

Er AND Yb ISOTOPE FRACTIONATION IN PLANETARY MATERIAL. E. Albalat¹, P. Telouk¹ and F. Albarède¹, ¹Ecole Normale Supérieure de Lyon, 46 allée d'Italie 69364 Lyon Cedex 7, France (emmanuelle.albalat@ens-lyon.fr)

Introduction: Multiple chemical features characterizing the Earth, Moon, and other planetary bodies are indicative of their strong depletion in lithophile volatile elements with respect to the solar composition. The case of high-temperature incomplete condensation can be made from heavy rare-earth elements (HREE), and their isotopes, as these elements have very similar crystal chemistry but different condensation temperatures from the nebular gas. Yb condenses at ≈ 1490 K from the vapor, where it is in metal form, whereas Er which is in oxide form, condense at ≈ 1660 K [1,2]. Although the atomic mass of HREE does not let us contemplate major isotopic fractionation, mass-dependent fractionation at the surface of nebular condensates should shed light on high-temperature volatility issues. This work presents a first investigation of Er and Yb isotopic variability in terrestrial material, meteorites, and lunar samples by multiple-collector inductively coupled mass spectrometry (MC-ICP-MS).

Sample description: In order to establish a solar system reference, we analyzed six carbonaceous chondrites, Murchison, ALH 83108, Allende, Sahara 00177, NWA 5240, and EET 92002, four ordinary chondrites, Korra Korrabes, Forest City, Mezô-Madaras, and NWA 987 35-6, and two enstatite chondrites, Sahara 97098 and Indarch. Planetary samples include three eucrite samples (Millbillillie, Stannern, and Bouvante) and provide a magmatic reference. For terrestrial samples, we analyzed a basalt from the Mid-Atlantic Ridge (RL-DR30), an ocean-island basalt from the Reunion Island, (Fournaise 986-251), the Hawaiian basalt BHVO2, and a 600 Ma old, kimberlite sample from Greenland (Kim14). In order to investigate fractionation in material relatively enriched in HREE, we also ran igneous garnet samples from the Beni Bousera ultramafic intrusion, and metamorphic garnets from Dora Maira, W. Alps, and Isua, Greenland. Finally, we included six lunar samples, one Ti-rich basalt (74275), the 'orange soil' 74220, which is better described as a pyroclastic glass, two soils (14163, 64501) and two breccias (62295 and 68815).

Analytical procedures: The option adopted here was to avoid the error amplification inherent in the double-spike technique and to monitor the mass bias by combining standard-sample bracketing plus and external isotopic reference [3] with peak-stripping of isobaric interferences. The HREE were therefore separated as a group, with the stringent constraint that only a separation yield approaching 100 % allows a control of the instrumental bias. Samples were digested by fluxing with conc. HF and HNO₃ and treated with HClO₄ and 6M HCl to decompose the fluorides formed

during the attack. Entrainment of the REE by hydroxide precipitation [4] of natural iron present in the samples was achieved by addition of ammonia solution remaining the pH to 6. The REE were separated from iron using AG1-X8 anion-exchange. The procedure for further purification from the remaining matrix elements was adapted from [5] and was achieved on AG50-X8 cation-exchange resin. Major elements were eluted with 2.5M HCl with traces of H₂O₂. The REE fraction was then collect with 6M HCl and thereafter divided into two groups by reversed-phase extraction chromatography on HDEHP-coated teflon beads using 1.5M HCl as the light REE eluent and 6M HCl for the HREE. All isotopic measurements were carried out with a Nu Instruments MC-ICP-MS Nu Plasma 1700 at ENS Lyon using a Desolvation Nebuliser System (DSN-100). The isotopic compositions of Er and Yb were measured simultaneously using a combination of standard bracketing and external normalization. An in-house standard solution of HREE was prepared to

