Petrology and hydrogen and sulfur isotope studies of mineral phases in Martian Meteorite ALH84001

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ALH84001 is a coarse-grained cataclastic orthopyroxenite consisting of orthopyroxene with minor maskelynite, clinopyroxene, chromite, and apatite (1). One of the unique features of ALH84001 is the occurrence of a carbonate-pyrite assemblage interstitially or in cataclastic zones within the meteorite. This assemblage is believed to be of hydrothermal origin (1,2) and may have preserved evidence of past biogenic activity on Mars (3). A low temperature origin of the carbonate assemblage is advocated by (4,5) on the basis of carbon and oxygen isotopic measurement. A high temperature origin (~ 650°C) on the basis of carbonate geothermometry is favored by (1,2). Ion probe measurements of oxygen isotopes of the carbonate (6) also suggest that at least some of the carbonate in ALH84001 was in isotopic equilibrium with the host rock at high temperatures. On the other hand, (7) favors shock melting and mobilization of the carbonate-plagioclase-silica assemblage during a single shock of ~ 50GPa that also formed the brecciated zones in the meteorite. Sulfur isotope measurements on pyrite (8,9) suggest that the enrichment of the heavy S isotope in the sulfide is due to inorganic hydrothermal processes and does not support a biogenic origin of pyrite by sulfate reducing bacteria.

In this phase of our investigation of ALH84001, we concentrated on the carbonate-pyrite assemblage and whitlockite. We studied their modes of occurrence, their textures, mineral chemistry, and their hydrogen and sulfur isotopic composition. We chose hydrogen isotope to assess whether the carbonate formed from hydrothermal fluids of magmatic affiliation or interacted with crustal fluids that equilibrated with an isotopically fractionated Martian atmosphere. Whitlockite, a mineral that occurs in association with the carbonate in ALH84001, was found in the much younger shergottite Zagami to have equilibrated with a Martian crustal water reservoir and has δD similar to that of present day atmosphere (10). If the whitlockite in ALH84001 reacted with crustal fluids on Mars, its hydrogen isotopes may provide clues about a much earlier Martian atmosphere ~ 4.5 by ago. Sulfur isotope measurements on pyrite were intended to expand the data base provided by (7,8) and to assess whether the $\delta^{34}S$ values on pyrite in the samples we investigated agree or differ from those in the samples they studied.

The ion probe analyses were performed at 10 kv with Cs primary beam of 2 nA. The analyzed area was ~ 5 to 25 µm. For H analysis of the carbonate and whitlockite, an amphibole standard was used. The mass fractionation factor is -128 ‰.

Mineral chemistry and stable isotopes: Carbonates occur interstitially or in cataclastic zones, as complexly zoned globules, or clusters of globules. Concentric zoning with Mg-rich layers alternating with Fe-rich layers is observed in some globules and reflect episodic changes in the activities of Fe and Mg in the hydrothermal fluids. Iron in the carbonates shows a positive correlation with Mn and Ca and a negative correlation with Mg. Similar zoning patterns were reported by (11). The average δD for three carbonate analyses (table 1) is 221 ± 9‰.

Pyrite occurs as anhedral grains (~ 5µm) associated with carbonate in the cataclastic zones and in some cases as inclusion in the carbonate. Rare pyrite was observed in association with chromite with no carbonate present. Both Co and Ni in pyrite were below the detection limit of microprobe analysis (~ 0.1 wt.%). The $\delta^{34}S$ for three pyrite grains falls within the range reported by (7,8). The two pyrite grains from cataclastic zones (6.8 ± 0.8 ‰ and 8.0 ± 1.8 ‰ have higher $\delta^{34}S$ values that a single pyrite grain within the carbonate (1.9 ± 1 ‰). The latter, however, overlap with the lowest $\delta^{34}S$ value reported by (8).

