

Lunar Monazites

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The monazite group minerals (LREE, Ca, Th)[PO₄] are the most important LREE-carriers in the rocks of the Earth. Monazite-(Ce) is considered the most abundant REE-bearing mineral [1]. The monazite group includes anhydrous monoclinic phosphates, arsenates, and silicates of LREE, Ca, and Th: monazite-(La), monazite-(Ce), monazite-(Nd), and monazite-(Sm) LREE[PO₄], cheralite-(Ce) (Ce, Ca, Th)[PO₄], gasparite-(Ce) Ce[AsO₄], brabantite CaTh[PO₄]₂, and huttonite Th[SiO₄]. Cheralite-(Ce) is the intermediate member in the brabantite–monazite-(Ce) series. The abundance of monazites sharply decreases from monazite-(Ce) to monazite-(Nd), monazite-(La), and monazite-(Sm).

Owing to the wide stability field (1200–300°C), chemical resistance, and mechanical strength, monazite occurs almost in all calc-alkaline and subalkaline magmatic and metamorphic rocks, as well as in different pegmatites, metasomatites, hydrothermal rocks, and many sedimentary rocks. Under high (ultraalpine) alkalinity, monazite becomes unstable and gives way to vitusite-(Ce) Na₃Ce[PO₄]₂. Since monazite is widespread, this mineral can be used as an indicator of formation conditions. Therefore, many researchers have studied the typomorphic features of monazites from different rocks and, primarily, REE and Th distribution [2–4]. Based on the available works, the average REE composition of monazite in the rocks is La₂₄Ce₄₆Pr₅Nd₁₉Sm_{3.9}Eu_{0.05}Gd_{1.9} at Y/REE = 0.1 [1]. As was shown in [3], the REE composition of monazite directly reflects that of the mineral-forming environment.

Experiments have shown that monoelement REE orthophosphates form crystals with monazite structure from La to Tb [2]. The TbPO₄ possesses dimorphism and crystallizes in monoclinic (monazite) and tetrago-

nal (xenotime) modifications. At the same time, Mineev showed that the natural REE mixture during mineral formation behaves as individual rare earth element with corresponding ionic radius [5]. To describe the behavior of REE mixture, the author developed “isotope” model and introduced the term “REE equivalent.” According to this model, the natural mixture Y₄₃La₆Ce₁₆Pr₂Nd₂₄Sm₉ has an average ionic radius of 1.172 Å, which corresponds to the Sm equivalent.

Thus, orthophosphates with significant amounts of HREE and Y can theoretically crystallize in monoclinic monazite structure, if equivalent radius is more than that of Tb. In nature, such monazites with complex REE composition can crystallize under high-temperature conditions. Therefore, they can be preserved in the absence of hydrothermal alteration, which is highly probable under lunar conditions. Otherwise, the low-temperature recrystallization of monazite with complex composition will produce a monazite–xenotime pair with selective REE composition.

Unlike the Earth, the Moon shows significantly less abundance of monazite relative to whitlockite and REE-bearing apatite, which are the main lunar REE-concentrators. Monazite was previously found on the Moon only as a tiny (10 × 3 μm) inclusion in hedenbergite from coarse-grained basalt in Mare Tranquillitatis (10047.68, Apollo 11), which is anomalously rich in apatite, whitlockite, tranquillityite, and zirconolite [6].

The lunar regolith was studied on an SEM JSM 5300 microscope (JEOL, Japan) equipped with EDS Link ISIS (Oxford Instruments, Britain) and on a low-vacuum SEM JSM 5610LV equipped with JED 2300 (JEOL, Japan).

