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Lithium Distribution in Proterozoic Sedimentary Rocks of the Southern Urals



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Abstract:

RESEARCH ARTICLE

Background: Lithium is currently a critically important resource for high-tech industries. However, data on the Li content in the sedimentary rocks of the Southern Urals have not been provided. The limited understanding of lithium geochemistry in the Proterozoic sedimentary rocks dictates the need for detailed geochemical studies.

Objective: The objective of this study was to determine the lithium distribution in the Proterozoic sedimentary rocks on the western slope of the Southern Urals and analyze the potential causes of enrichment.

Methods: Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used to analyze sandstones, shales, and carbonate rocks.

Results: Two stratigraphic intervals of lithium enrichment were identified in the Proterozoic sedimentary rocks on the western slope of the Southern Urals: the Suran and Avzyan Mesoproterozoic formations. The maximum enrichment of this alkali element occurred in carbonate rocks, where Li concentrations reached 125–268 ppm, exceeding the Clarke value by 5–12 times on average. In the Avzyan Formation, lithium showed a strong positive correlation with chlorite content. In the Suran Formation, lithium was highly correlated with fluorine (r = 0.97) and rubidium (r = 0.93), indicating its association with F-bearing phlogopite. The highest lithium concentrations, reaching industrially significant levels of up to 0.1 wt.% Li₂O, were confirmed within the fluorite ore halo of the Suran deposit. Cryolithionite was the dominant lithium-bearing mineral, accounting for 0.1–7 wt.% of the bulk composition.

Discussion: The lithium enrichment in the sedimentary rocks of the Suran and Avzyan Mesoproterozoic formations resulted from sedimentation under near-evaporitic conditions, as well as the subsequent influence of postmagmatic fluids during epigenesis caused by the intrusion of gabbrodolerite dikes. These findings are significant for both regional metallogeny and the broader pursuit of lithium resources, highlighting the substantial potential of sedimentary rocks.

Conclusion: The sedimentary rocks of the Suran and Avzyan formations on the western slope of the Southern Urals have the potential to host economically significant lithium concentrations. Of particular interest are the host rocks of the Suran Formation in the vicinity of the Suran fluorite deposit.

Keywords: Lithium, Carbonate rocks, Mesoproterozoic, Suran formation, Avzyan formation, Western slope of the Southern Urals.

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1. INTRODUCTION

In recent decades, lithium has become the focus of interdisciplinary research, including studies in geology, mining technology, and economics [1-8]. Due to the development of high-tech industries, including the production of electric vehicle batteries, portable electronics, and energy storage systems, the metal has rapidly become one of the most in-demand resources [9-11]. Global consumption of lithium in 2024 was estimated to be 220,000 tons, marking a 29% increase from 2023 [12]. Demand is projected to increase by 20-30% annually due to the global green-energy transition [13]. The majority of global lithium consumption (87%) is allocated to battery production, with the remainder used in ceramics, glass, lubricants, medicine, and other industries [12]. According to a report by the IEA [14], the global demand for lithium batteries is expected to grow thirtyfold by 2030 and more than a hundredfold by 2050 compared to 2020.

While lithium is relatively abundant in the Earth's crust (Clarke of carbonate rocks is 5 ppm, sandstones 15 ppm, shales 66 ppm [15]), mining poses significant challenges [16]. Over 90% of the Earth's total lithium resources are contained in oceans and seawater, currently unsuitable for mining. The measured and indicated global lithium reserves for 2025 are estimated to be about 115 million tons [12]. Half of these reserves, as salar brines, are contained in the so-called "Lithium Triangle" — comprising Argentina (23 million tonnes), Bolivia (23 million tonnes), and Chile (11 million tonnes) [17]. However, lithium extraction from salar brines requires large volumes of water and poses substantial environmental risks [18, 19]. The most significant deposits of lithium-bearing pegmatites [20, 21] are located in Australia and China, with reserves estimated at 8.9 million tons and 6.8 million tons, respectively [12]. Their primary advantage is the high lithium concentration, while their disadvantages include limited resource availability; only a small fraction hosts economically relevant lithium mineralization. In addition, the complexity of the lithium ore beneficiation process from these ores has ;ade scaling production more difficult [1, 22].

