HEATING EVENTS IN THE NASCENT SOLAR SYSTEM RECORDED BY RARE EARTH ELEMENT ISOTOPIC FRACTIONATION IN REFRACTORY INCLUSIONS.
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Introduction: It is widely accepted that the building blocks of the planets and other inner solar system objects have been vaporized and homogenized at the birth of the solar system. According to this view, solids condensed as the solar nebula cooled, with composition evolving from more refractory phases rich in Ca, Al, and Ti to more volatile phases rich in K and Na. This view has been supported by the observation of the depletions in both the least (Eu, Yb) and most refractory (Gd-Er, Lu) rare earth elements (REEs) in group II calcium-aluminum-rich inclusions (CAIs) \cite{1}. The formation of group II CAIs were thought to represent a snapshot of the condensation sequence, the partial condensate in equilibrium with the solar nebula as it cooled \cite{2,3,4}. However, this view of group II CAI formation was never tested other than through thermodynamic calculations that suffer from large uncertainties due to the paucity of thermodynamic data. To test this paradigm of equilibrium condensation of solar gas, we measured the isotopic compositions of Ce, Nd, Sm, Eu, Gd, Dy, Er, and Yb in 8 CAIs (7 with group II REE patterns). Contrary to expectations for equilibrium condensation, we found significant negative isotopic compositions for the most refractory REE and more subdued isotopic variations for the least refractory REEs, indicative of disequilibrium formation pathways.

Methodology: Seven fine-grained group II CAIs and one coarse-grained CAI with unfraccionated group V REE pattern were picked from a few Allende slabs. The CAIs were then digested in a mixture of HF:HNO\textsubscript{3} followed by HCl:HNO\textsubscript{3} acid attacks on hot plates. After digestion, 80% of the sample was taken and passed through 2 Eichrom UTEVA\textsuperscript{®} columns for U extraction \cite{5}. The matrix of U chemistry is recombined and processed through prepacked TODGA column for REE extraction \cite{6}. The extracted REEs were then loaded onto a FluoroPolymer Liquid Chromatography system (FPLC) developed at the University of Chicago for separation of all multi-isotopic REEs from one another \cite{7-9}. The purified REEs were analyzed using an Apex Omega desolvating nebulizer and a Thermo Scientific MC-ICPMS upgraded to Neptune Plus specifications.

Results and Discussion: The most refractory REEs (Gd, Dy, and Er) were found to have substantial negative isotopic fractionations ranging from 0 to -3 ‰/amu with averages approximately at -2 ‰/amu while the least and moderately REEs (Ce, Nd, Sm, Eu, and Yb) showed more subdued fractionations ranging from -1 to +1 ‰/amu with averages near 0 \cite{9}. For comparison, the CAI with unfraccionated REE pattern were also analyzed and show fractionations within 0.5 ‰/amu. According to the canonical snapshot scenario, group II CAIs formed from equilibrium condensation. At the temperature of CAI formation (1600 K) no equilibrium isotopic fractionations are expected for REEs. The discovery of substantial negative isotopic fractionations in the most refractory REEs indicates that processes that were far from equilibrium has been involved during the formation of group II REE pattern. The elemental and isotope pattern of group II CAIs could be most readily explained by a two-stage process involving CAI evaporation followed by recondensation. The evaporation and condensation timescales could be modeled based on the extent of elemental depletion and isotopic fractionations, which turned out to be hundred to thousands of days for evaporation and at least a few hundred days for condensation. Such a heating history could have taken place during rapid solar outbursts when the young Sun went through EXor or FUor events akin to those documented in remote stars. The chemical and isotopic compositions of CAIs with group II patterns might reflect the influence of several cycles of evaporation and condensation before final condensation in refractory inclusions.