Available online at www.sciencedirect.com
ScienceDirect
Geochimica et Cosmochimica Acta 71 (2007) 1074–1086
Geochimica
www.elsevier.com/locate/gca

Sm and Gd isotopic shifts of Apollo 16 and 17 drill stem samples and their implications for regolith history

Hiroshi Hidaka [a,*], Shigekazu Yoneda [b]

[a] Department of Earth and Planetary Systems Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan
[b] Department of Science and Engineering, National Science Museum, Tokyo 169-0073, Japan

Received 13 February 2006; accepted in revised form 23 October 2006

Abstract

The isotopic compositions of Sm and Gd in lunar regolith samples from the Apollo 16 and 17 deep drill stems showed clear isotopic shifts in $^{150}Sm/^{149}Sm$ ($\varepsilon = +124$ to $+191$ for A-16, and $+37$ to $+111$ for A-17) and $^{158}Gd/^{157}Gd$ ($\varepsilon = +107$ to $+169$ for A-16, and $+31$ to $+84$ for A-17) corresponding to neutron fluences of $(5.68–9.03) \times 10^{16}$ n cm^{-2} for A-16 and $(1.85–5.04) \times 10^{16}$ n cm^{-2} for A-17. The depth profiles of neutron fluences suggest that the regoliths at both sites were due to incomplete mixing of three different slabs which experienced individual two-stage irradiation before and after deposition of the upper slabs. The variations in REE compositions provide chemical evidence for incompletely vertical mixing of regoliths especially at upper layers of the two sites. The thermal neutron energy index estimated from the combination of Sm and Gd isotopic shifts, defined as $\varepsilon_{Sm}/\varepsilon_{Gd}$, shows a small variation (0.61–0.64) in the A-16 core except for the surface layer. On the other hand, a large variation in $\varepsilon_{Sm}/\varepsilon_{Gd} = 0.67$ to 0.83 in the A-17 core may result from complicated history such as two-stage irradiation and incomplete mixing during the gardening processes. Isotopic enrichments of ^{152}Gd and ^{154}Gd correlated with Eu/Gd elemental abundances and neutron fluences were also observed in almost all of 15 samples, showing evidence of neutron-capture from ^{151}Eu and ^{153}Eu, respectively.

1. Introduction

Thermalized neutrons are produced by the interaction of cosmic rays with planetary materials. Isotopes having large neutron-capture cross-sections such as ^{113}Cd, ^{149}Sm, ^{155}Gd and ^{157}Gd in planetary materials sensitively react with the neutrons produced near the surface of planetary bodies. Therefore, isotopic shifts of $^{114}Cd/^{113}Cd$, $^{150}Sm/^{149}Sm$, $^{156}Gd/^{155}Gd$ and $^{158}Gd/^{157}Gd$ in extraterrestrial materials have been used to characterize the exposure histories of lunar samples (e.g., Eugster et al., 1970; Russ et al., 1972; Curtis and Wasserburg, 1975; Sands et al., 2001). Up to the present, we have measured the isotopic compositions of Sm and Gd in terrestrial samples (Hidaka et al., 1995; Hidaka and Gauthier-Lafaye, 2001), meteorites (Hidaka et al., 1999, 2000a, 2006) and lunar samples (Hidaka et al., 2000b). In particular, the isotopic data of lunar surface samples obtained by the Apollo missions provide important information to understand the mechanism of neutron production by interaction of planetary materials with cosmic rays, because the depths of the samples are well-known. Three long drilling cores of lunar regoliths were collected from the Apollo 15, 16 and 17 landing sites (hereafter A-15, A-16 and A-17, respectively).

Sm and Gd isotopic studies of A-15, A-16 and A-17 drill-cores were previously performed, and the collected data were used to discuss the gardening processes on the lunar surface (Russ et al., 1972; Russ, 1973; Curtis and Wasserburg, 1975). Among the many lunar samples, A-15 drill-core samples often have been used to study the interaction of cosmic rays with regolith materials as a function of depth (e.g., Nishiizumi et al., 1997), because the A-15 regolith has not experienced major impacts in the last 500 Ma. On the other hand, the depth profiles of A-16 and A-17 neutron fluences are quite different from that of

* Corresponding author. Fax: +81 824 24 0735.
E-mail address: hidaka@hiroshima-u.ac.jp (H. Hidaka).

0016-7037/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.gca.2006.10.015

A-15 (Russ, 1973; Curtis and Wasserburg, 1975). Some models were proposed to explain the neutron fluence profiles, such as incomplete mixing of two slabs and rapid sedimentation (Russ, 1973; Curtis and Wasserburg, 1975), but additional analytical data are required for detailed discussion.

