NEBULAR CONDENSATION UNDER INCOMPLETE EQUILIBRIUM: IMPLICATIONS FOR THE FINE-GRAINED SPINEL-RICH CAIs.

M. I. Petaev[1,2], A.N. Krot[3] and J. A. Wood[1], [1]Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, USA; [2]Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, USA, [3]Hawai'i Institute of Geophysics and Planetology, SOEST, University of Hawai'i at Manoa, Honolulu, HI 96822, USA; e-mail contact: mpetaev@cfa.harvard.edu.

Introduction: For more than three decades the equilibrium condensation sequence has been successfully used to interpret the chemistry and mineralogy of primitive chondrites. Many observed deviations in mineralogy and chemistry of some nebular components from the classic condensation sequence calculated for a gas of solar composition at a nebular pressure of 10^{-3} bar [1] can be corrected either by the use of improved thermodynamic data [*e.g.*, 2-5], or by condensation in fractionated nebular systems [*e.g.*, 2, 4-6], or by condensation at different pressures [7, 8], or by the condensate isolation [9, 10]. However, none of these equilibrium condensation models can resolve the well-known discrepancy between the equilibrium condensation sequence and the structure of individual nodules of fine-grained CAIs, where spinel cores surrounded by melilite mantles provide unequivocal evidence for condensation of spinel prior to melilite. Two different explanations for this discrepancy have been put forward. First, it has been suggested [11, 12] that the equilibrium condensation of melilite was suppressed either for kinetic reasons or by extreme Ca/Al fractionation. However, neither of these mechanisms seems plausible [13]. For example, because both melilite and spinel under equilibrium conditions form by reactions of primary condensates – hibonite and/or grossite – with the residual nebular gas, it is difficult to understand why the reaction hibonite+gas → melilite which requires no evaporation would be delayed by ~100 K relative to the reaction hibonite+gas → spinel which requires Ca evaporation. An alternative explanation would be rapid (probably disequilibrium) condensation in a parcel of supercooled nebular gas [*e.g.*, 14] in which spinel nucleates before melilite. This hypothesis is numerically tested here.

Mineralogy of fine-grained CAIs: Fine-grained CAIs in primitive carbonaceous chondrites are aggregates of numerous small irregularly-shaped nodules consisting of spinel ± hibonite ± perovskite, each of which is surrounded by thin and nearly monomineralic layers of melilite and Al-diopside; melilite is often replaced by anorthite [13,15]. The similar mineralogical zoning of spinel-rich inclusions is observed in AOAs, but there melilite is almost completely replaced by anorthite [16].

Thermodynamic model: Condensation of a supercooled gas would undoubtedly involve some kinetic effects, which are currently difficult or impossible to include in a numeric study because of the lack of ap-

propriate data. To simplify the problem, we made the following assumptions: (1) equilibrium speciation of a gas of solar composition is maintained at all temperatures of interest; (2) minerals condense by nucleation from the gas, which takes place as soon as gas-solid equilibrium is reached.

The speciation of the gas was calculated over wide ranges of nebular temperatures and pressures using a version of the CWPI code [4, 10] with all condensed phases removed from the thermodynamic database. The condensation temperatures of corundum, hibonite, grossite, perovskite, spinel, gehlenite, anorthite, Ca-tschermakite, diopside, forsterite, and Fe-Ni metal were calculated using the thermodynamic database of the ZONMET code [10] and partial pressures of the most abundant gaseous species of each element (see Fig. 1 plus gaseous H_2 and H_2O for the H and O, respectively) calculated as described above. A few alteration reactions of primary condensates with the ambient gas such as hibonite+gas → melilite, hibonite+gas → spinel, and grossite+gas → spinel+periclase were also taken into consideration, but these were found to be metastable relative to the direct condensation reactions.

**Results:** Fig. 1 shows how the mole fractions of major gaseous species of interest vary with temperature


Figure 1
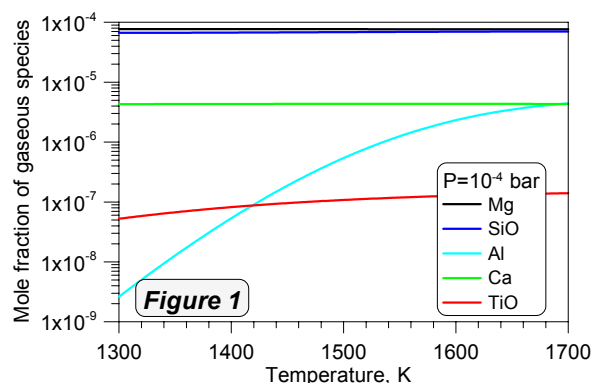
at a nebular pressure of 10^{-4} bar. Only the mole fraction of Al changes significantly with falling temperature, due to the formation of Al oxides, mainly Al_2O, but in the temperature range of condensation of spinel and melilite these changes are relatively minor. The equilibrium speciation of the gas is essentially independent of pressure, except that Al oxidation begins at lower temperatures with decreasing nebular pressure. Thus it appears that high-temperature equilibrium speciation of the nebular gas, once established, could be readily

maintained in the temperature range of interest.

The calculated condensation curves of the major minerals of fine-grained spinel-rich CAIs and AOAs are shown in Fig. 2. Spinel, melilite and perovskite (red, blue, and green curves, respectively) condense in a narrow temperature range, with the condensation sequence being pressure-dependent (see yellow insert). Corundum (not shown), hibonite, and grossite (not shown) would condense before the spinel-melilite-perovskite assemblage; clinopyroxene solid solution (ice-blue band), anorthite, forsterite, and metal condense later.

