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Sulfur isotopic compositions of individual sulfides in Martian meteorites ALH84001 and Nakhla: implications for crust-regolith exchange on Mars

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Abstract

Atmospheric chemical reactions on Mars have been invoked to explain non-mass-dependent Δ^{33} S anomalies (Δ^{33} S = δ^{33} S-0.516 δ^{34} S) reported from bulk analyses of Martian meteorites. To explore this signature in detail, a new ion microprobe multi-collector technique was developed to obtain precise in situ ³²S, ³³S and ³⁴S measurements of individual sulfide grains from Martian meteorites ALH84001 (>4.0 Ga) and Nakhla (1.3 Ga). This technique permits high-precision simultaneous measurement of multiple isotopes to uniquely evaluate Δ^{33} S at the grain scale (<30 µm). Our data reveal resolvable non-mass-dependent $\Delta^{33}S$ anomalies in two separate ALH84001 pyrite grains ($\Delta^{33}S$ = $-0.74 \pm 0.39\%$ and $-0.51 \pm 0.38\%$, 2σ ; none were detectable in Nakhla pyrrhotite (total range in $\Delta^{33}S = -0.4 \pm$ 0.5% to $-0.07 \pm 0.5\%$, 2σ). Our results might reflect a difference in how these meteorites exchanged sulfur with the Martian regolith and/or differences in their sources (atmospheric versus meteoritic) of anomalous sulfur. Nebular heterogeneities in sulfur isotope composition are indicated by Δ^{33} S anomalies preserved in, for example, the ureilites. The Δ^{33} S anomalies in ALH84001 pyrite could suggest that early (pre-4 Ga) additions of a meteoritic component carried isotopically anomalous sulfur to the Martian regolith, and was stored there as seen in the detection of Δ^{33} S anomalies from bulk measurements of Nakhla. Therefore, meteoritic contributions should also be considered in addition to atmospheric effects when explaining the large non-mass-dependent anomalies seen in Martian meteorites. These studies provide insight into how hydrothermal systems have facilitated exchange between volatile reservoirs on Mars, a planet that lacks efficient crustal recycling mechanisms and preserves ancient (and anomalous) $\Delta^{33}S$ signatures. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: sulfur; ALH84001; Nakhla Meteorite; Mars; regolith; isotope ratios; ion probe

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Table	1										
Sulfur	isotopic	compositions	of s	standard	minerals	measured	by	ion	microprobe	multi-co	llector

