
Introduction: The search for life in the universe is of paramount importance to current NASA objectives. How we will conclusively determine the existence of past (or present) biota needs to be evaluated now, not after samples are returned from Mars or Europa (or other solar-system bodies). The debate over evidence for relict life in martian meteorite ALH84001 has brought to the forefront the difficulty in such determinations. While the presence of morphological evidence in returned samples, such as unambiguous fossils, would be fantastic, the odds cannot be considered great. More reasonable and ubiquitous biomarkers would be stable isotopic fractionations of biologically important elements, such as C, N, O and S. Nitrogen has undergone significant isotopic fractionation and is rare as a rock-forming element. Carbon isotopes (12C, 13C) have been used successfully to document biological activity in the oldest terrestrial sediments [1] and makes determining the isotopic composition of C in martian reservoirs (hydrosphere, atmosphere, and lithosphere) of key importance. The potential of O isotopes as a biomarker has only been recently explored and could be useful for Mars sample return in two ways. The oxygen isotopic composition of phosphate (16O, 18O) appears to be a reliable biomarker in marine systems [2], and its extension to hydrothermal systems should be relatively straightforward. The three isotopes of oxygen (16O, 17O, 18O) have also been used as an indicator of paleoproductivity [3] in Greenland ice cores and holds promise for Mars. Some evidence for mass-independent fractionation of oxygen isotopes in martian meteorites has been ascribed to interactions with the martian atmosphere [4], although heterogeneous accretion cannot be ruled out [5]. The sulfur system has also been shown to have a mass-independent isotopic component in martian meteorites [6,7] and has been ascribed to interactions with the martian atmosphere [7]. Here we present measurements of 32S, 33S, and 34S in martian meteorites Los Angeles, ALH84001, and Nakhla by multicollector SIMS and discuss the implications for biological activity at the sites on Mars where these rocks originated. We also discuss the utility and importance of this method for future sample return from Mars and other solar system bodies.

Methods: 32S, 33S, and 34S were counted simultaneously with Faraday cups on the UCLA ims 1270 ion microprobe in multicollector mode. This method allows for greater precision (approaching that of laser ablation methods) than ion microprobe monocollector, while still maintaining very high spatial resolution (<25µm). Details of the methods employed are described in [6]. Data for the Los Angeles meteorite were not collected in the same session as ALH84001 and Nakhla. Precision of the Los Angeles measurements were much lower as evidenced by greater variability of the standard minerals in this analytical session.

Results: The δ33S vs. δ34S measurements of Los Angeles, ALH84001, and Nakhla are shown in Fig. 1. Los Angeles: The range of δ33S values measured in Los Angeles (-2.7±1.6‰ to 0.0±1.6‰, 2σ) are similar to the range found in EETA79001 [8]. No Δ33S anomalies were found in Los Angeles within our analytical precision.

Nakhla: The range of δ34S values found for Nakhla (-4.49±0.44‰ to +1.38±0.44‰, 2σ) extends the previously determined range to slightly lighter values [9]. No Δ33S anomalies were found.

ALH84001: The range of δ34S values measured in ALH84001 (-9.69±0.22‰ to +4.19±0.22‰, 2σ) extends the previously determined range to much lighter values [8]. Curiously, the two sulfides with the lightest values are associated with carbonate. Resolvable positive Δ33S anomalies in two sulfides not associated with carbonate were found (Δ33S: +0.74±0.39‰ and +0.51±0.38‰, 2σ).

Discussion: Previous work on martian meteorites by conventional techniques revealed resolvable Δ33S anomalies in the nakhlites and shergottites [7]. Large, heterogeneous negative Δ33S anomalies were found in Nakhla, while small, homogeneous positive Δ33S anomalies were found in Lafayette [7]. Shergottites were found to have heterogeneous Δ33S distributions [7]. While the conventional method is more precise than our multicollector SIMS method, grain-scale heterogeneity and possible petrographic associations of anomalous sulfides cannot otherwise be determined.

Los Angeles: No resolvable Δ33S anomalies were found in Los Angeles meteorite. The Δ34S values are similar to those found in a previous study of the shergottites [8], and are consistent with a purely magmatic source. The largest Δ33S anomaly found by [7] was for sulfate in Shergotty. Sulfate is a rare phase in martian meteorites and contributes only a small portion of the total sulfur in the samples. Sulfate is likely a late-stage alteration product; this suggests that Δ33S anomalies found in shergottites are best attributed to a small
quantity of highly fractionated material derived from the martian regolith and added to the rock at subsolidus temperatures. The possibility that these alteration products were added later cannot be ruled out.

*Nakhla:* No resolvable $\Delta^{33}S$ anomaly was found. We hypothesize that non-mass-dependent sulfur isotopic compositions found by [7] are concentrated in ‘iddingsite’ in this meteorite. Iddingsite alteration occurred well after igneous crystallization [10], and likely resulted from low-temperature alteration [11]. Again, this points to a highly fractionated mass-independent component of the martian regolith. The range in $\delta^{34}S$ is consistent with a magmatically-driven hydrothermal system.

*ALH84001:* We found a large range of $\delta^{34}S$ as well as two sulfides with resolvable $\Delta^{33}S$ anomalies in ALH84001. The large range of values cannot be explained by low-temperature alteration due to the long time-scales inherent in sulfur isotope exchange below 200°C [6]. We propose that ALH84001 experienced higher temperature hydrothermal alteration than Nakhla, consistent with the idea that ALH84001 experienced a more vigorous impact-driven hydrothermal system.

*Implications for life from martian meteorites:* Biological activity results in rapid homogenization of isotopic reservoirs. The finding of mass-independent $\Delta^{33}S$ anomalies in ALH84001 pyrite grains points to an isotopic system that was not homogenized, and therefore cannot be used to support the presence of biological activity by these data. The two sulfides associated with carbonate in ALH84001 that we measured did not have $\Delta^{33}S$ anomalies, and were lighter in $\delta^{34}S$. Were there multiple episodes of alteration?? A more complete sulfur isotopic study of sulfide grains associated with carbonate in ALH84001 would allow this question to be answered. The lack of a $\Delta^{33}S$ anomaly in Nakhla could be interpreted as resulting from biological activity, but all other evidence points towards a magmatic hydrothermal system as being responsible for the observed values. Los Angeles meteorite shows neither evidence of biological nor hydrothermal activity.

*Future work:* A thorough study of sulfides associated with carbonate in ALH84001 is necessary for evaluating the question of life in this sample. The three-isotope sulfur isotope biomarker will be important for evaluation of biogenic activity in returned samples. The coupling of conventional measurements with multicollector-SIMS will be a powerful tool. The limits of analytical precision for multicollector-SIMS currently rest on the characterization of more robust sulfur isotopic standards.

**References:**