

ON THE SEARCH FOR RARE EARTH ELEMENT RESOURCES: THE EARTH, MOON, AND BEYOND.

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Introduction: Rare Earth Elements (REEs) are a group of transition metals which include the lanthanide series of the periodic table (La-Lu, in addition to Sc and Y). The REEs are used throughout modern society on a daily basis as they are integral components of smart phones, computer monitors, catalysts, magnets, and fundamental constituents of many energy and military-based technologies [1,2,3,4]. Earth's REE resource budget is however limited with several of these elements estimated to have <2500 years of reserves left, based on current demand, mining operations and technologies (**Fig. 1**; [5]).

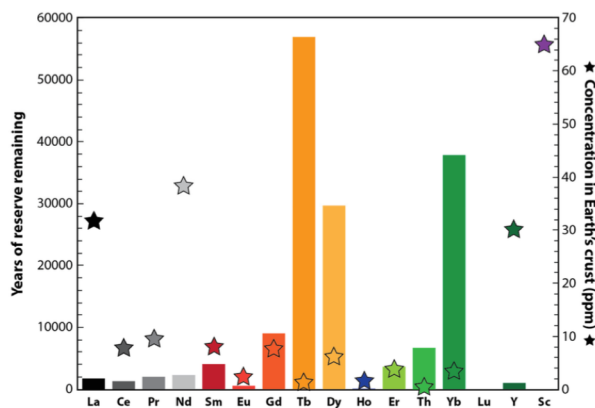


Figure 1: Estimated reserves of REEs (x-axis) on Earth in years (left y-axis) and their corresponding abundance in the Earth's crust (right y-axis) [5,6].

Terrestrial Ores and Resources: As of 2012, REEs had been produced from less than 20 minerals with bastnaesite ($\text{REECO}_3(\text{F},\text{OH})$), monazite ($(\text{REE},\text{Th},\text{Ca},\text{Sr})(\text{P},\text{Si},\text{S})\text{O}_4$), xenotime ($(\text{REE},\text{Zr})(\text{P},\text{Si})\text{O}_4$), loparite ($(\text{Na},\text{REE},\text{Ca})(\text{Ti},\text{Nb})\text{O}_3$), parisite ($\text{CaREE}_2(\text{CO}_3)_3(\text{F},\text{OH})_2$), and Al-clays accounting for the majority of REE production [1]. As of 2014, Earth's total REE resources were estimated at 140 million tonnes with 55 million in China and 13 million in the U. S. [7]. All of the REE uses are therefore primarily dependent on mined resources with recycling of REEs challenging and not widely practiced [8]. With Earth's human population projected to reach 8.5 billion by 2020 [9], and the downsizing of the mining industry largely associated with REE quotas and the reduction of illegal mining operations [4,10], material and energy resources on Earth are ultimately limited. Therefore, sustaining our reliance on raw materials will likely require investment in, and utilization of, extraterrestrial resources. A

natural, and logical, first step is the consideration of Earth's Moon, our nearest neighbor in space.

The Earth's Moon: At 99% crystallization, at the final stage of Lunar Magma Ocean (LMO) crystallization, remaining liquids would have been relatively enriched in incompatible trace elements and are hypothesized to have formed a late-stage reservoir between the solidifying lunar crust and mantle. This residuum from LMO differentiation is the urKREEP reservoir, the chemical signature of which is observed throughout the lunar sample collection [11]. On the lunar surface today, KREEP-rich lithologies are demonstrably associated with relative enrichments in Th and U, the distributions of which have been evaluated through gamma ray mapping and are largely associated with the Procellarum KREEP Terrain (PKT) [12,13]. The volume of KREEP lithologies underlying this region has been estimated at $2.2 \times 10^8 \text{ km}^3$ with potential REE reserves at $\sim 2.25 \times 10^{14}$ – $4.5 \times 10^{14} \text{ kg}$ [14]. **Figure 2** shows a compilation of normalized REE signatures for lunar lithologies and REE-bearing minerals (see later). As shown, the KREEP-rich lithologies and urKREEP reservoir exhibit the highest normalized abundances (compared to bulk lithologies) with concentrations orders of magnitude higher than the Ferroan Anorthosite Suite which characterizes the lunar highlands, as well as terrestrial crustal geochemical reservoirs, and chondrite.

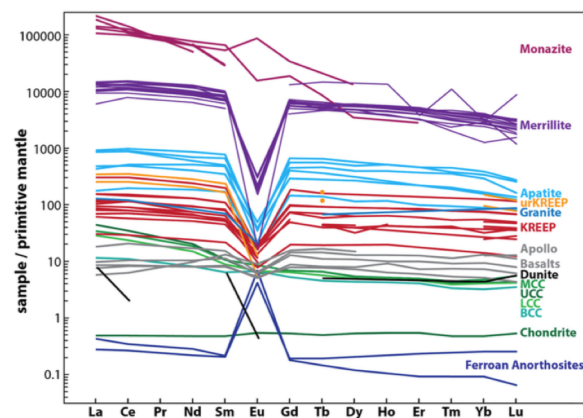


Figure 2: Earth's primitive mantle normalized concentrations of terrestrial and lunar geochemical reservoirs, and REE-bearing lunar minerals [6].

