

Implications from sulfur isotopes of the Nakhla meteorite for the origin of sulfate on Mars

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Abstract

The isotope geochemistry of sulfur in the SNC (Shergottite, Nakhlite, Chassignite) meteorites may carry important implications for the origin and chemistry of sulfates and sulfides in the Martian surface and subsurface. We report measurements of the sulfur isotope composition for three sulfur-bearing components of the Nakhla meteorite. These results yield a negative $\Delta^{33}\text{S}$ signal of -1.25‰ and a near zero $\Delta^{36}\text{S}$ signal for total sulfate as well as a small nonzero $\Delta^{33}\text{S}$ of -0.09‰ for sulfide phases. The $\Delta^{33}\text{S}$ of total sulfate measured here is more negative than the $\Delta^{33}\text{S}$ reported previously for water soluble sulfate and points to sulfur isotopic heterogeneity in the sulfate of Nakhla.

Current understanding of mass-independent isotope effects associated with sulfur oxidation reactions rules out hydrothermal oxidation mechanisms for producing nonzero $\Delta^{33}\text{S}$ and points to a significant role for photochemical effects (including hyperfine chemistry), likely located in the Martian atmosphere. The near zero $\Delta^{36}\text{S}$ signal allows for the possibility of hyperfine chemistry. Because of the relationship between SNC sulfate and the sulfate deposits seen on Mars, these results place constraints on the generation of sulfur (VI) at the Martian surface and provide a case for future direct measurements of $\Delta^{33}\text{S}$ (and $\Delta^{36}\text{S}$) of Martian sulfate.

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1. Introduction

Surface sulfate deposits on Mars are a focus of interest because they have been observed in a number of Martian environments, because they potentially preserve organic matter that can be studied in future Mars missions (Aubrey et al., 2006) and because they can hold water as hydrous phases in the near surface in Martian equatorial regions during periods of high and low orbital obliquity (Vaniman and Chipera, 2006). Their presence as sulfate salts in aerosols and as minerals at the surface and in the near surface of Mars is known from in situ data and

remote measurements (e.g., Settle, 1979; Pollack et al., 1990; Wanke et al., 2001; Klingelhofer et al., 2004; Squyres et al., 2004, 2006; Wang et al., 2006a,b), as well as measurements of the SNC meteorites (Gooding and Muenow, 1986; Wentworth and Gooding, 1988; Gooding et al., 1990, 1991; Gooding, 1992) which are thought to come from Mars (Ashwal et al., 1982; Bogard et al., 1984; McSween, 1984, 1985, 1994).

Martian sulfate minerals are thought to have been deposited in their present locations by a variety of chemical and physical processes (Grotzinger et al., 2005; Greenwood and Blake, 2006; Schiffman et al., 2006), and the oxidation of sulfur to a +6 oxidation state has been inferred to have occurred by reactions involving sulfide-rich hydrothermal solutions (Zolotov and Shock, 2005), oxidation of

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impact-related sulfides (Knauth et al., 2005), and atmospheric photochemical oxidation of volcanogenic sulfur dioxide (Settle, 1979; Farquhar et al., 2000c). The contributions of each of these processes to the Martian surface and near surface sulfate pools are relevant to our understanding of regolith processes — including the history of water and brines on Mars and of oxidation processes, but few tools exist to make direct tests of these possibilities.