An important strategy for sustainable lithium supply is the development of closed-loop technologies, particularly lithium recycling from spent batteries [23-25]. Recycling is projected to meet only about 5% of global lithium demand by 2035 (25% by 2050) [13]. However, the current battery recycling capacity is insufficient to meet the projected demand [26]. Additionally, it requires the improvement and scaling of extraction technologies and the development of efficient waste collection infrastructure [27, 28].

According to the USGS [12], estimated lithium reserves in Russia stand at 1 million tons. Greisenized granites were once the major source of lithium in the world, but are now only being mined in southeastern Russia [29]. In reality, the resources in Russia are much larger; proven mineral reserves amount to at least 1.65 million tons, while predicted hydromineral resources reach 4.2 million tons at the Znamenskoye deposit alone

[4, 8, 30]. Taken together, this puts Russia in 5th place worldwide, on par with China and Australia. This is crucial for strengthening Russia's resource base amid the energy transition [31]. At the same time, supply shortages, coupled with advances in mining technologies, are driving interest in untapped resources in unconventional deposit types.

In detailed studies of the Southern Urals examining the geochemical behavior of most trace elements in the Proterozoic sedimentary rocks [32-35], data on lithium content were not addressed. This is partly due to the fact that most of the studies in the region during the last century were performed using semi-quantitative spectral analysis, which underestimates lithium concentrations in rocks by 1.5-2 times compared to quantitative determination, for example, flame emission analysis [36]. Recent studies on trace element distribution in the Proterozoic rocks are based on modern analytical techniques related to inductively coupled plasma: mass spectrometry (ICP-MS) [37-40] and atomic emission spectroscopy (ICP-AES) [41-43]. A review of the results from these recent studies, conducted with contributions from one of the present article's authors [44], showed that in the Southern Urals there are two stratigraphic intervals of lithium enrichment in sedimentary rocks, in which the Suran and Avzyan (Kuzha) Mesoproterozoic formations exceed the Clarke value by 2-8 times. At the same time, the established dependencies were based on limited data, and the poor understanding of lithium geochemistry in the Proterozoic rocks of the Southern Urals underscores the need for further geological and geochemical research in this area.

In comparison to earlier studies [41-43], the authors have obtained new geochemical data from over 350 samples of sandstones, shales, and carbonates from various Proterozoic formations on the western slope of the Southern Urals (Fig. 1). The study focuses particularly on lithium-enriched sedimentary rocks of the Suran and formations, Avzvan (Kuzha) which account approximately half of the analyzed samples. This article presents these new results alongside previously published data from other researchers. The study aims to determine the lithium distribution in the Proterozoic sedimentary rocks of the western slope of the Southern Urals and to explain the possible causes of lithium accumulation in the Mesoproterozoic. The authors seek to answer the question of whether the described sediments could be promising for detecting elevated lithium concentrations.

1-5 - undivided deposits: 1 - Paleozoic (PZ), 2 - Vend (V), 3 - upper (RF₃), 4 - middle (RF₂), 5 - lower (RF₁) Riphean; 6 - Taratash metamorphic complex; 7 - Uraltau and Ufaley metamorphic complexes; 8 - igneous rocks: gabbro (a) and granites (b); 9 - geological boundaries; 10 - main tectonic disturbances: a - thrusts; b - faults; 11 - studied sections of various formations and section numbers (Neoproterozoic formations: Minyar - 3 (on the river Zilim near the Tolparovo village); Inzer - 4 (on the river Zilim); Katav - 5, 19: 5 - on the river Zilim, 19 - in the Aktash region. Mesoproterozoic formations: Avzyan - 1, 8, 15: 1 - on the river Tyulmen, 8 - near the Tukan village, 15 - near the Verkhny Avzyan village; Kuzha - 16,

17, 18, 20: 16 - on the river Tanasitkan, 17 - near the Islambaevo village, 18 - in the Aktash region, 20 - on the river Allakuyan; Zigazino-Komarovo - 14, 15: 14 - on the river Bolshoy Avzyan, 15 - near the Verkhny Avzyan village; Suran - 2, 7, 10, 13: 2 - near the Bagaryshta village, 7 - host rocks of the Suran deposit on the river

Suran, 10 – on the river Kuporda, 13 – near the Ismakaevo village; Paleoproterozoic formation: Bolsheinzer – 6, 9, 11, 12, 13: 6 – on the river Bolshoy Inzer, 9 – near the Bzyak village, 11 – borehole 31, 12 – borehole 26, 13 – near the Ismakaevo village, boreholes 18 and 21); 12 – rivers; 13 – settlements.

