

SULFUR ISOTOPE ANALYSIS OF THE NAKHLA METEORITE: IMPLICATIONS FOR THE ORIGIN OF SULFATE AND THE PROCESSING OF SULFUR IN THE METEORITE PARENT. J. Farquhar, Sang-Tae Kim and A. Masterson, All at: Department of Geology and Essic, University of Maryland, College Park MD 20742, jfarquha@geol.umd.edu, sangtae@geol.umd.edu, and masterso@umd.edu.

Introduction: We report new analyses of the sulfur isotope composition ($\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$) of a piece of the Nakhla meteorite (BM 1913.25) with the aim of understanding several questions raised by a prior study that we undertook [1]. These include: (a) providing new $\Delta^{36}\text{S}$ data that can be used to evaluate the origin of previously reported nonzero $\Delta^{33}\text{S}$, (b) providing data that can be used to evaluate the possibility that nonzero $\Delta^{33}\text{S}$ may also be present for sulfide minerals in this meteorite, and (c) evaluating whether the reactions that produced the nonzero $\Delta^{33}\text{S}$ in Nakhla share similar characteristics to those that are observed in other terrestrial and extraterrestrial samples.

Our findings support the suggestion that the non mass-dependent signal was transferred to sulfide minerals in this meteorite. Our findings also point to a part of the sulfur cycle that is distinct from known igneous, hydrothermal, and aqueous phase effects, and are also not accounted for by existing gas-phase photochemical experiments. We interpret the effects to be photochemical in origin, but work remains to identify the specifics details of the cause of the effect.

Methods: A single pieces of the Nakhla meteorite from the British Museum (BM 1913.25) with a mass of 1.9939 g was gently disaggregated using a steel mortar and transferred to a double necked boiling flask with a septum. The flask was assembled as a part of an apparatus similar to that described by [2], comprised of a nitrogen purged boiling flask, a water-cooled condenser, a bubbler filled with milli-Q water, and a sulfide trap filled with 0.2 M cadmium acetate trapping solution. All joints are sealed with PTFE sleeves. The apparatus was assembled, checked for leaks, and purged with nitrogen. After ten minutes, 25 ml of 5N HCl were injected through the septum into the reaction flask using a syringe and the boiling flask was heated for 3 hours. After three hours, approximately 5 mL of Milli-Q water was added to the trapping solution, along with 5 drops of 0.3 M silver nitrate solution. The sulfide trap was then replaced with a new trap containing fresh cadmium acetate trapping solution and 25 mL of a reduction solution containing preboiled HI, H_2PO_3 , and 12N HCl was injected into the hot boiling flask. After another three hours the second trapping solution was treated with Milli-Q water and 5 drops of 0.3 M silver nitrate solution. The sulfide trap was then replaced with a new trap containing fresh cadmium ace-

tate trapping solution and the acidic $\sim 0.3\text{M}$ Cr(II) solution was injected into the boiling flask and the reaction allowed to proceed for another three hours. After another three hours the third trapping solution was treated with Milli-Q water and 5 drops of 0.3 M silver nitrate solution. Silver sulfide from all three trapping solutions was transferred to 3 mL glass centrifuge tubes, centrifuged, washed and then dried in a 90 °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 -gas at 250 °C. Product SF_6 was frozen out of the remaining F_2 -gas which was passivated by reaction with hot KBr. The product SF_6 was then purified by cryogenic separation at -120 °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. The SF_6 peak 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 are generally better than 0.2, 0.01 and 0.2‰ for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ [3], but this is not the case for small samples like the AVS sample for which we would estimate uncertainties of 0.5, 0.03 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: Our analyses are reported in Table 1 and indicate the following:

1) The sulfate fraction and the Cr reducible fractionation have $\Delta^{33}\text{S}$ that are nonzero. These values are analytically resolvable from those reported for CDT and bulk sulfur from other meteorite populations (including the other SNC meteorites) [1,4-9].

2) Although the $\Delta^{33}\text{S}$ of the AVS fraction that we measured is very close to that for the Cr reducible fraction, the amount of sample is small and we do not believe that we resolve this value from zero. A prior analysis of AVS from Nakhla [1] yielded a similar negative $\Delta^{33}\text{S}$ value (like the Cr reducible sulfur reported here) and is considered to be distinct from other SNC meteorites.

3) All of our measurements of $\Delta^{36}\text{S}$ are within error of zero (smaller than ± 0.2 permil). These measurements are an improvement on earlier measurements of

$\Delta^{36}\text{S}$ for Nakhla (because of small sample sizes in the prior measurements).

4) Our results yield a different relationship between $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ than has been observed in natural and experimental sample sets. Our results yield $\delta^{33}\text{S}/\delta^{34}\text{S} \sim 0.3$ and $\Delta^{36}\text{S}/\Delta^{33}\text{S} \sim 0.2$, but within error of 0. These are distinct from those produced by mass-dependent processes, known non mass-dependent chemical processes, and non mass-dependent effects associated with nuclear reactions or shielding reactions [1, 10-14].

Discussion: Our analyses of Nakhla confirm earlier measurements of nonzero $\Delta^{33}\text{S}$ in SNC sulfate and point to part of the Martian sulfur cycle that is independent of typical terrestrial aqueous and geologic processes that cycle sulfur on earth.

The observation of nonzero $\Delta^{33}\text{S}$ in Cr reducible sulfur confirms earlier suggestions that the nonzero $\Delta^{33}\text{S}$ is also present in sulfides in Nakhla. This points to assimilation of sulfur from a surface sulfur (sulfate) pool, possibly during hydrothermal activity following the emplacement of Nakhla source rocks on Mars.

The origin of the nonzero $\Delta^{33}\text{S}$ remains unresolved. The small amount of data that we have collected so far does not fit with the $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ observed in experiments undertaken to date and in natural samples sets. Possibilities include photochemical gas-phase reactions and reactions that are influenced by nuclear spin of odd isotopes. Further investigation of candidate reactions is warranted as is revisiting the isotope compositions of different forms of sulfur in other SNC meteorites.

Table 1. Sulfur isotope compositions

	$\delta^{34}\text{S}$	$\Delta^{33}\text{S}$	$\Delta^{36}\text{S}$
Nakhla SO ₄	4.7	-1.25	-0.16
Nakhla Cr-red.	-1.6	-0.09	-0.24
Nakhla AVS	0.9	-0.06	0.06

Values given in permil and normalized to CDT. All for BM 1913.25.

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