Sample	$\delta^{34}S^a_{CDT}$	$2\sigma \operatorname{error}^{\mathrm{b}}$	$\delta^{33}S_{CDT}^{c}$	$2\sigma \operatorname{error}^{\mathrm{b}}$	$\Delta^{33}S^d$	2σ error	
	(‰)		(‰)		(‰)		
Ralmat nyrite							
Ball22	15.67	0.02	7 91	0.08	-0.17	0.08	
Ball23	14 73	0.02	7.56	0.08	-0.03	0.09	
Bal124	14.85	0.03	7.62	0.07	-0.04	0.07	
Ball26	15.16	0.02	7 72	0.10	-0.09	0.10	
Ball27	15.05	0.02	7.66	0.09	-0.10	0.09	
Ball28	15.09	0.04	7.81	0.06	0.03	0.07	
Bal129	15.12	0.02	7 80	0.09	0.01	0.09	
Bal21	14 88	0.02	7.58	0.09	-0.09	0.10	
Bal22	15.05	0.05	7.65	0.09	-0.11	0.10	
Bal23	15 19	0.04	7.82	0.09	-0.01	0.09	
Bal1210	14 14	0.09	7 49	0.11	0.21	0.14	
Bal1211	16.43	0.07	8 54	0.07	0.07	0.10	
Bal1212	14 86	0.08	7 69	0.08	0.04	0.11	
Bal1213	15.13	0.07	7.83	0.08	0.03	0.11	
Ball214	14.86	0.06	7.62	0.09	-0.04	0.11	
Bal1215	14.92	0.06	7 78	0.09	0.09	0.10	
Bal1216	14.18	0.08	7 39	0.11	0.08	0.13	
Bal1217	14 69	0.00	7 74	0.07	0.00	0.10	
Bal24	15 31	0.09	8.04	0.06	0.14	0.11	
Bal25	16.15	0.05	8 32	0.06	-0.01	0.08	
Mean	15.07	0.05	7 78	0.00	0.01	0.00	
Standard deviation	0.54		0.27		0.10		
True ^e	15.1		0.27		0.10		
Cañon Diablo troilite	15.1						
CDT1	-0.06	0.04	-0.16	0.12	-0.12	0.13	
CDT2	-0.18	0.04	-0.27	0.12	-0.12	0.15	
CDT3	0.53	0.04	0.23	0.15	-0.04	0.16	
CDT4	-0.58	0.05	-0.26	0.15	0.04	0.16	
CDT5	0.16	0.03	-0.06	0.11	-0.15	0.11	
CDT6	0.14	0.03	0.00	0.15	-0.07	0.16	
Mean	0.00	0.0.	-0.09	0.110	-0.09	0110	
Standard deviation	0.37		0.19		0.08		
123 Pyrite	0107		0117		0.00		
12311	0.89	0.03	0.56	0.09	0.10	0.09	
12312	0.61	0.02	0.35	0.11	0.04	0.11	
12313	1.64	0.02	0.84	0.10	-0.01	0.10	
12314	1.36	0.03	0.82	0.09	0.13	0.09	
12315	2.36	0.05	1.27	0.06	0.05	0.08	
12316	1.72	0.05	1.11	0.08	0.22	0.10	
12321	0.36	0.03	0.22	0.07	0.04	0.07	
12322	1.22	0.03	0.62	0.08	-0.01	0.09	
12317	2.11	0.08	1.17	0.07	0.08	0.11	
12318	2.42	0.05	1.32	0.08	0.07	0.09	
12319	1.78	0.05	1.11	0.06	0.19	0.08	
123110	1.24	0.05	0.81	0.09	0.17	0.11	
Mean	1.48		0.85		0.09		
Standard deviation	0.66		0.36		0.07		
True ^e	1.41						
Anderson pvrrhotite							
And11	1.98	0.03	0.89	0.16	-0.13	0.16	
And12	2.11	0.04	1.03	0.11	-0.06	0.12	
And13	2.37	0.04	1.05	0.09	-0.17	0.10	

Sample	$\delta^{34}S^a_{CDT}$	2σ errorb	$\delta^{33}S_{CDT}^{c}$	$2\sigma \operatorname{error}^{\mathrm{b}}$	$\Delta^{33}S^d$	2σ error
I	(‰)		(‰)		(‰)	
And14	1.19	0.14	0.38	0.16	-0.23	0.22
And15	1.96	0.03	0.98	0.09	-0.03	0.10
And221	0.29	0.04	0.04	0.11	-0.11	0.11
And212	0.17	0.03	0.07	0.07	-0.18	0.11
And16	1.45	0.04	0.70	0.12	-0.04	0.12
And17	1.44	0.03	0.61	0.11	-0.13	0.11
And18	1.26	0.07	0.55	0.08	-0.10	0.11
And19	1.19	0.06	0.57	0.06	-0.04	0.08
Mean	1.40		0.63		-0.10	
Standard deviation	0.70		0.36		0.07	
True ^e	1.4					

Table 1 (continued)

 ${}^{a}\delta^{34}S = 1000(({}^{34}S/{}^{32}S)_{sample}/({}^{34}S/{}^{32}S)_{standard} - 1)$. All values use the accepted reference ratio of Cañon Diablo Troilite (${}^{32}S/{}^{34}S = 22.220$; [16]) and are corrected for instrumental mass bias (see text).

^bErrors are from counting statistics, and do not include uncertainty in the composition of the standard or uncertainty in instrumental mass bias.

^cAll values use the $({}^{33}S/{}^{32}S)_{CDT}$ determined in this study (7.958×10⁻³). This value was determined by the intersection of the terrestrial fractionation line (TF) on a 3-isotope plot and the accepted value of $({}^{34}S/{}^{32}S)_{CDT}$. ${}^{d}\Delta^{33}S = \delta^{33}S + 0.516\delta^{34}S$.

