THE TEMPERATURE OF FORMATION OF CARBONATES IN MARTIAN METEORITE ALH84001: CONSTRAINTS FROM CATION DIFFUSION. A. J. R. Kent, I. D. Hutcheon, F. J. Ryerson and D. L. Phinney, L-202, Lawrence Livermore National Laboratory, Livermore CA. 94550. Email: kent5@llnl.gov.

Introduction: An important test of the hypothesis that Martian meteorite ALH84001 contains fossil remnants of an ancient Martian biota [1] is the thermal history of the carbonate rosettes associated with the proposed biomarkers. If carbonates formed at temperatures over ~110°C (the limit for terrestrial life), it is unlikely that these minerals are associated with a terrestrial-like biota.

Unfortunately, current estimates for the formation temperatures of ALH84001 carbonates (based on textural interpretations, phase equilibria, stable isotope geothermometry, paleomagnetism, and diffusion modeling; [1-8]) range between ~0 and >650°C. Clearly, if the temperature of carbonate formation is to be used to assess the possible presence of ancient Martian life in ALH84001, there is a need for robust and unequivocal estimates of formation temperatures.

We have used the rates of cation diffusion in carbonate minerals to constrain the formation temperatures of ALH84001 carbonates. Carbonate rosettes in ALH84001 are chemically zoned; evident as Mg-rich rims grading to Ca and Fe-rich cores, and also by more marked changes in Mg, Fe and Ca concentrations over shorter length scales. These occur adjacent to the Mg-rich rims of the rosettes as well as in intermediate locations and represent steep compositional gradients–with changes exceeding 10 mol cation % over distances of 1-5 μm [4]. Given an appropriate thermal history, diffusion will act to remove such sharp gradients, and thus the rates of cation diffusion can constrain the formation temperature and thermal history of ALH84001 carbonates.

We have measured the rates of diffusion of Ca in magnesite and Mg in calcite. Our method is similar to the recent study by [3], but differs in two important ways: (1) in addition to calcite, we have also obtained diffusion data for Ca in magnesite (which is more common than calcite in ALH84001); and (2) we have obtained diffusion data from experiments conducted at temperatures as low as 400°C (compared to 550°C in [3]), substantially reducing the amount of down temperature extrapolation required

Experimental method: Diffusion experiments used a simple powder source technique [9]. Cleavage fragments of calcite and magnesite were placed in platinum capsules with dried powder of the appropriate composition ($CaCO_3$ for magnesite and MgO for calcite). For calcite + MgO experiments a small amount of $CaCO_3$ was also added to enhance stability of the calcite surface [9]. Capsules were sealed in evacuated silica glass tubes and then annealed for periods ranging from 24h – 120 days. Experiments were run at tem-

peratures of 400-500°C for magnesite + $CaCO_3$ and 400-600°C for calcite + MgO.
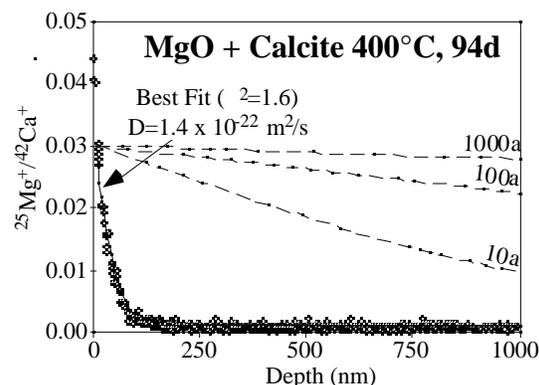
Fig. 1. Mg diffusion in calcite heated at 400°C for 94 days. Solid symbols show measured $^{25}Mg^+/^{42}Ca^+$ with depth and solid line shows best fit. Dashed lines show calculated profiles for heating times of 10, 100 and 1000 years.

Diffusion profiles were analyzed using a modified Cameca ims-3f ion microprobe. Results from a typical experiment are shown in Fig.1. Diffusion coefficients for each experiment were calculated by least-squares regression to the solution of Fick's diffusion equation for diffusion from a semi-infinite medium. Time series and replicate experiments indicate constant diffusion rates at a given temperature for annealing times varying by a factor of 3; diffusion coefficients are reproducible to ~ ± 0.3 log units.

Results and Discussion: On the Arrhenius plot in Fig. 2 measured diffusion rates form linear trends corresponding to activation energies of ~ 100 and 90 kJ/mol and log Do values of ~ –14 and –8 for diffusion of Mg in calcite and Ca in magnesite, respectively. Our measured diffusion rates for Mg in calcite overlap with the data reported by [3] for temperatures of 600 and 550°, but indicate a distinctly different temperature dependence at lower temperatures, with Mg diffusivity at 400°C ~100 times faster than predicted by [3]. The reason for this is unknown, but this difference may suggest a change in the dominant cation diffusion mechanism in calcite at temperatures below ~550°C.

