IN-SITU UV-LASER FLUORINATION OXYGEN ISOTOPIC ANALYSES OF AN EFREMOVKA CAI AND MATRIX: IMPLICATIONS FOR OXYGEN ISOTOPE EXCHANGE IN THE SOLAR NEBULA.

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Introduction: The oxygen isotope anomaly present in CAIs reveals the earliest evolution of solar system materials. Of specific concern in this study is how the oxygen isotopic composition of various mineral phases in an individual CAI can be related to its thermal and temporal history. Recent work has shown that many CAIs experienced multiple heating or shock events in their history, resulting in several recrystallization and evaporative episodes. Magnesium isotopic data from E44, a type B CAI from the CV3 meteorite Efremovka, verify that this is one such object [1]. A complimentary oxygen isotopic data set would serve to better understand the complicated thermal history of CAIs such as these. The oxygen data are also relevant to the origin of oxygen isotope variability in early solar system condensed phases.

We used the unique UV-laser ablation fluorination technique to obtain high-precision *in situ* data for E44. Using these results, as well as diffusive exchange coefficients for the phases in question [2], we determined that the oxygen isotopes in anorthite, melilite, and fassiate in E44 could be explained by solid-state oxygen isotopic exchange between this object and a nebular gas.

Sample: E44 is a type B CAI from the reduced CV3 Efremovka. There is a core composed of large anorthite and fassaite grains, with dense spinel crystals. A melilite-mantle with interstitial spinel surrounds this core. Alteration is negligible.

Technique: A UV-laser ablation microprobe has been constructed at UCLA. A 213 nm coupled Nd-YAG laser is used for laser ablation sampling. Samples, including the standard (San Carlos olivine), are ablated in the presence of purified F_2 gas. This *in-situ* technique has a resolution of 125-150 μm for the experiments reported here. Oxygen gas is isolated and then taken via He-carrier gas into a Thermo Finnigan 253 mass spectrometer for analysis. Precision is on the order of 0.2 to 0.3‰ in $\delta^{18}O$ and $\delta^{17}O$. All values are reported relative to SMOW.

Results: The *in-situ* data for E44 and surrounding matrix are shown in Figure 1 (matrix points only included in graph inset). There are 17 points from the interior of the CAI, with the phases anorthite and melilite are well-represented. Three data points were obtained for the matrix. The data from CAI phases fall along a line with a slope of 0.92. This line is distinctly different from the CCAM line (slope=0.94) and the Young-Russell slope-1 line. The matrix points also lie on this lower-slope regression.

Fassaite has a $\delta^{18}O$ =-37.7 ‰, anorthite $\delta^{18}O$ values range from -32.5 to -35.5 ‰, and melilite $\delta^{18}O$ values range from -1.2 to 7.4 ‰. While we cannot rule out minor contamination from spinel, the grain size of E44 is sufficiently large that we are confident that the UV laser data are a good representation of the individual phases. Phase mixtures, as determined from BSE images, are labeled as such.

Solid State diffusion calculations: We compared our oxygen isotope ratios for E44 with predictions based on the diffusion equations and diffusion coefficients described in [2] for appropriate grain sizes. The goal is to determine whether solid-state diffusion of oxygen could explain the oxygen isotope systematics of this object. Adopted grain sizes include 1 mm for fassaite and melilite and 2 mm for the larger anorthite crystals. A median spinel grain size of 50 μm was used for these calculations. The sluggish rate of anorthite exchange and the ^{16}O-poor nature of most anorthites was taken as evidence against the importance of solid-state diffusion in coarse-grained CAIs by Ryerson and McKeegan. However, the ^{16}O-rich anorthite found in E44 indicates that this process may be important in this particular object.

Discussion: Our calculations indicate that high-temperature solid-gas exchange is a potential explanation for the oxygen isotopic trends in mineral phases of E44. Previous work [1] showed that at 1600K, 300 years were required to reset Mg isotope ratios in E44 by solid-state diffusion between anorthite (An) and melilite (Me). Our calculations reveal that the oxygen isotope systematics are consistent with this thermal history. This is because Mg self diffusion is much faster at higher temperatures than that of oxygen. At 1600K, åkermanite (Ak) would be completely reset, fassaite (Fs) would remain largely ^{16}O-rich, and anorthite would be ^{16}O-rich, but less so than fassaite. Using the fractional equilibration parameters for phase *i*, f_i, described by Ryerson and McKeegan, one can show that after 100 years the following values for fractional approaches to oxygen isotopic equilibration with an external reservoir are obtained: $f_{Fs} = 0.15$, $f_{Ak} = 1$, and

f_{An}=0.19. The magnesium and oxygen isotopes are thus consistent with a proposed history of solid-state diffusion lasting on the order of hundreds of years.