^eThe actual δ^{34} S value measured by conventional mass spectrometry of standard grain splits. CDT is defined as δ^{34} S = 0 ‰.

1. Introduction

Sulfur isotopes (³²S, ³³S, ³⁴S and ³⁶S) are important tracers for igneous, hydrothermal and biological processes on Earth and in the solar system. Sulfur is abundant on the Martian surface [1,2] and the isotope composition of sulfur has been used as a biomarker in ancient terrestrial sediments [3]. Some fundamental questions regarding Mars, such as when and how the Martian 'soil' formed, the fate of an early atmosphere and if Mars has ever had incipient life, could be addressed by exploring the sulfur isotope composition of Martian rocks. Values of $\delta^{34}S$ ($\delta^{34}S$ % = $\{[(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{standard}]-1\}\times 1000)$ for sulfur-containing minerals generally exhibit a small range centered around 0% for terrestrial igneous $(0 \pm 5\%)$ and hydrothermal $(0 \pm 10\%)$ processes [3]. In addition, bacterial reduction of sulfate has been implicated for the over 150% variation in δ^{34} S of sulfates and sulfides found in the terrestrial rock record [3]. Claims that the ancient Martian meteorite ALH84001 preserves both microfossil and chemical evidence of Martian biota [4], as well as similar claims for the (younger) Martian meteorite Nakhla [5], compel further study and development of potential iso-

topic biomarkers. Non-mass-dependent chemical reactions involving UV photolysis of volcanogenic SO₂ and H₂S in the Martian atmosphere have been used to explain the anomalous Δ^{33} S values reported for some Martian meteorites (nakhlites and shergottites) [6]. Few mechanisms are known in nature that can fractionate isotopes independently of mass. Only atmospheric, or nuclear processes (as recorded in meteorites), appear as likely agents for producing both Δ^{33} S and Δ^{17} O anomalies. Laboratory photolysis experiments of SO₂ used to simulate atmospheric effects produce large fractionations in δ^{34} S rivaling that seen in the bacterial reduction of sulfate [6], which calls into question the utility of δ^{34} S alone as an isotopic biomarker. The majority of meteoritic materials analyzed for the minor isotopes ³³S and ³⁶S indicate that inhomogeneities in sulfur isotope compositions that could be related to stellar nucleosynthesis, spallation reactions of Fe, or gas-phase (ion-molecule) reactions, were mostly homogenized in the early solar system [7-9]. However, Δ^{33} S anomalies have been found in bulk ureilites (a class of igneous meteorites) [10], in organic compounds from carbonaceous chondrites [11] and in an acid-resistant residue of the Allende meteorite ('phase Q') [12]. This raises the possibility that infalling matter during late accretion carried heterogeneous distributions of the sulfur isotopes and imparted that signal into early planetary crusts, including that of Mars. Thus, exploration of the sulfur isotope geochemistry of Martian meteorites can provide unique information about early atmospheric, and possibly accretionary processes on Mars.

Previous studies of sulfur isotope compositions of the Martian meteorites (shergottites, nakhlites, Chassigny) have demonstrated a relatively large range of values ($\delta^{34}S = -6.1$ to +8.0%) compared to other meteorite classes. The $\delta^{34}S$ values of pyrrhotite (Fe_{1-x}S) grains in shergottites are similar to those measured in fresh ocean-floor basalts ($\delta^{34}S \sim 0\%$), suggesting that the Martian mantle resembles Earth's mantle and most meteorites in sulfur isotopic composition [13]. The $\delta^{34}S$ values of pyrrhotite grains in nakhlites are variable, and range from -6.1 to +4.9%. This varia-

tion has been explained by modification of the original sulfur signature by high-temperature (>200°C) hydrothermal fluids in communication with the Martian regolith [14]. The δ^{34} S values previously measured in ALH84001 pyrite (FeS₂) grains have a small, yet positive δ^{34} S range of +2.0 to +8.0% interpreted to indicate interaction between a mantle sulfur reservoir ($\sim 0\%$) and an isotopically heavier crustal reservoir (>0%) on Mars [13,15]. Pyrite in ALH84001 appears to be secondary in nature and is primarily found in impact-produced granular bands associated with secondary features such as carbonates. Here we present ³²S, ³³S and ³⁴S measurements on individual sulfide grains identified in petrographic thin sections prepared from ALH84001 and Nakhla. The new in situ ion microprobe multi-collector technique described here has the ability to resolve Δ^{33} S anomalies at the sub-grain scale (<30 µm), thus facilitating exploration of the magnitude and



Fig. 1. δ^{34} S versus Δ^{33} S plot of standard sulfide minerals measured by ion microprobe multi-collector. The total range found in Δ^{33} S is -0.23 to +0.22%.

