

Nuclear Instruments and Methods in Physics Research A 470 (2001) 422-425



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# Geochemistry of rare elements in different types of lunar rocks (based on µXFA-SR data)

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#### Abstract

Micro ( $\mu$ ) X-ray fluorescence (XRF) analysis using synchrotron radiation (SR) has been applied for the determination of rare element (Rb, Sr, Y, Zr, Nb, Ba, La, and Ce) distributions in a large collection of different lunar mare and highland rocks returned to the Earth by all successful missions of "Apollo" and "Luna". Consideration of all analytical data, obtained by  $\mu$ XFA-SR method shows that most of high aluminium (HA) and very high aluminium (VHA) basalts are results of partial melting of various basaltic magmas, which do not originate from the magmatic ocean. Fractionation trends of rare elements in different types of lunar rocks suggest that planetary processes (controlled by volatility of elements) took place at very early stages of the Moon planet formation. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 07.85.Qe; 92.70.G; 92.40.Ni; 91.35.Nm

Keywords: Synchrotron radiation; X-ray fluorescence analysis; Rare elements in lunar regolith; Geochemistry of lunar rocks; Lunar rocks

# 1. Introduction

One of the most important problems in the modern planetary geochemistry is connected with the origin of magmatic (mare and highland) lunar rocks. Trace element studies of highland rocks (making up the main part of the lunar crust, are very abundant and age more than  $4.0 \times 10^9$  years)

and mare basalts (usually younger and filling depressions on the surface of the Moon) contributed significantly to our understanding of the early stages of the Moon evolution and can provide information about some of the oldest accretion and igneous processes of the Moon. To resolve some problems in the petrogenesis of lunar rocks we continued our early studies (see Ref. [1] and the references therein) and investigated the distribution and fractionation of rare elements in a large collection of lunar fragments.

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## 2. Analytical techniques and samples

Samples for the present investigation were small fragments (from 0.x up to 2–3 mm in size) of lunar rocks returned from the Moon by all successful missions of "Apollo" and "Luna". More than 350 individual lunar fragments were selected for detailed geochemical studies. Each fragment (particle) was cleaned in alcohol and packed between two mylar films with a special acetate glue. Then this preparate was placed in the centre of the three-ring teflon supporter. Usually, the analytical set included 5–10 lunar fragments and 1–2 standards or reference samples.

The content of Rb, Sr, Y, Zr, Nb, Ba, La, and Ce in the selected fragments were determined by the micro-X-ray fluorescence analysis using synchrotron radiation (µXFA-SR) at the Element Analysis Stations at the VEPP-3 and VEPP-4 storage rings at Budker Institute of Nuclear Physics, Siberian Branch of Russian Academy of Science (Novosibirsk, Russia). For energies of 20-30 keV (typically used for determination of Rb, Sr, Y, Zr, and Nb) the monochromator was a flat crystal of pyrolitic graphite instrument with a 2500 mm<sup>2</sup> work area and a reflectivity coefficient of about 20%. For energies of 60-70 keV (measurement of the content of Ba, La, and Ce), an LiF-crystal was used for monochromatisation of continuum synchrotron radiation. The energy dispersive Si(Li) detector with a spectral resolution of 200 eV in the K<sub>a</sub>Mn-line was used for registration of fluorescent X-ray emission of Rb, Sr, Y, Zr, and Nd, and Ge(Li) detector with a spectral resolution of 170 eV in K<sub>a</sub>Mn-line, was used at relatively high energy (60-70 keV), when measurements of Ba, La, and Ce were performed. The semi-conductor detectors were mounted at  $90^{\circ}$  to the incident beam and at 8 cm from the sample. The count rate was 0.7-1.2 kHz. The exposure time per sample was usually 200 s (in special cases the exposure time was up to 500 s). Samples of BCR-1, W-1 and ST-1 were used as external and control standards.

The Rb, Sr, Y, Zr, Nb, Ba, La, and Ce contents were determined with precision of about  $\pm 10 \text{ rel}\%$  in the range of 100–200 ppm and more, about  $\pm 15 \text{ rel}\%$  for the content range of 50–100 ppm, and about  $\pm 20 \text{ rel}\%$  for contents < 50 ppm.

