Ca AND Mg TRACER DIFFUSION IN DIOPSIDE: EXPERIMENTAL DETERMINATION AND APPLICATIONS TO COOLING HISTORY OF PLANETARY SAMPLES.

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Introduction: Clinopyroxenes in slowly cooled igneous rocks in both planetary and terrestrial environments commonly show exsolution lamllae of augite and pigeonite (which may be inverted to orthopyroxene) normal to the c-axis. The lamellar thickness and Ca-Mg-Fe zoning in the exsolved phases can be modeled to retrieve the cooling rates of the host rocks [e.g. 1,2] if the diffuson properties of these cations are known. We have, thus, undertaken a study to measure the self diffusion coefficient of the divalent cations in clinopyroxene as a function of temperature. We report here the data that we have obtained so far in this on-going project, and discuss their potential implications.

Experimental studies and modeling: We used a gem quality diopside crystal of composition $Ca_{0.959}Na_{0.015}Fe_{0.018}Al_{0.006}Ti_{0.002}Fe^{3+}_{0.04}Si_{1.968}Al_{0.032}O_6$ for this study. Small slabs of the single crystal were oriented in a 4-circle diffractometer, and sections were cut and polished normal to c, b and a* directions with diamond pastes down to quarter-micron grit size. Finally, these surfaces were finished to mirror polish by a combination of chemical and mechanical polishing with silica suspension on OP-chem clothes (Struers). The polished wafers were pre-annealed at the T-fO$_2$conditions of the experiments for 21-24 hrs to heal the near surface damage that might have been caused by mechanical polishing, and also to equilibrate the point defects to the conditions of the diffusion experiments. Thin films of Ca and Mg diffusant material were deposited on the polished surfaces by evaporating a mixture of ^{44}Ca enriched CaO and ^{26}Mg enriched MgO. Diffusion experiments were carried at 1000 $^{\circ}$C (two crystals oriented normal to b and c axes) and 900 $^{\circ}$C (two crystals oriented normal to a* and c axes) in a one atmosphere furnace with fO$_2$ controlled by a flowing mixture CO/CO$_2$. The gas ratios held the environment at the fO$_2$ of the wüstite-iron buffer. Concentration profiles of the ^{44}Ca and ^{26}Mg tracer isotopes, along with those of other isotopes, were measured in an Ion-probe, and modeled to retrieve their diffusion coefficients.

Modeling of each measured concentration profile was carried out by usng both depleting and infinite source solutions of the one dimensional diffusion equation [3; Eqns 2.7 & 2.45]. The solutions were interfaced with a non-linear optimization program to find the best fits between the measured and modeled concentration profiles. The analytical solution using an infinite source was found to yield a better fit than the one with depleting source for the Ca profiles, while the reverse was true for the Mg profiles. (These suggest that during the co-evaporation of the oxides to form a diffusant layer, more Ca was deposited on a crystal surface than Mg). Fig. 1 shows a typical example of the measured and modeled profiles for ^{44}Ca and ^{26}Mg in diopside

Fig1: Diffusion profiles for ^{44}Ca and ^{26}Mg along the c direction at 1bar, 1000°C; fO$_2$ = WI buffer, annealing time = 44.65hr
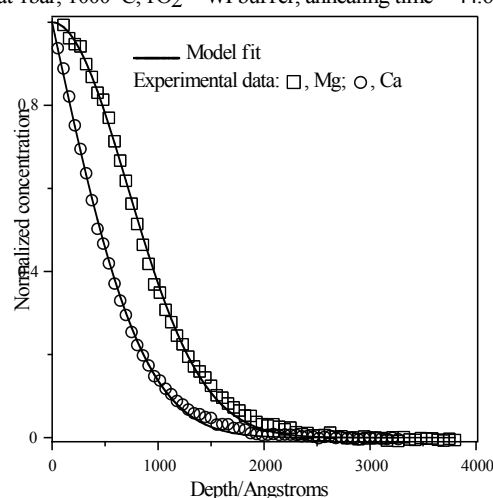

Results and comparison with previous studies: The measured tracer diffusion data of ^{44}Ca and ^{26}Mg along the c-direction are illustrated in Fig. 2 and compared with the results of earlier studies of Ca-(Mg + Fe) interdiffusion [4,5] and ^{44}Ca tracer diffusion [6] along the same direction. The inset of the figure shows our data along the a*, b and c directions at 900 and 1000 $^{\circ}$C. These data suggest a diffusion anisotropy according D(a*) ~ D(c) > D(b), with logD along the b direction being ~ 0.4 unit lower than that in the other directions.