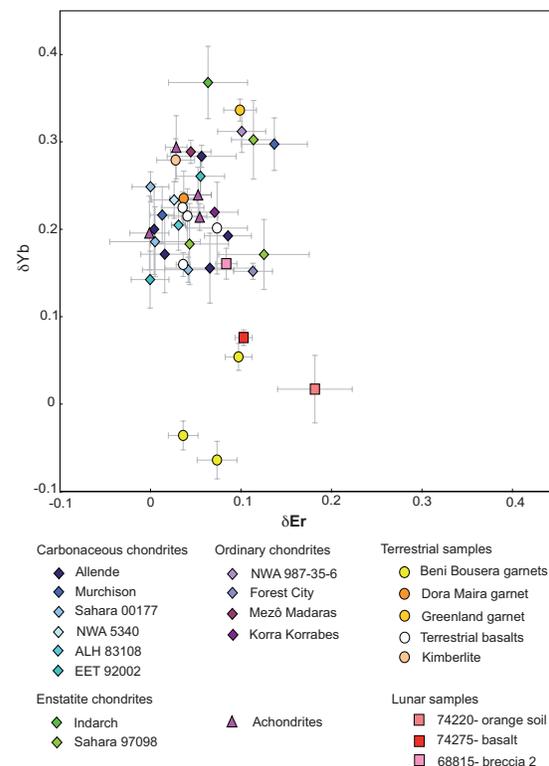


Fig. 1: Isotopic variability of Er and Yb in terrestrial and planetary samples. Note the smaller isotopic variability of Er with respect to that of Yb. Isotopically light Yb in lunar basalts may represent a signature of condensation of the Moon from silicate vapors produced during the Lunar Giant Impact.

match sample compositions. Gadolinium was added both to the Gd-free samples and to the standard solution, as external standard, to monitor and correct instrumental mass fractionation as it is well established for other elements [3, 6]. The mass bias correction using the $^{160}\text{Gd}/^{158}\text{Gd}$ ratio ($^{160}\text{Gd}/^{158}\text{Gd} = 0.87863$, [7]) is remarkably effective for correcting matrix effects. The isotopic data δEr and δYb are the average values of parts-per-1000 deviations per amu from the in-house standard solution for each isotopic ratio.

Yb isotope fractionation in planetary material:

The ranges of mass-dependent isotope fractionation are larger for Yb isotopes (0.44 ‰ per a.m.u.) than for Er (0.13 ‰), and exceed the standard reproducibility by a factor of 11 and 2.5, respectively (Fig. 1). For terrestrial rocks, the positive correlation between δYb and the La/Yb ratio (Fig. 2) suggests that the isotopic differences between Er and Yb can be accounted for by the presence of small fractions of Yb²⁺ in the mostly trivalent Yb. Yb seems to behave as Fe [8, 9...], with trivalent Yb fractionating preferentially into tighter bonds and, at the same time, being more incompatible than common Yb. The kimberlite sample is enriched in heavy Yb isotopes, whereas garnets from the Beni Bousera peridotite are depleted. A remarkable feature of this study is the apparently light Yb isotope compositions of lunar basalts 74275 and 74220 and soil 14163 which are 0.1-0.3 ‰ lighter than chondrites and terrestrial basalts. In spite of the fragmentary character of this observation, it suggests that, at the outset of the Lunar Giant Impact, the Moon may have condensed preferentially out of silicate vapors enriched in light Yb isotopes with respect to solids. The contrasting lack of Er fractionation between the Moon and the Earth indicates that this element was not vaporized and therefore suggests a range of vapor temperatures upon condensation of 1490-1660K.

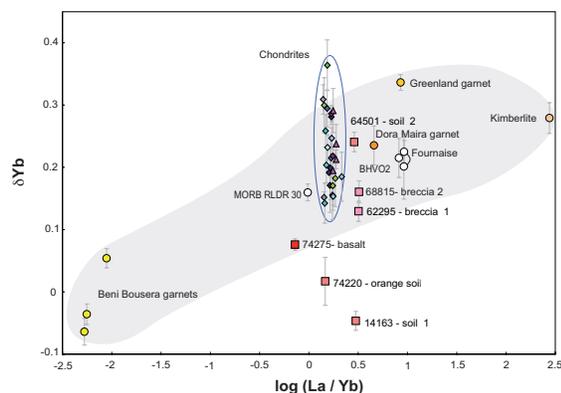


Fig. 2: Plot of δYb vs La/Yb ratios. The positive correlation observed for terrestrial samples (grey shade) shows that liquids formed by small degrees of melting (e.g., kimberlite) tend to be isotopically heavy, whereas residual garnets are isotopically light. Incompatibility of Yb isotopes therefore increases with masses of isotopes. See Fig. 1 for symbol key.

