

## Uranium-Bearing Srilankite from High-Pressure Garnetites of the Southern Urals: First Data

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**Abstract**—This work presents the results of studying srilankite, a rare zirconium titanate ( $ZrTi_2O_6$ ), associated with ilmenite, rutile, zircon, uraninite, and other minerals discovered in high-pressure garnetites of the Iherzolite Mindyak massif (Southern Urals). Srilankite occurs as inclusions in ilmenite and rutile of up to several tens of microns in size. It was established for the first time that srilankite contains a significant  $UO_2$  admixture (up to 20%). The negative correlation between Zr and U is evidence of isomorphism in the srilankite–brannerite system. The association of srilankite with high-Zr rutile indicates that formation of these minerals occurred at  $T > 850^\circ C$ .

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The mineral srilankite is a rare Zr–Ti-oxide mineral ( $ZrTi_2O_6$ ) with an orthorhombic  $PbO_2$  structure. It was first found in association with zirconolite, baddeleyite, geikielite, spinel, and perovskite in placers of Rakwana, Sri Lanka [1]. Later, this mineral was discovered as inclusions in pyrope–almandine garnets from lamprophyres of the Yagodka kimberlite pipe in the Tobuk–Khatysyr field (Aldan Shield, Yakutia) [2], in pyrope garnets from the Garnet Ridge kimberlite pipe (Plateau Colorado, United States) [3], in granulites of Western Norway and the Kola Peninsula [4, 5], and in gabbro of the Atlantis II transform zone in the Indian Ocean [6]. In the Urals, srilankite was first found in 2014 as intergrowths with ilmenite and rutile in sapphirine-bearing metamorphosed ultramafic rocks of the Ilmeny–Vishnevogorsk complex (V.G. Korinevskii, <http://webmineral.ru/deposits/item.php?id=2304>).

According to most chemical analyses available, the Zr/Ti stoichiometric ratio in srilankite is 0.5. Deviations from this value are attributed by the capturing of host minerals matrix during X-ray microprobe study of too small srilankite grains.

The following trace elements are found in srilankite (wt %): FeO = 0–1.6%, MgO = 0–0.75%, MnO = 0–0.03%, HfO<sub>2</sub> = 0.4–0.7%, Al<sub>2</sub>O<sub>3</sub> = 0–0.5%, CaO = 0–0.4%, SrO = 0–0.9%, Cr<sub>2</sub>O<sub>3</sub> = 0–0.62%, V<sub>2</sub>O<sub>5</sub> = 0–0.24%, Ta<sub>2</sub>O<sub>5</sub> = 0–0.2%, Nb<sub>2</sub>O<sub>5</sub> = 0–0.25% [1–3,

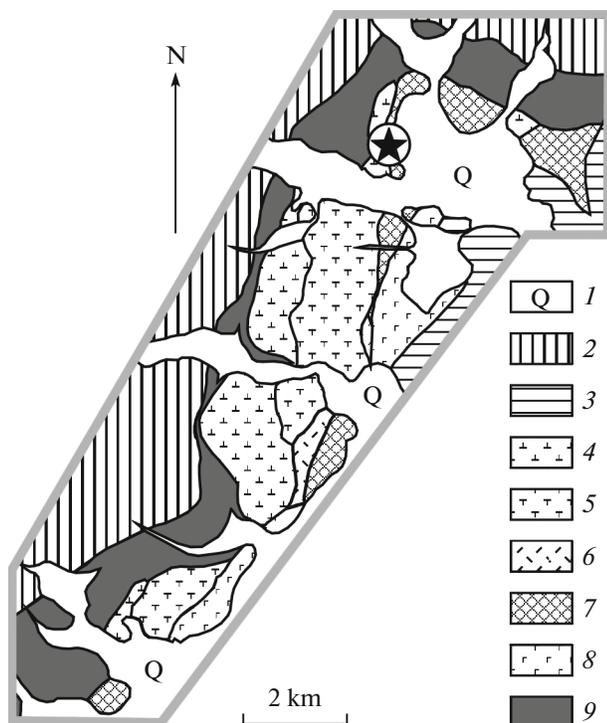
5, 6]. According to the data published, the U content in srilankite does not exceed a few tenths of a percent of  $UO_2$  [1]. As evidenced from Korinevskii's data, the  $UO_2$  content in srilankite from the Ilmeny–Vishnevogorsk complex reaches 10%.

