EXPERIMENTS TO CONFIRM CONDENSED PHASE ASSEMBLAGES PREDICTED BY EQUILIBRIUM THERMODYNAMIC CALCULATION IN DUST-ENRICHED SYSTEMS: PRELIMINARY RESULTS.

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Introduction: The Cr-bearing, O^{16}-poor, Mg-, Al-spinels (such as ALSP1) found in olivine-rich objects in the carbonaceous chondrites, Allende and Murchison, by [1] and [2] have been proposed to condense in a region of the solar nebula enriched 100 times in dust [2]. We have set out to explore experimentally the types of solid and liquid equilibrium assemblages that might form in these dust-enriched chemical systems at the temperatures where CAI-like liquids are stable condensates. These compositional regions lie near the border of where the CMAS model of [3] and the MELTS model of [4] begin to overlap, and experiments therefore allow an opportunity to clarify the nature of the phase boundaries, the phases present and the partitioning of trace elements among phases. Here, we investigate the spinels that form in the CMAS liquid + Al-spinel region and the adjacent CMAS liquid + spinel + perovskite field [5] .

Experimental Technique: Equilibrium crystallization experiments were performed using two bulk compositions. The first composition (#400) is the calculated bulk composition of liquid plus solid condensates stable at 1800K during condensation of a vapor of solar composition having a dust/gas enrichment of 100X at $P^{tot}=10^{-3}$ bars [6]. The second composition (#401) is that calculated for the bulk condensed assemblage for a dust/gas enrichment of 50X at $P^{tot}=10^{-3}$ bars and 1760K.

Table 1. Nominal Starting Compositions.

	#400	#401
SiO_2	34.01	26.48
TiO_2	1.17	1.82
Al_2O_3	26.18	35.17
Cr_2O_3	0.21	0.61*
FeO	0.02	0.02
MgO	17.58	7.76
CaO	20.83	28.14
Total	100.00	100.00

* See **Results** about an alteration to the #401 bulk composition.

The experimental charges were produced from spec pure oxide powders. The powders were mixed; pressed into 4mm diameter, 50 mg pellets; placed on Re wire loops and placed in a one atmosphere furnace at the Dept of Earth and Planetary Sciences, Rutgers University. An oxygen fugacity of IW-1 was maintained throughout the experiments with high precision flowmeters using a mixture of CO and CO_2. Although the oxygen fugacity in the condensation calculation is sig-

nificantly lower (~IW-3), we do not expect this difference to strongly affect phase stability for equilibria in the liquid + solid system. Each charge was held at 1600ºC (1873K) for 1 hour and then cooled at 5ºC per hour down to 1527ºC (1800K) for #400 or 1487ºC (1760K) for #401. Composition #400 was then held at 1527ºC for 125 hours, while #401 was held at 1487ºC for 145.5 hours to attain equilibrium. Both experiments were terminated by drop quenching into distilled water.

The experiments were analyzed first by X-ray diffraction to determine the phases present (courtesy of G. Harlow, AMNH). Both experiments contain only glass and Cr-bearing Mg-, Al- spinel. Perovskite, though predicted to be present in composition #401, was not found in the experiment. The charges were then mounted and polished for analysis using the Cameca SX-100 microprobe at AMNH. Run conditions were 15kV and 20nA with 40 second peak counting times. Well characterized minerals and glasses were used as standards.

Results: Both experiments were analyzed for the seven oxides they contained. The glass was quite homogeneous in both experiments, however the 100 to 800 micron, subhedral to euhedral, red spinel grains were mildly zoned from core to rim in Cr-Al. Table 2 shows the mean glass and spinel compositions from each experiment. Standard deviations are also given for the spinels, in parentheses. Modal estimates of the phase abundances for each experiment were made. In #400, 8% spinel and 92% glass is estimated. In #401, 9% spinel and 91% glass is estimated. The Cr_2O_3 abundance of #401, based on the condensation calculation should have been 0.06 wt%, however this was increased by ~10x to more easily obtain partition coefficients (D_{Cr}) derived from spinel and glass.

Discussion: Each experimental bulk composition explored here represents the sum of the solid(s) and liquid(s) of a calculated composition in equilibrium with a vapor at a specific temperature, pressure (10^{-3} bars) and dust-enrichment factor. It is important to recognize that the net bulk composition of solid(s) + liquid(s) at a specific dust enrichment factor will change with decreasing temperature, since a portion of the vapor will continue to condense (i.e., the composition of liqs + solids at 1800K and a dust enrichment factor of 100 are NOT equal to liqs + solids at 1600K at the same enrichment factor). Thus, each experiment represents a snapshot of the condensed matter at a specific temperature and enrichment factor. The experiment is

thus designed to test the prediction of equilibrium liquid-solid phase relations.

