

HYDROGEN ISOTOPIC COMPOSITIONS OF CARBONATE IN MARTIAN METEORITE ALH84001.

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Introduction: A recent Rb-Sr dating of carbonate [1] in ALH84001 showed that the carbonate was formed about 3.9 Ga. ago. Hence, isotopic compositions of volatile elements in the carbonate (and in the meteorite in general) is expected to reveal the early martian near-surface environment.

Previous studies: Some studies suggest that the isotopic compositions of volatile elements in ALH84001 are not very anomalous. A nitrogen isotopic composition ($\delta^{15}\text{N} = 46$ permil after cosmogenic correction) is reported by Murty and Mohapatra [2]. It was inferred that 4 Ga ago, the martian atmospheric nitrogen isotopic composition was lighter than that in the present atmosphere. However, heavier nitrogen isotopic compositions were, reported (or inferred) by other studies [3,4]. According to [4], the $\delta^{15}\text{N}$ of ALH84001 is higher than 400 permil after cosmogenic correction, which is the highest value ever reported for martian meteorites. The difference among various reported values could be either due to terrestrial contamination or due to mixing with different amounts of martian mantle nitrogen. Results on hydrogen isotopic compositions in ALH84001 are also somewhat discrepant. $\Delta D = 783$ permil was obtained by a stepped pyrolysis study of a bulk sample [5]. ΔD values obtained by SIMS studies [6,7] are less anomalous. The highest ΔD value for carbonate is 313 permil and that for whitlockite is 500 permil. Various explanations can be made for the difference between these results. It is tempting to propose that hydrogen in the early martian surface was less fractionated than now, but a simpler explanation may be that the SIMS results were affected by terrestrial contamination. Thus we performed our own H isotope measurements by SIMS.

Experimental: The H isotope measurements by SIMS (Cameca 6F) were made twice in 1998, once in August and another in December. Isotopic measurements of H suffers from large instrumental mass fractionation and severe contamination from terrestrial hydrogen.

Cs ions were used as the primary ions and negative hydrogen ions (with 9.5 K acceleration voltage) were measured. Strong ($>1\text{nA}$) primary beam was focused on a small area (30 micrometer across) to minimize the contamination of hydrogen originating within the SIMS chamber. The size of the carbonate ranges from 10 micrometer to 20 micrometer and is smaller than the size of the primary beam. Since appropriate carbonate standard samples which contain abundant hydrogen were not available, a hornblende sample was used as a standard. The instrumental mass

fractionation for this standard is about -120 permil. The 1 sigma reproducibility of H isotopic measurements is better than 20 permil for measurements on the same day under the same condition. If the same standard sample was measured on different days (within a week) under slightly different conditions, however, the average H isotopic compositions could be different by more than 20 permil. The average H isotopic composition measured in December was about 65 permil different from that measured in August. Thus, the results of D/H measurements are reported by normalizing to the ratio for the standard sample measured on the same day. The error due to counting statistics is about 10 permil and is insignificant compared with the uncertainty in the instrumental mass fractionation. All in all, the 1 sigma error of the results reported here is expected to be about 30 permil.

Polished sections of the ALH84001 were coated with Au. An electron gun was used for charge compensation. Liquid nitrogen trap was used to improve the vacuum of the chamber. Carbonates as well as maskelite whitlockite and quartz were examined, but only carbonates seemed to contain measurable amounts of hydrogen. In a couple of cases the isotopic composition was initially light and became heavier by repeated measurements. In such cases, the isotopic composition stabilized after 20-30 minutes of spattering. Thus the change in the isotopic composition is considered to have been caused by removal of terrestrial contamination, and only the highest ratio is reported.

Results: 14 carbonate grains were analyzed for the hydrogen isotopic composition. The ΔD value ranges from 293 permil to 1344 permil, with an average of 818 permil. The variation in the isotopic composition seems to be related to the size of the carbonate grain. The higher values were obtained for the larger (20 micrometer in size) grains and lower values were obtained for smaller grains (10 micrometer in size) or grains with cracks. Thus terrestrial contamination is suggested to be the main cause of the isotopic variation. Either isotopic exchange with terrestrial water, terrestrial contamination on grain boundary or hydrogen in the SIMS chamber could cause the grain size dependence. In any case, it is suggested that the real H isotopic composition is equal to or higher than the highest value (1344 permil). The present results are not inconsistent with the results (783 permil) obtained by pyrolysis [5], because usually SIMS analysis of small grains provides more extreme isotopic ratios than the pyrolysis which tends

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to give near-average values. The H isotopic composition for the ALH84001 is not much lighter than the H isotopic compositions for other martian meteorites [8]. Together with the high $\delta^{15}\text{N}$ values [3,4] for this meteorite, the present results of H isotopic composition of ALH84001 suggest that the isotopic compositions of martian surface volatiles had already significantly fractionated at 3.9 Ga.

References: [1] Borg et al. (1998) abstract of Workshop on "Martian meteorites: where do we stand and where are we going?". [2] Murty and Mohapatra (1997) *GCA* 61, 5417-5428. [3] Grady et al. (1998) *Meteoritics & Planet. Sci.* 33, 795-802. [4] Miura and Sugiura (1994) (abstract) *Antarctic Meteorite Symp.* 19, 151-153. [5] Leshin et al. (1996) *GCA*, 60, 2635-2650. [6] Boctor et al. (1998) *LPS XXIX* [7] Boctor et al. (1998) *Meteoritics & Planet. Sci.* 33, A18. [8] Watson et al. (1994) *Sci.* 265, 86-90.