 Table 2

 Sulfur isotopic compositions of pyrite in ALH84001 and pyrrhotite in Nakhla

Sample-spot	$\delta^{34}S^a_{CDT}$	$2\sigma \operatorname{error^{b}}$	$\delta^{33}S^c_{CDT}$	2σ error	$\Delta^{33} \mathbf{S}^{d}$	$2\sigma \operatorname{error}^{e}$
ALH84001						
ALHpy1_1	3.88	0.22	1.98	0.28	-0.02	0.36
ALHpy1_2	4.19	0.22	2.33	0.26	0.17	0.34
ALHpy2	3.00	0.20	1.36	0.20	-0.19	0.28
ALHpy4	-0.56	0.26	0.03	0.20	0.32	0.33
ALHpy5	3.60	0.22	1.81	0.30	-0.05	0.38
ALHpy9	-0.27	0.22	-0.38	0.34	-0.24	0.41
ALHpy10	2.16	0.22	0.60	0.30	-0.51	0.38
ALHpy11	3.45	0.20	1.55	0.20	-0.23	0.29
ALHpy12	3.95	0.22	1.88	0.18	-0.16	0.29
ALHpy14	0.26	0.24	-0.12	0.16	-0.26	0.29
ALHpy15	-0.05	0.24	-0.77	0.32	-0.74	0.39
ALHpy17_1	-9.07	0.24	-4.65	0.34	0.04	0.42
ALHpy17_2	-9.69	0.22	-5.04	0.40	-0.04	0.47
ALHpy17_3	-4.60	0.30	-2.16	1.06	0.21	1.10
ALHpy17b	-9.44	0.38	-5.61	1.24	-0.74	1.29
Nakhla						
Nakpo2	0.08	0.42	-0.38	0.22	-0.42	0.49
Nakpo13	-4.49	0.44	-2.60	0.30	-0.28	0.53
Nakpo14	-3.17	0.44	-1.73	0.32	-0.09	0.55
Nakpo16	1.38	0.44	0.64	0.24	-0.07	0.49
Nakpo17	-2.85	0.44	-1.55	0.24	-0.09	0.50
Nakpo18	-1.57	0.42	-0.91	0.22	-0.10	0.48

 ${}^{a}\delta^{34}S = 1000(({}^{34}S/{}^{32}S)_{sample}/({}^{34}S/{}^{32}S)_{standard} - 1)$. All values use the accepted reference ratio of Cañon Diablo Troilite (${}^{32}S/{}^{34}S = 22.220$; [16]) and are corrected for instrumental mass bias (see text).

^bErrors are from counting statistics and include uncertainty in reproducibility of the standard, but do not include uncertainty in the composition of the standard or uncertainty in instrumental mass bias.

^cAll values use the $({}^{33}S)_{CDT}$ determined in this study (7.958×10⁻³). This value was determined by the intersection of the terrestrial fractionation line (TF) on a 3-isotope plot and the accepted value of $({}^{34}S)_{CDT}^{32}S)_{CDT}$.

 ${}^{\mathrm{d}}\Delta^{33}\mathrm{S} = \delta^{33}\mathrm{S} + 0.516\delta^{34}\mathrm{S}.$

 eError is the propagated $\delta^{34}S$ and $\delta^{33}S$ errors.

distribution of sulfur isotope anomalies in natural samples.

