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Pentlandite and its alteration products in serpentinites of the Itkulsky ultrabasic massif (Southern Urals)

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Abstract

The relevance of the work is due to the need to study the mineralogy of the only indigenous manifestation of jewelry olivine within the Ural region.

The purpose of the work is to study pentlandite and the products of its supergene alteration in serpentinites of the Itkulsky ultrabasic massif in the Southern Urals.

Research methodology. The composition of some minerals was analyzed using a scanning electron microscope JSM-6390LV from Jeol with an energy dispersive attachment INCA Energy 450 X-Max 80 from Oxford Instruments (analyst L. V. Leonova). The same instrument was used to obtain images of minerals in BSE (back-scattered electron) mode. X-ray structural study of minerals was carried out on an XRD-7000 X-ray diffractometer from Shimadzu with polycapillary optics and a high-temperature attachment NTK-1200N from Anton Paar for operation in the temperature range 25–1500 °C (analyst O. L. Galakhova). Conditions: copper radiation, V = 40 kV, I = 30 mA, step size – 0.02°.

Results. Pentlandite is the main sulfide mineral of antigorite serpentinites; it is characterized by a fairly pure chemical composition; the only impurities in the mineral are cobalt (from 0 to 1.18 wt. %). According to the Ni/Fe ratio, the sulfide belongs to nickel and pentlandite proper. Smythite replaces pentlandite grains along the cracks and at the edges. Chemical composition, wt. %: S – 40.81; Fe – 37.65; Co – 1.66; Ni – 19.87, well calculated for the crystal chemical formula of smythite – $(Fe_{5.83}Ni_{2.93}Co_{0.24})_{9.00}S_{11.00}$. Cronstedtite replaces the pentlandite matrix in the form of veined segregations. It is distinguished by its chemical composition: SiO_2 – 17,82; Fe_2O_3 – 40,00; NiO – 11,02; FeO – 18,06; MnO – 0,57; MgO – 2,23; CaO – 1,30; H_2O – 9,00 (by difference in accordance with the standard), which is calculated based on the crystal chemical formula of Ni-Mg-bearing cronstedtite – $(Fe^{2+}_{0.95}Ni_{0.71}Mg_{0.21}Ca_{0.09}Mn_{0.03})_{1.99}Fe^{3+}_{1.01}[(Si_{1.12}Fe^{3+}_{0.88})_{2.00}O_5](OH)_{3.80}$.

Conclusions. Pentlandite from antigorite serpentinites of the Itkulsky ultrabasic massif (Southern Urals) was studied. Under the influence of weathering processes, most of the pentlandite grains were partially replaced by secondary sulfide – smythite and ferruginous serpentine – cronstedtite.

***Keywords*:** pentlandite, smythite, cronstedtite, antigorite serpentinite, Itkulsky massif, Southern Urals.

Introduction

The Itkulsky ultrabasic massif is located in the north of the Chelyabinsk region (Southern Urals) directly east of Lake Itkul (Fig. 1, *a*). About fifteen chromite ore occurrences were discovered within the massif [1], most of which were mined in tsarist times. Even at the beginning of the 20th century, it was mentioned that in some mines collection samples with plates of pink chrome chlorite were mined [2]. In the same massif on Mount Vishnyovaya in 1846, the only occurrence of jewelry olivine in the Urals was discovered, which was first mistaken for a new mineral – glinkite [3], but almost immediately correctly attributed to chrysolite [4]. Olivine was described in more detail much later [5, 6]. At the same time, the mineralogy of the host antigorite serpentinites was extremely poorly studied.

Geological position of the Itkulsky massif. Geologically, Mount Vishnyovaya is entirely composed of antigorite serpentinites, carbonated and talcized in areas, which occur in metamorphic rocks of the Middle Riphean Saitovskaya group (Fig. 1, *b*). This block of serpentinites, up to 3 km in size, is the eastern fragment of the Itkulsky ultrabasic massif, the main body of which is located directly on the eastern shore of Lake Itkul. The ultrabasic massif stretches along the eastern shore of the lake within 8 km in length and up to 2 km in width. In the eastern and northern parts of the massif, serpentinites are intruded by small bodies of granitoids of Carboniferous age.

