Evidence for a polysulfane species in CM chondrites

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I. Abstract

Isotopic analyses of meteorites have the potential to provide a pathway to characterize the processes that occurred early in our solar system and shaped the world around us. Sulfur is a common element in the solar system and it exists both as a volatile and a solid. The nature of isotopic heterogeneity of sulfur in primitive asteroids is still somewhat unknown. The scale of the variability helps to characterize the processes that led to the isotopic fractionation and also helps paint a more complete picture of the processes that occurred on these parent bodies. Sulfur isotope analyses of the Murchison meteorite demonstrated the isotopic variability at a scale of a single large meteorite, and implied that this variability exists on the scale of centimeters to meters. The intention with this study was to characterize the possibility for variability in paired meteorites. Paired meteorites come from a single meteoroid, and those meteorite samples could demonstrate variability on a scale of meters to 100 meters. The scale of the fractionation itself could tell us more about whether or not the signatures are isolated in certain areas or randomly distributed in the chondritic matrix. This information could potentially tell us about the nature of the fractionation itself, whether or not it's a result of parent body processes or nebular processes. All species of sulfur were extracted (elemental, sulfides, sulfates) from two paired meteorites through a sequential chemical procedure. The sulfur was then analyzed in the mass spectrometer. The data resulting from the extractions and the subsequent analyses provide support for an argument about the reaction pathway that extraterrestrial sulfur follows. The data obtained from this study supports the idea that sulfur that is initially condensed as sulfide and then oxidized to sulfate. The isotopic data also exhibit characteristics consistent with the presence of a previously unmeasured sulfur species in one of the meteorites.

II. Introduction

Historically, meteorites have been studied for the purpose of helping to piece together the unknown that is solar system processes. Meteorites hold this capability partially because of the variety of types of meteorites. They are characterized by their chemical make-up or their origin or size. Different information can be gained from different meteorite types and so overall a large amount of knowledge can be gained from studying meteorites in general. Meteorites can also be studied using a variety of methods to characterize different aspects of them in order to draw different conclusions. For example, one can learn something by studying a meteorite's density using a certain technique and one may learn something else by studying a meteorite's chemical makeup using another technique. One such technique uses chemistry and mass spectrometry and focuses on characterizing the isotopic ratios within the meteorite in order to draw conclusions about the solar nebula as well as the homogeneity or heterogeneity of the isotopic ratios across different meteorite types. Studies performed in the past by Gao and Thiemens (1993) (also referred to as GT93) and Labidi et al. (2017) (also referred to as L17) record isotopic ratios for the four stable sulfur isotopes (^{32}S, ^{33}S, ^{34}S, ^{36}S) of a group of primitive meteorites called CM Chondrites. These studies reveal isotopic heterogeneity for this group of primitive meteorites that are attributed to low temperature nebular processes. The data in this project was used to further characterize the sulfur isotopic heterogeneity seen in the $\Delta^{33}S$ as well. GT93 and L17 record variations of ratios of $^{33}S/^{32}S$ in sulfur, sulfates, and sulfides of the Murchison meteorite implying that isotopic variability is observed at a scale of at least one of the individual CM chondrites. My project sought to characterize the isotopic ratios of ^{33}S in the extracted sulfur components from paired meteorite samples. From that data I was able conclude something about the heterogeneity of sulfur in paired meteorites and evaluate these variations. I was also able to learn more about the extraction products of the meteorites and the different isotopic signatures that they provided.

a. **Meteorites**

i. Chondritic Meteorites

Chondritic meteorites qualify with some of the oldest and most primitive rocks in the solar system. They are interpreted to have formed as conglomerates with some grains predating the formation of the solar system and preserving interstellar grains that have survived processing in the solar nebula environment. Understanding these meteorites is complicated immensely by secondary processing in the nebula after the components have formed or on asteroid bodies after accretion. A great challenge to the study of these meteorites lies in distinguishing the effects of primary from secondary processes. Primary refers to processes that have affected the individual components during their formation. Secondary processes refer to any process that has altered the individual component after its formation. These processes can include aqueous alteration, thermal metamorphism, and shock metamorphism. The most abundant component within chondrites are nodules of sub-millimeter-sized, igneous spheres called chondrules. Chondrules consist primarily of ferromagnesian silicate materials such as olivine, pyroxene and feldspathic glass.

There are 12 well-established groups of chondritic meteorites. The groups are differentiated by factors including bulk chemistry, isotopic compositions, oxidation states, and the proportion of individual components. The primary groups within the chondrite classification are the carbonaceous (C), ordinary (O), and enstatite (E) classes. There are 8 types of carbonaceous chondrites, each named for an archetype of its group. The 8 different groups are the Ivuna, Mighei, Vigarano, Renazzo, Ornans, Karoonda, Bencubbin and High iron groups. There are 3 groups within the ordinary chondrite type, called H, L and LL. The 8 carbonaceous chondrite groups, the 3 ordinary chondrite groups and the enstatite class make up the total 12 chondritic meteorite groups (Brearley and Jones, 1998).

My project focused specifically on carbonaceous chondrites. More specifically, the project was a study of Mighei- type meteorites (CM meteorites). CM chondrites are primitive, but there is evidence that they have clearly experienced varying degrees of aqueous alteration but no thermal metamorphism (Rubin *et al.*, 2007). CMs are known to have isolated grains of olivine, pyroxene and spinel in the matrix. The mineralogy of CM meteorites is classified as primary and secondary mineralogy of calcium-aluminum-rich inclusions (CAIs), the mineralogy of the matrices, and the mineralogy of the opaque phases. The primary minerals within CAI phases in CM chondrites include corundum, hibonite, perovskite, and spinel. Other primary minerals do exist but they are much more rare. The most common phases within the secondary mineralogy of CAIs in CM chondrites are phyllosilicates and calcite. The mineralogy of the matrix is dominated by phyllosilicates, which is described as a major component.

CMs also contain one of the highest bulk S contents of any chondrite group (Burgess *et al.*, 1991). The sulfur exists as sulfide, sulfates and elemental sulfur. It also contains large amounts of tochilinite and an unidentified poorly characterized phases (PCP) that is rich in Fe, S, Ni, and O. There are also carbonates present, with the dominating phase appearing as calcite with the rare occurrence of aragonite as well. Sulfates are not widespread but several occurrences have been reported and include gypsum as well as hemihydrate and anhydrite. There is also an oxide component of the matrix though it is not especially common and it normally appears as magnetite. Opaque phases are not as common in CM chondrites. Generally, metallic iron is rare due to aqueous alteration, although there have been rare occurrences of Fe, Ni metal grains within the matrix (Papike 1998).

ii. Broad Classifications

There are a few broad classifications of meteorites that will be referenced throughout this paper and need to be fully defined. One of these classifications is the concept of a meteorite find as opposed to a meteorite fall. A "find" is a meteorite that is found on the ground unrelated to any sighting or known impact. It is characterized as a meteorite due to the finder recognizing it as a specimen clearly from a non-terrestrial origin. In comparison, a "fall" is a meteorite that is seen to fall from the sky and then tracked down and successfully recovered after the impact. The meteorite samples from this study were meteorite finds from Antarctic ice sheets (Allan Hills pairing group).

As stated above, samples for my study are paired meteorite samples. If a sample is declared a paired meteorite sample, it has been determined that there are other samples similar to it and that those samples are fragments of the same meteoroid. A meteoroid is a piece of material knocked off of a parent asteroid that has an Earth crossing orbit. When material from a meteoroid reaches Earth's surface, it is called a meteorite. The idea of paired meteorites became particularly important after thousands of meteorites were discovered on ice fields in Antarctica and in the hot desserts and it was realized that these fragments might be related, coming from the same meteoroid. The classification of pairing is still very individualized and depends on careful research, using a variety of analytical techniques to document similarities that suggest a relationship between two meteorites. Most pairing classification is determined based on three broad categories: physical characteristics, geographic proximity, and recent space/terrestrial history.

The physical characteristics used for pairing include parameters such as shock level. It is seen as supportive evidence of pairing when fragments of the same class display equivalence of shock stage. Although, within this classification it is known that shock effects are notoriously inhomogeneous so that a difference in shock stage does not rule out pairings. Another physical characteristic is the mineralogy and mineral composition and rarity. Composition can be a vital pairing tool in many meteorite types due to their distinct and unique mineralogical and chemical make-up. The meteorite types in which composition plays a key role in pairing include iron meteorites, basaltic meteorites, unequilibrated ordinary chondrites, and other rare meteorite classes like lunar meteorites.

Geographic proximity is the second category used in pairing meteorites. People justifying meteorite pairs with proximity arguments must consider the potential for terrestrial agents of transport such as wind or water or ice. This is loosely defined as; meteorite-find locations within a few kilometers of each other are supportive of pairing.

The final category used to indicate pairing is recent space/ terrestrial history. This refers to measures such as Cosmic Ray Exposure (CRE) age, weathering, surface exposure age, and terrestrial age as well as other parameters. Paired meteorite samples should have the same CRE age, though many meteorites display similar ages that correspond to large break-up events so although having the same CRE age is supportive of pairing, it is not definitive. Differing CRE ages are regarded as a strong argument against pairing. Weathering refers to the weathering histories of different fragments, although it is acknowledged that it is possible that fragments could have a different weathering history so that this may not be the strongest evidence for pairing. Natural Thermoluminescence (TL) measures the surface exposure age and it reflects the terrestrial thermal history. A similarity in natural TL levels is supportive of pairing but it is not definitive because of the possibility of differences in terrestrial histories. Lastly, the terrestrial age of fragments can be supportive of pairing. Natural TL measurements as well as a measure of the abundance of cosmogenic radionuclides can be used to help determine the terrestrial age.

