**GEOCHEMISTRY** =

## Peculiarities in the Behavior of Trace and Rare Earth Elements during Granitization and Migmatization of the Elgakan Complex (East Siberia, Nyukzha River)

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The behavior of major elements in the process of Neoarchean amphibolite-facies metamorphism was considered previously for occasionally pyroxene-bearing biotite-amphibole-plagioclase schists and amphibolites, which occur in the middle and lower reaches of the Nyukzha River and are identified as the Elgakan Unit [1]. Ultrametamorphism took place in several stages. At the first stage, plagiogranite gneisses  $(Lc_1)$ and rocks of an intermediate composition (sch\*) were sequentially developed from the volume replacement of schists (sch). At the second stage, the stromatic, network, and coarse-banded migmatite leucosomes (Lc<sub>2</sub>,  $Lc_3$ , and  $Lc_4$ , respectively) developed progressively in schists and plagiogranite gneisses [1, 2]. The two stages were separated by emplacement of intermediate and silicic dikes and minor intrusions. This paper is focused on behavior of trace and rare earth elements in these processes.

Without dwelling on the major element geochemistry of crystalline schists and amphibolites (27 analyses), let us note that their compositions correspond to basalt–trachybasalt and basaltic andesite–basaltic trachyandesite in the TAS diagram: SiO<sub>2</sub> 50.10 ± 3.50 and  $55.40 \pm 1.85$  wt %, respectively; (Na<sub>2</sub>O + K<sub>2</sub>O)  $5.22 \pm$ 1.86 and  $5.48 \pm 1.27$  wt %, respectively. Correlation links are typical of igneous rocks of this composition: Si displays negative correlation with Fe<sup>3+</sup>, Fe<sup>2+</sup>, Mn, Mg, and Ca; positive correlation with Na; and the absence of significant correlation with K, Ti, and Al. The absence of significant positive correlation with Ca, Na, and Al testifies to the insignificant effect of plagioclase fractionation.

The  $Lc_1$  group (26 samples) includes plagiogranite and granite gneisses with biotite (occasionally, amphibole). In terms of composition, this group varies from tonalite to trondhjemite and granite with predominance of rocks containing 68–73 wt % SiO<sub>2</sub>. In terms of proportions of normative Ab, An, and Or, the distribution of samples is as follows: trondhjemite 39%, granite 23%, and tonalite and granodiorite 19% each. The sum total of alkali metals shows a positive correlation with K and a negative correlation with Na, resulting in a negative correlation between K and Na (–0.60). In terms of ASI values, most samples fall within a range of 0.9–1.2 (maximum 1.0–1.1). Four samples (out of 26) are characterized by ASI = 1.2–1.4. The Fe index (*F*) varies from 50 to 70%, and the degree of Fe oxidation ( $f_0$ ) is 10–40% (maximum 20–30%). Si has negative correlation with Na and K.

Leucosomes Lc<sub>2</sub> (20 samples) always contain >68 wt % SiO<sub>2</sub>. In comparison with  $Lc_1$ , they are characterized by the prevalence of trondhjemite (50%), a higher content of granite (35%), and a lower content of tonalite (15%). The correlation between K and Na is negative (-0.58). Samples with ASI = 1.0-1.1 and 1.2-1.3 are most abundant. In terms of F and  $f_0$ , these rocks are close to Lc<sub>1</sub> but marked by more mafic compositions and higher percentages of rocks with elevated contents of alkali metals. Si is negatively correlated with Al,  $Fe^{2+}$ , and Mg. Rocks of group Lc<sub>3</sub> (8 samples) are similar to  $Lc_1$  in composition. They differ from  $Lc_2$ in their higher Mg and lower Si contents. Group Lc<sub>4</sub> (14 samples) is close in many parameters to Lc<sub>2</sub>. However, the percentage of granite is higher (64%), while tonalite (7%) and trondhjemite (29%) are subordinate. K and Na are not correlated. As in the preceding group, Si lacks any significant correlation with all major elements except Al. The samples are uniformly distributed in three ASI intervals (1.0–1.1, 1.1–1.2, and 1.2–1.3). The maximums of F(60-70%) and  $f_0(20-30\%)$  are distinct.

