REDOX CONDITIONS DURING NEBULAR CONDENSATION.

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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 $H_{2(g)}$. During condensation of a solar gas at 10^{-3} b, the P_{H_2O}/P_{H_2} ratio falls gradually from $4.27\text{x}10^{-4}$ at 2000K to $3.95\text{x}10^{-4}$ at 1417K, then more steeply to $2.66\text{x}10^{-4}$ at 1300K, and levels off, reaching $2.52\text{x}10^{-4}$ 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% melilite and 20% spinel, with accessory clinopyroxene (cpx) and perovskite, while Type Bs contain ~40% melilite, 30% cpx, 20% spinel and 10% anorthite. Type B1s have a monomineralic melilite 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_2O_3 and 1-20% TiO_2^{tot} (all Ti calculated as TiO_2). When $TiO_2^{tot} \geq 4$ wt%, chemical formulae calculated from EMP data on the basis of 6 oxygen anions and 1.00 Ca ion show Ti^{3+}/Ti^{tot} is 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±0.8 at 1500K, and that this applies to all 3 CAI types. This translates to IW-8.1±0.8, $\geq$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^{tot} [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 ^{17}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 co-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 μ grains from reaching x_{Fa}=0.001, even for 10^6-yr nebular cooling times [4], far short of the apparent minimum x_{Fa} 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.

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