

Cation diffusion in calcite: Determining closure temperatures and the thermal history for the Allan Hills 84001 meteorite

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Abstract—The presence of zoned Fe, Mg, Ca, and Mn in the carbonate phases associated with the cracks and inclusions of the Allan Hills (ALH) 84001 meteorite provides evidence for constraining the thermal history of the meteorite. Using self- and tracer-diffusion coefficients obtained from laboratory experiments on natural calcite, cooling rates are calculated for various temperatures and diffusion distances to assist in the evaluation of the compositional zoning associated with the carbonate phases in ALH 84001. The closure temperature model provides the average temperature below which compositional zoning will be preserved for a given cooling rate, that is, the temperature at which diffusion will be ineffective in homogenizing the phase. The validity of various theories for the formation of the carbonate globules may be examined, therefore, in view of the diffusion-limited kinetic constraints. Experiments using a thin film-mineral diffusion couple and ion microprobe for depth profiling analysis were performed for the temperature range of 550–800 °C to determine self- and tracer-diffusion coefficients for Ca and Mg and in calcite. The resulting activation energies for Ca ($E_a(\text{Ca}) = 271 \pm 80$ kJ/mol) and for Mg ($E_a(\text{Mg}) = 284 \pm 74$ kJ/mol) were used then to calculate a series of cooling rate, grain size, and closure temperature curves. The data indicate, for example, that by the diffusion of Mg in calcite, a 10 μm compositional zone would be completely homogenized at a temperature of 300 °C for cooling rates <100 K/Ma. These data provide no constraint on formation models that propose a low-temperature fluid precipitation mechanism; however, they indicate that the carbonate globules were not exposed to a high-temperature environment for long time scales following formation.

INTRODUCTION

Numerous uncertainties surround the scientific interpretations of the microscopic and mineralogical features of the Allan Hills (ALH) 84001 Martian meteorite collected in Antarctica. Specifically, there is much debate on the mode of occurrence of carbonate "globules" of varied composition and the thermal history of the rock after its formation (e.g., Harvey and MacSween, 1996; Leshin *et al.*, 1998). Further research of these areas is critical for supporting or refuting the various theories of the genesis of the microstructural features of the ALH 84001 meteorite. Of particular interest in the mineralogy of the meteorite are the compositionally zoned carbonate phases (Treiman, 1995). The event during which the carbonates formed may be associated with the features that are possibly of biological origin (e.g., Romanek *et al.*, 1994; McKay *et al.*, 1996). The carbonate compositions of the carbonate phases are less common than those in terrestrial rocks, bearing components that are consistent with calcite (CaCO_3), the less terrestrially common magnesite (MgCO_3), as well as those carbonates containing the multivalent cations, rhodochrosite (MnCO_3) and siderite (FeCO_3) that are associated with reducing conditions. The thermal history of the meteorite and the included carbonate phases has been examined by several different analytical approaches. Kirschvink *et al.* (1997) using the remnant magnetization of pyroxene phases near (and predating) the carbonates determined that the carbonates must have formed at low temperatures. Valley *et al.* (1997) showed that the C and O isotope signatures of the carbonate phases offered no evidence of a high-temperature formation. In contrast, Leshin *et al.* (1998), also using O isotopes, interpreted carbonate formation to occur no lower than 125 °C but as high as 500 °C and, therefore, suggested a nonbiological origin.

The assemblage of carbonates observed for the ALH 84001 meteorite is formed as a stable assemblage only at high temperatures

(e.g., Harvey and McSween, 1996). In addition, work by Scott *et al.* (1997) indicates that the complex carbonate, plagioclase, and silica breccia found in the pyroxene cracks are the result of local melting during a shock event. If the carbonate phases were formed at high temperatures, they must have cooled at a rate that is consistent with the preservation of the assemblage to the lower temperatures. A minimum cooling rate can be derived from knowledge of the kinetics of diffusion and the laboratory measurements of cation diffusion rates in carbonates. The diffusion rates of cations in carbonate minerals can be used to help constrain the thermal conditions expected during the formation and subsequent thermal history of the ALH 84001 Martian meteorite. Since homogenization of the carbonate globules can occur by lattice diffusion of cations at elevated temperatures, the extent being a function of diffusion distance and diffusion coefficient for a given temperature, one can examine the measured compositional zoning patterns of the carbonate phases to see how the profiles might be preserved or modified.

