HYDROTHERMAL SYSTEMS ON MARS. INSIGHTS FROM SULFUR ISOTOPIC SYSTEMATICS IN ALTERATION ASSEMBLAGES IN MARTIAN METEORITE ALLAN HILLS 84001. C.K. Shearer, M.N. Spilde, J.J. Papike, and G.D. Layne. Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131.

Introduction. Crustal processes and reactions during hydrothermal and biogenic activity result in extreme degrees of sulfur isotopic fractionation on Earth. For example, \( \delta^{34}S \) in terrestrial sulfides ranges from -70 \(^{\circ}\) to +70 \(^{\circ}\) on Earth [1]. In contrast, \( \delta^{34}S \) values for sulfides from other planetary bodies that have been sampled (Moon, asteroids) show a very limited mass fractionation. The standard deviation in the bulk isotopic composition of sulfur in meteorites of all types is less than 0.1 \(^{\circ}\) [2]. However, the isotopic composition of sulfides in meteorites shows slightly more variability. Troilit in Orgueil, a carbonaceous chondrite, has a \( \delta^{34}S \) of 2.6 \(^{\circ}\) [3]. Kaplan and Hulston [4] showed that sulfides in enstatite chondrites have \( \delta^{34}S \) of between +1.6 to +2.5 \(^{\circ}\). The \( \delta^{34}S \) in troilit from ordinary chondrites ranges from -2.7 \(^{\circ}\) to +2.5 \(^{\circ}\) [5]. The slight fractionation of \( ^{34}S \) into these sulfides has been attributed to nebular heterogeneity [5], low temperature (1000°C) reactions between water and elemental sulfur [3], and oxidation of FeS in an aqueous environment [2,4,5]. Lunar materials exhibit a much broader variation in bulk \( \delta^{34}S \) than has been observed in meteorites. Whereas bulk lunar rocks show variability on the order of +0.37 to +0.68, lunar soils have \( \delta^{34}S \) as high as +9.76 \(^{\circ}\) [6]. These high values in the bulk lunar soils have been attributed to preferential volatilization of \( ^{34}S \) during sputtering caused by micrometeorite bombardment [6]. Until now, \( S \) fractionation processes on the larger terrestrial planets such as Mercury, Venus, and Mars has been only speculative. With the discovery of a possible Martian meteorite with an imprint of a Martian hydrothermal system, we can gain insights into \( S \) fractionation on another planet.

SNC Meteorite ALH 84001. ALH84001 is a coarse-grained, clastic orthopyroxenite meteorite related to the SNC meteorite group [7]. A hydrothermal signature is superimposed upon the orthopyroxene-dominant igneous mineral assemblage. This hydrothermal overprint consists of carbonate assemblages occurring in spheroidal aggregates and as fine-grained carbonate and sulfide vug-filling structures [7,8,9,10]. The sulfide has been identified as pyrite [7]. Textural interpretations of shock features in the carbonates lead to the interpretation that the carbonate-sulfide mineralization was a result of influxes of fluids during Martian hydrothermal activity [7].

Isotopic Analysis of Pyrite in ALH 84001. The sulfur isotopic measurements were made using a Cameca IMS-4f ion microprobe operated by a University of New Mexico-Sandia National Laboratory consortium on the UNM campus. A Cs\textsuperscript{+} primary beam was focused to a spot of between 8 and 10 \( \mu \text{m} \). \(^{32}S \) and \(^{34}S \) were analyzed in the secondary ion beam. A S isotope pyrite standard was analyzed in order to measure the degree of instrument-induced fractionation, precision, accuracy, and instrument drift over the period of an analytical session. The analytical precision measured on the standards is better than \( \pm 0.2 \(^{\circ}\) \), whereas the analytical precision measured on the samples is better than \( \pm 0.5 \(^{\circ}\) \). These reported precision values far exceed those reported in the literature for ion microprobe analysis of sulfur isotopes in sulfides [5, 10].

Results. \( \delta^{34}S \) values for 5 pyrite grains were obtained from ALH84001. Values for the pyrite range from +4.8 to +7.8. These \( \delta^{34}S \) values are \(^{34}S \) enriched relative to Canon Diablo troilit. Based on the 2\( \sigma \) precision, there are real isotopic differences among pyrite grains.

Discussion. Sulfur isotopic characteristics of sulfides are constrained by a large number of variables, such as the sulfur isotopic characteristics of the hydrothermal fluid, temperature, pH, and \( f_{O_2} \) [11]. The stability field of pyrite also influences the range of expected \( \delta^{34}S \) values of the pyrite [11]. Therefore, although sulfur isotopic systematics provide some information concerning the hydrothermal system, they are best used in conjunction with other data (mineral stability, other stable isotopes). In comparison with sulfides from other meteorites, the \( \delta^{34}S \) of the pyrite from ALH84001 is enriched in \(^{34}S \). This signature implies that the planetary body represented by ALH84001 experienced processes capable of fractionating \( S \) isotopes that were not functional on asteroidal bodies represented by chondrite and achenchordite meteorites.