A particle of REE phosphate ~1.5 μm in size (Fig. 1a) was found among K-feldspar particles in a regolith from Mare Crisium (A/S Luna 24). The EDS spectrum of this particle contains peaks of both REE mineral (P, Ca, REE, O) and feldspar (Si, Al, K, Na, O). The phosphate formula was based on quantitative analysis (table, particle 1) without considering the elements of the matrix, the composition of which was recorded near the

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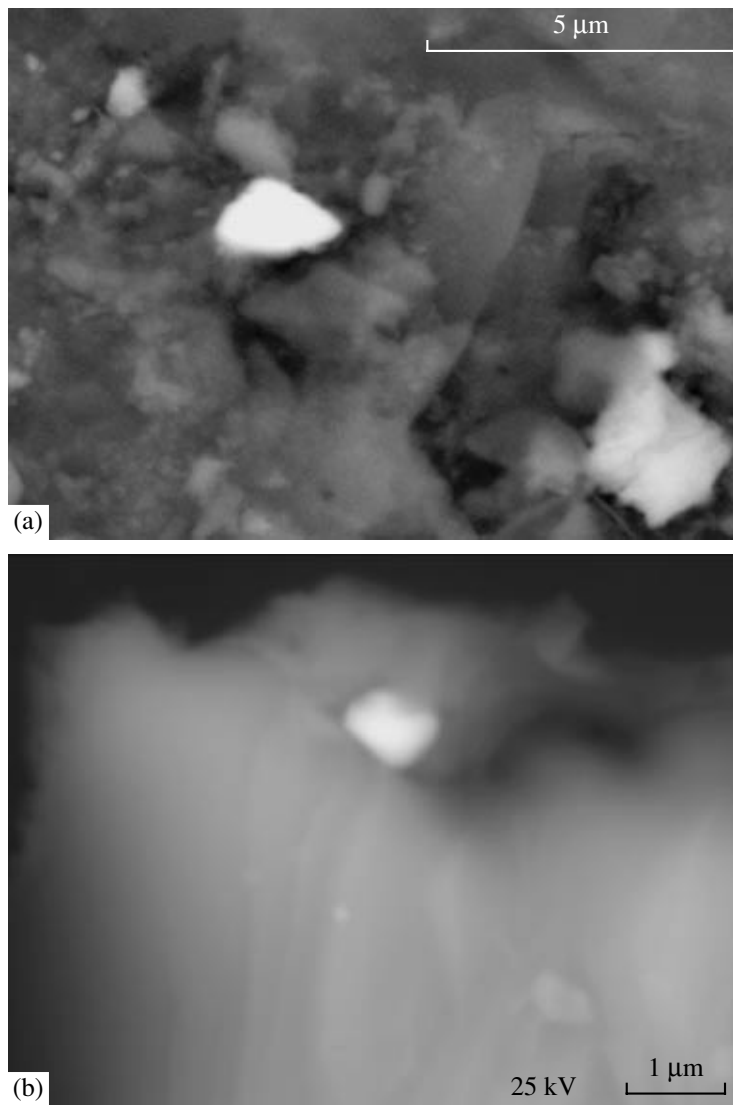


Fig. 1. Luna 16. BSE images of bright monazite particles among silicate particles.

phosphate inclusion. Obtained data showed that the phosphate belongs to the monazite group. The sharp Ce predominance indicates its affiliation to monazite-(Ce).

One more micrometer-sized Y-free and low-Th monazite particle was found in another sample from Mare Crisium (Fig. 1b; table, particle 2).

The BSE image shows the presence of a tiny bright particle (0.5 μm) on the native aluminum particle (10 μm) in the lunar regolith sample delivered by A/S Luna 20 (Fig. 2a). Its spectrum demonstrates characteristic peaks of REE, P, Al, and O. Omission of Al and normalization to 100% yields monazite-(Ce) compositionally close to monazite from Mare Crisium (table, particle 3). The same sample contains a larger (~3 μm) monazite particle lying separately on the tape (Fig. 2b). Therefore, only this particle was analyzed without normalization. Its composition (table, particle 4) can also

be ascribed to monazite-(Ce), despite the presence of Y and HREE and absence of Th.

