Volatility fractionation of the rare earth elements

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In most geological materials, rare earth element (REE) concentrations normalized to those in CI chondrites are smooth functions of ionic radius or atomic number, with a few very interesting "anomalies" of the redox-sensitive REE Ce and Eu. Calcium-. aluminum-rich inclusions (CAIs) in carbonaceous chondrites are a clear exception to this rule, with complex patterns owing to the fact that the volatilities of the REE are not a smooth function of ionic radius or atomic number. A surprisingly complex REE pattern was found by Tanaka and Masuda [1] in a fine-grained CAI, and they suggested that the pattern was volatility-controlled. Now known as group II REE patterns, they are best explained by high temperature gas-solid fractionation, in which the most refractory REE are removed from a gas of solar composition, and the remainder condenses to form objects with the group II patterns [2,3]. Despite this early progress, some puzzles remain. The refractory carrier that removed the most refractory REE from the gas prior to condensation of group II CAIs was probably hibonite, as mineral-melt partitioning suggests a strong preference for light vs. heavy REE, but activity coefficients for solid solution of REE into hibonite have not been measured. It is not even clear whether the volatility fractionation responsible for removal of the most refractory REE from group II CAIs was due to evaporation or condensation. Evaporation experiments have not succeeded in producing significant light/heavy REE fractionation [4]. Evaporation can produce mass fractionation effects, and a search for such effects in several REE in group II CAIs could reveal much about the events leading to their formation. The volatility of some REE is also redox sensitive: under oxidizing conditions, Ce becomes much more volatile and Eu, Tm, and Yb become more refractory compared to the rest of the REE [5]. With the advent of high precision isotope dilution MC-ICPMS measurement of REE patterns [6,7], there is much to be learned from volatility effects in the REE.

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