

DISEQUILIBRIUM MELTING OF REFRACTORY INCLUSIONS: A MECHANISM FOR HIGH-TEMPERATURE OXYGEN ISOTOPE EXCHANGE IN THE SOLAR NEBULA. James P. Greenwood, Dept. of Geology and Geophysics, Kline Geology Laboratory, Yale University, New Haven CT 0620-8109, (james.greenwood@yale.edu).

Introduction: Oxygen isotope compositions of individual minerals in calcium-, aluminum-rich inclusions (CAI) show a large isotopic range [1,2]. The oxygen isotope compositions of CAI minerals are incongruous with simple crystallization of CAI composition melts in a changing oxygen reservoir [2,3], in that spinel and fassaite are generally ^{16}O -rich, while melilite is ^{16}O -poor. Since melilite crystallizes before fassaite [4], and during equilibrium melting, fassaite will begin melting before melilite, we have an oxygen isotope paradox [2]. Here, I propose a simple solution to this paradox.

If CAIs were heated above the congruent melting temperature of individual CAI minerals, these minerals would transform to a liquid in less than seconds as determined by modeling melting rates using a normal growth model [5,6]. This is a very different process than that of equilibrium melting of CAIs, which is the reverse of equilibrium crystallization. The equilibrium crystallization sequence of a typical Type B CAI composition (CAIB; [4]), is: (1) spinel ($\sim 1550^\circ\text{C}$), (2) spinel+melilite ($\sim 1400^\circ\text{C}$), (3) +anorthite ($\sim 1260^\circ\text{C}$), and (4) +fassaite ($\sim 1230^\circ\text{C}$). Equilibrium melting would be the reverse, and would consist of: 1) melting of the four phase assemblage at $\sim 1230^\circ\text{C}$ until fassaite is completely melted, followed by 2) melting of anorthite, melilite and spinel until $\sim 1260^\circ\text{C}$ when anorthite would be completely melted, followed by 3) melting of melilite and spinel to $\sim 1400^\circ\text{C}$, and then 4) melting of only spinel until complete melting at $\sim 1550^\circ\text{C}$. Equilibrium melting is a slow process, which is appropriate for decompression melting of the mantle, but not for flash heating in the solar nebula.

During a rapid, high-temperature event (flash heating), wherein the CAI is heated to $T_{\text{peak}}=1500^\circ\text{C}$ on the order of seconds, only fassaite and melilite will melt; anorthite and spinel will not. For $T_{\text{peak}}=1700^\circ\text{C}$, anorthite, melilite and fassaite will melt.

Here I show that the melting rate of melilite will be higher than that of fassaite during high-temperature events. I also show that the diffusivity of oxygen will be higher in melilitic liquids than in fassaitic liquids. These two processes lead to a more rapid exchange of oxygen isotopes for melilite compared to fassaite in high-temperature events in the early solar nebula. These same hypotheses and the constraints therein, lead to an extended anneal at lower temperatures, above the glass transition of anorthite ($\sim 1000^\circ\text{C}$).

Melting rates of CAI minerals: The normal growth model for the movement of the solid-liquid interface reproduces experimental rates only within an order of magnitude, except for quartz (a factor ~ 20) and diopside (a factor of ~ 75). As diopside was the only mineral with a high ΔS_f , typical of geological minerals, I recently developed a new model for the melting rates of silicates and oxides [7]. This empirical model has a sound theoretical basis in Jackson's theory of crystal growth [8]. The 'smooth interface' (SI) model of [7] leads to calculated melting rates that reproduce 44 of the 45 experiments on the melting kinetics of silicates and oxides in the literature within a factor of four. More importantly, it reproduces the experimental data for the high ΔS_f minerals albite and diopside within a factor of two, and is thus appropriate for estimating the melting rates of CAI minerals such as melilite, fassaite, and anorthite. The normal growth and SI model use Wilson-Frenkel model:

$$U = fD^*/\lambda[1 - \exp(-\Delta G_m/kT)] \quad (1)$$

Where U is the growth rate, f is the fraction of sites available for melting, D^* is the kinetic transport factor for movement across the solid-liquid interface, and ΔG_m is the energy needed for this process. In the normal growth model for the melting of condensed phases, melting is limited by diffusive transport at the interface, as opposed to heat transport, which would be appropriate for metals. The normal growth model for melting is developed in [5,6]. The SI model of [7] differs in that the fraction of sites is no longer assumed to be equal to unity for melting. Instead, $f = A \exp(-B\alpha)$, where $\alpha = (\Delta S_f/R)$ and A and B are empirical constants. Consideration of the roughening of a smooth interface leads theoretically to $f = \exp(-\alpha)\phi$, where ϕ is related to the packing of the interface [8]. It should be pointed out that Jackson's theory of crystal growth is highly successful, in that it qualitatively predicts the external morphology of crystals from their entropy of fusion (e.g. [9]).