There are no principle differences between the four monazite particles found in the regolith from the lunar highland and Mare Crisium. Like the monazite from Mare Tranquillitatis in the sample delivered by *Apollo 11*, they belong to monazite-(Ce) (table, particle 5).

As seen from formulas, actinides are incorporated in lunar monazite according to the isomorphous schemes long known for the Earth's monazites $2\text{REE}^{3+} = \text{Ca}^{2+} + (\text{Th},\text{U})^{4+}$ и $\text{P}^{5+} + \text{REE}^{3+} = \text{Si}^{4+} + \text{Th}^{4+}$. This corresponds to the incorporation of 4 and 7 mol % brabantite and 1 mol % huttonite in monazite (table; analyses 1, 3, and 2, respectively). Analysis 4 corresponds to ideal monazite. The formula of the monazite from the sample delivered by *Apollo 11* is strongly distorted, probably

Chemical composition of lunar monazite

Oxide	Particle				
	1	2	3	4	5
P ₂ O ₅	30.17	29.87	30.17	30.95	26.36
SiO ₂	–	0.18	–	–	1.30
ThO ₂	4.34	0.83	7.24	–	0.76
UO ₂	–	–	1.08	–	0.03
Y ₂ O ₃	–	–	–	8.61	1.11
La ₂ O ₃	14.14	21.78	13.04	10.72	16.51
Ce ₂ O ₃	33.67	36.70	28.77	25.67	30.08
Pr ₂ O ₃	2.19	1.56	3.04	1.92	4.30
Nd ₂ O ₃	12.77	9.08	13.06	12.24	14.91
Sm ₂ O ₃	1.79	–	1.83	3.27	4.09
Eu ₂ O ₃	–	–	–	2.03	0.36
Gd ₂ O ₃	–	–	–	2.79	1.55
Tb ₂ O ₃	–	–	–	–	0.13
Dy ₂ O ₃	–	–	–	1.36	0.33
Er ₂ O ₃	–	–	–	–	0.18
CaO	0.93	–	1.77	–	0.60
Total	100.00	100.00	100.00	99.56	102.57
ΣREE	64.55	69.12	59.74	68.61	73.55
Equivalent	1.223 Ce	1.223 Ce	1.223 Ce	1.199 Nd	1.217 Ce
Sample	Luna 16	Luna 24	Luna 20	Luna 20	Apollo 11

Note: Formulas were calculated on the basis of one cation (REE + Ca + Th + U):

- (1) ((Ce_{0.48}La_{0.21}Nd_{0.18}Pr_{0.03}Sm_{0.02})_{0.92}Ca_{0.04}Th_{0.04})_{1.00}[PO₄],
 - (2) ((Ce_{0.53}La_{0.31}Nd_{0.13}Pr_{0.02})_{0.99}Th_{0.01})_{1.00}[(P_{0.99}Si_{0.01})_{1.00}O₄],
 - (3) ((Ce_{0.41}La_{0.19}Nd_{0.18}Pr_{0.04}Sm_{0.03})_{0.85}Ca_{0.07}Th_{0.06}U_{0.01})_{1.00}[PO₄],
 - (4) (Ce_{0.41}La_{0.19}Nd_{0.18}Pr_{0.04}Sm_{0.03})_{0.85}Ca_{0.07}Th_{0.06}U_{0.01})_{1.00}[PO₄],
 - (5) ((Ce_{0.40}La_{0.22}Nd_{0.19}Pr_{0.06}Sm_{0.05}Y_{0.02}Gd_{0.02}REE_{0.01})_{0.97}Ca_{0.02}Th_{0.01})_{1.00}[(P_{0.81}Si_{0.05})_{0.86}O_{3.61}].
- (–) Below detection limit; the detection limit for particles (1–4): Si 0.10–0.15%, REE and Y 0.6–0.8%, and U 0.8–1%.

owing to analytical underestimation of P content because of the poor analytical facilities of the early 1970s.

