Isotopy

#Ponomarchuk V.A., Lebedev Yu.N., Palessky S.V., Kiseleva V.Yu., Shevchenko D.O. Isotope microgeochemical heterogeneity of natural minerals.

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Basic petrological, geodynamic , historical-geological concepts are based to a large extent on isotope and elemental characteristics of rocks and minerals. For the investigation of the latter, at present analytical methods are often used to study the isotope, macro- and micro-geochemical composition of milligram and microgram weighed portions of minerals and rocks. These methods include SCHRIMP, ICP-MS, synchrotron radiation, laser spectrometry, microprobe methods. The results of analyses often show in-homogeneity of the isotope and chemical compositions. The latter circumstance is of substantial importance for the isotope and geochronological studies. Because of this, a problem arises to study the homogeneity of isotope compositions within mineral population isolated from the bulk rock. Its should be noted that this task is successfully solved in every specific case when applied to U-Th-Pb geochronological method for the accessories: zircon (apatite, monazite, etc.). However, in other isotope

and geochronological methods (Rb-Sr, K-Ar, $^{40}Ar/^{39}Ar$) involving rock-forming minerals (biotite, feldspar, hornblende, etc.) and accessories (sphene, apatite) no investigations of this type were performed.

For this purpose, in order to separate and individualise the grains of analogous minerals and determine K, Rb, Sr, Cl, Ca, $^{87}Sr/^{86}Sr$, $^{40}Ar/^{39}Ar$, we developed the instrumentation and techniques based on the differences in magnetic properties, density, structure and colour.

In the construction of magnetic separator, special attention was paid to the increase of magnetic field gradient along the trajectory of crystals movement. A maximum separation of the trajectories in the launder plane was achieved by selecting (in spherical coordinates) the angles for the electromagnet, launder, and the current of the electromagnet. As a result, along with the widely used procedure of the separation of rock-forming minerals and accessories with contrast magnetic susceptibility (the Frantz electromagnet), it is possible to perform further fractionation of minerals differing by this parameter in narrow range. An increase in the resolution is achieved by multiple passing of the fractionated concentrates through the electromagnet separator. Several fractions were obtained in the experiments on electromagnetic separation of phlogopite and feldspar concentrates from alkaline rock (Vietnam). The fractions differ by Rb and Sr contents (isotope dilution method) (Table 1). Thus determined Rb-Sr age of the sample was 40.9 ± 4.7 Ma. In this case, due to large error in the age, time uncertainty in the formation of elemental heterogeneity is 4.7 Ma starting from the crystallisation moment.

Table 1. Rb and Sr contents and isotopic composition of alkaline rock and its magnetically fractions

Sample fraction no.	Rock, mineral	Rb, ppm	Sr, ppm	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr\pm\sigma$
R9355	Bulk rock	336	10510	0.0927	0.70730±3
VB-2	Phlogopite	493	1420	1.00	0.70760±7
VB-3	»	601	742	2.34	0.70838±4
VB-4	»	525	1200	1.25	0.70775±5
VB-5	»	496	1184	1.21	0.70755±6
VB-6	»	392	4850	0.234	0.70716±6
Vb-1	»	572	1047	1.58	0.70795±5
Vb-5	»	570	851	1.94	0.70821±7
PSh-1	Feldspar	310	18950	0.0473	0.70728±2
PSh-2	»	309.8	19000	0.0468	0.70733±3
PSh-3	»	352	19500	0.0522	0.70738±4
PSh-5	»	310	17200	0.0526	0.70734±7
PSh-21	»	278	32200	0.0249	0.70706±3

The conclusion concerning elemental non-homogeneity during the crystallisation of minerals can be obtained by studying reference mineral samples. For the latter studies, the initial natural mineral is subjected to thorough control for the change indication and is rejected in the case if secondary processes are registered. The variation of potassium content from one fraction to another (5÷20 mg) in Russian reference materials is: Biotite-70 - 30 % (maximum K content is 8.2 %, minimum 6.15 %); Biotite Chernaya Salma - 12 % (maximum K content is 6.93 %, minimum 6.21); Biotite MSA - 11 - 20 % (maximum K content is 6.9 %, minimum 5.6 %). It should be noted that the International References materials of the Geological Survey of the USA Muscovite P-209 is also

characterised by geochemical non-homogeneity: the ratios $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ vary within the limits $198 \div 336$ and $0.994 \div 1.103$, respectively. So, indirect data point to the fact that the formation of elemental heterogeneity in such rock-forming minerals as biotite and muscovite occur at the crystallisation stage.

