ISOTOPE EVIDENCE FOR LINKS BETWEEN SULFATE ASSIMILATION AND OXIDATION OF MARTIAN MELTS FROM METEORITES MIL 03346, MIL 090030, MIL 090032, & MIL 090136.

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Introduction: Anomalous (mass independent) sulfur isotopic signatures have been recognized in a variety of phases from Martian meteorites [1-5]. These signatures have provided information relevant to our understanding of processes that cycle sulfur in Martian environments including the pathways for generation of sulfate, as well as understanding the pathways associated with assimilation of sulfate by Martian melts. The work presented here focuses on meteorites paired with the Nakhlite MIL 03346 [6,7]. These meteorites are oxidized compared to other martian meteorites and contain abundant Ti magnetite and magnetite [6-9]. We present data for sulfur extractions from MIL 090136, MIL 090030, MIL 090032 and compare our results with data from MIL 03346 obtained in a prior study [3] that (1) reveal different Δ^{33}S for sulfide from each of the MIL meteorites, (2) solidify relationships between Δ^{33}S, Δ^{36}S, and δ^{34}S that were suggested by analyses of other Martian meteorites [2] and to provide constraints that are useful for interpreting the origin of the anomalous signatures, and (3) support an important role for high – temperature assimilation of sulfate at the time of emplacement that resulted in significant oxidation of the melt, and may account for much of the skeletal magnetite observed in the mesostasis of the samples.

Methods: Sulfur was extracted from crushed whole rock meteorite samples using a sequential extraction protocol similar to [3]. Samples were first sonicated in milli-Q water to extract water-soluble sulfate. The water-soluble sulfate was precipitated with Ba and converted to sulfide by reaction with a mixture of concentrated HCl, HI, and H_2PO_3 [10]. The solids were acidified with 5N HCl, which releases and operationally defined acid volatile sulfur (AVS). For MIL meteorite samples the AVS fractions were too small to analyze. The 5N HCl extracts an acid soluble fraction of sulfate that was precipitated with Ba and analyzed using the Thode technique. The solid residues from acidification were then reacted with a mixture of 5N HCl and Cr(II) chloride, which releases sulfur as sulfide from the predominant sulfide minerals in the MIL samples. The sulfide was converted to silver sulfide form, which was fluorinated to SF_6, which was purified, and analyzed using dual inlet Isotope Ratio Mass Spectrometry (IRMS) at the University of Maryland. The data are presented in per mil using δ^{34}S, Δ^{33}S, and Δ^{36}S and normalized directly to the canyon diablo troilite (CDT) sulfur standard. The 2σ uncertainties for δ^{34}S, Δ^{33}S, and Δ^{36}S are estimated to be ± 0.3 ‰, ± 0.016 ‰, and ± 0.3 ‰, respectively. Sulfur concentrations were determined by gravimetric techniques. Uncertainties on sulfide concentrations are estimated to be on the order of ± 2%.

Magnetite/sulfide data were extracted using reflected light images obtained with a optical microscope that were analyzed using ImageJ (a image analyzing software). 15 melt pockets containing magnetite and sulfide grains were photographed for each of MIL090030, MIL090032, and MIL090136. ImageJ was used to construct histograms of the pixel by pixel intensity for the images of each melt pocket. This data was evaluated by matching histogram peaks to phases identified in the thin sections, and used to determine the magnetite/sulfide. These data are preliminary, and uncertainties are estimated to be at the level of ± 5%.

Table 1. Isotopic and concentration data for paired MIL samples

Meteorite	δ^{34}S	Δ^{33}S	Δ^{36}S	S(ppm)
MIL 03346,191‡				
Water-soluble sulphate	7.08	-0.207	-0.48	201
Acid-soluble sulphate	10.39	-0.254	-0.11	840
CRS	6.81	-0.434	-0.04	242
MIL 090030,41				
Acid-soluble sulphate	6.23	-0.474	-0.28	541
CRS	8.78	-0.538	0.12	212
MIL 090032,85				
Water-soluble sulphate	11.73	-0.226	0.38	143
Acid-soluble sulphate	9.01	-0.187	-0.67	674
CRS	8.85	-0.523	0.06	167
MIL 090136,32				
Water-soluble sulphate	12.75	-0.176	-0.32	129
Acid-soluble sulphate	9.7	-0.247	0.46	689
CRS	7.66	-0.476	0.18	109

‡data from Kim and Farquhar, LPSC 2008

Results: Table 1 reports isotopic data for the three paired martian meteorites and previously reported data for MIL 03346 [3]. The results are also shown in Figure 1 as δ^{34}S versus Δ^{33}S and Δ^{33}S versus Δ^{36}S. We observe positive δ^{34}S (6.23 to 12.75 ‰) and negative Δ^{33}S values (-0.538 to -0.176 ‰) for all samples. The Δ^{36}S values range from -0.67 to 0.46 ‰. Sulfur concentrations range from 109 to 689 ppm, and the most abundant fraction is the acid soluble sulfate fraction. The identity of this fraction is unclear. The sulfide fraction of the MIL samples ranges from 109 ppm to

242 ppm, with the highest value coming from the study of MIL 03346. Magnetite/sulfide data range from 90%/10% for MIL090030, 97%/3% MIL090032, and 95%/5% for MIL090136.