Fujino et al. [4] determined Ca-(Mg+Fe) interdiffusion coefficients by lamellar coasening experiments using a natural clinopyroxene. They measured the Ca and (Mg+Fe) profiles in the (001) exsolved lamellae of pigeonites and augites in an analytical TEM, and modeled these data to retrive the D values. These data show a change of diffusion mechanism at ~ 1100 $^{\circ}$C. The activation energy (Q) of interdiffusion below this temperature is much lower than that suggested by our tracer diffusion data. In fact,

our data suggest a Q value that seems to be similar to that corresponding to the higher temperature data of Fujino et al. [4]
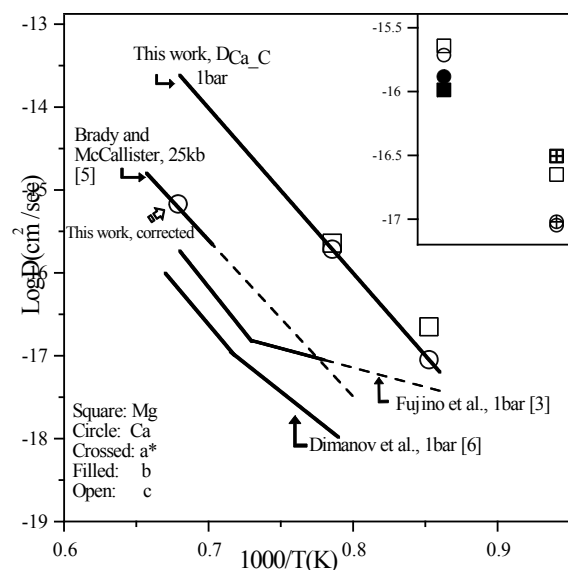
Brady and McCallister [5] determined Ca-(Mg+Fe) interdiffusion data at 25 kb, $1150 - 1250\,^{\circ}C$ from homogenization data of fine scale (001) coherent exsolution lamellae of pigeonite in a sub-calcic diopside megacryst from a kimberlite xenolith. Their data show a similar activation energy as that determined by Fujino et al. [4] above $1100\,^{\circ}C$. However, if the diffusion data are corrected for the pressure effect, assuming an activation volume, ΔV^+, of $\sim 5\text{-}7$ cm^3/mol, as commonly found for silicates and oxides [7], then the diffusion data of Brady and McCallister is about a factor of 10 greater than those of Fujino et al. [4]. This difference may be accounted for by considering the uncertainties of both experimental studies.

In a binary ionic system, the inter-diffsion coefficient, $D(i\text{-}j)$, can be calculated from the tracer diffusion coefficients, D_i and D_j, according to $D(i\text{-}j) = [D_iD_j/(X_iD_i+X_jD_j)][D(i\text{-}j)^{thermo}]$, where $D(i\text{-}j)^{thermo}$ accounts for the thermodynamic nonideality of the solution. According to the analysis of Brady and McCallister [5] $logD(i\text{-}j)^{thermo} \sim -1.14$ at $1200\,^{\circ}C$ and $X_{Ca} = 0.57$, which is the average composition of the augites in their experimental studies. In addition, assuming $\Delta V^+ \sim 5$ cm^3/mol, an increase of pressure from 1 bar to 25 kbar reduces logD by ~ 0.44 at $1200\,^{\circ}C$. After correcting for the cumulative effects of pressure and thermodynamic non-ideality, our tracer diffusion data, extrapolated to higher temperature,

yield D(Ca-Mg) that are in very good agreement with the interdiffusion data of Brady and McCallister. The [44]Ca tracer diffusion data of Dimanov et al. [6] seem to be in significant disagreement with all other data.

Implications for cooling rate calculations: Modeling of compositional zoning in the augite and pigeonite exsolved lamellae in planetary samples have so far relied on the diffusion data of Fujino et al.[4] below $1100\,^{\circ}C$, which seem questionable in the light of our diffusion data at 900 and $1000\,^{\circ}C$. In order to evaluate the probable error in these cooling rate calculations, we have considered the result of Miyamoto and Takeda [8] on the Moore County cumulate eucrite. They have modeled the exsolution lamellae in clinopyroxene to infer a cooling rate of $160\,^{\circ}C/Myr$, and a consequent burial depth of ~ 8 km in the parent body asteroid 4 Vesta, assuming a rock-like thermal diffusivity of 0.004 cm^2/s (the exsolution process was assumed to span a temperature interval of $990 - 730\,^{\circ}C$). Our data suggest a cooling rate for this sample ~ 3 times as fast. The probable increase of cooling rate value and consideration of the effect of a megaregolith blanket to reduce the therrmal diffusivity would result in a much smaller burial depth of this sample. Also, it may be mentioned incidentally that consideration of the effect of convolution [8] of microprobe spot analyses seems to obviate the need for a subsequent reheating effect that was proposed to account for some fine scale details of compositional profiles.

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