SULFUR ISOTOPIC VARIATIONS IN SULFIDES FROM SHERGOTTITES AND ALH84001 DETERMINED BY ION MICROPROBE: NO EVIDENCE FOR LIFE ON MARS.

James P. Greenwood[1], Lee R. Riciputi[2], and Harry Y. McSween, Jr.[1], [1]Department of Geological Sciences, University of Tennessee, Knoxville, TN 37996, [2]Chemistry and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

The proposal that carbonates in ALH84001 are products of extraterrestrial biogenic activity [1] necessitates a greater understanding of other potential biomarkers on Mars. The isotopic systematics of sulfur present an ideal case, as on Earth they are heavily fractionated as a result of biological processes [2,3]. There are two modes of occurence of Fe-sulfides in ALH84001. Minute Fe-sulfides are present with magnetite in the rims of carbonate globules in ALH84001. An origin of the Fe-sulfides in these rims as products of sulfate-reducing bacteria has been hypothesized [2]. The second mode is larger pyrite grains, commonly associated with carbonate globules, in the crushed zones of ALH84001. Recently reported sulfur isotopic measurements of three pyrite grains in crushed zones of ALH84001 [4] found δ^{34}S values ranging from +4.8 to +7.8‰. Origin of these pyrites by precipitation from a hydrothermal fluid, and not as a result of organic processes, was proposed [4]. While the secondary processes that have affected ALH84001 are hotly debated, the shergottites lack evidence of abundant secondary mineralization. The sulfides present in these meteorites are magmatic in origin; therefore, a record of sulfur isotopic systematics in martian rocks unaffected by biologic or hydrothermal activity can be obtained. Here we report results of *in situ* analyses of sulfur isotopes by ion microprobe in: 1) pyrrhotites from five shergottites (basaltic and lherzolitic), 2) eight pyrite grains in crushed zones of ALH84001, and 3) an Fe-sulfide zone within a carbonate globule of ALH84001.

Sulfur isotopic analyses of pyrrhotites from five shergottites are shown in Fig. 1. The range of δ^{34}S values (-2.6 to +3.5‰) overlaps reported ranges of sulfides in fresh ocean-floor basalts (-2.3 to +3.8‰) [5-7], suggesting that the mantle δ^{34}S value of Mars is akin to that of Earth and meteorites [7,8]. Positive δ^{34}S values, typical of subduction zone volcanism on Earth [9] are not seen in the shergottites, consistent with the idea that crustal recycling is not an important process on Mars [10]. The mean δ^{34}S value of -0.4 ± 0.4‰ for pyrrhotite grains determined by ion microprobe in this study is in excellent agreement with the value of -0.5 ± 1.5‰ determined for bulk rock analysis of Shergotty [11].

Our sulfur isotopic analyses of eight pyrite grains in crushed zones of ALH84001 have values of δ^{34}S in the range +2.0 to +7.3‰, confirming the analyses of [4] (Fig. 2). The sulfur isotopic composition of a fine-grained sulfide-rich zone in a carbonate of ALH84001 is +6.0 ± 6.7‰ (Fig. 2). The δ^{34}S value for the sulfide zone falls in the range of pyrite grains in the crushed zones of ALH84001, suggesting that both populations of sulfides in this meteorite are related. The significant enrichments in ^{32}S expected if the sulfides were products of sulfate-respiring bacteria, as suggested by [1], are not found. This argues strongly for formation of sulfides, as well as carbonates, in ALH84001 by inorganic processes.

If magnetite whiskers and platelets in the carbonates formed by condensation of a hot vapor, as proposed by [12], then the sulfides in ALH84001 may have formed by a similar mechanism. Pyrite and other sulfides have been identified in fumarolic deposits [13], and fumarolic gases can become markedly enriched in ^{34}S with decreasing temperature [14].

