

EXPERIMENTAL INVESTIGATION OF CONDENSATION PREDICTIONS FOR DUST-ENRICHED SYSTEMS G. Ustunisik¹, D. S. Ebel^{1,2}, D. Walker^{2,1}, J. S. Boesenber^{3,1}, ¹Department of Earth and Planetary Sciences, American Museum of Natural History, New York, NY, 10024 (gustunisik@amnh.org) ²Department of Earth and Environmental Sciences, Lamont Doherty Earth Observatory of Columbia University, Palisades, NY, 10964-8000, ³Department of Geological Sciences, Brown University, Providence, RI, 02912.

Introduction: Vapor-liquid interactions are important in the formation and evolution of the earliest solids including chondrules and Type B (igneous) Ca, Al- rich inclusions (CAIs) in protoplanetary disk environments. The bulk major element and mineral chemistry of CAIs and chondrules closely resembles that of the high temperature (T) solid/liquid assemblages predicted to be in equilibrium with high T vapor of solar or dust-enriched composition [1-6]. Testing equilibrium between a speciated H₂-rich vapor and high T condensates in the laboratory is extremely difficult. Here, we test the equilibrium mineralogy and chemistry of predicted condensates only.

The VAPORS code of [7] predicts equilibrium between silicate mineral solid solutions and silicate liquids, using the MELTS algorithm [8] in the olivine stability field, and the CaO-MgO-Al₂O₃-SiO₂ (CMAS) liquid model of [9] to address SiO₂-depleted liquids at higher T. These predictions for various dust enrichments [5, 6], neglecting metal, all at P^{tot} = 10⁻³ bar, are the basis for the experiments described here.

Experimental Design: Condensation from an H₂-rich vapor to an assemblage of solid(s) and/or liquid is controlled to first order by the difference in chemical free energy between vapor and condensates. We therefore assume that the VAPORS code of [7] correctly predicts the bulk total CMAS + TiO₂ + FeO + Cr₂O₃ composition of the condensate assemblage at every T. However, gas-condensate energy differences are an order of magnitude greater than liquid-solid energy differences. That is, the Gibbs free energy surface among the condensates is rather flat, and very sensitive to the data for thermodynamic and mixing properties of silicate liquid and minerals. What we can test by experiment are the predictions of the compositions of condensed liquid plus solid assemblages. We assume the predicted bulk chemistry of the condensate assemblage is correct at any particular T and total system composition (*d*, Fig. 1).

We performed crystallization experiments to systematically explore specific, narrow regions of temperature and total system composition space where either the CMAS model of [9] or the MELTS model of [8] were applied by [5, 6]. Each experiment tests whether the liquid + solid(s) assemblage that is calculated to be stable at a specific T, cooled from a vapor enriched by a specific dust enrichment factor, *d*, is the actual stable assemblage for the particular

condensate bulk composition predicted to coexist with H₂-rich vapor.

In Fig. 1, total system (w/ vapor) composition remains fixed at each *d* value, but the bulk *condensate* composition changes continuously with T. Therefore, the bulk condensate composition at 1760 K for a vapor enriched at *d* = 100 (#1, Fig. 1) is different from the bulk condensate composition at 1600 K and *d* = 100 (#15, Fig. 1), because a lot of Mg, Si, and O has condensed as olivine at the lower T. However, bulk condensate compositions are nearly identical at different T and *d* along systematic trend lines (stars in Fig. 1). Therefore we used certain starting compositions (yellow in Fig. 1) to probe phase stability at multiple points in T-*d* space (white in Fig. 1).

Experimental Details: Twelve bulk compositions (Fig. 1: #1, 4, 6, 7, 10, 11, 12, 14, 15, 16, 18, and 23) were prepared to test the equilibrium liquid plus solid assemblages predicted to be stable at twenty three points in seven phase fields of T-*d* space (Fig. 1). Six predicted condensate assemblages (#5, 8, 9, 17, 20, and 22) were tested only by proxy.

Target bulk compositions were prepared at the Department of Geosciences at Stony Brook University from mixtures of oxides, silicates, and carbonates by homogenization in ethanol in an automated mortar for >1 hr. and drying at 175°C under vacuum to remove any adsorbed water. Fidelity to target composition was tested by fusion of #23 at 1GPa and 1650°C.

Crystallization experiments were conducted at Lamont-Doherty Earth Observatory of Columbia University. Powders were pressed into 2-4 mm diameter and 1-2 mm thick pellets using polyvinyl alcohol (PVA) and hung on Pt-wire loops. CO - CO₂ gas mixtures kept *f*O₂ at or near the fayalite magnetite-quartz (FMQ) buffer. Due to the very low FeO content of starting compositions, oxygen fugacity was not expected to play an important role. Each charge was heated to the desired temperature and held there from 20 minutes to several days before drop-quenching into cold water. No seed crystals were added due to the fact that oxides nucleate and grow readily in SiO₂-depleted liquids.