Cooling histories of rocks can be quite complex and require appropriate diffusion models in order to correctly interpret the compositional zoning patterns. Dodson (1973), for example, derived an approximation for the relationship between cooling rate, grain size, and closure temperature for evaluating thermally activated diffusion processes in geological systems. The fundamental equation for the model can be solved in an iterative fashion to provide a series of closure temperatures as a function of cooling rate and grain radius. The closure temperature represents the weighted average temperature below which a nonequilibrium cation zoning pattern is essentially frozen or preserved. The Dodson model includes the assumption that the system under consideration cools to a temperature low enough that diffusion is no longer significant over the remaining life of the system. More sophisticated treatments of cooling models have been derived for modification of equilibrated high-temperature assem-

blages (Ehlers and Powell, 1994) and for the homogenization of orthopyroxene overgrowths (Ganguly *et al.*, 1994). The homogenization of compositional zoning of minerals in meteorites as a method of determining thermal histories was studied by Ganguly *et al.* (1994) using experimental cation exchange rates for Fe/Mg zoning to evaluate the overgrowths of the orthopyroxenes.

The complex and fine interzoning of cations in the carbonate phases of the ALH 84001 meteorite has not been unambiguously identified yet as resulting from a diffusional process. Therefore, the main impetus for the present study is to evaluate the possible temperatures and thermal histories that may have influenced the compositional zoning. In this effort, the cooling rate model from Ganguly *et al.* (1994) is employed to determine the thermal and spatial constraints for the effects of cation diffusion to be observed. The asymptotic cooling model assumes the inverse of the temperature T increases linearly with time t :

$$\frac{1}{T} = \frac{1}{T_o} + \eta t \quad \text{Eq. (1)}$$

where η is a time constant related to the cooling rate. The linear cooling rate dT/dt can be given, therefore, by the following approximation:

$$\frac{dT}{dt} \cong - \frac{D(T_o)RT_c^2}{E_a x^2} \quad \text{Eq. (2)}$$

where D is the diffusion coefficient at the initial temperature (T_o), R is the gas constant, T_c is interpreted at the closure temperature, E_a is the activation energy for diffusion, and x is the distance over which diffusion has occurred.

The homogenization of adjacent phases of the same mineral phase with different cation compositions may be accomplished, in the absence of a fluid phase, by the solid-state diffusion of cations through the lattice. The diffusion of C and O in calcite has been previously studied by several workers (Haul and Stein, 1955; Anderson, 1969; Kronenberg *et al.*, 1984) and the diffusion of Ca in a few recent studies (Farver and Yund, 1996). Diffusion mechanisms in minerals are controlled by either intrinsic (where the point defect concentration is thermally controlled) or extrinsic processes. In the latter case, the activation energy for diffusion is somewhat smaller due to the presence of impurities that fix the amount of point defects (*e.g.*, cation vacancies) available by which cation migration may occur. While intrinsic diffusion mechanisms dominate at higher temperatures, the diffusion at lower temperatures is extrinsically controlled by the preexistence of the point defects. In order to address the homogenization of the zoned ALH 84001 carbonates, it is important to determine diffusion rates at experimental temperatures as low as possible given the limitations imposed by the duration of the laboratory diffusion anneals. In addition, experiments using isotopic tracers typically measure self-diffusion rates for those ionic species in the mineral phase; while the problems addressed in this study are related to interdiffusion of cations, in which there is a gradient in the chemical potential of the diffusing species.