The proportions of individual REE and Th in two monazite grains from the highland regolith made it possible to estimate their relative timing. Th abundance in the monazite grain (table, particle 3) unambiguously indicates its magmatic origin, i.e., crystallization from residual basaltic melt enriched in incompatible REE and Th. Its position on the native aluminum particle testifies to transportation by a volcanic gas jet from the deeper fumarole zones. The study of terrestrial volcan-

ism indicates that REEs were transferred in fumaroles mainly as dustlike particles of REE minerals rather than in gas phase [8]. Another monazite grain (table, particle 4) from the same regolith sample lacks Th, but it is notably enriched in Y and MREE (especially Eu). The absence of Th may serve as indirect evidence for formation of the given monazite from aqueous solution. The Y and MRRE enrichment indicates its later formation relative to the first grain. Thus, the second grain could form during metasomatic alteration (possibly, with participation of aqueous solutions) of primary basalts and the subse-

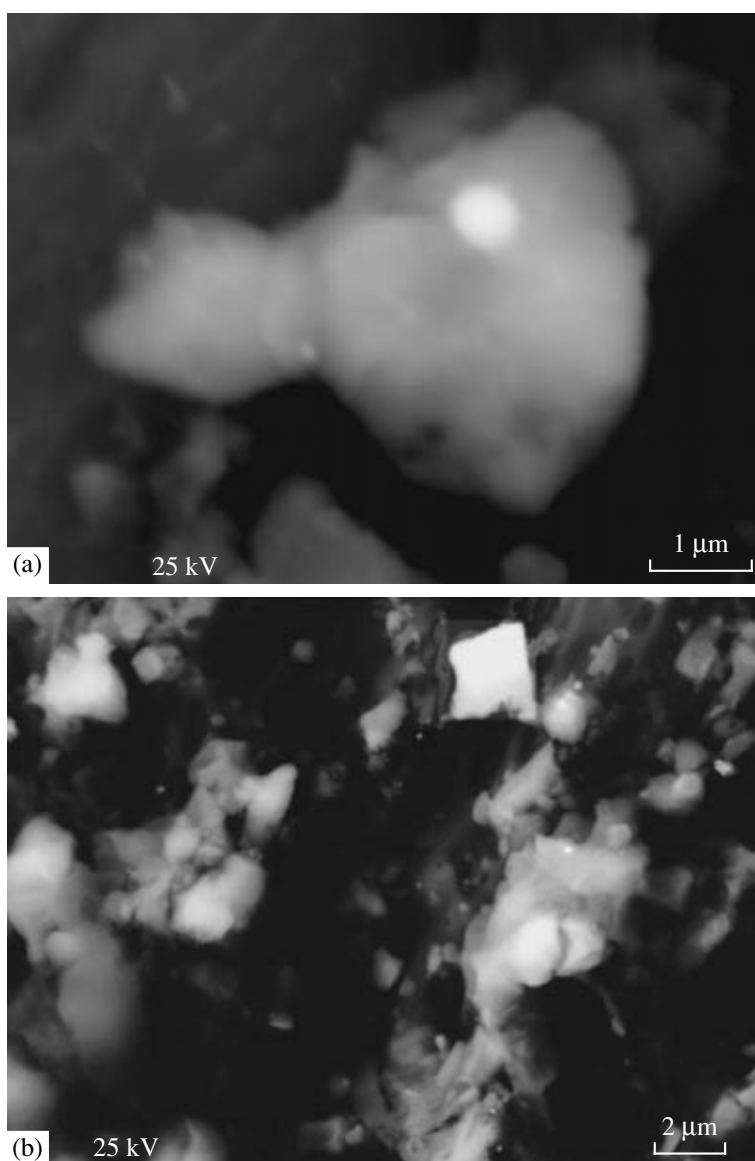


Fig. 2. Luna 20. BSE image of (a) bright monazite particle on native aluminum and (b) separate monazite particle on the tape (bright particle in the upper part of the image).

quent partial recrystallization of plagioclases and release of Eu. Recrystallization or decomposition of tranquillityite could additionally supply Y and MREEs. However, the given monazite could form at fairly high temperature and avoid simultaneous crystallization with xenotime phase (Y,HREE)[PO₄].

