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Oxygen isotopic constraints on the genesis of carbonates from Martian meteorite ALH84001

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Abstract—Ion microprobe oxygen isotopic measurements of a chemically diverse suite of carbonates from Martian meteorite ALH84001 are reported. The $\delta^{18}O$ values are highly variable, ranging from +5.4 to +25.3‰, and are correlated with major element compositions of the carbonate. The earliest-forming (Ca-rich) carbonates have the lowest $\delta^{18}O$ values and the late-forming (Mg-rich) carbonates have the highest $\delta^{18}O$ values. Two models are presented which can explain the isotopic variations. The carbonates could have formed in a water rich environment at relatively low, but highly variable temperatures. In this open-system case the lower limit to the temperature variation is ~125°C, with fluctuations of over 250°C possible within the constraints of the model. Alternatively, the data can be explained by a closed-system model in which the carbonates precipitated from a limited amount of CO_2-rich fluid. This scenario can reproduce the isotopic variations observed at a range of temperatures, including relatively high temperatures (> 500°C). Thus the oxygen isotopic compositions do not provide unequivocal evidence for formation of the carbonates at low temperature. Although more information is needed in order to distinguish between the models, neither of the implied environments is consistent with biological activity. Thus, we suggest that features associated with the carbonates which have been interpreted to be the result of biological activity were most probably formed by inorganic processes. *Copyright © 1998 Elsevier Science Ltd*

1. INTRODUCTION

ALH84001 is unique among the Martian meteorites. It is the only ancient Martian meteorite, with a crystallization age of ~4.5 Ga (Jagoutz et al., 1994; Nyquist et al., 1995), and the only Martian sample that contains an appreciable amount of carbonate (~1 vol%; Mittlefehldt, 1994). In addition, McKay et al. (1996) have made the provocative suggestion 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 important. The alleged biominerals (magnetite and pyrrhotite), the nanofossils, and the PAHs are all reportedly associated with the carbonates (McKay et al., 1996). However, regardless of whether the carbonates in ALH84001 were produced in association with biogenic activity, the presence of carbonate in Martian samples has important implications in a larger context. The early Martian environment is thought to have been more hospitable to life than today's cold, dry climate with perhaps an atmosphere of 1 bar or more of CO_2 (Fanale et al., 1992). Sequestration of CO_2 in carbonate has long been among the possible explanations for the lost CO_2 which must be accounted for in models of Martian atmospheric evolution. Additionally, the carbonates in ALH84001 are proposed to have been produced by fluid-rock interaction on Mars (e.g., Romanek et al., 1994; Jull et al., 1995; Leshin et al., 1996), but the secondary mineralization in ALH84001 is intriguingly different from that found in the other, younger Martian meteorites (Gooding, 1992). Clearly, understanding the environment under which the carbonates in ALH84001 formed is of critical importance for interpreting both the biological and geological significance of this unique Martian sample.

ALH84001 is a cumulate rock made up almost entirely of orthopyroxene, but as an impact breccia, it exhibits a range of petrographic domains, from relatively pristine cumulate regions to regions that have been crushed and mobilized by shock (Mittlefehldt, 1994; Treiman, 1995). Carbonate occurs in a wide variety of textures but predominantly within the crushed zones where it is often associated with feldspathic glass (e.g., Harvey and McSween, 1996). Overall, at least five textural types of carbonate both within crushed and uncrushed zones have been described (e.g., McKay and Lofgren, 1997; McKay et al., 1997), with the most distinctive and best studied being the globules or rosettes that form partial to fully circular exposures in thin section and on fracture surfaces.

The carbonates exhibit large chemical variability on the micron-scale with calcite ($CaCO_3$), dolomite-ankerite ($CaMg(CO_3)_2$-$CaFe(CO_3)_2$) and magnesite-siderite ($MgCO_3$-$FeCO_3$) compositions all observed within individual carbonate occurrences (e.g., Harvey and McSween, 1996; McKay and Lofgren, 1997). In addition, carbonates with metastable compositions between dolomite-ankerite and magnesite-siderite are observed. The rosettes allow the best assessment of chemical variability, and they show relatively continuous zoning from early Ca-rich cores (rarely calcite, but more often Mg-bearing ankerite) towards less Ca-rich compositions nearly on the magnesite-siderite join, and finally to pure magnesite rims (Harvey and McSween, 1996; McKay and Lofgren, 1997). There are fine-scale oscillations in the zoning, but these deviations from a smooth pattern are small, and the zoning is consistent from rosette to rosette (McKay and Lofgren, 1997).

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Numerous detailed studies of carbonate mineral chemistries have now been performed (Mittlefehldt, 1994; Treiman, 1995; Harvey and McSween, 1996; McKay and Lofgren, 1997; McKay et al., 1997; Scott et al., 1997; this study). Together these clearly demonstrate that all of the textural types of carbonate have the same basic mineral chemistries and zoning patterns, suggesting that the majority of carbonates in ALH84001 were formed by the same processes, with the different petrographic occurrences being controlled by local geometries.

There has been considerable disagreement concerning the nature of the environmental conditions (temperature, fluid composition, etc.) under which the carbonates formed, particularly as the hypothesis that biological activity was associated with their deposition (McKay et al., 1996) has been investigated (see McSween, 1997, for a review). Based on oxygen isotope data, Romanek et al. (1994) argued that the carbonates formed at temperatures between 0 and 80°C from a water-rich fluid. In contrast, Harvey and McSween (1996) used the distributions of major elements in the carbonate and the observed lack of coexisting hydrated minerals to argue that crystallization took place from a CO_2-rich fluid at much higher temperatures, ~ 650°C, perhaps during an impact-related metasomatic event. McKay et al. (1996) referenced the interpretations of Romanek et al. (1994) in support of their argument for the presence of biological signatures in ALH84001 and discounted the conclusions of Harvey and McSween (1996). However, if the carbonates truly did form in a temperature regime or from a fluid composition (such as a fluid of mostly CO_2) inconsistent with a biological environment, then a biological origin for the observations documented by McKay et al. (1996) would be highly unlikely. Subsequent studies have pointed out that the thermometry techniques utilized by Harvey and McSween (1996), which are based on the assumption of thermodynamic equilibrium to calculate temperatures, may not be applicable to the ALH84001 carbonates (Treiman, 1997; Valley et al., 1997). Additionally, reassessment of the assumptions of the Romanek et al. (1994) model have led to higher temperature estimates (Hutchins and Jakosky, 1997). Recently, Scott et al. (1997) have argued that the textural and chemical observations are best explained if the carbonates were deposited from shock-derived melts by locally mobilizing and redepositing pre-existing carbonates.

How can different studies come to such disparate conclusions about the environmental conditions of carbonate formation? One explanation for this discrepancy might be that interpretations based on chemical data obtained on a microscopic scale are not readily comparable with those derived from isotopic data obtained on a macroscale. The Romanek et al. (1994) study was on a bulk carbonate sample, while the Harvey and McSween (1996) conclusions were based on electron microprobe data obtained at the ~1-2 μm scale. The ion microprobe can address this problem of scale because it allows in situ analysis of oxygen isotopic compositions at a similar scale as electron microprobe analyses. Valley et al. (1997) recently reported oxygen isotopic measurements by ion microprobe in ALH84001 carbonates; however, the restricted range of carbonate compositions examined did not permit these authors to resolve any correlation of mineral chemistry with isotope composition.