Although our measured rates for diffusion of Ca in magnesite are considerably slower than those for Mg in calcite (Fig. 2), they are broadly co-linear with the diffusion rates for Ca in calcite measured by [3]. This observation suggests that as the rates of diffusion of Ca in magnesite and calcite are comparable, the rates of diffusion of Mg in magnesite and calcite are also simi-

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lar. This is an important conclusion for application of this data to ALH84001, as magnesite is a much more common component than calcite in carbonate rosettes [4,8].
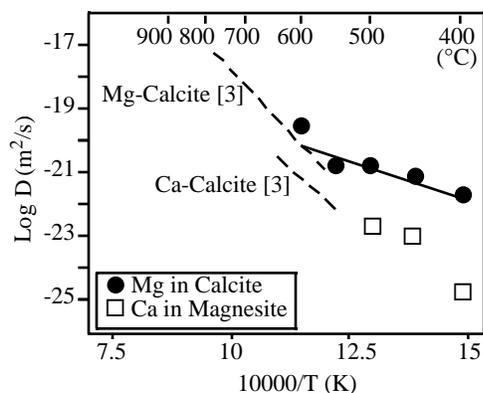

Fig. 2. Arrhenius plot for Mg diffusion in calcite and Ca diffusion in magnesite. Data for Ca and Mg diffusion in calcite from [3] is also shown.

To constrain the thermal history experienced by ALH84001 carbonates , we have chosen to interpret our data in two ways. The simplest is shown in Fig. 1, where we have taken the measured diffusion coefficient for Mg in calcite determined at 400°C and plotted curves representing the effect of diffusion at this temperature for time periods of 10, 100 and 1000 years. These curves show that, even over such geologically short time scales, Mg diffusion is sufficiently rapid at this temperature that short length scale chemical heterogeneity, such as that apparent in ALH84001, would rapidly disappear. This simple approach (our only assumption is that the Mg diffusivity in calcite is similar to the Mg diffusivity in ALH84001 carbonate) suggests that the carbonate rosettes in ALH84001 cannot have experienced temperatures above 400°C for any significant length of time. Carbonates formed at temperatures 400° must have cooled extremely rapidly to maintain the observed compositional variations.

Our second approach uses the formulation of Sheng et al. [10] to investigate the effect of cooling rates on the preservation of compositional heterogeneity in ALH84001 (Fig. 3). Assuming a cooling rate that is linear in 1/T, the diffusional homogenization of chemical (or isotopic) heterogeneities of a particular length scale (the vertical axis in Fig. 3) can be related to the cooling rate for a range of initial carbonate formation temperatures.

It is apparent from Fig. 3 that preservation of 1-5 µm scale Mg compositional heterogeneities in carbonates formed above ~200-300°C requires cooling rates of 100°C/Ma or higher. Such rapid cooling rates are outside the known range for rocks within the terrestrial crust, and are also unlikely in a coarse-grained crustal rock such as ALH84001. Given that Mg compositional heterogeneity in carbonate rosettes in ALH84001 oc-

curs down to the 1-2 µm scale [4], we suggest that carbonate formation probably occurred at temperatures below 200-250°C.

Both approaches used to interpret our data arrive at similar conclusions. A simple calculation requiring minimal assumptions suggests that carbonate rosettes in ALH84001 formed at temperatures that are *at least* below 400°C. Furthermore, the cooling rate approach of [10] strongly suggests that, unless cooling rates were substantially higher than realistic estimates, carbonate rosettes formed at temperatures less than 200-250°C. Models involving formation of ALH84001 carbonates at temperatures greater than 200-250°C [e.g. 4,6,8] appear much less suitable than models suggesting lower temperatures of formation.
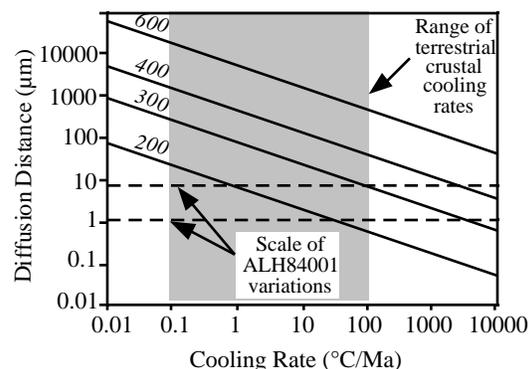

Fig. 3. Relation between cooling rate and distance over which diffusion will remove Mg compositional heterogeneity (after [10]). Solid curves show cooling from initial temperatures of 600–200°C. Dashed lines show scale of compositional variation in ALH84001 carbonate rosettes and the grey field shows approximate range of terrestrial crustal cooling rates.

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