2. Materials and methods

Prior to ion microprobe analysis, sulfides in ALH84001 and Nakhla were characterized by reflected light mapping of thin sections and subsequent analysis by electron microprobe with the Cameca CAMEBAX at UCLA. Sulfur isotopic measurements were carried out using the UCLA Cameca ims 1270 high-resolution ion microprobe in multi-collector detector mode by sputtering the sample with a ~2.5 nA, 20 keV Cs⁺ primary beam focussed to a ~25 μ m diameter spot. Analyses comprised 15 cycles of 10 s measurements;

including spot to spot setup time, total time per analyses was ~ 5 min. Negative secondary ions with initial energies in the range 0-25 eV were analyzed and a normal-incidence electron flood gun was used to neutralize positive charge buildup in the analysis area. Faraday cup collectors were used to detect the ${}^{32}S^-$, ${}^{33}S^-$ and ${}^{34}S^-$ beams which were amplified by Finnegan electrometers housed in a temperature-controlled evacuated chamber. Secondary beam currents are quoted here in counts per second (Hz). A mass resolving power of 4000 was sufficient to maintain the ${}^{32}S^{1}H^{-}$ contribution to the ${}^{33}S^{-}$ peak to <10 ppm. Measurements of the detection system baseline were made throughout the analysis session and were reproducible to ~1200 Hz (2σ , n = 12) for the ${}^{33}S^-$ and ${}^{34}S^-$ detectors. The integration



Fig. 2. δ^{34} S versus δ^{33} S plot of ALH84001 and Nakhla data. The 0.516 slope line is the best fit to our data for terrestrial sulfides and Cañon Diablo Troilite. Uncertainties are reported at the 2σ level. Two ALH84001 sulfides exhibit large non-mass-dependent anomalies (Δ^{33} S) of -0.74 ± 0.39 and $-0.51\pm0.38\%$. The inset also shows a subparallel line of slope +0.516 drawn through these two anomalous ALH84001 pyrite grains.

time for each baseline measurement was 150 s. Count rates on ${}^{33}S^-$ were in the range of 0.25–8 MHz, all except two of the ALH84001 analyses exceeded 1 MHz. Instrumental drift was not apparent over the 27 h of continuous measurements and, after baseline correction, no significant correlation between $\Delta^{33}S$ and count rate was observed. Instrumental mass fractionation was corrected for by means of measurements made on standards of the same sulfide phases as the unknowns. The ${}^{34}S/{}^{32}S$ instrumental mass fractionations measured were: pyrite, -12.7%; pyrrhotite, -18.0%; and troilite (FeS; Cañon Diablo, CDT), -20.0%. The terrestrial mass fractiona-

tion (TF) line on a 3-isotope plot was determined by 69 separate analyses of these and other sulfide standards (Table 1; only sulfide standards relevant to this study are listed). The measured ³³S/³²S ratios were corrected for instrumental mass fractionation assuming an exponential mass fractionation law. The ³³S/³²S of CDT was defined by the intersection of the experimentally determined TF line and the accepted value of $({}^{34}S/{}^{32}S)_{CDT} = 4.50045 \times 10^{-2}$ [16]. We obtained $({}^{33}\text{S}/{}^{32}\text{S})_{\text{CDT}} = 7.958 \times 10^{-3}$. Our reported $\delta^{34}\text{S}$ and δ^{33} S data use these reference ratios. The slope of our TF line on a plot of $\delta^{33}S$ against $\delta^{34}S$ is 0.516, therefore we use this to define $\Delta^{33}S =$ δ^{33} S-0.516• δ^{34} S. The entire range in Δ^{33} S found for our terrestrial sulfide standards was -0.23 to +0.22‰ (Fig. 1).

3. Results

We measured the Δ^{33} S of six pyrrhotite grains in Nakhla and 12 pyrite grains in ALH84001 (Table 2 and Fig. 2). The δ^{34} S range observed in this study for Nakhla, $-4.5 \pm 0.4\%$ to $+1.4 \pm 0.4\%$ (2σ), extends the previously determined range for this meteorite to slightly lighter values. Uncertainties in sulfur isotope data are reported at the 2σ level. The Δ^{33} S values for Nakhla do not appear fractionated (cf. [6]); all six grains were slightly negative, although they are not resolvable from average solar system sulfur (i.e. Δ^{33} S = 0‰) by the techniques outlined here.

