

THE STABILITY OF HIBONITE AND OTHER ALUMINOUS PHASES IN SILICATE MELTS: IMPLICATIONS FOR THE ORIGIN OF HIBONITE-BEARING INCLUSIONS.

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Abstract. Phase fields in which hibonite (Hib) and silicate melt coexist with spinel (Sp), CaAl_4O_7 (CA2), gehlenitic melilite (Mel), anorthite (An) or corundum (Cor) in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ (CMAS) were determined and activity models developed for melilite (Mel) and Hib solid solutions. Experimentally determined partition coefficients for Ti between Hib and coexisting melt, D_{Ti} , vary from 0.8 to 2.1 and generally decrease with increasing TiO_2 content in the liquid (L). Based on Ti partitioning between Hib and melt, bulk inclusion compositions and Hib-saturated liquidus phase diagrams, the Hib in Fluffy Type A inclusions (FTA's) from Allende and at least some of the Hib from Hib-rich inclusions is relict; much of the Hib from Hib-glass spherules probably crystallized from a melt under nonequilibrium conditions. Bulk compositions for all of these Ca-Al-rich inclusions (CAIs) are consistent with an origin as Mel + Hib + Sp + perovskite (Pv) proto-inclusions in which Mel was partially altered. In some cases, the proto-inclusion was partially or completely melted with vaporization occurring over a period of time sufficient to remove any Na introduced by the alteration process but frequently insufficient to dissolve all of the original hibonite. If equilibration temperatures based on Hib-bearing CAIs reflect condensation in a cooling gas of solar composition, then Hib + Cor condensed at $\sim 1260^\circ\text{C}$ (referenced to 10^{-3} atm) and Hib + Sp \pm Mel at $\sim 1215 \pm 10^\circ\text{C}$. Simple thermochemical models for the substitution of trace elements into the Ca-site of meteoritic Hib suggest that virtually all Eu is divalent in early condensate Hibs but that $\text{Eu}^{2+}/\text{Eu}^{3+}$ decreases by a factor of 20 or more during the course of condensation, primarily because the ratio is proportional to the partial pressure of Al, which decreases dramatically as aluminous phases condense. The relative sizes of Eu and Yb anomalies in meteoritic Hibs and CAIs may be influenced by this effect.

Introduction. Hib-bearing CAIs occur in carbonaceous, ordinary and enstatite chondrites but there is little consensus on how these inclusions formed. Based on textural, compositional and isotopic arguments, some appear to have crystallized from melts while others are interpreted to be vapor-to-solid condensates and/or vaporization residues (1-2). We conducted isothermal crystallization experiments in CMAS at 1 bar, 1350-1550°C. Our results are used to evaluate whether or not Hib could have crystallized from specific CAI bulk compositions and as a basis for constraining vapor-Hib equilibria in the primitive solar nebula.

Starting Compositions and Results. Fifteen bulk compositions with 0-5 wt% TiO_2 were selected to map out portions of the Hib saturation surface in CMAS by crystallization experiments. Hib is a binary [$\text{CaAl}_{12}\text{O}_{19}$ (HIB) - $\text{CaMgSiAl}_{10}\text{O}_{19}$ (MSH)] or ternary [HIB - MSH - $\text{CaMgTiAl}_{10}\text{O}_{19}$ (MTH)] solution, Ti^{4+} being slightly incompatible ($D_{\text{Ti}} \sim 0.8$) to strongly compatible ($D_{\text{Ti}} \sim 2.1$) with lower D_{Ti} at higher bulk Ti. Projected compositions of Hib-saturated melts (Fig. 1) are similar to those of (3) and are generally lowered by ~ 1 wt% HIB for every 1 wt% increase in TiO_2 . Hib is destabilized slightly under reducing conditions. There are also regions near the An and Sp vertices (shaded in Fig. 1) for which there are no Hib-saturated melts because Hib melts incongruently to Cor + L and if sufficient HIB is added to any Hib-saturated melt, Hib + L becomes unstable for the same reason. Hib is in a reaction relationship with L along Cor-Sp-Hib-L and CA2-Sp-Hib-L except possibly close to the Mel-CA2-Sp-Hib-L invariant point, CA2 along CA2-Mel-Hib-L and Cor along An-Cor-Hib-L.

Did Meteoritic Hibonite Crystallize from Melts? A few Hib-bearing inclusions contain glass and were therefore at least partially molten at some point. Most of these have bulk compositions consistent with near-liquidus Hib and apparent D_{Ti} values consistent with experimentally determined values. This suggests that there are at least Hib overgrowths on relict cores and possibly that all of the Hib crystallized from a melt. Glass compositions (1,4-5) are, however, well below the Hib-saturation surface suggesting that rapid cooling rates prevented nucleation of otherwise stable phases and that the liquid line of descent therefore passed through their saturation surfaces. Bulk compositions of some of the glass-bearing inclusions are far below the Hib saturation surface. Provided that sections used to obtain bulk compositions were representative, Hib is quite unlikely to appear early in the crystallization sequence, which suggests that at least some of the Hib is relict unless nucleation is much easier for Hib than for the other phases. Hib in FTA's is texturally early but bulk compositions are well below the saturation surface and Ti contents of Hib are often much higher than consistent with an early crystallizing phase. This suggests that Hib is relict with respect to melting events in these inclusions.

Condensation Sequences. We derived a binary solution model with one ordering parameter for Mel, a ternary model for Hib with perfect ordering of Mg-Si couples in adjacent tetrahedra, and used available thermodynamic data for end-member Sp, Mel, Hib, oxides and vapor species (6-8) to constrain the stability of meteoritic Hib-bearing phase assemblages. Based on the reactions [1] $\text{HIB} + \text{Mg}_{(\text{g})} + \text{SiO}_{(\text{g})} + \text{O}_{2(\text{g})} = \text{MSH} + \text{Cor}$ and [2] $\text{HIB} + \text{SiO}_{(\text{g})} + 2\text{Mg}_{(\text{g})} + 1.5\text{O}_{2(\text{g})} = \text{MSH} + \text{Sp}$ and assuming solar abundances of vapor species, we obtain temperatures for meteoritic Hib referenced to 10^{-3} atm of Hib + Cor $\sim 1260^\circ\text{C} \rightarrow$ Hib + Sp \pm Mel $\sim 1215 \pm 10^\circ\text{C}$.

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These refer to the points at which vapor-solid equilibrium ceased and may or may not correspond to initial condensation of phases. However, the relative temperatures are consistent with observed textures and therefore a condensation sequence. The equilibration temperatures of Hib-bearing inclusions with Sp but no Mel are indistinguishable from those with Sp+Mel+Hib although both they and the Cor + Hib temperatures are $>70^\circ$ below calculated equilibrium condensation temperatures of Mel for a cooling gas of solar composition (9). This may reflect the relative ease of nucleation in the vapor for Sp and Mel or fractionation of an aluminous phase.

Eu Anomalies. Available data are insufficient for accurate calculations of absolute concentrations of trace elements (TE) in condensate Hib, primarily because neither individual standard state free energies of formation for end-member components nor differences in free energies between them are known. Data of (10), however, constrain the relative free energies of formation from the oxides of $\text{Eu}^{2+}\text{Al}_{12}\text{O}_{19}$ (EuH2) and $\text{Eu}^{3+}\text{MgAl}_{11}\text{O}_{19}$ (EuH3) $[\bar{G}_{\text{EuH2}}^{\text{ox}} - \bar{G}_{\text{EuH3}}^{\text{ox}}]$ to -58 ± 8 kJ/mole at 1470°C . The exchange reaction [3] $\text{EuH3} + \text{Al}_{(\text{g})} = \text{EuH2} + \text{Mg}_{(\text{g})}$ can therefore be used to calculate $\text{Eu}^{2+}/\text{Eu}^{3+}$ in condensate Hib. This leads for trace Eu to [4] $X_{\text{EuH2}}/X_{\text{EuH3}} = [2X_{\text{MTH}}/(X_{\text{Hib}} + X_{\text{MTH}}/2)][P_{\text{Al}}P_{\text{Mg}}] \exp[-\Delta\bar{G}_{\text{r}(3)}^{\circ}/RT]$, where P_i are partial pressures in the vapor, X_i mole fractions in Hib and $\Delta\bar{G}_{\text{r}(3)}^{\circ}$ the standard state free energy of reaction [3]. Note that $\Delta\bar{G}_{\text{r}(3)}^{\circ}$ of an exchange reaction such as [3] that takes into account the phase that the TE is substituting into must be evaluated to describe correctly partitioning of a TE between Hib and vapor. This leads invariably to an explicit dependence of TE concentrations on P_i of one or more major element species in the vapor. Previous calculations (11-12) neglected this aspect of TE condensation but it can have a significant influence. Fig. 2 shows calculated $\text{Eu}^{2+}/\text{Eu}^{3+}$ in equilibrium condensate Hib based on (9). We increased the crystal chemistry term (i.e. the first expression in brackets in [4]) linearly from 0.11 at 1455°C to 1.94 at 1217°C to account for observed variations in meteoritic Hib. Initially, $\text{Eu}^{2+}/\text{Eu}^{3+}$ rises, an artifact of how the Hib composition was assumed to change that may not occur in natural systems, but the steadily declining P_{Al} due to condensation of aluminous phases soon causes a decline in $\text{Eu}^{2+}/\text{Eu}^{3+}$ that continues until Hib no longer coexists with vapor. Details of Fig. 2 are strongly dependent on various assumptions, but two features are likely to survive improvements in the thermodynamic database and condensation scenarios. {1} Most Eu in condensate Hib is divalent. Previous calculations used Eu^{3+} only and therefore underestimated total Eu concentrations, possibly by as much as 2-3 orders of magnitude. {2} $\text{Eu}^{2+}/\text{Eu}^{3+}$ decreases significantly during equilibrium condensation, by a factor > 20 in Fig. 2. Thus, the size of the Eu anomaly relative to that of the trivalent cation Yb can be expected to change in a way that reflects the degree of condensation (at least prior to the appearance of Pv) and this may be an important factor in determining the relative sizes of Eu and Yb anomalies in meteoritic inclusions.

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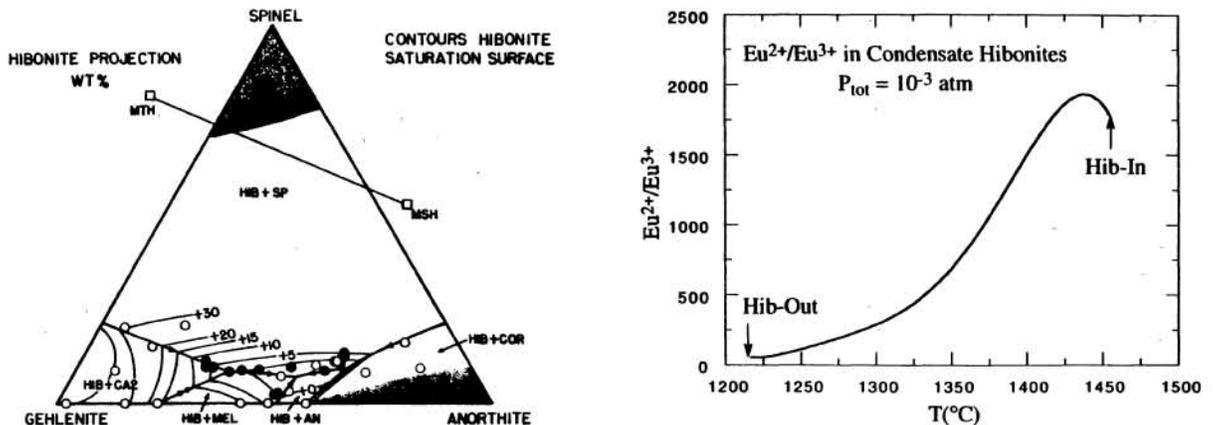


Fig. 1. Hib-saturated liquidus phase diagram (<2.5 wt% TiO_2) projected from Hib and TiO_2 onto the composition plane formed by gehlenite, anorthite and spinel contoured in wt% Hib. Multiply-saturated liquids from literature cited in 1 (open symbols) and this study (closed symbols).

Fig. 2. Calculated $\text{Eu}^{2+}/\text{Eu}^{3+}$ in condensate Hib assuming equilibrium condensation at a total pressure of 10^{-3} atm in a cooling gas of bulk solar composition.