2. PREVIOUS ISOTOPIC EVIDENCE CONCERNING ENVIRONMENTAL CONDITIONS OF CARBONATE PRECIPITATION

Previous oxygen and carbon isotopic analyses of ALH84001 are summarized by Valley et al. (1997); here we review two studies which specifically use their measurements of isotopic compositions to constrain the environmental conditions of carbonate formation. Romanek et al. (1994) concluded that the carbonates formed at low temperature (0-80°C) based on oxygen isotopic evidence. Analysis of the oxygen isotopic compositions of the carbonates is complicated by the compositional variability of the minerals. Traditionally, oxygen and carbon isotopes in carbonates are measured by the acid digestion technique (McCrea, 1950) in which CO_2 is released from carbonate by reaction with phosphoric acid. Because different carbonates react with the acid at different rates (with calcite reacting the most rapidly and magnesite the most slowly; Al Aasm et al., 1990), in principle by sampling the evolved gas at different times, it is possible to infer the isotopic compositions of the different minerals present in carbonate mixtures. Employing this stepped dissolution technique, Romanek et al. (1994) calculated the carbon and oxygen isotopic compositions of two carbonate endmembers: a "Ca, Fe-rich" composition with $\delta^{13}C = +39.5‰$ and $\delta^{18}O = +13.3‰$, and a "Mg-rich" composition with $\delta^{13}C = +41.8‰$ and $\delta^{18}O = +22.3‰$ (all δ values are reported relative to PDB for C and SMOW for O). According to Romanek et al. (1994), a low-temperature origin for the carbonates is indicated by the high $\delta^{18}O$ values relative to the host-rock value of +4.6‰ whereas if the carbonates formed at high-temperature, they should have $\delta^{18}O$ values of +6 to +8‰, in equilibrium with the host-rock. In addition to the general conclusion based on the high $\delta^{18}O$ values of the carbonates, Romanek et al. (1994) used the oxygen isotopic compositions of the two calculated carbonate endmembers to constrain the range of temperatures of carbonate deposition (0-80°C) and the mole fraction of water relative to CO_2 in the fluid that deposited them (finding that 58% of oxygen in the fluid was in the water, corresponding to a molar H_2O/CO_2 in the fluid of 2.8).

The recent ion microprobe study by Valley et al. (1997) found variation in carbonate $\delta^{18}O$ values from +9.5 to +20.6‰. Like Romanek et al. (1994), these authors concluded that equilibration at high temperature was inconsistent with the isotopic and petrographic data and that the carbonates probably formed by nonequilibrium processes at low temperatures. We present new ion microprobe analyses of oxygen isotopes in ALH84001 carbonates covering a significantly wider range of chemical compositions than analyzed previously. When considered with previous data, our results allow a more complete assessment of the environmental conditions under which the carbonates could have formed. The inferred conditions have important implications for the hypothesized biogenic origin of features associated with the carbonates in ALH84001 (McKay et al., 1996).

3. ANALYTICAL TECHNIQUES

Analyses were performed in two polished thin sections and one polished thick section. Carbonates from the two thin sections (PTS ALH84001,85 and ,168) were previously studied by Harvey and

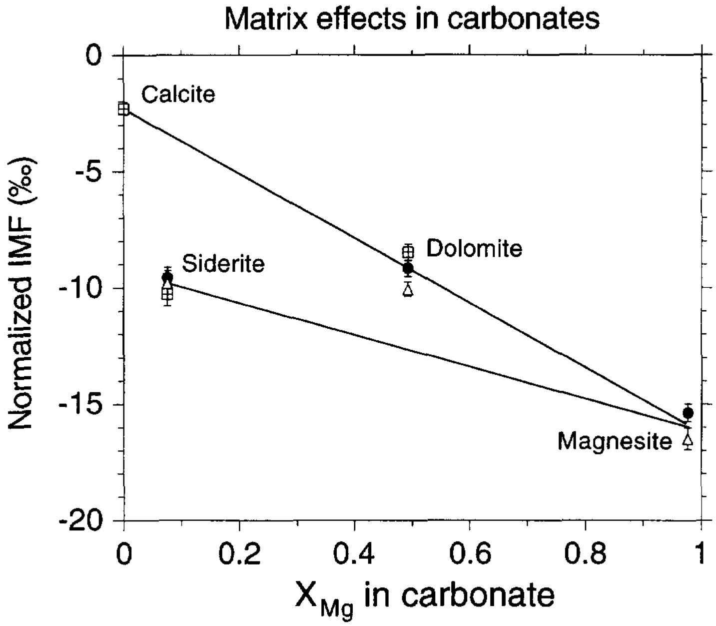

Fig. 1. Instrumental mass fractionation (IMF), the difference in per mil between the measured and true $^{18}O/^{16}O$ value, vs. chemical composition for carbonate minerals (displayed as mole fraction Mg in the minerals) used as standards for ion microprobe isotopic measurements. Each plotted data point represents the weighted mean (with standard error) of up to ten analyses of each standard, normalized to calcite measurements, during three different analysis sessions over which the ALH84001 measurements were made. The data show that the relative differences between IMF in carbonate minerals (the so-called matrix effect) were reproducible from session to session. As observed in previous ion probe studies of oxygen isotopes in carbonates, there is not a simple relationship between carbonate chemistry and IMF (Eiler et al., 1997; Valley et al., 1997). The reproducibility and relatively small magnitude of the matrix effects (especially between siderite, dolomite, and magnesite) allow a correction procedure for $\delta^{18}O$ values of the ALH84001 carbonates which is accurate to better than 2‰ (see text).

McSween (1996) for mineral chemistry. The thick section (TS1,68) was prepared at UCLA from chip ALH84001,68. All samples were allocated from the Antarctic Meteorite Collection at Johnson Space Center in Houston. For most of the carbonates analyzed isotopically, major element compositions were determined using the Caltech JEOL JXA-733 Superprobe equipped with five wavelength spectrometers and an energy-dispersive spectrometer (EDS). The remainder were analyzed with the CAMECA SX-50 electron microprobe at the University of Tennessee and constitute part of the data set reported by Harvey and McSween (1996). At Caltech, carbonate mineral standards were used (Calcite USNM 136321, Dolomite USNM 10057, Siderite USNM R2460, and Rhodochrosite Caltech P-561, for Ca, Mg, Fe, and Mn, respectively). Analyses were performed at 15 KV and 10 nA, with an area beam raster of 10 × 10 μm to minimize volatilization of CO_2 and a total count time of 60 s. The EDS spectrum was monitored as a quality control during each analysis to detect the presence of any silicate or sulfide component from the perimeter of the carbonate analysis area; any such analyses were discarded. Electron microprobe data were obtained either prior to ion microprobe analysis, or in some cases, following isotopic analysis in or adjacent to the sputtered crater.

