

**Mg SELF-DIFFUSION IN SPINEL: CONSTRAINTS ON THE THERMAL HISTORY OF PLAGIOCLASE-OLIVINE INCLUSIONS.** Y.J. Sheng, G.J. Wasserburg, and I.D. Hutcheon. The Lunar Asylum, Division of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125.

A prominent feature of Plagioclase-Olivine Inclusions (POIs), which distinguishes them from most coarse-grained CAIs and chondrules, is the Mg isotope heterogeneity both between coexisting spinel and silicates and among spinels. Sheng *et al.* [1] characterized POIs and proposed that the variation in Mg isotope fractionation among coexisting phases within POIs is the result of incomplete melting of silicate-rich precursors containing relict spinel with isotopically fractionated Mg. The preservation of isotopic heterogeneity indicates that the thermal event which partially melted the precursor and produced an igneous texture either had too low a temperature or was too brief to allow complete Mg isotope homogenization. Differences in thermal history are proposed to be the major factor leading to differences in isotopic composition and textures between POIs and CAIs. The temperature history required to homogenize Mg isotopes depends on the diffusion rate of Mg in spinels. In order to establish this critical rate we designed experiments to determine the self-diffusion coefficients of Mg in spinel at temperatures reflecting possible melting conditions of POIs.

We investigated Mg self-diffusion in  $\text{MgAl}_2\text{O}_4$  spinel (Sp) by an isotope tracer method. Experiments were made on single crystal gem quality Sp. Polished Sp wafers were annealed for 24 hrs. at  $1500^\circ\text{C}$ . The diffusion couple consists of a piece of the annealed polished Sp wafer placed together with  $^{25}\text{Mg}$ -doped  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  (CMAS) glass and held at the run temperature at 1 atm in air for different times. The wetting of the melt yielded a boundary of Sp to glass that was a sharp welded contact. The glass was produced by adding  $^{25}\text{MgO}$  to CMAS mixture and melted at  $1550^\circ\text{C}$  for 24 hours. The glass was verified to be both chemically and isotopically homogeneous. Initial ratios of the starting glasses were  $^{25}\text{Mg}/^{24}\text{Mg}=1.2$  to  $1.6$  and  $^{26}\text{Mg}/^{24}\text{Mg}\sim 0.140$ . The glasses contained 13.6-14.7 wt. % MgO. The bulk compositions of starting glasses were chosen so that they are spinel-saturated at the run temperature of a given experiment. Deviations from the saturation composition would be compensated by nucleation of Sp from the melt or dissolution of the Sp wafer. Since in our experiments, the starting glasses were chosen to be close to Sp-saturated compositions and that the Sp/melt volume ratio is relatively large ( $\sim 1:5$ ), slight deviations from Sp-saturated condition in the melt will be compensated with negligible effects to the Sp-melt diffusion couple. Variations in Mg isotopes in Sp and glass were measured with the PANURGE ion microprobe using methods described by [2,3]. Analyses were made across a traverse perpendicular to the diffusion interface. Diameter of the primary ion beam was approximately  $3\text{ }\mu\text{m}$ . The  $2\sigma$  error for measured  $^{25}\text{Mg}/^{24}\text{Mg}$  ratios is  $\pm 3\%$  and  $^{26}\text{Mg}/^{24}\text{Mg}$  is  $\pm 2\%$ .

The results are shown in Figs.1 and 2. Fig.1 shows the variation of  $^{25}\text{Mg}/^{24}\text{Mg}$  across a traverse in the Sp wafer from one experiment. The fitted curve is the calculated diffusion profile. The self-diffusion of Mg in Sp is modeled as diffusion in an infinite composite medium. The Sp-melt diffusion couple is in chemical equilibrium but with Mg isotopic exchange. The solution to the diffusion equations was taken to account for the complementary diffusion of  $^{24}\text{Mg}$ ,  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$  in both phases with the total concentration of Mg in each phase to be constant. This approach implies that the Sp-glass boundary has constant Mg isotopic composition. A diffusion coefficient (D) for each run is extracted by using a least square best fit to the measured data. The temperature dependence of D for Mg self diffusion in Sp is obtained from the Arrhenius relation  $D=D_0 \exp(-Q/RT)$  (Fig.2). The activation energy (Q) and pre-exponential factor  $D_0$  derived by a linear regression of the experimental diffusion data are, respectively,  $356\pm 26\text{ kJ}$  and  $7.77\pm 1.17\text{ cm}^2/\text{s}$ .