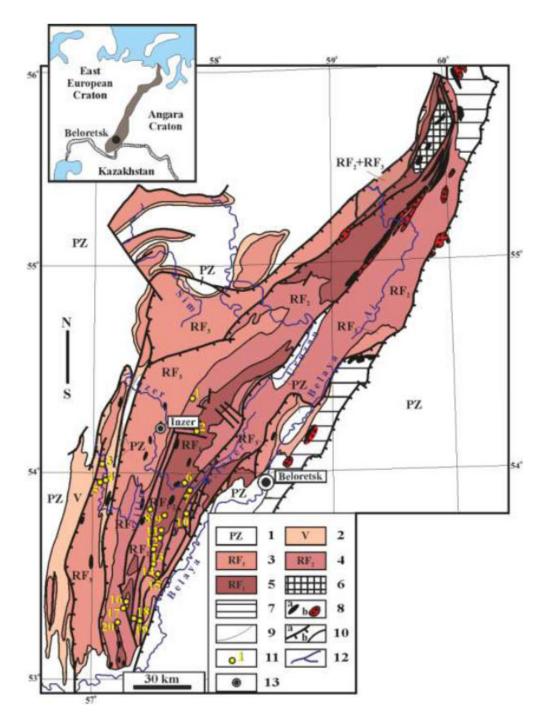


Fig. (1). Schematic geological map of the Bashkirian uplift on the western slope of the Southern Urals according to a previous study [45] (with additions), showing the locations of the studied sections.

2. STRATIGRAPHY OF THE PROTEROZOIC SEDIMENTS OF THE SOUTHERN URALS

Stratigraphy of the Proterozoic sediment of the Bashkirian uplift, located on the western slope of the Southern Urals, is shown in Fig. (2). The distribution area of these sediments within the Bashkirian uplift covers approximately 15,000-20,000 km² [34]. The total thickness of the Proterozoic sediment in the Bashkirian uplift exceeds 12 km, with sedimentation occurring from approximately 1750 to 660 Ma. According to the ISC [44-47], this age interval corresponds to the Paleoproterozoic, Mesoproterozoic, and Neoproterozoic, and according to the GSCR [48], to the Lower, Middle, and Upper Riphean (see Fig. 2). Figure 1 shows the boundaries of the Burzyanian, Yurmatinian, and Karatavian stratons in accordance with the GSS.

Ages are given as per recent studies [46, 49-51].

In the northern and central parts of the Bashkirian uplift, the Proterozoic stratotype formations include Ai (volcanogenic-sedimentary), Satka (terrigenouscarbonate). Bakal (carbonate-terrigenous), Mashak (sedimentary-volcanogenic), Zigalga (sandstonedominated), Zigazino-Komarovo (terrigenous), Avzyan (terrigenous-carbonate), Zilmerdak (terrigenous), Katav (limestone-dominated), Inzer (terrigenous-carbonate), Minyar (carbonate-dominated), and Uk (terrigenouscarbonate). The thicknesses of these formations are shown in Fig. (2). In the central and southern parts of the Bashkirian uplift, stratigraphic facies analogues have been identified for the Paleo- and Mesoproterozoic Ai. Satka. Bakal, and Avzvan formations, which correspond to the Bolsheinzer, Suran, Yusha, and Kuzha formations, respectively.

	ISG			H±5	SCR	Formation		Age, Ma	Lithology	Thickness, m	
Proterozoic	Neoproterozoic	Cryo- genian	or 600			Uk		669±16 663±9	Mudstones, siltstones, sandstones, limestones, including stromatolite ones	300-400	
		Tonian		Upper	Karatau	Minyar		820±77	Limestones and dolomites, including stromatolite ones, mudstones, siltstones	500-800	
						Inzer		844±24 836-805	Sandstones, siltstones, shales, mudstones, limestones, including stromatolite ones	100-1000	
						Katav			Clay limestones, marls, limestones, shales	250-400	
						Zilmerdak		<964±57	Shales, siltstones, sandstones, including arkosic and quartz ones, gravelites, and conglomerates	up to 1500-3000	
	Mesoproterozoic	Stenian	Riphean	Middle Middle	Yurmatau	Avzyan	Bretyak Biktimir Kuzha	>1270	Dolomite and limestones, including stromatolite ones, siltstones, shales, sandstones	1600- 2300	430 1200-1240 700-900
		S	×			Zigazino-Komarovo		1330±20	Shales, siltstones, sandstones	750-1500	
		Ectasian 1200				Zigalga			Quartz sandstones with interbeds and lenses of conglomerates, siltstones, shales	500-700	
			١.			Mashak		1383±31 1386±6	Sandstones, siltstones, shales, conglomerates, metabasalts	1600-3000	
		Calym- mian 0091		1400	Burzyan	Bakal	Yusha	1430±30	Shales, siltstones, sandstones, dolomites and limestones, including stromatolite ones	1500- 1650	900- 1100
		1600		Lower		Satka	Suran	1550±30	Dolomites, including stromatolite ones, limestones, shales, siltstones, sandstones	up to 3000- 3500	1700- 1900
	Paleopro- terozoic Statherian			0±10		Ai	Bolsheinzer	1752±11	Shales, siltstones, sandstones, gravellites, metabasalts, dolomites, limestones	1700- 2500	2150

