Genesis of Positive Eu Anomalies in Acid Rocks from the Eastern Baltic Shield

E. N. Terekhov and T. F. Shcherbakova

Institute of the Lithosphere of Marginal and Epicontinental Seas, Russian Academy of Sciences, Staromonetnyi per. 22, Moscow, 109180 Russia

> *e-mail: tereh@ilran.ru* Received May 17, 2005

Abstract—The eastern part of the Baltic Shield contains an abundance of acid rocks with positive Eu anomalies. These rocks are vein granites and blastomylonites of similar chemical composition but with variable K₂O concentrations. The rocks are depleted in Ti, Fe, Mg, Ca, Rb, Zr, and REE, but are enriched in Ba and Sr, a fact suggesting a deep-seated nature of the fluids that participated in the genesis of these rocks. A zone favorable for the derivation of these rocks was transitional from brittle to ductile deformations. The rocks were produced during the tectonic exhumation of lower and middle crustal material a horizontal extension. Shock decompression facilitated the inflow of reduced fluids, which, in turn, ensured the partial melting of the host rocks along open fractures and controlled REE fractionation with the development of Eu maxima.

DOI: 10.1134/S0016702906050028

INTRODUCTION

Long-term studies of high-grade metamorphic rocks in the eastern part of the Baltic Shield resulted in the finding of their abundant acid varieties with positive Eu anomalies. Rocks exposed at the Earth's surface most commonly have negative Eu anomalies (if any) [1], and thus, studying rocks with positive anomalies is of significant interest and may hopefully provide insight into the behavior of Eu in the Earth's crust. Most of our samples were collected at the Lapland–Belomorian Belt (LBB) and the closest surroundings (Fig. 1), although analogous or fairly similar rocks with positive Eu anomalies were also found elsewhere at the Baltic Shield [2, 3].

The Eu anomaly is calculated by dividing the chondrite-normalized Eu concentration of a rock by the halfsum of the normalized concentrations of Sm and Gd (the two neighboring elements) and is denoted Eu/Eu*. The deepest negative Eu anomalies, which likely determine the composition of the upper crust, occur in granites and metasomatic rocks, whose Eu/Eu* are sometimes less than 0.01 [4], i.e., their Eu concentrations are 100 or more times lower than they can be expected judging from the concentrations of other REE. No volcanic rocks of mantle provenance show Eu depletion $(i.e., Eu/Eu^* = 0.65)$ typical of the average composition of the upper crust [1], and MORB, within-plate volcanics, and volcanic rocks of island arcs equally rarely display positive and negative Eu anomalies. This puts forth the question as to where is Eu concentrated. The wide occurrence of post-Archean rocks with negative Eu anomalies and, as a consequence, the typical REE patterns of post-Archean sediments (the PAAS line reflects the average composition of the eroded rocks) provides indirect evidence of the occurrence of deepseated (lower and middle crustal) rocks with complementary REE patters, i.e., with positive Eu anomalies. However, most rocks of granulite complexes that are now exposed at the surface (and could previously be located in the lower crust) only occasionally have positive Eu anomalies. Persistently present positive Eu anomalies are typical only of anorthosites, which account only for insignificant volumes in granulite complexes. Anorthosites commonly consist of cumulus plagioclase. Plagioclase, a mineral thought to be responsible for the development of Eu anomalies [1], is known to be unstable at depths of >40 km, and, hence, Eu anomalies should be related to some crustal processes. It is worth noting that rocks with positive Eu anomalies are quite often found in Precambrian complexes and become progressively rarer in younger complexes, whereas the amount of rocks with negative Eu anomalies increases. Hence, one of the mechanisms responsible for Eu enrichment can be its temporary accumulation at a certain structural–geochemical boundary of the Earth's crust. Similar to the apparent horizon, some boundaries in the Earth's crust seem to always occur at a distance. For example, the boundary between ductile and brittle deformations always occurs at approximately the same depth (10–15 km from the surface), regardless of the processes that can take place.

ANALYTICAL TECHNIQUES

All of our rock samples were analyzed for La, Ce, Nd, Sm, Eu, Gd, Er, and Yb by plasma spectroscopy on

Fig. 1. Schematic geological map of the Lapland–Belomorian Belt and surrounding structures with our sampling sites of acid rocks with positive Eu anomalies. (*1*) Alkaline intrusions: (*a*) Paleozoic, (*b*) Late Paleoproterozoic; (*2*) Paleoproterozoic granitoids: (*a*) postkinematic (1.8–1.7 Ga), (*b*) synkinematic (1.85–1.8 Ga), (*c*) prekinematic (2.6–2.4 Ga); (*3*) Sumian intrusive magmatic rocks (2.5–2.45 Ga) layered intrusions, coronites (drusites), and gabbro-anorthosites of the Lapland–Belomorian Belt); (*4*) volcanosedimentary rocks of the Karelian Formation (2.6–1.8 Ga): (*a*) Ludicovian, Jatulian, (*b*) Sumian, Sariolian; (*5*) Late Archean (*a*) greenstone belts and (*b*) kyanite-bearing rocks of the Belomorian Belt; (*6)* Archean granite-gneisses of tonalite–trondhjemite– granodiorite composition; (*7*) Late Archean–Paleoproterozoic (*a*) migmatites and (*b*) garnet amphibolites; (*8*) granulites: (*a*) Late Archean and (*b*) Paleoproterozoic; (*9*) major faults and the Lapland–Belomorian detachment (heavy line), a normal fault that controlled the exhumation of the lower and middle crustal rocks to the surface; (*10*) sampling sites of acid rocks with positive Eu anomalies (sample numbers correspond to those in (*a*) Tables 1, 2 and (*b*) in [2]). KM—Karelian Massif, BB—Belomorian Belt, LB— Lapland Belt, CKB—Central Kola Block, MB—Murmansk Block, PS—Pechenga Structure, I-V—Imandra–Varzuga Structure.