Oxygen isotopic compositions of eighteen individual spots in eight separate carbonate-bearing regions within the three polished sections of ALH84001 were measured with the UCLA CAMECA ims 1270 ion microprobe. Mounts were coated with ~350 Å of Au. Negative secondary ions were sputtered by a ~0.1-0.3 nA Cs^+ primary beam defocused to a ~12-20 μm diameter spot. A normal-incidence electron gun was utilized to flood the analysis area with low energy electrons for charge compensation (Slodzian, 1980). Secondary ions with initial kinetic energies of ~0-30 eV were measured at a mass resolving power (M/ΔM) of ~4500, sufficient to eliminate any hydride interferences. Each measurement comprised twenty cycles of counting ^{16}O for 2 s and ^{18}O for 10 s. The secondary ^{16}O current was measured with a faraday cup (FC) equipped with a Keithley 642 electrometer, and ^{18}O ions were counted with an electron multiplier (EM). The analysis conditions resulted in typical count rates of thirty to forty million counts per second of ^{16}O; peak intensities were corrected for background (FC) and deadtime (EM). The Si^- signal was monitored before and after analyses in order to check for contamination from surrounding silicate phases, and the ion probe pits were documented by scanning electron microscope after analysis. The reported data all represent analyses of carbonate without any contamination from silicate. The combination of the tuning configuration, the low beam current, and the short analysis times resulted in the formation of shallow analysis pits approximately 1 μm in depth.

The data were corrected for instrumental mass fractionation (IMF) by using the known $\delta^{18}O$ value for standards analyzed during each session and applying a matrix effect correction. Matrix effects are the variation in the IMF due to changes in the chemical and physical properties of the samples being analyzed. Attention to matrix effects is particularly important in this case because the major element

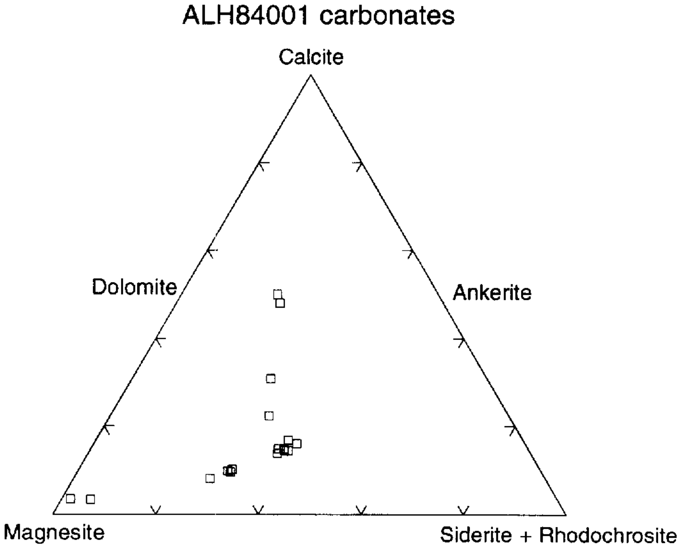

Fig. 2. Ternary diagram showing the chemical compositions of the carbonate spots in ALH84001 for which oxygen isotopic data are reported. Iron and manganese carbonate components have been combined to form the siderite + rhodochrosite endmember. We have studied carbonates covering nearly the entire compositional range found in ALH84001.

chemistry of the ALH84001 carbonates varies widely. Thus, standards covering the entire Ca, Mg, Fe-carbonate ternary were obtained (from Z. Sharp, U. Lausanne, in the case of dolomite, magnesite, and siderite, from the UCLA collection in the case of calcite) and analyzed during the same analysis sessions as the ALH84001 samples. The results of these analyses of standards are shown in Fig. 1. Similar to previous studies (Eiler et al., 1997; Valley et al., 1997), we do not find a single correlative between the magnitude of the instrumental mass fractionation and any chemical parameter (such as Mg content, as shown in Fig. 1) for carbonates covering the entire calcite-magnesite-siderite ternary. Thus the problem of matrix effects in carbonates forces a choice of an empirical correction procedure. We have chosen to correct the ALH84001 carbonate data by interpolating their chemical compositions from those of the standards and assuming linear variations in IMF with composition along calcite-dolomite-magnesite and magnesite-siderite (Fig. 1). Although linear behavior of the IMF with chemical composition is an assumption (except in the case of dolomite, where it is clearly observed), we emphasize that the total magnitude of the matrix effect between magnesite, dolomite, and siderite is small under our analytical conditions. Therefore, any small nonlinearities in the IMF should not affect the overall accuracy of the ALH84001 measurements by more than ~2‰ in the worst case.

The analyzed ALH84001 carbonates typically contain <3 but range up to ~7 mol% $MnCO_3$ component. Analysis of a rhodochrosite standard (provided by I. Hutcheon, LLNL) performed after the ALH84001 analyses, but under the same instrumental conditions, has revealed no measurable matrix effect between siderite and rhodochrosite under our analysis conditions; thus, both for standards and unknown measurements, Mn and Fe were combined to form the siderite endmember.

Reported uncertainties on individual analyses reflect both the internal measurement precision and an additional factor introduced by the scatter of the standard measurements during a given analysis session (represented in the error calculation by the standard deviation of measurements of the most frequently analyzed standard, typically 0.7-1.0‰ in $\delta^{18}O$ for an analysis session). Possible systematic errors, due to the assumption of linearity of the matrix effect correction or uncertainties in the composition of the standards, are not included in the reported uncertainty estimates.

4. SAMPLE DESCRIPTION

Here we describe briefly the petrographic setting of each of the regions analyzed in this study within the context of the five different types of carbonate occurrences in ALH84001 described by McKay et al. (1997). TS1,68 Areas 1 and 2 are fracture filling carbonates in pockets within cumulus pyroxene grains. Both areas are within 500 μm of a carbonate-rich crushed zone. TS1,68 Areas 3, 4, and 5 are all within crushed zones in a region of the thick section away from Areas 1 and 2. PTS,85 Area 4 is a region of intergrown globules with associated feldspathic glass within a pocket in a crushed zone and is pictured in Harvey and McSween (1996; Fig. 2). PTS,85 Area 5 is a single globule with associated with feldspathic glass in a crushed zone and is also pictured in Harvey and McSween (1996; Fig. 1). PTS,168 Area A contains many intergrown rosettes, is magnesite-rich, and contains mixed carbonate-silica intergrowths. This area is within a crushed zone but is difficult to fit into the categories described by McKay et al. (1997). Finally, PTS,168 Area D is similar to the interstitial carbonate fillings between feldspathic glass described by McKay et al. (1997) although, unlike the example given by these authors, Area D contains approximately equal amounts of feldspathic glass and carbonate. Despite varying petrographic setting, the carbonates present in all the areas studied here span nearly the entire range of major-element compositions previously reported for ALH84001 carbonates (except calcite, which is present only rarely). Thus our observations support the interpretation discussed above that nearly all of the current generation of carbonates in ALH84001, regardless of local depositional controls, were probably formed by the same processes.