Fig. (2). The generalized Proterozoic sequence of the Bashkirian uplift on the western slope of the Southern Urals, according to a previous study [46] (with additions).

The terrigenous rocks of the Bashkirian uplift sediments are predominantly represented by sandstones, siltstones, and shales (occasionally mudstones), with rare low-thickness interlayers of gravellites and conglomerates. The carbonate sediments consist of limestones and dolomites.

3. MATERIALS AND METHODS

A total of 20 outcrops from 8 different formations were studied in the central, western, and southern parts of the Bashkirian uplift (see Fig. 1). These outcrops were found along riverbanks and were exposed during the construction of highways, including: Minyar – 1, Inzer – 1, Katav – 2, Avzyan – 3, Kuzha – 4, Zigazino-Komarovo – 2, Suran – 4, and Bolsheinzer – 5. Core samples for the study were also taken from 4 boreholes (Nº 18, 21, 26, 31), which were drilled through Bolsheinzer formation sediments in 2003–2006 (see Fig. 1, numbers 11–13). Along with limited samples from our previous studies [42-44], this investigation analyzes a total of 403 samples: sandstones (66), shales (74), and carbonate rocks (263).

ICP-AES analysis for major elements (Na, Mg, Al, P, Ca, Ti, Mn, Fe) and trace elements (Li, Sc, V, Cr, Co, Ni, Cu, Zn, Sr, Y, Zr, Pb) was carried out on an ICPE-9000 (Shimadzu, Japan) spectrometer at AO INKhP (Joint-Stock Company Institute of Petroleum Refining and Petrochemistry), Ufa (analysts A.M. Karamova and Z.R. Biktimerova), following the technique of Musina and Michurin [52]. The ICP-AES method was selected for this study due to its ability to provide rapid, precise, and accurate multi-element data. The detection limits of the method are sufficient for the quantitative determination of lithium and associated elements in the studied

sedimentary rocks. Compared to ICP-MS, this method is less dependent on the matrix element content in the analyzed solution (up to 1–2 vol.% or higher). It is reliable and cost-effective for analyzing large numbers of samples. Potential spectral interference was minimized through the selection of alternative analytical wavelengths and the application of background correction algorithms. Calibration curves were constructed using multi-element and single-element standard solutions produced by High-Purity Standards (USA).

To ensure measurement accuracy, CRMs of rocks were used: sandstone SA-1, carbonate-silicate loose sediments SGHM-1 and SGHM-3, carbonates SI-1, SI-2, and SI-3, produced by the A.P. Vinogradov Institute of Geochemistry of the Siberian Branch of the RAS (Russia). Both the studied rock samples and CRMs were decomposed in open Teflon vessels using a stepwise acid treatment with HF, HNO₃, HClO₄, and HCl. The acid treatment was carried out at temperatures of 70–150°C for 20 hours until a dry residue was obtained. The chlorides were converted to nitrates and diluted to the required volume with 15 vol.% HNO₃. The detection limit of the method was 0.1 ppm; the sample weight was 0.10–0.25 g.

4. RESULTS AND DISCUSSION

4.1. The lithium concentrations in the Proterozoic formations of the Southern Urals

The data obtained by the authors of this article on the lithium content in sedimentary rocks from the Proterozoic formations of the western slope of the Southern Urals are presented in Table 1. The results of these data, along with previously published research [36-43], are graphically displayed in Fig. (3).

