

U AND Th ABUNDANCES AND REE MASS BALANCE OF EXTRATERRESTRIAL Ca-PHOSPHATES

D. Ward¹, A. Bischoff¹, J. Roszjar², J. Berndt³ and M. J. Whitehouse⁴

¹Institut für Planetologie, WWU Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany, d.ward@wwu.de.

²Institute of Mineralogy and Petrography, Natural History Museum Vienna, Burgring 7, 1010 Vienna, Austria.

³Institut für Mineralogie, WWU Münster, Corrensstraße 24, 48149 Münster, Germany.

⁴Swedish Museum of Natural History, SE-104 05 Stockholm, Sweden.

Introduction: Ca-phosphates are ubiquitous accessory phases and represent the predominant phosphorous (P) reservoir in meteorites. The most common meteoritic Ca-phosphates are merrillite [$\text{Ca}_{18}\text{Na}_2\text{Mg}_2(\text{PO}_4)_{14}$] and apatite-group minerals [$\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$], which are important carrier phases of REEs and other trace elements [1-4].

Methods: The trace element concentrations (REE, Sc, Ti, V, Cr, Mn, Co, As, Rb, Sr, Y, Zr, Nb, Ba, Hf, Ta, Pb, Th and U) of meteoritic Ca-phosphates were analyzed by LA-ICP-MS and/or SIMS (REE only). This systematic investigation includes 99 apatite and 149 merrillite analyses derived from eleven different (sub)groups [2-4], spanning from primitive to highly differentiated rock types, as well as variable thermal- and shock-metamorphic stages.

Results and Discussion: *U and Th in apatite:* Based on the investigated samples, U and Th are positively correlated. Their concentrations increase almost linearly with (1) their host rock's grade of thermal metamorphism (petrologic type) and (2) with increasing degree of differentiation of their respective parent body [Fig. 1]. Apatite from Devgaon and Ybbsitz (type 3.8 and 4 ordinary chondrites) has the lowest contents of $<0.5 \mu\text{g/g}$ U and $<0.3 \mu\text{g/g}$ Th, while apatite from thermally metamorphosed type 6 samples Bruderheim, Villalbeto de la Peña, Portales Valley and from type 6 fragments of the Adzhi-Bogdo (stone) breccia, has abundances of 2-6 $\mu\text{g/g}$ U and 2-8 $\mu\text{g/g}$ Th [2]. Achondritic apatite has higher concentrations, starting with 3-11 $\mu\text{g/g}$ U and 5-17 $\mu\text{g/g}$ Th in acapulcoites, followed by Martian meteorites with $\sim 5 \mu\text{g/g}$ U and 17-21 $\mu\text{g/g}$ Th [2]. Eucritic apatite has the highest content observed here, with 36-164 $\mu\text{g/g}$ U and 22-105 $\mu\text{g/g}$ Th [2], but is exceeded by apatite in lunar samples [5] and terrestrial lherzolites [6].

Samarium mass balance: The high REE abundances in apatite and merrillite raise the question of how to quantify the proportion they incorporate from the host rock's bulk REE budget. Mass balance calculations of Sm were conducted, based on the modal abundances of both species, their respective Sm concentrations, and on available bulk Sm concentration of the host meteorites. The accuracy of the evaluated modal abundances of the Ca-phosphates is the limiting factor within these calculations. For instance, in the Millbillillie eucrite, 0.01 vol% of merrillite accounts for approximately 20% of the bulk REE Sm budget [2], but the available modal data is far from precise enough for a reliable discrimination at this level. Despite of the constant REE patterns for a Ca-phosphate species within a given sample, their REE enrichments may vary and hence, depending on whether the average, minimum or maximum concentration of the corresponding species is taken into account, the fraction of the bulk REE budget that they host may vary significantly in some samples. Moreover, the abundance and size distribution of Ca-phosphates within a given sample is often observed to be heterogeneous, especially in brecciated samples.

Conclusions: The linear positive correlation of apatite Th vs. U concentrations with increasing petrologic type has not been reported previously and merits further investigation. Despite the uncertainties imparted by the limited accuracy of required modal abundances (<1 vol%) and also by the observed range of REE abundances of Ca-phosphates within a given meteorite [2], the distribution of REE among its various carrier phases is essential to understand the igneous and secondary alteration processes that have shaped extraterrestrial samples. We advise caution concerning the modal fractions and, more importantly, encourage discrimination of apatite and merrillite, rather than labelling them as "phosphates". Modal proportions should be based on several thin sections if available and different lithologies from (polymict) breccias (e.g., Adzhi-Bogdo (stone) [2, 7]) should be treated individually.

References: [1] Crozaz G. et al. (1989) *Earth and Planetary Science Letters* 93:157-169. [2] Ward D. et al. (2017) *American Mineralogist* (accepted). [3] Ward D. et al. (2015) *Meteoritics & Planetary Science* 50, Special Issue, #5056. [4] Ward D. et al. (2016) *Meteoritics & Planetary Science* 51:A649. [5] Nemchin A. A. et al. (2009) *Meteoritics & Planetary Science* 44:1717-1734. [6] O'Reilly S.Y. and Griffin W. (2000) *Lithos* 53:217-232. [7] Bischoff A. et al. (1993) *Meteoritics* 28:570-578.

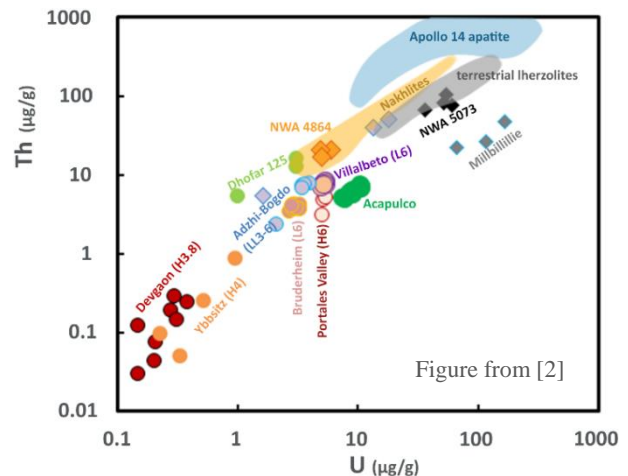


Fig. 1: U and Th concentrations of extraterrestrial apatite in $\mu\text{g/g}$. Points correspond to [2], colored areas to [5,6]