The compositional variation of basic rocks during the granitization and evolution of leucosomes may be traced by comparing the average major element contents in the rock series from the basic protolith to the granitized basic rocks, plagiogranite gneisses, and leu-

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**Fig. 1.** Average contents of major oxides in basic rocks (sch), granitized basic rocks (sch\*), plagiogranite gneiss ( $Lc_1$ ), and migmatite leucosomes ( $Lc_2$ ,  $Lc_3$ ,  $Lc_4$ ) normalized to the bulk crust (BC) composition [3].

cosomes of different generations: sch  $\rightarrow$  sch<sup>\*</sup>  $\rightarrow$  Lc<sub>1</sub> $\rightarrow$  $Lc_2 \rightarrow Lc_3 \rightarrow Lc_4$ . At the stage of  $Lc_1$  formation, one can see a distinct sequential trend of an increase in Si, Na, and K combined with a decrease in mafic elements and P. This trend is retained during the transition from  $Lc_1$  to  $Lc_2$  and  $Lc_4$ . (Fig. 1). The similarity of average Si, Al,  $Fe^{2+}$ , and Mg contents in Lc<sub>1</sub> and Lc<sub>3</sub> reflects the formation of  $Lc_3$  due to the mobilization of  $Lc_1$ . As has been shown previously by the method of discriminant functions and factor analysis [2], the compositional variations in pairs sch  $\rightarrow$  Lc<sub>1</sub> (28 pairs) and Lc<sub>1</sub>  $\rightarrow$  $(Lc_2 + Lc_3) \rightarrow Lc_4$  (18 pairs) are different (threshold value at 95% confidence level is 0.011). This is related to a more significant increase in Si and a decrease in all other elements in the first series relative to the second series.

Trace elements were determined by the ICP-MS method in 38 samples. They show typical wide variations of REE, Zr, Th, Hf, and Y contents in rock groups, probably, as a result of the nonuniform distribution of accessory minerals. The basic rocks reveal typical unfractionated REE patterns without Eu anomaly or with a slight Eu minimum (Fig. 2). The La/Yb ratio increases toward  $Lc_1$  as a result of depletion in Yb. In six samples (among 11),  $Eu/Eu^* > 1$ , the total LREE content grows, while the HREE content falls. In Lc<sub>2</sub>, Lc<sub>3</sub>, and Lc<sub>4</sub>, the La/Yb and Sm/Nd ratios and LREE and HREE contents decrease, while the Eu/Eu\* ratio increases. The transition from basic rocks to  $Lc_1$  is marked by variation in the REE pattern and enrichment in Th, Zr, Hf, and Zn. Their contents decrease in the subsequent leucosome generations.  $Lc_2$  and  $Lc_4$  are close to each other in this respect, while  $Lc_3$  is distinguished by the lower concentrations of these elements (Fig. 3).

Another variation trend is typical of the LILE group. Relative to basic rocks, leucosomes are characterized



**Fig. 2.** Chondrite-normalized REE patterns of basic rocks (sch), plagiogranite gneiss  $(Lc_1)$ , and migmatite leucosomes  $(Lc_2, Lc_3, Lc_4)$ . Chondrite composition was taken from [3]. See Fig. 1 for legend.

by a sequential increase in Rb, Ba, Sr, and Pb but a decrease in Nb and Ta, as well as in coherent and transitional elements (Co, Cr, Ni, and V). The analysis of correlations between certain elements in the rock groups revealed the following trend: the sum total of TiO<sub>2</sub>, FeO\*, MnO, and MgO, which characterize the mafic property of rocks, has positive correlation with the sum total of Co, Cr, Ni, and V; the groups show individual trends; REEs (LREE and HREE) have positive correlation with P<sub>2</sub>O<sub>5</sub>, Zr, Hf, Th, Y, U, and, less frequently, Nb in all rock groups, demonstrating the crucial contribution of accessory minerals (apatite, zircon, titanite, and allanite). The typical positive correlation between Y and HREE reflects the influence of not only accessory minerals, but also garnet. Correlation of mafic components with LREE and HREE is positive in



**Fig. 3.** Spidergram of BC-normalized [3] average chemical element contents in basic rocks (sch), plagiogranite gneiss  $(Lc_1)$ , and migmatite leucosomes  $(Lc_2, Lc_3, Lc_4)$ . See Fig. 1 for legend.