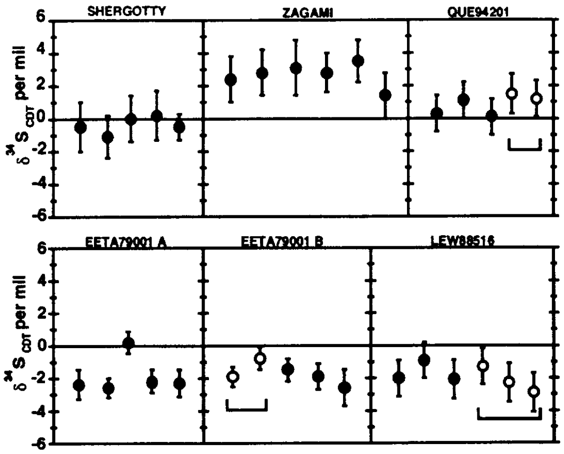

FIG. 1 (above left) Sulfur isotopic analyses of sulfides in shergottites relative to Cañon Diablo Troilite (CDT). All sulfides are pyrrhotites ($Fe_{92-94}S$). Open symbols denote multiple analyses on an individual sulfide grain. Error bars (2σ) represent the uncertainties arising from the statistics of each analysis, calibration to a known standard, deadtime uncertainty, and standard uncertainty. Analytical details are reported elsewhere [8,15,16].

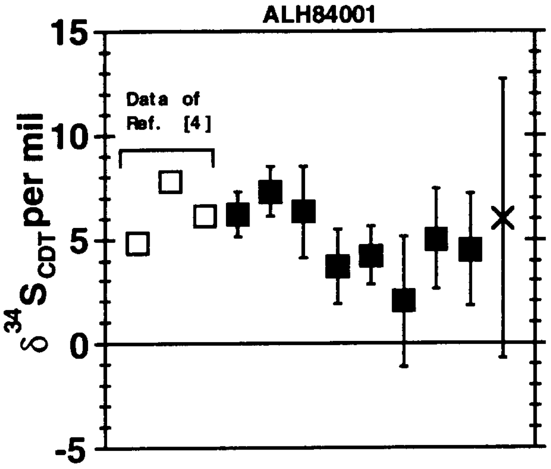

FIG. 2 (below left) Sulfur isotopic analyses of sulfides in ALH84001 relative to Cañon Diablo Troilite (CDT). Open symbols are the three pyrite analyses from Ref. 4; closed symbols are pyrite grains analyzed in this study. The (X) symbol is the analysis of a fine-grained sulfide rim within a carbonate globule (assumed to be pyrrhotite) Error bars (2σ) for each analysis are included; none are shown for data from Ref. 4 since individual errors were not cited.

References: [1] McKay D. S. et al. (1996) *Science* **273,** 924-930. [2] Kemp A. L. W. & Thode H. G. (1968) *GCA* **32,** 71-91. [3] Nielsen H. (1979) in *Lectures in Isotope Geology* (eds Jager E. & Hunziker J. C.) 283-312 (Springer-Verlag, Berlin). [4] Shearer C. K. et al. (1996) *GCA* **60,** 2921-2926. [5] Sakai H. et al. (1984) *GCA* **48,** 2433-2441. [6] Puchelt H. & Hubberten H. -W. (1980) *Init. Rept. Deep Sea Drilling Proj.* **51,** 1145-1148. [7] Chaussidon M. et al. (1989) *EPSL.* **92,** 144-156. [8] Paterson B. A. et al. *GCA* in press. [9] Ueda A. & Sakai H. (1984) *GCA* **48,** 1837-1848. [10] Carr M. H. & Wänke H. (1992) *Icarus* **98,** 61-71. [11] Burgess R. et al. (1989) *EPSL* **93,** 314-320. [12] Bradley J. P. et al. *GCA,* in press. [13] Symonds R. (1993) *Geochem. J.* **26,** 337-350. [14] Mizutani Y. & Sugiura T. (1982) *Geochem. J.* **16,** 63-71. [15] Riciputi L. R. (1996) *Rapid Comm. Mass Spec.* **10,** 282-286. [16] McSween H. Y. Jr. et al. *Meteor. Planet. Sci* in press.