We have found srilankite in high-pressure garnetite from the Mindyak Iherzolite massif, located in the Main Uralian Fault Zone (MUF) in the Southern Urals (Fig. 1). It was established for the first time that srilankite is characterized by a wide variation of  $UO_2$  (up to 20 wt %). Garnetite along with other high-pressure garnet-bearing rocks occurs as blocks varying in size from a few centimeters to several meters in rodinized polymictic breccias with aluminosilicate or serpentinite cement, confined to the contact zone between Iherzolites and banded dunite–clinopyroxene–gabbro series in the northern part of the massif (Fig. 1). The geological characteristics of the Mindyak massif, breccias, and compositions of high-pressure rocks are given in [7, 8]. According to these data, the  $P$ – $T$  conditions of garnetite formation are as follows: pressure of 12–16 kbar and temperature of 800–1000°C. The U–Pb (SHRIMP-II) age of zircons from garnetites is 408–399 Ma [8], which corresponds as a whole to that of high-pressure rocks of the Mindyak massif [9, 10].

The chemical composition of srilankite was studied using CAMECA SX 100 X-ray microprobe at the “Geoanalitik” Center (Institute of Geology and Geochemistry, Ural Branch, Russian Academy of Sciences). Analyses were performed using a focused beam (1–3 μm) with an accelerating voltage of 15 kV and a

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**Fig. 1.** Geological scheme of the Mindyak massif after E.A. Denisova [7]. (1) Quaternary deposits, (2) Proterozoic sedimentary rocks, (3) Devonian and Carboniferous volcanogenic rocks, (4) Iherzolites, (5) plagioclase Iherzolites, (6) harzburgites and dunites, (7) wehrlite and clinopyroxenites, (8) gabbro, (9) zone of serpentinite mélangé. The location of breccias with high-pressure garnet-bearing rocks is shown with a star.

beam current of 30 nA. The following certified standards were used: diopside, orthoclase, rutile,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{LiNbO}_3$ ,  $\text{ZrSiO}_4$ . The following are the standard deviation of estimating contents of elements (wt %): ~0.02 (Si), 0.75–1.15 (Ti), 0.01–0.03 (Al), 0.09–0.15 (Fe), 0.35–0.46 (Zr), 0.20–0.55 (U), 0.09–0.13 (Hf). The duration of the measurement of the intensity at the peak of the analytical lines was 10 s, and that on either side of the peak was 5 s.

The results of the chemical analysis of srilankite and associated minerals are given in Tables 1 and 2.

Garnetite (80–90%) is composed of large (up to 1–1.5 cm) grains of pale orange high-Ca garnet of pyrope–almandine composition, and the intergranular space is filled with greenish to reddish-brown high-alumina amphibole. The rock contains higher contents of rutile, ilmenite, apatite, and zircon, occurring as inclusions in garnet as well as in the intergranular space, sometimes as intergrowths with other minerals. This is a reason for the anomalous geochemistry of rocks, enriched in Ti, Zr, Nb, P, and REEs. In terms of the chemical composition (Table 2), garnetite does not correspond to igneous rocks and can be considered as a metasomatic rock developed after a mafic

protolith under high-pressure conditions. Locally, garnetite has pockets of irregular shape (up to 15 cm with coarse grained and pegmatoid texture. These pockets are composed of large crystals of pale brown amphibole and rutile of up to several centimeters in size. Rutile contains regularly oriented ilmenite plates (Ilm-I) up to few millimeters long, as well as tiny lamellae of ilmenite (Ilm-II) and uraninite of a few tens of microns long and 1–2 microns wide (Fig. 2). We suppose that these lamellae were formed during an exsolution of the U-Fe-rich rutile.

