



Sulfide isotopic compositions in shergottites and ALH84001, and possible implications for life on Mars

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Abstract—The shergottite and ALH84001 meteorites hold keys for understanding geologic and possibly biologic processes on Mars. Recently, it has been proposed that carbonates in ALH84001, and the Fe-sulfides they contain, are products of extraterrestrial biogenic activity (McKay et al., 1996). Here we report ion microprobe analyses of sulfides in shergottites and ALH84001. The sulfur isotope ratios of igneous pyrrhotites in shergottites (mean $\delta^{34}\text{S}_{\text{CDT}}$: Shergotty = -0.4‰ , Zagami = $+2.7\text{‰}$, EETA79001A = -1.9‰ , EETA79001B = -1.7‰ , LEW88516 = -1.9‰ , QUE94201 = $+0.8\text{‰}$) are similar to those of terrestrial ocean-floor basalts, suggesting that the sulfur isotopic composition of the Martian mantle may be similar to that of the mantle of the Earth. The sulfur isotopic systematics of ALH84001 sulfides are distinct from the shergottites. Measured sulfur isotope ratios of eight pyrite grains ($\delta^{34}\text{S}_{\text{CDT}}$ = $+2.0$ to $+7.3\text{‰}$) in crushed zones confirm previously reported analyses of isotopically heavy sulfides (Shearer et al., 1996) and are indistinguishable from an Fe-sulfide zone within a carbonate globule ($\delta^{34}\text{S}_{\text{CDT}}$ = $+6.0\text{‰}$). Analyses of synthesized, fine-grained mixtures of sulfide, carbonate, and magnetite indicate that the measured sulfur isotope ratio is independent of the presence of carbonate and magnetite in the sputtered volume, confirming the accuracy of the analysis of the fine-grained sulfide in the carbonate globule. Terrestrial biogenic sulfate reduction typically results in light isotopic enrichments. The similarity of $\delta^{34}\text{S}$ values of the sulfides in ALH84001 imply that the Fe-sulfide zones within ALH84001 carbonates are probably not the result of bacterial reduction of sulfate. Copyright © 1997 Elsevier Science Ltd

1. INTRODUCTION

Deciphering the pre-terrestrial history of martian meteorites, and especially ALH84001, has become a matter of great interest. The claim that ALH84001 preserves evidence of former biologic activity on Mars (McKay et al., 1996) makes unraveling the events that have affected this rock particularly important. Specifically, it has been proposed that submicroscopic sulfides and magnetites within rims of carbonate globules in ALH84001 are of biogenic origin, and that the Fe-sulfides in these rims are products of bacterial reduction of sulfate (McKay et al., 1996; C. S. Romanek, pers. commun.). Sulfate-respiring bacteria on Earth are known to cause large sulfur isotopic fractionations (Kemp and Thode, 1968; Nielsen, 1979). Recently reported sulfur isotopic measurements of three pyrite grains in crushed zones of ALH84001 found $\delta^{34}\text{S}$ values ranging from $+4.8$ to $+7.8\text{‰}$ (Shearer et al., 1996). Origin of these pyrites by precipitation from a fluid, and not as a result of organic processes, was proposed. This accords with other studies of the carbonates in this meteorite, which call for precipitation from either a low-temperature fluid (Romanek et al., 1994; Treiman, 1995; Valley et al., 1997a; Kirchvink et al., 1997), or a high-temperature supercritical fluid or vapor (Mittlefehldt, 1994; Harvey and McSween, 1996; Bradley et al., 1996). Here we report sulfur isotopic measurements of presumed biogenic Fe-sulfide within ALH84001 carbonate, eight analyses of pyrite in the crushed zones of the same meteorite, and pyrrhotites previously identified in five shergottites (Shergotty and Zagami, Stolper and McSween, 1979;

EETA79001, Steele and Smith, 1982; QUE94201, McSween et al., 1996; and LEW88516, Harvey et al., 1993).