DOKLADY EARTH SCIENCES Vol. 411 No. 8 2006

basic rocks, negative in  $Lc_{2-4}$ , and absent in  $Lc_1$ . Zr and Hf show a similar relation to the mafic components. This can be related to the following fact: in basic rocks and Lc1, accessory minerals are not confined to darkcolored minerals. In veined leucosomes, apatite and zircon are mostly incorporated into biotite and rare garnet and amphibole grains. Similar relationships were also established in other igneous complexes [5, 6]. The significant correlation of Si with LREE and HREE is only observed in veined leucosomes (Lc<sub>2</sub>, Lc<sub>3</sub>, and Lc<sub>4</sub>). As usual, K is correlated with Rb and Ba, but the K/Rb ratio decreases toward Lc<sub>4</sub>. The positive correlation between K and Rb/Sr was established only in Lc<sub>1</sub>. This correlation was not revealed in other groups. Therefore, crystallization of potassium feldspar cannot be considered the main factor responsible for their compositional variations and the generation of leucosomes was not caused by the fractionation of a single melt.

The positive correlation of K with LREE and HREE is typical of  $Lc_1$ . In  $Lc_2$ , K demonstrates a positive correlation with LREE. Such correlation is absent in other groups. In  $Lc_1$ , the highest LREE contents are characteristic for the K-rich varieties, and K has positive correlation with Y, Zr, Hf, Nb, Ta, Th, and U. The groups mentioned above show positive LREE–HREE correlations not only between the total concentrations, but also between neighboring REEs.

To estimate the difference in transformation of rocks, the chemical element contents in leucosomes of various generations were normalized to the respective substrate composition. Basic rocks are regarded as a substrate for  $Lc_1$ ;  $Lc_1$ , for  $Lc_2$ ; migmatites and  $Lc_1$ , for  $Lc_3$  and  $Lc_4$ . It can be seen that, relative to the basic protolith, Lc<sub>1</sub> is substantially depleted in V, Cr, Co, Ni, and, to a lesser degree, HREE as compared with veined leucosomes (Fig. 4). Variations of Cs, LREE, Eu, Zr, Hf, Th, and U contents in  $Lc_1$  relative to  $Lc_{2,3,4}$  are differently directed and more significant in the first case. Patterns in veined leucosomes are unstable. Only the migmatites and  $Lc_1 \rightarrow Lc_3$  series demonstrate the maximal depletion in LREE, HREE, Zr, Hf, Th, U, Y, Nb, and Ta. In terms of the major element contents,  $Lc_1$  and  $Lc_3$  are closest to each other. Probably,  $Lc_1$  serves as restites for Lc<sub>3</sub> in relation to elements associated with accessory minerals and amphibole, which sporadically occurs in  $Lc_1$  and disappears in  $Lc_3$ . Rb, Sr, Ba, and Pb concentrations are higher in the sch  $\rightarrow$  Lc<sub>1</sub> series only relative to the  $Lc_1 \rightarrow Lc_2$  series, whereas the reverse relationships are established in the migmatites and  $Lc_1 \rightarrow Lc_3$  (partly, migmatites and  $Lc_1 \rightarrow Lc_4$ ) series because of higher potassium feldspar contents in the late generations of leucosome.

Thus, the established differences in the degree of enrichment (or depletion) in chemical elements, as well as specific features of correlation and composition, in various groups of rocks are related to different styles of volume replacement and development of veined leucoLeucosome/Protolith



**Fig. 4.** Average element ratios for pairs: (1)  $Lc_1/sch$ , (2)  $Lc_2/Lc_1$ , (3)  $Lc_3/mig$ ,  $Lc_1$ , and (4)  $Lc_4/mig$ ,  $Lc_1$ .

somes. The gradual transition from metabasic rocks to  $Lc_1$ , the absence of melanosomes, the mismatch of concentrations of elements in  $Lc_1$  with experimental results, lower real temperatures and pressures of granitization than those necessary for the melting of basic rocks, and the considerable volume of rocks produced during the granitization [7–10] indicate the substantial role of metasomatic granitization with progressive sequential melting (anatexis and diatexis) during the formation of veined leucosomes in the open system. The confinement of veined leucosomes to axial planes of folds ( $Lc_2$ ,  $Lc_4$ ), shear zones ( $Lc_3$ ), and crystallizational schistosity planes testifies to percolation of the produced melt. Granitization was accompanied by the gain of LILE, LREE, Zr, Hf, and Th and the loss of HREE, Y, Nb, V, Cr, Co, and Ni. The concentration of LILEs in the veined leucosomes was accompanied by their depletion in REE, Zr, Hf, Th, Y, U, Nb, and Ta. Such variations of chemical element contents cannot be obtained in models of equilibrium or nonequilibrium melting [11, 12]. They are possible only if accessory minerals (zircon, apatite, titanite, and allanite) did not participate in melting and concentrated in restites as a result of screening by refractory minerals.

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