It was previously established that the olivine veins at Mount Vishnyovaya are represented by metasomatic olivinites [6]. The thickness of the veins usually does not exceed 10 cm (Fig. 2), and in places of swelling it reaches 30 cm. In the host serpentinites, olivinitization, talcification and carbonatization are noted at the contact with the veins. In addition to olivine veins, the antigorite serpentinites of Mount Vishnyovaya contain clinochlore and tremolite veins up to 10 cm thick. When studying the antigorite serpentinites, scattered dissemination of pentlandite was discovered, which underwent secondary alterations. The study of this mineralization is presented in this work.

Research methods

All analytical studies of the samples were carried out at the Institute of Geography, Ural Branch, Russian Academy of Sci-

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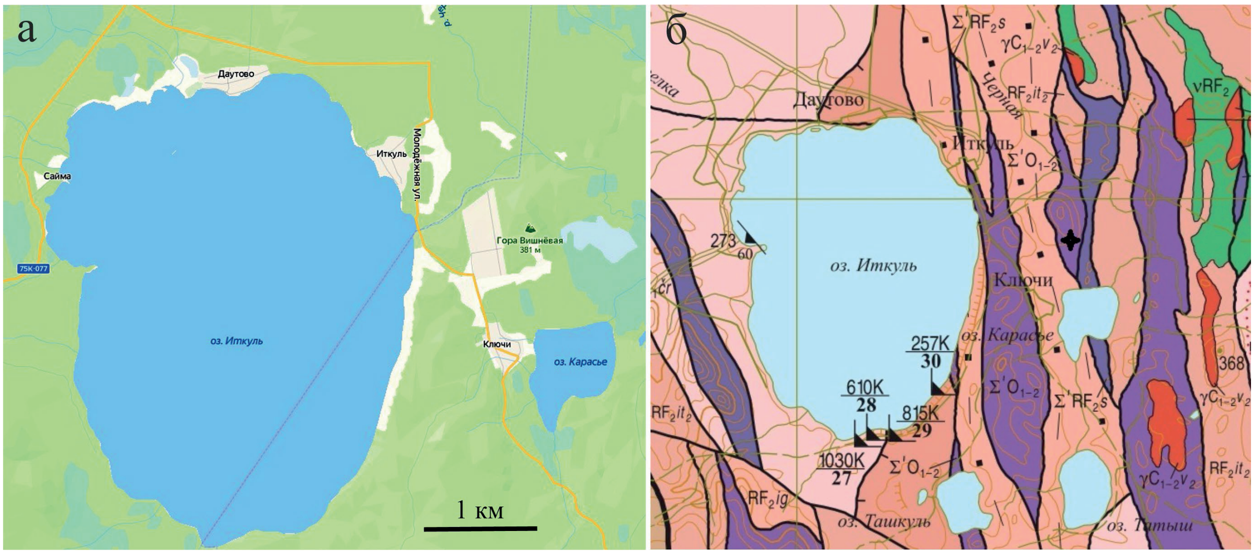

Figure 1. Sampling site (indicated by a star) on Mount Vishnyovaya in the vicinity of Lake Itkul: *a* – topographical diagram, given using Yandex Maps; *b* – geological diagram, given according to [7]

Рисунок 1. Место отбора образцов (обозначено звездочкой) на горе Вишневая в окрестностях озера Иткуль: *а* – топографическая схема, дано с использованием Яндекс Карты; *б* – геологическая схема, дано по [7]

Figure 2. Olivine (brown) vein, almost without talc, in antigorite serpentinite (light green). Photo by Yu. V. Erokhin

Рисунок 2. Оливиновая (коричневого цвета) жила, почти без талька, в антигоритовом серпентините (светло-зеленого цвета). Фото Ю. В. Ерохина

ences, in the Laboratory of Physicochemical Research Methods. The composition of some minerals was analyzed using a scanning electron microscope JSM-6390LV from Jeol with an energy dispersive attachment INCA Energy 450 X-Max 80 from Oxford Instruments (analyst L. V. Leonova). The same instrument was used to obtain images of minerals in BSE (back-scattered electron) mode.

