

**DIRECT CONDENSATION OF FERROMAGNESIAN LIQUIDS FROM 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.

**Introduction.** Wood [1] rejected the idea of direct condensation of liquids of chondrule composition by showing that forsterite could condense in equilibrium with a melt of its own composition from a solar gas only at unreasonably high total pressures ( $P^{\text{tot}} > 100$  atm). It was subsequently realized in [2] and [3] that the minimum  $P^{\text{tot}}$  for condensation of forsterite + liquid assemblages in a solar gas might be much lower than this because forsterite coexists stably with silicate liquids of many compositions to temperatures well below the melting point of pure forsterite. Also, Grossman and Clark [4] estimated that high-temperature, Ca-, Al-rich assemblages would condense in a partially molten state at a  $P^{\text{tot}}$  as low as only  $5 \times 10^{-3}$  atm. Wood [5] was the first to point out that liquid condensates might become stable at  $P^{\text{tot}}$  below that estimated in [1] in gases made by complete vaporization of dust in regions which had become enriched in interstellar dust relative to gas compared to solar composition. By assuming that the silicate liquid is an ideal solution, various attempts were made to model the condensation of liquids, in a solar gas [3], at  $P^{\text{tot}} = 1 \times 10^{-3}$  atm in systems enriched in dust compared to gas by factors of 20-25 relative to solar abundances [6,7], and at  $P^{\text{tot}} = 1 \times 10^{-5}$  bar in systems enriched in dust relative to gas by factors of  $10^3$  to  $10^7$  [8]. A large body of experimental work shows, however, that most multicomponent silicate liquids of petrologic significance are quite non-ideal [9], causing these liquid condensation models to be highly inaccurate. Using the non-ideal solution model of [10] for liquids in the CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) system in full equilibrium condensation calculations, Yoneda and Grossman [11] showed that forsterite + CMAS liquid is a stable condensate assemblage in a gas of solar composition at  $P^{\text{tot}}$  at least as low as  $5 \times 10^{-2}$  atm and in systems enriched in dust relative to gas by a factor of at least as low as 16 at  $P^{\text{tot}} = 1 \times 10^{-3}$  atm. Ebel and Grossman [12] were able to lower these estimates to  $P^{\text{tot}} = 5 \times 10^{-3}$  bar in solar gas, and to dust/gas enrichments of  $\sim 3.5$  at  $P^{\text{tot}} = 1 \times 10^{-3}$  bar and  $\sim 165$  at  $P^{\text{tot}} = 1 \times 10^{-6}$  bar. Wood [5] was also the first to show that cosmic gases made by vaporization of nebular regions enriched in dust relative to gas are more oxidizing than a gas of solar composition, possi-

bly leading to stabilization of FeO-bearing, liquid condensates at high temperature, and condensation of chondrules.

**Technique.** In order to investigate the condensation temperatures of ferromagnesian liquids and their coexisting solid condensates as well as changes in the compositions of coexisting solids and liquids with falling temperature, non-ideal liquid solution models applicable to a much broader range of compositions than those restricted to CMAS must be incorporated into equilibrium condensation calculations. Consequently, we have re-written our condensation program in order to use the same free energy minimization technique, the same silicate liquid composition-activity relations, and the same thermodynamic data base for both pure solids and solid solution phases compatible with that liquid as are used in MELTS, a program written by Ghiorso and Sack [13]. This program describes a fifteen-component silicate liquid with a regular solution model which has been successfully applied to such petrologic problems as the melting of mantle peridotite [14], the crystallization history of Hawaiian basalts [15] and the evolution of andesitic magma [16].

