

OXYGEN ISOTOPIC CONSTRAINTS ON THE GENESIS OF CARBONATES FROM MARTIAN METEORITE ALH84001; Laurie A. Leshin¹, Kevin D. McKeegan¹, and Ralph P. Harvey²; ¹Dept. of Earth and Space Sciences, University of California, Los Angeles, CA 90095-1567; ²Dept. of Geological Sciences, Case Western Reserve University, Cleveland, OH 44106-7216.

Introduction: With a crystallization age of ~4.5 Ga [1,2], ALH84001 is unique among the martian meteorites. It is also the only martian meteorite that contains an appreciable amount of carbonate [~1 vol. %; 3], and significantly, this carbonate occurs without associated secondary hydrated minerals. Moreover, McKay et al. [4] have suggested that ALH84001 contains evidence of past martian life in the form of nanofossils, biogenic minerals, and polycyclic aromatic hydrocarbons (PAHs).

The presence of carbonate in ALH84001 is especially significant. The early martian environment is thought to have been more hospitable to life than today's cold, dry climate. It is possible that early Mars had an atmosphere of 1 bar or more of CO₂ and sequestration of CO₂ in carbonate has long been among the possible explanations for the "lost" CO₂ which must be accounted for in models of martian atmospheric evolution [e.g., 5]. The carbonates in ALH84001 are thought to have been produced by fluid-rock interaction on Mars [e.g., 6,7], which is an important geologic process that appears to have affected nearly all of the martian samples we have [7,8]. Additionally, the alleged biominerals, the nanofossils, and the PAHs are all found to be associated with the carbonates [4].

One of the central areas of debate concerning the carbonates is their temperature of formation, which obviously is an extremely important factor in assessing the suggestion made by McKay et al. [4]. Based on the oxygen isotopic compositions of the carbonates, calculated from compositions measured by acid-dissolution, Romanek et al. [6] argued that the carbonates formed at temperatures below 100°C. However, Harvey and McSween [9] used the distributions of major elements in the carbonates to argue that the crystallization took place at much higher temperatures, perhaps even >600°C. If the carbonates truly did form at temperatures significantly above 100°C, a biological origin for features associated with them [4] would be highly unlikely.

The oxygen isotopic data collected by Romanek et al. [6] may not adequately constrain the conditions of formation of the carbonates because of experimental difficulties associated with analyzing mixtures of complex carbonates [10]. In order to better assess the true $\delta^{18}\text{O}$ values, as well as the isotopic diversity and complexity of the ALH84001 carbonates, direct measurements of the oxygen and carbon isotopic compositions of individual carbonate phases are needed. Here we report *in situ* analyses of $\delta^{18}\text{O}$ values in carbonates from two polished thin sections of ALH84001 performed using the UCLA CAMECA ims1270 ion microprobe.

Experimental procedure: Oxygen isotope measurements were performed using a defocused Cs⁺ beam to sputter a flat-bottomed crater ~15x20 μm in diameter (Fig. 1). A normally incident electron flood gun was used to compensate for sample charging during analysis and measurements were performed at high mass resolving power (>4500) in order to eliminate molecular interferences. The data were collected with no energy filtering by measuring the intense (up to ~10⁸ cps) ¹⁶O peak in a Faraday cup (FC) equipped with a Keithley 642 electrometer while the ¹⁸O peaks were pulse counted in an electron multiplier (EM) using the UCLA-built ion counting system. Measurements of standards (discussed below), which were mounted independently from the thin sections, were made interspersed with those of the 84001 carbonates. The raw data were corrected for deadtime (small effect), instrumental mass fractionation, EM yield, and matrix effects using data from the standards. Precision is typically ~1‰ per analysis spot even accounting for the uncertainties due the EM yield and mass fractionation corrections.

The primary issue that must be dealt with in the analysis of the complex carbonates, such as those in ALH84001, is the so-called matrix effect, which results in minerals of different chemistries exhibiting different magnitudes of instrumental mass fractionation (presumably due to differences in ionization processes). Our systematic survey of carbonate standards revealed only a 1.8‰ difference in instrumental mass fractionation between dolomite and siderite (this difference is the matrix effect), suggesting that for the "Ca, Fe-rich" carbonates, most of which are intermediate in composition falling between dolomite and an intermediate magnesite-siderite composition on a carbonate ternary diagram (e.g., Fig. 3 of Harvey and McSween [9]), matrix effects are not an insurmountable problem for oxygen isotopic analysis.

To date, we have performed a total of eight oxygen isotopic analyses of carbonates in ALH84001. We have examined four different carbonate-bearing regions; two in each of two thin sections studied (.85 and .168). We purposely did not analyze calcite or magnesite in this first round of analyses, but only studied carbonates with compositions ranging from the more Fe-rich magnesite-siderite compositions to the Fe-bearing dolomitic compositions documented by Harvey and McSween [9]. The data were corrected for matrix effects using the average of instrumental mass fractionation factors determined on our dolomite and siderite standards and are reported relative to SMOW.

Results and discussion: The eight measurements are reported in Table 1 and the data from .168 area D

MICROSCALE OXYGEN ISOTOPES IN ALH84001: Leshin L. A. et al.

are shown in Fig. 1. Two important observations can be made: (1) all except one of the analyses have lower $\delta^{18}\text{O}$ values than the “Ca, Fe-rich” end-member of Romanek et al. [6], and (2) large heterogeneities over small distances can be seen, even within these carbonates which all have similar major-element chemistries.