Table 1. The average, minimum, and maximum lithium content (in ppm) in the Proterozoic formations of the western slope of the Southern Urals.

Formations	Sandstones	Shales	Carbonates
Minyar	-	-	2.3±2.9 0.0-23.4 (n=27)
Inzer	-	-	1.1±1.3 0.0-7.6 (n=29)
Katav	-	-	10.9±7.6 0.0-33.6 (n=36)
Kuzha	13.9±3.2 9.7-16.3 (n=4)	29.3±28.0 8.3-103.6 (n=10)	7.4±8.4 0.0-38.2 (n=30)
Avzyan	-	52.1±38.4 12.1-221.2 (n=33)	60.0±57.1 0.0-267.5 (n=58)
Zigazino-Komarovo	9.3±5.8 4.9-19.2 (n=8)	21.9±2.9 20.0-25.3 (n=3)	5.9±1.6 4.1-7.5 (n=4)
Suran	-	87.5±101.8 15.4-302.5 (13)	25.1±32.9 0.0-125.2 (n=41)

(Table 3) contd.....

Formations	Sandstones	Shales	Carbonates
Bolsheinzer	7.6±7.2	43.1±14.6	11.4±13.9
	0.0-33.0	5.0-65.1	0.0-39.0
	(n=54)	(n=15)	(n=38)

Note: The numerator shows the average value and standard deviation; the denominator shows the range of values. n — the number of analyzed samples — is shown in parentheses. A dash (—) indicates no data available.

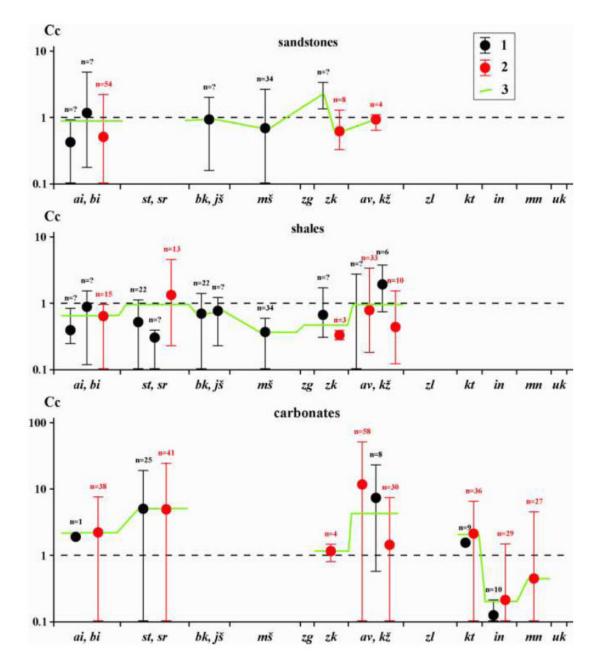


Fig. (3). Variations in lithium concentration coefficients in the Proterozoic formations of the western slope of the Southern Urals

Cc - concentration coefficient of lithium. Cc is calculated as the ratio of the average lithium content in the lithological rock type (sandstones, shales, carbonates) to its Clarke value according to [15]. 1 - calculated Cc values based on data from the literature [36-43]; 2 -

calculated Cc values based on data from the present study (see Table 1); 3 - trend line showing the variation of average Cc values across formations. Circles show the average Cc values. The vertical range bars indicate the minimum and maximum Cc values. n - the number of

analyzed samples. Abbreviations of formation names: ai – Ai, bi – Bolsheinzer, st – Satka, sr – Suran, bk – Bakal, $j\check{s}$ – Yusha, $m\check{s}$ – Mashak, zg – Zigalga, zk – Zigazino-Komarovo, av – Avzyan, $k\check{z}$ – Kuzha, zl – Zilmerdak, kt – Katav, in – Inzer, mn – Minyar, uk – Uk. The differing distances on the horizontal axis correspond to the stratigraphic thickness of each geological formation (Fig. 2). Formations ai-bi, st-sr, bk- $j\check{s}$, and av- $k\check{z}$, grouped closely together, are stratigraphic analogues.

