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Magnesium diffusion in plagioclase: Dependence on composition, and implications for thermal resetting of the ^{26}Al–^{26}Mg early solar system chronometer

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ABSTRACT

Experimental data are reported on Mg diffusion in plagioclase crystals with a range of anorthite content (x_{An}), at temperatures between 800 and 1150 °C. Oriented and polished single crystals of anorthite ($x_{An} = 0.93$), labradorite ($x_{An} = 0.67$), andesine ($x_{An} = 0.43$) and oligoclase ($x_{An} = 0.23$) were each embedded in powered source material enriched in natural MgO or ^{25}MgO and suspended in a furnace at constant temperature. Diffusion profiles in quenched samples were measured from the polished surface using SIMS depth profiling. The diffusion coefficient does not depend significantly on the Mg concentration gradient, and little anisotropy is observed between the *b* and *c* directions in labradorite. Diffusion coefficients increase systematically with decreasing x_{An}, and the entire data set is described by $\ln D = (-6.06 \pm 1.10) - (7.96 \pm 0.42)x_{An} - \frac{287\pm10\ \text{kJ/mol}}{RT}$, where R is the gas constant, T is absolute temperature, and the diffusion coefficient D is in m^2/s. ^{26}Al–^{26}Mg ages in albite-rich plagioclase are much more easily reset than in anorthite, with closure temperatures up to 120–150 K lower.

1. Introduction

The ^{26}Al–^{26}Mg radioactive decay system is one of the most important sources of information on the timing of events in the early solar system. In situ decay of ^{26}Al (half-life of 0.705 Ma) produces a detectable excess of ^{26}Mg in phases with high Al/Mg ratios, and its presence provides unequivocal evidence for the formation of the object within several million years of the synthesis of ^{26}Al. Excess radiogenic ^{26}Mg has been found in refractory inclusions (CAIs) in chondritic meteorites (e.g., MacPherson et al., 1995; Kita et al., 2013, and references therein), in chondrules (Kita and Ushikubo, 2012, and references therein) and even in metamorphosed ordinary chondrites and achondrites (e.g., Srinivasan et al., 1999; Zinner and Göpel, 2002), and hence may provide a fine-scale chronometer not only for condensation and heating events within the solar nebula but for the assembly and thermal history of planetesimals. ^{26}Al–^{26}Mg chronometry depends, however, on the ability to determine the significance of the age implied by excess ^{26}Mg. Does it correspond to the time of formation of the object, or has it been partially or fully reset by later processing? Perhaps the most important, and best understood, mechanism for resetting of ^{26}Al–^{26}Mg ages is by thermally activated diffusive loss of ^{26}Mg from high Al/Mg phases. Because plagioclase is the most common high Al/Mg phase in meteorites, and the one in which excess ^{26}Mg is usually best resolved (Lee et al., 1977; Kurahashi et al., 2008; Goodrich et al., 2010; Kita et al., 2012), diffusion data for Mg in plagioclase are critical to determine the susceptibility of ^{26}Al–^{26}Mg ages to modification by thermal events. LaTourrette and Wasserburg (1998) determined Mg self-diffusion coefficients in nearly pure anorthite (An$_{95}$; i.e. 95 mol% anorthite) single crystals at 1200–1400 °C. The results of this study provide strong constraints on the resetting of ^{26}Al–^{26}Mg ages at high temperatures, in CAIs and other materials that contain anorthitic plagioclase. However, a long extrapolation is required to extend these data to thermal resetting at the much lower temperatures characteristic of metamorphism within planetesimals. Furthermore, application of these data to the more albite-rich plagioclase that is found in high-FeO (Type II; Kunihiro et al., 2004; Kurahashi et al., 2008) chondrules, equilibrated chondrites, and other meteoritic materials such as ureilites (Goodrich et al., 2010), is highly uncertain because no experimental data have yet been published on the dependence of Mg diffusion on plagioclase composition. Studies of other cations in plagioclase indicate a significant dependence of diffusivities on An content, with diffusion faster in more albite-rich plagioclase (Behrens et al., 1990; LaTourrette and Wasserburg, 1998; Cherniak and Watson, 1992, 1994; Giletti and Casserly, 1994; Cherniak, 1995, 2002, 2003).

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Magnesium diffusion in plagioclase also provides the basis for time constraints on magmatic processes (Costa et al., 2003, 2008; Druitt et al., 2012). Plagioclase phenocrysts commonly preserve chemical zoning in both trace and major elements that can only be preserved if the crystals' residence at high temperature was short enough to prevent diffusive homogenization. The compositional zoning profiles can be modeled to provide quantitative constraints on the time these phenocrysts experienced in the magma chamber between development of the original zoning profile and eruption. Magnesium profiles in plagioclase are particularly well suited to this purpose because Mg often can be analyzed with sufficient precision by electron microprobe and because its diffusivity is relatively rapid, providing access to information on the annual to millennial timescale. The influence of plagioclase composition on Mg diffusion is particularly important for these applications, because the zoning of trace elements such as Mg is commonly correlated with strong zoning in the major components (i.e. the anorthite content). Variation in Mg diffusivity with plagioclase composition must be taken into account in modeling the profiles. Costa et al. (2003) suggested that the dependence of Mg diffusion on plagioclase composition was similar to that for Sr and other large cations – which exhibit strong increases in diffusivity with decreasing anorthite content – and was able to obtain good fits to natural Mg diffusion profiles in plagioclase phenocrysts by assuming that the relative dependence on composition of Mg diffusion was identical to that of Sr. However, as noted above, the compositional dependence of Mg diffusivity in plagioclase has not yet been investigated experimentally.