The observation of $\delta^{18}\text{O}$ values substantially lower than those reported by Romanek et al. [6] is especially important. Our data suggest that the technique of sampling gas evolved at different times from acid-treated samples does not provide an accurate estimate of the oxygen isotopic composition of the carbonates. In fact, using the end-member compositions and abundances reported by Romanek et al. [6], if there was 10% contamination in the reported “Ca, Fe-rich” composition (this end-member has $1.50\mu\text{g C}$ and $\delta^{18}\text{O} = +13.3\text{‰}$) by the “Mg-rich” end-member ($6.16\mu\text{g C}$; $+22.3\text{‰}$) this would drive the true $\delta^{18}\text{O}$ of the “Ca, Fe-rich” end-member down to $\sim+7\text{‰}$, more consistent

with our observations. Our preliminary analysis indicates that at least some of the carbonates were in isotopic equilibrium with the host rock at high temperatures (Romanek et al. [6] argued against high temperatures because their analysis of the $\delta^{18}\text{O}$ of the carbonates revealed them to be out of the range of $+6$ to $+8\text{‰}$). The situation is clearly more complicated than simple high temperature isotopic equilibrium, however, as evidenced by the small-scale variability within and among different carbonate regions. The value of $+21.6\text{‰}$ is particularly intriguing. This value was measured in a small rosette of major element chemistry similar to the other carbonates analyzed, but within a region that has a high abundance of magnesite. Comparison of this magnesite to other occurrences of magnesite, to be accomplished in the near future, will reveal if this region could perhaps represent “late” crystallizing carbonate formed after fluids had evolved isotopically or cooled.

REFERENCES: [1] Nyquist L.E. et al. (1995) *Lunar Planet. Sci. XXVI*, 1065-1066. [2] Jagoutz E. et al. (1994) *Meteoritics*, 29, 478-479. [3] Mittlefehldt D.W. (1994) *Meteoritics*, 29, 214-221. [4] McKay D.S. et al. (1996) *Science*, 273, 924-930. [5] Fanale F.P. et al. (1992) in *Mars*, The University of Arizona Press: Tucson, 1135-1179. [6] Romanek C.S. et al. (1994) *Nature*, 372, 655-657. [7] Leshin L.A. et al. (1996) *Geochim. Cosmochim. Acta*, 60, 2635-2650. [8] Watson L.L. et al. (1994) *Science*, 265, 86-90. [9] Harvey R.P. and McSween H.Y., Jr. (1996) *Nature*, 382, 49-51. [10] Al-Aasm I.S. et al. (1990) *Chem. Geol.*, 80, 119-125.

Table 1. Ion probe analyses of ALH84001 carbonates

Sample description	$\delta^{18}\text{O}_{\text{SMOW}} (\text{‰}) \pm 1\sigma$
ALH84001,85 area 4 spot 1	$+10.6 \pm 0.7$
ALH84001,85 area 4 spot 2	$+8.2 \pm 0.7$
ALH84001,85 area 5 spot 1	$+10.1 \pm 0.8$
ALH84001,168 area A spot 1	$+8.5 \pm 1.1$
ALH84001,168 area A spot 2	$+21.6 \pm 1.1$
ALH84001,168 area D spot 1	$+5.6 \pm 0.9$
ALH84001,168 area D spot 2	$+11.6 \pm 1.4$
ALH84001,168 area D spot 3	$+6.8 \pm 0.8$

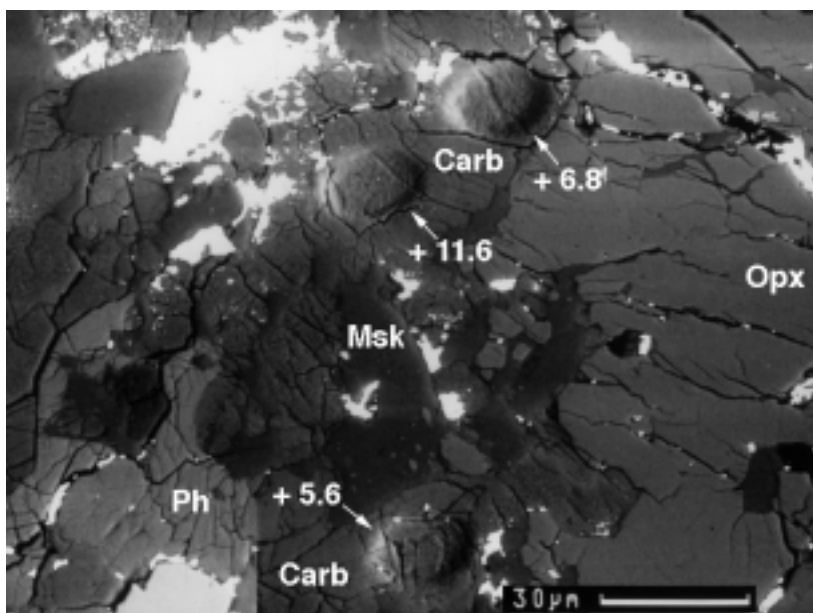


Figure 1. SEM BSE image of carbonates (carb) in ALH84001 after isotopic analysis with the ims1270 ion microprobe. Orthopyroxene (Opx), maskelynite (Msk), and phosphate (Ph) are also present. Three ion probe pits, labeled with their measured $\delta^{18}\text{O}$ values (corrected for matrix effects and instrumental mass fractionation), are visible. The $\delta^{18}\text{O}$ values of these “Ca,Fe-rich” carbonates are lower than the value calculated by Romanek et al. [6] for carbonates of this composition. The results indicate heterogeneities at the microscale, but also that some of the carbonates could have isotopically equilibrated with the host-rock at high temperatures.