TRACE ELEMENT INVENTORY OF METEORITIC CA-PHOSPHATES.

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Introduction: The most common meteoritic phosphate species are apatite [$Ca_5(PO_4)_3(F,Cl,OH)$] and merrillite [$Ca_9NaMg(PO_4)_7$]. Both are important accessory phases in numerous meteorite classes which formed under varying conditions, such as oxidizing (e.g. martian meteorites) as well as reducing (e.g. winonaites) environments [1,2]. Both of them occur in varying abundances and their grain sizes range from µm to mm. Moreover, they are the dominating carrier phases for REEs as well as for halogens and therefore provide insight into the genesis and evolution of their host rocks. Nevertheless, their abundances, distribution and formation mechanisms – especially within the early Solar System – still remain poorly constrained [3-6].

Material and Methods: Despite their rarity in some meteorite groups, intensive search by EPMA and SEM has established a chemically and petrographically well-documented pool of over 600 phosphates covering nine different meteorite classes. The trace element concentrations – with particular emphasis on the REE – of selected grains were analyzed by LA-ICP-MS at the University of Münster (Germany) and/or SIMS at the NORDSIM Laboratory in Stockholm (Sweden). This dataset includes analyses of 133 apatites and 163 merrillites from 7 ordinary chondrites, 1 carbonaceous chondrite, 3 acapulcoites, 1 ureilitic trachyandesite [7], 1 eucrite, 4 shergottites, 1 winonaite, 1 mesosiderite and 1 IAB iron meteorite.

Results: Ca-phosphates are major hosts for REE in all observed samples, accounting for the majority of the bulk REE budget. This entails enrichments of up to two orders of magnitude compared to the bulk rock concentrations in their hosts. The REE appear evenly distributed within the single phosphate grains, as multiple analyses of the same grains overlap within error.

Achondritic phosphates generally show significantly higher REE contents than those of chondritic samples (up to 3000x CI vs. up to 300x CI). Within a single sample, each phosphate species displays a uniform REE-pattern and variations are mainly restricted to their enrichments. Furthermore REE concentration in merrillite predominantly exceeds those of apatite by an order of magnitude. The latter shows two different shapes of REE patterns (Figs.1a and b): The first is featured in the apatite of the acapulcoites Acapulco and Dhofar 125, the winonaite Hammadah al Hamra (HaH) 193, and the ureilitic trachyandesite ALM-A [7]. The shapes of their REE-patterns are flat with prominent negative Eu anomalies (Eu/Eu* ≈ 0.03-0.7) and except for HaH 193 an additional depletion in the HREE (La/Lu ≈ 1.2-5.4) (Fig.1a). In contrast, those of apatite in the ordinary chondrites Devgaon (H3.8), Ybbsitz (H4), Portales Valley (H6) and Villalbeto de la Peña (L6) exhibit a distinct enrichment in the LREE (La/Lu ≈ 2.6-8.4) with slight Eu anomalies (Eu/Eu* ≈ 0.6-6.2). These anomalies are either positive or negative but coincide within each sample (Fig.1b).

Merrillite on the other hand shows three main REE patterns again with varying enrichments (Fig.1c-e):

(1) In ordinary chondrites (as listed above, additionally Aguemour 009 (L3.8), Allegan (H5) and Bruderheim (H6)), acapulcoites (Acapulco, NWA 1052) and the eucrite NWA 5073, merrillite has flat REE-patterns, slightly depleted in the HREE (La/Lu ≈ 1.2-3.8) and a striking negative Eu anomaly (Eu/Eu* ≈ 0.02-0.7) (Fig.1c).

(2) Merrillite in the enriched shergottites Zagami and NWA 4864, as well as in the mesosiderite Dalgaranga exhibits unfractionated patterns without pronounced anomalies (Eu/Eu* ≈ 0.9-1.2, La/Lu ≈ 0.8-1.4) (Fig.1d).

(3) In the depleted shergottites SaU 005 and DaG 1051 merrillite shows highly LREE-depleted patterns (La/Lu ≈ 0.1-0.18) with a minor negative Eu anomaly (Eu/Eu* ≈ 0.4-0.6) (Fig.1e).

The Ca-phosphates in both enriched and depleted shergottites mimic the REE pattern of the bulk meteorite but compared to their hosts, their REE concentrations are elevated by two orders of magnitude.

Discussion: LA-ICP-MS and SIMS analyses provided concordant data, which is also consistent with previous work on meteoritic Ca-phosphates [8-10].

