

MULTIPLE SULFUR ISOTOPE COMPOSITIONS IN MARTIAN METEORITE MIL 03346. Sang-Tae Kim¹ and James Farquhar¹, ¹Department of Geology and ESSIC, University of Maryland, College Park, MD, 20742, sangtae@umd.edu and jfarquha@geol.umd.edu.

Introduction: Sulfur isotope compositions of SNC meteorites have been determined on the basis of either stable isotope mass spectrometric or secondary ion microprobe techniques [1-6]. The range of the reported $\delta^{34}\text{S}$ values from each group of the martian SNC meteorites in the literature has been used to suggest that (a) the sulfur isotope signature of the Martian mantle may be very similar to that of the Earth's mantle and (b) chemical and physical processes, such as magmatic hydrothermal activity, were probably at play in the Martian surface or subsurface. In addition, based upon the determination of $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ values in Nakhla and Lafayette, it was proposed that atmospheric photochemical processes played an important role for the genesis of sulfate-bearing minerals on Mars [1, 5]. Furthermore, an unexpected covariation between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ in Nakhla, which is distinct from those observed from ancient terrestrial analogs and existing photochemical experiments, was found [1] and this new observation prompted us to investigate and characterize the nature of the $\Delta^{33}\text{S}$ - $\Delta^{36}\text{S}$ relationship for other SNC meteorites. As a first step of these efforts, the analyses of the sulfur isotope compositions ($\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$) in MIL 03346 Martian meteorite were carried out and the results for the water-soluble sulfate, Cr-reducible (assumed to be pyrite), and acid-soluble sulfate fractions are reported.

Method: A fragment of MIL 03346 from NASA (MIL 03346, 191) was gently disaggregated using a steel mortar and subsequently grinded with an agate pestle and mortar set. A mass of 2.938g powdered meteorite was then transferred to a 15 mL centrifuge tube and 10 mL of degassed Milli-Q water was added to the tube. The powdered meteorite and water in the tube were sonicated for 30 minutes to promote the dissolution of water-soluble sulfate phases in the meteorite. Subsequently, the sample and the solution were centrifuged for 10 minutes and the solution was carefully separated from the meteorite using a pipette and then transferred to a double necked boiling flask with a septum. This process was repeated twice and a total of a 20 mL solution was recovered. The reduction for the water-soluble sulfate of the meteorite was carried out for 3 hours and the protocol was the same as that for the acid-soluble sulfate fraction described in the following section. The remaining powdered meteorite was transferred to another double necked boiling flask for a sequential sulfur extraction. The boiling flask was assembled as a part of an apparatus similar

to that described by [7] that consisted of a nitrogen purged boiling flask with a silicone septum, a water-cooled condenser, a bubbler filled with Milli-Q water, and a sulfide trap made of a mixture of a silver nitrate solution and a nitric acid. All ground glass joints were sealed with PTFE sleeves. This apparatus was assembled, checked for leaks, and purged with nitrogen for 10 minutes. Following this initial step, 20 mL of 5N HCl were syringe injected through the septum into the boiling flask where the ground meteorite was placed and the acid was heated to $\sim 60^\circ\text{C}$ for the collection of AVS (acid volatile sulfur). After 3 hours, the first sulfide trap and the bubbler were replaced with a new trap containing a fresh silver nitrate trapping solution and fresh Milli-Q water, respectively, and the reaction was continued for 30 minutes. After the second sulfide trap and the bubbler were removed and replaced with a new trap and a bubbler filled with fresh Milli-Q water, 15 mL of acidic $\sim 0.3\text{M}$ Cr(II) solution was then injected into the hot boiling flask ($\sim 60^\circ\text{C}$) and the reaction was allowed to proceed for 4 hours for the extraction of Cr-reducible sulfur. After 3 hours, the third sulfur trap and the bubbler were removed and a new sulfur trap and a bubbler were placed for the remaining 1 hour of the reduction. Again, after a new sulfur trap and a bubbler were placed, a 20 mL reduction solution containing preboiled and nitrogen-purged HI, H_2PO_3 , and 12N HCl was injected into the hot boiling flask for the reduction of acid-soluble sulfate. During the course ~ 40 hours of heating ($\sim 85^\circ\text{C}$) and purging with nitrogen, the sulfide trap and the bubbler were changed 7 times with a new trap containing fresh silver nitrate trapping solution and Milli-Q water, respectively. All of the trapping solutions were left in a dark cabinet for a minimum of 7 days, and then silver sulfide from all trapping solutions was vacuum filtered, rinsed with ammonium hydroxide and Milli-Q water, and then dried in a 55°C drying oven. The silver sulfide precipitates were weighed, wrapped in Al-foil boats and placed into separate Ni-reaction vessels for fluorination by reaction with ~ 10 times excess purified F_2 at 250°C . Product SF_6 was frozen out of the remaining F_2 which was passivated by reaction with hot KBr. The product SF_6 was then purified by cryogenic separation at -110°C and gas chromatography using a 1/8 inch diameter composite column consisting of a 6 foot 5A molecular sieve followed by an 8 foot Haysep Q[®] column. Sulfur hexafluoride was trapped as it exited the column and frozen into the sample inlet of a dual inlet ThermoFinnigan MAT 253 where $m/z = 127^+$,

128⁺, 129⁺, and 131⁺ were monitored. Reproducibility of these measurements is estimated on the basis of long-term measurements of IAEA reference materials and is generally better than 0.2, 0.01 and 0.2‰ for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$. The $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ values are normalized to measurements of CDT.

Results and Discussion: The results of our isotopic analyses of MIL 03346 are reported in Table 1. It should be noted that sulfur isotope compositions of the 2nd fraction of the Cr-reducible sulfur and the 3rd to 7th fraction of the acid-soluble sulfate fractions are not determined yet and thus can not be reported in this abstract; however, their multiple sulfur isotope data will be collected. The water-soluble sulfate and Cr-reducible fractions have positive $\delta^{34}\text{S}$ values (7.26 and 6.98‰, respectively) that are close to each other and also lie within the range of the reported $\delta^{34}\text{S}$ values from other SNC meteorites [2-4]. In contrast, the acid-soluble sulfate fractions show a wide range of $\delta^{34}\text{S}$ values (-1.40 to 15.46‰). It is not clear at this stage whether this variation is a real representation of the isotopic ratios of the acid-soluble sulfate phases in the meteorite or simply originated from kinetic isotope effects during the course of sample reduction/collection processes. Additional data from the remaining acid-soluble sulfate fractions will help us to characterize the nature of this unexpected variation. All of our measurements of $\Delta^{33}\text{S}$ have negative values (-0.21 to -0.46) implying that the water-soluble as well as acid-soluble sulfates and Cr-reducible sulfides (assumed to be pyrite) in the meteorite are probably secondary minerals formed on Mars. Our $\Delta^{33}\text{S}$ data also confirm the previous findings that the non-mass dependent signature was transferred to sulfur-bearing minerals in the SNC meteorites [1, 5, 6] and atmospheric chemical reactions played a significant role in the Martian sulfur cycle. Furthermore, regardless of its magnitude, the $\Delta^{36}\text{S}$ of all sulfur-bearing fractions has negative values (-0.04 to -0.78). Consequently, our sulfur isotope data yield a different covariation between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ than those have been observed in terrestrial and experimental sample sets as well as that observed in Nakhla. This observation requires additional analyses of other SNC meteorites and laboratory experiments to characterize the nature of the $\Delta^{33}\text{S}$ - $\Delta^{36}\text{S}$ covariation.

Table 1. Sulfur isotope compositions of MIL 03346 191

	$\delta^{34}\text{S}$	$\Delta^{33}\text{S}$	$\Delta^{36}\text{S}$
MIL 03346 191 Water-soluble Sulfate	7.26	-0.23	-0.47
MIL 03346 191 Cr-reducible Sulfur-1	6.98	-0.46	-0.04
MIL 03346 191 Acid-soluble Sulfate-1	-1.40	-0.21	-0.78
MIL 03346 191 Acid-soluble Sulfate-2	15.46	-0.25	-0.24

References: [1] Farquhar J. et al. (2007) *Earth Planet. Sci. Lett.* 264, 1-8. [2] Greenwood J. P. et al. (1997) *Geochim. Cosmochim. Acta* 61, 4449-4453. [3] Greenwood J. P. et al. (2000a) *Geochim. Cosmochim. Acta* 64, 1121-1131. [4] Shearer C. K. et al. (1996) *Geochim. Cosmochim. Acta* 60, 2921-2926. [5] Farquhar J. et al. (2000) *Nature* 404, 50-52. [6] Greenwood J. P. et al. (2000b) *Earth Planet. Sci. Lett.* 184, 23-35. [7] Forrest J. and Newman L. (1977) *Anal. Chem.* 49, 1579-1584.