a Monospec 1000 analyzer [5] at the Institute of the Lithosphere of Marginal and Epicontinental Seas, Russian Academy of Sciences. Ni, Rb, Ba, Sr, Zr, and Y were determined on a TEFa device at the same institute. Conventional silicate analyses were conducted at the Vinogradov Institute of Geochemistry, Siberian Division, Russian Academy of Sciences. The quality of the analyses was checked by using internationally certified standards and by comparing the results obtained by different techniques for the same samples.

BRIEF GEOLOGICAL–PETROGRAPHIC OVERVIEW

According to their morphological characteristics, acid rocks with positive Eu anomalies from the eastern Baltic Shield (Fig. 1) are classed into two groups (Fig. 2). One of them occurs as relatively thin veins of granites and orthotectites, which usually cut across the host rocks or, more rarely, are conformable with them. The other group comprises linearized rocks (blastomylonites).

The *granites* occur as veinlets a few centimeters thick and as veins up to 1–50 cm or, occasionally, up to 1.5 m. The granites sometimes occur as orthotectites that compose irregularly shaped patches or lenses 20– 30 cm across. More rarely, orthotectite lenses are arranged along two perpendicular directions. Both the granites and the orthotectites are very leucocratic rocks and contain no more than 2–5% biotite. A distinctive feature of the orthotectites is their texture, which varies from coarse-grained to pegmatoid. Another of their noteworthy features is biotite rims along boundaries between the orthotectites and the host rocks, a feature that reportedly [6] testifies that the rocks were formed by melting in situ. When the granites with positive Eu anomalies occur among complicatedly folded gray gneisses or dome structures of charnockites and enderbites, they occur as randomly oriented veins (Figs. 2d, 2f). In the monoclinal sequences of the Lapland and Belomorian complexes, the granites most commonly develop as veins with strikes parallel to those of the host structures but with opposite dips (Figs. 2a–2c, 2e). The granites usually compose of cutting veins, some of which filled the fractures of brittle deformations. Some minerals of the host rocks, for example, hypersthene, bluish quartz, kyanite, and hornblende can be contained in the granite veins (although in smaller amounts and recrystallized). We are not aware of any data on the radiological ages of these granites, and their host rocks were dated at 3.1 (gray gneisses and amphibolites) to 1.75 Ga (subalkaline granites) [2]. In the southeastern part of the Lapland granulite belt (in the Por'ya Bay area), the granites are intruded by 1.72-Ga lamproites [7]. Geological evidence indicates that the latter rocks were emplaced into material within a zone of brittle deformations and inherit the structural style from the granite veins.

The *vein rocks* that looked like granites in the exposures turned out to comprise of more than one petrographic variety (as can be seen in thin sections). These are biotite nebular plagioclase migmatites, leucocratic granites, orthotectites, and muscovite–quartz rocks. The rocks have granoblastic and, in places, hypidiomorphic-granular textures, and many of them exhibit traces of deformations, which are variably pronounced in individual veins (samples 24/1, 9405/2, N41/2, and N033/3). Due to this, the textures of the rocks are cataclastic: along with grains 1–2 mm, which are most typical of these rocks, as they also contain smaller (0.1– 0.2 mm) grains, which have uneven, ragged outlines and occur between larger grains. Large plagioclase grains are flattened and have a patchy extinction, and biotite plates have stringy habits. All of the rock varieties have analogous compositions: they consists of plagioclase, quartz, microcline, biotite, and occasional muscovite and secondary aggregates of epidote-zoisite. The proportions of leucocratic minerals vary, particularly the amounts of microcline, which can be contained in the rocks in the form of antiperthitic inclusions, anhedral interstitial grains, or large porphyroblasts. Some samples (sample 24/1) contain single anhedral large $(12 \times 7 \text{ mm})$ microcline prisms. In this rock, a large microcline grain contains small anhedral domains of brown older plagioclase and myrmekites with small vermicular quartz grains that display simultaneous extinction. The groundmass of this rock contains no microcline. Quartz is also unevenly distributed in the rock: the mineral can be contained in the form of small equant or randomly and irregularly shaped grains in the interstitial space or lens-shaped aggregates up to 3–7-mm long. The quartz shows no traces of deformations and was likely recrystallized after the cataclasis and mylonitization of the rock. Its amount varies from 30% (of the total rock volume) in sample 24/1 to 50% in the samples 94103/4 and 9405/2. The strongly silic-

Fig. 2. Schematic vertical sections showing the structural settings of acid rocks with positive Eu anomalies: (a)–(f) vein granites, (g, h) blastomylonite zones in various complexes in the eastern part of the Baltic Shield. Sketches correspond to (a) the central, (b) upper rear, and (c) lower rear parts of the Lapland Belt; Belomorian Belt (d) western part (area with overprinted granulite mineral assemblages) and (e) central (amphibolite–migmatite) parts and (f) the pre-Karelian basement. The structural situations (g) and (h) can occur in any of the compositions in the eastern Baltic Shield metamorphosed to the granulite and amphibolite metamorphic facies.

ified rocks contain minor amounts of muscovite in the form of thin elongated (2–3 mm) laths. These granites seem to be related to acid leaching zones and compose their axial parts. In some instances, the granites affected by acid leaching are completely devoid of their original features and transformed into muscovite– quartz rocks (sample 9435/1) or preserve their original features in relict grains, as in sample 767/21, which is a muscovite–quartz rock with patches of old plagioclase and skeletal kyanite prisms. The latter indicate that the pristine rock was kyanite–garnet–biotite gneiss affected by leaching. The mafic mineral of the vein rocks is dark olive biotite, whose contents vary from single platelets to 2–5%. In places, the biotite is replaced by zoisite or earthy aggregates of epidote.