EXPERIMENTAL APPROACH

Unfortunately, few experimental data exist for the diffusion of cations in carbonate minerals that can be directly applied to the determination of closure temperatures. However, the experimental approach that uses a thin film-mineral diffusion couple provides an accurate means of obtaining relatively low-temperature diffusion data for cations in minerals. The technique is briefly discussed here;

however, the studies of Schwandt *et al.* (1993, 1998) present considerable detail of the experimental technique. The calcite samples used in the diffusion experiments included natural clear single crystals from Chihuahua, Mexico. Electron microprobe analysis of over 200 points on these samples indicate a composition equal to CaCO_3 with 0.25 wt% MgO, 0.02 wt% MnO, no detectable SrO, and 0.02 wt% FeO.

A thin film ($\sim 1000 \text{ \AA}$) coating of an isotopically enriched oxide was deposited in a high vacuum onto a cleaved (104) surface of the calcite samples by resistively heating a W crucible containing either MgO (enriched 98.8% in the ^{25}Mg isotope) or CaO (enriched 98.5% in the ^{44}Ca isotope). The calcite samples were then annealed in 1 atm of pure CO_2 for ~ 24 to 4000 h at temperatures from 500–800 °C. According to Goldsmith (1959), this temperature range is within the stability field of calcite at 1 bar CO_2 . However, all samples were optically examined following the diffusion anneal and, in almost all experimental runs, no sign of decomposition of the calcite to $\text{CaO} + \text{CO}_2$ was observed. Decomposition was observed following one experiment in which the CO_2 supply was depleted and another experiment performed at 900 °C as a test of the calcite stability field. Farver and Yund (1996) observed no crystallographic anisotropy for diffusion of Ca in calcite; therefore, only diffusion normal to the cleavage (104) surface of calcite was examined in the present study.

Following the annealing experiments, diffusion samples were analyzed using a Cameca IMS 4f ion microprobe with a 50 or 100 nA and negatively charged O primary beam accelerated at 12.5 V, 45 μm spot size, and 250 μm raster. Depth profiles of counts/s vs. analysis time were obtained for various secondary ions and normalized to ^{40}Ca . An example of the microprobe intensity (secondary ion concentration) as a function of analysis cycle for a Ca self-diffusion run is shown in Fig. 1. The plot clearly exhibits the diffusional penetration of ^{44}Ca into the bulk calcite along with the exchange and diffusion of ^{40}Ca out to the thin film. Cations ^{42}Ca and ^{24}Mg also show slight diffusional zoning near the calcite surface but are secondary effects being several orders of magnitude less intense. It was not possible to remove the isotopically enriched surface layer for these experiments, as some previous workers have done (*e.g.*,

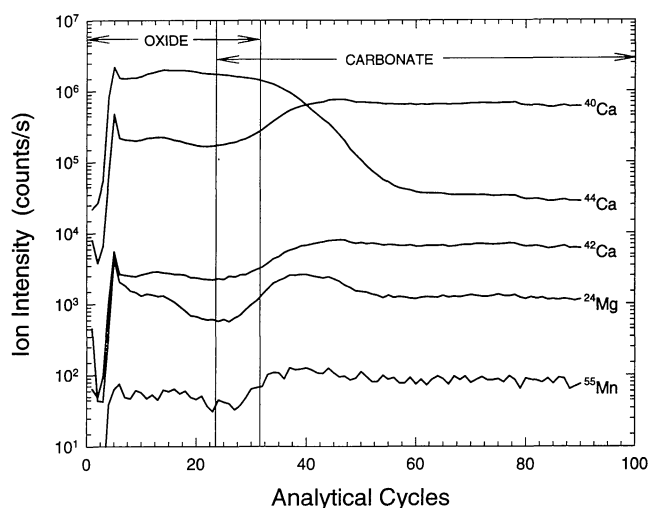


FIG. 1. Ion microprobe analysis of various isotopes as a function of analysis cycle (time) in a calcite diffusion sample, which was initially coated with an isotopically enriched ^{44}Ca tracer film and annealed at 600 °C for 912 h. The two vertical lines indicate the interface region of the diffusion couple (see text).