The methods of isotope microgeochemistry register also the induced in-homogeneity which is formed with a substantial time gap (several million years) from the crystallisation period. This is especially evident in the $^{40}Ar/^{39}Ar$ spectrum of the hornblende from the residual rock of gabbroid among the granitoids of the Sora Cu-Mo porphyry deposit (Fig. 1). As Fig. 1 shows, the concentrate of the mineral (50 mg.) is non-homogeneous with respect to the Ca/K ratio. High-temperature argon fraction shows the age of 438 ± 2.3 Ma while the age of the main part of hornblende crystals is 481 ± 2.3 Ma. This apparent paradox is quite understandable if we take into account the geological situation at the deposit in general. A rhythmic occurrence of endogenic processes is registered by the $^{40}Ar/^{39}Ar$ method within the area of the deposit: surrounding rocks - $479 \div 480$ Ma, $465 \div 466$, $454 \div 455$ and $421 \div 422$ Ma; pre-ore dikes - $402 \div 405$ Ma, sub-alkaline porphyries I - $388 \div 389$ Ma, sub-alkaline porphyries II - $363 \div 357$ Ma. This list of magmatism stages allows to understand the essence of dating of the high-temperature fractions of the $^{40}Ar/^{39}Ar$ spectrum. This is the time when a part of the crystals of hornblende were transformed due to fluids that usually accompany the magmatism. The time when the latter took place was $421 \div 422$ Ma.

Not only rock-forming minerals but also accessories are characterised by the isotope and chemical non-homogeneity. The $^{87}Sr/^{86}Sr$ ratio in the apatite from different sites of the granitoid body is rather homogeneous and only insignificantly differs from the primary isotope composition which is the genetic label of magmatite. However, in titanites sampled under the same conditions, the $^{87}Sr/^{86}Sr$ ratio varies substantially. In dark-coloured titanite varieties the $^{87}Sr/^{86}Sr$ ratio is the lowest, only slightly different from the primary isotope composition characteristic of a granitoid. In light (colourless) varieties coexisting with the dark ones, the $^{87}Sr/^{86}Sr$ ratio is high. This is explained by late-magmatic re-crystallisation (or new formation) of titanites in the presence of fluids with increased concentration of radiogenic strontium. Thus, the isotope microgeochemical approach allows us to reveal the isotope and elemental heterogeneity of rock-forming minerals and accessories with the identification of crystallisation and post-crystallisation stages of its formation.
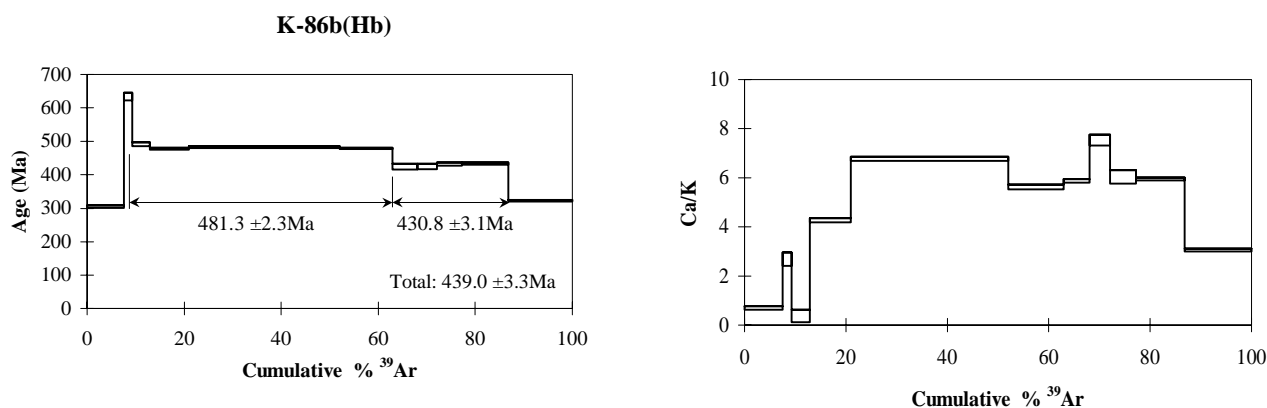
K-86b(Hb)

Fig. 1. Argon-argon age spectrum and Ca/K ratio of hornblende, which indicates heterogeneity of mineral concentrate.