We found that two of the 12 pyrites analyzed in ALH84001 show clearly resolvable negative Δ^{33} S anomalies: -0.74 ± 0.39 and -0.51 ± 0.38 % (Ta-



Fig. 3. $\delta^{34}S$ versus $\Delta^{33}S$ plot of ALH84001 and Nakhla data.



Fig. 4. Mixed secondary and backscattered electron images of (a) grain ALHpy11, (b) grain ALHpy10, (c) grain ALHpy1 and (d) ALHpy15. The ion microprobe pits are $18 \times 25 \ \mu m$ in size. Scale bars for (a), (b) and (c) are 25 \ \mu m. Pyrite grains (Pyt) are outlined in black. The textural relationships of these grains to orthopyroxene (Opx), chromite (Chr), and plagioclase-composition glass (Pg) are shown. ALHpy10 and ALHpy15 have Δ^{33} S anomalies; ALHpy1 and ALHpy11 are isotopically normal.

ble 2 and Figs. 2 and 3). These two sulfides are otherwise indistinguishable from other grains analyzed. Variable alteration at low water/rock ratios, as has been suggested to explain variable δ^{34} S values in the nakhlites [14], could have been an important process in ALH84001. Sulfides in ALH84001 commonly occur in close association with chromite; it is possible that the sulfides are replacing chromite, although unambiguous evidence is lacking. There is also no spatial association of these sulfides apparent in the plane of the thin-section that would link them to each other. Electron images of the two ALH84001 sulfides with resolvable Δ^{33} S anomalies (grains ALHpy10 and ALHpy15) as well as two isotopically normal sulfides (ALHpy1 and ALHpy11) are shown in Fig. 4. The ion microprobe spots overlap onto pyroxene and chromite for all four of these grains (ALHpy1 was analyzed twice). Unfortunately, the two anomalous sulfides were not subjected to repeat analysis; an instantaneous data reduction procedure for Δ^{33} S does not exist, so that we were unaware at the time of analysis that these two grains were isotopically anomalous in Δ^{33} S.



Fig. 5. Backscatter (a) and secondary (b) electron images, and Fe K α (c) and S K α (d) X-ray maps of pyrite grains ALHpy17 and ALHpy17b and their complex textural relationship to carbonate (Cb), whitlockite (Wh), chromite (Chr) and plagioclase-composition glass (Pg) are shown. These two pyrite grains have the lightest δ^{34} S values so far measured in an extraterrestrial material. Pyrite grain ALHpy17 is located in a crack in chromite, and ALHpy17b is located at a carbonate and whitlockite contact (denoted by the arrowhead in (d)). Scale bars are 25 µm.

Our δ^{34} S values measured in ALH84001 pyrites range from -9.69 ± 0.22 to $+4.19 \pm 0.22\%$ and extend the previously determined range (+2 to +8%; [13,15]) to much lower values. These are the lightest δ^{34} S values yet described for extraterrestrial materials (Table 2). The total range in δ^{34} S for ALH84001 is now -9.7 to +8.0%. This new ion microprobe technique allows us to uniquely evaluate sulfide grains carrying Δ^{33} S anomalies in their petrographic context and to detect intragranular heterogeneities. During the analytical session, it was realized that ALHpy17 was significantly lighter than the other ALH84001 sulfides analyzed, and we repeated the measurement 4 h later (ALHpy17_2). Subsequently, the ALH84001 sample was removed from the analysis chamber of the ion microprobe so that other samples could be investigated. Seven h after ALH-py17_2, the same ALH84001 thin section was returned to the analysis chamber and a third measurement was taken of this same grain (ALH-py17_3). Thus, grain ALHpy17 was analyzed

three times (δ^{34} S = -9.07 ± 0.24, -9.69 ± 0.22, and -4.60 ± 0.30 %); the third analysis is heavier by $\sim 5\%$, suggesting that this grain is zoned roughly normal to the plane of the thin section. A second, smaller, sulfide (ALHpy17b) was found nearby and analyzed after ALHpy17_3 and gave $\delta^{34}S = -9.44 \pm 0.38 \%$. Curiously, these two pyrite grains with the lightest $\delta^{34}S$ values in ALH84001 are intimately associated with carbonate, and are partially enclosed by it (Fig. 5). An earlier study reported a far less precise, but consistently heavier δ^{34} S value of $+6.0 \pm 7.2\%$ for Fe-sulfide rims in carbonate globules from ALH84001 [13]. This suggests that the association of isotopically light sulfide and carbonate may be coincidental to this sample.