The sulfur and oxygen isotopic composition of sulfate and carbonate in Martian samples (e.g., SNC meteorites) also bears on questions about oxidation chemistry. Karlsson et al. (1992) documented isotopic evidence for water in the Martian subsurface that carried the signature of an oxygen reservoir independent of the silicate planet, and initiated a series of sulfur and oxygen isotope studies of secondary phases from SNC meteorites that provide indications of a rich record of chemistry and mixing between juvenile and evolved sources of sulfur. In the case of oxygen, this record provides information about the atmospheric inputs of oxidants to the Martian regolith, and the transfer of species that carry the imprint of non mass-dependent atmospheric signals to deeper levels in the Martian subsurface. The residual $\Delta^{17}\text{O}$ signal in SNC hydrous minerals by Karlsson et al. (1992) and Romanek et al. (1998) was found to be similar to that observed in carbonate but distinct from that of sulfate (Farquhar and Thieme, 2000). Sulfur isotope studies of sulfides in SNC meteorites using secondary ion mass spectrometry (SIMS) documented heterogeneity of $\delta^{34}\text{S}$ that point to assimilation of surface and atmospheric components into hydrothermal sulfides at least as early as ~ 3.9 Ga and extending to ~ 1.3 Ga (Shearer et al., 1996; Greenwood et al., 1997, 2000a). These meteorites also preserve evidence for incorporation of surface sulfate since ~ 700 Ma (Farquhar et al., 2000c). The Nakhla meteorite is reported to possess a variety of different sulfide phases (troilite, pyrrhotite, chalcopyrite, and pyrite) (Bunch and Reid, 1975; Weinke, 1978; Greenwood et al., 2000b) as well as a variety of different sulfate phases (Ca-sulfate and Mg-sulfate) (Wentworth and Gooding, 1988).

In this short communication, we revisit the sulfur isotope composition of the Nakhla meteorite, presenting sulfur isotope data for sulfide and sulfate from the SNC meteorite Nakhla that includes high precision measurements of $\Delta^{36}\text{S}$, in addition to $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ for sulfate and sulfide from a fragment supplied by the British Museum of Natural History (Nakhla BM 1913.25). Our new $\Delta^{36}\text{S}$ data for this meteorite are more accurate than that reported in our prior studies principally because we extracted a greater amount of sulfate from this fragment, but also because of improvements in mass-spectrometer precision. The new data provide better characterization of the isotope

fractionation effects associated with sulfate sulfur and for understanding the cycling of sulfur in near surface Martian environments. It also provides constraints that can be used (1) to evaluate whether the signal is the product of extra-planetary processes or is a product of Martian atmospheric chemical processes, (2) to determine the types of processes that may have produced the signal, and (3) to evaluate its implications for the models of sulfur cycling in near surface Martian environments as well as prevailing hypotheses about the formation of S(VI) on Mars.

2. Methods

A fragment of the Nakhla meteorite from the British Museum (BM 1913.25) with a mass of 1.9939 g was disaggregated using a steel mortar and pestle and transferred to a double necked boiling flask. The flask was assembled as a part of an apparatus similar to that described by Forrest and Newman (1977) 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 filled with 0.2 M cadmium acetate trapping solution. All ground glass joints were sealed with PTFE sleeves. This apparatus was assembled, checked for leaks, and purged with nitrogen for 10 min. Following this, 25 mL of 5 N HCl were injected using a syringe through the septum into the reaction flask and the solution heated to ~ 100 °C. After 3 h, 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 trapped sulfide is referred to as acid volatile sulfide (AVS) and is considered to consist mostly of monosulfides (troilite, pyrrhotite, and chalcopyrite), although it has been shown by Rice et al. (1993) that disulfides can in some cases partially react during this step. The sulfide trap was then replaced with a new trap containing fresh cadmium acetate trapping solution. Addition of 25 mL of a reduction solution containing preboiled and nitrogen-purged HI, H_2PO_3 , and 12 N HCl was injected into the hot boiling flask. After another 3 h of heating and purging with nitrogen, approximately 5 mL of Milli-Q water and 5 drops of 0.3 M silver nitrate solution were added to the second trapping solution. This fraction is referred to as the acid soluble sulfate fraction and the reduction solution (Thode et al., 1961) is considered to be specific to sulfate (Mayer and Krouse, 2004)¹. The second sulfide trap was removed

¹ Tests conducted to evaluate the extent of carry-over of sulfur between the different extraction fractions did not yield evidence for reaction of sulfate or pyrite in the first step: the latter is in contrast with the findings of Rice et al. 1993. The tests did however yield minor reaction of pyrite with the sulfate reduction solution and carry over of a minor amount of the AVS fraction to the subsequent step(s).