It should be emphasized that the vein rocks sometimes bear relics of hornblende–biotite (sample 24/1) or biotite (sample N033/30) plagioclase migmatites, containing 15–20% biotite. Relics of these pristine rocks are also distinguishable by the occurrence of older plagioclase, which is completely saussuritized. The rocks often display traces of cataclasis, partial mylonitization, and blastesis, which suggest brittle deformations in the vein rocks during their final evolutionary stages. The data presented above and the fairly uneven distri-

bution of microcline in the vein rocks indicate that they were formed in situ.

The geological nature of the vein granites with positive Eu anomalies is uncertain and was interpreted variably. To some extent, this is explained by the fact that these rocks often occur among gray gneisses, whose genesis is also disputable. Most foreign researchers believe that gray gneisses were produced via magmatic crystallization, and veins of granites with positive Eu anomalies are the final products of this process [8]. Most Soviet and Russian geologists consider gray gneisses to be the products of metasomatic alterations in mafic rocks, and the granites with positive Eu anomalies are thought to correspond to the final stage of granitization: the microcline stage of this process [9]. The results of our research indicate that granites with positive Eu anomalies are present not only among gray gneisses, but also among granulites, anorthosites, massive and gneissose charnockites and enderbites, subalkaline granites, quartz monzonites, and kyanite-bearing rocks, and hence, studying these rocks may shed light onto global events in the evolution of the Earth's crust.

The *blastomylonites* compose tectonic zones ranging from a few to a few hundred meters in thickness. These are pale, small-grained finely scaled rocks, often

Fig. 3. Al₂O₃/(Na₂O + K₂O) vs. Al₂O₃/(CaO + Na₂O + K_2O) diagram for (I) potassic granite, (2) sodic granite, and (*3*) blastomylonite. Compositional fields of granites from various geodynamic environments (after [11]): CAG—continental arc granites, CCG—continental collisional granites, RRG—rift-related granites, POG—postorogenic granites, CEUG—continental epeirogenic granites.

Fig. 4. (Na₂O + K₂O) vs. SiO₂ diagram. ($1-4$) Acid rocks with positive Eu anomalies: (*1, 2*) vein granite: (*1*) potassic, (*2*) sodic; (*3*, *4*) blastomylonite: (*3*) potassic, (*4*) sodic; (*5*) host rocks. (I) Tonalite; (II) plagiogranite, (III) granite, (IV) leucogranite; (V) subalkaline granite, (VI) subalkaline leucogranite. Compositional fields of granitoid series: Al alkaline, Ca—calc–alkaline, Th*—*tholeiitic (after [12]).

444

TEREKHOV, SHCHERBAKOVA

Table 1. (Contd.)

Table 1. (Contd.)

446

Table 1. (Contd.)

Table 1. (Contd.)

mafic granulite, 19—migmatite-charnockite; 20—granite; 21, 22—15 km north of the settlement of Umba; 21—migmatite, 22—granite); (23–32) northern Norway (23–26— Kirkenes area: 23—plagioclase migmatite, 24—granite, 25—migmatite, 26—granite; (27, 28) Jarfiord mouth: 27—plagioclase migmatite with cordierite, 28—granite; 29–32— Karasjok area: 29, 30—20 km south of it: 29—subalkaline granite, 30—vein granite, 31, 32—35 km west of the town of Karasjok, Archean Jargul basement complex: 31—gray

gneiss, 32—vein granite. Dashes mean not analyzed; n.f. means not found due to low concentrations. Printed in italics are vein granites, normal face—host rocks.

GEOCHEMISTRY INTERNATIONAL Vol. 44 No. 5 2006

Belomorian Belt, Notozero Lake area, (7–9) blastomylonites with lenticular quartz developing after gray gneisses; (10) intrusive enderbite and (11) blastomylonite developing after it; (12) acid gneissose granulite, Belozerskaya Bay, Kolvitsa structure; (13) anatectic acid granulite, 10 km southeast of the settlement of Inari, northern Finland. Printed in italics

are blastomylonites and other rocks in fluid-reworking zones, normal face—host rocks.

Fig. 5. (a) CaO vs. Sr and (b) K_2O vs. Ba diagrams for acid rocks with positive Eu anomalies from the eastern part of the Baltic Shield.

with augen textures and variable amounts and sizes of the augen. The schistosity of these rocks is accentuated by the orientation of biotite flakes, with quartz lenses elongated conformably with this orientation. The blastomylonites most commonly contain augen of feldspars (which sometimes account for 25% of the rock by volume) and, more rarely, garnet. The schistosity planes of the blastomylonites often bear slickensides, which testify to their development at brittle deformations during the final stages of the process.

