

MAGNESIUM DIFFUSION IN PLAGIOCLASE. J. A. Van Orman¹, D. J. Cherniak², N. T. Kita³ ¹Dept. of Earth, Environmental and Planetary Sciences, Case Western Reserve University, Cleveland, OH 44106, ²Dept. of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, NY 12180, ³Dept. of Geoscience, University of Wisconsin-Madison, Madison, WI 53706.

Introduction: The ²⁶Al-²⁶Mg system provides important constraints on the timing of events in the early solar system, including the formation of refractory inclusions (CAIs) and chondrules, and the assembly and differentiation of planetesimals [1-4]. Age data from this system are often based on the internal isochron method, in which excess ²⁶Mg in plagioclase usually has a critical role in constraining the initial ²⁶Al/²⁷Al ratio [4-6]. Full interpretation of ²⁶Al-²⁶Mg isochron ages depends on an understanding of the susceptibility of the system to thermal resetting. A young isochron age, for example, may indicate late formation of an object, or may result from diffusive redistribution of ²⁶Mg.

To understand the conditions required for thermal disturbance of ²⁶Al-²⁶Mg ages, it is necessary to obtain data on the diffusivity of Mg and its temperature dependence. LaTourrette and Wasserburg [7] performed experiments to measure Mg self-diffusion coefficients in anorthite, at temperatures of 1200-1400 °C. The present study was undertaken to investigate whether the diffusivity of Mg varies with plagioclase composition. Prior studies on Sr, Ba, Pb and the REE show that diffusion rates increase strongly as the anorthite content of the plagioclase decreases [8]. If this is also true for Mg, it would imply that the more sodic plagioclase found in some FeO-rich (Type II) chondrules and equilibrated chondrites is significantly more prone to thermal resetting of ²⁶Al-²⁶Mg ages than is anorthite from CAIs and FeO-poor (Type I) chondrules.

Experiments: The diffusion experiments were performed using natural single crystals of anorthite (An93), labradorite (An66), andesine (An43) and oligoclase (An23). Each crystal was oriented, sectioned with a low speed saw and mirror polished on one side, then surrounded by a source of diffusant within a Pt capsule. Source materials consisted of a mixture of MgO (usually enriched in ²⁵Mg), Al₂O₃ and SiO₂ powders in 1:1:2 molar proportions, mixed in a 6:1 ratio (by wt) with plagioclase powder of the same composition as the sample. Each sample was suspended in the hotspot of a 1 atm furnace at constant temperature between 850 and 1150 °C, for times ranging from 25 minutes to 24 days. Following the experiment, the plagioclase single crystal was removed and rinsed in purified water and ethanol, mounted in epoxy with the polished surface exposed and coated with a thin layer of gold.

Diffusion profiles were analyzed by SIMS depth profiling, using a Cameca IMS-1280 ion microprobe at the University of Wisconsin-Madison. We used a focused 30 nA O⁻ primary ion beam rastered over a 70 μm square area, and inserted a field aperture to restrict sampling to secondary ions originating within the central 20 μm of the rastered area. The mass resolution power was set to ~3000, high enough to separate interference peaks. An energy offset of -50 V was used to filter out low energy secondary ions, which are affected by charging of the sample surface during the analysis.

To determine the diffusion coefficient, each profile was fit to the equation for one-dimensional diffusion in a semi-infinite medium, with constant surface concentration [9]:

$$\frac{C(x,t) - C_{surf}}{C_{init} - C_{surf}} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right). \quad (1)$$

Here, C represents the concentration at depth x after time t , C_{surf} is the concentration at the crystal surface, C_{init} is the initial concentration within the crystal, and D is the diffusion coefficient. Figure 1 shows an example of an Mg isotopic concentration profile in labradorite, for diffusion parallel to the b direction, along with an error function curve showing the least squares fit of Eq. 1 to the data.

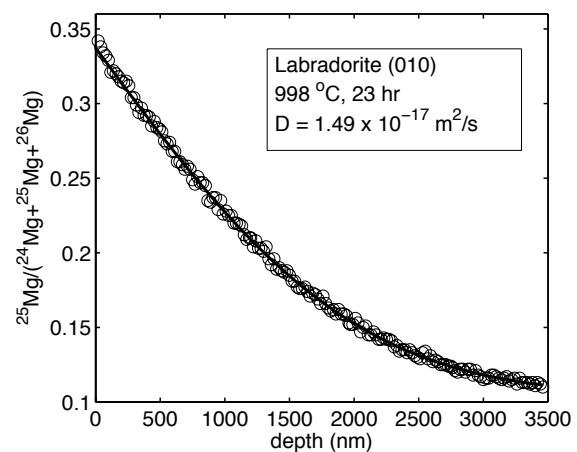


Figure 1. Example of an Mg isotopic diffusion profile in labradorite. Circles represent measured isotope compositions along the depth profile, and the solid curve is a least-squares fit to Eq. 1.

Results: The diffusion coefficients determined from each experiment are shown on an Arrhenius plot in Figure 2. Separate experiments on the same compo-

sition at the same temperature yield consistent diffusion coefficients, for diffusion times varying over more than an order of magnitude. Diffusion parallel to the *b* and *c* crystallographic axes was examined in labradorite, and little anisotropy was observed. Our results for anorthite are in excellent agreement with those of LaTourrette and Wasserburg [7], which were obtained at higher temperatures using different experimental and analytical methods.