The meteorite samples in this study come from the ALH pairing group. The letters are indicative of a more precise location of the find (Bennoit *et al*., 2000). The samples are all pairing groups of the carbonaceous chondrite meteorite class, so primarily major element composition or the modal mineralogy, and the induced TL determined the pairing status (Bennoit *et al*., 2000).

b. Stable isotope Analysis

An isotope is a variation of an element due to a differing number of neutrons in the nucleus. A stable isotope is an isotope that does not experience decay as a radioactive isotope of an element does. It is normally one or two neutrons heavier than the more common isotope of that element. The fundamental principle behind stable isotope systems is that "in any multiphase system, there is a preferential fractionation of isotopes, with one phase preferentially incorporating the heavy (or light) isotope relative to other coexisting phases" (Sharp, 2017). The fractionation occurs because the mass differences of the isotopes results in subtly differing thermodynamic and other chemical properties, so that one isotope is favored during equilibrium or during a kinetic process (Sharp, 2017).

i. Delta Notation

It is easier to comprehend relative differences in isotopic ratios rather than absolute isotopic ratios. The δ notation was introduced by McKinney *et al.* (1950) to display these relative differences in a more precise way than absolute ratios could be reported. The δ value is given by

$$\delta=\left(\frac{R_x-R_{std}}{R_{std}}\right)\times 1000$$

(Equation 1)

where R is the ratio of the abundance of heavy to light isotope, *x* denotes the sample, and *std* is the standard. For sulfur, R is given by $^{34}S/^{32}S$, $^{33}S/^{32}S$, and $^{36}S/^{32}S$. The δ values are reported in parts per thousand (‰). In this notation, a positive value means that the ratio of heavy to light isotope is higher in the sample than the standard, and a negative value means the opposite. The δ notation is an excellent way to express small relative differences in isotopic ratios within samples or between samples and standards that are measured by isotope ratio mass spectrometry.

Another quantity used to measure differences in isotopic ratios is Δ, a value commonly used to report differences in isotopic composition between substances and also unusual relationships between three or more stable isotopes in a single substance. The first use of Δ is calculated using the δ values of the two ratios being compared

$$\Delta_{A-B}=\delta_A-\delta_B$$

(Equation 2)

where δ_A and δ_B are calculated using equation 1. The values reported in this study are in δ notation and the final numbers used for the comparison of isotopic variability are in Δ notation (Sharp, 2017). The second use of Δ is calculated using the different δ values ($\delta^{33}S$, $\delta^{34}S$, and $\delta^{36}S$) for a single substance relative to a reference mass-dependent composition. In this case:

$$\Delta^{33}S = \delta^{33}S - 1000*((1+\delta^{34}S/1000)^{0.515}-1), \quad \text{(Equation 3)}$$

$$\Delta^{36}S = \delta^{36}S - 1000*((1+\delta^{34}S/1000)^{1.9}-1). \quad \text{(Equation 4)}$$

Note that this is like equation 2, but with δ_B representing the composition ($\delta^{33}S$) of a sample with the same $\delta^{34}S$ that was on the mass fractionation array which is given by $\delta^{33}S = 1000*((1+\delta^{34}S/1000)^{0.515}-1)$ and $\delta^{36}S = 1000*((1+\delta^{34}S/1000)^{1.9}-1)$ and reflects the role of mass in equilibrium (thermodynamic) isotopic fractionation.

ii. Mass Independent Fractionation

This project focused specifically on the mass independent fractionation of sulfur. Mass dependent fractionation is related specifically to partitioning of isotopes by a process that minimizes energy. Vibrational, rotational, and translational energy levels associated with atomic bonds change with the different masses of the isotopes in a relatively predictable way (Urey, 1947) that defines mass dependent fractionation. Mass independent fractionation occurs by a different mechanism. The effect was first observed in the oxygen isotopes of ozone, which display a non-zero $\Delta^{17}O$ signal. The idea is that instead of fractionation driven by lower energies relating to different masses of isotopes, the fractionation is determined by other factors, such as how molecules transition from one excited state to another or between excited and ground states. These states are determined by the orbitals that electrons occupy. Absorption of UV light often initiates mass-independent reactions by driving electrons from the ground state orbitals to higher orbitals that are unoccupied at ground state. This results in an altogether different energy and chemistry. Another way for mass independent fractionation to occur is when there is selective excitation of specific isotopic forms of molecules by specific wavelengths of light. In space, the spectrum of available light can be modified by molecules absorbing (removing) specific wavelengths, and creating a spectrum that selectively excites some isotopic species over others. This process known as shielding can occur for any molecule, and when it involves molecules closer to thei source of radiation that are of the same composition as the reacting molecule, it is referred to as self shielding. In this case, these photochemical processes occur as a function of abundance rather than mass (Thiemens *et al.*, 2012). Both mass independent processes are particularly important when studying the early solar system. In sulfur, mass independent fractionation is evaluated by comparing the ^{33}S and ^{36}S isotope variation with that for ^{32}S and ^{34}S.

III. Discussion of Hypotheses

My project focuses on the isotopic ratios of sulfur of compounds from two paired CM chondrite samples. Specifically, I evaluated 2 meteorite samples from the ALH pairing group of the CM subclass. Because the samples are CM chondrites, they are believed to have come from the same parent body. Furthermore, because the samples are paired meteorites, they are thought to come from the same the same meteoroid and broken up in the atmosphere to create a group of paired meteorites. The various forms of sulfur within these paired meteorite samples include sulfates, sulfides, elemental and organic sulfur, and these were extracted from using a sequential extraction strategy modified from L17, (2017). Then the abundances of the four sulfur isotopes (32, 33, 34, 36) in each of those components were measured.

My initial plan was to characterize the ratio of the ^{33}S compared to the ^{34}S, and the ratio of ^{36}S to ^{34}S to identify signatures that were formed prior to the time of the CM parent body formation. Two of these isotopes $^{(33}$S and ^{36}S) can be measured in the context of the other two ^{32}S and ^{34}S to reveal mass independent fractionation effects that are characteristic of chemical reactions occurring prior to parent body formation. Previous research indicated the presence of analytically resolvable variability for mass independent sulfur isotopes within a single meteorite for sulfates, sulfides, and elemental sulfur and indicated that at least some variability of precursor materials existed at the scale of that meteorite. The meteorite that was tested was the Murchison meteorite, a CM chondrite that fell in Australia in 1969. My project planned to test if this result also applies more broadly to CM chondrite materials and focused on paired meteorites, separate rock samples believed to be from the same parent body.

As time went on the project evolved and incorporated different focuses in addition to the initial goal. After studying the data obtained from the analyses and the past data obtained by L17, it was clear that a new unknown species was extracted from one of the ALH samples. The compound has an isotopic signature (^{33}S) that is distinct from the other sulfur species. Because of the extraction procedure and the sequential way in which the compounds are taken out, the compound is thought to be released by a reaction occurring during sample processing with the sequential methods developed by GT93 and LT17., I believe this compound is an organic polysulfane species.

At the start of this project, my hypothesis was purely a statement on the presence of the isotopic variability in the Δ^{33}S of the paired meteorite samples. More specifically my hypothesis was that measurements of the Δ^{33}S value for paired meteorite samples would show the same compositional variability that is seen in Murchison. After the analyses performed on the meteorite samples from the ALH pairing group, and comparing those data to data from an ALH sample characterized by L17, this hypothesis was anticipated to be valid. There was a question about the scale of that variability and whether it would be found in other samples. At the time that Murchison fell in 1969, people were able to collect about 100 kg of the meteorite indicating that the variability observed within this meteorite is measurable up to the 100 kg scale. However, paired meteorites are believed to be fragments of the same parent body and same meteoroid that traversed space from that parent body in an Earth-crossing orbit. This means that the study of this variability in paired meteorites has the potential to further define the scale to something much larger than 100 kg.

After studying the data, an additional hypothesis was developed. This hypothesis specifically focuses on the new sulfur species that was unexpectedly extracted during this project. The hypothesis reads that one of the sulfur compounds analyzed from the ALH 83100 related meteorite pairs is derived from an organic polysulfane species that was decomposed by the acidification procedure.

There were a few considerations taken into account with this study. The paired meteorites that were studied were all meteorite finds, meaning that they were found in Antarctica after significant time had passed. This opens up the question of contamination due to prolonged exposure to the surrounding environment. Another consideration is related to the difference of scale between a meteorite and its parent body, or the meteoroid that transported it. One cannot know if the meteorite collection samples the parent body in an un-biased way. This study, therefore focused on documenting the whether heterogeneity seen for Murchison is also seen for other CM chondrites that are paired, which can tell us about the part of the parent body from which these meteorites are derived.

Observations taken into consideration in the part of this study that aims to characterize the possibility of an organic polysulfane focus on the isotopic composition of sulfates, sulfides, and elemental sulfur extracts as well as the protocols used to obtain these. From the process the compound must undergo a reaction with HCl to produce elemental sulfur as well as a component extractable with the acidic Cr(II) solution. From there it became a literature search as to what the compound could be based on what I learned from the analysis and extraction process, but the compound is not specifically identified in the project. These are the considerations that have been evaluated when conducting the research.