Table 1. Chemical and Isotopic Analyses of Carbonates from ALH84001.

Analysis Description	X_{Mg}*	X_{Ca}	X_{Mn}	X_{Fe}	$\delta^{18}O \pm 1\sigma$ (‰)
TS1,68–Area 1–spot 1	0.610	0.098	0.007	0.285	20.1 ± 0.8
TS1,68–Area 1–spot 2	0.947	0.036	0.002	0.015	19.6 ± 1.1
TS1,68–Area 1–spot 3	0.612	0.098	0.006	0.284	20.5 ± 0.8
TS1,68–Area 2–spot 1	0.600	0.102	0.008	0.290	18.2 ± 0.8
TS1,68–Area 2–spot 2	0.488	0.147	0.027	0.338	8.0 ± 1.1
TS1,68–Area 2–spot 3	0.423	0.308	0.041	0.228	6.4 ± 1.2
TS1,68–Area 2–spot 4	0.608	0.095	0.008	0.289	22.1 ± 1.3
TS1,68–Area 3–spot 1	0.479	0.144	0.028	0.349	11.6 ± 1.5
TS1,68–Area 4–spot 1	0.495	0.138	0.020	0.347	12.9 ± 1.1
TS1,68–Area 5–spot 1	0.911	0.033	0.001	0.055	23.2 ± 1.3
PTS,85–Area 4–spot 1	0.470	0.144	0.034	0.352	12.8 ± 0.7
PTS,85–Area 4–spot 2	0.458	0.168	0.033	0.341	10.0 ± 0.8
PTS,85–Area 5–spot 1	0.445	0.160	0.030	0.365	12.0 ± 0.8
PTS,168–Area A–spot 1	0.476	0.148	0.026	0.350	10.6 ± 0.8
PTS,168–Area A–spot 2	0.654	0.081	0.005	0.260	25.3 ± 0.8
PTS,168–Area D–spot 1	0.468	0.224	0.035	0.273	7.0 ± 0.9
PTS,168–Area D–spot 2	0.314	0.499	0.073	0.114	10.0 ± 1.4
PTS,168–Area D–spot 3	0.319	0.480	0.064	0.137	5.4 ± 0.8

*Chemical compositions are reported as mole fraction of cations in carbonate.

5. RESULTS

The chemical and oxygen isotopic compositions of eighteen spots in eight occurrences of ALH84001 carbonates are reported in Table 1. We analyzed a wide range of carbonate compositions from Mg-bearing ankerite to nearly pure magnesite (Fig. 2). The $\delta^{18}O$ values are plotted against cation content of the carbonate in Fig. 3.

The measured $\delta^{18}O$ values range from +5.4 ± 0.8‰ to +25.3 ± 0.8‰ relative to SMOW. As expected when going from bulk measurements to a microscale technique, the range of oxygen isotopic compositions we observe encompasses and expands the range measured by Romanek et al. (1994). In addition, despite significantly different analytical conditions, where the data sets overlap, our results are consistent with the ion probe measurements of Valley et al. (1997) as shown in Fig. 3. The data presented here are also in general agreement with ion probe results of Saxton et al. (1997).

6. DISCUSSION

The $\delta^{18}O$ values of carbonates in ALH84001 vary by approximately 20‰, a significantly larger range than previously reported (Valley et al., 1997; Romanek et al., 1994). These large oxygen isotopic variations are observed over small spatial scales (Fig. 4) indicating that isotopic, in addition to chemical, heterogeneity is preserved in ALH84001 carbonates (Valley et al., 1997; this study). However, the large range of carbonates analyzed in this study for the first time permits the observation of a clear correlation between the mineral chemistry and isotopic composition (Fig. 3). The Ca-rich carbonates have the lowest $\delta^{18}O$ values and the Mg-rich carbonates have the highest $\delta^{18}O$ values, with a smooth variation in between. As can be seen in Fig. 3, the previous ion probe data of Valley et al. (1997) are consistent with this observation.

Based on petrographic relationships and core-rim zoning in the rosettes, previous studies have concluded that the earliest formed carbonates are Ca-rich and as crystallization proceeds the compositions follow a trajectory toward the magnesite-siderite join and then towards the magnesite endmember (Romanek et al., 1994; Harvey and McSween, 1996; McKay and Lofgren, 1997). This same basic pattern is observed on the $\sim$10 μm scale in virtually all carbonates where zoning can be easily followed. Although our data set was acquired as distinct spots from several carbonate occurrences rather than as a single continuous zoning profile across an individual rosette, the ranges of chemical composition observed in all carbonates in ALH84001 are essentially identical suggesting that the isotopic analyses sample a representative sequence of carbonate growth. The reason that the correlation of $\delta^{18}O$ with Fe content shown in Fig. 3 is complicated is because the carbonates first increase, then decrease in Fe concentration as precipitation proceeds. Because no single chemical parameter (e.g., Ca content) changes linearly with extent of crystallization, we have no quantitative measure of $\delta^{18}O$ variation with the percentage of carbonate precipitation. Nonetheless, the correlation of oxygen isotopic compositions with mineral chemistry indicates that the isotopic record is indeed related to the extent of carbonate crystallization. Whatever processes are responsible for the carbonate formation must be consistent with this correlation between major element chemistries and oxygen isotopic compositions.

At equilibrium, the partitioning of oxygen isotopes between a carbonate mineral and the fluid from which it precipitates is a function of temperature, providing a means for determining the temperature of formation from carbonate oxygen isotopic compositions. For example, paleo-ocean temperatures can be inferred from isotopic measurements of terrestrial marine carbonates, as first suggested by Urey (1947). One difficulty with applying this technique to ALH84001 carbonates is that the isotopic composition of the co-existing fluid is unknown. In some cases this problem can be circumvented by analyzing the isotopic compositions of two minerals which simultaneously equilibrated with the fluid, so-called mineral pair thermometry.