The microtexture of the rocks is blastomylonitic and is accentuated by small (0.3–0.5 mm) biotite flakes, some of which are recrystallized and reach 1.5 mm in length. The texture is characterized by a fine-grained (<1 mm) groundmass with larger plagioclase relics, which were preserved during shattering and mylonitization. These relics are usually rounded or ellipsoidal and have patchy extinction. These can be porphyroclasts ("augen") and porphyroblasts. The latter are usually large (up to 3–5 mm) grains of quartz and feldspar. The blastomylonites sometimes contain chains of small $(0.1 mm) plagioclase grains, which develop as com$ plete or incomplete rims around larger grains. Some porphyroblasts are surrounded by biotite flakes. Sample 9431/1 is a typical blastomylonite with a characteristic schistose–banded structure. The schistosity is accentuated by systematically oriented biotite laths and flakes, and the banding is defined by thin (0.2–0.4 mm) equally spaced laminae of recrystallized quartz elongated conformably with the schistosity, which impart a look of thin lamination to the rocks.

The blastomylonites consist of plagioclase, quartz, microcline, and biotite. The secondary minerals are epidote, epidote–zoisite aggregates, and earthy epidote– saussurite masses. Accessory minerals are generally atypical. The quantitative proportions of major minerals vary (with greater or lesser amounts of plagioclase and microcline). The contents of biotite range from 3–5 to 15%. Some mylonite varieties are more recrystallized, so that the mineral grains in them reach 1–2 mm, and traces of mylonitization can be identified by the presence of single flattened plagioclase crystals or aggregates of small $(0.1 mm) plaqio \text{class}$ grains with ragged outlines between larger grains of other minerals (samples 9422/2 and 9435/1). The mineralogy of the blastomylonites corresponds to that of biotite plagio migmatites, their nebular varieties, and granites. Some 15–20 years ago, most mylonites were considered to be components of stratified Early Precambrian complexes. Now their affiliation with tectonic zones is beyond doubt, although some researchers still continue to class these rocks with banded metasediments [10].

PETRO- AND GEOCHEMISTRY OF ACID ROCKS WITH A POSITIVE Eu ANOMALY

Regardless of their affiliation with certain tectono– stratigraphic complexes, all of the rocks with positive Eu anomalies are rich in $SiO₂$ (70–76%), and most of them are highly aluminous (Fig. 3). The highest silica contents were detected in rocks affected by acid leaching. These varieties are strongly depleted in $K_2O(0.35-$ 0.58 wt $\%$) and are relatively rich in CaO (3–4 wt $\%$). Note that most of the rocks bear as little as $1-1.5$ wt % CaO. Most of these rocks are rich in K_2O , whose contents occasionally reach anomalously high values (7– 10 wt $\%$), a fact definitely suggesting the metasomatic introduction of this element (Tables 1, 2). Another notable feature of these rocks is their depletion in such elements as Ti, Fe, Mn, Mg, and P, which makes the rocks leucocratic. According to their proportions of the sum of alkalis to silica, most of them can be classed with subalkaline granites, with a few samples corresponding to leucogranites and subalkaline leucogranites (Fig. 4). Figure 4 also shows the compositional fields of rock series, and it can be seen that the data points of the vein granites plot within the fields of the tholeiitic and alkaline series. At the same time, the host rocks and blastomylonites (which usually inherit compositions from the host rocks) affiliate with the calc–alkaline series.

A notable feature in the distribution of trace elements is the depletion of the rocks in *rubidium*, whose concentrations are 1.5–3.5 (and occasionally even 7– 14 times) times lower than the average rubidium concentration in lithospheric granite [13]. It should be mentioned that some of the rocks have Rb concentrations approaching the clarkes for granites (184 as com-

Fig. 6. Chondrite-normalized REE patterns for vein granites and their host rocks from various areas in the eastern Baltic Shield. Sample numbers correspond to those in Tables 1 and 2.

pared with 210 ppm) or even slightly exceeding them (237 ppm), but these petrographic varieties are rare. Although we did not identify any clearly pronounced tendencies in the distribution of Rb and K in the rocks, the highest Rb concentrations were found in their varieties with anomalously high concentrations of $K_2O(8-$ 9 wt %). The general poorness of rocks in Rb is explained by their insignificant contents of biotite, since Rb contained in acid rocks is known [14] to be preferably concentrated in micas compared to other K-bearing minerals. It was demonstrated previously that the Rb concentration in biotite from granites and plagioclase granites from the White Sea area (Belomorie) is 370–510 ppm [15].

Zirconium. Similar to Rb, these rocks are depleted in Zr, whose contents are two–five times lower than granite clarke. When granitization of mafic rocks was studied, it was determined that Zr is correlated with Ti [15]. Conceivably, the low contents of $TiO₂$ in the granites (mostly 0.03–0.13 wt %) and the absence of accessory zircon cause low Zr concentrations.

GEOCHEMISTRY INTERNATIONAL Vol. 44 No. 5 2006

Barium and strontium. The distribution of Ba is known to be controlled by the ability of this element to enrich K-bearing minerals. All of our rocks (except only their occasional varieties) contain very little biotite, and their potassic feldspar is the only mineral able to concentrate Ba. The potassic feldspar of the Belomorian biotite granites contains 744 ppm Ba [15], whereas the concentration of this element in our rocks is often much higher. The Ba concentrations in the vein rocks vary from 120 to 6600 ppm (Table 1), and the contents of this element in the blastomylonites are notably lower (89–1600 ppm (Table 2)). As can be seen from the tables, all samples, including those of rocks with low K_2O concentrations, are much higher in Ba than the average crustal granite (830 ppm). There seems to be a direct correlation between the concentrations of Ba and K_2O in our rocks, although this correlation is not very strong (Fig. 5). All rocks with no more than 1 wt $\%$ K₂O are the poorest in Ba, but the varieties with approximately 7% K₂O have Ba concentrations as high as 1600, 2600, and 6600 ppm.