The shergottites studied are basaltic lithologies, with the exception of LEW88516, which is lherzolitic (Harvey et al., 1993). The sulfide in these meteorites is pyrrhotite ($\text{Fe}_{0.92-0.94}\text{S}$). These meteorites are igneous rocks which have been heavily shock metamorphosed (McSween, 1994), and they differ from ALH84001 in that they lack evidence for abundant secondary mineralization. The sulfides in these rocks are interpreted as being magmatic and not the result of biologic activity; therefore, a record of sulfur isotopic systematics in martian rocks unaffected by either possible sulfate-respiring bacteria or pervasive hydrothermal fluids can be obtained.

ALH84001 is a coarse-grained cataclastic orthopyroxenite consisting of centimeter-sized orthopyroxene with minor maskelynite, augite, chromite, and apatite (Mittlefehldt, 1994). Crushed zones in this meteorite contain abundant carbonates and pyrite. On the basis of textures (Treiman, 1995) and carbon and oxygen isotopic measurements (Romanek et al., 1994; Valley et al., 1997a) of the carbonates, it has been argued that the carbonates formed at temperatures less than 300°C . Evidence cited to support the recent claim that the carbonates formed as a result of low-temperature biogenic activity (McKay et al., 1996) includes: (1) identification of PAHs on fresh fracture surfaces which also contain carbonates, (2) possible biogenic minerals (single domain magnetites and Fe-sulfides), and (3) microparticles within the carbonates which are interpreted as fossilized nanobacteria. In contrast, a high temperature origin for carbon-

ates in ALH84001 is favored by the composition of the carbonates (Mittlefehldt, 1994; Harvey and McSween, 1996), the oxygen isotope study of Leshin et al. (1997), the presence of included magnetite morphologies with growth mechanisms suggesting vapor condensation (Bradley et al., 1996), and textural evidence for shock remobilization of carbonates (Scott et al., 1997).

2. ANALYTICAL METHODS

$^{34}\text{S}/^{32}\text{S}$ ratios of sulfides were measured with the Cameca 4f ion microprobe at Oak Ridge National Laboratory, using a Cs^+ primary beam and monitoring S^- secondary ions with extreme energy filtering of 350 eV (Riciputi, 1996). The normal incidence electron gun was employed to neutralize potential sample charging arising from analysis of fine-grained sulfides contained in an insulating silicate and carbonate matrix. Analytical details are described elsewhere (Riciputi, 1996; Paterson et al., 1997; McSween et al., 1997). Pyrite and pyrrhotite standards were used to correct for instrumental mass bias. Prior to ion microprobe measurement, sulfide elemental compositions were determined by electron microprobe using the Cameca SX-50 at the University of Tennessee, and compositional homogeneity was verified. The overall precision and accuracy for each isotope analysis includes errors arising from counting statistics of each individual analysis, calibration to a known standard, uncertainty in the composition of the standard mineral, and uncertainty in deadtime corrections resulting from variable count rates. In general, the overall precision ranged between ± 0.3 and 0.8% (1σ), although the errors ranged as high as $\pm 1.6\%$ for very small ($< 8 \mu\text{m}$) sulfide grains.

Individual sulfide grains within the carbonate globules from ALH84001 are far smaller than the spatial resolution of the ion microprobe. The single successful analysis of a sulfide-rich zone within a carbonate globule is a composite of many individual grains; use of the electron flood gun and extreme energy filtering allowed stable ion signals to be obtained. This analysis was corrected for minor oxygen dimer interferences on the sulfur peaks (primarily $^{16}\text{O}_2$ on ^{32}S); the correction results in a change of $< 2\%$ in the measured isotope ratio. Due to the low abundance of sulfur ions (resulting in poor counting statistics), this analysis had a much higher error ($\pm 3.4\%$).

