

**EFFECT OF DUST ENRICHMENT ON SOLID AND LIQUID COMPOSITIONS IN EQUILIBRIUM WITH COSMIC GASES.** D.S. Ebel<sup>1</sup> and L. Grossman<sup>1,2</sup>, <sup>1</sup>Department of the Geophysical Sciences, 5734 South Ellis Ave., <sup>2</sup>Enrico Fermi Institute, University of Chicago, Chicago, IL 60637 (debel@midway.uchicago.edu).

**Introduction.** If chondrules formed by the partial or complete melting and rapid quenching of agglomerated solids [1, 2] then their rate of loss or gain of oxide components, particularly FeO and Na<sub>2</sub>O, during that process depends upon the degree to which they were out of equilibrium with their surrounding vapor [3]. Another suggestion is that chondrule liquids formed by direct condensation from nebular gas enriched in precondensed dust [4]. Both ideas require chondrules to coexist with nebular gas, or freely evaporate into vacuum, for some time period at high temperature. The composition of surrounding gas, however tenuous, influences the chemistry of chondrules either strongly or weakly, depending on their time/temperature history [5, 6]. Equilibrium calculations provide bounds to constrain this chemistry.

Because the silicates in chondrites are so rich in FeO, many cosmochemists have speculated that the formation region of chondrite constituents was more oxidizing than a gas of solar composition [7, 8, 9]. The most plausible cause of such an oxidized state is enrichment in precondensed dust [10, 11]. We have mapped equilibrium compositions of liquid+solid condensate assemblages in vapors enriched up to 1000x, relative to a system of solar composition, in dust of C1 composition. Current results are complete for  $P^{\text{tot}} = 10^{-3}$  bar, from temperatures of complete vaporization to the solidus of silicate liquid, in 10° intervals. Above 1400K, the dust enrichment factors consistent with FeO-bearing olivine (Fa>2) are sufficient to stabilize large amounts of silicate liquid over wide temperature ranges.

**Technique.** We have continued development of, and calculations using, the VAPORS code described previously [12, 13]. This code is fundamentally new in including both the silicate liquid model and solid solution models embodied in the MELTS code of Ghiorso and Sack [14]. We have extended our calculations of gas-solid-liquid equilibria to include the CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) liquid of Berman [15], and also non-ideal Fe-Ni-Si-Co-Cr metal alloy, described using an asymmetric binary solution model calibrated against the data used by [16]. Because MELTS liquid is modeled with Mg<sub>2</sub>SiO<sub>4</sub> and CaSiO<sub>3</sub> instead of MgO and CaO as basis components, CAI-like liquids are outside its accessible composition range. In condensation calculations, we find a temperature range where use of either the CMAS liquid model [15] or the MELTS liquid model yields a liquid with only very small amounts of non-CMAS components. Very similar liquid compositions ( $\pm$  less than 2 wt%) are predicted by both models in this temperature range, suggesting that they are thermodynamically consistent with each other. We therefore use the CMAS liquid model at high temperatures where CAI-like liquids are found, and switch to the MELTS model at the onset of olivine condensation

where both models give similar results. A consequence is small (<5% relative) offsets in CMAS oxide concentrations over the 1° step in which olivine appears. A slight discontinuity due to the presence of TiO<sub>2</sub> in the MELTS liquid also occurs, because trace amounts of Ti-bearing spinel, present with CMAS liquid at high temperatures, dissolve into the MELTS liquid when olivine appears. We have also corrected for a previously unreported error in  $\Delta_f G^\circ$  and  $\log K_f$  data for HS(gas) which we detected in the JANAF Tables [17], and which had resulted in a slight over-stability of silica in condensates in earlier calculations, and under-stability of sulfide at lower temperatures.

**Results.** Appearance temperatures of phases encountered below the appearance of olivine are illustrated in Figure 1. Above 20x dust enrichment, silicate liquid always appears at a higher temperature than olivine. The assemblage olivine + orthopyroxene (opx) + metal + spinel + liquid occupies a very wide temperature range even at relatively low dust enrichments. As dust enrichment increases, the minimum condensation temperature of sulfide (Fe<sub>0.977</sub>S pyrrhotite of [17]) increases rapidly, rising above the Fe-FeS eutectic (1263K) at ~140x dust enrichment. Because we do not model Fe-Ni-S liquid, the predicted sulfide + metal alloy assemblage is metastable with respect to such liquid, and the “sulfide in” curve is therefore a lower bound on the condensation temperature of Fe-Ni-S liquids. The silicate liquid disappears at progressively lower temperatures as dust enrichment is increased, due to the increasing concentrations of FeO and Na<sub>2</sub>O in the liquid. The temperatures of the solidus illustrated in Figure 1 are probably ~50° too low at enrichments <600x, due to exaggerated concentrations of trace oxides, particularly TiO<sub>2</sub>, in residual liquids. At dust enrichments approaching 800x, opx becomes unstable relative to olivine + liquid near 1500K, only reappearing near the solidus. Above ~930x enrichment, opx is absent above ~1400K. This is due to the enhanced stability of FeO-rich olivine relative to orthopyroxene.

