



# The lunar neutron energy spectrum inferred from the isotope compositions of rare-earth elements and hafnium in Apollo samples



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## ABSTRACT

The isotopic abundances of Sm, Gd, Dy, Er, Yb, and Hf have been measured in nine lunar samples by MC-ICP-MS. The data were corrected for both instrumental mass bias and natural isotope fractionation. We used the data to calculate the total flux and energy spectrum of the neutrons absorbed by the rocks. We write the constitutive equations of the isotopic changes for these elements induced by neutrons and solve the inverse problem by computing local energy averages. Resonant absorption peaks can be used as convenient kernels to define the spectrum of epithermal neutrons. We find that  $^{149}\text{Sm}$  and  $^{157}\text{Gd}$  anomalies correlate with neutron flux density for  $E < 0.015$  eV ( $r^2 > 0.98$ ) and  $E \approx 0.13$  eV ( $r^2 > 0.85$ ), while no significant correlation exists between the ratio of these anomalies and the epithermal/thermal flux ratio at any value of energy. Neutron flux density variations can be used to trace the proportions of neutrons scattered out of the samples. The spectrum in the thermal region follows the expected  $E^{-1/2}$  dependence but with 'notches' corresponding to neutron absorption. A major notch at the lowest end of the epithermal neutron spectrum (0.2–0.8 eV) is possibly due to absorption of neutrons by  $^{151}\text{Eu}$ ,  $^{167}\text{Er}$ , and  $^{149}\text{Sm}$ . In general, we find a rather good correlation between the neutron flux density at specific energies and the exposure age, which suggests a mean residence time of the samples at the surface of the regolith of 2–300 Ma. Another correlation of epithermal neutrons with sample wt% FeO + TiO<sub>2</sub> is consistent with orbital reflectance observations.

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## 1. Introduction

The orbital measurement of neutron fluxes by neutron and gamma detectors in various ranges of energy can be used to infer the abundances of some elements at the surface of planets (Lingenfelter et al., 1961). This has allowed for surface compositions to be estimated for the Moon (Feldman et al., 1998a, 1998b, 2000, 2002; Maurice et al., 2000; Gasnault et al., 2000), Mercury (Feldman et al., 1997), and Mars (Feldman et al., 2002). Most importantly, the neutron energy spectrum has been used to suggest the presence of hydrogen, and therefore water, at the surface of the Moon (Lingenfelter et al., 1961; Feldman et al., 2000). Lunar neutrons are produced by spallation upon interaction of galactic cosmic rays with planetary soils and surface rocks. A typical reaction producing secondary neutrons is that of  $^{56}\text{Fe}(p, n)^{56}\text{Co}$  (Reedy and Arnold, 1972). Neutrons produced in the process quickly lose energy by both elastic and inelastic collisions with surrounding material and produce a steady-state energy spectrum down to the thermal energy range ( $E < 0.3$  eV), where they are absorbed by Fe,

Ti, K, Gd, and Sm. Resonance escape probability defines the proportion of slowing down neutrons escaping resonant absorption. Hydrogen, when present, is a major contributor to the production of epithermal neutrons ( $E > 0.3$  eV) (Feldman et al., 1998a, 1998b). In the thermal range, neutrons absorb as much energy per collision on average as they transfer to ambient material by collision and hence their energy remains relatively unaffected until they are absorbed by nuclei (Lingenfelter et al., 1972). In order to assess the potential of a planetary surface for hosting hydrogen it is therefore important to determine how the energy is reduced during the cascade of collisions and scattering (neutron lethargy). The isotope compositions of some critical elements in planetary samples add independent information to that determined from orbital observations.