Figure 2
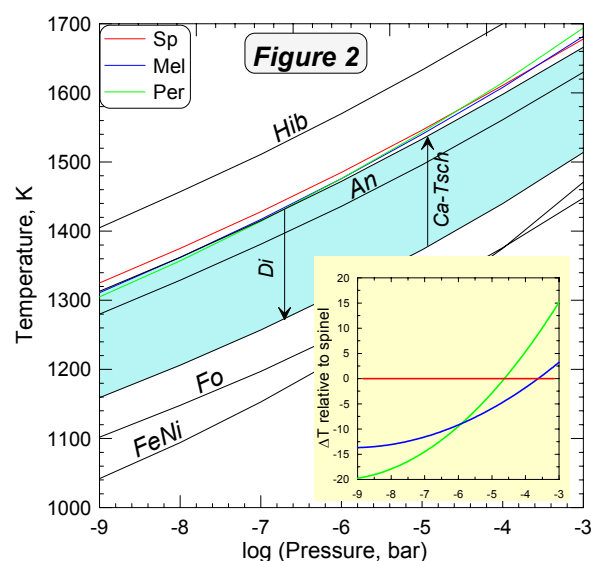
The yellow insert in Fig. 2 shows condensation temperatures of melilte and perovskite relative to that of spinel ($T_{min} - T_{sp}$). Depending upon the nebular pressure, there are four different condensation sequences: perovskite $\rightarrow$ melilite $\rightarrow$ spinel ($P_{tot} > \sim 2.5 \times 10^{-4}$ bar); perovskite $\rightarrow$ spinel $\rightarrow$ melilite ($\sim 3 \times 10^{-5} - 2.5 \times 10^{-4}$ bar); spinel $\rightarrow$ perovskite $\rightarrow$ melilite ($\sim 1.3 \times 10^{-6} - 3 \times 10^{-5}$ bar), and spinel $\rightarrow$ melilite $\rightarrow$ perovskite ($< 1.3 \times 10^{-6}$ bar).

Figure 3
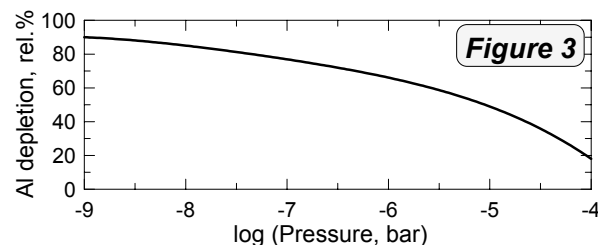
So far our thermodynamic analysis has been based on the assumption that early Ca,Al-bearing condensates do not deplete the nebular gas, which may or may not be true in nature. Fig. 3 shows to what degree the nebular gas can be depleted in Al (and corresponding amounts of Ca) and still be able to condense spinel prior to melilite. The admissible depletion increases from ~ 20 % at 1×10^{-4} bar to ~ 90 % at 1×10^{-9} bar.

Discussion: Our thermodynamic analysis of condensation reactions of major minerals of CAIs and AOAs clearly shows that at nebular pressures lower than $\sim 2.5 \times 10^{-4}$ bar spinel can condense before melilite under conditions that are rather far from equilibrium. First, there should be no metasomatic reactions between the condensates and the ambient residual gas. This requirement seems to be consistent with our calculations as well as with general textures of the individual nodules, which show no such reactions. A second and more important condition is the incomplete condensation of all minerals condensing before spinel. Unfortunately, here no direct evidence, either pro or con, exists. Obviously, incomplete condensation of a mineral can only occur if the cooling rate of a parcel of gas is higher than the growth rate of the mineral condensing from this gas. The small sizes and high abundance of individual nodules in their nebular source regions seems to be consistent with rapid condensation from a supercooled gas. The chemical compositions of the outermost Al-diopside layer of the individual nodules seem to provide additional support for incomplete condensation. These Al-diopside layers never contact perovskite grains, but they always contains up to a few wt.% TiO_2, which could have come only from the ambient gas, implying incomplete condensation of perovskite. If Al-diopside itself is a direct nebular condensate, as the textures of the individual nodules suggest, then its Al must have also been acquired from the ambient gas, pointing to incomplete condensation of Al even after the formation of Ca-aluminates, spinel, and melilite.

References: [1] Grossman L. (1972) *GCA, 36,* 597-619. [2] Wood J. A. and Hashimoto A. (1983) *GCA, 57,* 2377-2388. [3] Yoneda S. and Grossman L. (1985) *GCA, 59,* 3413-3444. [4] Petaev M. I. and Wood J. A. (2000) *LPS XXXI,* #1608. [5] Ebel D. and Grossman L. (2000) *GCA, 64,* 339-366. [6] Larimer J. W. and Bartholomay M. (1979) *GCA, 43,* 1455-1466. [7] Petaev M. I. and Wood J. A. (1998) *MAPS, 33,* A122. [8] MacPherson G. J. et al. (2004) *LPS XXXV,* #1838. [9] Petaev M. I. and Wood J. A. (1998) *MAPS, 33,* 1123-1137. [10] Petaev M. I. et al. (2003) *GCA, 67,* 1731-1751. [11] Beckett J. R. and Grossman L. (1988) *EPSL, 89,* 1-14. [12] Beckett J. R. and Stolper E. (1994) *MAPS, 29,* 41-65. [13] Krot A. N. et al. (2004) *MAPS, 39,* 1517-1553. [14] Wood J. A. (2004) *GCA, 68,* 4007-4021. [15] Aléon J. et al. (2002) *MAPS, 37,* 1729-1755. [16] Krot A. N. et al. (2004) *Chem. Erde, 64,* 185-239.