CONDENSATION FROM CLUSTER-IDP ENRICHED VAPOR INSIDE THE SNOW LINE: IMPLICATIONS FOR MERCURY, ASTEROIDS, AND ENSTATITE CHONDRITES.

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Introduction: Enstatite chondrites (EC) contain highly reduced matrix minerals (e.g.- (Mg,Fe,Mn)S solid solution, CaS) that probably formed in thermodynamic equilibrium with a vapor phase. EC chondrules contain enstatite, Fs_5 to Fs_{30}, in which iron was reduced after formation, also by interaction with vapor [1, 2]. The origin and location of this reducing vapor bears upon the formation of the terrestrial planets (Mercury to Mars), the remnant chemical zoning of the asteroid belt (E, S, C, D-types), and the cosmochemistry of metals in the early solar system.

The protoplanetary disk contained an isopleth of total pressure (P^{tot}) - temperature (T) conditions at which water sublimed or condensed as ice [3]. This 3D 'snow line' moved radially and azimuthally as the disk evolved, but is variously placed at 3 to 5 AU in the disk midplane during formation of the asteroid belt [4]. Particularly in late disk time, the midplane is expected to have been enriched in dust (condensable material), relative to a chemical system of solar composition. [5] explored the thermodynamic stability of FeO in silicates as a function of P, T, and enrichment in a dust of CI chondrite composition. A better analog to primordial dust composition might be that of highly unequilibrated, anhydrous, interstellar organic- and presolar silicate-bearing cluster IDPs (C-IDPs) [6, 7]. CI chondrites have been aqueously altered and heavily oxidized. C-IDPs have chondritic compositions and are generally considered to be more primitive than chondrites - they are highly unequilibrated and have higher abundances of presolar organics, oxides and silicates than any chondrite [8, 9]. C-IDPs likely represent cometary ejecta and debris from C-rich asteroidal bodies, about which the STARDUST mission samples will provide a wealth of new information. C-IDP dust enrichments would create reducing conditions due to their very low FeO, and high C contents, stabilizing EC minerals in the absence of condensed water ice [10]. A preliminary exposition of this idea is in [11].

Methods: Thermodynamic stabilities of mineral, silicate liquid, and vapor phases were calculated using a chemical equilibrium code, for 23 elements [5]. The solar composition [12, Tab 1, col 3] incorporates lower O [13] and lower C abundances than [14]. The C-IDP dust analog is H-, N-, F-, Cl-free Orgueil (CI) dust [14] with all C elemental (~organic), all S as FeS, Co+Ni as metal, and only enough O to make oxides of the remaining Fe and of all Si, Mg, Ca, Al, Na, P, K, Ti, Cr, Mn. This C-IDP dust is almost identical to the CI dust of [5], with chondritic elemental ratios (e.g.- Mg/Si=1.074), except C-IDP dust contains 0.7561 atoms C per Si, and less O. Our analog remains more oxidizing than true, FeO-poor C-IDPs. Dust was added to complementary solar composition vapor (enrichment of 1 = solar) to make bulk compositions [5]. Thermodynamic equilibrium between fully speciated vapor, silicate liquid, and solid minerals was calculated at 5° steps at fixed P^{tot} for each bulk composition. Calculations span P^{tot} of 10^{-2}, 10^{-4}, 10^{-6}, 10^{-8}, at C-IDP dust enrichments of 100x; and, at $P^{tot}=10^{-4}$, 10x, 300x, 500x, 1000x.

Results: Figure 1 illustrates oxygen fugacities in cooling systems enriched in different dusts. At high T (vapor only), the $f(O_2)$ differs by one log unit, for constant dust enrichment. When oxides begin to condense from the C-IDP-enriched, $f(O_2)$ dips steeply (where curves are marked with black squares).

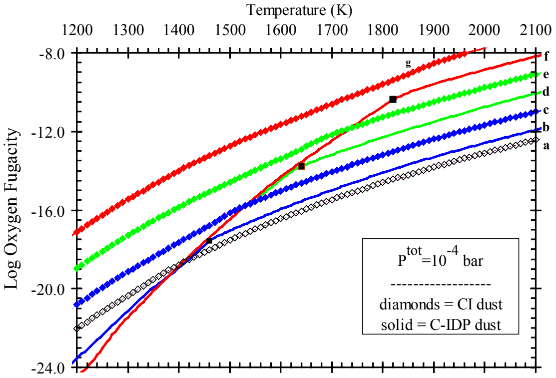

Fig. 1: Oxygen fugacity in cooling vapors of solar composition enriched in dust of CI composition [3] (diamonds), and C-IDP composition (solid). Curve **a** is solar[5], **b** through **g** are for 10x (blue), 100x (green), and 1000x (red) enrichments.