Figure 2 explores the entire time-temperature paramater space that satisfies the oxygen isotopic data of E44 in the context of solid-state oxygen self diffusion. The diagram is contoured for f_{An}. The ^{16}O-poor anorthite indicates that this phase has been largely equilibrated with its environment (f_{Me}~1). This diagram reveals that when T>1300K, it is possible to completely equilibrate melilite and maintain ^{16}O-rich anorthite grains as at reasonable timescales of ~days to 10^3 years at lower temperatures.

While a few recent studies have also found ^{16}O-rich anorthite in CV CAIs, it is generally uncommon, especially in large objects that appear to have undergone extensive processing. Both reports of ^{16}O-rich anorthite in reduced CVs argued for rapid disequilirium melting (melilite prior to anorthite) and subsequent recrystallization to reproduce the oxygen isotope systematics [3,4]. We maintain that solid-state diffusion is an alternative explanation for the high-precision E44 data shown here. Another complication that should be explored is solid-state diffusion between melilite and anorthite grains.

These diffusion calculations include the implicit assumption of exchange with a CO/CO_2 gas reservoir (diffusivities refer to dry conditions). A more likely scenario is that H_2O vapor, not CO, is the primary gaseous exchange reservoir. Previous studies performed on chondrule melts in an He+H_2O gas mixture resulted in extensive exchange between water vapor and silicate melt [5] while similar experiments on exchange between isotopically-labelled CO and chondrule material resulted in no exchange [6]. H_2O exchanges oxygen with condensed phases readily while CO does not. ^{16}O-poor nebular water is consistent with self shielding models for early solar system oxygen.

Conclusions: We obtained *in situ*, high-precision data for most mineral phases in E44, in addition to several analyses of surrounding matrix (the first obtained for Efremovka to our knowledge). This CAI is rare in that it shows extensive processing while preserving ^{16}O-rich anorthite. Our data for anorthite, melilite, and fassaite are consistent with a solid-state isotopic exchange at high temperatures for ~10^2 yrs. Obtaining diffusion coefficients for these phases with water vapor, however, may prove important for elucidating the thermal history and evolution of CAIs based on oxygen isotopes.

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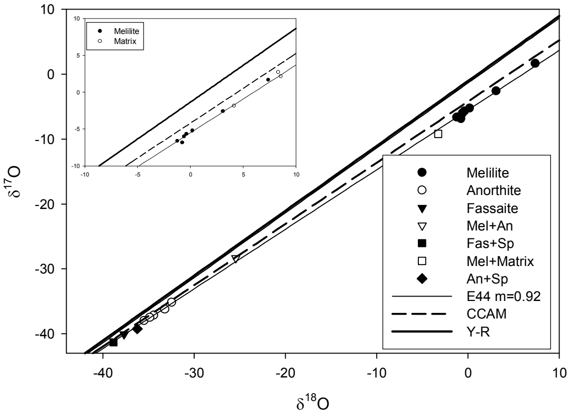

Figure 1: UV laser fluorination data obtained from E44 and Efremovka matrix. All points fall on a line with slope m=0.92. Inset plots melilite and matrix data points in a more restricted range.

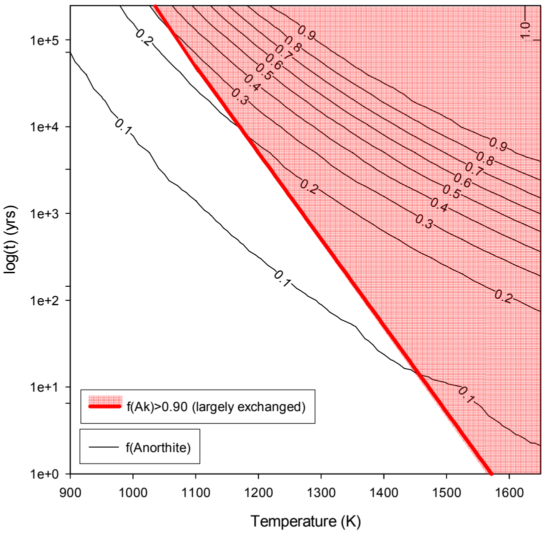

Figure 2: Log(time) vs. temperature plot for conditions of interest. Contours correspond to f_{An}. The red line and shaded area delineate the region where melilite is fully equilibrated (f_{Ak}>0.90) with a surrounding exchangeable gas.