

**THERMAL DECOMPOSITION OF SIDERITE-PYRITE ASSEMBLAGES: IMPLICATIONS FOR SULFIDE MINERALOGY IN MARTIAN METEORITE ALH84001 CARBONATE GLOBULES:** <sup>1</sup>D. C. Golden, <sup>2</sup>D. W. Ming, <sup>3</sup>H. V. Lauer, Jr., and <sup>2</sup>R. V. Morris; <sup>1</sup>Hernandez Engineering Inc., Houston, TX; <sup>2</sup>ARES, NASA Johnson Space Center, Houston, TX; <sup>3</sup>Lockheed Martin, Houston, TX (\*e-mail: douglas.w.ming@nasa.gov)

**Introduction:** Although magnetite crystals in ALH84001 have received considerable attention in the literature as a potential biomarker, the sulfide component is important because the coexistence of magnetite and sulfides has also been suggested as a marker for past biogenic activity [1]. Very little research, however, has focused on the formation of sulfides in ALH84001. Early research on the sulfides in ALH84001 indicated that pyrite grains (>10  $\mu\text{m}$  in size) are associated with chromite, maskelynite, and/or carbonate globules [2,3]. Fine-grained sulfides, which are found in the black rims of the carbonate globules, were tentatively identified as pyrrhotite and greigite by [1]. The presence of greigite has not been confirmed but the presence of pyrrhotite has been confirmed by [4].

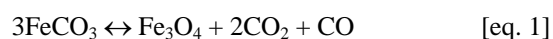
An alternative hypothesis to the biogenic origin for the carbonate-magnetite-sulfide assemblage in ALH84001 is the inorganic formation of this mineral assemblage by aqueous or hydrothermal precipitation of carbonate globules with Fe-sulfides followed by a heat pulse that was sufficient to decompose siderite to magnetite and pyrite to pyrrhotite [5,6,7]. We have previously precipitated Fe-sulfides (pyrite and pyrrhotite) and magnetite along with synthetic carbonate globules in laboratory experiments [5]. The pyrite precipitated along with the Fe-rich carbonate layers, and then was thermally converted to pyrrhotite upon heating to 470°C in a CO<sub>2</sub> atmosphere.

The thermal decomposition of pyrite-siderite assemblages to pyrrhotite-magnetite assemblages depends on a number of environmental variables, e.g., the partial pressure of S and CO<sub>2</sub>, presence/absence of volatile sinks, and open versus closed reaction environments. The objective of this paper is to report the effects of these environmental variables on the thermal decomposition of siderite-pyrite assemblages and to discuss their implications for the formation of the carbonate-sulfide-magnetite assemblage in ALH84001.

**Materials and Methods:** Siderite (Nova Scotia, <150  $\mu\text{m}$  size fraction with Mg and Mn impurities), pyrite (origin unknown, <150  $\mu\text{m}$  with minor silicate inclusions), and mixtures thereof were heated to 550°C in gas mixing furnaces under a stream of 95% CO<sub>2</sub> + 5% CO. The endmember and mixture samples (200 mg siderite and/or 50 mg pyrite) were heated in open (quartz crucibles) and sealed (SiO<sub>2</sub> glass tubes) containers to simulate open and closed systems, respectively. Temperatures were measured with

thermocouples placed next to the sample containers. Another set of closed-system experiments was conducted with CaO placed in a separate crucible inside the sealed silica glass tube to act as a getter for CO<sub>2</sub>. The temperature in all experiments was ramped from room temperature to 550°C at 1°C/min, held at 550°C for 1h, and then cooled to room temperature at 200°C/min. Mineralogical and chemical properties of run products were characterized by X-ray diffraction analysis, scanning electron microscopy, electron microprobe analysis, and Moessbauer spectroscopy. Treatments and reaction products are summarized in Table 1. We also characterized sulfides in ALH84001 thin sections using electron beam techniques (see above).

**Results from Experimental Studies:** Siderite-only decomposition in the open-system experiments yielded magnetite as the only product (Table 1). Magnetite and residual siderite were present in closed-system experiments. The extent of thermal decomposition is a function of the partial pressure of CO<sub>2</sub>, so that siderite decomposition stops once an equilibrium pressure is reached inside the sealed quartz tubes:



Pyrite-only decomposition in the open system yielded exclusively pyrrhotite. The boiling point of S is 445°C at 1 bar, so that the thermal decomposition of pyrite [eq. 2] is facilitated in the open system by the removal of S in the CO<sub>2</sub>:CO gas stream. In contrast to the open system, we did not detect decomposition of

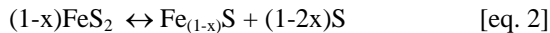
**Table 1.** Starting materials, experimental conditions and reaction products.

| Exp. #                                   | Sample*                  | System | Product (XRD)*                              |
|--|--------------------------|--------|---|
| Open vs Closed Systems                   |                          |        |   |
| 1  | sid                      | open   | mt  |
| 2  | sid                      | closed | sid > mt                                    |
| 3  | py                       | open   | ph  |
| 4  | py                       | closed | py  |
| 5  | sid + py                 | open   | mt, ph                                      |
| 6  | sid + py                 | closed | sid > mt, ph                                |
| Closed System with CO <sub>2</sub> Sink* |                          |        |   |
| 7**                                      | [(sid) + (py)]<br>+(CaO) | closed | [(mt, ph) + (ph)] +<br>(CaCO <sub>3</sub> ) |

\*sid = siderite; py = pyrite; ph = pyrrhotite, mt = magnetite.

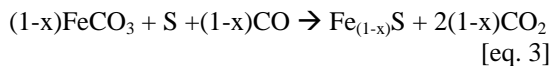
\*\*parentheses indicate individual open containers within quartz tube.

pyrite in the closed system, suggesting that the vapor pressure of S within the quartz tube was sufficient to inhibit the forward reaction:



This reaction in the closed system may simulate the conditions under which pyrite crystals trapped in the Opx (and glass) matrix experience in ALH84001, i.e., S vapor pressure builds up in the Opx matrix around the pyrite crystal and prevents thermal decomposition to pyrrhotite.

Starting materials of siderite + pyrite in the open system yielded magnetite and pyrrhotite. The grains of the original siderite and pyrite transformed pseudomorphically to magnetite and pyrrhotite, respectively (not shown). A small S concentration was detected even among magnetite grains; this S may be adsorbed on the surfaces of magnetite grains or be very fine-grained pyrrhotite. Siderite + pyrite in a closed system decomposed into pyrrhotite [eq. 1], magnetite [eq. 2], and unreacted siderite. Sulfur driven off during the thermal decomposition of pyrite also reacted with siderite to form pyrrhotite (eq. 3, data not shown). These pyrrhotite crystals were hexagonal plates and distributed among the submicron-sized magnetite crystals.



Siderite + pyrite decomposition in a closed system in the presence of the CO<sub>2</sub> getter produced magnetite and pyrrhotite; there was no detectable residual pyrite. Pyrrhotite crystals were randomly dispersed among magnetite grains and residual siderite (Fig. 1). This type of association has been observed in the rim region of ALH84001 carbonate globules [1,4].