There is also some question about instrumental mass bias on analysis of fine-grained material in a matrix of different composition (J. Valley, pers. commun., 1996; 1997). Recent experiments (L. R. Riciputi, unpubl. data) confirm that the instrumental mass bias is controlled only by the minerals which contain the element of interest, and that the presence of other materials in the analyzed area does not change the mass bias. In the present experiments, four pressed pellets containing mixtures of fine-grained ($< 1 \mu\text{m}$) pyrite (5–50 wt%), dolomite (50–95 wt%), and magnetite (0–5 wt%) were analyzed using extreme energy filtering and the electron gun for charge compensation. The instrumental mass bias measured on these four samples was statistically identical ($\pm 1.4\%$; precision of each analysis 1–3%), and matched that measured on 100% pyrite. These results indicate that the analysis of the fine-grained sulfide in the carbonate matrix is accurate within the precision limit imposed by counting statistics.

3. RESULTS

The results of our sulfur isotopic analyses are listed in Table 1. Sulfur isotopic analyses for five shergottites are shown in Fig. 1. The $\delta^{34}\text{S}$ values range from -2.6 to $+3.5\%$. This range of values is similar to reported ranges of sulfides in fresh ocean-floor basalts (-2.3 to $+3.8\%$) (Sakai et al., 1982; Puchelt and Hubberten, 1980; Chaussidon et al., 1989), suggesting that martian mantle $\delta^{34}\text{S}$ values are similar to that of Earth and chondritic meteorites (Paterson et al., 1997; Chaussidon et al., 1989). Significant enrichments of ^{34}S , typically associated with subduction zone volcanism on

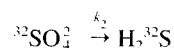
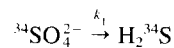
Earth (Ueda and Sakai, 1984), are not seen in these meteorites, consistent with the hypothesis that crustal recycling is not important on Mars (Carr and Wänke, 1992). EETA79001 contains two distinct igneous lithologies, designated lithologies A and B. Sulfur isotopic analyses of sulfides from both lithologies are virtually identical (mean $\delta^{34}\text{S}$ EETA79001A = -1.9% ; EETA79001B = -1.7%). The range of $\delta^{34}\text{S}$ values found in EETA79001A (-2.6 to $+0.2\%$) is similar to the range reported for Kilauea east rift basalts (-2.3 to -0.1% ; Sakai et al., 1982). A $\delta^{34}\text{S}$ = $-0.5 \pm 1.5\%$ reported for bulk rock analysis of Shergotty (Burgess et al., 1989) is the same as the mean value of $-0.4 \pm 0.4\%$ determined on sulfide grains by ion microprobe in this study.

The eight sulfur isotopic analyses of individual pyrite grains in crushed zones of ALH84001 have values of $\delta^{34}\text{S}$ in the range $+2.0$ to $+7.3\%$ (Fig. 2); this extends the range of $\delta^{34}\text{S}$ values that have been previously reported in this meteorite based on three analyses ($+4.8$ to $+7.8\%$; Shearer et al., 1996). The sulfur isotopic composition of a fine-grained sulfide-rich zone in a carbonate of ALH84001 is $+6.0 \pm 3.4\%$ (1σ). Images of the analyzed zone are shown in Fig. 3. We were unable to locate another sulfide-rich zone containing sufficient sulfur for analysis in our samples of ALH84001, preventing acquisition of additional data on the fine-grained sulfides.

4. DISCUSSION

The $\delta^{34}\text{S}$ value for the sulfide-rich zone in the carbonate falls in the range of pyrite grains in the crushed zones of ALH84001. The pyrite grains in the crushed zones are not believed to be biogenic (Gibson et al., 1996); consequently, the finding that the fine-grained sulfide-rich zone in carbonate has the same $\delta^{34}\text{S}$ value as the associated pyrites argues for a related origin by inorganic processes. If the fine-grained sulfide zone was the product of sulfate-reducing bacteria (McKay et al., 1996), a significant enrichment in ^{32}S would be expected. The action of sulfate-reducing bacteria is the main cause for large variations (over 150%) documented in terrestrial $\delta^{34}\text{S}$ values (Kemp and Thode, 1968; Nielsen, 1979).