#### 3. Results and discussion

Most of the bi-elemental diagrams show that similar petrochemical rocks from different regions of the Moon can form compact or stretch fields (see Fig. 1). Since successive crystallization of olivine—(Mg, Fe)<sub>2</sub>SiO<sub>4</sub>, pyroxene—(Mg, Fe, Ca)-SiO<sub>3</sub>, and plagioclase—(Na, Ca)Al(Si, Al)<sub>3</sub>O<sub>8</sub> (main minerals in the lunar rocks) takes place usually in magmatic evolution process, some part of rare (non-coherent) elements (these elements can not be isomorphyc occurrencies in the crystal structure of rock-forming minerals) will

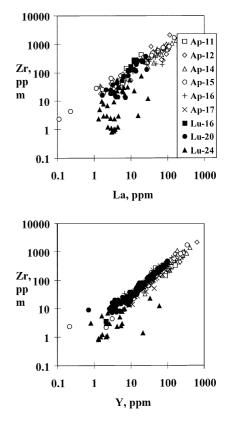


Fig. 1. Bi-elemental diagrams of Zr vs. La and Zr vs. Y for lunar rocks returned by the Apollo (Ap) and Luna (Lu) missions.

accumulate in residual melts. Therefore, as a first approximation, we may assume that an increase of the degree of enrichment of rocks with noncoherent elements should be a quantity criteria for the degree of magmatic differentiation of silicate melts. Bi-elemental diagrams for rocks of similar petrochemical types show clearly different degrees of geochemical differentiation of the parent magmas. The most differentiated lunar rocks are HA and VHA basalts from regolith of Apollo 12, 14, and 15.

The fractionation of chemical elements in the lunar regolith is a result of several planetary processes, which took place at different stages of the Moon evolution as a planet. For example, most of the investigated lunar fragments show that fractionation process(es) was(were) controlled by volatility of the elements: with relatively low fractionation degrees of extremely refractory (Zr, Y), moderately refractory (La, Ce), and moderately volatile (Ba, Nb) elements, a significant decrease in the content of other moderately volatile (Sr) and volatile (Rb) elements (Fig. 2) is observed. It is possible that the process which controlled the low content of moderately volatile and volatile elements in modern lunar rocks was related with "hot" Moon accretion. Our analytical data contradict the model of "cold" Moon accretion, which was suggested in the literature earlier. However, some lunar fragments show clear positive anomaly of Sr (Fig. 2) that cannot be explained by the model of "hot" accretion. The Sr anomaly is a result of the high content of feldspar component in some lunar fragments.

Thus, the patterns of the element fractionation in the lunar regolith were conditioned not only by selective evaporation events during "hot" accretion of the Moon but also by the following processes of magmatic differentiation, as well as by the crystallochemical similarity of ions of some rare elements and major cations in the structure of rock-forming minerals. Diagrams of CI-normalized concentrations of rare elements in single lunar fragments vs. degree of non-coherence of rare elements (Fig. 3) show similarity with the fractionation trends calculated for crystallization events in different models of lunar magmatic ocean (LMO). However, a detail analysis of the analy-

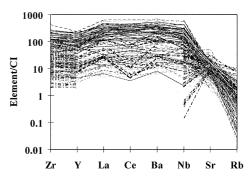


Fig. 2. Fractionation of rare elements in lunar rocks. The elements are in the order of their increasing volatility.

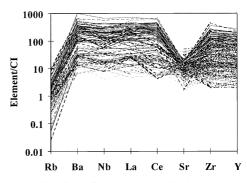


Fig. 3. Fractionation of rare elements in lunar rocks. The elements are in the order of the increasing degree on non-coherence.

tical and theoretical data shows the difference in Rb fractionation. It is possible that the loss of volatile Rb at "hot" Moon accretion was a more essential process than it was postulated in the LMO models.

## 4. Conclusions

Consideration of all analytical data obtained by the  $\mu$ XFA-SR methods shows that most of the HA and VHA basalts are the results of partial melting of various basaltic magmas but do not originate from the magmatic ocean. This conclusion as well as the conclusion about the possible proceeding of some very early planetary processes (controlled by volatility of the elements) influencing fractionation trends of rare elements in different lunar rocks are the most important results obtained by our  $\mu$ XFA-SR studies of small lunar fragments in the large collection of lunar regolith particles.

# Acknowledgements

We are grateful to A.N. Skrinsky and G.N. Kulipanov for their support and keen interest in this work. The support by the Program

"Universities of Russia—Fundamental Investigations" grant 5305 and RFBR grant 99-05-64831 are gratefully acknowledged.

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