Natural versus Synthetic Spinels: A comparison of the ALSP1 spinel composition from [2] with the experimentally produced #400 spinel yields amazingly good agreement. The experimental Cr_2O_3 contents (1.36-2.87 wt%) are well within the range seen in ALSP1 (0.74-8.5 wt%) as are TiO_2, CaO, and Al_2O_3. The major difference in the compositions is FeO, with ALSP1 containing between 0.49 and 16.1 wt% FeO, while the experiment contains a mere 0.03 wt%. How such an Fe-rich spinel might form in equilibrium with a nebular vapor however is difficult to envision, since the stability field for more iron-rich spinel should require temperatures to be some 200K lower (near 1600K) than that run here (Fig. 1).

Table 2.

| | #400 | | #401 | |
	Glass	Spinel	Glass	Spinel
SiO_2	36.57	0.14 (0.02)	28.85	0.08 (0.01)
TiO_2	1.25	0.14 (0.01)	2.28	0.09 (0.01)
Al_2O_3	23.61	69.42 (0.63)	32.54	66.34 (1.41)
Cr_2O_3	0.06	2.14 (0.46)	0.16	6.30 (1.17)
FeO	0.03	0.03 (0.01)	0.03	0.03 (0.01)
MgO	15.96	28.01 (0.36)	5.28	27.37 (0.55)
CaO	22.35	0.02 (0.03)	30.33	0.04 (0.02)
Total	99.83	99.90	99.47	100.25

Formation of the aluminous diopside and forsterite that are associated with the ALSP1 spinel [2] appear consistent, assuming the remaining glass from experiment #400 glass were allowed to fractionally crystallize. However, fine-grained nepheline and Fe-rich olivine reported by [2] are not consistent with thermodynamic calculations. These phases require formation at much lower temperature or, more likely, are late stage alteration products.

Missing Perovskite: As mentioned earlier, experiment #401 did not crystallize perovskite despite its composition being well within the calculated CMAS liquid + spinel + perovskite field (Fig. 1). The residual glass contains over 30 wt% CaO and 2.28 wt% TiO_2. It seems likely that either a slightly lower temperature or the added presence of perovskite nuclei is required to initiate its crystallization.

Spinel Cr and Ti Partitioning: Partition coefficients for Ti and Cr between spinel and melt were obtained from the experiments. For experiment #400, D_{Ti} = 0.112 and D_{Cr} = 35.7, while in experiment #401, D_{Ti} = 0.040 and D_{Cr} = 39.4. These are a bit lower than D's from [7], who looked at co-existing olivine, spinel and liquid at oxygen fugacities near the IW buffer and in the range of 1300-1350°C. They found spinel D_{Ti} = 0.56-0.57 and D_{Cr} = 51.2-62.8.

Figure 1. Calculated phase relations during condensation in CI dust-enriched systems [5]. Red phase appearance "in" or disappearance "out" labels apply during decreasing temperatures only. Experiments were run to simulate compositions inside the CMAS liq. + Al-spinel (#400) and the liq. + perovskite + Al-spinel fields (#401). See [5] for mineral abbreviations.
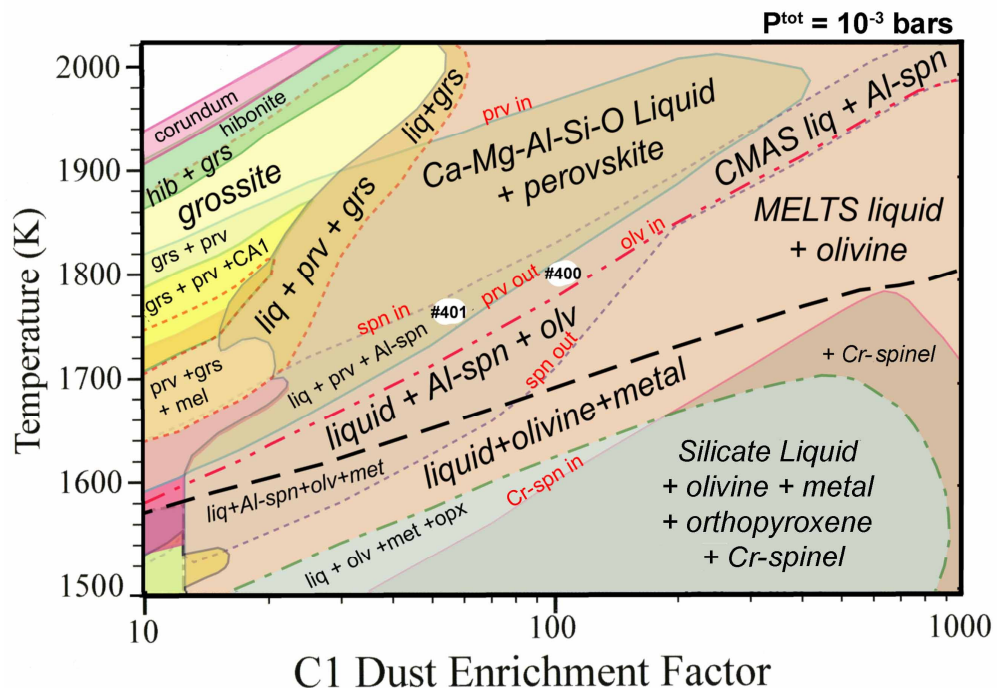
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