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GEOCHEMISTRY

First Data in Favor of the Crystallization Model of Lithium Isotope Fractionation in the Pegmatitic Process

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In recent decades, the geochemistry of stable metal isotopes has achieved significant progress due to the application of multicollector mass spectrometers with inductively coupled plasma (MC-ICP-MS) that makes it possible to measure weak isotope variations with an accuracy better than 0.5‰. This facility, primarily for the investigation of lithium, has appeared now in Russia (Isotope Research Center, Karpinskii All-Russia Research Institute of Geology, St. Petersburg). As is known, lithium has two isotopes (^{6}Li and ^{7}Li) with the maximal mass discrepancy (15.5%) relative to all other metals. Therefore, one can also expect the most appreciable Li isotope shifts in natural processes. We propose to estimate the isotope shift relative to the ^{7}Li/^{6}Li ratio in the international standard of synthetic lithium carbonate (LSVEC) as δ^7Li‰, where $\delta^7\text{Li} = [(^7\text{Li}/^6\text{Li})_{sam} - (^7\text{Li}/^6\text{Li})_{st}]/(^7\text{Li}/^6\text{Li})_{sam} \cdot 10^3$). The available scanty data on this issue [1–5] suggest the following main regularities in the behavior of Li isotopes in natural objects.

The isotopic composition of Li in crystalline rocks of the upper mantle and continental crust differs little from the standard value (δ^7Li = –2…+5‰). High-temperature processes of magmatic differentiation do not provoke significant effects of isotope fractionation [2–4]. However, the Li isotope in seawater appeared unexpectedly heavy (+32‰) [1–5]. The most notable δ^7Li variations are attributed to low-temperature exogenous processes, such as halmyrolysis of marine basalts [1, 3, 5], weathering of rocks, and diagenesis of sediments [1–3]. Trends of the Li isotope fractionation in metamorphic, postmagmatic, and hydrothermal-metasomatic processes in the Earth's crust are poorly studied.

Meanwhile, the behavior of Li isotopes in these processes is an interesting issue [4]. For example, the Li isotope in pegmatite-bearing systems, which serve as an intermediate member between magmatic and hydrothermal objects, deserves particular interest. The available publications devoted to this issue only provide data on the Li isotope in minerals from separate rare-metal pegmatite bodies with prominent concentric zonality [6, 7]. Large δ^7Li variations (> 15‰) in these minerals characterize the Li isotope shift related to the temporal intrachamber differentiation of matter in the course of decrease in crystallization temperature. However, we do not know the main reason for the Li isotope fractionation within the framework of the evolution of integral pegmatite-forming systems that include numerous units (separate vein bodies).

We investigated lithium minerals in two contrasting pegmatite-forming systems (PS) of the rare-metal association in the Kolmozero–Voron'ya pegmatite-bearing zone (Kola Peninsula) confined to the Late Archean Kolmozero–Voron'ya greenstone belt (GB) [8]. Pegmatites genetically associated with granitoids of the granodiorite–leucogranite association are similar in terms of concentrations of Li, Rb, Ta, Be, and other fluophile chemical elements. However, they drastically differ in the degree of intrachamber differentiation, fluorine concentration, and pegmatite-forming medium fractionation. We can assess the latter parameter based on the K/Rb ratio in the major minerals of pegmatites (micas and feldspars). All of these mineralogical–geochemical indicators of the PS evolution in space and time [9] are consistent with the erosion level of the

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δ^7Li isotope shift in lithium minerals and its correlation with the K/Rb ratio in paragenetic micas as an indicator of fractionation level of the system

Ord. no.	Sample no.	Mineral	+ δ^7Li, ‰	K/Rb in micas	T_c, °C
Low-F (Kolmozero) system					
1	KO-100	Holmquistite	5.3	16.2	
2	K-2616	Spodumene I	6.7	10.8	500
3	K-1033	Spodumene II	6.9	6.7	420
Correlation, $n = 3$			r δ^7Li – K/Rb; –0.946		
High-F (Voron'ya Tundra) system					
4	BP-100	Holmquistite	8.8	14.5	
5	B-1158	Spodumene I	12.7	10	480
6	BP-0	Spodumene II	15.1	2.8	450
7	3B-6	Lepidolite	20.3	1.1	420
Correlation, $n = 4$			r δ^7Li – K/Rb; –0.938		r δ^7Li – T; –0.42, $n = 5$
Correlation for all systems, $n = 7$			r δ^7Li – K/Rb; –0.805		

Note: Crystallization temperature is based on the Pb content in the paragenetic microcline and albite (according to [12]).

lithostructural zone in the pegmatite-hosting areas. For example, the Kolmozero PS located in an area corresponding to a deep erosion level of the greenstone belt is characterized by a weak intrachamber differentiation of sufficiently thick and extended spodumene-type pegmatite bodies, low F content (<0.15% F in muscovite; lack of natural fluorine minerals), and a relatively low degree of fractionation (K/Rb from 7 to 15) [10]. The Voron'ya Tundra PS confined to a lower erosion level of the greenstone belt shows a very high degree of intrachamber differentiation of pegmatites. This is reflected in the following features: the concentric-zonal structure; high F concentrations (>0.5% F in muscovite; the presence of F-rich minerals, such as lepidolite and amblygonite); high contents of all fluophile chemical elements, particularly Rb, Cs, and Ta; and an anomalously high degree of fractionation (K/Rb in minerals decreases to –2.5) [9, 11].