Fig. 7. Chondrite-normalized REE patterns for vein granites and their host rocks from (a–e) various areas at the Baltic Shield and (f–i) blastomylonites of acid composition.

All of the granitoids contain up to 1.5–6 Sp clarkes typical of lithospheric granites (except only occasional samples, whose Sp contents are close to the clarkes: 90–150 ppm and 110 ppm, respectively) (Table 1). Sr is commonly isomorphous with Ca in various Ca-bearing

Fig. 8. Magnitude of Eu anomalies (Eu/Eu*) as a function of REE fractionation (La/Yb)*n*.

minerals of magmatic rocks, mostly in plagioclase [16]. As can be seen from Fig. 5, the increase in the Sr concentrations in our rocks is not correlated with the increase in their Ca contents. Similar to Ba, the accumulation of Sr in the feldspars of magmatic rocks is directly correlated with their crystallization temperature [17]. Hence, the Ba and, particularly, Sr concentrations of the rocks are not correlated with the concentrations of major "host" elements (K and Ca), and the enrichment of the former was likely controlled by some other phenomena. One of the reasons for the significant enrichment of these elements in the granites and blastomylanites could be their anomalously high temperatures, which is also corroborated by experimental data [16].

Rare earth elements. The rocks in question are characterized by very low concentrations of REE (Figs. 6, 7). Practically all the samples (except only two) bear 2– 30 times less La, Ce, Nd, and Sm than crustal granites. The granitoids are depleted even more in HREE, whose concentrations in some samples are close to chondritic.

The depletion of the granites in REE is particularly conspicuous in comparison with the host acid rocks (Figs. 6, 7). At the same time, the granites often have very high (La/Yb) _n ratios (>130). There is no clear correlation between the magnitudes of the positive Eu anomalies and the (La/Yb)*n* ratios (Fig. 8). The low HREE concentrations are related to the leucocratic character of the rocks, which contain relatively few mafic minerals (2–5%), mostly biotite. The rocks typically bear no accessory minerals (some of which are known to be enriched in REE). The aforementioned configurations of REE patterns and positive anomalies are characteristic of plagiogranite and granites of mostly metamorphic or anatectic genesis [18], although our rocks span a broader petrographic spectrum: they are not only plagiogranites and granites but also plagiomigmatites and migmatites, their nebular varieties, plagioclasites, blastomylonites of granitic composition, and muscovite– quartz rocks from acid leaching zones. All of them have positive Eu anomalies. As can be seen from Tables 1 and 2 and from Figs. 8–10, the height of the Eu anomaly in the rocks is independent of their chemical composition.

All REE are trivalent, but $Eu³⁺$ is transferred into $Eu²⁺$ in reducing environments. Because of this, melting in the presence of reduced fluids (hydrogen or hydrocarbons) is favorable for the preferential generations of Eu²⁺. Sites available for Eu²⁺ are unavailable for Eu3+. For example, feldspars more easily accommodate Eu²⁺, whose ionic radius is closer to that of Sr^{2+} , and Eu^{2+} can substitute Ba^{2+} in Ba-bearing minerals [20]. The ionic radius of Eu^{2+} is larger than that of Eu^{3+} [19], and, thus, the reduction of Eu^{3+} to Eu^{2+} is facilitated, in addition to the presence of a reduced fluid, also by extensional environments.

Several researchers (for example, A.A. Beus) addressed themselves to the experimental data [16] and pointed out the preferable accommodation of Eu^{2+} (compared to Eu^{3+}) in the feldspar structure. This implies that the origin of granites with positive Eu anomalies is associated with a shift of the $Eu^{2+} – Eu^{3+}$ equilibrium toward Eu^{2+} . According to this scheme, the magnitude of the Eu anomaly should be directly proportional to the Ca and Sr concentrations, but this is not the case with our rocks (Figs. 9, 10). The absence of correlations between high positive Eu anomalies and the Sr concentrations was also mentioned by other researchers [21]. The highest Eu anomalies are typical of granites enriched in Ba, i.e., an element whose enrichment in a rock is often thought to be caused by deep-seated fluids [22]. The vein granites also show clear correlations between the height of the positive Eu anomalies and the Ba concentrations, but no such correlations were detected in the blastomylonites (Fig. 11). The Eu concentrations in the vein granites decrease compared to the concentrations of this element in the amphibolite-facies rocks. At the same time, the granites

Fig. 9. Magnitude of Eu anomalies (Eu/Eu*) as a function of Sr concentration in the rocks.

Fig. 10. Magnitude of Eu anomalies (Eu/Eu*) as a function of CaO concentration in the rocks.

Fig. 11. Magnitude of Eu anomalies (Eu/Eu*) as a function of Ba concentration in the rocks.

cutting across the rocks with granulite assemblages are practically always notably enriched in Eu (Figs. 6, 7).