Anomalies in the isotope abundances of Sm, Gd (Eugster et al., 1970; Russ et al., 1971, 1972; Russ, 1972; Lugmair et al., 1975; Hidaka et al., 1999, 2000; Hidaka and Yoneda, 2007), Cd (Sands et al., 2001; Kruijjer et al., 2013), and W (Leya et al., 2000) attest to neutron capture by meteorites and lunar samples and have been used to determine the total flux of thermal neutrons that affected a particular sample. Albalat et al.'s (2012) Er isotopic data and Kruijjer et al.'s (2013) Cd isotopic data suggest that the neutron energy

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spectrum is richer in high-energy neutrons than that proposed by Lingenfelter et al. (1972). The neutron energy spectrum absorbed by rock samples provides a useful hint at the amount of hydrogen present at the surface of terrestrial planets. Correction for neutron capture is also a major concern for the isotope geochemistry of lunar samples, notably for Sm (Nyquist et al., 1995; Boyet and Carlson 2007; Sprung et al., 2013) and W (Leya et al., 2000; Touboul et al., 2007) isotope compositions.

The present work reports isotope compositions of Sm, Gd, Dy, Er, Yb, and Hf in nine lunar samples including soils and a plutonic rock. Selective sensitivity of some elements to thermal (Sm, Gd) and epithermal (Er, Dy, Hf) neutrons suggests that a combination of analytical data can constrain the lunar energy spectrum below the lunar surface and provide a new perspective on the search for water in the Moon. A novel method is proposed here to calculate an approximation of the energy spectrum based on the multiplicity of analytical observations.

The original motivation behind the present sample selection strategy was not an attempt to constrain the neutron fluxes affecting the lunar surface but a prior study of mass-dependent Er and Yb isotope fractionation in the Moon (Albalat et al., 2012). For this reason, no emphasis has been placed on the effect of depth, composition, and density of the samples on the neutron energy spectrum.

## 2. Samples

The following information was taken from the NASA lunar sample compendium (<http://curator.jsc.nasa.gov/lunar/lsc/>). Sample 12002 is a ~3.3 Ga old low-Ti olivine basalt. Sample 15597 is a low-Ti pigeonite basalt with a similar but poorly constrained Ar–Ar age. Sample 74275 is a high-Ti basalt dated at ~3.85 Ga and associated with pyroclastic ‘orange’ glass. Sample 75055 is a ~3.8 Ga old high-Ti ilmenite basalt. Sample 78236 is a ~4.34 Ga old heavily shocked norite. Sample 62295 is an impact melt breccia dated at ~3.87 Ga, while sample 68815 is a polymict glassy breccia with clasts dated from 3.6 to 4.1 Ga. Samples 14163 and 64501 are soils. Exposure ages have been summarized by Arvidson et al. (1975) and are listed in the lunar compendium. The only sample for which exposure ages are missing is soil 14163. Exposure ages of soil samples vary with grain size and systematically represent mixtures of different components.

## 3. Analytical techniques

### 3.1. Chemical separation

Sample preparation, digestion, and separation chemistry was done at the Ecole Normale Supérieure de Lyon (ENS Lyon). The following description repeats to some extent the procedure used for Er and Yb purification by Albalat et al. (2012). The lunar samples were crushed in an agate mortar. For each sample the powder was divided into two splits that went through two independent procedures from digestion to chemical separation: one procedure for the separation of each of the five rare-earth elements (REEs) and another procedure for the separation of Hf. Sample sizes depended on sample availability and element concentrations and varied from 0.15 to 0.3 g for the REE digestions and from 0.03 g to 0.1 g for the Hf digestions. In both cases, samples were digested in a 3:1 mixture of double-distilled concentrated HF:HNO<sub>3</sub> under high-pressure and high-temperature conditions using a double enclosed Savillex system as described by Albalat et al. (2012). After evaporation to dryness, residues were taken up twice in a few ml of double-distilled 6 N HCl and a few drops of double-distilled concentrated HClO<sub>4</sub> to eliminate fluorides and ensure complete sample dissolution. The REEs were separated as a group from the sample matrix following the three-step procedure described by Albalat et al.

**Table 1**

Extraction of REE by reversed-phase chromatography in three steps using columns of HDEHP-coated PTFE beads.