Table 1
Sulfur isotope compositions and concentrations of Nakhla

Nakhla sample	$\delta^{34}\text{S}$ ($\sigma_{\text{estimated}}$)	$\Delta^{33}\text{S}$ ($\sigma_{\text{estimated}}$)	$\Delta^{36}\text{S}$ ($\sigma_{\text{estimated}}$)
BM 1913.25 total sulfate 170 ppm S	4.7 (0.2)	-1.25 (0.01)	-0.16 (0.2)
BM 1913.25 CRS 94 ppm S	-1.6 (0.2)	-0.09 (0.01)	-0.24 (0.2)
BM 1913.25 AVS 12 ppm S	0.9 (0.5)	-0.06 (0.03)	0.06 (0.2)

AVS refers to acid volatile sulfur (extracted with hot 5 N HCl, and CRS refers to chrome reducible sulfur extracted with hot acidic Cr(II) solution. The inferred sulfur concentrations of each extraction are also reported.

and replaced with a new trap containing fresh cadmium acetate trapping solution. Following this, 25 mL of acidic ~ 0.3 M Cr(II) solution was injected into the hot boiling flask and the reaction was allowed to proceed for another 3 h. After another 3 h the third trapping solution was augmented with 5 mL of Milli-Q water and 5 drops of 0.3 M silver nitrate solution. This fraction is referred to as the Cr-reducible fraction and would include disulfides (pyrite) and any elemental sulfur, including elemental sulfur produced from monosulfide during the extraction of AVS (Mayer and Krouse, 2004). The trapping solutions were left in a dark cabinet overnight, and then 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 stoichiometric excess purified F_2 (200–300 μmol) 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 -120 °C and gas chromatography using a 1/8 in. diameter composite column consisting of a 6 ft 5A molecular sieve followed by an 8 ft 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 are generally better than 0.2, 0.01 and 0.2‰ for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$, but this is not the case for small samples like the acid volatile sulfur fraction 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.

3. Results

The results of our analyses of Nakhla are reported in Table 1 and in Figs. 1 and 2. They are briefly summarized as follows. The sulfate fraction has a positive $\delta^{34}\text{S}$ (4.7‰)

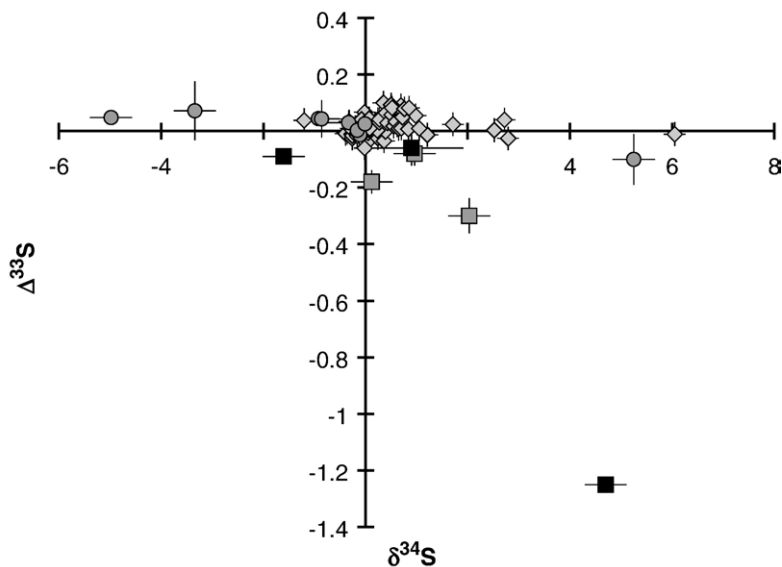


Fig. 1. Plot of $\Delta^{33}\text{S}$ versus $\delta^{34}\text{S}$. Grey diamonds include acid volatile sulfur extracted from analyses of chondrites, iron meteorites, and basaltic achondrites reported by Farquhar et al. (2000c), Gao and Thiemens (1991, 1993a,b), Farquhar et al. (2000b), Rai and Thiemens (2007) and Rai et al. (2005). Grey discs are for SNC meteorites other than Nakhla, analyses from Farquhar et al. (2000c). Grey filled square symbols are for analyses of sulfur extracted from Nakhla reported by Farquhar et al. (2000c). Black filled square symbols are for analyses of sulfur extracted from Nakhla reported in this study. Error bars represent estimates of the 2 sigma uncertainty.