The most prevalent REE-bearing phases found throughout the lunar sample collection are apatite, merrillite and monazite (**Fig. 2**). The majority of lunar samples contain apatite and/or merrillite as a trace phase

and in samples which exhibit a KREEP signature, merrillite (H-free whitlockite) is almost always present, often co-existing with apatite [15]. While significant proportions of the KREEP REE budget are associated with merrillite, which can constitute up to 3% of a lithology's volume in the PKT, this amount is too small for economical extraction, based on current understanding and practices [16]. In addition to apatite and merrillite, monazite is also present on the Moon but up until 2006 had only been identified as small ($10\mu\text{m} \times 3\mu\text{m}$) inclusions in pyroxene from Apollo 11 basalts. For a mineral to be mined as an ore (as a resource), the concentration of the desired element must be high enough for economic extraction, meaning that its initial abundance must also be high enough so that a differentiation process can concentrate it. While there are REE-bearing phases on the Moon they are present only as trace phases are a volumetrically minor component of the lunar geological record, and at present cannot be considered viable REE

REEs beyond the Moon: The only other planet from which samples are known to be derived from is Mars. Like the Moon, following ~99% of solidification of a Martian Magma Ocean, a late-stage liquid enriched in incompatible trace elements has been modelled with characteristics similar to lunar KREEP [18]. While like the Moon, evidence of REE ore deposits is lacking, REE-bearing phases have been identified throughout the meteorite collection, the most common of which is merrillite which has been found in shergottites, the orthopyroxenite, and the regolith breccia (NWA 7034). Compared to lunar merrillite, martian merrillite is two orders of magnitude lower in REEs [6] indicative of different planetary differentiation histories [15]. The first occurrence of Martian apatite-hosted monazite was recently documented in NWA 7034 alongside monazite-chevkinite-perrierite [19].

Beyond the Moon and Mars, other REE-bearing phases have been documented in other meteorites. A summary of the REE characteristics of these, broadly classified as stony-type, is shown in **Fig. 3**. From the 63 bulk rock signatures shown in **Fig. 3**, 61 are chondrites and 2 are achondrites. The two aubrite samples represent the most REE-depleted samples, consistent with their differentiated nature. As with lunar and martian samples, REE-bearing minor phases are also present with sub-mm phosphates (apatite, whitlockite, merrillite) and oldhamite common REE carriers (up to ~1600 ppm). Broadly, these REE-bearing phases are enriched by 1-2 orders of magnitude comparison to the bulk samples but do not extend to the same degree of enrichment as observed in lunar or Martian phases.

Concluding Remarks: The daily use of REEs by society is placing an undeniable demand for their extraction from limited terrestrial resources.

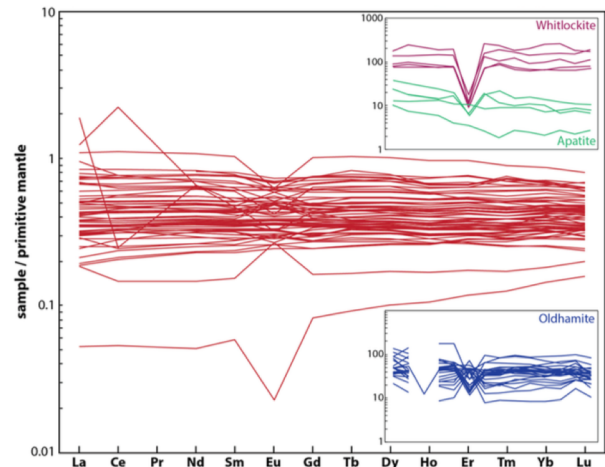


Figure 3: From [6], REE characteristics of stony meteorites (16 chondrite types and 2 achondrites, aubrite). Two inset graphs illustrate the REE signatures of REE-bearing phases. Oldhamite from aubrites Bustee and Mayo Belwa, EL6 Jajh deh Jot Lelu and Khairpur. Apatite and Whitlockite from H4 Yamato-74371.

Although to date there is a lack of evidence in support of REEs being present as viable extraterrestrial resources on the Moon, Mars, or other parent bodies, future explorations may change this. With numerous future space explorations currently planned (e.g. NASA, ESA, JAXA, ISRO, Virgin Galactic, SpaceX, Google Lunar XPRIZE), science and society stand to benefit.

References: [1] Chakhmouradian and Wall (2012), *Elements*, v. 8; 333-340; [2] Navarro and Zhao (2014), *Front in Energy Res*, v. 2; 1-17; [3] Grasso, (2013), *Congressional Res Service* 7-5700, R41744; [4] DOE (2011), *U.S. Department of Energy Critical Materials Strategy*; [5] Haque et al. (2014), *Resources*, v. 3; 614-635; [6] McLeod and Krekeler (2017), *Resources*, v. 6; 40; [7] USGS Mineral Commodities Survey (2014), U. S. Department of the Interior; [8] Goonan et al. (2011), *USGS Scientific Investigations Report* 2011-5094; [9] United Nations (2015), *UNFPA Revision of Population Prospects*; [10] Ali et al. (2017), *Nature*, v. 453; 367-372; [11] Warren and Wason (1985), *LPSC*, 185-217; [12] Lawrence et al., (1999), *Geophys Res Lett*, v. 26; 2681-2684; [13] Haskin et al. (2000), *J. Geophys Res*, v. 105; 20403-20415; [14] Zou et al. (2004), *Chin J of Geochem*, v. 23; 65-70; [15] Jolliff et al. (2006). *Am Min*, v. 91; 1583-1595; [16] Yazawa et al. (2012), *Moon Perspective Energy and Material Resources*, Springer New York, 771p; [17] Crawford (2015), *Prog Phys Geog*, v. 39; 137-167; [18] Borg et al. (2003), *Met Planet Sci*, v. 38; 1713-1731; [19] Liu et al., (2016), *EPSL*, v. 451; 251-262.