Thermal neutron capture by ^{167}Er : In lunar soils 14163 and 64501 and in breccia 62295, mass-independent fractionation of $^{167}\text{Er}/^{166}\text{Er}$ and $^{168}\text{Er}/^{166}\text{Er}$ (Fig. 3) indicates an excess of ^{168}Er . Such excesses reflect the particularly high cross-section of ^{167}Er of neutron capture with respect to those of ^{166}Er and ^{168}Er , both in the thermal domain. The presence of mass-independent isotopic anomalies is definitely not correlated with the strength of the thermal neutron fluxes at the locality where the samples were collected, and is better accounted for by different exposure ages. The presence of thermal neutrons, which are produced by interaction of cosmic rays with the lunar regolith, is well established from isotopic anomalies [10-13], and the neutron measured by orbiters. The cross-section for the capture of thermal neutrons (≈ 0.025 eV) by ^{155}Gd and ^{157}Gd , two nuclides commonly used to infer neutron fluxes on the Moon, strongly drops above 0.02 eV, whereas the first resonance for the capture of 0.1-0.5 eV 'hot' neutrons by ^{167}Er is very strong. ^{167}Er anomalies may help refine the knowledge of the neutron energy spectrum on the Moon and other planets.

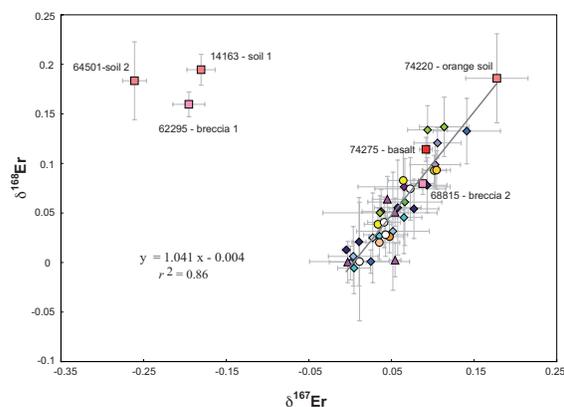


Fig. 3: The +1.0 slope of the correlation between $\delta^{167}\text{Er}$ and $\delta^{168}\text{Er}$ observed for all but a few lunar samples indicates that the small fractionation of Er isotopes is mass-dependent. The two lunar soils and breccia 62295 are displaced above the mass-fractionation line as a result of neutron capture by ^{167}Er . See Fig. 1 for symbol key.

References: [1] Boyton W.V. (1975) *GCA*, 39, 569-584. [2] Lodders K. (2003) *Astroph. J.*, 591, 1220-1247. [3] Maréchal C. et al. (1999) *Chem. Geol.*, 156, 251-273. [4] Goldberg E.D. et al. *J. Geophys. Res.* 68, 4209-4217. [5] Blichert-Toft J. et al. (1997) *Contrib. Mineral. Petrol.*, 127, 248-260. [6] White W.M. et al. (2000) *Chem. Geol.*, 167, 257-270. [7] Dubois J.C. et al. (1992) *Intern. J. Mass Spectrom.* 120, 163-177. [8] Dauphas N. et al. (2009) *EPSL*, 288, 255-267. [9] Schoenberg R. and Blankenburg F. (2006) *EPSL*, 252, 342-359. [10] Eugster O. et al. (1970) *EPSL*, 8, 20-30. [11] Lingenfelter R.E. et al. (1972) *EPSL*, 16, 355-369. [12] Sands D.G. et al. (2001) *EPSL*, 186, 335-346. [13] Leya I. et al. (2003) *GCA*, 67, 529-541.