In terms of composition, rutile is characterized by high contents of  $\text{FeO} = 0.2\text{--}0.6\%$ ,  $\text{ZrO}_2 = 0.4\text{--}0.6\%$ ,  $\text{Nb}_2\text{O}_5 = 0.2\text{--}0.4\%$ ,  $\text{V}_2\text{O}_3 = 0.4\text{--}0.6\%$ , and U up to 500 ppm. The high Zr content in rutile in the presence of coexisting zircon is an evidence that it was formed under a temperature of at least  $850^\circ\text{C}$  [11, 12]. Ilmenite, occurring as large plates in rutile, contains insignificant admixtures of MnO up to 1% and MgO up to 3.5%.

Srilankite occurs often as subidiomorphic inclusions of rectangular or rhomboidal habit or more complex morphology in ilmenite-I (Ilm-I) (Figs. 2b–2d). Srilankite grains vary in size from a few to one hundred microns. Sometimes, they form chains (Fig. 2a). Srilankite occurs rarely as inclusions in rutile and intergrowths with ilmenite or uraninite (Fig. 2d). In reflected light under the microscope, srilankite is characterized by a high reflectivity and white color. The morphology of srilankite and its relationships with host minerals do not allow to interpret its origin with certainty.

The study of srilankite using X-ray microprobe has revealed that it contains unusually high uranium contents varying from 1 to 20%  $\text{UO}_2$ , which had not been noted earlier for this mineral. It was established that srilankite have zoning, expressed by decreasing of U content from core to rim of grains (Table 1). The concentrations of U and Zr in srilankite have a negative correlation that was established by X-ray microprobe data and element mapping (Fig. 3, Table 1). Uranium complements zirconium up to one formula unit in srilankite stoichiometry, while iron in a small amount up to 1.5% FeO, occupies the position with titanium.

These facts allow to assume the existence of a solid solution between srilankite ( $\text{ZrTi}_2\text{O}_6$ ) and brannerite ( $\text{UTi}_2\text{O}_6$ ). The formula of the studied uranium-bearing srilankite from garnetites of the Mindyak massif can be represented as:  $(\text{Zr}_{0.74\text{--}0.98}\text{U}_{0.01\text{--}0.25}\text{Fe}_{0.05}\text{Ti}_{1.94\text{--}1.97})\text{O}_6$ . Hafnium occurs as an admixture in srilankite (from 0.2 to 1.4%  $\text{HfO}_2$ ). The uranium-enriched central parts of srilankite grains contain small inclusions of up to 3  $\mu\text{m}$ , enriched in U, Ca, and Fe and depleted in Zr and Ti relative to the host mineral. Because of the small size of these inclusions, it is hardly possible to determine the real composition or to identify these inclusions.