Schwandt *et al.*, 1993, 1995). Therefore, the depth profiles are corrected by subtracting the surface oxide layer and redesignating the surface of the carbonate as $x = 0$. Sputtering through an interface using an ion microprobe introduces some analytical "smearing" of the interface. To determine the significance of these undesirable artifacts, sets of diffusion experiments were performed for different anneal durations at several temperatures. No time dependence beyond the uncertainty in the diffusion coefficient was observed. In addition, zero-time experiments were performed and indicate that the analytical "smearing" or convolution effect extends $\sim 50 \text{ \AA}$ into the carbonate. Because of this effect, the penetration of the diffusion tracer at very low temperatures ($< 550 \text{ }^\circ\text{C}$) is beyond the analytical capability of the ion microprobe.

In previous experiments using this techniques (*e.g.*, Schwandt *et al.* 1998), the location of the interface has been determined by obvious discontinuities in the ratio of minor elements to major elements. Such sharp discontinuities were rarely observed in the present study. The position of the interface between the mineral and the oxide coating was identified by a number of qualitative factors, including the initial point of increase of ^{12}C relative to the normal calcite composition and the location of the maximum tracer isotope concentration. Because the diffusion coefficient calculated using an analytical error function (see below) is dependent on the curvature of the diffusion profile, identification of the precise position of the interface is not crucial. Nonetheless, the larger the diffusion profile that was used, the more statistically accurate the least-squares fit and diffusion coefficient that was obtained. The results presented here are calculated using the maximum isotopic composition as a consistent choice for the beginning of the diffusion profile.

The raw concentration profile (*e.g.*, Fig. 1) can be transformed to concentration *vs.* depth by multiplying the analysis time (analytical cycle) by the ion sputtering rate determined from the depth of a sputtered crater using a contact profilometer on an uncoated sample (samples are typically gold-coated prior to ion microprobe analysis to prevent surface charging). The diffusion coefficient is obtained by fitting the final diffusion profile to an error function solution to Fick's diffusion equations (Crank, 1975), dependent on surface concentration C_s , the natural concentration in the sample at infinite depth C_b , and the diffusion coefficient D . In all cases, C_b is equal (within 5%) to the natural abundance of ^{25}Mg and ^{44}Ca in the original sample of calcite as determined by the ion microprobe analysis and the known natural abundances. The variation of concentration as a function of depth x and experimental anneal time t is based on a semi-infinite model and is described by:

$$C_x = C_s + (C_b - C_s) \text{erf}(x/4Dt) \quad \text{Eq. (3)}$$

Figure 2 provides an example of the Ca diffusion profile from an experiment performed at $650 \text{ }^\circ\text{C}$ for 510 h. The profile exhibits the expected decrease of the Ca tracer (^{44}Ca) content up to a depth of $\sim 0.15 \text{ } \mu\text{m}$. The best statistical fit of the diffusion model based on Eq. (3) to the observed depth profile is also presented and suggests a Ca self-diffusion coefficient of $4.0 (\pm 2.0) \times 10^{-21} \text{ m}^2/\text{s}$, where the error in the diffusion coefficient is dominated by the uncertainty in determining the distance.