At any particular temperature above the appearance of Ca-rich pyroxene (cpx) and feldspar, relative amounts of liquid, olivine, opx and metal, measured as mole% of the condensed matter, vary systematically with dust enrichment. At high temperatures, the olivine/liquid mole% ratios decrease with increasing dust enrichment. At lower temperatures this ratio increases with dust enrichment, primarily because the amount of olivine increases more than liquid at the expense of opx and metal. For example: at 500x, liquid and olivine are both ~50 mol% when metal appears (1780K), and liquid is ~18 mol%, olivine ~28 mol%, opx ~8 mol%, and metal ~46 mol% when feldspar appears (1430K); at 1000x, liquid is 67 mol%, olivine 33 mol% when metal appears (1800K), and liquid comprises

~20 mol%, olivine ~44 mol%, sulfide ~8 mol%, and metal ~23 mol% when feldspar appears (1430K).

The FeO and Na<sub>2</sub>O contents (wt%) of silicate liquid, and the fayalite mole fraction of coexisting olivine, are contoured in Figure 2. Even at a moderate dust enrichment such as 300x, liquids with >1 wt% FeO coexist with olivines of Fa1.7 to Fa8 over a 400° range. At all dust enrichments, the iron contents of both olivine and liquid increase rapidly with falling temperature until metal alloy becomes stable. Below this temperature, the fraction of Fe condensed as FeO becomes nearly constant and, because FeO partitions preferentially into olivine, the liquid FeO content reaches a maximum, then decreases with falling temperature. Sodium contents of liquids increase rapidly with decreasing temperature, reaching a maximum at the solidus. At high enrichments, Na<sub>2</sub>O contents of liquids reach % levels only within 100-150° of the solidus, which becomes depressed by the presence of FeO and Na<sub>2</sub>O. At 1000x enrichment, the final liquid has >8 wt% Na<sub>2</sub>O and 1.4 wt% K<sub>2</sub>O, and disappears >100° lower than at 200x.

The major element composition of silicate liquid changes systematically with increasing dust enrichment. At 1800K the liquid has 8.19 wt% CaO, 25.30% MgO, 10.73% Al<sub>2</sub>O<sub>3</sub>, 48.63% SiO<sub>2</sub> and 6.33% FeO at 500x enrichment, while at 1000x the liquid has 3.94, 23.38, 5.06, 41.79, and 24.51 wt% of these respective oxides. Nearer the solidus, at 1430K, the liquid has 11.47 wt% CaO, 6.83% MgO, 13.27% Al<sub>2</sub>O<sub>3</sub>, 61.89% SiO<sub>2</sub>, 3.57% FeO, and 1.72% Na<sub>2</sub>O at 500x enrichment, while at 1000x the liquid has 9.49, 5.38, 13.08, 58.07, 9.81, and 3.10 wt% of these oxides. At any given dust enrichment between 100x and 1000x, the CMAS oxide compositions of these liquids follow nearly linear trends between the appearance T of metal and the appearance T of feldspar.

Preliminary results at lower  $P^{\text{tot}}$  indicate that the maximum mass fraction of silicate liquid in the condensate assemblage, and the temperature range of its stability, are both approximately halved when  $P^{\text{tot}} = 10^{-6}$ , compared to  $P^{\text{tot}} = 10^{-3}$ . The solidus curve of Figure 2 shifts to the right with decreasing  $P^{\text{tot}}$ , because it is primarily a function of liquid composition. Decreasing  $P^{\text{tot}}$  dramatically decreases the maximum Na<sub>2</sub>O content of liquid at the solidus, at a given dust enrichment. By contrast, the maximum FeO content of liquid and the maximum FeO content of olivine and pyroxene coexisting with it are less sensitive to  $P^{\text{tot}}$ .