Within the different samples, both merrillite and apatite mostly show variations in REE enrichment, but not in the particular shape of their REE-patterns, suggesting the phosphates of each sample formed under similar conditions. Despite this uniformity within single samples, their REE-patterns are not unique for distinct meteorite groups, except for the depleted shergottites (Fig.1). Suprisingly no clear correlations of the patterns exist with the grade of metamorphism, petrologic type, adjacent mineral assemblages or grain size. The variations of Ca-phosphate REE patterns within the different meteorite groups were generated during their formation. For instance, in shergottites merrillite is a primary, late-crystallizing phase featuring two different REE patterns (enriched and depleted; Fig.1d and e) depending on the characteristics of its source region and, hence, different basaltic melts [5]. In chondrites on the other hand, both apatite and merrillite are presumed to be almost exclusively secondary phases [3,4], which might lead to lower enrichment of REE in both phosphate phases compared to achondritic samples. Nevertheless chondritic merrillite shows similar REE-patterns to that in acapulcoites and eucrites, although significantly less enriched (Fig.1c). Furthermore the apatites from these groups clearly exhibit different patterns than those of ordinary chondrites (Fig.1a and b), hence primary versus secondary origin cannot be the only factor affecting REE enrichment. In addition apatite from the ALM-A sample and from the primitive achondrites Acapulco and HaH 193 show similar REE-patterns (Fig.1a and b). The smooth decrease from LREE to HREE may simply be a function of the REEs decreasing ionic radii and the large Eu anomalies caused by the preference of the plagioclase crystal structure during ionic substitution. However, as there is no resolvable correlation between the Eu anomalies and the plagioclase modal abundance in the given assemblage, plagioclase cannot be the solitary factor controlling the Eu anomaly.

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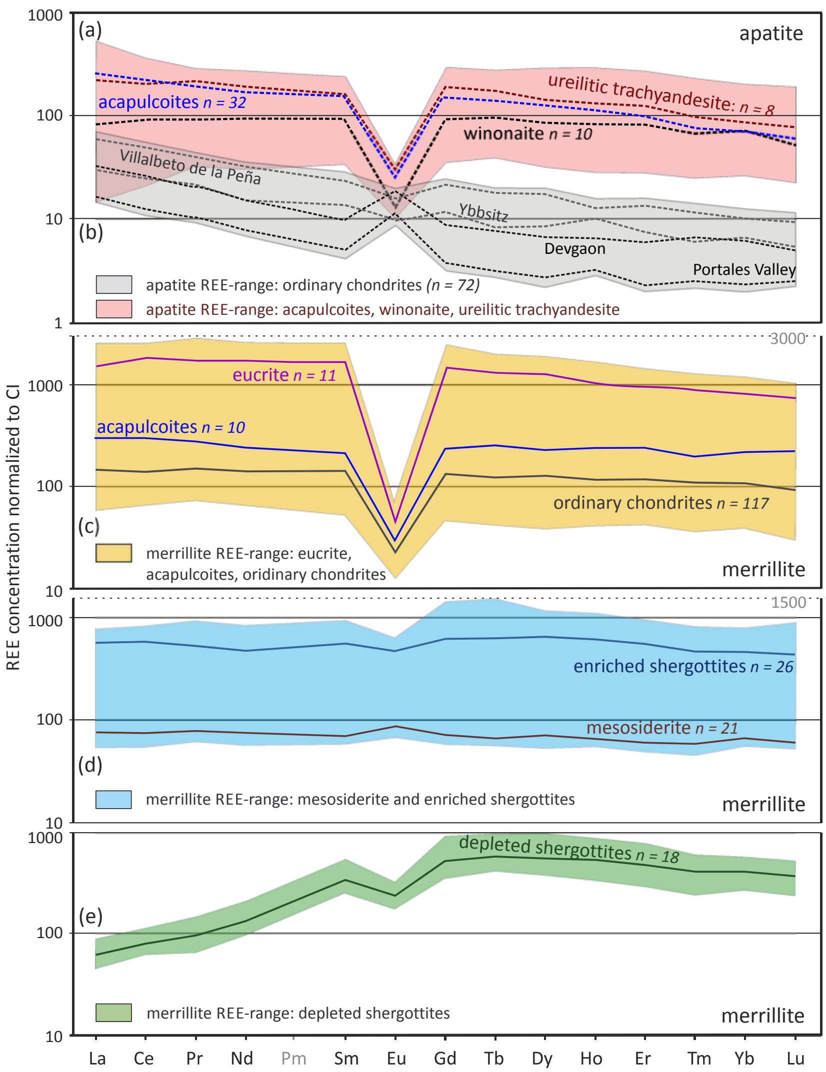

Fig.1 Apatite and merrillite REE concentrations normalized to CI [11]. Red field (a): Apatite REE-range from Dhofar 125, Acapulco, ALM-A and HaH 193, averages for each group indicated by dashed lines. Gray field (b): REE-range of apatites from ordinary chondrites, averages for each sample indicated by dashed lines. Orange field (c): Merrillite REE-range of eucrites, acapulcoites and ordinary chondrites, averages for each group indicated by solid lines. Blue field (d): Range of the flat patterns exhibited by merrillites in enriched shergottites (average = dark blue line) and mesosiderites (average = dark brown line). Green field (e): REE-range of merrillites from depleted shergottites, average corresponds to the solid line.