**Table 1.** Composition of the uranium-bearing srilankite from garnetite of the Mindyak massif (Mk-163), wt %

Component	Inclusions in ilmenite-I								Inclusions in rutile		
	1**c	1 r	2	3	4	5	6	7	8	9	10
TiO <sub>2</sub>	48.63	54.57	48.27	49.87	51.21	51.43	52.58	54.18	49.79	53.72	56.01
Al <sub>2</sub> O <sub>3</sub>	0.40	0.22	0.38	0.40	0.38	0.32	0.33	0.26	0.34	0.17	0.28
FeO*	1.09	1.39	1.11	1.18	1.51	1.09	1.17	1.41	0.38	0.42	0.10
ZrO <sub>2</sub>	28.74	39.43	28.67	31.39	33.19	35.92	37.43	39.32	30.64	38.56	42.98
UO <sub>2</sub>	20.77	3.25	20.53	16.26	14.23	10.50	8.65	2.70	18.03	5.95	0.76
HfO <sub>2</sub>	0.28	1.34	0.20	0.32	0.46	0.64	0.78	1.13	0.21	1.38	1.21
Total	99.91	100.20	99.16	99.42	100.98	99.90	100.94	99.00	99.39	100.20	101.34
Formula coefficients based on six oxygen atoms											
Ti	1.956	1.981	1.955	1.962	1.960	1.952	1.954	1.983	1.974	1.979	1.986
Al	0.025	0.013	0.024	0.025	0.023	0.019	0.019	0.015	0.021	0.010	0.015
Fe <sup>2+</sup>	0.049	0.056	0.050	0.052	0.064	0.046	0.048	0.057	0.017	0.017	0.004
U	0.247	0.035	0.246	0.189	0.161	0.118	0.095	0.029	0.211	0.065	0.008
Zr	0.749	0.928	0.753	0.800	0.823	0.884	0.901	0.933	0.787	0.921	0.976
Hf	0.004	0.018	0.003	0.005	0.007	0.009	0.011	0.016	0.003	0.019	0.016

FeO\*, total iron as FeO. 1\*\*, numbers of different srilankite inclusions; c, core and r, rim of a zonal grain.

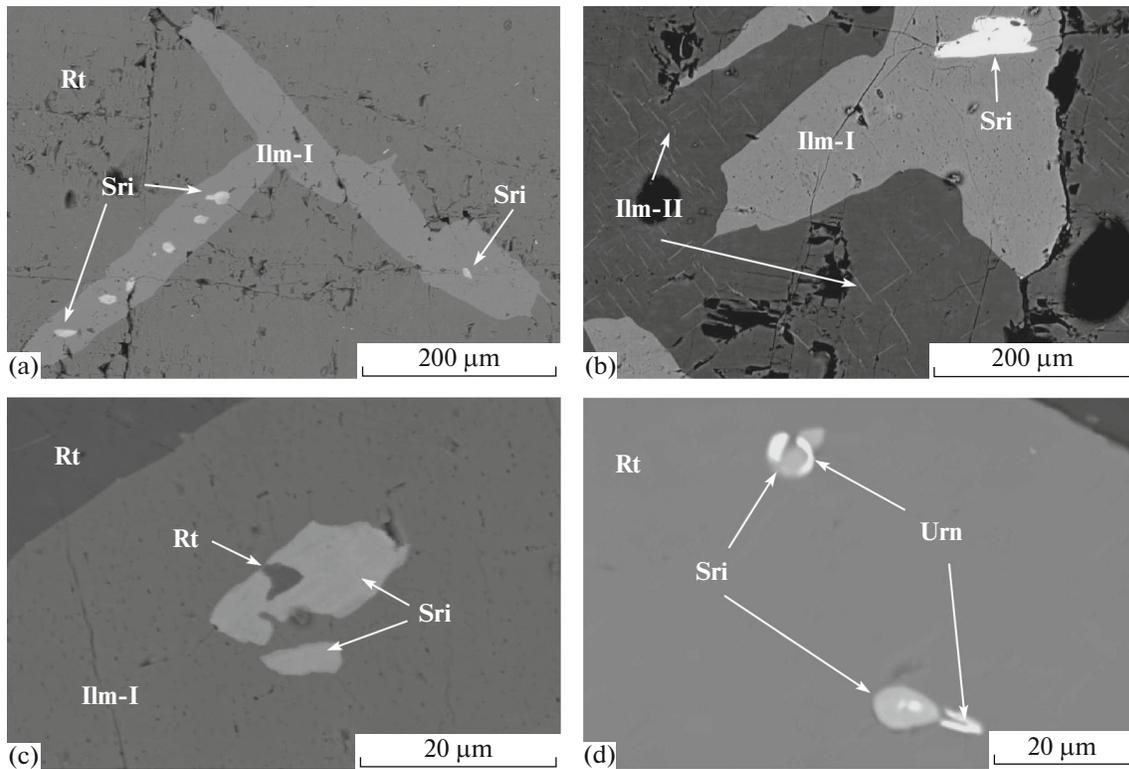
**Table 2.** Composition of garnetite and rock-forming minerals, wt %