Diffusion experiments on calcite were performed for Ca from $550\text{--}660 \text{ }^\circ\text{C}$ and for Mg at temperatures from $500\text{--}900 \text{ }^\circ\text{C}$. The diffusion rates at temperatures $< 550 \text{ }^\circ\text{C}$ were too slow even for the excellent depth resolution provided by the ion microprobe. No diffusion values are reported for the Mg experiment at $900 \text{ }^\circ\text{C}$. Although the ion microprobe analysis of this sample showed the ex-

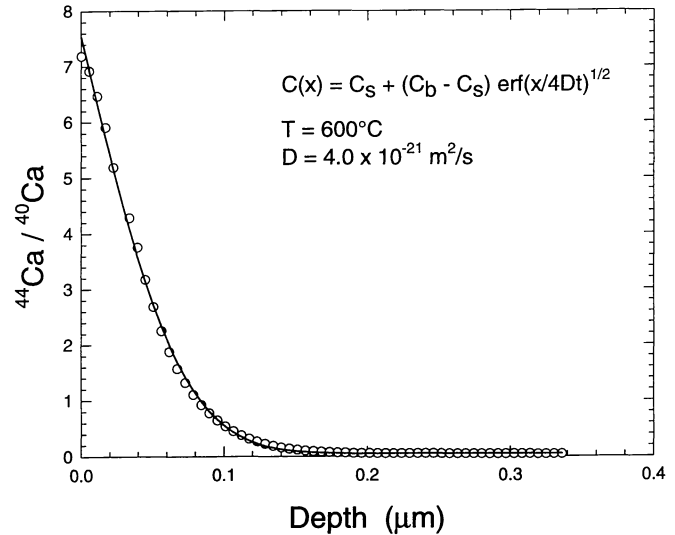


FIG. 2. Compositional profile for ^{40}Ca self-diffusion in calcite in terms of isotope ratio *vs.* depth as derived from the data of Fig. 1. A primary ion sputtering rate determined by profilometry was used to obtain the depth scale. The sample was annealed at $600 \text{ }^\circ\text{C}$ for 912 h. Best fit of the error function model to the analytical data is shown by the solid line.

pected natural Ca to C ratios for bulk calcite, the resultant zoning profiles due to enhanced transport along minute cracks were questionable. In addition, several experiments were performed on clear natural single crystals of magnesite; and although the results from the ion microprobe were reasonable in terms of composition, there was extensive cracking of the magnesite surface upon examination by optical microscope.

RESULTS AND DISCUSSION

Values for the activation energy E_a and preexponential term D_0 for the Arrhenius relation were obtained by fitting the diffusion coefficients determined at the various temperatures to the following equation:

$$D = D_0 \exp(-E_a/RT) \quad \text{Eq. (4)}$$

For Mg, tracer diffusion in calcite $\log D_0 = -3.26 \text{ m}^2/\text{s}$ and $E_a = 284 \pm 74 \text{ kJ/mol}$; while for Ca, diffusion in calcite $\log D_0 = -5.30 \text{ m}^2/\text{s}$ and $E_a = 271 \pm 80 \text{ kJ/mol}$. An Arrhenius plot exhibiting these relations for the experimental diffusion data is presented in Fig. 3. The experimental data of Kronenberg *et al.* (1984) for C diffusion and Farver and Yund (1996) for a Ca diffusion are also noted. The Ca results for the latter study were obtained at higher temperatures ($700\text{--}850 \text{ }^\circ\text{C}$) than the present study and provide an activation energy of 382 kJ/mol .

The data for Mg and Ca diffusion in the calcite lattice along with the asymptotic cooling equation of Ganguly *et al.* (1994) (Eq. (2)) were used to generate a series of temperature *vs.* cooling rate curves as a function of cation type and diffusion distance (Fig. 4). A minimum estimate of initial temperature of $500 \text{ }^\circ\text{C}$ was used in these calculations. The results indicate the temperature at which diffusion will be able to homogenize a particular distance in a zoned carbonate crystal for a particular rate of cooling. For example, a $10 \text{ } \mu\text{m}$ grain cooling at a rate of 100 K/Ma would have a uniform Mg content at $\sim 300 \text{ }^\circ\text{C}$. In contrast, a $5 \text{ } \mu\text{m}$ grain would require a cooling rate of 400 K/Ma at that temperature in order to homogenize. In general, the cooling curves for Ca fall at much higher temperatures