4. Discussion

4.1. Nakhla

We interpret the lack of a resolvable $\Delta^{33}S$ anomaly in the six pyrrhotites analyzed in this study as indicating a strongly heterogeneous distribution of sulfur in Nakhla. Large pyrrhotite grains associated with mesostases regions represent the major sulfur store in Nakhla. A smaller quantity of sulfur is associated with a later alteration event on Mars. Olivine has cracks filled with what has been termed 'iddingsite', but is actually a mixture of ferroan clays and oxides, with sulfur probably in the form of sulfate but also possibly in clays and oxides [17,18]. Iddingsite-rich samples have been dated to 671 ± 91 Ma [19], significantly vounger than the crystallization age of Nakhla at ca. 1.3 Ga [20]. We propose that the sulfur associated with the iddingsite is derived from the regolith and carries a signal of non-mass-dependent fractionated sulfur. Therefore, a small quantity of strongly fractionated regolith sulfur associated with the iddingsite in Nakhla could explain the heterogeneous Δ^{33} S distribution reported in a previous whole-rock study [6].

4.2. Origin of $\Delta^{33}S$ anomaly in ALH84001

The Δ^{33} S signature, if established when the car-

bonates formed ~ 4.0 Ga [21], coupled with prior observations of elevated Δ^{17} O in ALH84001 carbonate [22], suggests that the pre-4 Ga Martian regolith already had a significant non-mass-dependent component of sulfur and oxygen isotopes. This non-mass-dependent signature was transferred to ALH84001. Periodic inputs of volcanic SO₂ and H₂S, photolysis of these species and their short lifetimes in the Martian atmosphere [23], and the absence of effective crustal recycling, would have favored the production of isotopically heterogeneous reservoirs in the crust of Mars [6]. Alternatively, the environment of early Mars was characterized by high rates of volcanism, a denser atmosphere, and a faint young Sun which would mitigate against the production and preservation of atmospherically derived isotopic anomalies. Accretion of a late meteoritic (or cometary?) veneer on early (>4 Ga)Mars, similar to what could have occurred on early Earth, should therefore be taken into consideration as a mechanism for creating large isotopically distinct reservoirs of sulfur and oxygen in the Martian crust. The isotopic compositions of comets are poorly known, but variable oxygen isotopes in meteorites [24], as well as small, but significant variations in sulfur isotopes of some meteorites and meteoritic components [10-12] suggest that heterogeneous accretion is a viable mechanism for generating non-mass-dependent isotopic anomalies in the Martian regolith. $\Delta^{33}S$ anomalies in a class of igneous meteorites (ureilites) [10] strongly suggest that nebular heterogeneities in sulfur were present, and preserved, late into the accretionary epoch of the planets.

4.3. Large range of Δ ³³S and δ ³⁴S in ALH84001

Low-temperature aqueous fluids ($< 100^{\circ}$ C), invoked for the iddingsite alteration in the nakhlites [18], does not explain the wide range of δ^{34} S values in ALH84001 due to the very long timescales necessary for sulfide sulfur isotope exchange below 200°C [14,25]. Alteration by hydrothermal fluids at low fluid/rock ratios and above 200°C has been used to explain the δ^{34} S systematics of the nakhlites [14]. A likely scenario for this process would be at subsolidus temperatures during initial cooling of the nakhlite parent magma. While this can explain the $\delta^{34}S$ of the nakhlites, this model must be modified significantly to explain the extended δ^{34} S range and anomalous Δ^{33} S in ALH84001. Pyrite is a secondary mineral in ALH84001; it occurs almost exclusively within the impact-produced granular bands of the meteorite and is probably contemporaneous with carbonate formation. Pyrite is unstable above 742°C at 1 atm [26] arguing against a magmatic origin. The ultramafic lithology of ALH84001 would necessitate either pyrrhotite or monosulfide solid solutions [26] rather than pyrite. The extreme zoning of major elements [27] and oxygen isotopes [28] in ALH84001 carbonates suggest that a high-temperature hydrothermal system ($> 200^{\circ}$ C) affecting this meteorite must have been sufficiently shortlived to still preserve micrometer-scale chemical variations. The large range of δ^{34} S values and heterogeneous Δ^{33} S distribution in ALH84001 reported here are consistent with a short-lived, impact-driven hydrothermal system, wherein the majority of sulfur was derived from a regolith source as opposed to a magmatic source.

