Carbonates in ALH 84001 Formed in a Short-Lived Hydrothermal System

Itay Halevy[1] and John M. Eiler[1], [1]California Institute of Technology, Pasadena, CA, USA (itay.halevy@gmail.com)

Introduction: The martian meteorite ALH 84001 is a ~4.1 billion-year-old [1] orthopyroxenite that contains ~1 w% carbonate minerals of variable composition and an age of 3.9–4.0 billion years [2]. On the basis of several petrographic studies, the carbonates can be divided into *i)* chemically and isotopically zoned concretions and void fillings, *ii)* veins, and *iii)* regions of massive carbonate, variably intergrown with feldspathic glass and orthopyroxene [3, 4]. Most concretions are ovoid in shape and belong to two size populations, 100–250 and ≤50 μm. The cores of the larger concretions are Ca-Fe-rich and have $\delta^{18}O$ as low as ~5‰ (versus the SMOW standard) and their rims are Mg-rich and have $\delta^{18}O$ as high as ~25‰ [4–7]. The smaller concretions display only the latter, Mg-rich and isotopically heavy part of the sequence. Massive carbonates are usually internally homogeneous, though significant variability between occurrences is observed in both chemical and isotopic composition. Several studies have reported a Ca-rich and isotopically light ($\delta^{18}O = 0$ to 10‰) composition for the massive carbonates [e.g. 7].

Various scenarios have been suggested for formation of the carbonates, including impact melting of preexisting carbonates [8], reaction between CO_2-rich fluids and the parent rock at temperatures exceeding 650°C [3, 9], precipitation in low-temperature (0–200°C) hydrothermal systems [5–7, 10] and precipitation from a rapidly-evaporating water reservoir, perhaps at sub-freezing temperatures and with a receding water table [11, 12]. Small, pure and apparently ordered magnetite crystals, as well as sulfide grains and organic matter associated with the concretion rims have been used to argue for a biological origin of the carbonates [13]. Understanding how the carbonates formed is crucial to evaluating hypotheses such as those presented above, as well as to unravelling the history of aqueous processes near the surface of Mars. In addition, irrespective of their formation mechanism, the carbonates in ALH 84001 hold valuable information about the hydrological and carbon cycles of ancient Mars. Here we present isotopic analyses of the carbonates in ALH 84001, which suggest that the carbonates formed in shallow, ephemeral hydrothermal systems, at temperatures just below 100°C, out of equilibrium with the silicates in the rock and from water that was isotopically light.

Methods: We determined the temperature of carbonate formation from the abundance of multiply-substituted or "clumped" isotopologues of CO_2 evolved from acid digestion of the carbonate. The measured abundance of mass 47 CO_2 (mostly $^{13}C^{18}O^{16}O$) relative to the abundance expected from a random distribution of the heavy isotopes is denoted Δ_{47} and is temperature-dependent. The theoretical and technical details are given in [14, 15]. Unlike traditional $\delta^{18}O$ thermometry, clumped isotope thermometry arises from equilibrium within a single phase (the carbonate), and therefore requires no knowledge of the $\delta^{18}O$ of the water from which the carbonate formed.

We dissolved ~220 mg of bulk meteorite and an additional ~1.2 mg of nearly pure carbonate in 102% phosphoric acid, at a temperature of 90°C, in three steps. Due to their faster dissolution kinetics, the first extraction step (0–1 hour) is expected to have sampled the calcic carbonates in the meteorite, though separation of the Ca-rich massive carbonates ("ankeritic domains," e.g. [7]) from the concretion cores is not possible in this way. The second and third steps (1–4 and 4–12 hours, respectively) dissolved increasingly Mg-rich carbonates (Fig. 1). To remove water and other contaminants, the evolved CO_2 was passed through glass cold traps held at ~−75°C and ~−125°C, a 0.3 m long, 1/4" outer diameter quartz tube packed with silver wool and a 2.5 m long, 1/8" outer diameter stainless steel Porapak Q column held at −20°C. The isotopic composition of the purified gas was measured on a dual-inlet Thermo Finnigan MAT 253 gas-
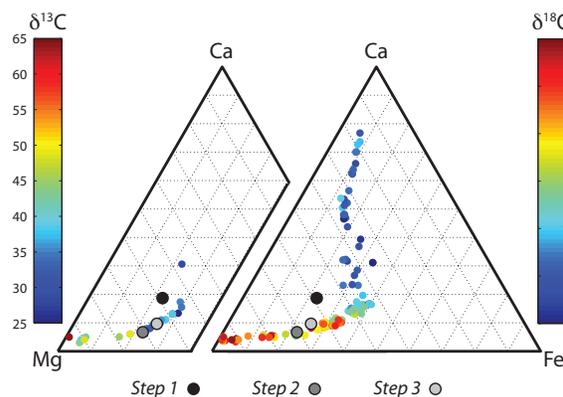

Figure 1: Likely chemical composition of the carbonates dissolved in the extraction steps, given their measured $\delta^{18}O$ and $\delta^{13}C$ (mean of normal distributions of Mg, Fe and Ca mole fractions with similar isotopic composition to those measured). The colored points are values of $\delta^{18}O$ and $\delta^{13}C$ measured by *in situ* methods [6, 7, 16, 17] and located on the ternary diagrams according to their chemical composition. $\delta^{18}O$ and $\delta^{13}C$ are reported relative to the SMOW and PDB standards, respectively. The inferred chemical composition of step 1 suggests that it is a physical mixture of "ankeritic domains" and concretion cores.

source mass spectrometer. A large, reaction duration- and sample size-dependent contamination was measured on mass 48, but subsequent experiments on materials with known isotopic composition suggest that this contamination does not affect the measured Δ_{47} and the calculated temperatures.