IV. Background

a. Gao & Thiemens (1993)

GT93 (referred to as GT93) describe a multistep extraction process by which different types of sulfur where freed from various carbonaceous chondrite meteorite samples. The study examined meteorite samples from 7 sources of various types of carbonaceous chondrites. The 7 meteorite sources include 6 falls and 1 find and CM, CI, CV, CO subtypes (Table 1).

Table 1: Meteorites studied by GT93, the meteorite class, and the status as a fall or a find

Name	Class	Fall/find
Orgueil	CI	Fall
Allende	CV	Fall
Vigarano	CV	Fall
Murchison	CM	Fall
Mighei	CM	Fall
ALH84029.29	CM	Find
Warrenton	CO	Fall

The chemical extraction process first required crushing the samples before beginning a multistage chemical procedure to yield elemental sulfur, sulfates, sulfides and organic sulfur compounds. The chemical extraction process is described in more detail below

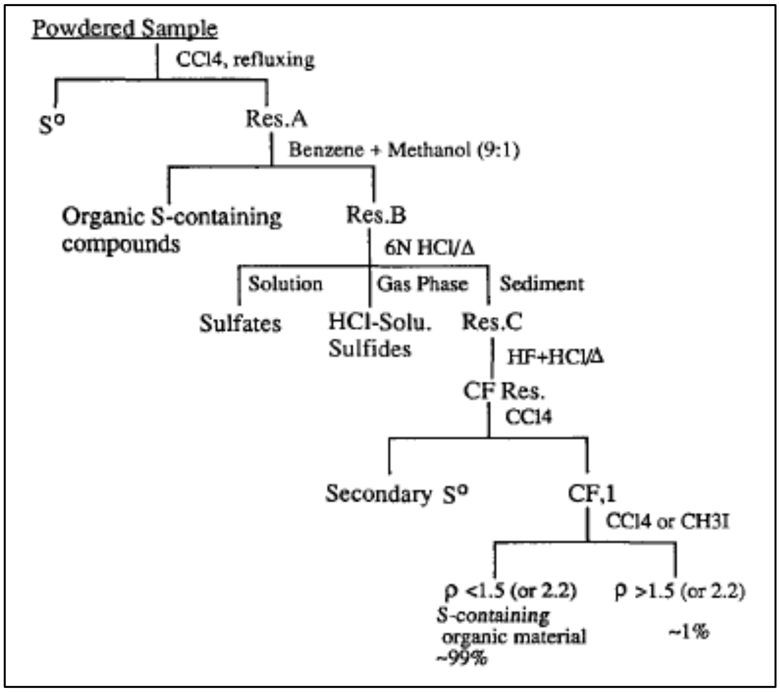

Figure 1: Chemical extraction process used by GT93 of Orgeuil meteorite .

These different sulfur components were then converted to silver sulfide (Ag_2S) and then underwent a reaction with bromine pentafluoride (BrF_5) to create sulfur hexafluoride (SF_6). The mass spectrometer is used to analyze SF_6 and the results were reported as δ values. For this study, the δ values reported by GT93 were converted to Δ notation by me, so that a comparison could be made to values reported by subsequent literature studies.

Table 2: Results reported by GT93 for Murchison 1 and 2 as $\delta^{33}S$ and $\delta^{34}S$, and converted to $\Delta^{33}S$. Analytical uncertainty $\delta^{33}S$= -0.04 (+-) 0.02‰ (1σ)
$\delta^{34}S$= -0.27 (+-) 0.05‰ (1σ). Analytical uncertainty for $\Delta^{33}S$ is thought to be comparable to that for $\delta^{33}S$.

Murchison 1	$\delta^{33}S$	$\delta^{34}S$	$\Delta^{33}S$
Sulfates	0.22	0.37	**0.03**
Sulfide	1.44	2.72	**0.04**
Murchison 2			
Sulfates	-0.12	-0.29	**0.03**
Sulfide	1.30	2.52	**0.00**

b. Labidi et al. (2017)

Labidi et al. published a paper in 2017 (referred to as L17) detailing a similar study to GT93. This paper, titled "Mass independent sulfur isotope signatures in CMs: Implications for sulfur chemistry in the early solar system", sampled 4 meteoric falls and 9 meteorite finds that were all of CM type.

Table 3: CM chondrite meteorites studied by L17.

Name	Fall/find
Banten	Fall
Cold Bokkeveld	Fall
Murchison	Fall
Nogoya	Fall
ALH 84029	Find
DOM 08003	Find
DOM 08013	Find
GRA 98074	Find
LEW 85412	Find
LEW 87022	Find
MCY 05230	Find
PCA 91084	Find
TIL 91722	Find

Samples went through an extraction process similar to the one carried out in 1993 by GT93, with some minor modification. GT93 relied heavily on carbon tetrachloride (CCl_4) when extracting the elemental sulfur from the powdered sample (Table 1). Alternatively, L17 used ethanol to extract and Cr(II) to react the elemental sulfur. The process yielded sulfates, sulfides in the form of AVS, elemental sulfur, and organic sulfur compounds.

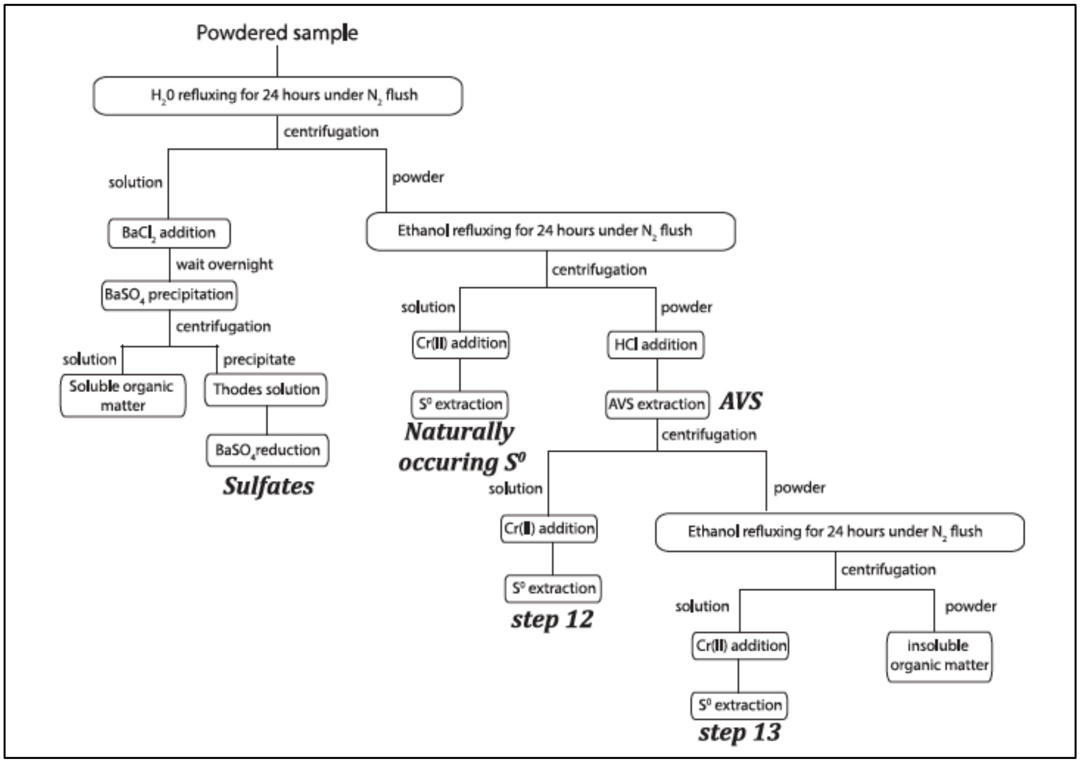

Figure 2: Chemical extraction process conducted by L17. This is the procedure that my extraction process followed.

The sulfur components were then converted to SF_6 and the isotopic analysis was made with an isotope ratio gas-source mass spectrometer. The results of the isotopic analysis were reported as both δ and Δ values (Labidi et al., 2017).

c. Overlapping samples from GT93 and L17

The connection between these two studies lies in the overlap of the analysis of samples from the Murchison meteorite. Murchison is a 100 kg CM chondrite that fell on September 28th, 1969 near Murchison, Victoria, in Australia. Both studies analyzed samples from Murchison and obtained very different results. GT93 reported $\delta^{33}S$ values that, when converted to Δ notation, display at or near zero homogeneous $\Delta^{33}S$ values with no variability outside of analytical uncertainty. L17 report values that are much more positive than the those of GT93, and much more varied across the different types of sulfur components (sulfates vs. sulfides vs. elemental, etc.) indicating variability of the $\Delta^{33}S$ value within the Murchison meteorite.

Table 4: Table detailing the differences in $\Delta^{33}S$ values obtained in 1993 and in 2016. Analytical uncertainty for the values recorded by L17 is (+/-)0.012 ‰ (2σ) and (+-) 0.02‰ (1σ) for GT93

Reference	$\Delta^{33}S$ (Sulfates)	$\Delta^{33}S$ (Sulfide)
Gao & Thiemens 1993	0.029	0.040
Gao & Thiemens 1993	0.029	0.003
Labidi et al., 2017	0.263	0.156

This differences in the recorded values for sulfates and sulfide are essential to this study. It allowed one to form questions about the degree and consistency of variability within CM chondrite meteorites. My study focused on testing if the variability exists in paired CM chondrite meteorites.