The moderate-Th monazite from mare regolith (grains 1 and 2) is presumably postmagmatic mineral. Grain 1 with more primitive REE spectrum and higher Th content presumably crystallized earlier than grain 2 enriched in La and depleted in Th and Pr.

Chondrite-normalized REE spectra of lunar monazites are shown in Fig. 3. The lunar monazite has a steep HREE pattern typical of this mineral. All spectra of the

studied grains have a relatively distinct Pr minimum, unlike the sample with Pr maximum from Mare Tranquillitatis. We can distinguish two groups of spectra with more or less selective REE compositions (group 1, grains 1–3; group 2, grains 4 and 5). Two latter spectra differ in the sign of Eu anomaly. The monazite from Mare Tranquillitatis has a deep Eu minimum, reflecting crystallization from the late basaltic portions, when most Eu was incorporated in plagioclase. The monazite from highland regolith differs in an unusually high Eu maximum. This, presumably, suggests that it formed owing to hydrothermal alteration of Eu-rich plagioclase rocks and dissolution of the primary REE minerals (REE-bearing apatite, whitlockite, and tranquillityite). Similar spectra and a similar formation mechanism

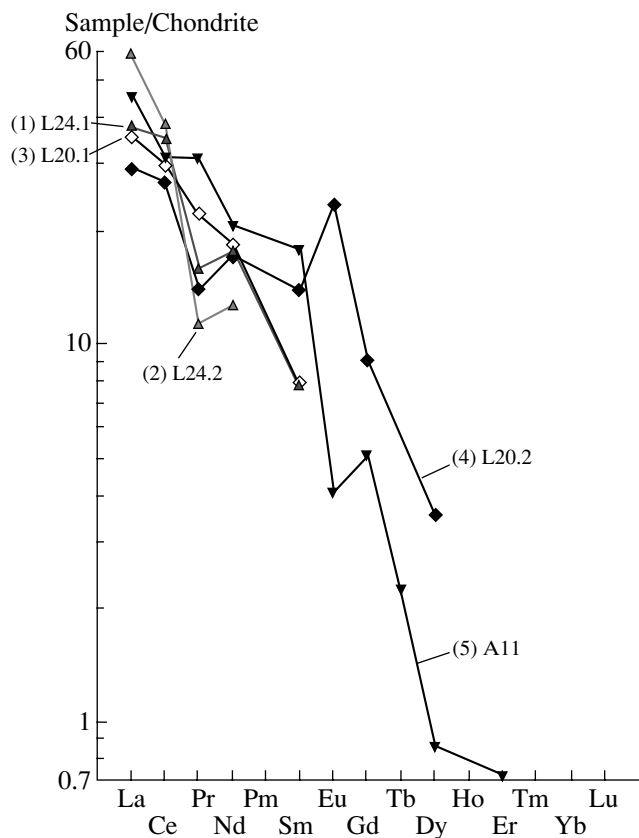


Fig. 3. Chondrite-normalized REE distribution patterns in lunar monazites.

have been previously described for REE-bearing epidote with a strong Eu maximum [7].

Hence, the studied monazites are the late crystallization products of lunar basalts. It should be noted that monazite was found in samples of both highland and mare soils.

CONCLUSIONS

The discovery of Eu-rich monazite on the Moon presumably indicates that lunar rocks experienced metasomatic alteration by aqueous solutions prior to regolith formation. This information expands our concepts on the lunar fluid regime, which was traditionally considered “dry,” on the one hand, and confirms the importance of monazite as indicator of different settings of the mineral formation, on the other hand.

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