Petrogenic components were determined on an XRF 1800 X-ray fluorescence wave spectrometer from Shimadzu, which is equipped with a powerful (4 kW) X-ray tube (Rh anode), TAP, PET, Ge, LiF (200) analyzer crystals, as well as a vacuum stabilizer, flow-proportional and scintillation counters (analyst N. P. Gorbunova). Losses on ignition were determined by the wet chemistry method (analyst G. S. Neupokoeva).

X-ray structural study of minerals was carried out on an XRD-7000 X-ray diffractometer from Shimadzu with polycapillary optics and a high-temperature attachment NTK-1200N from Anton Paar for operation in the temperature range 25-1500°C (analyst O. L. Galakhova). Conditions: copper radiation, V = 40 kV, I = 30 mA, step size – 0.02°.

Results and their discussion

Pentlandite in serpentinites forms scattered dissemination in the form of individual isometric and weakly elongated grains, up to 50 μm in size, and their clusters. The sulfide forms both independent segregations (Fig. 3, *a*, *b*) and intergrowths with magnetite (Fig. 3, *c*, *d*). In this case, iron oxide contains a high admixture of chromium (Cr_2O_3 up to 11.4 wt. %), which, when recalculated, gives 17% of the chromite end value. Other impurities in it include magnesium (MgO up to 1.0 wt. %), nickel (NiO up to 0.6 wt. %), manganese (MnO up to 0.2 wt. %), vanadium (V_2O_3 up to 0.2 wt. %) and cobalt (CoO up to 0.1 wt. %). The crystal chemical formula is as follows – $(Fe^{2+}_{0.91}Mg_{0.06}Ni_{0.02}Mn_{0.01})_{1.00}(Fe^{3+}_{1.66}Cr_{0.34})_{2.00}O_4$. Apparently, this chromium-containing magnetite appeared as a result of the replacement of the primary accessory chromium spinel [6].

Antigorite serpentinite is characterized by the following chemical composition (in weight %) – SiO_2 46,63; Al_2O_3 1,15; Fe_2O_3 1,60; FeO 3,52; MgO 35,22; LOI 11.26; The amount is 99.38, i. e. its iron content is 7%. According to X-ray phase analysis, the rock consists almost entirely of serpentine – antigorite. Olivine from antigorite serpentinites, in contact with olivinite veins, belongs to forsterite and contains 14% fayalite component. It contains an admixture of manganese (MnO up to 0.1 wt. %) and traces of calcium. The crystal chemical formula is as follows – $(Mg_{1.72}Fe_{0.28})_{2.00}[Si_{1.00}O_4]$. Talc from antigorite serpentinites is weakly ferrous (FeO 1.4–1.6 wt. %) and contains an admixture of chromium (Cr_2O_3 up to 0.05 wt. %). The crystal chemical formula is as follows – $(Mg_{2.89}Fe_{0.09}Cr_{0.01})_{2.99}[Si_{4.00}O_{10}](OH)_2$. The carbonate in antigorite serpentinites belongs to ferruginous magnesite (FeO up to 11.6 wt. %) with the crystal chemical formula – $(Mg_{0.86}Fe_{0.14})_{1.00}[CO_3]$. In addition