DISCUSSION

Granites depleted in LREE and with well-pronounced negative Eu anomalies are spread quite widely. Depletion in LREE in the course of crystalliza-

Setting of fluid systems before the development of the normal fault

Fig. 12. Structural setting of acid rocks (granites and blastomylonites) with positive Eu anomalies in the vertical section of the Earth's crust during the development of a normal fault and changes in the fluid regime.

crust

Zones of blastomylonites

 with positive Eu anomalies (not to scale)

tion in the sequence from granodiorites to granites with the development of negative Eu anomalies is usually explained by the crystallization of minerals concentrating REE (such as monazite and apatite) and their removal from the magma [23]. Granites with positive Eu anomalies are rarer and occur mostly in the Precambrian TTG series or, occasionally, in modern geodynamic environments [12]. With rare exceptions [9, 18], their genesis is also thought to be related to magma differentiation [3, 8]. Considering REE distribution in rocks, most researchers either do not explain the genesis of the Eu anomalies at all or, if the anomalies are positive, relate them to high plagioclase contents in the rocks (i.e., high concentrations of Sr, an element isomorphous with Eu [1]). When the orthogneisses of tonalite–granodiorite composition in the Inner Hebrides were studied, it was determined that granulite-facies gneisses have low REE concentrations and positive Eu anomalies, whereas the amphibolite-facies gneisses commonly have higher REE concentrations but negative Eu anomalies. The Eu enrichment in these rocks was explained by the formation of plagioclase cumulates, which appear at depths corresponding to the granulite facies [24]. The study of trondhjemites in southwestern Finland revealed a gradual transition from gabbro to trondhjemites, as follows from the REE patterns of these rocks. This rock series is characterized by a decrease in the contents of LREE and HREE and an increase in the positive Eu anomalies with the transition from varieties of intermediate composition $(SiO₂ = 65.7%)$ to trondhjemites $(SiO₂ = 72.4%)$. This behavior of REE in the rocks from southwestern Finland can be explained by fractional crystallization [3]. It was demonstrated that the granitoids of the Belomorian Belt are high in Al_2O_3 (15–16 wt %) and SiO₂ (up to 74 wt $\%$), bear much plagioclase (61–74%), and are depleted in REE, but enriched in Eu [15]. According to [18], positive Eu anomalies were detected in enderbites, plagiogranites, anorthosites, syenites, and leucogranites (orthotectites) of the Ol'khon metamorphic complex in the western Baikal area. The anomalous behavior of Eu was explained by the ability of Eu^{2+} to form stable aluminosilicate complexes in strongly polymerized water-poor melts. This fact confirms the preservation of Eu concentrations at broad variations in the contents of other REE, particularly HREE.

It is sometimes hypothesized that plagiogranites with positive Eu anomalies could be produced by partial melting. Rocks of this type were found in the Karmoy ophiolite complex in western Norway, in which they are associated with dikes and occur as thin (a few centimeters thick) layers parallel to shear zones or as branching veinlets in brecciated mafic magmatic rocks [25]. The simulations of REE behavior indicate that the Karmoy plagiogranites were produced by partial melting of amphibolites (40% hornblende and 60% plagioclase). The aforementioned examples of positive Eu anomalies pertained to plagioclase granites. However, analogous anomalies quite often occur in potassic rocks. For example, the general decrease in the concentrations of REE in the TTG series with increasing silicity and the concept that the granites of these series correspond to the final stages of the metasomatic alterations of basic rocks led some geologists to regard the positive Eu anomalies as residual (all REE during the final stage were removed, because of a decrease in the amount of mafic minerals, whereas the Eu concentrations did not change) [2, 9]. In other natural materials, positive Eu anomalies were detected in oil, coal [19], phosphorites [20], and Archean BIF [26]. An Eu excess in these rocks is considered to be an indication of strongly reduced conditions. Inasmuch as the Eu^{2+}/Eu^{3+} ratio is a function of the redox potential of the mineralizing environment, it is reasonable to think that granitoids with positive Eu anomalies were produced under reduced conditions [13].

The origin of high-Al granites was related for a long time to the melting of crustal rocks during continental collision [8, 12]. However, the past 10–15 years witnessed the development of models of the origin of such granites via partial melting triggered by the emplacement of hot mantle magmatic masses into lower crustal levels (underplating) [27]. The genesis of small granite veins scattered over vast areas in the eastern Baltic Shield (Fig. 1) cannot be explained within the scope of either of these models. The REE patterns of these granites and blastomylonites can be most probably accounted for by the reduced conditions in the environments where these rocks were formed. We propose the following model of the geodynamic environment, where these rocks could be formed. The boundary between brittle and ductile deformation zones to which the origin of these rocks is thought to be restricted lately attracted much attention from geologists, geophysicists, and geochemists. This boundary is now often considered to be a significant discontinuity in the Earth's crust (its "barrier zone") that can control the uplift of fluids and plastic rocks to the surface [28]. Under extreme conditions, for example, at crustal extension, this barrier is destroyed and becomes permeable to deep, mostly reduced fluids.

