

HYDROGEN ISOTOPE STUDIES OF CARBONATE AND PHOSPHATE IN MARTIAN METEORITE ALH84001; N. Z. Boctor¹, J. Wang², C. M. O'D Alexander², E. Hauri², C. M. Bertka¹, and Y. Fei¹, ¹Geophysical Laboratory, Carnegie Institution of Washington, 5241 Broad Branch Rd., NW, Washington, DC 20015; ²Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd., NW, Washington, DC 20015.

Carbonate and phosphate minerals in ALH84001 are minor but significant constituents. Previous investigations [1–6] were concerned with the origin of the carbonates, their O and C isotope compositions, and their potential as biomarkers of ancient life on Mars. Phosphate minerals received less attention than carbonates. Because whole rock hydrogen isotope data on ALH84001 [7] indicate the presence of a high temperature hydrogen component, we investigated the hydrogen isotopic composition of the carbonate and whitlockite in this meteorite [8]. In view of the low δD values of whitlockite and carbonate relative to the whole rock, there was concern that epoxy contamination may have contributed to the measurements. In this investigation, we report additional ion microprobe analysis of the carbonate and whitlockite in ALH84001. We measured the C/H ratio on the epoxy and on the minerals and corrected the δD values for any possible contribution of the epoxy. To maximize the correction, we assumed that all carbon counts in whitlockite analyses are derived from epoxy. The analyses were performed at 12.5KV with oxygen primary beam of 2nA. The analyzed area was ~5 to 25 μm , and an amphibole standard was used. Based on the H count rates measured in two amphibole standards, and assuming that all H (after epoxy correction) in the samples is present as water, we have estimated the water contents of the whitlockite and carbonate. The results are given in table 1 and are compared to our previous analyses using a Cs primary beam.

The δD values of whitlockite from ALH84001 are much lower than those reported by (9) from Zagami ($\delta D + 4000\text{‰}$) which reacted with crustal waters that equilibrated with the Martian atmosphere. They are also lower than the δD values (~ +1680 to +3570 ‰) in apatite from the shergottite QUE94201 (10). There also is a positive correlation between δD and water contents of the whitlockite and carbonate, contrary to what was observed by (10) in apatite from the shergottite QUE94201. The δD values of the carbonate and whitlockite show that there is an extraterrestrial hydrogen component in ALH84001. The report by (11) of phyllosilicates in ALH84001 adds credence to the notion that extraterrestrial water was present in this meteorite. This is consistent with the presence of a high temperature hydrogen in the whole rock ($\delta D + 800\text{‰}$) reported by (7). Because there is a low temperature terrestrial hydrogen component released

during stepwise heating of ALH84001 whole rock (7), it is possible that there is also a terrestrial component to our measurements of whitlockite and carbonate and that the indigenous δD of whitlockite and carbonate are heavier. The δD of +800 ‰ of the whole rock high temperature hydrogen constrains the upper limit of the δD of whitlockite and carbonate; however, diffusive fractionation of D/H ratios during stepped heating may also bias the whole rock δD to high values. If the hydrogen component in ALH84001 is magmatic, this would imply that hydrous magma with a low activity of water may have existed in the Martian mantle ~ 4.5 Gyr ago. Alternatively, the hydrogen signature may represent an interaction of ALH84001 with crustal fluids that equilibrated with a primitive atmosphere that was much less fractionated than the present day Martian atmosphere.

References: [1] Harvey and McSween (1996) *Nature*, 382, 49. [2] McKay et al. (1996) *Science*, 273, 924. [3] Romanek (1994) *Nature*, 372, 655. [4] Valley et al. (1997) *Science*, 275, 1633. [5] Scott et al (1997) *LPS XXVIII*, 1271. [6] Leshin et al. (1998) *GCA*, 62, 3. [7] Leshin et al. (1996) *GCA*, 60, 2635. [8] Boctor et al. (1998) *LPS XXIX*. [9] Watson et al. (1994) *Science*, 265, 86. [10] Leshin (1998) *LPS XXIX*. [11] Breatly (1998) *LPS XXIX*.

Table 1. Ion Probe Analyses of Hydrogen Isotopes of Whitlockite and Carbonate in ALH 84001

Mineral Beam	O Beam		Cs	
	δD ‰	δD_{Corr}^* ‰	Water ppm	δD ‰
Whitlockite	+477±17	+500	1600	+287±12
	+270±22	+280	1100	+216±12
	+166±20	+181	800	+201±14
Carbonate	+209±22		700	+313±5
	+175±23		400	+185±10 +165±11

* Corrected for possible contribution from epoxy.