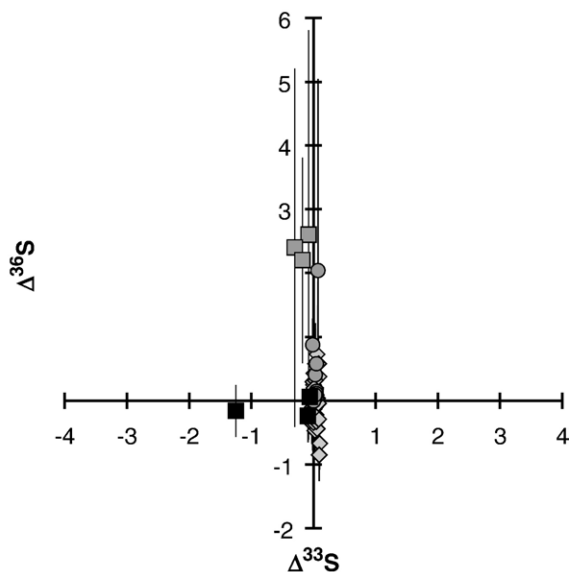


Fig. 2. Plot of $\Delta^{36}\text{S}$ versus $\Delta^{33}\text{S}$. Grey diamonds include acid volatile sulfur extracted from analyses of chondrites, iron meteorites, and basaltic achondrites reported by Farquhar et al. (2000c), Gao and Thiemens (1991, 1993a,b), Farquhar et al. (2000b), Rai and Thiemens (2007) and Rai et al. (2005). Grey discs are for SNC meteorites other than Nakhla, analyses from Farquhar et al. (2000c). Grey filled square symbols are for analyses of sulfur extracted from Nakhla reported by Farquhar et al. (2000c). Black filled square symbols are for analyses of sulfur extracted from Nakhla reported in this study. Error bars represent estimates of the 2 sigma uncertainty. The grey square symbols with $\Delta^{36}\text{S}$ values between ~ 2 and 2.5% have large uncertainties (reported by Farquhar et al., 2000c) and are within 2 sigma of zero $\Delta^{36}\text{S}$.

while the Cr-reducible and acid volatile fractions have slightly negative (-1.6%) and near zero (0.9%) values respectively. The sulfate fraction and the Cr-reducible fraction have negative $\Delta^{33}\text{S}$ values (-1.25 and -0.09% , respectively) that are distinct from those measured in CDT and for bulk sulfur from other meteorite populations (including analyses of Shergotite meteorites) (Gao and Thiemens, 1991, 1993a,b; Farquhar et al., 2000b,c; Rai et al., 2005; Rai and Thiemens, 2007). The $\Delta^{33}\text{S}$ of the sulfate fraction of Nakhla is presently the most negative value reported from the meteorite literature (-1.25%) and is distinct from a prior measurement of sulfate from another piece of Nakhla (-0.302%) (Farquhar et al., 2000c). The $\Delta^{33}\text{S}$ value of the acid volatile sulfur fraction measured here is identical (within uncertainty) to that for the Cr-reducible sulfur, and to a prior published analysis of acid volatile sulfur fraction from Nakhla (Farquhar et al., 2000c), but the larger uncertainty of the acid volatile sulfur fraction measurement makes it within 2σ of a value of zero. This lower precision reflects the small size of the acid volatile sulfur fraction sample extracted in this study.

