MAGNESIUM, SILICON, AND OXYGEN ISOTOPIC CONSEQUENCES OF CAI EVAPORATION AND INVERSION FOR PRIMORDIAL MELT COMPOSITIONS. 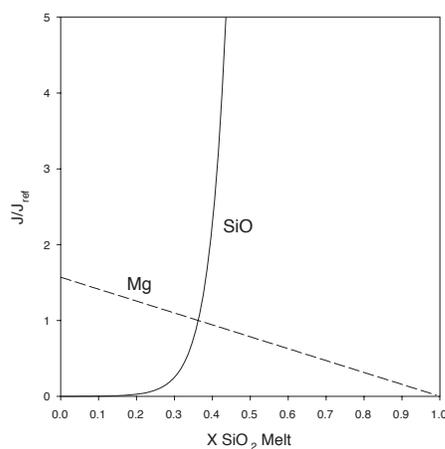Edward. D. Young[1] and Anat Shahar[2], [1]Department of Earth and Space Sciences, University of California Los Angeles, Los Angeles, CA, USA, eyoung@ess.ucla.edu, [2]Geophysical Laboratory, Carnegie Institution of Washington, Washington DC, USA, ashahar@ciw.edu.

Introduction: Igneous calcium aluminum-rich inclusions (CAIs) experienced various degrees of evaporation near the time of their formation in the early solar system. The physical chemistry of this process is sufficiently well known that the isotopic effects of evaporation can be used as tools for reconstructing the evolution of these ancient objects.

In prior work [1, 2] we used the enrichments in $^{25}Mg/^{24}Mg$ and $^{29}Si/^{28}Si$ common in these objects in attempts to reconstruct the times, temperatures, pressures (P_{H_2}) and initial compositions. The method involves a Monte Carlo search of composition space to determine those initial compositions (wt % SiO_2, MgO, Al_2O_3 and CaO) of CMAS melts that upon evaporation yield the measured shifts in Mg and Si isotope ratios. Our prior searches could not account for accurate activity-composition relations in SiO_2 and MgO for the melts because these relationships are calculated using relatively elaborate codes [3, 4] not easily adapted to large-scale random searches of composition space.

Parameterization of Melt Activities: Here we present results based on parameterizations of activity-composition relations in CMAS melts that afford rapid and accurate searches of compositon space suitable for reconstructing the initial concentrations of SiO_2 and MgO in igneous CAIs (Figure 1).

Building on the approach in [1], we modify published reference fluxes of Si and Mg [5, 6] with parameterizaed activity ratios for SiO_2 and MgO. For the former, we use a non-ideal formulation:

$$J_{SiO} = J_{SiO,ref} \exp\left(8.0(x_{SiO_2} / x_{SiO_2,ref} - 1)\right) \quad (1)$$

and for the latter an ideal formulation:

$$J_{Mg} = J_{Mg,ref}\, x_{MgO} / x_{MgO,ref} \quad (2)$$

where the ref subscript refers to the reference fluxes for a material of known composition. In addition to application of Equations (1) and (2), we find that experimental constraints on the temperature dependence of SiO fluxes from CMAS melts are reproduced when the activation energy of Si evaporation is increased by 20% relative to that in [5]. These simple parameterizations of the effects of melt activity on evaporative fluxes yield accurate depictions of evaportion of CMAS melts (Figure 2). The form of Equation (1) is consistent with many non-ideal activity-composition relationships and is generally consistent with thermodynamic models for CMAS melts (e.g., [3]).