More than three decades after the first analysis of the lunar samples, the Sm and Gd isotopic compositions in the lunar long drill-cores are worth repeating because of recent improvements in mass spectrometric instrumentation and chemistry procedures. Hidaka et al. (2000b) obtained new high-precision Sm and Gd isotopic compositions of A-15 samples and addressed (1) the detailed depth dependence of neutron energy spectra suggested from the combination of Sm and Gd isotopic shifts and (2) clearly resolved isotopic enrichments of both ^{152}Gd and ^{154}Gd due to neutron-capture for ^{151}Eu and ^{153}Eu, respectively. These results were already indicated in some extent in earlier studies (Russ et al., 1972), though new high-precision data significantly improved quality of the discussion. In this paper, we show the newly measured Sm and Gd isotopic data of A-16 and 17 drill-core samples, and construct the fine structure of neutron stratigraphy from the combination of our data with previously published data to improve the understanding of the depositional history of lunar regoliths at the A-16 and 17 sites.

2. Experimental

2.1. Samples

2.1.1. Apollo 16 core

The Apollo 16 drill-core is 224 cm long. The core is divided into seven sections from 60001 (bottom) to 60007 (upper). In this study, six samples were selected from each of the individual sections except 60005. 60005 is not assigned in the core, because a part of the core corresponding to the section 60005 located between 60 and 100 cm deep from the surface was originally missing. Although the A-16 core may not be suitable for the study of neutron stratigraphy, because it lacks a part of the core, it is nevertheless interesting to compare the isotopic data of the A-16 samples with those of A-15 and A-17 core samples. Isotopic analyses of Sm and Gd in the A-16 samples were initially performed by Russ (1973) for the study of interaction between cosmic rays and the lunar surface. It is known that the A-16 core shows the highest neutron fluences among lunar materials. Because the Gd and Sm data from 60002 and the Sm data of 60006 have not been reported in the previous works (Russ, 1973), in this study we completely measured a pair of Sm and Gd isotopic ratios from all sections of the core except 60005.

2.1.2. Apollo 17 core

Nine samples were selected from the 284 cm deep drill-core of the Apollo 17 landing site. The core is divided into nine sections from 70001 (bottom) to 70009 (upper). The upper 20 cm of the A-17 core corresponding to 70009 is well-mixed in the layer, which is known as a reworked zone. Curtis and Wasserburg (1975) already measured the isotopic abundances of Sm and Gd of the A-17 samples. Among the A-17 samples, Sm isotopic data from the 70002, 70004, 70005, 70007 and 70009 layers have not been studied yet. Here, we report the Sm and Gd isotopic data of the A-17 samples from all nine layers including the Sm data of 70002, 70004, 70005, 70007 and 70009 samples.

2.2. Chemical procedures

Prior to the isotopic work, a new method of chemical separation of lighter rare earth elements (LREE) including Sm and Gd was developed. For the isotopic analysis, effective separation of the target element from isobaric interferences is required. Cation exchange chromatography has been often used for mutual REE separation (Lugmair and Marti, 1971; Hidaka et al., 1988). However, the previous REE separation method using a cation exchange resin in ammonia form with α-hydroxy isobutyric acid (α-HIBA) as an eluent requires complicated processes for the conditioning of the resin and for the purification of α-HIBA (Hidaka et al., 1995).

In this study, the elution behavior of LREE was calibrated using a lanthanide-specific resin (LN resin) commercially manufactured by Eichrom Technologies Inc., and then the technique was applied for the mutual separation of Sm and Gd in the lunar samples. This resin comprises di-(2-ethylhexyl)-phosphoric acid (HDEHP) loaded on a polymeric substrate (Pin and Zalduegui, 1997).

Twenty to thirty micrograms of each sample was digested by HF-$HClO_4$. The sample was then taken to dryness and redissolved in 1 mL of 2 M HCl. The solution was divided into two portions: the main portion for Sm and Gd isotopic measurements and the rest for the determination of REE abundances. The sample solution was loaded onto a cation exchange resin column (Bio-Rad AG50WX8, 200–400 mesh, H^+ form, 50 mm length, 4.0 mm i.d.) and washed with 4.7 mL of 2 M HCl before REE were eluted with 3 mL of 6 M HCl. This REE fraction from the first column was evaporated until dry and redissolved in a drop of 0.1 M HCl. The solution was loaded onto a second column packed with LN resin (particle size of 100–150 μm, 100 mm length, 2.5 mm i.d.) to separate Nd, Sm and Gd using 0.25, 0.35 and 0.5 M HCl, respectively. The recovery rate of each element through this procedure is more than 90%. The total procedural blanks of Sm and Gd were less than 100 pg for each element. The elution behaviors of Nd, Sm, Eu and Gd are illustrated in Fig. 1. This method using LN resin is more convenient and simpler than the previous method using α-HIBA.

Another aliquot of the sample solution was used for the determination of REE abundances by inductively coupled plasma mass spectrometry (ICP-MS).