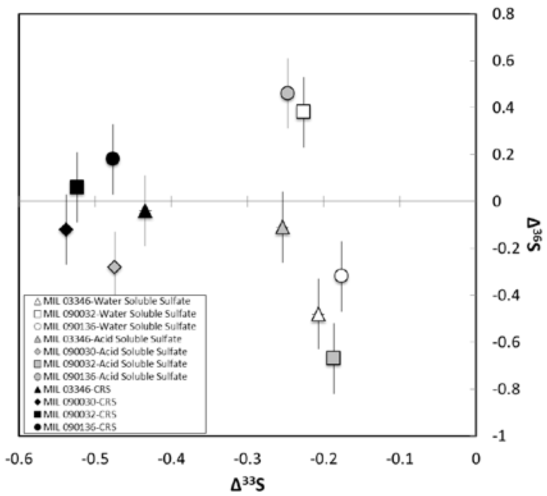

Figure 1. Plot of $\Delta^{36}S$ vs $\Delta^{33}S$ for MIL samples. Sulfide is filled symbols, acid soluble sulfate is grey filled symbols, and water soluble sulfate is unfilled symbols. Uncertainties are 1σ.

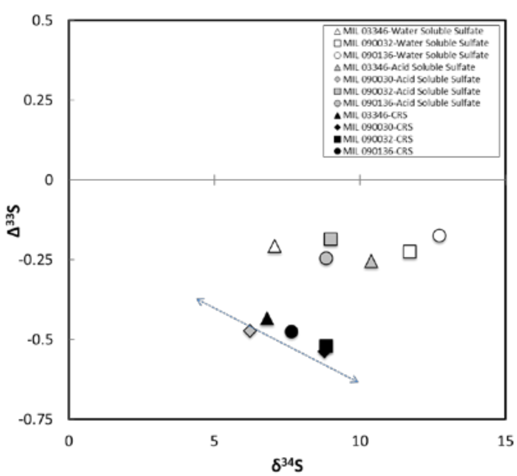

Figure 2. Plot of $\Delta^{33}S$ vs $\delta^{34}S$ for MIL samples. Sulfide is filled symbols, acid soluble sulfate is grey filled symbols, and water soluble sulfate is unfilled symbols. Dashed line represents a possible mixing line between igneous sulfide sulfur and contributed mass-independent sulfur.

Discussion: The IRMS data indicate that the most negative $\Delta^{33}S$ (for sulfide phases from the three paired MIL meteorites) lacks negative excursions for $\Delta^{36}S$. This is different from the signature seen in terrestrial analogs and implies a difference in the MIF source reactions.

The data indicate that while the water soluble and acid soluble sulfate fractions possess anomalous $\Delta^{33}S$, the most significant $\Delta^{33}S$ are observed for sulfide minerals. The sulfate fractions are inferred to derive from Ca sulfate and jarosite, with the acid soluble fraction most likely representing the latter.

The data also reveal a link between the high sulfide $\Delta^{33}S$ and the high oxidation state of MIL samples because the paired MIL samples are presently the martian meteorites with the most anomalous $\Delta^{33}S$ that have been identified [compare with 1,2,5]. This observation is consistent with assimilation of sulfate that is reduced in the parent melt to the MIL meteorites and then crystallized from the melts as sulfide. The high sulfide concentrations of the MIL samples compared to other Nakhlites is also consistent with this interpretation.

The data also reveal clear differences for $\Delta^{33}S$ of sulfide in different martian MIL meteorites. This observation points to real heterogeneity in the proportions of assimilate sulfate that was subsequently reduced to form sulfide. It indicates that the process of assimilation that occurred on emplacement was heterogeneous.

Data from image analysis may link the copious amount of skeletal type magnetite grains to sulfate assimilation. Assuming the Fe in the magnetite originates from the melt (or possibly pyroxene xenocrysts), the magnetite may be explained by a redox reaction involving pyroxene such as: 13Fe(II) in px/ol + $CaSO_4 \cdot 2H_2O \rightarrow 4Fe_3O_4 + FeS +$ Ca (in silicates) + $2H_2O$. This reaction yields 90% magnetite and 10% pyrrhotite, which is slightly lower (but comparable) ratio to that observed in the image analyses. This suggests an important role for assimilation of salts in determining the redox state of the crystallizing melt [9]. It also may indicate that other magnetite rich rocks from/on Mars will have anomalous $\Delta^{33}S$.

We believe that as the Martian lava flow traveled across the Martian regolith and assimilation of sulfate occurred. The sulfate reacted with the melt and xenocrysts to force an oxidation reaction yielding magnetite and pyrrhotite. The amount and crystallographic form of magnetite in these paired, sulfur rich meteorites, are uncommon and unlike other petrographically observed Martian Meteorites [7]. An additional interpretation to make from this data is that magnetite rich meteorites are possibly an important characteristic in searching for sulfur rich meteorites.

References: [1] Farquhar et al. (2000) Nature, 404, 50. [2] Farquhar et al. (2007) EPSL, 264, 1. [3] Kim & Farquhar, LPSC 2008. [4] Franz et al. (2011), LPSC. [5] Franz et al. (2012) LPSC. [6] Hallis &. Taylor (2011) MAPS, 46, 1787. [7] A. Udry et al. (2012) MAPS, 211. [8] Kuebler (2013) JGR, 118, 347. [9] McCanta et al. (2009) MAPS, 44, 725. [10] Righteret al. (2008) MAPS, 43, 1709. [11] Dayet al.(2006) MAPS, 41, 581. [12] Thode et al. (1961) GCA, 25, 159.