Kinetic fractionation of sulfur isotopes during unidirectional processes depends on the difference between the two reaction rates



where $k_1 \neq k_2$. Theoretical calculations suggest that $k_1/k_2 \approx 0.978$ at 25°C (Harrison and Thode, 1957); this predicts an isotopic fractionation of $\approx -22\%$ during the production of sulfide from sulfate. The extent of reaction will ultimately depend on the supply of reactant. An open system implies an infinite concentration of reactant; in a closed system, the reactant reservoir is limited. The ratio k_1/k_2 is appropriate for describing sulfur isotopic fractionation in an open system. In a closed system, the concentration of reactant will diminish as the reaction proceeds; preferential utilization of the

Table 1. Sulfur isotopic compositions of sulfides in martian meteorites.

ALH84001,85 [†]		Shergotty (USNM321-2)*		Zagami (UNM 993)*		EETA79001,317A*	
$\delta^{33}\text{SCDT}$ (‰)	1 σ Error [§] (‰)	$\delta^{33}\text{SCDT}$ (‰)	1 σ Error [§] (‰)	$\delta^{33}\text{SCDT}$ (‰)	1 σ Error [§] (‰)	$\delta^{33}\text{SCDT}$ (‰)	1 σ Error [§] (‰)
+2.0	1.6	-0.5	0.8	+2.4	0.7	-2.4	0.5
+5.0	1.2	-1.1	0.7	+2.8	0.7	-2.6	0.3
+4.5	1.4	0.0	0.7	+3.1	0.9	+0.2	0.4
+6.2	0.6	+0.2	0.8	+2.8	0.6	-2.2	0.4
+7.3	0.6	-0.5	0.4	+3.5	0.7	-2.3	0.4
+6.3	1.1			+1.4	0.7		
+3.7	0.9						
+4.2	0.7						
+6.0 ^{‡,*}	3.4						
		QUE94201,5*		LEW88516,22*		EETA79001,318B*	
$\delta^{33}\text{SCDT}$ (‰)	1 σ Error [§] (‰)	$\delta^{33}\text{SCDT}$ (‰)	1 σ Error [§] (‰)	$\delta^{33}\text{SCDT}$ (‰)	1 σ Error [§] (‰)	$\delta^{33}\text{SCDT}$ (‰)	1 σ Error [§] (‰)
		+0.3	0.6	-2.0	0.6	-1.9 [°]	0.3
		+1.1	0.6	-0.9	0.6	-0.8 [°]	0.4
		+0.1	0.6	-2.1	0.6	-1.5	0.4
		+1.5 [°]	0.6	-1.3 [°]	0.6	-1.9	0.4
		+1.2 [°]	0.6	-2.3 [°]	0.6	-2.6	0.6
				-2.9 [°]	0.6		

Notes: $\delta^{34}\text{SCDT}$: Results reported relative to Cañon Diablo Troilite.

* Sulfide phase is pyrrhotite.

[†] Sulfide phase is pyrite, except for the Fe-sulfide rim in carbonate (see below).

[‡] Multiple analyses of an individual grain.

[§] McKay et al. (1996) identified the sulfide within carbonate globule rims as 4C monoclinic pyrrhotite, based on its basal spacing of 0.57 nm corresponding to the (111) reflection. According to Morimoto et al. (1975), the basal spacing for this phase is 0.53 nm, corresponding to the (002) reflection, and the (111) spacing is 0.47 nm. Most Fe-sulfides (Fe/S = 0.9–1) have a strong 0.57–0.59 lattice spacing, which suggests that this is among the least diagnostic spacings. Moreover, their quoted Fe/S ratios of 0.92–0.97 require careful calibration with standards and counting statistics which are difficult to achieve using nanoprobe thin-film EDS analysis. Although the identification of this sulfide is uncertain, we have calculated the $\delta^{34}\text{SCDT}$ value for pyrrhotite.