Our program runs on a time-shared Silicon Graphics Power Challenge, equipped with R-8000 microprocessors under a UNIX operating system at I-EEE quadruple precision, equivalent to computational resolution of  $2 \times 10^{-34}$ . In the runs described herein, convergence is defined such that mass balance is preserved to within  $1 \times 10^{-27}$  of the amount present for each element, and the accuracy of equilibration of condensed phases with the gas, as measured by the difference in the chemical potential of each component between the gas and condensed phase, is always  $< 1 \times 10^{-6}$  % of the chemical potential. This required from 7 minutes to 4 hours of computer time per temperature step, depending on the number and complexity of condensed phases, but increased to  $> 12$  hr/step when the machine was heavily used.

**Results.** No condensate liquids were found in a gas of solar composition at  $P^{\text{tot}} = 1 \times 10^{-3}$  bar. All other runs were performed at  $P^{\text{tot}} = 1 \times 10^{-3}$  bar and a dust/gas enrichment factor of 200 relative to solar composition, assuming that the aggregate composition of the original interstellar dust

had the bulk chemical composition of C1 chondrites. At 200x enrichment in C1 dust at  $P^{\text{tot}}=1 \times 10^{-3}$  bar, the only condensate at 1900 K is a liquid containing all of the Ca, Al and Ti. It contains 35 wt%  $\text{SiO}_2$ , 30%  $\text{Al}_2\text{O}_3$ , 23% CaO, 10% MgO, 1.3%  $\text{TiO}_2$  and  $5 \times 10^{-3}$ % FeO. The MgO and FeO concentrations rise rapidly and the  $\text{SiO}_2$  concentration slowly with falling temperature. By 1850 K, the liquid contains 41 wt%  $\text{SiO}_2$ , 31% MgO and  $5 \times 10^{-2}$ % FeO and coexists with one-tenth as many moles/liter of olivine containing 0.33 mole % Fa and 1.4% monticellite. At 1740 K, the condensate consists of olivine ( $\text{Fa}_{2.4}$ ;  $\text{Mont}_{0.8}$ ) and liquid (containing 48 wt%  $\text{SiO}_2$ , 23% MgO and 1.2% FeO) in 5 : 3 molar proportions. Metallic nickel-iron ( $X_{\text{Ni}}=0.11$ ) condenses by 1730 K and, at 1700 K, the condensate consists of approximately equal molar proportions of olivine ( $\text{Fa}_{3.3}$ ), metal ( $X_{\text{Ni}}=.08$ ) and liquid (56 wt%  $\text{SiO}_2$ , 20% MgO and 1.4% FeO). At 1700 K, 56% of the Fe, 21% of the Si and only 2% of the Mg are gaseous. By 1680 K, orthopyroxene ( $\text{Fs}_{2.7}$ ) has begun to form at the expense of gaseous SiO, olivine and liquid. By 1660 K, spinel [ $(\text{Mg}_{0.91}\text{Fe}_{0.09})$  ( $\text{Al}_{0.52}\text{Cr}_{1.47}\text{Ti}_{0.01}$ )  $\text{O}_4$ ] has become stable; the metal contains 6.5 mole % Ni, 0.30% Co, and 0.63% Cr; the olivine is  $\text{Fa}_{3.6}$ ; the orthopyroxene is  $\text{Fs}_{2.8}$ ; and the liquid contains 60 wt%  $\text{SiO}_2$ , 17% MgO and 1.2% FeO. The condensate assemblage remains remarkably constant for at least the next 70 K. At 1590 K, the molar proportions of metal (5.7 mole % Ni, 0.26% Co, and 0.33% Cr) : liquid (60 wt%  $\text{SiO}_2$ , 14% MgO, 13%  $\text{Al}_2\text{O}_3$ , 10% CaO, 1% FeO, 0.9% MnO, 0.6%  $\text{TiO}_2$  and 0.4%  $\text{Cr}_2\text{O}_3$ ) : olivine ( $\text{Fa}_{3.8}$ ) : orthopyroxene ( $\text{Fs}_{3.0}$ ) : spinel [ $(\text{Mg}_{0.91}\text{Fe}_{0.09})$  ( $\text{Al}_{0.61}\text{Cr}_{1.38}$ )  $\text{O}_4$ ] are  $\sim 2.3 : 1 : 0.9 : 0.4 : 0.01$ . Although the concentrations of alkali metals are negligible at very high temperature, a potentially important phenomenon is the steepness of the rise in  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  concentrations in the liquid, from  $1.3 \times 10^{-3}$  wt% at 1730 K to  $2.4 \times 10^{-2}$  wt% at 1590 K for  $\text{K}_2\text{O}$  and from  $9.6 \times 10^{-4}$  wt% at 1610 K to  $1.7 \times 10^{-3}$  wt% at 1590 K for  $\text{Na}_2\text{O}$ . At the time of writing, we had not yet completed computations at lower temperatures; however, it is quite conceivable that the liquid found at 1590 K persists to low enough temperatures that % levels of  $\text{Na}_2\text{O}$  may condense into it. Stabilization of alkali metals in high-temperature condensate liquids is greatly enhanced by the high partial pressures of Na and K species which result from enrichment in the

