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Planetary-scale volatility-controlled fractionation of the rare earth elements in the early Solar System

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Introduction: Chemically, CI1-chondrites are regarded as the most primitive meteorites and are thus used as proxy for the composition of the Solar System. We present high-precision data on REEs. We demonstrate that CI1 chondrites may not be the best proxies for solar REE ratios.
Materials and Methods: We selected a large number of terrestrial samples (including 616 MORBs and OIBs, [1]), differentiated meteorites (Moon, Mars, Vesta) and analyzed these samples along with different aliquots of CI1 (Orgueil, Ivuna, Alais) and other chondrites in the same analytical sessions. The bulk rock samples were prepared using a container- and flux-less melting technique [2]. LA-ICPMS analyses were conducted at the RSES at ANU Canberra (Australia) using an Agilent 7500S Quadrupole ICPMS equipped with a 193 nm Lambda Physique excimer laser and an in-house constructed ablation cell. We used NIST SRM 612 as external standard (data from [3]), but report the REE abundances directly relative to the data obtained from the CI1 chondrite Orgueil.
Results and Discussion: Five aliquots (~100-740 mg) of Orgueil show within uncertainty identical REE patterns. They have a standard error of 1% and are in good agreement with data from [4] and [5]. One aliquot, which we analyzed by ID-MC-ICPMS at the University of Bonn, however, has anomalous concentrations in W and Ta and anomalous Lu/Hf. This may suggest that Hf, W and Ta are likely not hosted by the same phases as the REEs. Decoupling has been documented for Ta/Lu, but has not been shown for Hf/Lu [6]. The terrestrial samples show very smooth Orgueil-normalized REE patterns. Relative to Orgueil the terrestrial, Lunar, Martian and HED samples show some variation in Eu, and a resolvable negative Tm anomaly relative to the neighbouring HREEs (Earth: -4.4 $\pm$ 0.2 %, Moon: -4.8 $\pm$ 0.8 %, Mars: -3.4 $\pm$ 0.7 %, Vesta -4.1 $\pm$ 0.4 %). We also calculated the Tm anomaly for the data from [4] (terrestrial standards and Post Archean Australian Shales relative to Orgueil) and obtain a Tm anomaly of -3.9 $\pm$ 0.8 %, which is within uncertainty identical to our value. The observed Tm anomaly indicates that either Tm is depleted in the Earth, Moon, Mars, and Vesta or that the CI1-chondrites are enriched in Tm relative to the large, differentiated bodies. We suggest that Earth, Moon, Mars and Vesta likely have unfractionated Tm/HREE relative to the Sun. Thus CI1 chondrite Orgueil has a small ~4.2 $\pm$ 0.2 % positive Tm anomaly. Such an anomaly can be due to incorporation of high-T fractional condensates with a group-II REE pattern. The CV, CK and some CM chondrites analyzed in this study also have a clearly resolvable positive Tm anomaly; making anomalous Tm a characteristic of some carbonaceous chondrites, including CI1.
We conclude that high-precision REE ratios should be best normalized to concentrations measured in CI1 chondrites with consideration of the 4.2% positive Tm anomaly as best proxy for the Solar composition. Other chondrites typically show distinct volatility-controlled REE fractionation and are not suitable for normalization.
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