[°] The error reflects uncertainties arising from the counting statistics of each analysis, calibration to a known standard, deadtime constant, and value of the standard.

light isotope will lead to changes in the isotopic composition of both product and reactant with time. The relationships between the initial reactant, residual reactant, total product, and product at any time (instantaneous product) are given by Rayleigh distillation equations (Nakai and Jensen, 1964). In a closed system, at approximately 75% completion of

reaction, the instantaneous product sulfide could have the isotopic composition of the initial reactant. With further reaction, the instantaneous product would be enriched in ^{34}S relative to the initial reactant sulfide. However, the $\delta^{34}\text{S}$ value of the integrated product sulfide will not reach that of the reactant until the sulfate has been completely consumed.

The observed isotopic fractionation between sulfide and sulfate due to bacterial sulfate reduction is generally on the

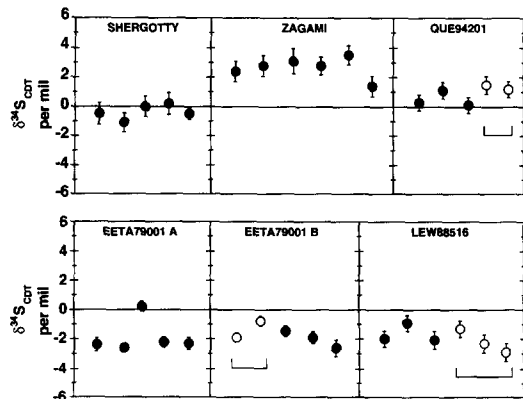


Fig. 1. Sulfur isotopic analyses of sulfides in martian meteorites relative to Cañon Diablo Troilite (CDT). All sulfides are pyrrhotites (Fe_{0.92–0.94}S). Open symbols denote multiple analyses on an individual sulfide grain. Error bars (1 σ) represent the uncertainties arising from the statistics of each analysis, calibration to a known standard, deadtime uncertainty, and standard uncertainty.

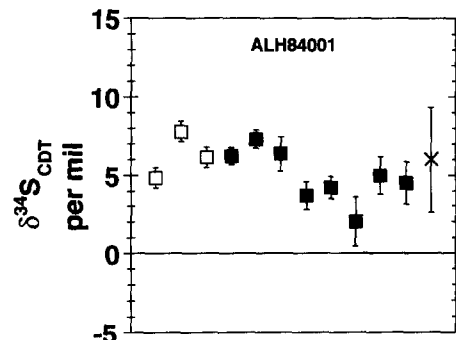


Fig. 2. Sulfur isotopic analyses of sulfides in ALH84001 relative to Cañon Diablo Troilite (CDT). Open symbols are the three pyrite analyses of Shearer et al. (1996); closed symbols are pyrite grains analyzed in this study. The (X) symbol is the analysis of a fine-grained sulfide rim within a carbonate globule (assumed to be pyrrhotite; see Table 1). Error bars (1 σ) for each analysis are included.



Fig. 3. Backscattered-electron image (left), iron $K\alpha$ (center), and sulfur $K\alpha$ (right) X-ray maps showing the analyzed Fe-sulfide zone (Fe-S) in carbonate (cb). Other phases are chromite (cr), maskelynite (mk), orthopyroxene (opx), and pyrite (py). The pyrite shown has a $\delta^{34}\text{S}_{\text{py}} = +4.5 \pm 1.4\text{‰}$ (Table 1). Scale bar in the backscattered-electron image is 100 μm .

order of $-45 \pm 20\text{‰}$, although this value might be greatly reduced if the concentration of sulfate is extremely low (Nielsen, 1979). The high contents of sulfur in martian soils measured by the Viking lander (Clark et al., 1982), coupled with the oxidizing nature of the Martian atmosphere (Hunt, 1979), suggest that there should be ample sulfate in the fluid or vapor that precipitated the carbonates and sulfides found in ALH84001, so that any sulfate-reducing bacteria should have concentrated ^{32}S in sulfides (Kemp and Thode, 1968; Nielsen, 1979). The observed lack of fractionation in the fine-grained Fe-sulfide zone argues against formation as a result of biologic activity if terrestrial analogs are appropriate. Alternatively, if sulfate-respiring bacteria were active in ALH84001, the measured $\delta^{34}\text{S}$ value of the fine-grained sulfide zone would imply that the precursor sulfate had a $\delta^{34}\text{S} \approx +50\text{‰}$, or that the fine-grained sulfides are the instantaneous product resulting from extended reduction of sulfate in a system that is closed to input of additional sulfate. However, given that the $\delta^{34}\text{S}$ value of the fine-grained sulfides are in the same range as those of the inorganic pyrites in the sample, an inorganic origin for the fine-grained sulfide is a simpler and more likely explanation.