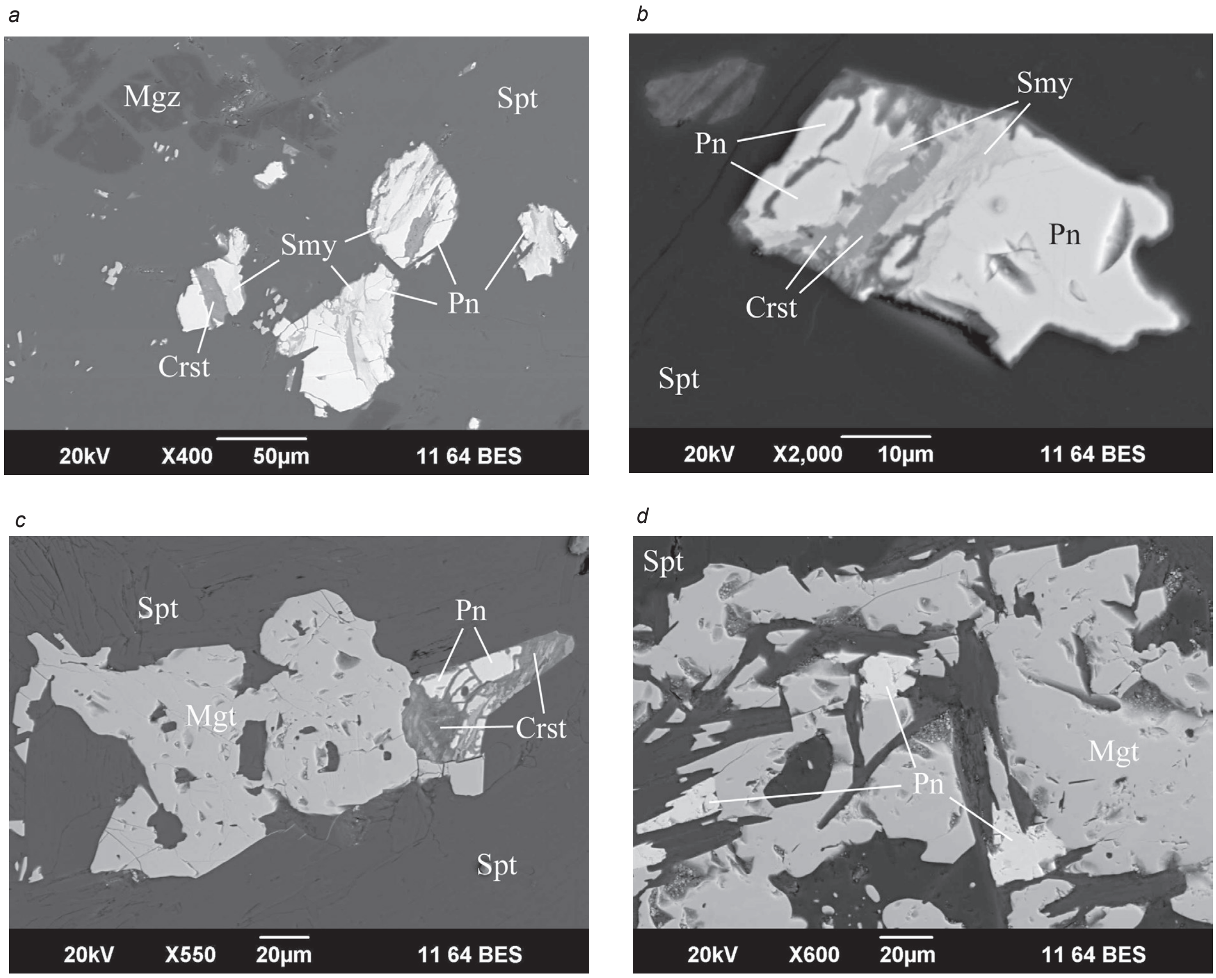

Figure 3. Pentlandite in antigorite serpentinites of the Itkulsky massif: *a*, *b* – independent segregations; *c*, *d* – intergrowths with magnetite. BSE photo, SEM JSM-6390LV; Pn – pentlandite, Smy – smythite, Crst – Cronstedtite, Mgt – magnetite, Spt – serpentine, Mgz – magnesite

Рисунок 3. Пентландит в антигоритовых серпентинитах Иткульского массива: *а*, *б* – самостоятельные выделения; *в*, *г* – срастания с магнетитом. BSE-фото, СЭМ JSM-6390LV; Pn – пентландит, Smy – смизит, Crst – кронстедтит, Mgt – магнетит, Spt – серпентин, Mgz – магнезит

to iron and magnesium, the carbonate contains small impurities of manganese (MnO up to 0.3 wt. %) and nickel (NiO up to 0.2 wt. %) [6].