Finally, all of our measurements of $\Delta^{36}\text{S}$ are within 2σ of zero (smaller than $\pm 0.4\%$). These measurements have smaller uncertainties than earlier measurements of $\Delta^{36}\text{S}$ for Nakhla. 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 such as those for Archean samples (Farquhar et al., 2000a) and modern atmospheric samples. A feature of our results that has not been observed in these other datasets (except for a few mid-Archean samples (Ono et al., 2006a)) is the presence of variation in $\Delta^{33}\text{S}$ with little resolvable variation for $\Delta^{36}\text{S}$. These values are also distinct from those observed and predicted for mass-dependent isotopic effects (Johnston et al., 2006; Ono et al., 2006b). The extractions yielded 0.8 , 10.4 , and $5.9 \mu\text{mol}$ of sulfur as AVS, sulfate sulfur and CR-reducible sulfur, which corresponds to 12 ppm, 170 ppm, and 94 ppm S, respectively.

4. Discussion

4.1. Implications for the origin of the isotope signal in the SNC meteorites

Farquhar et al. (2000c) argued that nonzero $\Delta^{33}\text{S}$ reflected photochemistry involving sulfur species in the Martian atmosphere because (1) the atmosphere of Mars transmits incident solar ultraviolet radiation down to wavelengths of approximately 190 nm (Kuhn and Atreya, 1979), (2) no large negative $\Delta^{33}\text{S}$ had been observed for total sulfur extracted from other meteorite populations (Gao and Thiemens, 1991, 1993a,b; Farquhar et al., 2000b,c), an observation recently reinforced by Rai and coworkers (Rai et al., 2005; Rai and Thiemens, 2007), and (3) negative $\Delta^{33}\text{S}$ were observed in closed cell photochemical experiments with sulfur dioxide and hydrogen sulfide (Farquhar et al., 2000c, 2001). Greenwood et al. (2000a) argued that the nonzero (negative) $\Delta^{33}\text{S}$ may reflect photochemistry, but it also may reflect influx of exotic meteoritic or cometary material to Mars. While ongoing efforts associated with the Stardust mission are likely to provide constraints on the isotopic composition of cometary sulfur that can be used to evaluate the validity of these two hypotheses about the origin of the non mass-dependent effects observed in the SNC meteorites, we favor a photochemical, Martian origin rather than an extraplanetary origin. While nonunique, one of our reasons includes the presence and absence of this signal in samples that span a significant portion of the entirety of Martian evolutionary history (approximately 3 Ga), which implies that it was heterogeneously distributed across surface environments for snapshots of Martian

history provided by the meteorites, yet persistent over the longer term which implies an ongoing production mechanism rather than the persistence of an early signal.

Another part of the argument for an atmospheric effect for Mars sulfur is based on parallels with a similar observation for early Earth samples which exhibit covariation between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ (Farquhar et al., 2000a; Thiemens, 2006), which recently has been demonstrated to possess intervals with similar negative $\Delta^{33}\text{S}$ and near zero $\Delta^{36}\text{S}$ (Ono et al., 2006a; Farquhar et al., 2007). Gas-phase non mass-dependent isotope effects have been interpreted to reflect different reaction rates for some isotopic species resulting from differences in molecular symmetry or rovibronic overlap between intermediate electronic bound states in photochemical reactions (e.g., Zmolek et al., 1999; Bhattacharya et al., 2000; Gao and Marcus, 2001; Babikov et al., 2003a,b). The absence of a clear $\Delta^{36}\text{S}$ signal complicates this interpretation because it permits an explanation that is related to a second type of isotope effect where reaction rates are affected by coupling between electron spin and unpaired nuclear spins of isotopologues with odd-mass isotopes (Buchachenko, 2001). These effects, referred to in the literature as hyperfine coupling or magnetic isotope effects (MIE), have been documented for photochemical reactions involving radicals in liquid phase (Buchachenko, 2001). A third type of non mass-dependent effect, nuclear field shift effect (Bigeleisen, 1998) are not thought to be significant for sulfur (Schauble, 2007), and are therefore not considered to be a likely explanation of our observations.