	Eluant	Elements collected
HDEHP column 1		
Cleaning (HCl 6 N), conditioning, and loading (HCl 1.5 N)		
LREE fraction	HCl 1.5 N	La Ce Pr Nd Sm Eu → HDEHP column 2
HREE fraction	HCl 6 N	Er and Yb → Er and Yb MC-ICP-MS with Tm, Lu and Y
HDEHP column 2		
Cleaning (HCl 6 N), conditioning, and loading (HCl 0.5 N)		
Sm fraction	HCl 0.5 N	La Ce Pr Nd Sm Eu → HDEHP column 3
Gd fraction	HCl 1.2 N	Gd with Eu Tb → Gd MC-ICP-MS
Dy fraction	HCl 6 N	Dy with Tb and Ho → Dy MC-ICP-MS
HDEHP column 3		
Cleaning (HCl 6 N), conditioning, and loading (HCl 0.25 N)		
Nd fraction	HCl 0.25 N	
	HCl 0.5 N	La Ce Pr Nd → discard
Sm fraction	HCl 0.5 N	Sm → Sm MC-ICP-MS

(2012). This included extraction of the REEs by Fe-hydroxide precipitation. Co-precipitation of other hydroxides such as those of Ca and Mg was minimized by keeping the pH at 6. After separation from the supernatant by centrifugation, the solid hydroxide was rinsed with distilled water and dissolved in double-distilled 6 N HCl. Iron was then removed from the solution on a 2 ml BioRad anion exchange column (AG1-X8) in HCl medium. The iron hydroxide precipitation step was repeated to improve the REE yield. Finally, the group of REEs was separated from the remaining sample matrix on a 5 ml cation exchange column (AG50W-X8) in HCl medium with traces of H<sub>2</sub>O<sub>2</sub>.

Samarium, Gd, Dy, Er, and Yb were separated from each other by reversed-phase extraction chromatography using HDEHP as a stationary phase coated on PTFE powder (Cerrai and Testa, 1963). The separation procedure included the three successive steps summarized in Table 1. Column specifications including the volume and nature of eluents are reported in the Supplementary Material Table S1. The first HDEHP column step separated the REEs into two groups, the light REEs (LREE) and the heavy REEs (HREE). The HREE fraction was analyzed by MC-ICP-MS to determine simultaneously the isotopic compositions of Er and Yb. The detailed chemical procedure, including blank issues, yield, and the presence of other elements, such as Tm, Lu, and Y, in the final solution, is described in Albalat et al. (2012). Gadolinium, Sm, and Dy were separated from the LREE fraction during HDEHP column steps 2 and 3 (Table 1). After elution of the light REEs on column 2 with 0.5 N HCl, Gd was collected using 1.2 N HCl and Dy using 6 N HCl. All purified Gd solutions were free of Sm and Dy (see paragraph below on Gd mass spectrometry), but still contained about 60% and 40% of the original Eu and Tb, respectively. The Dy fractions contained 60% and 16% of the original Tb and Ho, respectively. The presence of these elements in the Dy fractions were of no consequence to the isotopic analysis by MC-ICP-MS as none of them interfere isobarically with Dy. Typical Dy/Ho and Dy/Tb ratios were ~30 and ~10, respectively. The LREE fraction from the second HDEHP column step was taken through a third HDEHP column to completely separate Sm from the other LREEs. Lanthanum, Ce, Pr, and Nd were eluted with 0.25 N HCl and some 0.5 N HCl, and Sm was collected using 0.5 N HCl. The Sm purification step was repeated to ensure complete removal of Nd, which interferes isobarically with Sm. For all samples, the REE yield was better than 95% except for the Dy fractions with yields of only about 70%. The missing 30% were lost with the Er and Yb fractions during the first HDEHP column step (Albalat et al., 2012). The blanks of the total digestion and purification procedures were better than 0.1 ng for all REEs.

For Hf separation, the samples were attacked as described above and followed the three-stage column procedure of Blichert-

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