METHODS

The Li isotopic composition was determined in ThermoFinnigan Neptune MC-ICP-MS at the Isotope Research Center, Karpinskii All-Russia Research Institute of Geology, St. Petersburg. Samples were prepared with the maintenance of all conditions warranting the correctness of results, i.e., achievement of the maximal separation of Li from Na for the suppression of matrix effects in the ICP source and the maximal Li yield from chromatographic columns for the minimization of its isotope fractionation during the measurement procedure. Processes of the decomposition of samples and the two-stage chromatographic Li extraction were carried out in accordance with the method described in [5]. Therefore, we could obtain solutions with the Li/Na value exceeding 1 and the total Li yield in columns was no less than 98%. In order to check the correctness of chemical operations, solutions of the isotope standard LSVEC (δ^7Li = 0‰) and seawater (δ^7Li from +30 to +33‰) were passed through the columns. Measurements were carried out using Li-bearing solutions (Li ~0.5 ppm in 3% HNO_3) sprayed with a Teflon Nebulizer at a rate of ~50 μl/min. The intensity of the ^{7}Li signal varied from 3 to 5 V. Samples, blank solutions, and standards were introduced with a Cetac autosampler. Deviation from standardized values during the run did not exceed ±0.9‰. The typical measurement error did not exceed ±0.4‰ (2σ).

DISCUSSION

The table presents results of the measurement of δ^7Li. They show the ^{7}Li/^{6}Li isotope shift in minerals of rare-metal pegmatites and Li–Cs metasomatites from the pegmatite-forming systems. The δ^7Li value increases in objects with a higher degree of fractionation. Based on these data, we calculated pair coefficients between δ^7Li and K/Rb in paragenetic micas. The results demonstrate a close reverse correlation between the parameters mentioned above and the existence of two types of PS. The first PS corresponds to the low-F crystallization setting with low degree of fractionation and low δ^7Li values (5.3–6.9‰). In contrast, the second PS corresponds to the fluoride system with a very high degree of fractionation and significantly high δ^7Li values (8.8–20.3‰).

Our original data are consistent with data on the Li isotope shift in the Tin Mountain rare-metal pegmatite [6, 7]. In terms of the K/Rb ratio and δ^7Li value, the Tin Mountain pegmatite occupies an intermediate position between the objects studied. Hence, ^{7}Li is obviously concentrated in later products of PS. Since the geochemical evolution of PS is undoubtedly stipulated

by the accumulation of fluophile chemical elements in the course of fractional crystallization [9], this mechanism is also valid for fractionation of the heavy Li.

One can assess the influence of the intrachamber differentiation and temperature regime on the $^7Li/^6Li$ isotope shift in the course of pegmatite formation based on discrepancies in the Li isotopic composition of two spodumene generations in each PS. It is worth mentioning that the early PS is represented by spodumene from the medium-grained quartz–spodumene–albite assemblage metasomatically developed after a microcline, whereas the late PS is represented by spodumene from the coarse-grained quartz–spodumene–two-feldspar aggregate with block texture [9–11]. The table shows that increase in the δ^7Li value in younger crystallization products is rather well recorded for each PS type. Calculations based on the method described in [12] indicate the lack of a significant correlation ($r - 0.42$, $n = 5$) between the Li isotope shift and crystallization temperature in the paragenetic assemblages mentioned above (see table).

Thus, increase in the δ^7Li value in the pegmatite-forming process is primarily related to the mechanism of fractional crystallization. We believe that this isotope parameter can be used as a reliable tracer of fractionation and other metasomatic processes in space and time. We also believe that further investigations in this field can yield very interesting results.

CONCLUSIONS

We detected and quantitatively estimated the increase in the δ^7Li value (up to +20‰) as the result of fractional crystallization during the evolution of Early Precambrian postmagmatic systems of rare-metal pegmatites. This is a new fact in the lithium isotope geochemistry.

The Li isotope shift can serve not only as a quantitative measure of the fractionation degree of postmagmatic geochemical systems, but also as a useful tool for solving pressing issues of their genesis and ore potential.

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