Pentlandite is characterized by a fairly pure chemical composition (Table 1); among the impurities in the mineral, only cobalt is noted (from 0 to 1.18 wt. %). In the well-known classification of pentlandites [8], low-cobalt sulfide (Co <10 at. %) according to the Ni/Fe ratio is divided into three varieties: nickel pentlandite (Ni/Fe >1.30), pentlandite proper (Ni/Fe within 0. 90–1.30) and ferruginous pentlandite (Ni/Fe < 0.90). Itkul analyzes have a Ni/Fe ratio in the range of 1.20–1.39, i. e. belong to nickel and pentlandite proper. Sulfide is a common mineral of ultrabasic and basic rocks, as well as metasomatites and metamorphites after them, i.e. it was formed as a result of serpentinization of ultrabasic rocks [9].

Sulfide grains often have secondary alterations, which is explained by the influence of weathering processes, because sampling was carried out from rock outcrops. Alterations in pentlandite manifest themselves in the form of the development of secondary sulfide – smysite and ferruginous serpentine – cronstedtite (Fig. 3, *a*, *b*, *c*).

Smythite replaces pentlandite grains along the cracks and at the edges; it is clearly distinguished in the BSE image by its darker color compared to the pentlandite matrix. Chemical composition (wt. %): S 40.81; Fe 37.65; Co 1.66; Ni 19.87, well calculated for the crystal chemical formula of smythite – $(Fe_{5.83}Ni_{2.93}Co_{0.24})_{9.00}S_{11.00}$. This sulfide was first described in 1956 in sedimentary rocks near Bloomington (Indiana, USA), where, together with pyrrhotite, it formed

Table 1. Chemical composition of pentlandite from serpentinites of Mount Vishnyovaya, wt. %

Таблица 1. Химический состав пентландита из серпентинитов г. Вишнёвая, мас. %

Analysis number	Elements				Crystal chemical formula
	S	Fe	Co	Ni	
1	33.60	27.74	–	38.66	$(Ni_{5.09}Fe_{3.83})_{8.92}S_{8.08}$
2	33.26	28.40	0.58	37.75	$(Ni_{4.97}Fe_{3.93}Co_{0.08})_{8.98}S_{8.02}$
3	33.08	29.16	0.79	36.97	$(Ni_{4.88}Fe_{4.04}Co_{0.10})_{9.02}S_{7.98}$
4	33.56	26.60	0.92	38.92	$(Ni_{5.12}Fe_{3.68}Co_{0.12})_{8.92}S_{8.08}$
5	32.95	28.25	1.00	37.80	$(Ni_{4.99}Fe_{3.92}Co_{0.13})_{9.04}S_{7.96}$
6	33.20	28.99	1.11	36.69	$(Ni_{4.83}Fe_{4.01}Co_{0.15})_{8.99}S_{8.01}$
7	32.85	28.65	1.18	37.33	$(Ni_{4.93}Fe_{3.97}Co_{0.16})_{9.06}S_{7.94}$

Note: SEM JSM-6390LV from Jeol with EMF attachment INCA Energy 450 X-Max 80 from Oxford Instruments, analyst L. V. Leonova.

inclusions in calcite [10]. A similar nickel-bearing smythite was described as a secondary mineral after pyrrhotite and pentlandite in copper-nickel deposits of Canada [11]. In the Urals, smythite was described in hydrothermal formations of the Komsomolsk sulfoantimonite-gudmundite deposit (Polar Urals) [12].