The research results on the western slope of the demonstrate Southern Urals elevated concentrations in the following Proterozoic formations: 1) Bolsheinzer (Cc_{carbonates}=2.3); 2) Suran (Cc_{shales}=1.3; Cc_{carbonates}=5.0); 3) Zigazino-Komarovo (Cc_{sandstones}=2.4 (?); Cc_{carbonates}=1.2); 4) Avzyan (Cc_{shales}=1.4; Cc_{carbonates}=12.0); 5) Kuzha ($Cc_{shales}=1.9$; $Cc_{carbonates}=7.6$); 6) $(Cc_{carbonates}=2.2)$. At the same time, the concentration coefficients of average lithium content in the shales of the Suran, Avzyan, and Kuzha formations range from 1.3 to 1.9, and in carbonates from 5.0 to 12.0, which indicates the maximum concentration of this element in these formations, as well as lithological control and significantly greater enrichment in carbonate rocks compared to terrigenous ones. A similar pattern is observed for the formation, where elevated Bolsheinzer concentration coefficients are recorded in carbonates compared with the lower-clarke content of sandstones and shales. For sandstones of the Zigazino-Komarovo formation and shales of the Avzyan formation, the data (see Fig. 3) were sourced from [40], providing only the range of obtained values without indicating the number of analyzed samples and their average values. In this case, we compared the average value of the established variations with the clarke value, which is not entirely correct for understanding the real distribution of lithium. Consequently, the current data cannot reliably determine the enrichment levels in rocks of the Zigazino-Komarovo formation. The obtained data confirm the stratigraphic confinement of enriched intervals to the Suran and Avzyan (Kuzha) Mesoproterozoic formations.

It should be noted that a comparative analysis of lithium behavior in Mesoproterozoic sedimentary formations of various regions of the world faces certain challenges. These are primarily due to the limited amount of published geochemical data [53]. For example, a recent study [54] provided data on the average lithium content in greywackes only for Mesoproterozoic sediments of China as a whole. While in another recent review [55], focused on lithium metallogeny in Europe throughout the Earth's evolution, the time interval from 1800 to 1140 Ma was not considered. However, these researchers demonstrate in their global review that exogenous processes in Paleo- and Neoproterozoic sedimentary formations can lead to significant lithium enrichment.

4.2. Reasons for lithium enrichment in the Proterozoic formations of the Southern Ural

Possible reasons for lithium enrichment in the

sedimentary rocks of the identified stratigraphic intervals are its endogenic input due to magmatic and hydrothermal activity and/or the primary enrichment of sediments of the Suran and Avzyan (to a lesser extent, possibly the Bolsheinzer and Katav) formations, which accumulated under conditions close to evaporitic sedimentation. Lithium enrichment in the host sedimentary rocks of the Avzyan and Kuzha formations, which are intruded by magmatic bodies (gabbro-dolerite dikes), supports an endogenic source. For example, in the section on the Tyulmen River (see Fig. 1, outcrop number 1), three gabbro-dolerite dikes intrude the dolomite host rocks of the upper part of the Avzyan formation [43]. In this section, the lithium concentration in carbonate rocks increases toward the contacts with the dikes, reaching peak values of 267.5 ppm, with an average content of 84.5 \pm 46.4 ppm (n = 34). At the same time, changes in the geochemical and crystallochemical characteristics are observed in the dolomites due to the influence of postmagmatic fluids [56]. In contrast, lithium enrichment is typically absent in the sedimentary rocks of the Kuzha Formation where dikes are not present. For example, in the dolomite section near Islambaevo village (Fig. 1, outcrop number 17), the average lithium concentration is 3.4 ± 2.7 ppm (n = 7), consistent with near-Clarke values.

The positive correlation between Li, F, and Mg, or between Li, F, Fe, and Mg (and possibly B), serves as evidence for a magmatic lithium source in enriched sedimentary rocks [57-59]. In the shales and carbonates of the Kuzha Formation, the observed co-enrichment of lithium and fluorine similarly indicates an endogenic source [36].

It is well known that felsic igneous rocks contain significantly higher lithium concentrations compared to mafic ones [15], and large deposits of this metal are often associated with them [20, 21]. At the same time, only dikes of mafic igneous rocks have been found in the studied sedimentary rock sections on the western slope of the Southern Urals. Recent studies have provided substantial evidence that mafic and intermediate igneous rocks in modern volcanic eruptions can also exhibit significant lithium enrichment [60-64]. However, it is currently difficult to unequivocally determine whether the lithium enrichment in the sedimentary rocks of the Suran and Avzyan formations is related to magmatic influence, given the limited available data on lithium content in magmatic complexes of various ages on the western slope of the Southern Urals [44, 65].