In calculating Δ_{47}, we accounted for the anomalous oxygen isotopic composition ($\Delta^{17}O = 0.8‰$) determined for ALH 84001 carbonates [18]. We used empirical calibrations for inorganically precipitated calcite and dolomite to calculate the formation temperature from Δ_{47}. Using this temperature, and temperature-dependent siderite–H_2O and siderite–CO_2 equilibrium fractionation factors [19], we determined the $\delta^{18}O$ of the water and the $\delta^{13}C$ of the CO_2 from which the carbonates formed.

Results and Discussion: The isotopic compositions of the three reaction steps, the temperatures derived from them and the isotopic compositions of the ancient martian surface reservoirs are shown in Table 1. We include the Δ_{47} measured for the third extraction step, but note that too little gas was evolved for an accurate Δ_{47} measurement (but enough for $\delta^{18}O$ and $\delta^{13}C$ measurements). Step 1 likely represents a mixture of the carbonate cores and the "ankeritic domains" (Fig. 1), whereas steps 2 and 3 are mixtures of core and rim carbonates, with a dominance of the latter. The carbonates dissolved in steps 1 and 2 formed at relatively high temperatures ($>80°C$), whereas it appears that the concretion rims, sampled in step 3, formed at a much lower temperature ($\sim20°C$). The isotopic composition of the water from which the carbonates formed is not in equilibrium with the coexisting silicates at the measured temperature for any of the extraction steps. The initial low $\delta^{18}O$ of the water is consistent with a meteoric or a meltwater source. Neglecting the value calculated for step 2 due to the large uncertainty in temperature, the decrease in $\delta^{18}O$ of the water with time is consistent with Rayleigh distillation due to carbonate precipitation or refreezing.

The near-constant $\delta^{13}C$ of the three extraction steps suggests a system open to a large gas-phase CO_2 reservoir, such as the atmosphere. If this is true then the early martian atmosphere appears to have been isotopically heavy ($\delta^{13}C \sim 30‰$). Additionally, for the water to reach a temperature of $79°C$ without boiling, the total pressure must have exceeded ~0.5 bar. Taken together with the near-constancy of the $\delta^{13}C$ of the gas-phase reservoir, this may indicate a very shallow hydrothermal system, under either a thicker early martian atmosphere or a few meters of water and a thin atmosphere.

Our results suggest a system that began at relatively high temperatures and cooled by $>60°C$ over the formation time of the carbonate concretions. The absence of

Step	1	2	3
t　(hr)	0–1	1–4	4–12
$\delta^{18}O_c$ (‰)	13.3±0.02	16.8±0.01	19.0±0.02
$\delta^{13}C_c$ (‰)	35.7±0.004	41.1±0.004	41.1±0.006
Δ_{47} (‰)	0.515±0.018	0.445±0.047	*0.664±0.067*
T　(°C)	79^{+10}_{-9}	120^{+39}_{-30}	22^{+16}_{-14}
$\delta^{18}O_w$ (‰)	−8.4	−0.1	−13.5
$\delta^{13}C_g$ (‰)	27.8	34.5	30.0

Table 1: Measured isotopic composition of carbonates in ALH 84001 and calculated formation temperatures and isotopic composition of the water and CO_2 from which the carbonates formed ($\delta^{18}O_w$ and $\delta^{13}C_g$, respectively). The Δ_{47} and temperature of step 3 (italicized) are highly uncertain. $\delta^{18}O$ and $\delta^{13}C$ are reported relative to the SMOW and PDB standards, respectively. Uncertainty is 2 standard errors.

other hydrous alteration phases in ALH 84001 [3] and the preservation of anomalous oxygen fractionations in the carbonates [18] suggest that this cooling occurred rapidly. A scenario consistent with these constraints is that the heat required for the warm aqueous conditions recorded by the carbonates may have been supplied and then dissipated very rapidly, perhaps by impact ejecta or a nearby lava flow. Transient, impact-induced precipitation or melting of ground ice could have supplied the isotopically light water, which then reacted with the rock and precipitated carbonates. After the heat-supplying event, the rocks near the surface cooled and the water refroze too rapidly for hydrous alteration phases to form in detectable abundances. This is consistent with Ar thermochronology, which indicates that ALH 84001 could have only been exposed to temperatures above $0°C$ for very brief periods [20].

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