V. Methodology

a. Sample Preparation

Meteorite samples are obtained as rock fragments from a source the meteorites in this study were obtained from NASA. In order to prepare the samples for the analysis they had to be weighed as rock samples and then crushed into a fine homogeneous powder. The samples are weighed again as a powder with masses recorded for each sample.

b. Chemical Extraction

The chemical extraction process is very similar to the one outlined by L17. Water is allowed to undergo a degassing process for about 24 hours before beginning a N_2 and H_2O flush of the samples. The samples go through an H_2O cycle with 60-80 ml of milliQ water continually flushing through the sample for 3 to 4 hours. The samples are then run through the centrifuge and put into a sonicator. This process dissolves sulfate and soluble organic compounds.

The powder samples from the previous step are transferred to 50 ml centrifuge tubes and filled with N_2 gas and 20 ml of degassed water. After agitating the mixture it is placed in the sonicator for about 20 minutes and then allowed to sit for 24 hours before undergoing an ethanol wash. The ethanol wash is performed with a soxhlet extractor. Each sample is transferred into an absorbent tube and placed in the soxhlet extractor. Ethanol is added to the bottom and N_2 gas is flushed through the whole system. After the extraction is finished, the tube with the powder is covered with parafilm and the flask with the ethanol and dissolved elemental sulfur is covered with parafilm. This process serves to extract the elemental sulfur from the samples.

The residue from the H_2O and N_2 flush is dried and then placed in the soxhlet extractor again with ethanol and N_2 cycling through. The liquid from this process is reduced by the chromium reduction (CRS) method with ethanol and produces the elemental sulfur. The residue from the ethanol extraction in the soxhlet is dried and then degassed with 5N HCl. This extracts the acid volatile sulfur (AVS), which is believed to be the sulfides, as a gas and then produces a liquid, which is reduced with CRS and ethanol to extract more sulfides in the form of elemental sulfur. The residue from the HCl degassing is then dried and placed in the soxhlet extractor with ethanol and N_2. The liquid from this is reduced with CRS and isolates sulfur compounds believed to be the same as the sulfides from the AVS (Labidi et al 2017) as well as the polysulfane species detected in this study. The residue from this final ethanol extraction is the insoluble organic matter.

c. Chemical Conversion

Each component of sulfur needed to be converted to Ag_2S and then to SF_6 before it can be analyzed in the mass spectrometer. Sulfates are precipitated out of solution as $BaSO_4$, then reduced to H_2S, and then recovered as Ag_2S using Thode solution. The elemental sulfur is extracted during the ethanol flush and then it is reduced to H_2S using by adding 12N HCl and Cr(II) solution to the ethanol, and heating in a nitrogen purge. Sulfide released from this process is recovered as Ag_2S. The sulfides are present as the total amount of acid-volatile sulfide phases, and are extracted during a chemical procedure involving a digestion in sub-boiling 5N HCl solution for 3 hours. H_2S was evolved and then be recovered as Ag_2S (Labidi et al., 2017).

After the chemical conversion of the sulfur components to Ag_2S, they must then be converted to SF_6. This is completed by wrapping the samples in Al-foil and placing them within Ni-reaction vessels so that they may undergo fluorination with at least 10x excess of pure F_2 gas at 250°C overnight. SF_6 was produced from this fluorination and then it was isolated cryogenically and chromatographically from all possible impurities (Labidi et al., 2017).

d. Isotopic Analysis

The δ value is computed from intensities of ion signals measured in the mass spectrometer. Mass spectrometers are based on the principle of the deflection of an energetic ion beam in a magnetic and/or electrostatic field. The degree of this deflection is a function of mass and charge. One can then measure the relative intensities of different ion beams corresponding to different masses in order to calculate isotope ratios.

Mass spectrometers are consistently made up of three parts: the source, the analyzer, and the collector. The source is the area of the instrument where the sample is ionized and accelerated to a given energy and collimated into a well-focused beam. The analyzer works to deflect the ion as a function of mass, and the collector measures the relative intensities of the different ion beams.

The mass spectrometer used in this study is an isotope ratio gas-source mass spectrometer (IRMS). Sulfur can be introduced into the mass spectrometer as either SO_2 or SF_6. In this study all of the extracted sulfur components were converted to SF_6 before running them through the mass spectrometer. The mass spectrometer measures ion beams as m/z= 127, 128, 129 and 131 for measuring abundances of ^{32}S, ^{33}S , ^{34}S and ^{36}S.

The sample raw data was normalized to analyses of IAEA S1, a reference material that was analyzed along with the materials in a single, 4-day long mass spectrometry session. It was assumed that these IAEA S1 analyses, run in parallel with sample analyses, share the same systematic mass spectrometry uncertainties. It has been found, in other studies, that this improves data reproducibility. Uncertainties typically are +/- 0.3 for **$\delta^{34}S$ (‰)**,+/- 0.08 for **$\Delta^{33}S$ (‰)**, and +/- 0.3 for **$\Delta^{36}S$ (‰)** (2σ). Uncertainties for these specific analyses are discussed in the results section. The normalized data were then converted to the CDT scale using a second normalization based upon a calibration of IAEA S1. To test for instrumental drift, the standard is rerun periodically to make sure that the values remain consistent. Though there is some indication of instrumental drift, it was too small to make a significant contribution to the data.

e. Preliminary Tests of Methods to Extract Sulfur From IOM

A process of extending the previously-established protocol to develop techniques that can be used to isolate different insoluble sulfur species from insoluble organic matter (IOM) has also been started (figure 3). The first test was to extract the total organic sulfur from the insoluble organic matter, but this approach will not resolve specific compounds and therefore will not be the preferred approach.

First the Raney nickel reduction method was tested on a laboratory standard of L cysteine, and gave back very poor yields. The Raney nickel method involves the activation of the Ni-Al alloy in 2.5 M NaOH for 24 hours. Then the catalyst must be washed with deoxygenated water, with a pH of 7. Next the organic sulfur can be introduced into the reaction flask with a chilled EtOH solvent for volatiles and with water for non-volatiles. After the organic sulfur is in the reaction flask, 1 mL of 1.0 M NaOH into the flask. The reaction is then heated to a boil for 20 minutes under a flow of N_2 gas. The heat is then shut off and 15 mL of HCl in dropwise amount is added to the flask to convert the S into H_2S once the heat is turned back on for an hour with the N_2 still flowing. The H_2S is then trapped with a zinc acetate acid buffer and recovered as ZnS and Ag_2S precipitates after adding $AgNO_3$. After the process is completed the samples are dried and weighed to get yields. Unfortunately, this attempt failed even though the method has been demonstrated to work.

The temperatures as well as the general procedure were varied slightly to see which would give the best result and obtained consistently low yields of about 50-60% and 70-75%.

The Thode reduction method was also tested to see if it could be used to extract the insoluble organic matter. This method starts by adding the sample and 25 mL of the Thode solution into a sealed flask. The flasks are heated and flushed with N_2. A silver nitrate trap solution is added to the chemical apparatus so that the reduced sulfur will precipitate out as silver sulfide (Ag_2S). 5 mL of ethanol was added to the reaction flasks and then the reaction was left for about 4 hours. At the end, the glass tubes containing the trap solution and the reaction product were wrapped in parafilm and moved to storage until they could be dried and weighed to test yields. This method was carried out with $BaSO_4$ first and then on the L cysteine. Yields from the first test were between 90 and 100% and have yet to be weighed out for the second test. The hope with this is to find a method to use to successfully extract the final sulfur product from the meteorites. This approach yielded AgI from secondary chemistry that produced an ethyl iodide. Neither the Raney Ni method or the Thode method were successful tests, and further work is needed to develop a strategy for analyzing sulfur in different components of insoluble organic matter. Further work will be needed to refine these techniques.

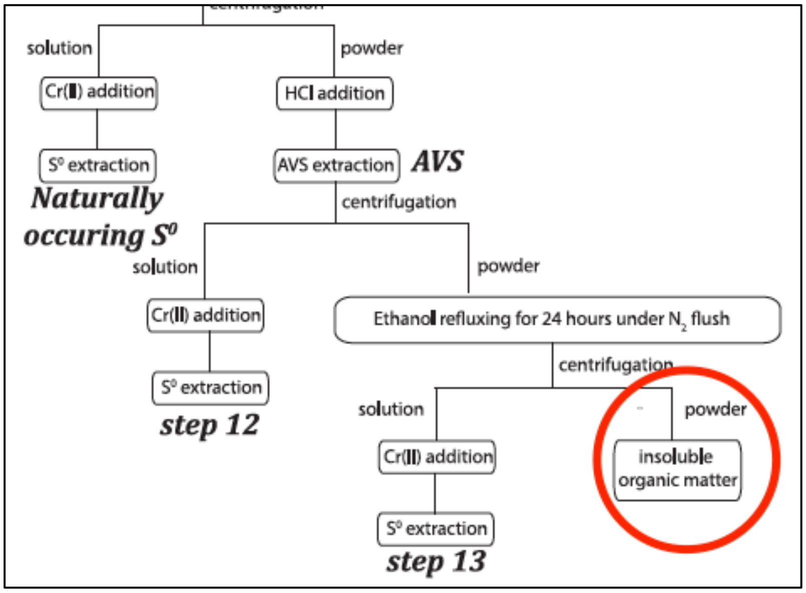

Figure 3: Image from the flow chart depicting the extraction process from L17. The insoluble organic matter(circled in red) was not extracted in L17. In this study, the Raney nickel reduction method and the Thode reduction method were tested on laboratory standards of $BaSO_4$ and L cysteine in order to find the best method to use for the insoluble organic matter.

VI. Results

Tables 5 and 6 present the uncertainty and isotopic and abundance data for the samples studied.

Table 5: 2σ uncertainty from this study for different components of the meteorite samples.