The large range of δ^{34} S values found in ALH84001 is inconsistent with deposition of carbonates as flood evaporites [29,30]. The terrestrial oceans have mixing times of $\sim 10^3$ yr [31]. and large reservoirs of surface water on Mars would have quickly become isotopically homogeneous. The Δ^{33} S anomalies found in two of 12 ALH84001 pyrite grains, coupled with the reported elevated Δ^{17} O of ALH84001 carbonate [22], implies non-mass-dependent isotopic anomalies were present in the Martian crust prior to 4.0 Ga. The ubiquity of non-mass-dependent isotope anomalies of oxygen [32-34] and sulfur [6] in the younger Martian meteorites suggests that the regolith has continued to maintain anomalous isotopic signatures of sulfur and oxygen for >4 billion years. This observation is consistent with the paucity of effective crustal recycling mechanisms on Mars [35].

Exchange of volatile components between regolith and crust on early Mars may have been dominated by impact-driven hydrothermal systems; after the late heavy bombardment (~ 3.9 Ga) magmatic hydrothermal systems took over as the dominant means of regolith-crust exchange. The lack of a detectable Δ^{33} S anomaly in Nakhla pyrrhotite grains points to a different hydrothermal system from that which affected ALH84001. We propose that a magmatic hydrothermal system is responsible for the sulfur isotope composition of the nakhlites and that ALH84001 was affected by an impact-driven hydrothermal system. These two meteorites may be considered bookend examples of how the regolith and crust of Mars have interacted in the last 4 billion years. If ALH84001 and Nakhla are representative samples, this would imply that regolith-crust exchange occurred more readily on early Mars and is a widespread phenomenon for the crust of the cratered highlands of the planet.

4. Conclusions

The presence of a $\Delta^{33}S$ anomaly in two ALH84001 pyrites has implications for the role that hydrothermal systems have had in facilitating exchange between regolith and crustal reservoirs of volatiles such as sulfur, and may have implications for the evolution of the Martian atmosphere. The present study shows that non-mass-dependent fractionated sulfur was present on early Mars (>4.0 Ga) and that this isotopic signature was transferred to the crust. We propose that the addition of a late meteoritic veneer on Mars should be considered, in addition to atmospheric chemistry, in explaining the isotopic anomalies present in Martian meteorites. Low-temperature (<200°C) inorganic isotopic fractionation of sulfur is inadequate to explain the range in δ^{34} S values reported here. The lack of a resolvable Δ^{33} S anomaly in Nakhla pyrrhotite can be reconciled with reported heterogeneous whole-rock $\Delta^{33}S$ anomalies in Nakhla if the $\Delta^{33}S$ anomaly is present only in sulfur associated with the younger iddingsite alteration. The ALH84001 sulfur isotopic results are consistent with a short-lived impact-driven hydrothermal system, an environment that may have been commonplace early in Martian history. Nakhla, being younger, experienced a magmatic hydrothermal system. The ubiquity of oxygen and sulfur isotopic anomalies in the

younger Martian meteorites [6,32–34] points to a Martian regolith that has remained isotopically distinct from the Martian mantle which is consistent with the absence of effective crustal recycling (i.e. widespread and long-lived plate tectonics) on Mars [35]. Cosmic-ray exposure ages of ALH84001, the nakhlites (and Chassigny), and the shergottites are different, meaning that these meteorites represent different sampling locations of the Martian crust [36]. The finding of Δ^{33} S anomalies at three sites in three groups of Martian meteorites would therefore suggest that sulfur affected by non-mass-dependent fractionations is commonplace on Mars.

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