**Discussion.** Thermal histories for porphyritic chondrules have been proposed based on dynamic crystallization experiments [3, 18]. In light of the evidence for very rapid evaporation of Na<sub>2</sub>O from chondrule liquids [5], these hypotheses are more tenable if dust enrichment and/or  $P^{\text{tot}}$  are (1) sufficiently high that Na<sub>2</sub>O and FeO evaporate less rapidly from liquid into gas than would be the case in a solar gas at very low  $P^{\text{tot}}$ , or (2) even higher, such that Na<sub>2</sub>O partitions into the liquid from surrounding gas as cooling liquid nears its solidus.

FeO-rich chondrule liquids and olivines could be direct equilibrium condensates only under what have heretofore been considered extreme conditions of nebular

composition and pressure. In a preliminary survey of the current results at  $P^{\text{tot}} = 10^{-3}$  and C1 dust enrichments to 1000x, we have not yet identified conditions at which specific porphyritic chondrule compositions can be shown to result from direct equilibrium condensation.

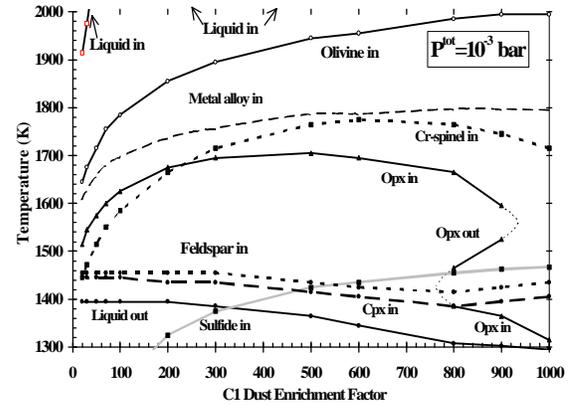


Figure 1: Stability fields of phases at  $P^{\text{tot}} = 10^{-3}$  bar as a function of C1 dust enrichment (above 20x) and temperature. Symbols represent calculated values ( $\pm 5^\circ$ ).

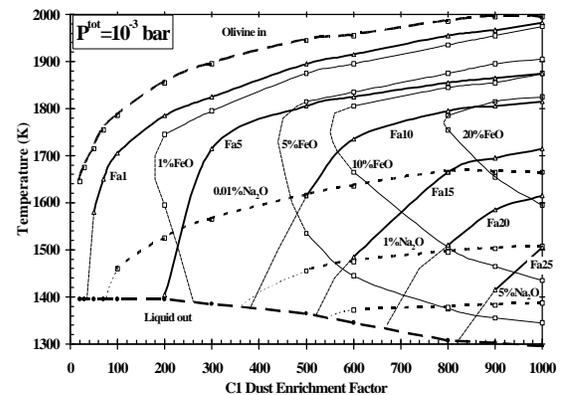


Figure 2: Contours of fayalite in olivine (heavy), and FeO (light) and Na<sub>2</sub>O wt% (dashed) in silicate liquid. Data set and 'olivine in' and 'liquid out' lines are as in fig. 1.

**References.** [1] Whipple (1966) *Science* **153**: 54-56. [2] Weisberg & Prinz (1997) In *Chondrules and the Protoplanetary Disk*, ch. 13. [3] Radomsky & Hewins (1990) *GCA* **54**: 3475-3490. [4] Wood & McSween (1977) In *Comets, Asteroids, Meteorites* (ed. A.H. Delsemme), p. 365. [5] Tsuchiyama *et al.* (1981) *GCA* **45**, 1357. [6] Hewins (1991) *GCA* **55**: 935-942. [7] Weinbruch *et al.* (1990) *Meteoritics* **25**:115-125. [8] Mason (1963) *GCA* **27**: 1011-1023. [9] Palme & Fegley (1990) *EPSL* **101**: 180-195. [10] Wood (1967) *GCA* **31**, 2095. [11] Rubin *et al.* (1988) In *Meteorites and the Early Solar System*, 488-511. [12] Ebel & Grossman (1997) *LPSC XXVIII* 317-318. [13] Ebel & Grossman (1997) *Meteoritics Supp.* **32**: A37. [14] Ghiorso & Sack (1995) *Contrib. Mineral. Petrol.* **119**, 197. [15] Berman (1983) Ph.D. Thesis, U.B.C. [16] Yoneda & Grossman (1995) *GCA* **59**, 3413. [17] Chase *et al.*, 3<sup>rd</sup> ed. (1985). [18] Lofgren (1997) In *Chondrules and Prot. Disk*, ch. 20.