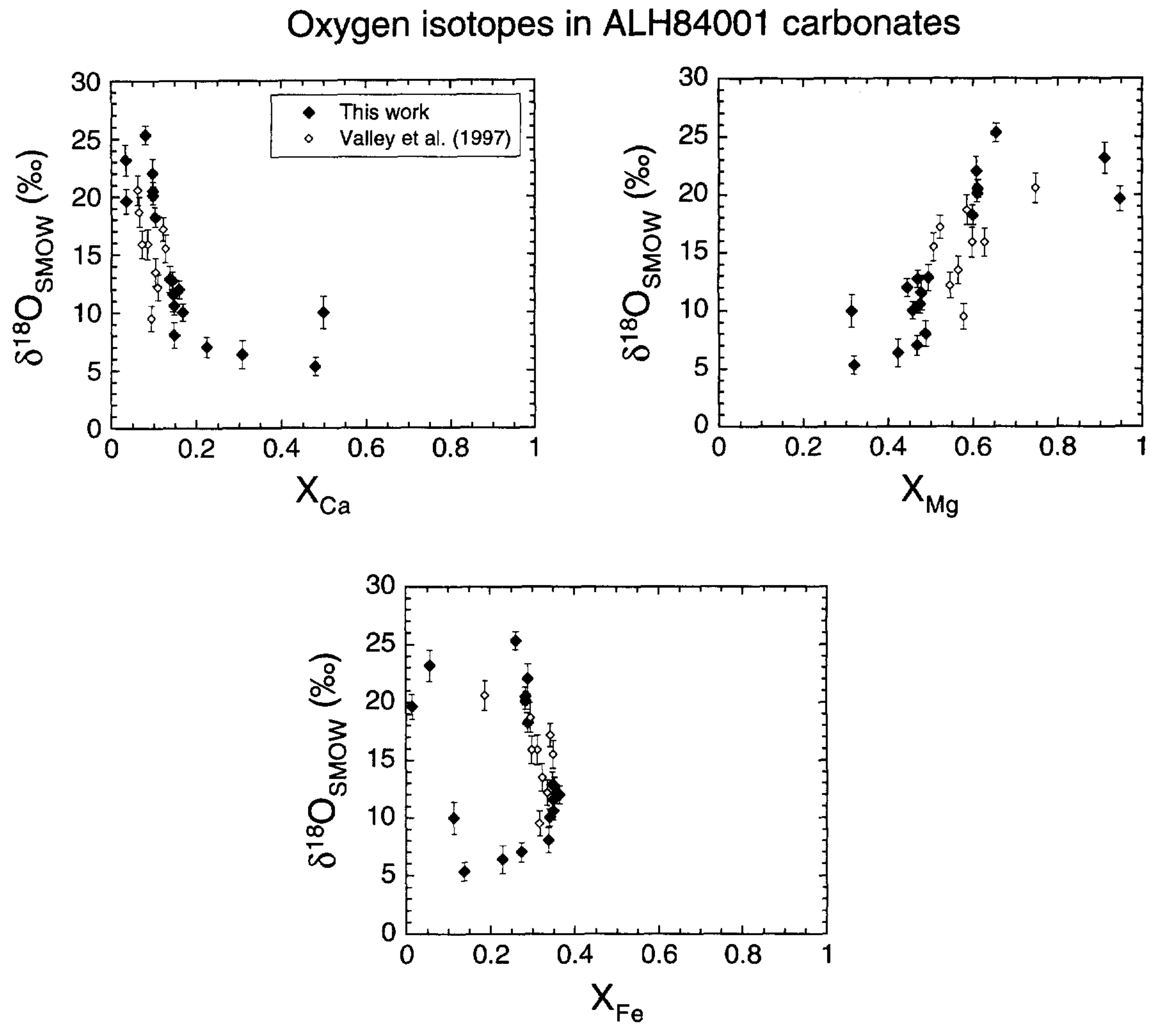

Fig. 3. Oxygen isotopic compositions of ALH84001 carbonate as a function of major element composition (displayed as cation mole fraction). Filled symbols are data from this work, and open symbols are from the recent ion microprobe study of Valley et al. (1997). The $\delta^{18}O$ values are correlated with extent of carbonate crystallization, with the Ca-rich, Mg-poor, early-forming carbonates having lower $\delta^{18}O$ values than the Ca-poor, Mg-rich, late-forming carbonates.

However, in the case of ALH84001, the heterogeneous compositions of the carbonates clearly precludes application of such an approach.

The existence of isotopic (and chemical) zoning sets some constraints on the thermal environment experienced by the carbonates in ALH84001. Primary isotopic zoning will be relaxed by diffusive exchange following carbonate precipitation; however, because oxygen self-diffusion rates are slow at all temperature-time histories considered plausible for carbonate formation, this has a minor effect. For example, at 500°C, the characteristic time for diffusive equilibration of oxygen isotope heterogeneities across distances of ~50 μm is of order 10^3 yr under hydrous conditions or 10^9 yr for water-absent conditions (Farver, 1994). Thus, while the preservation of isotopic zoning indicates that the carbonates could not have formed in a prolonged high temperature event, it does not provide a means for ruling out high temperatures for short time periods. Chemical zoning has been documented at the micron scale in the carbonates; however, this does not currently provide quantitative thermal constraints since the data on cation diffusion in carbonates similar to those in ALH84001 are limited. Nonetheless, the existing diffusion data (Ca in calcite) indicates that chemical homogenization would occur more slowly than oxygen isotopic equilibration over the temperature range of interest (Farver and Yund, 1996).

Despite the complications discussed above, oxygen isotopic data may be used to constrain the environmental conditions under which the carbonates in ALH84001 formed. Under the assumption that local isotopic equilibrium is maintained, the isotopic zoning preserved in the carbonates implies systematic changes in temperature and/or fluid isotopic composition during carbonate precipitation. In this case, the isotopic composition of the forming carbonate is governed by the equilibrium fractionation factor between fluid and carbonate. While kinetic isotope fractionation effects cannot be ruled out, it is not clear why such effects would result in a correlation with mineral chemistry and, as shown below, they are not required to explain the isotopic observations.

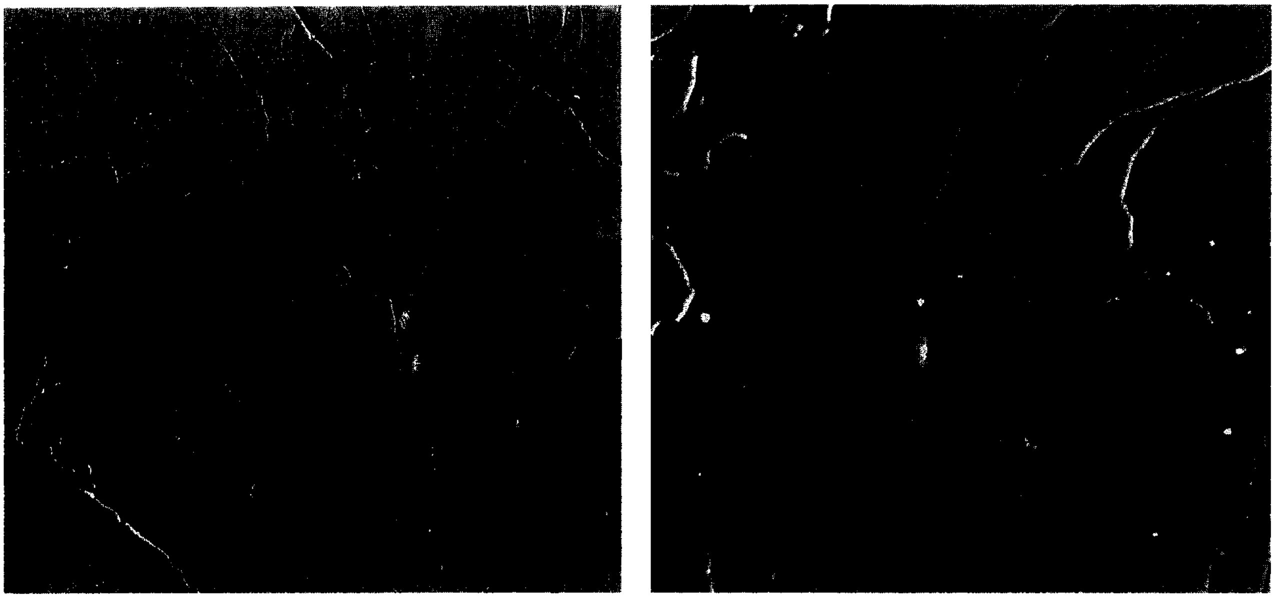

Fig. 4. Scanning electron microscope backscattered electron images of two carbonate occurrences in ALH84001. The host orthopyroxene is also indicated (opx). Each of the five ion microprobe pits shown is marked with the $\delta^{18}O$ value of the analyzed carbonate. The images show the small (~15 μm), shallow (~1 μm) ion microprobe analysis pits and demonstrate the small-scale isotopic heterogeneity of the ALH84001 carbonates.