Uncertainty (+/-‰) 2σ	$\delta^{34}S$ (‰)	$\Delta^{33}S$ (‰)	$\Delta^{36}S$ (‰)
ALH 83100.235 Sulfate	0.30	0.008	0.30
ALH 83100.235 1st Elemental Sulfur	0.30	0.008	0.30

ALH 83100.235 AVS	N/A	N/A	N/A
ALH 83100.235 HCl-Sol CRS	0.30	0.010	0.30
ALH 83100.235 2nd Elemental Sulfur	0.30	0.008	0.30
ALH 84042.15 Sulfate	0.30	0.008	0.30
ALH 84042.15 1st Elemental Sulfur	0.30	0.008	0.30
ALH 84042.15. AVS	0.50	0.016	0.30
ALH 84042.15 HCl-Sol CRS	0.30	0.010	0.30
ALH 84042.15 2nd Elemental Sulfur	0.30	0.008	0.30

The uncertainty reported for measurements of $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$ in the table above reflects the long-term reproducibility on standards. Uncertainty on $\delta^{34}S$ primarily reflects uncertainty associated with chemical extractions of sulfur. Alternatively, the uncertainty associated with $\Delta^{33}S$ and $\Delta^{36}S$ measurements reflects analytical uncertainties associated with counting statistics, mass and isobaric interferences, and contaminants introduced during the analysis. Note, uncertainty on $\Delta^{33}S$ differs between S^0, sulfate, and 2nd S^0 in the ALH samples. The differing uncertainty on $\Delta^{33}S$ is attributed to differences in the number of measurements performed on a single reservoir of gas from the associated species.

Table 6: Depicts the data obtained from this study for the $\delta^{34}S$, $\Delta^{33}S$, $\Delta^{36}S$, and abundance for the different sulfur components.

SF6 No.	Sample ID	Abundance (ppm)	$\delta^{34}S$ (‰)	$\Delta^{33}S$ (‰)	$\Delta^{36}S$ (‰)
SF16476	ALH 83100.235 Sulfate	7145	-1.2	0.056	-0.38
SF16478	ALH 83100.235 1st Elemental Sulfur	2524	2.6	0.049	-0.05
	ALH 83100.235 AVS	30	N/A	N/A	N/A
SF16486	ALH 83100.235 HCl-Sol CRS (Step 13)	209	9.7	0.014	0.42
SF16479	ALH 83100.235 2nd Elemental Sulfur (Step 12)	1116	-1.8	0.101	0.69
SF16480	ALH 84042.15 Sulfate	7216	-1.0	0.029	-0.19
SF16482	ALH 84042.15 1st Elemental Sulfur	1038	3.6	-0.006	0.16
SF16487	ALH 84042.15. AVS	92	1.2	0.007	0.44
SF16485	ALH 84042.15 HCl-Sol CRS (Step 13)	446	8.2	-0.006	0.21
SF16483	ALH 84042.15 2nd Elemental Sulfur (Step 12)	3467	0.5	0.021	-0.07

Abundances range from an extreme low values for the AVS extraction (30 and 92 ppm) to very high values for sulfate (7145 and 7216 ppm). The $\delta^{34}S$ data range from -1.8 (‰) for the 2nd Elemental Sulfur of the ALH 83100.235 meteorite sample and 9.7(‰) for the HCl-Sol CRS of the ALH 83100.235 meteorite. The $\Delta^{33}S$ shows range as well with the lowest value coming in at -0.006 (‰) for both the 1st Elemental Sulfur and the HCl-Sol CRS for ALH 84042.15. The highest $\Delta^{33}S$ value is 0.101 (‰) for the 2nd Elemental Sulfur of the ALH 83100.235, and this is about 2x larger than the next highest value. The $\Delta^{36}S$ data has more negative values than the $\Delta^{33}S$ with the most negative value being -0.38 (‰) for the sulfate of the ALH 83100.235 and the most positive value being 0.69 (‰) for the 2nd

Elemental Sulfur of the ALH 83100.235. In general the $\Delta^{36}S$ shows a much larger range than the $\Delta^{33}S$ data. Also generally the ALH 84042.15 has slightly lower $\boldsymbol{\Delta^{33}S}$ values than the ALH 83100.235 measurements, and the $\boldsymbol{\delta^{34}S}$ between the two meteorites shows a similar general trend with a couple of outliers. There is definitely more variation between the data from this study and the data from the ALH 84029 meteorite that was analyzed in 2017 by L17 Specifically, there is significant variation between the HCl-Sol CRS series with a lot of separation between the $\delta^{34}S$ values. There is also variation between the 1st elemental sulfur series in the $\Delta^{33}S$ and the 2nd elemental sulfur species for the $\Delta^{33}S$ and the $\delta^{34}S$.

VII. Discussion

Mass independent fractionation of the ^{33}S value indicates, as L17 hypothesized, that there is another pathway to mass independently fractionated sulfur reaching the outer solar system in addition to the proposal by Rai et al. (2005, 2007) of transport by the X-wind hypothesized by Shu *et al.* (1997). In the Rai et al. (2005, 2007) hypothesis, the inner solar nebula is bombarded with UV rays from the sun, which then causes photolytic reactions that lead to mass-independently fractionated sulfur in materials that are then blown into the outer solar nebula by the X-wind, a coronal solar wind. This process that has been debated provides one explanation of the mass independent fractionation of sulfur seen in chondrules. The data showing an absence of a MIF sulfur signal in CM chondrites from GT93 might have been seen as supporting this hypothesis because a non-zero signal was expected due to low formation temperatures that CM chondrites are believed to display. From L17, however, it is clear that CM carbonaceous chondrites contain MIF sulfur, and that this sulfur is present in components that formed at lower temperatures than the predominant mineral sulfides. This observation of MIF sulfur in Murchison generated a need for a different pathway that would explain the MIF sulfur present in phases other than the high temperature FeS phases of CM meteorites. With this result, L17 proposed a different possible pathway in addition to the X-wind hypothesis. In this model, the outer surface of the nebular disk is bombarded by UV, which causes the MIF signature while shielding protects the interior (midplane) of the disk. Then, because of vertical mixing, new materials are exposed so that there is a variable distribution of MIF sulfur. Our results are consistent with the results seen by L17 in that there is a MIF signature in the $\Delta^{33}S$ supporting this complementary pathway.

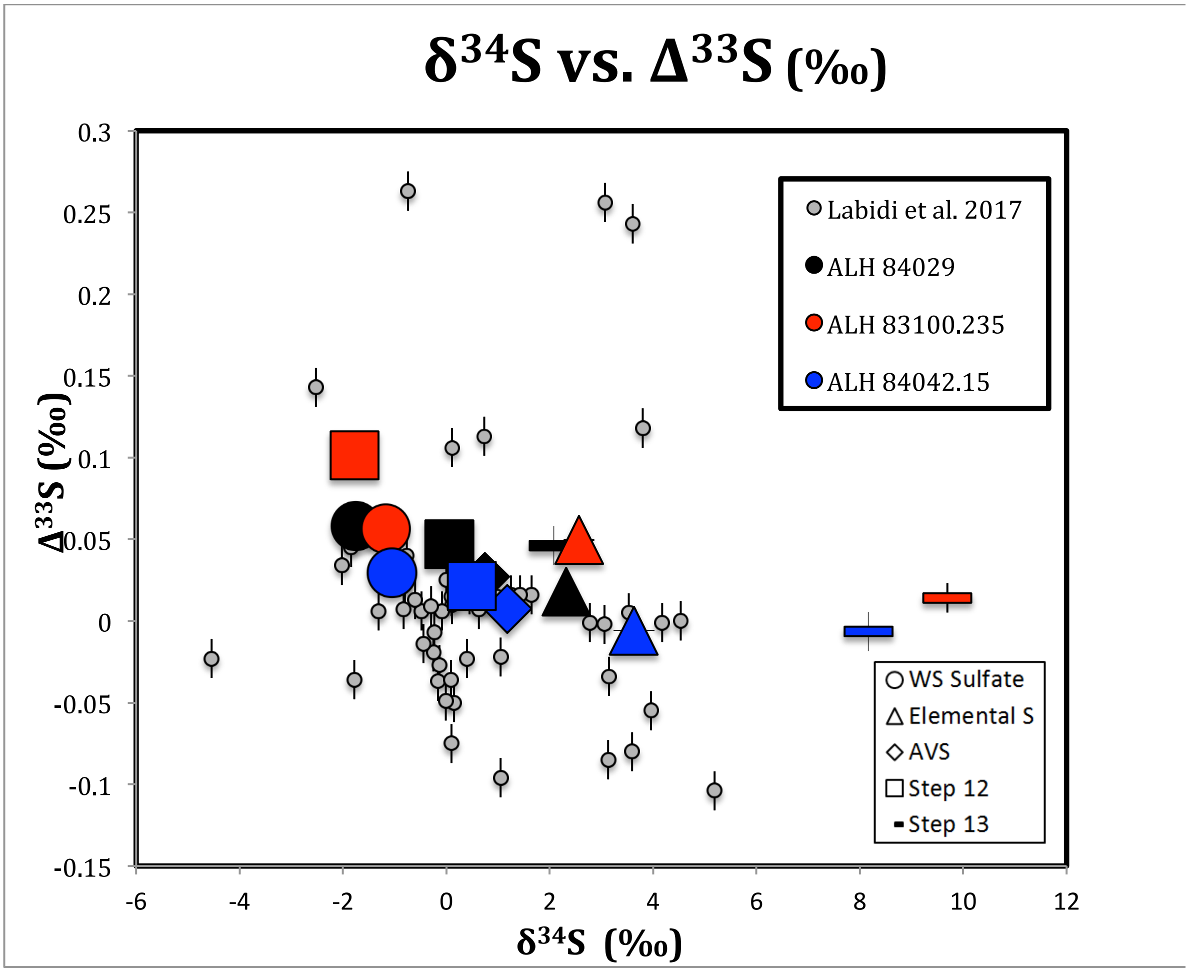

Figure 4a: A plot depicting the δ34S vs. Δ33S of the different components. The gray data points are from L17. The larger symbols correspond to the size of 2σ uncertainties. The black data points are also from L17 and are isolated because the ALH 84029 meteorite is from the same pairing group as the ALH 83100.235 and ALH 84042.15 meteorites that were analyzed in this study. The different data point styles in the enlarged data series correspond to different sulfur species. The squares are the 2nd elemental sulfur (step 12), the circles are the water soluble sulfate, the triangles are 1st elemental sulfur, the diamonds are the AVS sulfur, and the horizontal bars are the HCl-Sol CRS (step 13).