The two lines of evidence that lead us to favor an atmospheric origin for the observed effects are (1) the effects appear to be present in sulfur from two SNC meteorites with very different ages of formation and in Martian environments with very different amounts of surface water, and (2) recent evidence from the terrestrial geologic record suggests that similar $\Delta^{36}\text{S} / \Delta^{33}\text{S}$ relationships are present in the terrestrial record and appear to be part of a record that possesses variable $\Delta^{36}\text{S} / \Delta^{33}\text{S}$ (Ono et al., 2006a), (3) the negative sign of the $\Delta^{33}\text{S}$, and (4) experiments with sulfur dioxide in closed photocells yielded a change from positive $\Delta^{36}\text{S} / \Delta^{33}\text{S}$ to negative $\Delta^{36}\text{S} / \Delta^{33}\text{S}$ as a consequence of the light source used for the experiments (Farquhar et al., 2001). This result, combined with the observation that products and reactants from these experiments did not form a single line on plots of $\delta^{33}\text{S}$ versus $\delta^{34}\text{S}$ and $\delta^{34}\text{S}$ versus $\delta^{36}\text{S}$, led to the suggestion that more than one non mass-dependent reaction was present in the experiments (Farquhar et al., 2001). It is not known if one of these reactions produces an odd-mass ^{33}S magnetic isotope effect (hyperfine cou-

pling), or whether a balance between these reactions can occur as a result of different wavelengths, or other changes in photochemical pathways. It is known that some reactions inferred to occur in the photocells involve changes in electron spin (e.g., intersystem crossing between upper singlet and triplet states of SO_2^*).

4.2. Implications for the origin of S(VI) in Martian environments

There are a number of hypotheses about the oxidation of sulfur to a +6 oxidation state that may be evaluated in the context of the data presented here. One broad class of interpretations calls upon atmospheric oxidation processes, which if photochemical in nature would be broadly consistent with our observations. These include: suggestions by Hurowitz et al. (2006) who argue that weathering surfaces for Wishstone and Watchtower class rocks (a class enriched in P, Ti, and Al) could be best explained by two component mixing that was overprinted by secondary processes that included addition of an SO_3 component, likely by aeolian processes; suggestions by Schiffman et al. (2006), who argue that some Martian jarosite may have formed in an analogous environment to jarosite formed on Kilauean outcrops in areas with nearly continuous acidic aerosol fallout (acid fog); and suggestions by Greenwood and Blake (2006), who argue that while the chlorine and sulfur derive from volcanic sources, with atmospheric oxidation of sulfur dioxide as the principal sulfate source, the principal source of the high phosphorous concentrations is best explained by weathering of calcium phosphate minerals in igneous rocks. Greenwood and Blake (2006) argue further that the covariation of sulfur, chlorine, and phosphorous (S/Cl and S/P) requires a process capable of mixing these elements on a global scale, and assert that this reflects the presence of early acidic Martian oceans where sulfate, chloride, and phosphate were mixed in constant proportions. Similar arguments about mixing have been made on the basis of analog studies of acid weathering (Bullock and Moore, 2004; Bullock et al., 2004) and point to dilution and homogenization of a sulfur concentration signal. While the origin of sulfate in these models are consistent with our observations and a significant source of sulfate is inferred to be atmospheric, the assertion that this is the principal source of sulfate, exclusive of oxidation of sulfide minerals is not required by our data, provided the atmospheric chemical source has a very large non mass-dependent isotopic fractionation signature.

The second group of interpretations that are not consistent with our observations, but that can be reconciled with them if a second (atmospheric source) of sulfate was

included are: suggestions that sulfate in jarosite derives from oxidation of sulfide in hydrothermal fluids (Zolotov and Shock, 2005) and the suggestion that sulfate is derived from in situ oxidation of sulfides after an impact event (Knauth et al., 2005). The isotopic composition of sulfate produced in photochemical experiments by Farquhar et al. (Zmolek et al., 2001) had $\Delta^{33}\text{S}$ between -10 and -30% , and if the atmospheric contribution had a similar $\Delta^{33}\text{S}$, it would represent between 10 and 30% of the total sulfate. The relevance of this to Meridiani sulfates and to other Martian sulfates is not known, but should be taken into consideration and the ultimate resolution of these depends on the actual $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ of these deposits, highlighting the importance of undertaking these measurements in future missions either in situ or with return samples.