An alternative explanation is the primary lithium enrichment in the carbonate rocks of the Suran and Avzyan formations, possibly related to evaporitic sedimentation. Lithium compounds in evaporite basins precipitate during the late stages of evaporation. Host sediments contain 30-1500 ppm Li in closed-type basins and 20-150 ppm Li in open-type basins [66]. Large lithium deposits are known to occur in evaporites [17]. The most noteworthy of several lithium brine systems in China is Zabuye Lake in Tibet [58]. It is an evaporite basin where a lithium salt (Li_2CO_3) precipitates as part of the evaporite

mineral sequence, and where there is no volcanism or hydrothermal activity [17].

The sedimentary carbonates of the Satka, Suran, Avzvan, and Kuzha formations are characterized by indicators of the former presence of evaporites [67-72]. Evaporitic sedimentation conditions during Satka-Suran period are evidenced by the presence of gypsum crystals in the carbonate sediments of the Suran Formation [67] and by collapse breccias in the Satka Formation, located at the same stratigraphic levels and formed through the dissolution of interbeds and nests of evaporite minerals [71]. In the fluorites of the Suran deposit, localized within the Suran Formation, highsalinity fluid inclusions and the correspondence of oreforming brines to the evaporite trend have been established [72]. The study of various geochemical features of the fluorites showed that earlier generations of gray and violet fluorites precipitated from fluorineenriched evaporitic brines, whereas green fluorites, formed through metasomatic replacement of earlier generations, had another fluorine source likely associated with granitoids [34, 72]. Gypsum pseudomorphs have been found in the dolomites of the Avzyan Formation [68], and large gypsum crystals with sulfur isotope characteristics of sedimentary origin have been found in the dolomites of the Kuzha Formation [70]. Thus, lithological and isotopic data confirm that sedimentation conditions during the Satka-Suran and Avzyan-Kuzha periods were close to evaporitic.

In general, it can be assumed that in the established stratigraphic intervals of the Southern Urals, the Li enrichment of sedimentary rocks was caused by two combined factors: sedimentation under near-evaporitic conditions, as well as the subsequent influence of postmagmatic fluids on sedimentary rocks due to the intruding of gabbrodolerite dikes. Lithium in deposits associated with evaporites is redistributed to varying degrees by hydrothermal activity, superimposed on primarily enriched sedimentary rocks in this metal [17, 55, 73].

4.3. Lithium-bearing minerals in the Proterozoic rocks of the Southern Urals

In the carbonate rocks of the Avzyan formation section on the river Tyulmen and near the Tukan village (see Fig. 1, outcrops numbers 1 and 8, respectively), and the intruding igneous rocks, lithium shows a direct correlation with chlorite content [43, 65]. It is known that lithium can replace Mg and Fe in chlorite to some extent [74], and most likely, lithium in the rocks on the River Tyulmen is associated with chlorite.

In carbonate rocks of the Suran formation near Bagaryshta village (see Fig. 1, outcrop number 2), lithium is most likely contained in phlogopite [41]. This is indicated by the significant presence of F-bearing phlogopite and strong positive geochemical correlations between F and Li (r=0.97) and between F and Rb (r=0.93). According to Shirobokova [36], lithium in rocks of the Kuzha ore field occurs in micas. As proof, the author

of this study also demonstrates a high positive correlation between F and Li.

Elevated lithium concentrations have been established in carbonate-terrigenous sediments of the Suran formation, which hosts the Suran fluorite deposit [75]. Fluorides of the cryolite group, including ussingite $(Ba_2MgAl_2F_{12})$, pachnolite $(NaCaAlF_6\cdot H_2O)$, and particularly cryolithionite $(NaLi_3[AlF_6]_2)$, play an important role in the structure of the near-ore halo. Diffraction studies have confirmed the presence of lithium-bearing minerals in 11 boreholes [75]. According to spectral analysis, the lithium oxide content reaches industrial values of 0.1 wt. %. Cryolithionite is the dominant lithium-containing mineral, accounting for 0.1-7 wt. % of the bulk composition.

4.4. Prospects for finding industrial lithium concentrations in the Proterozoic formations of the Southern Urals

The study shows that lithium-enriched sedimentary rocks of the Suran and Avzyan formations have prerequisites for hosting industrial concentrations of this alkali metal. From this perspective, the host rocks of the Suran formation and ores from the Suran deposit are of particular interest, as they contain independent lithium minerals and almost economic concentrations. Moreover, the patterns of lithium distribution in the rocks of the deposit have not yet been identified [75], and this issue requires focused attention in future studies.