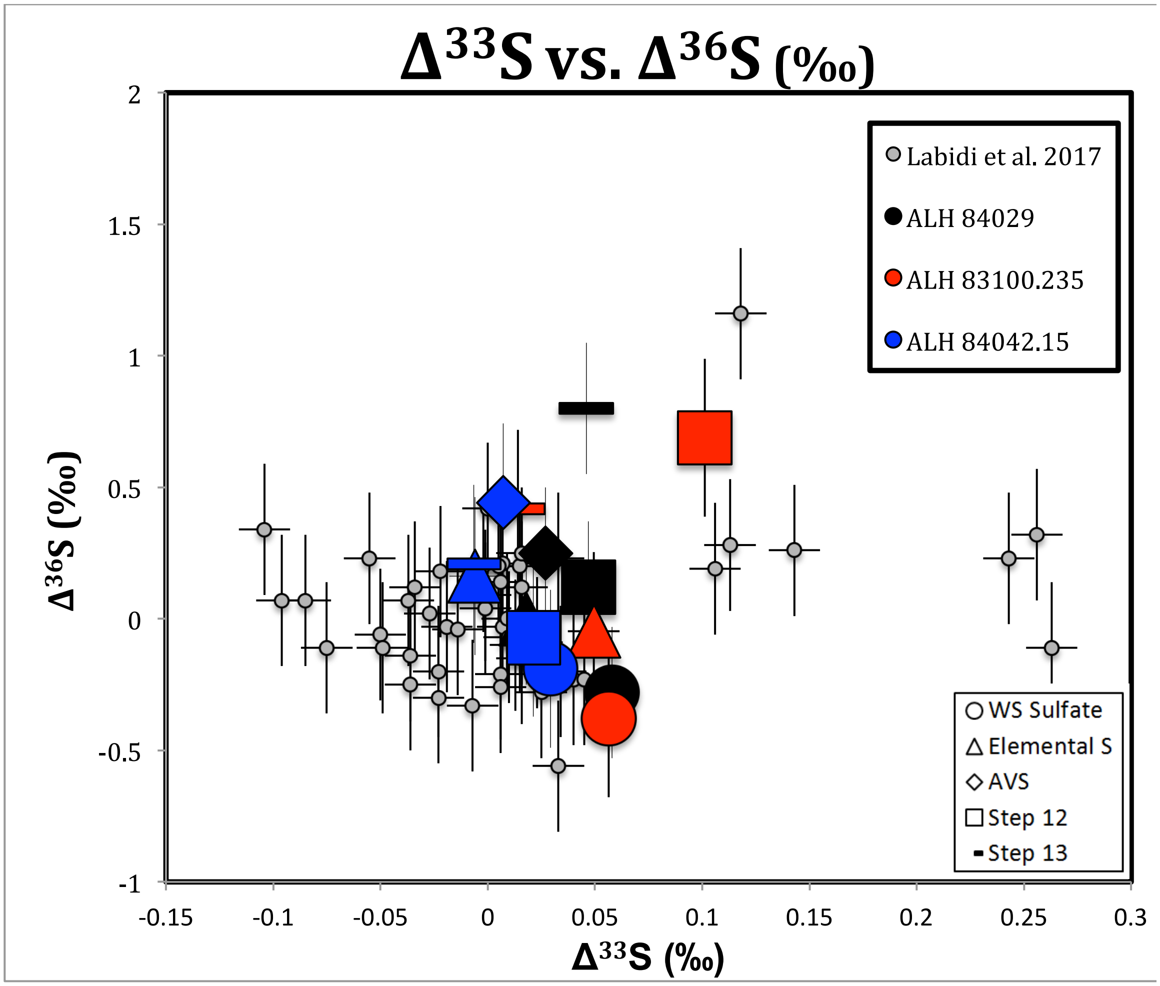

Figure 4b: This plot depicts the $\Delta^{33}S$ vs. $\Delta^{36}S$ of the different components. Both the data from this study and the data from L17 and the data from this study show a general trend going down and to the left with a few outliers (though the outliers from this study and from L17 deviate in a similar way).

a.) Testing for Homogeneity of Sulfur Among Paired Meteorites

The data displayed in Figure 4a, suggests a degree of heterogeneity for sulfur isotopes in paired meteorites. Figure 4a depicts the $\delta^{34}S$ vs. $\Delta^{33}S$ data from this study and from L17. The ALH 84029 meteorite, which was analyzed in the previous study, is also part of the same pairing group as the samples from this study. When looking at the 1st Elemental Sulfur data points, variability outside of analytical uncertainty between the three meteorites can be seen for the $\Delta^{33}S$ values. The 1st Elemental Sulfur is thought to truly exist in the meteorite as elemental sulfur as opposed to an extraction product that was altered from some different compound to begin with (2nd elemental sulfur). Because this species is believed to be elemental sulfur from the meteorite and it displays variability in the $\Delta^{33}S$ values outside of analytical uncertainty, this points towards an irregular MIF pattern in the solar nebula. In this scenario, sulfur would exist in a gaseous state attached to hydrogen and then it would dissociate due to the solar UV radiation. This photodissociation of the H_2S gas would then become the elemental sulfur carrying the nebular signal that is recorded in the data. Put a different way, this could be supportive of nebular heterogeneity of sulfur that is captured by the material accreting to form the CM parent body. Also, specifically looking at the contrast in the $\Delta^{33}S$ of 1st Elemental Sulfur of the larger data points demonstrates that this variability does in fact exist in paired meteorites in addition to single, larger meteorites like Murchison. It is also important to note that some of the species like the sulfates for example, do not contrast as strongly and actually display quite a bit of overlap. This could be indicative that instead of processes directly related to the solar nebula, the sulfate species could have evolved from some sort of parent body processes. This would make the $\Delta^{33}S$ signature within those species less varied than species that arise as a direct result of nebular processes. There also appears to be some similarity between the HCl-Sol CRS values of the two meteorite samples from this study, but they both display very different $\delta^{34}S$ values than the ALH 84029 as well as variability outside of analytical uncertainty in the $\Delta^{33}S$. These findings are supportive of my initial hypothesis and speaks to the scale of the variability on the meteorites. From previous studies, it was clear that variability within this value existed at a meter scale (Murchison), but with this study the potential scale for the variability could be similar size, or possibly larger, given that the size of the meteoroid from which the ALH pairs are derived is not known.

b.) Evidence for a Polysulfane Species

Evidence for the presence of a new compound is revealed by differences for the $\Delta^{33}S$ values of both 2nd Elemental S extracted (step 12 and step 13) for both samples analyzed, and by the difference between Step 12 and AVS in the case of ALH 84042.15. L17 argue that both step 12 and step 13 are derived from partial oxidation of sulfide sulfur during the AVS extraction. Their arguments rely on prior findings of sulfide oxidation by reactive Fe(III) during acidification to produce elemental sulfur (which would contribute to both steps 12 and 13) and on a general correspondence of $\Delta^{33}S$ between AVS, Step 12, and Step 13 (Grey points in Figure 5 and Supplemental figures in L17). The bulk sulfide species from L17 are the AVS, the step 12 and the step 13. These were all thought to be zero valence sulfur (ZVS) compounds resulting from the conversion of Fe3+ to Fe2+ and an exchanging of electrons between the S and Fe species.

$$\mathbf{S^{2-}+2Fe^{3+}\rightarrow 2Fe^{2+}+S^{o}}$$

The differing isotopic values convey that the residues are not purely ZVS produced by the previously described exchange.

The data collected in this study does not show this correspondence, and points to a contribution of sulfur to Step 12 and Step 13 that are not only different from that of AVS chemistry, but also different from each other. The $\delta^{34}S$ value also differs between Step 12 and 13, but since both include products of the extraction protocol chemistry, it is possible that these differences do not reflect two additional compounds. The logical conclusion is that in addition to extracting the sulfide compound that L17 reported, an additional organic S compound was reduced in the extraction process. Then when the measurement is taken on the mass spectrometer, the signal has the isotopic signature of the sulfide compound and the new organic S compound resulting in a new signal. Such contributions were also not ruled out by L17 for some data that did not fall on the 1:1 line, and they briefly discussed this, but did not identify the origin of the contaminant.