As was noted previously, the terrestrial \( \delta^{34}S \) exhibits a wide variability. In particular, the large negative values in terrestrial \( \delta^{34}S \) has been attributed, in many cases, to the bacterial reduction of sulfate to sulfide. The positive \( \delta^{34}S \) measured in the ALH84001 pyrite, therefore suggests that the sulfur in this hydrothermal sulfide was not processed by bacteria in a manner analogous to terrestrial processes.

The positive \( \delta^{34}S \) measured in the ALH84001 pyrite may be attributed to several different processes that may be functioning on the Martian surface or in the shallow Martian crust:

(Model 1) Assuming that the \( \delta^{34}S \) in the fluid was essentially 0, the pyrite may be enriched in \( ^{34}S \) by pH,
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temperature, and \(f_{O_2}\) conditions during precipitation. The pH and the fugacity of oxygen may be approximated using the \(\delta^{34}S\) data presented here, \(\delta^{13}C\) data on the carbonates [12], a relatively low \(\Sigma S\), a temperature of precipitation of \(= 100^\circ\) C [12] and the coexistence of pyrite and carbonate[11]. Making these assumptions, precipitation occurred in a reduced and moderately alkaline environment with the dominant sulfur-bearing species in solution being HS\(^{-}\). At higher temperatures (= 700° C) as suggested by [7,9], the \(\delta^{34}S\) of pyrite in the stability fields of carbonate + pyrite will not have values that approach +5 to +8 \(\%_o\).

(Model 2) The above interpretation makes the assumption that the \(\delta^{34}S\) in the fluid was equal to 0. At more acidic conditions than suggested above (but at the same reducing conditions), \(\delta^{34}S\) will not be strongly fractionated during pyrite precipitation from an aqueous solution [11]. Therefore, under these conditions, the pyrite will approximate the \(\delta^{34}S\) in the fluid [11]. There are several potential processes that can generate positive \(\delta^{34}S\) in the fluid under these pH and \(f_{O_2}\) conditions: 

(2a) Previous isotopic studies of SNC meteorites indicated that the present Martian atmosphere is isotopically heavy in O, C, N, and H [14]. Therefore, it is perhaps not surprising that other stable isotopes in the Martian atmosphere such as S should also be isotopically heavy. 

(2b) Alternatively, it has been documented that during lunar regolith formation and evolution, the bulk \(\delta^{34}S\) increases [6]. Therefore, impact-generated hydrothermal system models as suggested by [9] may result in the preferential volatilization of \(^{32}S\) relative to \(^{34}S\) during impact. 

(2c) Assessments of Martian soil mineralogy based on Viking XRF measurements and SNC documentation have suggested that phases such as clays, Fe-oxides, carbonates, and Ca- and Mg-sulfates will be stable in the oxidizing Martian environment [15]. It is expected that under such weathering environments, particularly with the stabilization of sulfates, \(^{34}S\) should be enriched in water soluble components (Ca- and Mg-sulfates) in the soil. Leaching of the \(^{34}S\)-enriched water-soluble minerals in Martian soil produced by processes 2a,b,c will result in a positive \(\delta^{34}S\)fluid. Model (2a,b,c) implies that the source for the sulfur is rather shallow and that this groundwater-hydrothermal system is in isotopic communication with processes occurring at the Martian surface. Under this second model, the temperature of precipitation cannot be constrained by the sulfur data.

Conclusions. Our data indicates that the sulfur isotopes \(^{32}S\) and \(^{34}S\) in the sulfides in meteorite ALH84001 have been fractionated to a greater extent than what has been documented in other meteorites. This, in itself, is another piece of information that links this orthopyroxenite to a planetary body that has experienced processes not present onchondrite and achondrite parent bodies. Mineralogical data suggests that the alteration assemblages were deposited under reducing conditions and that \(SO_4^{2-}\) was not a dominant species in the solution. Therefore, the extent of sulfur isotopic fractionation during pyrite precipitation from the hydrothermal solution was moderate, at alkaline conditions \(\delta^{34}S_{\text{fluid}} < \delta^{34}S_{\text{pyrite}}\), to minor at low pH conditions \(\delta^{34}S_{\text{fluid}} = \delta^{34}S_{\text{pyrite}}\). This suggests two different models for the generation of positive \(\delta^{34}S\) in the pyrite. If the pyrite precipitated at low temperature \(100 - 150^\circ\) C) reducing conditions and high pH < 9>, a \(\delta^{34}S_{\text{fluid}}\) equal to 0 \(\%_o\) would precipitate pyrite with \(\delta^{34}S_{\text{pyrite}}\) between 5 \(\%_o\) and 8 \(\%_o\). Under more acidic conditions, the \(\delta^{34}S_{\text{fluid}}\) will be equal to that of the pyrite. This requires the positive \(\delta^{34}S_{\text{fluid}}\) signature to be produced prior to pyrite deposition. The positive \(\delta^{34}S\) in the fluid may be attributed to upper atmospheric processes, impact processes or low temperature weathering reactions enriching the soil in \(^{34}S\). These components may then be leached and their \(\delta^{34}S\) signature transported to the location of precipitation. This process requires isotopic communication between the “hydrothermal system” and the Martian surface. If the isotopic signature of the sulfide reflects communication with surficial-atmospheric processes, it may constrain additional aspects of Martian atmosphere evolution.