Melting rates for akermanite, diopside, anorthite, melilite, and fassaite calculated by the SI model are shown in Table 1. The methods and references for thermodynamic quantities can be found in [5-7]. For melilite, I chose an Ak61 from [10], and a viscosity from [11] for this composition. Melting temperature was determined from [12] and the ΔH_f of akermanite was used. For fassaite, a composition from

[10] was used, with a calculated viscosity from [12]; melting point and ΔH_f were assumed to be similar to diopside.

Table 1. Melting rates (m/s) of CAI minerals calculated using the Smooth Interface model of [7].

Mineral	1500°C	1600°C	1700°C
Diopside	7×10^{-4}	2×10^{-3}	4×10^{-3}
Akermanite	2×10^{-3}	1×10^{-2}	3×10^{-2}
Anorthite	-----	1×10^{-4}	1×10^{-3}
Melilite	3×10^{-3}	1×10^{-2}	3×10^{-2}
Fassaite	5×10^{-4}	2×10^{-3}	4×10^{-3}

Oxygen self-diffusion in melilitic and fassaite liquids: Oxygen self-diffusion has been experimentally determined for diopside melts [13]. A model relating the viscosity of melts in the CMAS system to oxygen self-diffusion was used to calculate the oxygen self-diffusion coefficient at 1500°C [14]. Using $x^2 = Dt$, for $x = 100 \mu\text{m}$, we get $t = 121 \text{ s}$ for an Ak61 [10], and $t = 375 \text{ s}$ for diopside.

Fassaite is likely more viscous than diopside, according to a viscosity model [12]. Melilitic liquids will likely always be more fluid than fassaite liquids. A qualitative use of the Eyring equation would predict from this simple analysis that oxygen isotope exchange will be always be faster in melilitic liquids as compared to fassaite liquids.

CAIs that contain anorthite offer additional information. Anorthite liquid is much more viscous than melilitic or fassaite liquids, and would be the slowest to equilibrate with an ^{16}O -poor gas. A prolonged anneal would seem to be necessary to isotopically exchange oxygen in CAI anorthite. The problem is that fassaite cannot exchange oxygen during this prolonged anneal. A possible solution is that the time spent above the melting point of fassaite was short, and that this time was insufficient to exchange oxygen, but was sufficient in time to exchange oxygen in melilite. The diffusion of oxygen differs by only a factor of three at 1500°C between diopside and melilite, suggesting that multiple, short-lived, heating events were necessary to promote the exchange of oxygen in melilite relative to that of fassaite. If this model is correct, we should find that fassaite has a range of oxygen isotope compositions along the CCAM or slope 1 line, and that it may be petrographically correlated. Small fassaite grains embedded in melilite in the outer zones of Type B1 CAIs may not show primordial oxygen signatures.

Proposed thermal history of CAIs for oxygen isotope exchange: If CAIs formed by the condensation of a nebula gas, followed by remelting

and slow cooling to produce igneous textures and promote evaporation of Mg and Si [15], then these CAIs were ^{16}O -rich and their oxygen resembled that of ^{16}O -rich materials in CAIs. These objects were then heated to $T_{\text{peak}} < T_m$ of spinel and perovskite, but above T_m of anorthite ($\sim 1600\text{-}1900^\circ\text{C}$) for less than a second, and then cooled quickly to a temperature below or near the solidus ($< 1230^\circ\text{C}$). The temperature near the solidus was maintained for a longer duration, so that anorthite could crystallize and equilibrate with the ambient ^{16}O -poor gas. The rapid cooling from T_{peak} to $T < 1230^\circ\text{C}$ is necessary so that fassaite liquid does not equilibrate with the nebula gas.

Conclusions: Here I have shown a simple mechanism for the exchange of oxygen isotopes of CAI minerals during disequilibrium melting events of short duration in the solar nebula. This history is reconcilable with past descriptions of the thermal histories of refractory inclusions [15]. The thermal histories proposed herein could be accomplished if CAIs were formed in the inner nebula, were then subsequently melted in a disequilibrium fashion, such as by multiple, short-duration flare events, and were then heated for several days at $\sim 1000\text{-}1200^\circ\text{C}$, such as might occur in an X-wind [16]. The disequilibrium melting would necessarily take place in a region of the disk that was enriched in heavy isotopes of oxygen, such as the inner edge of the gas disk [17].

More importantly, I have demonstrated the importance of transient heating events in the thermal history of the CAIs. One could extend this model to explain the oxygen isotopic systematics of the smaller CAIs in ordinary and CH chondrites. The model I propose is testable. Oxygen self-diffusion measurements in melilitic and fassaite liquids are desperately needed. Melting rate data on CAI minerals would also be an important addition to our knowledge and for our ultimate understanding of the oxygen isotope anomaly.

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