

Condensation at Varying Total Pressures and Metallicities: Rare Earth Elements .

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Introduction: The solar-normalized, relative abundances of the rare earth elements (REE) in chondrites are diagnostic of volatility related fractionation processes in the early solar nebula. Except for Eu and Yb, the REE are among the more refractory lithophile elements. They condense into refractory Al, Ca, and Ti-bearing phases such as hibonite ($\text{CaAl}_{12}\text{O}_{19}$) and perovskite (CaTiO_3) which observed in Ca,Al-rich inclusions [1]. There are several REE patterns observed in CAIs that are related to volatility: Group I and V patterns are relatively unfractionated (REE present around 10x solar) corresponding to complete REE uptake. The group III pattern has relative depletions in the most volatile REE Eu and Yb, otherwise roughly solar relative abundances. The group II pattern is characterized by extreme depletions in highly refractory and volatile REE ranging over 2-3 orders of magnitude. This pattern, observed in hibonite and perovskite, is clearly caused by fractional condensation: The first condensates must have removed Gd, and Tb to a large extent, but even larger amounts of Dy, Ho, Er, and Lu from the gas before the phase carrying the group II pattern formed. The LREE and Tm condense to around 10-20x solar. This phase must be removed from equilibrium with the gas before Eu and Yb could fully condense. The models for fractional condensation, however require that the first phase has to be removed from equilibrium with the gas with in a few tenth of a degree, and it has been a long-standing question how this can be accomplished physically.

Effects of Total Pressure (P): An increase in total P typically increases the condensation temperature (TC) for compounds and widens the T-intervals in a condensation sequence. A change in P also can change the condensation sequence (e.g., the well known switch in the order of Mg-silicate and iron)[2].

Effects of Metallicity [M/H]: Metallicity is the enrichment or depletion of all elements (M) heavier than H and He relative to the solar composition using the Brigg's logarithm. The abundance scale is set so the number of H atom is $\log A(\text{H}) = 12$. The metallicity notation is $[\text{Fe}/\text{H}] = \log (A(\text{Fe})/A(\text{H}))_{\text{sample}} - \log (A(\text{Fe})/A(\text{H}))_{\text{sun}}$. An increase in metallicity increases TC, affects condensation sequence, and other stable condensed phases can appear. These effects are of particular importance for the modelling of the group II pattern because the oxides of the heavy rare earth elements become stable before any Ca-bearing condensates. Removal of "REE-oxide nuggets" (in analogy with ultrarefractory metal nuggets) would leave the gas depleted in the refractory REE and hibonite or perovskite condensation from such a gas can easily lead to the observed group II patterns. It can be shown that a change in [M/H] corresponds to a change in oxidation state (given by $\text{H}_2\text{O}/\text{pH}_2$) as long as CO is the major carbon gas. Note that a change in [Fe/H] is not equal to a change in the dust/gas ratio since CNO and the noble gases change by the same factor as rock-forming elements.

Conclusions: Condensation of the ultrarefractory REE as oxides before Ca-bearing condensates at lower total pressures and [Fe/H] removes the need for removal of hibonite or perovskite from equilibrium with gas within an extremely small T interval after they become stable.

References: [1] Boynton, W.V. 1975, *Geochim. Cosmochim. Acta* 39, 569-584; Davis, A.M. and Grossman, L. 1979, *Geochim. Cosmochim. Acta* 43, 1611-1632. Fegley, B. and Ireland T.R. 1991, *Eur. J. Solid State Inorg. Chem.* 28, 335-252, Fegley B. and Kornacki, A.S., 1984, *EPSL* 68, 181-197; [2] Lodders, K. 2003, *Astrophys. J.* 591, 1220-1247.