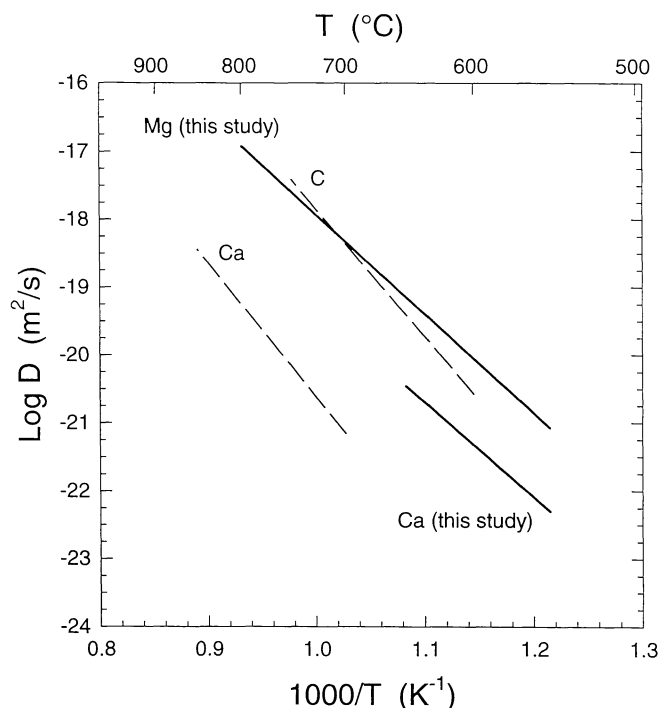


FIG. 3. Arrhenius plot of the diffusion coefficients for Mg and Ca in calcite (this study), and previous measurements of Ca diffusion in calcite (Farver and Yund, 1996) and C diffusion in calcite (Kronenberg *et al.*, 1984).

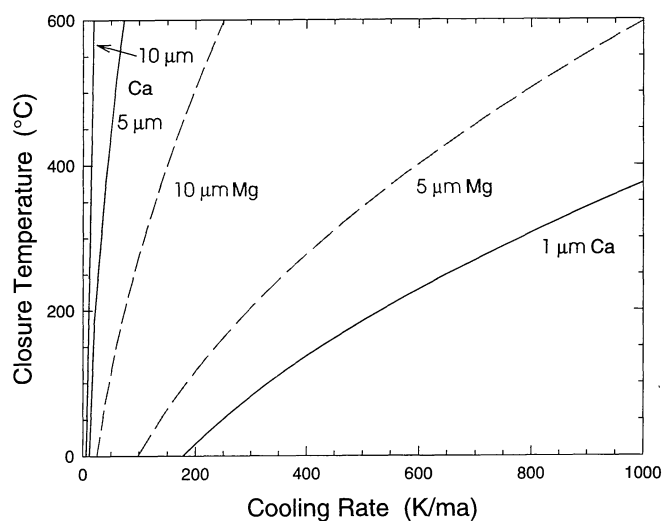


FIG. 4. Plot of the temperature required for the homogenization of the specified distance as a function of cooling rate for Ca and Mg diffusion in calcite. Calculations are based on the asymptotic cooling model using an initial temperature of 500 °C. The rate for the homogenization of Mg in a 1 μm grain is relatively fast; the temperature values fall <0 °C and are not plotted.

compared to those for Mg. This behavior is related to the slower diffusion rate for Ca and the greater difficulty in reequilibrating as the crystal is being cooled. Of interest is that the faster diffusion of Mg in calcite allows the cooling curve for the 1 μm distance to occur well below 0 °C (not plotted in Fig. 4).