We have explored two possible scenarios (modeled as open- and closed-systems) each of which can explain the variation of $\delta^{18}O$ values we observe, with the early carbonates having $\delta^{18}O$ values as low as +6‰ and the fairly smooth variation of the values to +25‰. Although the data are not sufficient to allow us to eliminate either model as a possible mode of carbonate formation, each scenario has important implications for the petrogenetic history of ALH84001 and in turn for the suggestion that features associated with the carbonate are biogenic in origin (McKay et al., 1996).

7. OPEN-SYSTEM MODEL

In an open-system scenario, the fluid from which carbonates are formed is considered to be an infinite reservoir. In other words, this is a fluid-rich environment such that the formation of carbonate does not affect the isotopic composition of the remaining fluid reservoir. The large variation in $\delta^{18}O$ values in an open-system model must, therefore, be due to changes in temperature. It was utilizing such a model, with several assumptions (further discussed below), that Romanek et al. (1994) calculated a temperature range of 0-80°C for ALH84001 carbonate formation. Valley et al. (1997) considered only open-system models and argued that the large variation in $\delta^{18}O$ observed by them and Romanek et al. (1994) were inconsistent with formation of the carbonates at the high temperatures (>600°C) indicated by the cation chemistries (Harvey and McSween, 1996). Indeed, in a fluid-rich environment, considering the temperature dependence of the carbonate-water isotopic fractionation factor (Friedman and O'Neil, 1977), the range of measured $\delta^{18}O$ values indicates that some of the carbonate must have formed at temperatures well below 600°C. However, the data also require substantial temperature variations.

Attempts at converting the observed isotopic compositions into quantitative temperature estimates are frustrated by the lack of direct information about the isotopic composition of the fluid from which the carbonates formed. Thus, the only way to proceed is to make some assumptions about the isotopic composition of the fluid. Romanek et al. (1994) chose to follow the lead of an earlier model proposed by Clayton and Mayeda (1988) to explain the isotopic composition of carbonates from Martian meteorite EET79001. In this model, carbonates are formed from a mixed H_2O/CO_2 fluid assumed to be in equilibrium with Martian basalt at magmatic temperatures, and in which the H_2O and CO_2 subsequently equilibrated with each other to the lower temperatures at which carbonates were precipitated. However, the carbonates in ALH84001 probably formed hundreds of millions or perhaps billions of years after their mafic host rock (Knott et al., 1995; Ash et al., 1996; Wadhwa and Lugmair, 1996), and the evolution of Martian fluid reservoirs during this interval is not well constrained. For example, other light elements, such as C and H, are thought to have undergone isotopic modification after degassing due to preferential loss of light isotopes from the Martian atmosphere (e.g., Bjoraker et al., 1989; Jakosky, 1991). Although the oxygen isotopic composition of the Martian atmosphere is not well known, considering possible Martian atmospheric evolution, Hutchins and Jakosky (1997) assumed an atmospheric $\delta^{18}O$ value of +20‰ and revised the temperature estimates of Romanek et al. (1994) up to 40-250°C.

In spite of the uncertainties regarding fluid composition inherent in the open-system model, we can use the same approach as Romanek et al. (1994) to derive a range of temperatures of carbonate formation. We observe a wider range of $\delta^{18}O$ values, thus a wider range of temperatures is implied. The results of our re-evaluation of the Romanek et al. (1994) model

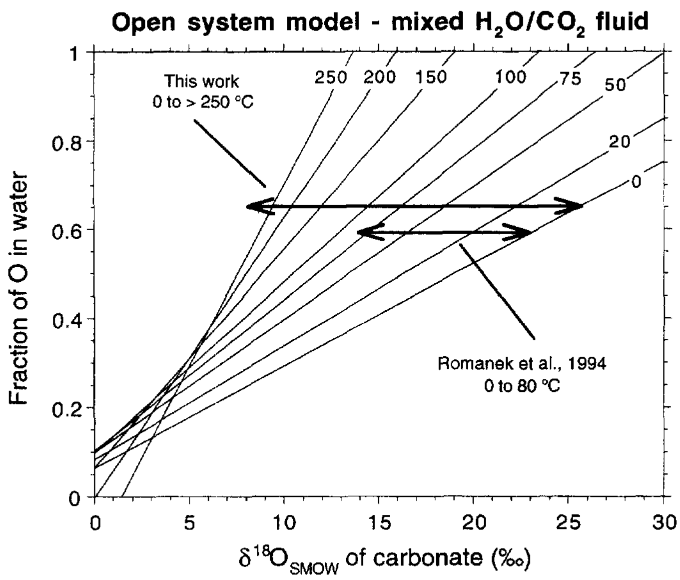

Fig. 5. Extension of an open-system model for ALH84001 carbonate formation after Romanek et al. (1994). Isotherms are calculated following the method of Clayton and Mayeda (1988) and show the isotopic composition of carbonate produced at a given temperature (°C) and H_2O:CO_2 ratio (displayed here as the fraction of O in water). Given the assumptions of the model discussed in the text, Romanek et al. (1994) derived the temperature range of 0-80°C (shown on the figure) for precipitation of ALH84001 carbonates by assuming that the calculated $\delta^{18}O$ value of their Mg-rich endmember was produced at 0°C in order to determine the H_2O:CO_2 ratio in the fluid. The $\delta^{18}O$ value of their calculated Ca,Fe-rich endmember then constrains the high temperature end of the range. The longer arrow shows the range of carbonate isotopic compositions measured by ion probe. The model fluid has a slightly higher H_2O:CO_2 ratio, and the temperature range implied is over 250°C. The value of 250°C represents a lower limit because the isotopic fractionation factors involved in the calculation of the isotherms become less sensitive to temperature changes at higher temperatures.

are shown in Fig. 5. In such a model, the carbonate with the highest $\delta^{18}O$ value is assumed to have formed at 0°C, and this constrains the H_2O/CO_2 of the fluid. The temperature range is then derived from the variation in the $\delta^{18}O$ values. As seen in Fig. 5, a temperature range of more than 250°C is required to explain all of the carbonate isotopic compositions in an open-system with this fluid composition. The first carbonates to form (with the lowest $\delta^{18}O$ values) do so at the highest temperatures implied, and as temperature drops, further crystallization produces carbonate with higher $\delta^{18}O$ values. Temperatures >250°C clearly are necessary; however, the highest temperatures indicated in this model are not very well constrained and could be even higher due to the decreasing sensitivity of the carbonate-water fractionation factor to changes in temperature at higher temperatures.