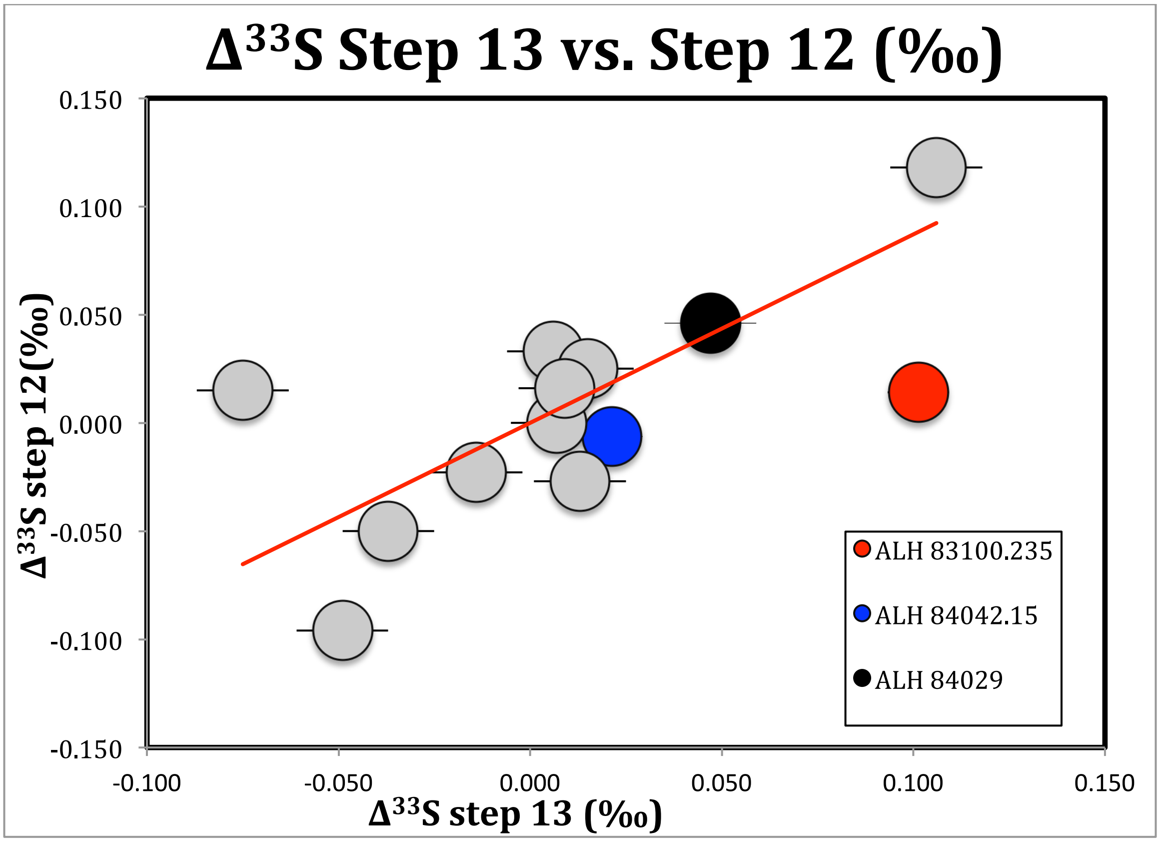

Figure 5: This plot depicts the data from L17 and this study and shows the difference between the step 13 and step 12 species in the ALH 83100.235 sample. The data from L17 show a general 1 to 1 trend for the two species, and it was decided that they were the same species along with the AVS sulfur and were termed the bulk sulfide content. Some of the data from this study is consistent with that (ALH 84042.15) but the ALH83100.235 does not follow that trend and thus the species are distinguishable from each other.

To determine the nature of this likely organic S phase we consider the extraction procedure. Both 2nd Elemental S extracts (Step 12 and Step 13) were extracted following reaction with hot 5N HCl. Step 12 was a soluble form that was extracted using acidified Cr(II) (reduction) in the presence of ethanol. Because the sample had previously undergone an ethanol and CRS wash, the new species must have only become available after the sample was reacted with hot 5N HCl. During this step, a completely separate ethanol soluble, chromium reactive compound was produced. Then in the following steps of the extraction. After a literature search about organic sulfur compounds, I propose that the unknown component that was traced in the ALH 83100.235 sample is an organic polysulfane compound with a structure of R-S_x-R. The organic polysulfane most likely underwent a reaction with the 5N HCl during the extraction process that resulted in products that were reduced by the subsequent CRS and ethanol reductions. A sample reaction could be as follows:

$$\mathbf{R—S_x—R + 2HCl \rightarrow 2RSH + S_nCl_2}$$

(Steudel 2002)..

This is the reverse reaction of a process that describes the synthesis of organic polysulfanes from a review paper by Steudel in 2002. It is also important to address the origin of the organic polysulfane. Another possibility for the decomposition of the organic polysulfane could have been caused by an initial addition of sulfur trioxide (partial oxidation of the polysulfane), possibly from the being on the Earth's surface. Then, the new compound would be susceptible to continue reacting with sulfur trioxide and exist as this partially oxidized component, which could then be susceptible to a reaction with HCl.

$$\mathbf{R\text{—}S\text{—}SO_3^{-} + SO_3^{2-} == R\text{—}S\text{—}SO_3^{-} + SO_3^{2-}}$$

(Steudel 2002).

The meteorites that were sampled are meteorite finds, so they are susceptible to alteration and have experienced interaction with terrestrial water and also possibly biota. Because of this fact, it is important to establish a degree of confidence that the organic polysulfane is not of terrestrial origin. However, because the organic polysulane displays a nonzero MIF signature, it is unlikely to be of terrestrial origin.

One question arises from the apparent absence of the trace of the separate species in the data from L17, indicating that the species is present in some samples and not in others. Additionally, the new compound displays a MIF signal that could potentially carry a signature remnant from the planetary nebula or from parent body processes. Steudel 2002 outlines several possible syntheses for organic polysulfanes, one of which is described by the equation below

$$\mathbf{2R\text{—}S\text{—}X + M_2S_x \rightarrow R\text{—}S_n\text{—}R + 2MX}$$

X: Cl, Br; M: H, Na, Ag, Hg, Tl, Pb

$$\mathbf{x = 1, 2; \quad n = x+2}$$

(Steudel 2002).

This could potentially describe a formation pathway for the polysulfane and if so then part of the MIF signature would be carried from the H_2S gas. The gas would carry a nebular MIF signature and therefore would provide a strong argument for nebular heterogeneity of sulfur. Additional testing would be required for this hypothesis. It would be best to get more samples in order to find additional traces of this compound. Additional tests on the chemical reactions responsible for extracting the polysulfane compound would also be crucial.

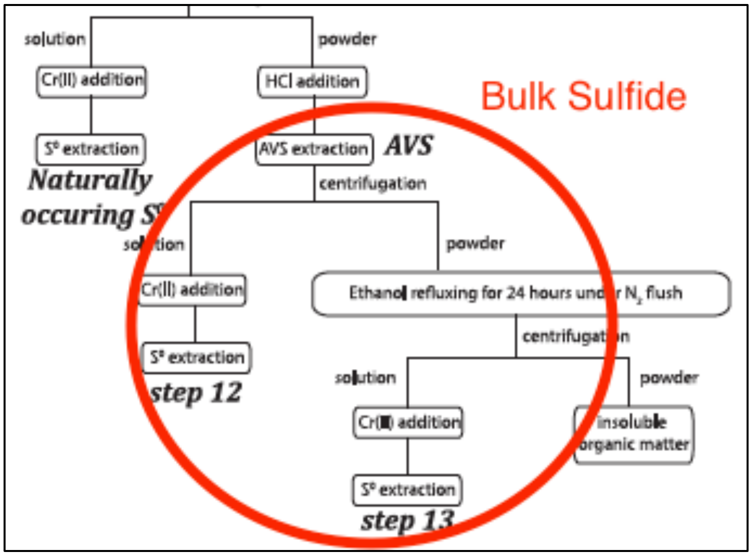

Figure 7: This image is from the flow chart depicting the extraction process followed by L17. The circled portion isolates the extraction products all attributed to be part of the bulk sulfide in the meteorite. The distinct signal that was measured in this study was from the step 13 (2nd elemental sulfur) of the ALH 83100.235 meteorite sample.

