REDOX CONDITIONS DURING NEBULAR CONDENSATION. L. Grossman, Dept. of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, 5734 South Ellis Ave., Chicago, IL 60637. yosi@midway.uchicago.edu.

Theory: In thermodynamic calculations of molecular equilibria in high-temperature cosmic gases, \( CO_{(g)} \) is so stable that it consumes the entirety of whichever of C or O is the lower in abundance, leaving the excess of the more abundant element to form other molecules and condensates. The best estimate of the solar C/O ratio is 0.50 \([1,2]\), yielding oxide and silicate condensates, and of the H/O ratio is 2041 \([3]\), yielding a very reduced system. Virtually all oxygen in excess of that in \( CO_{(g)} \) and condensates reacts with hydrogen to form \( H_2O_{(g)} \), and virtually all of the remaining hydrogen forms \( H_2 \). During condensation of a solar gas at \( 10^5 \) K, the \( \frac{P_{H_2}}{P_{H_2O}} \) ratio falls gradually from \( 4.27 \times 10^4 \) at 2000K to \( 3.95 \times 10^3 \) at 1417K, then more steeply to \( 2.66 \times 10^4 \) at 1300K, and levels off, reaching \( 2.52 \times 10^4 \) at 900K \([4]\), yielding \( log f_{O_2} \) from IW-6.8 (1500K) to IW-7.1.

Refractory Inclusions: Near-spherical white inclusions (CAIs), up to 1 cm in diameter, are found in CV3 chondrites at the ~5% level. Type As contain ~80% melilitte and 20% spinel, with accessory clinopyroxene (cpx) and perovskite, while Type Bs contain ~40% melilitte, 30% cpx, 20% spinel and 10% anorthite. Type Bs have a monomineralic melilitte mantle, B2s do not. The mineralogy of CAIs indicates that their precursors are high-temperature solid condensates from the solar nebula \([5]\), and their major element chemical and isotopic compositions indicate that they underwent later melting and partial evaporation \([6]\). The cpx, called “fassaite”, contains 25% CaO, 10-22% Al\(_2\)O\(_3\) and 1-20% TiO\(_2\)\(_{an}\) (all Ti calculated as TiO\(_2\)). When TiO\(_2\)\(_{an} \geq 4 \text{ wt\%} \), chemical formulae calculated from EMP data on the basis of 6 oxygen anions and 1.00 Ca ion show \( Ti^{3+}/Ti^{4+} = 0.2 \) to 0.8, agreeing with optical \([7]\) and XANES \([8]\) spectral identification of Ti\(^{3+}\). The assemblage spinel+melilite+fassaite, the latter of the same composition as that in CAIs, was crystallized from liquids having the compositions of CAIs under controlled \( f_{O_2} \) at 1500K \([9]\), near the CAI solidus. From compositions of the synthetic phases and a non-ideal solution model for fassaite, equilibrium constants were determined for 2 reactions involving spinel, melilite and fassaite in which \( O_{2(g)} \) converts Ti\(^{3+}\) into Ti\(^{4+}\). From these and analyses of coexisting CAI phases, it was found that the \( log f_{O_2} \), at which the fassaite crystallized was \(-19.5 \pm 0.8\) at 1500K, and that this applies to all 3 CAI types. This translates to IW-8.1\(\pm 0.8\), \( \pm 0.5 \) log unit below that of a solar gas. Ti\(^{3+}\)-bearing fassaite is the only oxygen barometer that says that anything in chondrites formed in a gas that was near-solar in composition. This argues against CAI formation by repeated evaporation and condensation due to solar flares in a reconnection region close to the protosun, as one prediction of this is that CAIs would have formed from a very dust-enriched, and thus very oxidizing, gas \([10]\). Depletions of W and Mo relative to other refractory siderophiles in whole CAIs suggest they may contain trace components formed at higher \( f_{O_2} \) \([11]\), and the presence in CAI rims of both pyroxene with low Ti\(^{3+}/Ti^{4+} \) \([12]\) and Fe\(^{3+}\)-bearing andradite \([5]\) implies that CAIs were affected by later events under much more oxidizing conditions. One idea is that such redox variability accompanied secondary exchange of \(^{16}O\) and \(^{18}O\) in disequilibrium reactions using atomic oxygen made by CO photolysis \([13]\).

Fayalite in Chondritic Olivine: Solar gas is so reducing that metallic NiFe and pure forsterite condense at high T. FeO is eventually stabilized as fayalite, but only at such low T that slow Fe-Mg interdiffusion in olivine prevents 1 \( \mu \) grains from reaching \( x_{Fe} = 0.001\), even for 10\(^{4}\)-yr nebular cooling times \([4]\), far short of the apparent minimum \( x_{Fe} \) of the precursors of chondrules in UOCs, ~0.15. Models involving enhancement of O/H and O/C ratios by vaporization of regions enriched in dust relative to gas, formed by reasonable degrees of vertical settling \([14]\) or radial transport \([15]\) of dust, yield too low an \( f_{O_2} \) to overcome this major obstacle to understanding the oxidation state of chondrites.