Another approach to modeling the temperature in the open-system environment is to hypothesize that the carbonates formed from a nearly pure aqueous fluid (i.e., a fluid where $H_2O/CO_2 >> 1$). In this case, two extremes can be considered. If the isotopically heaviest carbonates are assumed to have formed at 0°C (the most optimistic case for a biological environment), then the $\delta^{18}O$ of the water would be approximately −9‰ and the temperature variation required is 0-125°C (Fig. 6, curve A). Alternatively, if the isotopically lightest carbonate is assumed to have formed in equilibrium with host orthopyroxene, corresponding to a $\delta^{18}O$ of water of ~+6‰, then temperatures of >800°C are implied, and subsequent cooling to temperatures below 100°C during precipitation would be required to account for the isotopically heavy carbonates (Fig.

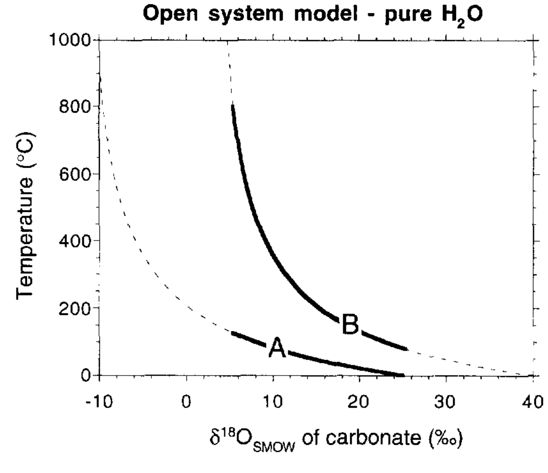

Fig. 6. Temperature ranges required for formation of the ALH84001 carbonates from a pure H_2O fluid in an open-system model are shown for two extreme cases. Curve A shows the $\delta^{18}O$ value of carbonate formed in equilibrium with water where the highest measured $\delta^{18}O$ value (+25‰) is produced at 0°C. Curve B shows the case where the carbonate with the lowest $\delta^{18}O$ formed in isotopic equilibrium with the host orthopyroxene, suggesting temperatures of at least 800°C. Calcite-water fractionation factors are from Friedman and ONeil (1977). The bold portions of the curves correspond to the range of measured $\delta^{18}O$ values of ALH84001 carbonates (Table 1). Curve A suggests a temperature variation of 0-125°C, and curve B implies variation from 80 to 800°C would be necessary to produce the range of $\delta^{18}O$ values we observe. Thus, in all cases, significant temperature variation and temperatures below 100°C are required to explain the isotopic data within the context of an open-system model.

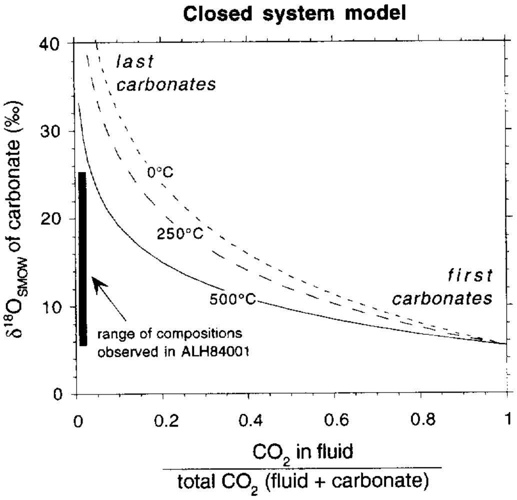

Fig. 7. Isotopic composition of carbonates crystallized from a limited amount of CO_2 for three different temperatures. The initial carbonate is fixed in the calculation to have $\delta^{18}O = +5.4$‰, the lowest value measured in ALH84001 carbonates, and crystallization proceeds from right to left on the diagram. This closed-system model is capable of reproducing the range of isotopic compositions measured (shown on the figure by the black bar) and also qualitatively matches the observation of isotopic variation with degree of crystallization because the $\delta^{18}O$ value of the carbonates is predicted to increase as the carbonates are deposited. The range of values observed in the ALH84001 carbonates can be reproduced even at relatively high temperatures in a closed-system model.

6, curve B). Finally, precipitation from CO_2-rich fluids is not feasible in the open-system model because the variation of the carbonate-CO_2 fractionation factor for oxygen is not large enough to produce the variations in $\delta^{18}O$ values we observe over any range of temperatures (Chacko et al., 1991).

To summarize, an open-system, fluid-rich environment requires low but changing temperatures and water-rich fluids in order to explain the isotopic variation observed. The temperatures implied are model-dependent, but must vary by between 125 and >250°C. Because larger variations in $\delta^{18}O$ values may be found if still smaller regions of carbonate could be analyzed (we are still averaging the $\delta^{18}O$ values over our ~15 μm analysis spot), all of the temperature ranges discussed above must be considered lower limits.

8. CLOSED-SYSTEM MODEL

In a closed-system a model, the amount of fluid is limited so that the fluid composition changes as a result of carbonate formation. For example, at 500°C, calcite forming from CO_2 will have a $\delta^{18}O$ value about 6‰ lower than the CO_2, as dictated by the calcite-CO_2 fractionation factor (Chacko et al., 1991). The remaining fluid is thus depleted in ^{16}O relative to ^{18}O as the carbonate forms, and if the fluid remains isotopically well-mixed, the next carbonate to crystallize will have a slightly higher $\delta^{18}O$ value. This is a Rayleigh process and can be modeled at a given temperature (e.g., Faure, 1986) if the carbonate-CO_2 fractionation factor and initial fluid composition are known. In principle, either a kinetic or equilibrium fractionation factor can govern the isotopic distribution produced in the Rayleigh process. In this model, we have taken equilibrium fractionation factors from Chacko et al. (1991) and require that the initial fluid must produce the lowest $\delta^{18}O$ carbonate (+5.4‰) at a designated temperature. The observation that the earliest carbonates have the lowest $\delta^{18}O$ values is reproduced only if the fluid is CO_2-rich, because precipitation from water-rich fluids would drive the later carbonates to lighter $\delta^{18}O$ values as crystallization proceeds. Thus, we have assumed a pure CO_2 fluid and have used the calcite-CO_2 fractionation factor because relevant isotopic partitioning data for other carbonate compositions have not been experimentally determined.