dust/gas ratio, and by non-ideal solution effects in the liquid. For example, the activity coefficients computed for the  $\text{KAlSiO}_4$  and  $\text{Na}_2\text{SiO}_3$  components in the liquid at 1590 K are 0.4 and  $3 \times 10^{-3}$ , respectively.

This system is more oxidizing than a solar gas because its composition arises from an enrichment of dust relative to gas compared to solar composition, and the dust has higher atomic ratios of O/H and O/C than solar composition. When massive condensation of silicates and oxides occurs, however, a significant fraction of this excess oxygen condenses, actually causing the gas to become slightly less oxidizing, and the FeO/(FeO+MgO) ratios of oxide and silicate minerals to rise only very slightly, with falling temperature. In systems enriched in C1 dust relative to gas by a factor  $>200$ , condensation temperatures and the maximum FeO/(FeO+MgO) ratios of condensed phases will increase, while condensation from systems equally enriched in less oxidized dust, *e.g.* having the composition of ordinary chondrites, will illustrate the opposite effect. In order for the condensate liquid to appear at the same temperature at lower  $P^{\text{tot}}$ , higher dust/gas enrichment factors are required. When cosmic gases are made oxidizing enough to stabilize FeO in high-temperature silicate and oxide condensates, copious amounts of ferromagnesian condensate liquids are inevitable.

**References.** [1] Wood J.A. (1963) *Icarus* **2**, 152. [2] Wood J.A. & McSween H.Y.Jr. (1977) In *Comets, Asteroids, Meteorites* (ed. A.H. Delsemme), 365. [3] Wagner R. & Larimer J.W. (1978) *LPS IX*, 1191. [4] Grossman L. & Clark S.P.Jr. (1973) *GCA* **37**, 635. [5] Wood J.A. (1967) *GCA* **31**, 2095. [6] Bartholomay H.A. & Larimer J.W. (1982) *Meteoritics* **17**, 180. [7] Larimer J.W. & Bartholomay H.A. (1983) *LPS XIV*, 423. [8] Wood J.A. & Hashimoto A. (1993) *GCA* **57**, 2377. [9] Ghiorso *et al.* (1983) *Contrib. Mineral. Petrol.* **84**, 107. [10] Berman R.G. (1983) Ph.D., U.B.C. [11] Yoneda S. & Grossman L. (1995) *GCA* **59**, 3413. [12] Ebel D.S. & Grossman L. (1996) *Meteoritics* **31**, A40. [13] Ghiorso M.S. & Sack R.O. (1995) *Contrib. Mineral. Petrol.* **119**, 197. [14] Baker M.B. *et al.* (1995) *Nature* **375**, 308. [15] Hirschmann M.M. & Ghiorso M.S. (1994) *GCA* **58**, 4109. [16] Lange R.A. & Carmichael I.S.E. (1996) *Contrib. Mineral. Petrol.* **125**, 167.