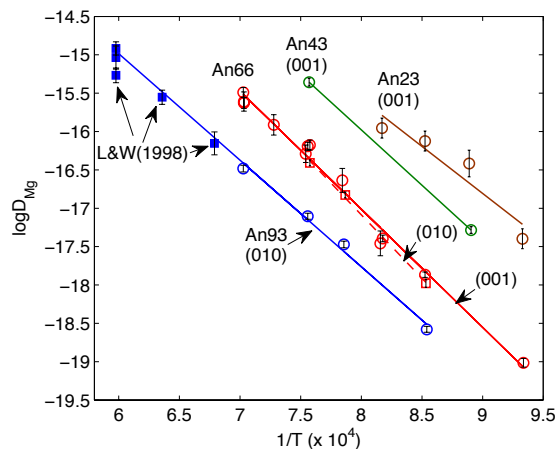


Figure 2. Arrhenius plot summarizing the diffusion data from this study, and from [7].

Magnesium diffusion coefficients increase systematically with decreasing anorthite content (Fig. 3), similar to the behavior of other divalent cations in plagioclase [8]. In oligoclase (An23) D_{Mg} is more than two orders of magnitude faster than in anorthite. The calculated closure temperatures [10] for 50 μm grains cooling from high temperature at cooling rates between 10 and 1000 $^{\circ}\text{C}/\text{Myr}$ are shown in Fig. 4. The closure temperature for An23 plagioclase is more than 100 $^{\circ}\text{C}$ lower than for anorthite.

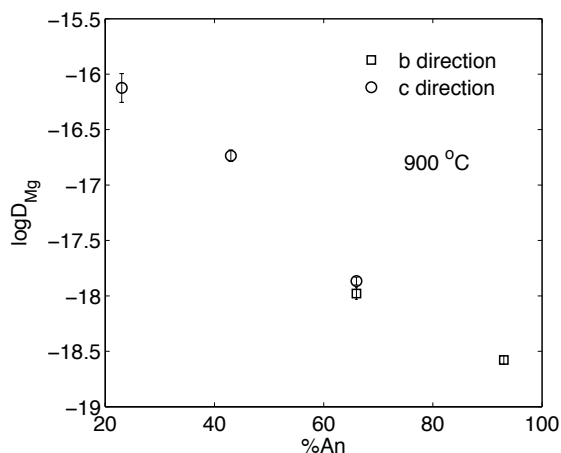


Figure 3. Variation of the Mg diffusion coefficient with plagioclase composition.

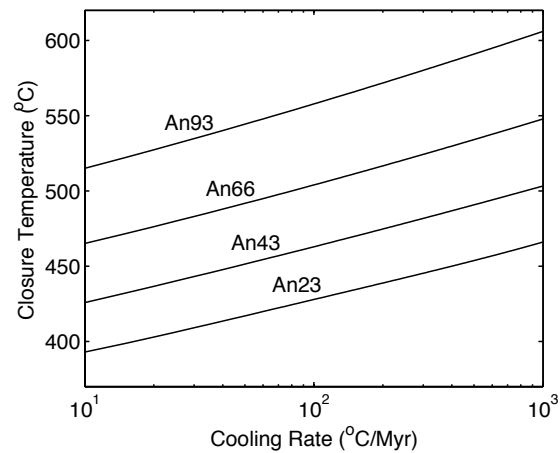


Figure 4. Calculated ^{26}Al - ^{26}Mg closure temperatures [10] for 50 μm plagioclase grains.

Nagashima et al. [11] found recently that plagioclase in a type B1 CAI from the Allende CV chondrite was sharply zoned in $^{24}\text{Mg}/^{27}\text{Al}$ but nearly homogeneous in $\delta^{26}\text{Mg}$, and inferred that Mg isotopes had been redistributed by a heating event that did not significantly affect the bulk Mg/Al distribution. In our experiments, we find that $^{24}\text{Mg}/^{27}\text{Al}$ and $^{25}\text{Mg}/\Sigma\text{Mg}$ profiles yield similar diffusion coefficients. Bulk diffusion of Mg in our experiments is evidently uncoupled from the much slower interdiffusion of CaAl-NaSi [8], but that may not be the case in natural crystals, such as those examined by [11], that exhibit sharp zoning in major elements. In such cases Mg may partition between anorthite-rich and anorthite-poor regions, thus maintaining sharp zoning in $^{24}\text{Mg}/^{27}\text{Al}$ despite the rapid self-diffusivity of Mg.

References: [1] MacPherson G. J. et al. (1995) *Meteoritics* 30, 365-386. [2] Jacobsen B. et al. (2008) *EPSL* 272, 353-364. [3] Kita N.T. et al. (2000) *GCA* 64, 3913-3922. [4] Spivak-Birndorf L. et al. (2009) *GCA* 73, 5202-5211. [5] Kurahashi E. et al. (2008). [6] Kita N. T. et al. (2010) *LPS XLI*, #2154. [7] LaTourrette T., Wasserburg G.J. (1998) *EPSL* 158, 91-108. [8] Cherniak D.J. (2010) *Rev. Mineral. Geochem.* 72, 691-733. [9] Crank J. (1975) *The Mathematics of Diffusion*, 2nd Ed., Clarendon Press, Oxford, 424 pp. [10] Dodson M.H. (1973) *Contrib. Mineral. Petrol.* 40, 259-274. [11] Nagashima K. et al. (2011) *LPS XLII*, #2447.