Figure 1. Evaporative fluxes relative to reference fluxes used in present calculations as functions of mole fraction of SiO_2 in the parental CMAS melt.
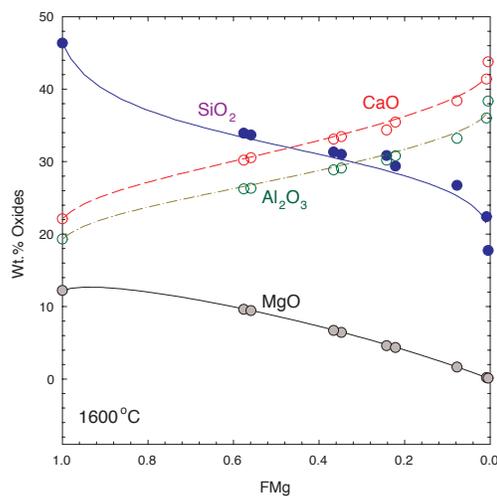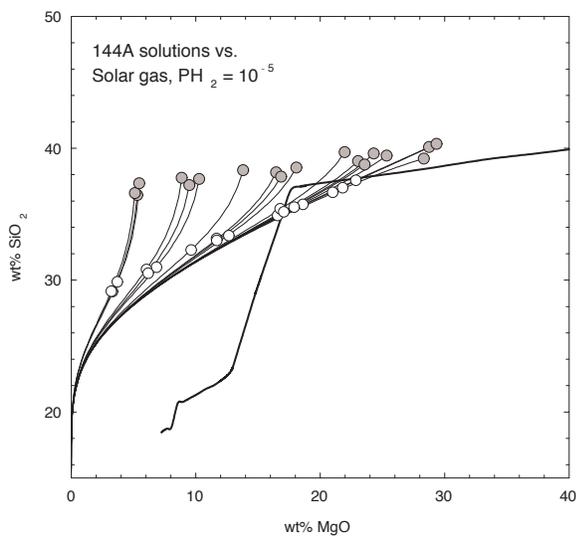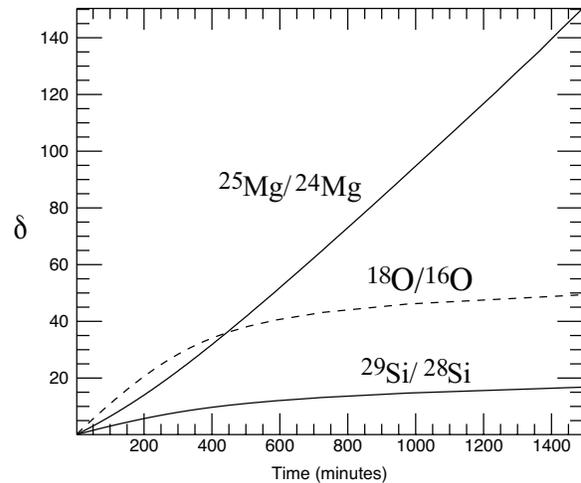

Figure 2. Comparison of measured (circles, [7]) and calculated (curves, this study) evaporation histories for a type B CAI-like melt at 1873K. FMg is the fraction of Mg remaining.

Applications: Comparisons with experimental data reported at this meeting last year [4] suggest that Si and Mg isotope ratio data constrain the initial concentrations of SiO_2 tightly but offer only lose constraints on the initial concentrations of MgO in the precursor melt. Estimates of plausible final MgO concentrations can be used to define a unique evaporation path. When applied to natural CAI data, where even final concentrations are not well known, an array of initial and final elemental concentrations is obtained that match the $\delta^{25}Mg$ and $\delta^{29}Si$ measurements (Figure 3). Comparisons with equilibrium condensation calculations suggest that in view of reasonable uncertainties, the precursor to the CAI studied in depth thus far could well have been a primary condensate from a solar gas at ~10^{-5} bar. If a primary condensate, the primary melt had an MgO concentration greater than ~ 18 wt% and condensed at T ~ 1310K.

Figure 4. Calculated changes in Mg, Si, and O isotope ratios with evaporation (as measured in time) for a single high-MgO model shown in Figure 3. Fits to the Mg and Si isotope ratios occur after ~100 minutes of evaporation, indicating an expected shift in $^{18}O/^{16}O$ of 10 per mil.

References: [1] Shahar A. and Young E.D. (2007) *EPSL* 257, 497-510. [2] Young E.D. and Shahar A. (2010) *LPSC XLI*. [3] Alexander C.M.O.D. (2001) *MAPS* 36, 255-283. [4] Ebel D.S. et al. (2011) *LPSC XLII*. [5] Richter F.M. et al. (2002) *GCA* 66, 521-540. [6] Grossman L. et al. (2000) *GCA* 64, 2879-2894. [7] Richter F.M. et al. (2007) *GCA* 71, 5544-5564.

Figure 3. Calculated initial (grey circles) and final (open circles) compositions of melts that reproduce the Mg and Si isotopic shifts measured in the fiducial CAI Leoville 144A. Also shown is the curve for equilibrium condensation from a solar gas at $P_{H2} = 10^{-5}$ bar (solid, Grossman, pers. comm.).

Oxygen: A corollary of these evaporation calculations is that the effects on oxygen isotope ratios are readily calculated. In the example of the fiducial CAI Leoville 144A presented in this abstract, the predicted shift in $\delta^{18}O$ with evaporation is ~ 10 per mil (Figure 4). Such shifts are not seen routinely in this or other similar igneous CAIs, suggesting post-evaporative exchange of oxygen with ambient gases.