A very important tectonic event in the evolution of the Lapland–Belomorian Belt was the exhumation of deep rocks to the surface, i.e., their transfer from the zone of ductile deformation to that of brittle deformations. It was thought until quite recently that most Precambrian complexes were exposed at the surface by erosion. However, now numerous lines of evidence were obtained that these rocks were brought to the surface mostly by tectonic processes. There is still no consensus concerning the geodynamic environment of these processes. Many geologists are prone to relate them to collision and the "squeezing" of deep rocks. The LBB, the largest structural feature in the eastern Baltic Shield is often believed to be a collision zone, whose development was controlled by the convergence of the Karelian and Kola massifs, a process that forced out lower crustal rocks [2, 10]. However, modern studies in several territories, including such a classic collisional area as the Himalayas, indicate that deep rocks are brought to the surface in extensional environments [29]. Although the driving forces of the extensional processes can vary, the exhumation of deep rocks to the surface is related exclusively to extensional environments, a concept that provokes no doubt in light of the results of modern research [30]. The structural mechanism facilitating the exhumation of deep rocks to the surface is a normal fault at gentle angles. During this process, the rocks of the lying limb are brought to the surface and pass from the zone of ductile deformations to that of brittle deformations [31]. A principally important component of the evolution of low-angle faults is the decompressional melting of their footwall rocks and the spontaneous release of deep fluids [32]. The structure of the Lapland–Belomorian Belt can also be considered in the context of extension processes: the moving of the Kola and Karelian massifs in opposite directions away from the axis of the belt. The tectonic denudation of the 15- to 25-km-thick rocks sequence overlying the Lapland–Belomorian Belt created conditions favorable for shock decompression at certain depths and the release of huge amounts of fluids, which accompanied the post-tectonic magmatism in the area. The 1.8- to 1.7-Ga rocks of this stage intruded the rocks of the Lapland–Belomorian Belt when the latter were close to the surface, whereas our granites were produced somewhat earlier, at the boundary between the brittle- and ductile-deformation zones, when deep-seated rocks were brought to the surface. The blastomylonites were produced at depths greater than those where the granite veins were emplaced, and all of these rocks marked the exhumation of deep rocks to the surface. Judging from the occurrence of positive Eu anomalies in the rocks, the latter process was associated with a flow of reduced fluids. Diverse models for fluid transfer within the crust can be grouped into two major types: fluid migration along systems with open pores and cracks, and fluid movement along "viscous" tectonic boundaries [33], which can be compared in general terms with the granite veins and blastomylonitization zones. The early evolutionary stages of most LBB rocks were marked by their transformations under the effect of reduced fluids, which later gave way to oxidized fluids, i.e., the boundary between the fluid systems continuously shifted downward. However, the shock decompression that occurs during normal faulting can be associated with the release of reduced fluids, which start to ascend along blastomylonite zones or open fractures (in the zone of brittle deformations). The reduced fluids typically bear and release much more heat than oxidized fluids can [33], and this facilitates partial melting along open fractures and the generation of granites. The latter are depleted in mafic components (which are removed by flows of hydrogen fluids) and have positive Eu anomalies (an indication of a reduced environment). The ascending fluids oxidize and produce various metasomatic rocks with negative Eu anomalies (Fig. 12). This process results in the complementary differentiation of Eu, which is concentrated in the transitional zone, where reduced fluids are periodically injected. After this, the fluids (that are already depleted in Eu and oxidized) migrate upward and largely control the composition of the upper crust.

CONCLUSIONS

(1) The eastern part of the Baltic Shield was found to contain abundant acid rocks with positive Eu anomalies. These rocks are mostly vein granites and, to a lesser degree, plagiogranites and blastomylonites. The granites and blastomylonites have similar chemical compositions, but varying K_2O concentrations.

(2) The rocks described in this publication have low concentrations of Rb and Zr, are strongly depleted in REE (whose concentrations approach those of basalts), and are enriched in Sr and Ba, a feature suggesting that the fluids came from a significant depth.

(3) The transition zone from ductile to brittle deformations was favorable for the origin of these rocks. Horizontal extension periods were characterized by the inflow of reduced fluids into the zone and the partial melting of the host rocks along open fractures. This process facilitated the melting of the host rocks along open fractures and controlled the REE distribution in the rocks and the occurrence of positive Eu anomalies in them.

REFERENCES

- 1. S. R. Taylor and S. M. McLennan, *The Continental Crust: Its Composition and Evolution* (Blackwell, Oxford, 1985; Mir, Moscow, 1988).
- 2. M. V. Mints, V. N. Glaznev, A. N. Konilov, et al., *Early Precambrian of the Northeastern Baltic Shield: Paleogeodynamics, Structure and Evolution of the Continental Crust* (Nauchnyi Mir, Moscow, 1996) [in Russian].
- 3. J. G. Arth, F. Barker, Z. E. Peterman, and J. Friedman, "Geochemistry of Gabbro–Diorite–Tonalite–Trondhjemite Suite of Southwest Finland and Its Implications for the Origin of Tonalitic and Trondhjemitic Magmas," J. Petrol. **19**, 289–316 (1978).
- 4. Yu. A. Kostitsin, "Accumulation of Trace Elements in Granites," Priroda, No. 2, 26–34 (2000).
- 5. L. B. Efremova and N. A. Sorokina, "REE Determination in Geological Samples by Atomic Emission Spectroscopy with Inductively Coupled Plasma after Ion-Exchange Extraction," Zh. Anal. Khim. **46** (11), 2259– 2262 (1991).
- 6. K. Mehnert, *Migmatites and the Origin of Granitic Rocks* (Elsevier, Amsterdam, 1968; Mir, Moscow, 1971) [in Russian].
- 7. L. P. Nikitina, L. K. Levskii, K. I. Lokhov, et al., "Proterozoic Alkaline–Ultramafic Magmatism in the Eastern Part of the Baltic Shield," Petrologiya **7** (3), 252–275 (1999) [Petrology **7**, 246 (1999)].
- 8. S. Sheppard, T. J. Griffin, I. M. Tyler, and R. W. Page, "High- and Low-K Granites and Adakites at a Paleopro-

terozoic Plate Boundary in Northwestern Australia," J. Geol. Soc. (London) **158**, 547–560 (2001).