The phosphate is whitlockite, which generally occurs as anhedral crystals (up to 800 µm). It occurs in association with either clinopyroxene or carbonate. Most of the crystals are unzoned and are almost Cl and F free. We encountered one crystal, however, that was zoned. The core of this crystal was highly rich in chlorine (2.98 – 3.72 wt.%) and fluorine (0.92 – 1.17 wt. %). The rim contained only traces of chlorine and no detectable fluorine, but was enriched in Na (1.60 – 1.98 wt.% Na_2O) and Mg (1.9 – 2.09 wt.% MgO) relative to the core. Two δD measurements on a large whitlockite crystal associated with clinopyroxene and containing Mg-rich carbonate inclusions (whitlockite 1, table 1) average 244 ± 13 ‰). The Cl-rich core of the zoned whitlockite crystal which is also associated with pyroxenes has a negative δD value (-20 ± 7 ‰) that is remarkably different from the rim (216 ± 12 ‰).

Discussion: One of the interesting results of this investigation is the low δD values of the carbonates and whitlockite relative to the values reported for kaersutite and whitlockite in chassigny and the shergottites by (10). Hydrogen isotope studies of the composition of water extracted by stepwise heating of ALH84001 and other whole rock SNC meteorites (12) suggest that water in these samples originated from two sources: a terrestrial contaminant released at low temperature and an extraterrestrial component released at high temperature. The δD of the higher temperature hydrogen in ALH84001 is + 800‰. The terrestrial δD values range approximately between - 400‰ and + 100‰ (13). If we exclude the δD value for the Cl-rich core, which has a terrestrial hydrogen signature, all the δD values reported in table 1 clearly contain an indigenous extraterrestrial hydrogen component, unless the terrestrial contamination is very large. The low δD values of the carbonate and whitlockite imply that they have not significantly interacted with the present day Martian atmosphere. Since the crystallization age of ALH84001 is ~ 4.5 Gyr., and the Martian atmosphere was probably less fractionated than now, it is possible these compositions reflect magmatic or atmospheric compositions at the time of crystallization. The similarity between the δD of hydrogen released at high temperature by stepwise pyrolysis of ALH84001 and that of the much younger Nakhlites (12) seem to preclude this hypothesis. It is possible that there is a water reservoir on Mars which has not fully equilibrated with the atmosphere.

The sulfur isotope data on pyrite support a hydrothermal origin. The upper stability limit of pyrite is 743°C at 1 bar (14). This temperature represents the upper temperature limit for formation of this mineral at surface conditions. Pressure tends to increase the stability limit by 10°/Kbar. Preliminary experiments (Boctor, Bertka and Fei, unpublished data) show that pyrite in equilibrium with a Martian mantle composition (15) is stable at 1350°C. at 7GPa. Hypothetically, therefore, the pyrite associated with chromite could have formed at high temperature and pressure. This pyrite, however, should show little or no isotopic fractionation. The $\delta^{34}S$ of magmatic pyrrhotite in shergottites ranges between – 1.9‰ and 2.7‰ (9). All the pyrites in ALH84001 show enrichment in the heavy isotope which suggests a hydrothermal origin at temperatures much lower than magmatic temperatures. The sulfur isotope data also preclude a biogenic origin of the pyrite, if we assume that microorganisms, if they existed on Mars, used the same nutrients, had the same metabolic behavior, and produced the same kinetic isotope effects as sulfate reducing bacteria on earth.

Table 1. Ion probe analyses of hydrogen and sulfur isotopes of minerals from ALH84001

Mineral	δD_{smow}	$\delta^{34}S_{CDT}$
Whitlockite I	201 ± 14	
	287 ± 12	
Whitlockite 2 core	-20 ± 7	
Whitlockite 2 rim	216 ± 12	
Carbonate	313 ± 5	
	185 ± 10	
	165 ± 11	
Pyrite		8.0 ± 1.8
		6.8 ± 0.8
		1.9 ± 1.0

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