In C-IDP-enriched systems, condensates draw oxygen from the vapor, sharply decreasing $f(O_2)$. In contrast to CI-dust enriched systems [5, Fig. 8], silicate FeO content *decreases* with decreasing T. Systems become so reduced that at $P^{tot}=10^{-4}$ CaS (oldhamite) becomes stable at 1340 K at 100x, and 1365 K at 1000x; and MgS at 1195 K and 1230 K for the same C-IDP dust enrichment factors (Fig. 2). With declining $f(O_2)$, FeO becomes *less* stable as a component of the condensates, and orthopyroxene dominates over olivine in the condensate assemblage. In oxidized systems (e.g.-solar, CI dust-enriched), after CO(g) forms, excess O forms the highly stable SiO(g) molecule. In the C-IDP enriched systems, $SiO_{(g)}$ is less stable relative to $CO_{(g)}$ in the vapor, with declining $f(O_2)$. The calculated stability fields in Fig. 2 are quite similar in general, but shifted down in T with increasing enrichment in less oxidizing C-IDP dust. The only sulfide that appears in the CI dust case is FeS at high enrichments.

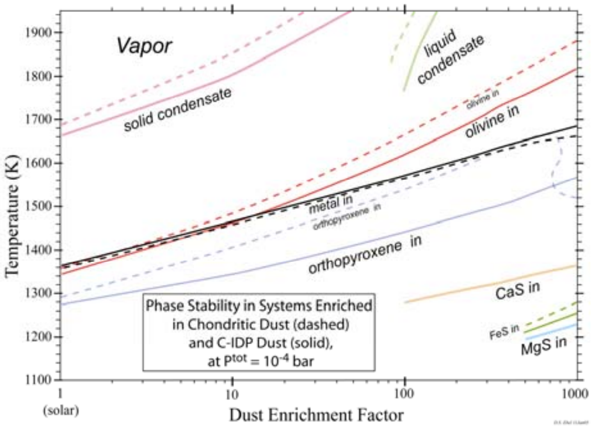

Fig. 2: Appearance temperatures of major phases with increasing dust enrichment, for CI (dashed) and C-IDP (solid) dust compositions. Data are interpolated from 1, 10, 100, 500 and 1000 K results. Liquid stability has not been calculated in detail, but solidi are ~1380 K.

Comparison with CI-dust enrichment: At 1000 x CI dust enrichment [5], C/O=0.100, Si/O=0.131. At 1000 x C-IDP dust enrichment, C/O=0.204, Si/O=0.268. A dust enrichment of 1000xCI (atomic) corresponds to a dust/gas *mass* enrichment of only ~6.7, a not unreasonable expectation for the protoplanetary disk midplane [15]. Enrichment to the same degree in C-IDP dust (~5.1x by *mass*) leads to very different midplane chemistry. At 1000x dust, at $P^{tot}=10^{-4}$ bar, >99% of Si speciates as $SiO_{(g)}$ above 1900 K. At 1000x**CI** dust, at 1400 K, Si is 7% in silicate liquid, 70% in olivine, 16% in opx, the remainder in anorthite and Ca-pyroxene, with $X_{fa}=0.32$ in olivine, $X_{fs}=0.24$ in opx. For 1000x**C-IDP** dust at this T and P (10^{-4} bar), Si is ~7% in liquid, but only 28% in olivine, 44% in opx, 7% in anorthite, and ~13% remains in the vapor. At 1400 K, X_{fa} and X_{fs} are <0.001, and over 90% of the 13% Si in the vapor is speciated as $SiS_{(g)}$, the remainder $SiO_{(g)}$. With decreasing T, olivine disappears at 1200 K, but ~3% of Si remains in the vapor as $SiS_{(g)}$ at 1200 K.

Discussion: In these analog C-IDP dust-enriched systems, reduced phases (CaS, MgS) become stable at equilibrium with orthopyroxene above 1000 K, at dust enrichments >300x at $P^{tot}=10^{-4}$ bar. Ca-, Al-rich solids in these systems are the same minerals as calculated for CI dust-enriched systems [5], and olivine, pyroxenes and feldspar are all calculated to condense before CaS and MgS. Increased elemental C in dust-enriched systems is predicted to stabilize E chondrite assemblages, relative to the oxidized assemblages seen in carbonaceous chondrites.

If dust enrichment at the midplane was a function of the position of the snow line, then these results indicate that EC parent bodies formed inside the snow line, where dust included C but not ices. High dust enrichments, relative to the gas, are necessary to produce the EC-like assemblages we predict. If the inner planets preserve condensates stable in narrow radial annuli of a dust-enriched midplane, then Mercury should contain a higher bulk sulfur abundance than Earth. Similar arguments may apply to Io in a Jupiter subdisk.

The distribution of the refractory lithophile elements among host phases becomes difficult to predict, in circumstances where the equilibration of perovskite, hibonite, and liquid at high temperatures, is followed by formation of crystalline silicates and then oldhamite at lower T. CaS must form in these cases by reaction of previously formed CaO-bearing phases with the vapor. Different Ca-bearing precursors might be differentially enriched in trace elements, leading to heterogeneous CaS refractory lithophile contents [16].

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This work was supported by U.S. N.A.S.A. grants NAG5-12855 (DSE) and NAG5-13040 (CA).