4.3. Implications for recycling of sulfur into the Martian subsurface

Shearer et al. (1996) provide evidence using SIMS sulfur isotope analyses for a secondary origin of pyrite in ALH 84001 that involves surface chemistry (hydrothermal or weathering) and reduction of surface sulfate, and Greenwood et al. (1997) extended this research with SIMS measurements of six basaltic shergottite meteorites and the orthopyroxenite, ALH 84001 and made arguments for incorporation of a surface component of atmospheric or soil-related origin with positive $\delta^{34}\text{S}$. A subsequent study by Greenwood et al. (2000b) examined three related Nakhrites — Nakhla, Governador Valadares and Lafayette and noted that sulfide minerals from each of these three meteorites spanned a greater range of $\delta^{34}\text{S}$ values than had been observed in the shergottites, and that the mean $\delta^{34}\text{S}$ of the three meteorites varied in a systematic way with the meteorite Nakhla having the highest $\delta^{34}\text{S}$ and Lafayette having the lowest $\delta^{34}\text{S}$. They interpreted these observations to reflect reworking of sulfur from surface pools with sulfur from juvenile sources and implied mobility of sulfur in the Martian near surface environments. They also argued for a ^{34}S -enriched source of S(VI) that was transferred to SNC sulfide by hydrothermal processes, making arguments that sulfide minerals are located in mesostasis areas and are associated with late-stage crystallization features (Greenwood et al., 2000b). Greenwood et al. (2000b) suggest these events occurred shortly after emplacement of the meteorite protolith (~ 1.3 Gya — Nakamura et al., 1982) and predated the formation of low temperature weathering products (iddingsite and sulfate) (~ 650 and 700 Ma — Swindle and Olson, 2004).

The data presented here are largely consistent with these suggestions, and confirm nonzero $\Delta^{33}\text{S}$ for sulfide

from Nakhla both as the acid volatile fraction (assumed to be monosulfide) and the Cr-reducible fraction (assumed to be pyrite). We suggest that this provides strong evidence in support of the model and assertions of Greenwood et al. (2000b) that sulfide minerals in Nakhla carry the signature of an (atmospheric) soil sulfur component and that the sulfur cycle at ~ 1.3 Gya carried this signal. This also lends support to similar assertions for ALH 84001 made by Shearer et al. (1996) and Greenwood et al. (2000b) for sulfides very early in Martian history, (~ 3.9 Ga (Borg et al., 1999; Bogard and Garrison, 1999; Terada et al., 2003).

Tosca and McLennan (2006) describe a precipitation sequence for salt assemblages in Nakhla that initiates with precipitation of Fe carbonate, and is followed by precipitation of sulfates and ultimately halides. The different $\Delta^{33}\text{S}$ of sulfate reported in this study (-1.25%) compared to that reported previously (-0.302% : Farquhar et al., 2000c) indicates that the sulfate in Nakhla was not well-mixed. While these analyses were undertaken on two fragments of Nakhla, and extracted using two different techniques (extraction of water soluble sulfate by Farquhar et al. (2000c) and extraction of total sulfate here), this difference is significant from the standpoint of analytical uncertainties (the values differ by more than 10σ). The statistically significant difference in the $\Delta^{33}\text{S}$ values for Nakhla sulfide and total sulfate reported here, as well as for water soluble sulfate reported in Farquhar et al. (2000c), provides evidence that sulfide and sulfate in Nakhla formed in more than one event and may have spanned a significant interval in the history of the meteorite target rocks and provides a rationale for future studies that seek to document this signal in the sulfate present at the Martian surface.

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