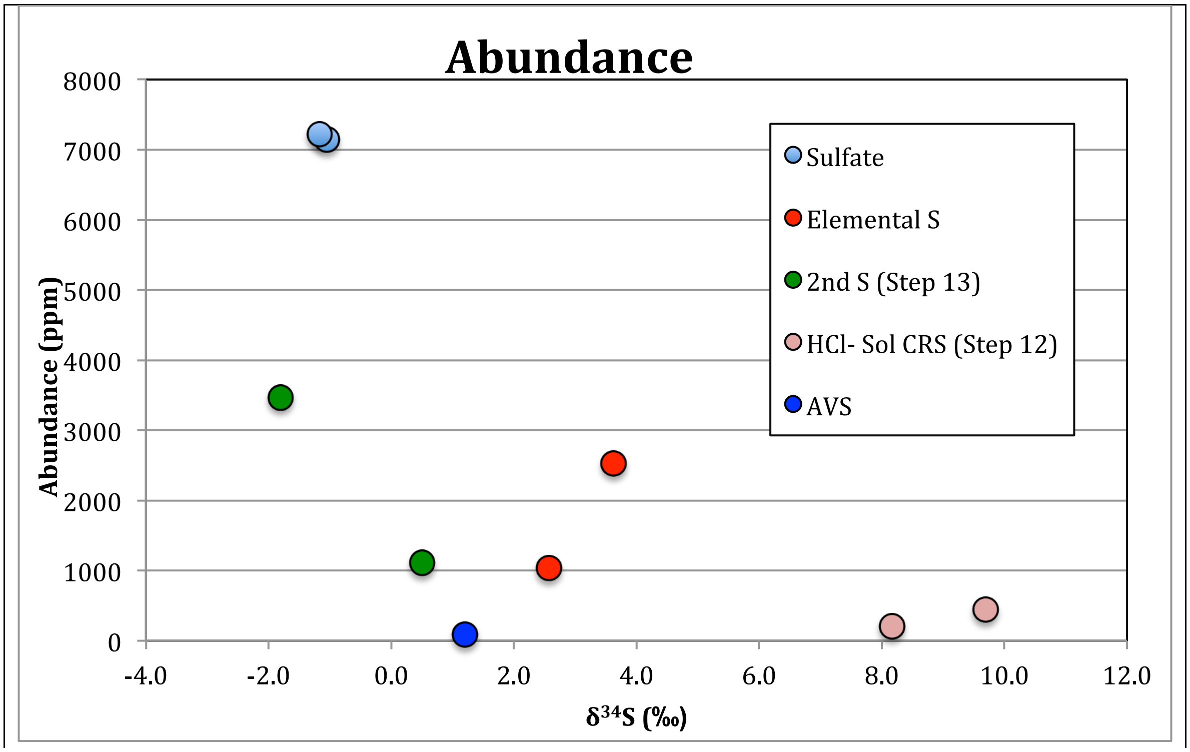

Figure 8: This plot depicts the abundance of the extraction products in this study compared o the δ^{34}S. It is important to note the relatively high abundance of the sulfates. It is also important to note that the overall abundance is much lower than that obtained by L17. This has been attributed to loss of certain components (AVS) to oxidation processes on the Earth's surface.

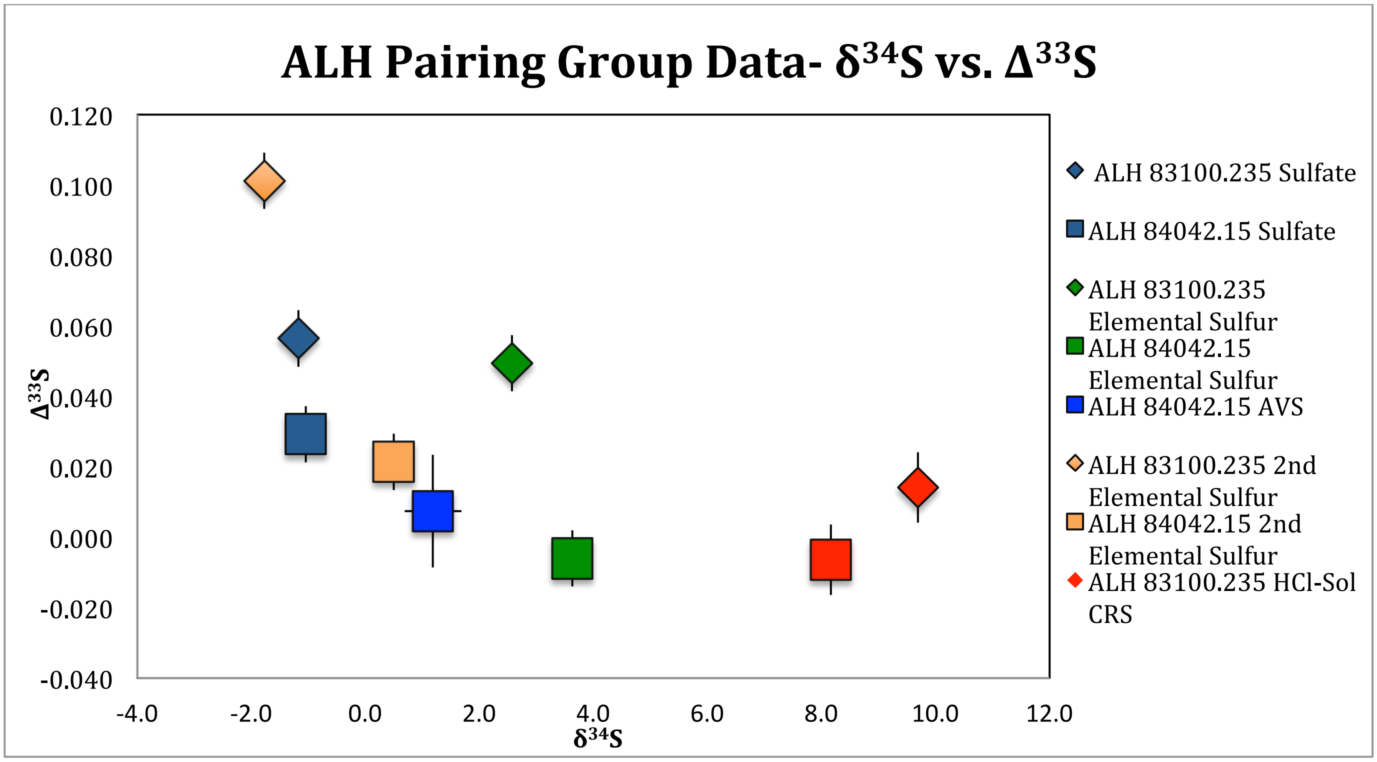

Figure 9: Depicts the data from this study as δ34S vs. Δ33S. Note the different colors corresponding to different sulfur species, and the different shapes corresponding to meteorite sample. Also note that in this plot, the ALH83100.235 can also be seen to have a distinct isotopic signature from the other 2nd elemental sulfur data point (yellow) and from the general downward and to the left trend that the data appears to follow. Also note the negative δ34S values that the sulfate species display.

The sulfides indicated by the blue dots and the sulfates indicated by the red dots both lay on the mass dependent fractionation line. The sulfates also gave very high abundances where the sulfides recorded extremely low abundances; this is unusual and not consistent with what is normal in meteorites. Some speculation arose as to whether the sulfate could be a terrestrial product both in terms of abundance and in terms of the isotopic signature due to the meteorite's presence on Earth's surface. A prior study by Airieau *et al*. (2005) explores this potential issue and addresses it by characterizing the oxygen isotope data in meteorite samples to test for terrestrial alteration. Specifically, the study looked to characterize the Δ17O value in the sulfates. A non-zero Δ17O could indicate preterrestrial origin of the sulfates found in meteorites. Theoretically, the sulfate would arise from oxidation of sulfides by some oxygen rich fluid (H_2O) on the parent body. Complications have been shown by Tyra et al. (2007) for carbonates that are attributed a terrestrial origin because they have live ^{14}C from nuclear testing. These carbonates had negative Δ17O that was attributed to buffering of the alteration water under water-limited weathering conditions in Antarctica. The sulfates studied by Airieau et al. (2005) have positive Δ17O, which cannot be explained by terrestrial water or by oxidation under water limited conditions where the Δ17O was controlled by the meteorite minerals. This implies that at least some sulfate is extraterrestrial and preserves the signature of the fluids at the time of oxidation and by extension preserve information about the aqueous alteration process that occurred within the CM parent body. There is a clear possibility that some sulfate in these samples could be due to terrestrial alteration but the different Δ33S of sulfate, relative to sulfide indicates that a significant enough amount of it is sources from other S compounds. Exchange is ruled out because it is known that sulfate, even in aqueous ionic form, is inhibited from oxygen isotope exchange with water unless it is heated significantly above 100 degrees C or the pH falls below 2 (Airieau *et al.* 2005). Because our samples are meteorite finds that were found in Antarctica both a cold and pH neutral environment, it is reasonable to assume that the sulfate signature, though still vulnerable to alteration, is extraterrestrial.

VII. Conclusion

Sulfur is a very common phase in CM chondrites and is present in many different phases. It also carries isotopically distinct signatures that help to unravel the possible nebular processes and parent body processes that took place in the past. Because of this, confident knowledge of the extraction process and the products that are being extracted is extremely important to make correct conclusions about the data.

From this study, variability within the $\Delta^{33}S$ values was demonstrated in the ALH pairing group. This result is supportive of my initial hypothesis. The variability is present at a scale outside of analytical uncertainty and is consistent with the results reported by L17. This heterogeneity in the $\Delta^{33}S$ values is important when determining the scale of the variability. Because variability was demonstrated in paired meteorites, it could be indicative that the variability exists on a scale much larger than previously known.

Progress has also been made on establishing a protocol for the extraction of the insoluble organic sulfur compounds in the meteorites. Both the Raney-Ni and Thode reduction methods have been performed on laboratory samples of $BaSO_4$ and L-Cysteine. Unfortunately, neither the Raney Ni method or the Thode method were successful tests, and further work is needed to develop a strategy for analyzing sulfur in different components of insoluble organic matter.

Finally, results indicate that an additional extraction product was analyzed that is different from the sulfides, sulfates and elemental sulfur. As stated in my additional hypothesis, this compound is thought to be an organic sulfur phase, specifically a polysulfane compound. This thought was built off of literature describing organic sulfur chemistry and off of the appearance of the product in the lab after the HCl extraction step. This led me to believe that the compound reacted with the HCl to form a reducible, ethanol-soluble product that was measured on the mass spec. Even though meteorite finds are vulnerable to terrestrial contamination and alteration, I can tell that this organic polysulfane is not of terrestrial origin because of its mass- independent fractionation signature compared to terrestrial material. It is also clear that the organic polysulfane species carries a unique isotopic signature that could potentially carry a nebular signature, although additional testing is needed for this hypothesis.

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