Cronstedtite replaces the pentlandite matrix in the form of veined segregations and irregularly shaped clusters, which are clearly distinguished in the BSE image by a dark gray color against the background of light sulfides. It is distinguished by its chemical composition – SiO_2 17,82; Fe_2O_3 40,00; NiO 11,02; FeO 18,06; MnO 0,57; MgO 2,23; CaO 1,30; H_2O 9,00 (by difference in accordance with the standard), which is calculated based on the crystal chemical formula of nickel-magnesium-containing cronstedtite – $(Fe^{2+}_{0.95}Ni_{0.71}Mg_{0.21}Ca_{0.09}Mn_{0.03})_{1.99}Fe^{3+}_{1.01}[(Si_{1.12}Fe^{3+}_{0.88})_{2.00}O_5](OH)_{3.80}$. Interestingly, Ni-Mg-bearing cronstedtites are characteristic of meteorites – carbonaceous chondrites [13]. In metabasites, this mineral replaces copper-iron sulfides (chalcopyrite, bornite, etc.) and is characterized by an increased copper content [14]. In the Urals, classical cronstedtite was discovered in the crushing zones of pyrite-pyrrhotite ores of the Uzelginksoye copper pyrite deposit [15].

Conclusions

Thus, the author has studied in detail pentlandite from antigorite serpentinites of the Itkulsky ultrabasic massif (Southern Urals). According to the Ni/Fe ratio, they belong to nickel and pentlandite proper. Under the influence of weathering processes, most of the pentlandite grains were partially replaced by secondary sulfide – smythite and ferruginous serpentine – cronstedtite.

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Пентландит и продукты его изменения в серпентинитах Иткульского гипербазитового массива (Южный Урал)

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Аннотация

Актуальность работы обусловлена необходимостью изучения минералогии единственного коренного проявления ювелирного оливина в пределах Уральского региона.

Цель работы – исследование пентландита и продуктов его гипергенного изменения в серпентинитах Иткульского гипербазитового массива на Южном Урале.

Методология исследования. Состав некоторых минералов проанализирован с помощью сканирующего электронного микроскопа JSM-6390LV фирмы Jeol с энергодисперсионной приставкой INCA Energy 450 X-Max 80 фирмы Oxford Instruments (аналитик Л. В. Леонова). На этом же приборе были получены изображения минералов в режиме BSE (обратно рассеянных электронов). Рентгеноструктурное изучение минералов проведено на рентгеновском дифрактометре XRD-7000 фирмы Shimadzu с поликапиллярной оптикой и высокотемпературной приставкой HTK-1200N фирмы Anton Paar для работы в диапазоне температур 25–1500 °С (аналитик О. Л. Галахова). Условия съемки: медное излучение, $V = 40$ kV, $I = 30$ mA, размер шага – 0,02°.

Результаты. Пентландит – главный сульфидный минерал антигоритовых серпентинитов, он характеризуется достаточно чистым химическим составом, из примесей в минерале отмечается только кобальт (от 0 до 1,18 мас. %). По Ni/Fe-отношению сульфид относится к никелистому и собственно пентландиту. Смизит (или смайтит) замещает зерна пентландита по трещинам и с краев. Химический состав, мас. %: S – 40,81; Fe – 37,65; Co – 1,66; Ni – 19,87, хорошо рассчитывается на кристаллохимическую формулу смизита – $(Fe_{5.83}Ni_{2.93}Co_{0.24})_{9.00}S_{11.00}$. Кронстедтит замещает матрицу пентландита в виде прожилковатых выделений. Выделяется по химическому составу: SiO_2 – 17,82; Fe_2O_3 – 40,00; NiO – 11,02; FeO – 18,06; MnO – 0,57; MgO – 2,23; CaO – 1,30; H_2O – 9,00 (по разности в соответствии с эталоном), который рассчитывается на кристаллохимическую формулу Ni–Mg-содержащего кронстедтита – $(Fe^{2+}_{0.95}Ni_{0.71}Mg_{0.21}Ca_{0.09}Mn_{0.03})_{1.99}Fe^{3+}_{1.01}[(Si_{1.12}Fe^{3+}_{0.88})_{2.00}O_5](OH)_{3.80}$.

Выводы. Изучен пентландит из антигоритовых серпентинитов Иткульского гипербазитового массива (Южный Урал). Под влиянием процессов выветривания большая часть зерен пентландита частично заместилась вторичным сульфидом – смизитом и железистым серпентином – кронстедтитом.

***Ключевые слова*:** пентландит, смизит, кронстедтит, антигоритовый серпентинит, Иткульский массив, Южный Урал.

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