#### Results from analysis of sulfides in ALH84001:

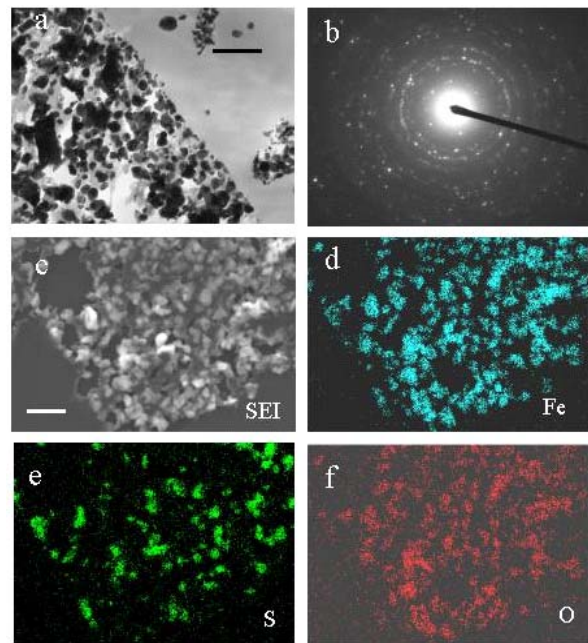
Sulfide grains in the Opx matrix of ALH84001 were pyrite and appeared to be completely “sealed” in the rock matrix. Presumably, pyrite isolated in the Opx matrix is inhibited from undergoing thermal decomposition to pyrrhotite because S vapors could not be transported away from crystal surfaces even if temperatures were high enough to drive the reaction. Sulfides exposed in fractures in ALH84001 were depleted in sulfur, suggesting that these grains had undergone partial thermal decomposition (not shown); fractures allowed passages for S vapors to escape away from pyrite surfaces. Sulfides in the rim regions of carbonate globules are mostly pyrrhotite. We suggest that pyrite in the rim regions was thermally decomposed into pyrrhotite because the S could either escape through cracks around globules or react with siderite to produce pyrrhotite.

**Discussion and Conclusions:** Experimental studies presented here show that the sulfide phase produced by heating siderite + pyrite is pyrrhotite,

which implies a similar formation mechanism for the recent identification of pyrrhotite in the rim regions of the carbonate globules of ALH84001 [4]. The large pyrite crystals in the Opx (and glass) matrix are largely not altered in ALH84001 because the S vapor pressure around the crystal is sufficiently high to prevent the thermal decomposition of the pyrite. The thermal decomposition of pyrite to pyrrhotite should have an appreciable kinetic isotopic effect on the sulfur; the evolved sulfur will be depleted in the heavier isotope (i.e., decrease in <sup>34</sup>S/<sup>32</sup>S in the vapor and an enrichment in <sup>34</sup>S in the pyrrhotite). ALH84001 sulfur isotopic data is consistent with this hypothesis [8,9].

In conclusion, the magnetite and pyrrhotite assemblage in the black rims of the ALH84001 carbonates can be direct decomposition products of siderite and pyrite in a closed or nearly closed system during a heating event. This scenario is consistent with the inorganic formation hypothesis for the carbonate-magnetite-sulfide assemblage in ALH84001 [5].

**References:** [1] McKay D.S. et al. (1996) *Science* **273**, 924–930. [2] Mittlefehldt D.W. (1994) *Meteoritics* **29**, 214–221. [3] Treiman A.H. (1995) *Meteoritics* **30**, 294–302. [4] Weiss B. et al. (2002) *Earth & Planet. Sci. Lett.*, **201**, 449–463. [5] Treiman A.H. (2003) *Astrobiol.*, **3**, 369–392. [6] Golden D.C. et al. (2001) *Am. Min.*, **86**, 370–375. [7] Golden D.C. et al. (2004) *Am. Min.*, submitted. [8] Shearer C. et al. (1996) *GCA* **60**, 2921–2926. [9] Greenwood J. et al. (2000) *Earth & Planet. Sci. Lett.*, **184**, 23–25.



**Figure 1:** (a) TEM image of a pyrrhotite + magnetite assemblage replacing siderite in experimental studies; (b) selective area electron diffraction of pyrrhotite and magnetite in (a); (c) SEM image of a thin section of transformed siderite showing a random mix of pyrrhotite + magnetite submicron-sized crystals; (d) Fe, (e) S, and (f) O x-ray dot maps of (c). Bar = 1 μm.