Component	Garnetite	Garnet		Amphibole		Rutile		Ilmenite-I	
SiO <sub>2</sub>	36.50	41.05	40.50	41.37	40.21	0.01	0.02	n.d.	n.d.
TiO <sub>2</sub>	1.87	0.16	0.10	0.73	1.33	98.35	98.67	54.25	54.68
Al <sub>2</sub> O <sub>3</sub>	19.13	21.65	21.92	19.05	18.40	n.d.	0.06	0.08	n.d.
FeO*	12.32	10.69	12.08	7.50	4.75	0.54	0.36	42.26	41.69
MnO	0.23	0.52	0.24	0.11	n.d.	n.d.	n.d.	0.27	0.45
MgO	11.80	13.47	12.46	13.46	15.26	0.01	n.d.	2.59	3.53
CaO	14.41	13.40	12.71	12.63	12.88	n.det.	n.det.	n.det.	n.det.
Na <sub>2</sub> O	0.60	n.det.	n.det.	1.89	1.69	n.det.	n.det.	n.det.	n.det.
K <sub>2</sub> O	0.05	n.det.	n.det.	0.67	1.86	n.det.	n.det.	n.det.	n.det.
ZrO <sub>2</sub>	n.det.	n.det.	n.det.	n.det.	n.det.	0.51	0.50	n.d.	n.d.
V <sub>2</sub> O <sub>3</sub>	n.det.	n.det.	n.det.	n.det.	n.det.	0.50	0.60	0.13	0.20
Nb <sub>2</sub> O <sub>5</sub>	n.det.	n.det.	n.det.	n.det.	n.det.	0.32	0.21	n.d.	n.d.
P <sub>2</sub> O <sub>5</sub>	0.52	n.det.	n.det.	n.det.	n.det.	n.det.	n.det.	n.det.	n.det.
LOI	1.90	n.det.	n.det.	n.det.	n.det.	n.det.	n.det.	n.det.	n.det.
Total	99.33	100.94	100.00	97.41	96.38	100.24	100.43	99.64	100.56

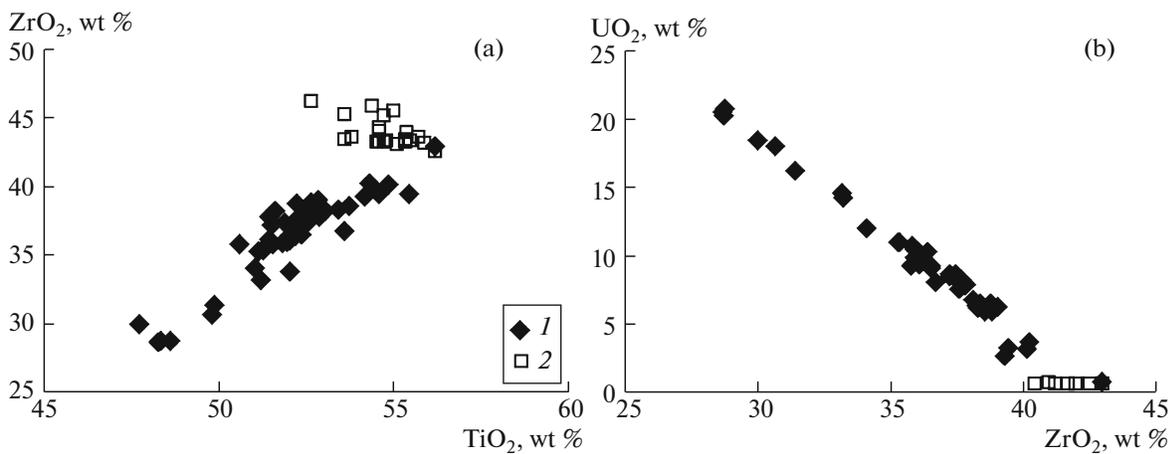
FeO\*, total iron as FeO. n.d., not detected; n.det., not determined. Ilmenite-I, ilmenite inclusions in rutile.