If the temperature of formation of the carbonate zoning features in the ALH 84001 meteorite was >500 °C, a grain diameter (or zoning

feature in this case) of 5 μm would be completely homogenized in Mg at cooling rates from geologically extremely slow (1 K/Ma) to very rapid (800 K/Ma). The presence of fine Mg zoning on the order of 5–10 μm has been observed in the ALH 84001 carbonate phase (*e.g.*, Thomas-Kepra *et al.*, 1997). This observation constrains the closure temperature to between 350 and 450 °C for typical geologic cooling rates (<100 K/Ma). Figure 4 clearly illustrates the constraints that the detection of finer compositional zoning places on cooling rates. Even for fairly rapid cooling rates, a 1 to 10 μm nonequilibrium zone will be homogenized at temperatures >350 –400 °C.

As a necessary precursor to interpreting their studies of grain boundary diffusion, Farver and Yund (1996) measured Ca diffusion rates in natural single crystals at temperatures from 700 to 900 °C. No dependence on crystallographic orientation was observed. Using the activation energies and D_0 values reported by Farver and Yund (1996), the closure temperatures using Eq. (2) are ~ 100 degrees higher for a given cooling rate. The activation energy derived in Farver and Yund (1996) is larger than the activation energies reported here, although it is similarly based on the tolerance for the reported errors in the measurements. Another possible interpretation of the discrepancy is the lower temperature range of the experiments in this study, which indicates that perhaps a different mechanism for cation diffusion occurs at the lower temperatures. This possibility emphasizes the difficulties involved in extrapolating many hundreds of degrees in temperature in order to apply laboratory results to systems occurring at significantly lower temperatures.

The present study has directly measured the self-diffusion of Ca and the tracer diffusion of Mg in calcite. However, the chemical diffusion process that would account for the homogenization of the ALH 84001 carbonate phases is best represented by a binary diffusion coefficient where the composition of the carbonate will determine what combination of the two diffusion coefficients will dominate. For diffusion in ionic systems, the binary diffusion coefficient is given by Lasaga (1979) as:

$$D_{MgCa} = \frac{D_{Mg}^o D_{Ca}^o}{X_{Mg} D_{Mg}^o + X_{Ca} D_{Ca}^o} \quad \text{Eq. (5)}$$

where D_i^o represents the tracer (or self-) diffusion coefficient and X_i represents the cation mole fractions. Inspection of Eq. (5) suggests that the value for D_{MgCa} will be similar to D_{Ca}^o for magnesite-component-rich carbonates and D_{Mg}^o for calcite-component-rich carbonates, while intermediate carbonate compositions would be somewhere in between. The cooling rates presented in Fig. 4 provide the upper and lower compositional bounds for this analysis. Additionally, at much lower temperatures, the process of homogenization may be controlled by an extrinsic diffusion process. Some recent experiments by Cherniak (1997) have suggested smaller activation energies for diffusion of the rare earth elements in various carbonate phases. Therefore in the region of extrinsic diffusion, activation energies may be slightly lower than those reported here, and diffusion at very low temperatures may be faster than the present results would indicate. As such, the results represent a minimum cooling rate; homogenization may occur at faster rates and would require a faster cooling rate for a given closure temperature than those presented in Fig. 4.

CONCLUSION

The analysis of closure temperatures based on the available experimental cation diffusion data demonstrates that any model for the

high-temperature formation (>500 °C to 600 °C) of the carbonate assemblages associated with the ALH 84001 meteorite requires a very fast cooling rate for the preservation of compositional zoning reported in several papers describing the formation of the phases (e.g., Harvey and McSween, 1996; Scott *et al.*, 1997). The presence of extremely complex fine-scale zoning in these carbonate phases limits the closure temperature to even lower temperatures for geologically common cooling rates. A theory for the formation of the carbonate phases that postulates high temperatures must incorporate extremely rapid geologic cooling rates in order to avoid modification of the observed compositional zoning features. Low-temperature theories for formation of the zoned carbonates are unconstrained by the experimental diffusion data; crystallization from shock melting would result in rapid cooling rates that are consistent with preservation of such textures. In both cases, the cooling model requires that the carbonates do not experience high temperatures for long periods of time in the postdeposition environment.

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