The sediments of the Avzyan Formation, probably enriched during sedimentogenesis, may exhibit very high lithium concentrations in areas that were intensively exposed to magmatic fluids during epigenesis. Our studies show that lithium concentrations in the carbonate rocks of this stratigraphic level, where they are intruded by gabbro-dolerite dikes, exceed the Clarke value by 53.5 times.

CONCLUSION

Two stratigraphic intervals of lithium enrichment have been identified in the Proterozoic sedimentary rocks of the western slope of the Southern Urals: the Suran and Avzyan Mesoproterozoic formations. The maximum enrichment of this alkali element occurs in carbonate rocks, where the average lithium concentration exceeds the Clarke value by 5-12 times, compared to terrigenous rocks, in which it exceeds the Clarke value by 1.3-1.9 times.

On the western slope of the Southern Urals, the identified stratigraphic intervals of lithium-enriched carbonate rocks in the Suran and Avzyan formations are characterized by indicators of evaporitic sedimentation, which may explain the presence of elevated lithium concentrations. However, the same studied sections clearly demonstrate the influence of postmagmatic fluids on lithium enrichment in the sedimentary rocks. Overall, our analysis suggests that lithium enrichment in the Satka-Suran and Avzyan-Kuzha intervals likely resulted from two combined factors: sedimentation under near-

evaporitic conditions, and the subsequent influence of postmagmatic fluids on the sedimentary rocks due to the intrusion of gabbro-dolerite dikes. The combination of both factors likely makes the sediments of these formations particularly prospective for further exploration of lithium occurrences.

The presented data demonstrate that the Suran and Avzyan Mesoproterozoic formations on the western slope of the Southern Urals have the potential to host economically significant lithium concentrations. Of particular interest are the host rocks of the Suran Formation in the vicinity of the Suran fluorite deposit.

STUDY LIMITATIONS

This study provides new insights into lithium enrichment in Proterozoic sedimentary rocks on the western slope of the Southern Urals. However, certain limitations should be considered. First, the interpretation of a magmatic source for lithium-rich fluids remains hypothetical due to incomplete geochemical data on magmatic complexes of various ages in the region. Second, evidence for evaporitic sedimentation conditions, which is crucial for the proposed primary enrichment model, is based on local lithological indicators, such as gypsum pseudomorphs and collapse breccias. Variability in the preservation and distribution of these indicators across the studied sections introduces uncertainty into the precise reconstruction of paleofacies and limits the universal applicability of this model to all formations.

Future research should focus on the quantitative assessment of the proposed genetic model of postmagmatic fluid interaction with evaporite-bearing sediments, which would test the hypothesis of lithium leaching and redistribution. In addition, isotopic data (e.g., lithium, strontium, and magnesium) could serve as robust indicators to distinguish between the contributions of evaporitic brines and postmagmatic hydrothermal fluids, as well as to better constrain the lithium source and sedimentation conditions.

Finally, direct geochemical comparisons with other similar lithium-enriched Proterozoic sedimentary rocks worldwide are limited due to the scarcity of detailed published geochemical data. This limitation restricts the ability to fully compare our results with global conditions and to determine universal mechanisms for lithium enrichment in sedimentary rocks.

AUTHORS' CONTRIBUTIONS

The authors confirm their contributions to the paper as follows: study conception and design: S.V. Michurin and G.M. Kazbulatova; data collection: S.V. Michurin and Z.R. Biktimerova; analysis and interpretation of results: S.V. Michurin, Z.R. Biktimerova, and G.M. Kazbulatova; draft manuscript: S.V. Michurin. All authors reviewed the results and approved the final version of the manuscript.

LIST OF ABBREVIATIONS

IEA = International Energy Agency

USGS = United States Geological Survey

ICP-MS = Inductively Coupled Plasma Mass

Spectrometry

ICP-AES = Inductively Coupled Atomic Emission

Spectroscopy

CRMs = Certified Reference Materials

ISC = International Stratigraphic Chart

GSCR = General Stratigraphic (Geochronological)

Chart of Russia

GSS = General Stratigraphic (Geochronological)

Scale

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The data and supportive information are available within the article.

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise. $\ \ \,$

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