Here, we report the results of experiments to determine Mg diffusion coefficients in natural plagioclase crystals of a wide range of composition, from An_{93} (anorthite) to An_{23} (oligoclase), over a wide range of temperature extending downward to 800 °C. The experiments also address whether Mg chemical diffusion rates, which are relevant to the relaxation of Mg zoning profiles in plagioclase, may be different than Mg self-diffusion rates, which are relevant to ^{26}Al–^{26}Mg resetting where the net flux of Mg among phases is negligible.

2. Experimental

The diffusion experiments were performed using natural single crystals of anorthite (An_{93}), labradorite (An_{66}), andesine (An_{43}) and oligoclase (An_{23}). Each crystal was oriented, sectioned with a low speed saw and mirror polished on one side, then placed in an open Pt capsule surrounded by a powder consisting of MgO, Al_2O_3 and SiO_2 in 1:1:2 molar proportions, mechanically mixed in a 6:1 weight ratio with plagioclase powder of the same composition as the crystal. Two sets of experiments were performed, one with highly enriched ^{25}MgO in the powder source and the other with isotopically normal MgO. The experiments with ^{25}MgO provided better resolution in the measurement of the Mg diffusion profiles, and, as described below, allowed for a comparison between Mg self-diffusion coefficients (in experiments where there was a negligible net flux of Mg) and Mg chemical diffusion coefficients.

The open Pt capsule containing each crystal/powder diffusion couple was suspended in air within the hotspot of a 1 atm furnace and maintained at constant temperature, between 798 and 1150 °C, for times ranging from 25 min to 24 d. Following the experiment, the plagioclase single crystal was removed from the powder and rinsed in purified water and ethanol, mounted in epoxy with the polished surface exposed and coated with a 60 nm layer of gold, which provided a conductive surface layer for SIMS depth profiling analyses.

2.1. SIMS depth profiling analyses

Depth profiles of major elements (Na, Al, Si, and Ca) and Mg isotopes were performed using the WiscSIMS Cameca IMS-1280 ion microprobe at the University of Wisconsin-Madison (Valley and Kita, 2009; Kita et al., 2012). An O^- primary ion beam was used, with total impact energy of 23 keV to the sample surface (−13 kV primary ion and +10 kV secondary ion acceleration voltages). The primary beam was focused to ∼30 μm diameter with 30 nA intensity and raster size of 70 μm square, which leaves a sputtered crater that is flat over a ∼40 μm square area. The field aperture was set to a 1600 μm square that restricted sampling to a central 20 μm square area on the sample surface (the magnification of the transfer lens was set to 80), with the beam position carefully adjusted at each analysis location so that only secondary ions produced from the center of the raster area were collected in the mass spectrometer. Mass resolution power was set to ∼3000, high enough to separate interference peaks. The isotope peaks were detected by magnetic peak switching on the fixed axial detector (mono-collector), which is switchable between electron multiplier (EM) and Faraday Cup (FC), in the following order: ^{23}Na (2 s, EM), ^{24}Mg (10 s, EM), ^{25}Mg (10 s, EM), ^{26}Mg (10 s, EM), ^{27}Al (2 s, FC), ^{28}Si (2 s, FC), and ^{40}Ca (2 s, FC). A single cycle took ∼54 s including waiting time to settle the magnetic field at each isotope. For the first set of samples, with natural Mg isotope abundances in the source powder, the minor Mg isotopes (^{25}Mg and ^{26}Mg) were not included in the analysis and a single cycle took ∼30 s. For a natural labradorite standard containing 0.1 wt% MgO (Lab1, An_{60}; Kita et al., 2012), typical secondary ion intensities were 6×10^4 cps for ^{23}Na, 3000 cps for ^{24}Mg, 8×10^5 cps for ^{27}Al, 6×10^5 cps for ^{28}Si, and 4×10^5 cps for ^{40}Ca.

The secondary ions with higher initial energy were selected by using an energy offset (−50 V), similar to the conditions applied in previous diffusion profile studies (e.g., Ito and Ganguly, 2006). We note that this energy filtering was required to reduce molecular interferences for small radius ion microprobes, but not for the IMS-1280 which is capable of resolving interference peaks by applying high mass resolution power without losing secondary ion transmission. However, the sample surface becomes charged up to ∼30 eV under our analytical conditions, which drastically changes the secondary ion intensity of low energy ions at the beginning of the depth profiling. The energy filtering method works well in keeping the secondary ion intensity relatively stable despite surface charging, with only a slight gradual decrease in ion counts with increasing depth over the first ∼1 μm of sputtering. To correct for this small charging effect, Mg ion intensity at each depth is normalized to that of ^{27}Al. Thus, in experiments with isotopically normal MgO in the source materials, ^{24}Mg/^{27}Al is used as a proxy for relative Mg concentration along the depth profile. Similarly, in experiments conducted with ^{25}Mg-enriched source materials, (^{24}Mg + ^{25}Mg + ^{26}Mg)/^{27}Al is used as a proxy for total Mg concentration, and the Mg isotope composition is recorded as ^{25}Mg/(^{24}Mg + ^{25}Mg + ^{26}Mg).

Following SIMS depth profiling analyses, the sputtered pits were measured using a Zygo 3D optical surface profilometer. The central 20 μm square area of the pit that was sampled during the SIMS analysis was considered for depth measurement. The variation in depth within this central area was within 10–50 nm for each pit, compared to total depths between 1.26 and 9.57 μm, corresponding to a 2σ precision in depth measurement between 0.22% and 1.7% for each of the sputtered pits. The sputtering rate, for the beam conditions noted above, was found to be ∼0.012–0.015 nm/s/nA, and increased slightly with the albite content of the plagioclase.