Diffusion of oxygen in diopside and spinel: implications for oxygen isotopic anomalies in CAIs. K. D. McKeegan and F. J. Ryerson, Lawrence Livermore National Laboratory, Livermore, CA 94550.

It has been 13 years since the discovery of the heterogeneous distribution of oxygen isotopic anomalies among different mineral phases in Allende refractory inclusions [1]. While more recent data for other C3 meteorites [2,3] and for anorthite from 3 type-B Allende calcium-aluminum-rich inclusions (CAIs) [4] indicate that the quantitative detailed understanding of the isotopic patterns is complicated, the most plausible model for interpreting the broad features remains the gas-solid isotope exchange process proposed by Clayton and Mayeda [5]. In this model the initially uniform $^{16}$O-enriched oxygen of the CAI undergoes partial isotopic exchange with more "normal" oxygen in the surrounding nebular gas. The extent of exchange in each mineral phase depends on its oxygen self-diffusion coefficient and its time-temperature history. This model demands that, at the relevant temperatures, the oxygen diffusion coefficients for spinel and (probably) hibonite are smaller than those for pyroxene and olivine which, in turn, must be much smaller than those for melilite and anorthite.

Recent laboratory data for oxygen self-diffusion in refractory silicates have led to divergent answers on the ability of the gas-solid exchange model to explain the CAI data. Muehlenbachs and co-workers [6,7] have measured oxygen diffusion in melilite and diopside by a bulk exchange technique and concluded that diffusion in melilite is sufficiently fast - especially at low temperatures - compared to that in diopside for the Clayton and Mayeda model to work. However, Yurimoto et al. [8], based on ion probe measurements of oxygen diffusion in melilite, conclude that the Hayashi and Muehlenbachs [6] data are systematically high and that the observed CAI isotope patterns are unlikely to be the result of post-crystallization diffusion. Because of systematic uncertainties, diffusion data obtained by different techniques in different laboratories are often in disagreement. We have begun to measure oxygen self-diffusion in a suite of refractory oxides and silicates by gas-solid exchange followed by ion probe depth profiling. Results for spinel and diopside are reported here; data for melilite will be presented at the meeting.

The self-diffusion of oxygen parallel to the c-axis has been measured for two diopsides, from DeKalb, N.Y., (Wo$_{50.6}$En$_{48.3}$Fs$_{1.1}$) and from Rajasthan, India (Wo$_{49.2}$En$_{47.1}$Fs$_{2.2}$), and for a synthetic magnesium aluminate spinel between 1086°C and 1400°C under NNO-f$_{02}$ conditions. Sample surfaces were prepared by polishing followed by etching in dilute (10%) HF. The samples were then pre-annealed in flowing isotopically normal CO/CO$_2$ mixtures at the conditions (T, f$_{O2}$) to be used in the subsequent diffusion anneals. The diffusion anneals were performed in a static atmosphere of 99% $^{18}$O-enriched mixtures of CO-CO$_2$ along with solid buffers of Ni-Ni$^{18}$O. The $^{18}$O profiles were measured as negative ions with a CAMECA IMS-3f ion microprobe, and inverted through the appropriate solution to Fick's Law to obtain the diffusion coefficient.

The results for oxygen diffusion in the two diopsides agree well and are described by,

$$D = 53.4 \exp(-114 \text{ kcal mol}^{-1}/RT) \text{ cm}^2 \text{ s}^{-1}$$

which is significantly slower than has been seen in previous studies (Figure 1). The activation energy is in good agreement with the value of 97 kcal mol$^{-1}$ determined by Connolly and Muehlenbachs for gas-solid exchange[7], but is much higher than the value of 54 kcal mol$^{-1}$ measured under hydrous conditions at 1 kB [9]. Discrepancies between diffusivities obtained from bulk exchange and from
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Profiling techniques are typically observed in the pre-exponential term rather than the activation energy due to overestimates of the effective diffusion radius and/or unanticipated fast diffusion pathways in the bulk-exchange method. The results in Figure 1 are consistent with this observation. The difference in diffusivities observed under hydrous and anhydrous conditions appear to demonstrate the real effect of dissolved hydrogen-bearing species in enhancing diffusion rates in diopside.

Our results for spinel are in excellent agreement with the down-temperature extrapolation of the data of Reddy and Cooper [10] and are described by:

\[ D = 5.7 \times 10^{-4} \exp \left( -91.4 \text{ kcal mol}^{-1}/RT \right) \text{ cm}^2 \text{ s}^{-1} \]

Diffusion coefficients for oxygen in diopside, melilite, and spinel from this and a number of other investigations are also shown in Figure 1. At temperatures below the melting point of diopside (\(-1390^\circ\text{C}\)), diffusion is most rapid in melilite (regardless of composition), followed by diopside and then spinel. This pattern of relative diffusivities is consistent with that required to produce the pattern of oxygen isotopic anomalies in Ca-Al-rich inclusions by diffusive exchange [5].

Figure 1. Oxygen diffusion data from this study (\(\bullet = \text{spinel, } \square = \text{DeKalb diopside, } \mathbf{\square} = \text{Rajasthan diopside}\) and melilites [8], diopside [7,9] and spinel [10] from other workers.

REFERENCES: