

HIBONITE CONDENSATION IN THE SOLAR NEBULA. M.B. Fegley, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138.

Hibonite (CaAl_2O_9) has been observed in refractory inclusions in several carbonaceous chondrites, e.g. Allende, Leoville, Vigarano and Murchison. However despite the frequent occurrences of hibonite in refractory inclusions and the potential importance of hibonite for deciphering the history of these inclusions, no comprehensive chemical equilibrium calculations for hibonite and other calcium aluminates have been made. Grossman (1) suggested that hibonite, rather than corundum (Al_2O_3) is the first major element-bearing condensate in a solar composition system. However, the lack of thermodynamic data for hibonite prevented him from actually doing any condensation calculations. Blander and Fuchs (2) used slag activity measurements to estimate free energy values for hibonite and CaAl_4O_7 and calculated condensation temperatures for both phases at 10^{-3} bars pressure. However accurate and internally consistent thermodynamic data for all five calcium aluminates were not available until the very careful study by Allibert et al (3). The present work uses these data to calculate the stabilities of hibonite, all other calcium aluminates, and corundum over a wide range of temperatures and pressures in solar composition matter.

The results of the chemical equilibrium calculations illustrate that hibonite and CaAl_4O_7 are the only two aluminates which are stable in solar composition matter. Corundum is also stable but only at pressures less than about $10^{-2.7}$ bars. Above this pressure hibonite is the initial condensate until a pressure of $10^{0.06}$ bars where CaAl_4O_7 becomes the first condensate. In turn CaAl_4O_7 is the first condensate until $10^{0.45}$ bars where $\text{CaO-Al}_2\text{O}_3$ melts become stable. The results of Blander and Fuchs (2) for corundum, hibonite, and CaAl_4O_7 formation at 10^{-3} bars are in qualitative agreement with the present results (at the same pressure). However no previous study included all five calcium aluminates, used internally consistent thermodynamic data, or covered as wide a range of temperatures and pressures.

The calculations predict the following condensation sequence and mineralogical assemblages. At pressures less than $10^{-2.7}$ bars corundum is the initial condensate. It reacts with the cooling nebular gas to form hibonite, which in turn is converted to CaAl_4O_7 . Thus assemblages such as relict corundum surrounded by hibonite or relict hibonite surrounded by CaAl_4O_7 might be expected in hibonite-bearing refractory inclusions. Perovskite (CaTiO_3) is formed at comparable temperatures and can stably coexist with hibonite and phases formed at lower temperatures. Perovskite crystals on the surface of hibonite crystals or perovskite crystals enclosed by CaAl_4O_7 --which condenses just below perovskite--or perovskite enclosed by melilite are assemblages predicted by the calculations. As the temperature decreases further CaAl_4O_7 reacts with the nebular gas to form gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and the akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) content of the melilite increases. CaAl_4O_7 crystals surrounded by melilite or contiguous CaAl_4O_7 -melilite crystals displaying a reaction relationship are the assemblages expected. The melilite and CaAl_4O_7 coexist until CaAl_4O_7 is consumed during spinel (MgAl_2O_4) formation. Relict CaAl_4O_7 enclosed by spinel is the predicted mineral assemblage.

How do the observed mineralogies of hibonite-bearing inclusions compare with the predictions of the chemical equilibrium calculations? Grossman et al (4) have described a corundum-rich inclusion (BB-5) from Murchison which is composed of hibonite (77% by area), corundum (23%) and traces of perovskite. The inclusion mineralogy and textural relations are consistent with a vapor-solid condensation origin. BB-5 could have condensed at pressures less than $10^{-2.7}$ bars and then have been isolated from the nebular gas after perovskite formation but before CaAl_4O_7 formation.

Several authors (5) have described coarse-grained pure hibonite inclusions in Murchison. Some of these are irregular clumps of hibonite while another one is a single hibonite crystal 90 μm in longest dimension. Textural and isotopic evidence suggest a primary origin for these inclusions. The coarse-grained hibonite inclusions can be viewed as hibonite crystals which condensed and were then isolated from further interactions with the nebular gas. They could be formed at pressures greater than $10^{-2.7}$ bars and be samples of a different P-T region of the nebula than inclusion BB-5.

However BB-5 is (sofar) an isolated occurrence and the primary origin of the coarse-grained hibonite inclusions is uncertain. Many other hibonite-bearing inclusions in Murchison, as well as in Allende and Leoville, do not have mineralogies and textural features consistent with the predictions of the chemical equilibrium calculations. Several different observations by other workers support this assertion. For example, hibonite is frequently found associated with spinel (5), but only rarely with CaAl_4O_7 or melilite which both condense after hibonite but before spinel. Second, CaAl_4O_7 , which is stable over a

HIBONITE CONDENSATION

Fegley, M.B.

large P-T range, is almost never found in refractory inclusions. In fact, CaAl_4O_7 has been observed in only one inclusion, labelled L2, in Leoville (6). Also the mineralogy, chemistry and textural features in L2 do not necessarily imply a vapor-solid condensation origin. Third, the hibonite-bearing rims (overlying more volatile phases) found on some inclusions (2,7) are not predicted by the chemical equilibrium calculations which predict instead that refractory phases will be enclosed by less refractory phases, e.g. corundum mantled by hibonite and hibonite mantled by CaAl_4O_7 . These latter two cases have been rarely if ever observed. Fourth some hibonite-bearing inclusions contain hibonite which has inclusions of perovskite in it (2). This feature is exactly opposite to the textural relations predicted by the chemical equilibrium calculations. Last some hibonite-bearing spherules in Murchison have textures such as an almost solid core with intergrown phases and splays of crystals which apparently grew inward from a cooling exterior which suggest that these spherules were once molten (8). It is not certain whether the spherules are the result of melting pre-existing condensates or are the product of direct vapor-liquid condensation. However, their spherical shape, mineralogy and texture are inconsistent with the predictions of the chemical equilibrium calculations.

Taken together these observations strongly suggest that processes much more complex than a simple sequential condensation process were involved in the formation of many hibonite-bearing inclusions. Although some inclusions such as BB-5 and the coarse-grained hibonite inclusions in Murchison have mineralogies and textural features consistent with a vapor-solid condensation origin many other inclusions described in the literature do not have such features. Rather than adapting the simple first-order condensation model to fit this evidence I suggest that a much more promising approach seems to be the development of second order models incorporating features such as grain and vapor transport in the nebula, consideration of kinetic effects in reactions, and the study of vapor-liquid condensation processes. Although this suggestion is not original, the comprehensive equilibrium calculations for the calcium aluminates and the comparison with the actual inclusion mineralogies and textures indicate that deviations from the first order condensation model occurred at much higher temperatures and are more widespread than previously assumed. Thus work on second order models is even more imperative than before. Our companion abstract (9) describes work which is being done along these lines.

References: (1) Grossman, L. (1972) *GCA* **36**, 597; (2) Blander, M. and Fuchs, L.H. (1975) *GCA* **39**, 1605; (3) Allibert, M. et al (1981) *J. Am. Ceram. Soc.* **64**, 307; (4) Grossman, L. et al (1980) *Meteoritics* **15**, 296; (5) MacDougall, J.D. (1979) *EPSL* **42**, 1; MacPherson, G.J. et al (1980) *LPSC XI*, p. 660; (6) Kurat, G. (1981) per. comm.; (7) Allen, J.M. et al (1980) *GCA* **44**, 685; (8) MacDougall, J.D. (1981) *GRL* **8**, 966; (9) Cameron, A.G.W. and Fegley, M.B. (1981) These abstracts.

Acknowledgments: I thank A.G.W. Cameron for supporting this research under NASA Grant NGR-22-007-269.