The isotopically heavy sulfur found in the pyrite grains of ALH84001 has been explained as a result of the equilibrium isotopic fractionation of a hydrothermal fluid from which the pyrite precipitated (Shearer et al., 1996). There are other possible mechanisms which can explain the enrichment of ^{34}S in the sulfides of ALH84001. Recently discovered magnetite whiskers and platelets within carbonates of ALH84001 have been attributed to condensation from a vapor or hot, supercritical fluid (Bradley et al., 1996). The Fe-sulfide in the fine-grained zones may also have a similar origin. For example, pyrite and other sulfides have been identified in fumarole sublimates (Symonds, 1993), and outgassing of SO_2 from basalts can result in variable and heavy $\delta^{34}\text{S}$ values (Sakai et al., 1982). Thus, the sulfur isotopic compositions of sulfides found in crushed zones of ALH84001 may be the result of proximity to a volcanic center on Mars.

Studies of the compositional zoning of the carbonates sug-

gest kinetically-controlled growth (McKay and Lofgren, 1997). Also, the wide range of $\delta^{18}\text{O}$ found for the carbonates (Valley et al., 1997a; Leshin et al., 1997) allows the possibility that isotopic equilibrium may not have been maintained during formation of the carbonates (and the sulfides they contain) in ALH84001. The available oxygen isotopic data can be explained by mixing between a magmatic ($+4$ to $+6\text{‰}$) and an atmospheric reservoir ($> +20\text{‰}$). The carbon isotopic data for the carbonates also suggests input from an atmospheric source (Romanek et al., 1994). Similarly, the sulfur isotopic systematics of ALH84001 can be explained by mixing lighter, igneous sulfide and heavier "atmospheric" (possibly as soil sulfate) sulfur. Such mixing between igneous and "atmospheric" sources could occur as a result of an impact event. The likely large range of temperatures and rapid cooling associated with such an impact event could potentially result in both isotopic disequilibrium and formation of sulfides and carbonate across a range of temperatures, explaining observed textural and chemical features of the carbonates and sulfides in ALH84001.

5. CONCLUSIONS

Sulfur isotopes of sulfides have been measured by ion microprobe in five shergottites and ALH84001. The sulfur isotopic ratios of the shergottites ($\delta^{34}\text{S} = -2.6$ to $+3.5\text{‰}$) are similar to those measured in fresh ocean-floor basalts (Sakai et al., 1982; Puchelt and Hubberten, 1980; Chaussidon et al., 1989). The $\delta^{34}\text{S}$ values determined in this study for ALH84001 inorganic pyrites (Gibson et al., 1996) range from $+2.0$ to $+7.3\text{‰}$. These measurements extend the previously determined range ($+4.8$ to $+7.8\text{‰}$) for pyrite in this meteorite (Shearer et al., 1996). The analysis of a fine-grained sulfide zone within a carbonate globule ($\delta^{34}\text{S} = +6.0 \pm 3.4\text{‰}$) falls in the range of values found for the associated pyrites. If the fine-grained sulfide zone was formed by the action of sulfate-respiring bacteria (McKay et al., 1996), a significant sulfur isotopic fractionation would be expected (on the order of $-45 \pm 20\text{‰}$; Kemp and Thode, 1968; Nielsen, 1979). The finding that the putative biogenic sulfide

has a $\delta^{34}\text{S}$ value that is in the range of the inorganic sulfides in the same meteorite argues for a related origin for both types of sulfide by inorganic processes. Our results do not support the hypothesis that ALH84001 preserves evidence of relic biogenic activity.

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