Run products were lightly crushed, mounted in epoxy and polished for optical examination and quantitative analysis using the Cameca SX100 electron microprobe at the AMNH. Backscattered electron (BSE) images and X-ray intensity maps were used to differentiate between quench versus equilib-

rium spinels. Mass balance calculations using the initial and final compositions were done using the least squares methods of the IgPet software [10] to determine mineral abundances (wt%) and test that no phase was missed during analysis.

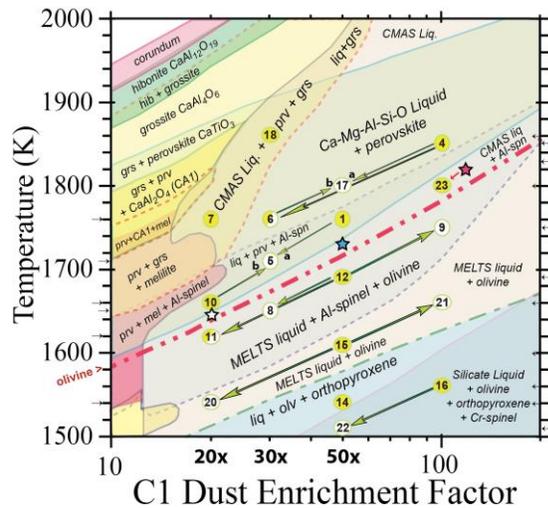


Fig. 1. Predicted phase fields. Arrows indicate use of proxy compositions (e.g., #8 tested using composition #12; #17 tested using both #4 and #6). Half yellow circles used both that starting composition and a proxy (e.g., #6 used #4, and was also prepared as #6). From plate 10 of [6].

Results and Discussion: Perovskite CaTiO_3 did not grow in any high-T silicate liquid, even in runs where Ti built up outside the rims of growing melilite crystals (e.g., #17a). This result explains the absence of perovskite in most melted, Type B CAIs [11]. Perovskite is observed to be common in non-igneous "fluffy" CAIs, and is, indeed, predicted to form at high T and $d < \sim 15x$ (Fig. 1). Nearly all Ti condenses above the stability field of olivine at all d , so absence of TiO_2 does not inhibit growth of perovskite. We conclude that perovskite is not a stable phase in dust-enriched systems in which liquid is present at high T.

Spinel was seen in glass where it was predicted above the T of olivine stability, but only experiment #11 had spinel with olivine. Spinel only reappeared with the growth of orthopyroxene (enstatite) at significantly lower temperature. Al-rich spinel was *not* predicted with orthopyroxene. The absence of Al-spinel in the large liquid + olivine field is consistent with the observed rarity of spinel in ferromagnesian chondrules. Cr-rich spinel appeared only in #16.

Grossite CaAl_4O_7 appeared where predicted (#7, #18). The stability of melilite (near-pure gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$) with grossite in #6 was verified directly and by proxy using composition #4. The melilite field extended to #17, but not to #4. This difference between experiment and prediction is likely due to

the inadequacy of the melilite solid solution model used in the prediction. These experiments confirm that C1 dust enrichments up to nearly 100x are, contrary to predictions, entirely consistent with the ubiquity of melilite in igneous Type B CAIs [11].

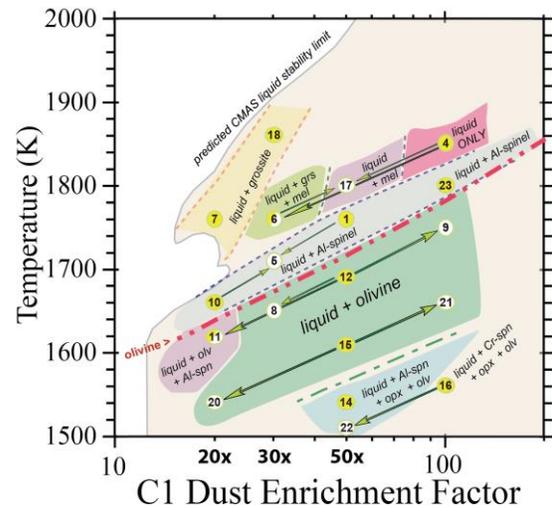


Fig. 2. Experimentally determined phase fields. Phase boundaries are estimated.

Our results demonstrate the importance of experimental testing of predictions that are based on thermodynamic models, even when the models are based on sound, internally consistent equations of state. Generally, predictions using the MELTS model [8] were found to match experimental results better than predictions using the CMAS model [9]. The experiments expand the scope of tested crystal-liquid equilibrium phase relations (e.g., LEPR [12]) to calibrate and test future models for liquid-crystal equilibration, particularly in silica-poor compositions.

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