The results of the closed-system modeling are displayed for three hypothetical temperatures in Fig. 7. This figure shows the variation in $\delta^{18}O$ value of the carbonate as crystallization proceeds (from right to left in the diagram) and clearly demonstrates that it is possible in a closed-system environment to produce the range in oxygen isotopic values observed at a range of temperatures, including relatively high temperatures of >500°C. Therefore, it is incorrect to conclude that isotope variation necessarily requires low temperatures. However, the model is relatively insensitive to temperature so that a thermal history in which the temperature was falling from above 500°C during the closed-system crystallization process would still be consistent with the isotopic data. As noted above, post-crystallization isotopic redistribution by diffusion does not rule out temperatures considered in this scenario because equilibration times are long at the relevant temperatures (Farver, 1994). In principle, the preservation of metastable carbonate compositions within the ankerite-magnesite solvus may provide time-temperature constraints, but the kinetics of the decomposition reactions are not known. Mineralogical considerations (Valley et al., 1997) may imply that if carbonate crystallization took place at relatively high temperatures, then the time scales involved must have been rapid, perhaps as short as minutes to hours.

The calculated endmembers derived from the bulk carbonate carbon isotopic data of Romanek et al. (1994) suggest that the $\delta^{13}C$ values of the carbonates increase as crystallization proceeds. If the closed-system model is correct, the change in sign of the carbonate-CO_2 fractionation factor near 200°C (Chacko et al., 1991) indicates that temperatures higher than this are needed. Romanek et al. (1994) recognized this possibility but rejected a closed-system model, concluding that such temperatures were "perhaps rather high for near-surface aqueous processes on Mars." In contrast to Romanek et al.(1994), we conclude that there is no justification for dismissing a closed-system model based on the available data.

In a closed-system crystallization process, the bulk isotopic composition of the carbonates equals that of the initial fluid. Thus, in principle, given this bulk composition and that of the first carbonate to crystallize, a temperature estimate may be made. In the case of ALH84001, however, the bulk $\delta^{18}O$ of carbonate is not known with sufficient accuracy to derive a meaningful temperature estimate. For example, acid dissolution data yield values of bulk $\delta^{18}O$ that differ by nearly 3‰ (Romanck et al., 1994; Jull et al., 1995), possibly because of the long times needed to obtain accurate isotopic analyses of magnesites and siderites by this technique (Al-Aasm, 1990), or because of the difficulties in obtaining a representative sample.

Additionally, it is likely that calcite was the earliest phase to crystallize, but we have not yet analyzed any carbonate of this composition due to its rare occurrence.

In summary, the closed-system, fluid-poor model can reproduce the range of $\delta^{18}O$ values observed, even at relatively high temperatures. In this model, the carbonates are formed from a limited amount of CO_2-rich fluid, with the variation in $\delta^{18}O$ values produced by a Rayleigh fractionation process. Such a closed-system model of carbonate crystallization is consistent with a geological environment of the type discussed by Scott et al. (1997) involving small-scale mobilization and redeposition of pre-existing carbonates in the parent-rock during a shock event.

9. IMPLICATIONS FOR BIOGENIC ORIGIN OF FEATURES IN ALH84001

Although the currently available isotopic data cannot be used to exclude either of the two possible models discussed above, we can examine the implications that each scenario would have for the hypothesis of McKay et al. (1996) that ALH84001 contains within the carbonates evidence of ancient life on Mars. In assessing possible biological environments on Mars, we restrict our view to the one example of biological systems that we know of: Earth-based life.

One of the arguments discussed by McKay et al. (1996) was their assertion that the carbonates formed at temperatures consistent with biological activity on Earth in a water-rich environment (also a necessity for life). However, this interpretation of the 0-80°C results of Romanek et al. (1994) is misleading in that they imply that the calculated temperature range brackets a fairly constant ambient temperature. Our results, within the context of an open-system model, clearly indicate that systematic temperature variations are required to precipitate ALH84001 carbonates and that the oxygen isotope data do not reflect an error around some central temperature. Studies of the distributions of alleged biogenic minerals were used to suggest that the same population of microorganisms is present throughout the growth-cycle of carbonate, from core to rim (McKay et al., 1996; Thomas-Keprta et al., 1997). For example, although many features described by McKay et al. (1996) are found in the globule rims, a chain of magnetites, specifically compared to terrestrial magnetosomes produced by magnetotactic bacteria, was reported within the interior of a globule, in the Ca,Fe-rich orange carbonate (Thomas-Keprta, 1997). Although terrestrial extremophile microorganisms can adapt and live in conditions with temperatures as high as ~110°C or as low as roughly 0°C, no known single organism lives in an environment where they are subjected to temperature swings covering this entire temperature range (Yayanos, 1995; Stetter, 1996; Trent, 1996). Thus, although in some cases the open-system scenario does indicate temperatures that overlap those in which life is known to operate, the temperature ranges required exceed even those which the most extreme extremophiles are likely to tolerate.

The implications of our closed-system model for possible biogenic activity are straightforward; with its CO_2-rich (essentially anhydrous) fluids and possible high temperatures, it operates far outside the boundaries of known biological systems. Thus we conclude that none of the environments which can reasonably explain the regular variation of the observed isotopic values is consistent with a biological origin for features associated with the carbonates.

10. CONCLUSIONS AND FUTURE WORK

We have performed in situ oxygen isotopic measurements of a wide range of ALH84001 carbonates, both from globules and from other types of occurrences, covering the major element compositional range from ankerite to magnesite. The $\delta^{18}O$ values are highly variable, ranging from +5.4 to +25.3‰, and are correlated with the major element compositions, such that the earliest-forming, Ca-rich carbonates have the lowest $\delta^{18}O$ values and the Mg-rich, late-forming carbonates have the highest $\delta^{18}O$ values.

Two possible models are presented which can explain the isotopic variations; however, more information is needed in order to distinguish between the models. On the one hand, the isotope data can be explained by low, but highly variable temperature in an open-system, water rich environment in which case the lower limit to the temperature variation implied is ~125°C, with variations of over 250°C possible within the constraints of this assumption-dependent model. Alternatively, the data can be explained by a closed-system model in which the carbonates precipitate from a limited amount of CO_2-rich fluid. This scenario can produce the isotopic variation observed over a range of temperatures, including relatively high temperatures (>500°C). We conclude that neither of these environments is suitable for biological activity and thus suggest that features associated with the carbonates that have been interpreted to reflect biological activity (McKay et al., 1996) were in fact formed by inorganic processes. In particular, our study, when combined with the observations of Bradley et al. (1996), Scott et al. (1997), and McKay and Lofgren (1997) suggest that the hypothesis involving deposition of the observed carbonates during a shock event (Scott et al., 1997) warrants additional study.

Further work is needed to fully explore the implications of the preserved isotopic record of environmental conditions experienced by ALH84001 in its complicated history. In particular, microscale carbon isotopic analysis of the carbonates, when correlated with mineral chemistry and oxygen isotopes, could help distinguish between the possible scenarios presented here. In addition, an assessment of the oxygen isotopic heterogeneity of the feldspathic glass and silica occurrences in ALH84001 would be valuable. Finally, determinations of carbonate-fluid isotopic fractionation factors as well as oxygen and cation diffusion rates in carbonates of major element chemistries similar to those in ALH84001 are needed in order for accurate constraints to be placed on the environmental history of this important Martian sample.

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