Data on the conditions of srilankite crystallization are scarce. This mineral was synthesized in the presence of water at  $P < 1.5$  kbar and  $T = \sim 900^\circ\text{C}$  [1]. Other experiments showed that srilankite can also be stable under high pressure and temperature [13, 14]. The occurrence of a srilankite inclusions in mantle garnets confirms this conclusion [2]. Wang et al. [3]

suggested that srilankite, occurring as inclusions in kimberlitic pyropes, could have originated from high-magnesian and low-silica melts at  $T = 600\text{--}800^\circ\text{C}$  and a pressure ranging from 1.5 to 30 kbar [3]. Srilankite crystallized under conditions of the granulite and eclogite facies metamorphism at  $P > 10$  kbar and  $T = 800\text{--}850^\circ\text{C}$  [4, 5]. Morishita et al. [6] discovered a



**Fig. 2.** BSE images of intergrowths of U–Zr–Ti minerals in garnetites (JSM-6390 scanning electron microscope, “Geoanalitik” Center, Institute of Geology and Geochemistry, Ural Branch, Russian Academy of Sciences. (a–b) Idiomorphic inclusions of srilankite (Sri) in ilmenite-I (Ilm-I) in intergrowths with rutile (Rt) with thin ilmenite-II lamellae (Ilm-II), formed as a result of an exsolution of the rutile solid solution; (c) subidiomorphic srilankite inclusions in ilmenite-I; (d) intergrowths of srilankite with uraninite (Urn), occurring as inclusions in rutile.



**Fig. 3.** Diagrams  $ZrO_2$ – $TiO_2$  (a) and  $UO_2$ – $ZrO_2$  (b) for srilankite: (1) from garnetite of the Mindyak massif, (2) compositions of srilankites after [3, 5, 6].

rutile–ilmenite–srilankite association in a gabbro dike, cutting MOR peridotites and suggested that these minerals crystallized at the magmatic stage before the metamorphic recrystallization of rocks. However, a good consensus exists among researchers that the formation of srilankite occurred in a system enriched in highly charged elements and depleted in  $SiO_2$ .

Garnetites of the Mindyak massif are highly undersaturated in  $SiO_2$  and enriched in highly charged elements. Srilankite occurs in association with rutile and ilmenite. If we assume that the large ilmenite plates (Ilm-I), containing srilankite inclusions, intergrowth with rutile and don't represent a result of exsolution, like fine ilmenite nets (Ilm-II) within rutile, then the

uranium-bearing srilankite is most likely a primary mineral equilibrated with Zr-bearing rutile, ilmenite, almandine–pyrope garnet and high-alumina amphibole. In addition, this is confirmed by idiomorphic shape and zoning of srilankite grains. As was noted above, the  $P$ – $T$  parameters of such equilibrium are 12–14 kbar and 800–1000°C. The high Zr content in rutile is evidence that the temperature of its formation was >850°C [11, 12]. Therefore, srilankite crystallized in the course of metasomatic transformation of mafic substratum to garnetites and its enrichment by Ti, Zr, Nb, U and P under these high- $T$  and high- $P$  conditions. The most likely geological setting where such processes took place is a mantle wedge above the subducted oceanic plate with a break off zone and upwelling of high- $T$  mantle material through this window. It creates a positive thermal anomaly and provides a migration of ascending fluids carrying rare elements. This process was preceded by or coincided in time with the formation of high-pressure rocks in Late Silurian–Early Devonian [8–10].

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