	4253.1	20.3	15.1	0.17	Oct 18 10:45 2019
7	Mn	2.011E-08	3222.9	24.3	19.3	0.23	Oct 18 13:00 2019
8	Si	2.003E-08	9305.5	45.8	23.4	0.16	Oct 18 10:45 2019
9	Co	2.002E-08	14776.5	75.9	61.1	0.11	Oct 18 10:38 2019

Standard Factors

Element	f(chi)	If/Ip	abs-el	1/s-el	r-el	c/k-el
Na	0.4390	0.0055	0.5240	0.9768	0.9922	1.9582
Fe	0.9812	0.0000	0.9972	0.7981	1.0583	1.1872
Cr	0.9813	0.0175	1.0026	0.8776	1.0384	1.0757
Ca	0.9341	0.0025	0.9675	0.9039	1.0501	1.0862
Al	0.6409	0.0108	0.7188	0.9530	1.0071	1.4339
Mg	0.5652	0.0054	0.6478	0.9961	0.9986	1.5435
Mn	0.9804	0.0000	0.9991	0.8357	1.0454	1.1456
Si	0.7007	0.0003	0.7689	0.9760	1.0138	1.3141
Co	0.9858	0.0000	1.0000	1.0000	1.0000	1.0000

Data table on next sheet.

Appendix C: LA-ICP-MS Parameters and Data Table

ICP MS parameters

Power	1270 W
Cool gas (Ar)	16 l min^{-1}
Auxiliary gas (Ar)	1.10 l min^{-1}
Sample gas (Ar)	0.73 l min^{-1}
Ablation carrier gas (He)	0.73 l min^{-1}
Extraction voltage	2000 V

Laser parameters

Spot size	40-80 μm
Repetition rate	7 Hz
Fluence	2.54-4 J cm^{-2}

Standards

NIST 610 synthetic doped alumino-silicate glass with nominally 400 ppm of a suite of trace elements

Reference material BHVO2g (USGS) vitrified Hawai'in Basalt

Silicon was used as the internal standardization element for the data reduction

All data reduction is performed by Lamtrace

Appendix D: Method Specifications for Mass Spectrometer

The method used by the mass spectrometer was to measure the isotopes in the list (100 times) in counting mode. Then collect 20 seconds of background data and then 50 seconds of gathering quality data. The background data was used to reduce any noise and reduce any uncertainty for the next 50 seconds of data collection.

The exact specifications will be on the next sheet.

Appendix E: Average, Standard Deviation, and RSD Calculations