The results from this study indicate that Mg isotopic reequilibrium can be achieved in a relatively short time at melting temperatures of POIs determined from the phase diagrams [4]. As suggested by [4], maximum melting temperature ( $T_{\text{max}}$ ) for POIs is  $\sim 1500^\circ\text{C}$ . Assuming a spinel grain size (x) in POIs of about  $10\text{ }\mu\text{m}$  (typically  $< 5\text{ }\mu\text{m}$ ), the homogenization time of Mg isotopes in a Sp-saturated silicate melt at temperatures above  $1500^\circ\text{C}$ , using the approximation  $D \approx x^2/t$ , is  $< 1\text{ hr}$ . For temperatures between  $1500\text{-}1400^\circ\text{C}$  the homogenization time (t) is 1-4 hrs, and at  $1400\text{-}1300^\circ\text{C}$   $t \sim 4\text{-}20\text{ hrs}$ . Thus for the range of expected melting temperatures of POIs, the Mg diffusion data provides limits on the maximum time the POI melt could have remained at a specific temperature. The dependence of cooling rate (r) with  $T_{\text{max}}$  for given x calculated using the relation  $x = D(T)tRT^2/rQ$  [5] is shown in Fig.3. The initial rates at  $T = 1500^\circ\text{C}$  for x of 5, 10, and  $15\text{ }\mu\text{m}$  are, respectively, 305, 76, and  $34^\circ\text{C/hr}$  (Fig.3). The nature of the heating process is thus required by our data to be short, such as flash heating or impact melting.

These grain-size dependent bounds on cooling rates are comparable to or up to  $10\times$  greater than those inferred from experimental and textural studies of synthetic systems [6,7]. It appears that the igneous textures of

POIs are compatible with the cooling rates determined in this experiment, but much faster rates, which would preserve isotopic heterogeneity, are probably inconsistent with petrographic observations. The cooling rates for POIs are much lower than radiative loss cooling rates of mm-size droplets, requiring formation of POIs in a hot region of the nebula. For  $T_{\text{max}} = 1420^\circ\text{C}$  and  $r \leq 20^\circ\text{C}$ , as suggested for some Type B CAIs [7], our data suggests that Sp with  $x \leq 10 \mu\text{m}$  would be isotopically homogenized in Mg. If CAIs initially contained Sp with fractionated Mg or other similar relict phases, they would be consequently reequilibrated at this slower cooling rate. The presence of Mg isotope heterogeneity in POIs and the results of our diffusion experiments provide one of the most direct means of establishing a constraint on the thermal history of these inclusions. The presence or absence of Mg isotopic heterogeneity could be used as a measure of the  $T_{\text{max}}$  and cooling rate not only of POIs but also of other types of refractory inclusions and chondrules if we assume that these objects had sampled similar material.

**Acknowledgement.** We thank D. Burnett for generously allowing use of his lab, M. Johnson and T. LaTourette for their kind support.

**References.** [1] Sheng Y. *et al.* (1991) GCA 55, in press; [2] Huneke J. *et al.* (1983) GCA 47, 1635; [3] Hutcheon I. *et al.* (1987) GCA 51, 3175; [4] Sheng Y. *et al.* (1991) LPSC XXII; [5] Kaiser T. and Wasserburg G. (1983) GCA 47, 43; [6] Wark D. and Lovering J. (1982) GCA 46, 2651; [7] Stolper E. and Paque J. (1986) GCA 50, 1785.

**Captions.** Fig.1. Variation of  $^{25}\text{Mg}/^{24}\text{Mg}$  across a traverse in Sp from Sp-glass interface. The fitted curve is the calculated diffusion profile. Fig.2. Arrhenius plot showing the least square best fit of the experimental data. Fig.3. Dependence of cooling rate ( $r$ ) upon temperature ( $T$ ) for Sp grain sizes of 5, 10, and 15  $\mu\text{m}$ .