- 9. N. M. Kunina and M. V. Mints, "Behavior of the Rare-Earth Elements during Granitization," Byull. Mosk. O-va Ispyt. Prir., Otd. Geol. **67** (4), 86–94 (1993).
- 10. N. E. Kozlov, A. A. Ivanov, and M. I. Nerovich, *Lapland Granulite Belt: Primary Nature and Evolution* (Geol. Inst. Kol. Fil. AN SSSR, Apatity, 1990) [in Russian].
- 11. P. D. Maniar and M. Piccoli, "Tectonic Discrimination of Granites," Geol. Soc. Am. Bull. **101**, 635–643 (1989).
- 12. H. Martin, "Adakitic Magmas: Modern Analogues of Archaean Granitoids," Lithos **46**, 411–429 (1999).
- 13. A. A. Beus, *Geochemistry of the Lithosphere* (Nauka, Moscow, 1981) [in Russian].
- 14. A. Erlang, "Correlation between Potassium and Rubidium Contents in the Earth's Rock," in *Origin and Distribution of the Elements* (Pergamon, Oxford, New York, 1968; Mir, Moscow, 1972).
- 15. T. F. Shcherbakova, *Amphibolites of the Belomorian Complex and Their Granitization* (Nauka, Moscow, 1988) [in Russian].
- 16. A. A. Beus and T. F. Shcherbakova, "Comparative Geochemical Characteristics of Amphibolite– Trondhjemite–Granite Series of the Baltic (Belomorian Complex) and Ukrainian (Dnepropetrovsk Complex) Shields," Geokhimiya, No. 11, 1547–1567 (1994).
- 17. V. A. Makrygina and Z. I. Petrova, "Geochemistry of Migmatites and Granitoids of Priol'khon'e and Ol'khon Island, Baikal Region," Geokhimiya, No. 7, 637–649 (1996) [Geochem. Int. **34** (7), 574 (1996)].
- 18. Z. I. Petrova, V. A. Makrygina, and V. A. Bobrov, "Rare-Earth Elements as Indicators of the Geodynamic Evolution in the Continental Block of Ol'khon Island and Adjacent Areas, Western Baikal Region," Geokhimiya, No. 12, 1286–1297 (1999) [Geochem. Int. **37** (12), 1158 (1999)].
- 19. Yu. A. Balashov and K. S. Tsoi, "Role of the Redox Conditions in Accumulation of Eu²⁺, Yb²⁺, and Sm²⁺ in Oils," Dokl. Akad. Nauk SSSR **309** (5), 1189–1192 (1989).
- 20. G. N. Baturin, J. Lucas, and L. Prévö-Lucas, "The Europeum Anomaly in Oceanic Phosphorites," Dokl. Akad. Nauk **379** (5), 647–650 (2001) [Dokl. **379A** (6), 701 (2001)].
- 21. M. D. Norman, W. P. Leeman, and S. A. Mertzmam, "Granites and Rhyolites from the Northwestern U.S.A.: Temporal Variation in Magmatic Processes and Rela-

tions to Tectonic Setting," Trans. R. Soc. Edinburgh, Earth Sci. **83**, 71–81 (1992).

- 22. V. I. Levitskii, "Classification of Metasomatites of the Precambrian Continental Crust," Zap. Vseross. Mineral. O-va **127** (2), 26–40 (1998).
- 23. C. F. Miller and D. W. Mittlefehdt, "Depletion of Light Rare-Earth Elements in Felsic Magmas," Geology **10** (3), 129–133 (1982).
- 24. J. Arth, "Some Trace Elements in Trondhjemites—Their Implication to Magma Genesis and Paleotectonic Setting," in *Trondhjemites, Dacites and Related Rocks*, Ed. by F. Barker, (Elsevier, Amsterdam, 1979; Mir, Moscow, 1983).
- 25. R. B. Pedersen and J. Malpas, "The Origin of Oceanic Plagiogranites from the Karmoy Ophiolite, Western Norway," Contrib. Mineral. Petrol. **88**, 36–52 (1984).
- 26. A. Danielson, P. Moller, and P. Dulski, "The Europium Anomalies in Banded Iron Formation and the Thermal History of the Oceanic Crust," Chem. Geol. **97**, 89–100 (1992).
- 27. B. J. Williamson, H. Downes, and F. M. Trirlwall, "The Relationship Between Crustal Magmatic Underplating and Granite Genesis: An Example from the Velay Granite Complex, Massif Central, France," Earth Sci., No. 83, 235–245 (1992).
- 28. S. N. Ivanov and A. I. Rusin, "Continental Rift Magmatism," Geotektonika, No. 1, 6–19 (1997) [Geotectonics **31** (1), 3 (1997)].
- 29. K. Hodges, S. Bowring, K. Davidek, et al., "Evidence for Rapid Displacement on Himalayan Normal Faults and the Importance of Tectonic Denudation in the Evolution of Mountain Ranges," Geology **26** (6), 483–486 (1998).
- 30. J. F. Dewey, "Extensional Collapse of Orogens," Tectonics **7** (6), 1123–1139 (1988).
- 31. B. Wernicke, J. D. Walker, and M. S. Beaufait, "Structural Discordance between Neogene Detachments and Frontal Sevier Thrusts, South Nevada," Tectonics, No. 2, 112–132 (1985).
- 32. D. McKenzie and M. J. Bickle, "The Volume and Composition of Melt Generated by Extension of the Lithosphere," J. Petrol., No. 29, 625–679 (1988).
- 33. F. A. Letnikov, "Fluid Regime of Endogenous Processes in the Continental Lithosphere and Problems of Metallogeny," in *Proceedings of Theoretical Seminar OGGGGN RAN on Problems of Global Geodynamics, Moscow, 1998–1999* (GEOS, Moscow, 2000), pp. 204– 224 [in Russian].