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Keywords (separated by '-')	Rayisite - Gemology - Ray-Iz massif - Mineralogy of jewelry raw materials - Spectroscopy
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Mineralogy and Gemmology of a New Jewelry Stone of Raiizite

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Abstract. This paper presents the research of a new jewelry and ornamental stone-rayizite. Comprehensive studies of the mineralogical and chemical composition of rayisite were carried out. The main gemological characteristics and features of the nature of the color of this jewelry material are revealed.

Keywords: Rayisite · Gemology · Ray-Iz massif · Mineralogy of jewelry raw materials · Spectroscopy

1 Introduction

The Rai-Iz massif, with an area of about 400 square kilometers, is located near the Arctic Circle. It is one of the most thoroughly studied ultrabasic massifs of the Polar Urals. Together with the Syum-Keu and Voikaro-Syninsky massifs, it forms the northern end of the Main Ultrabasic Belt of the Urals and is one of the largest in the Urals. N. A. Kulik discovered the massif in 1913. The geological position of the massif is described by A. N. Zavaritsky (1932), G. B. Rudnik, G. L. Kashintsev, I. E. Kuznetsov (1971); Yu. E. Moldavantsev and A. P. Kazak (1977); and by Ural geologists—E. P. Tsaritsyn (1981f), B. V. Perevozchikov (1990, 1995, etc.), V. N. Puchkov, I. F. Tavrín, I. S. Chashchukhin, Yu. A. Volchenko, V. Yu. Alimov, etc. (1990). The last major scientific work on the array was published in 2018 (Vakhrusheva et al., 2018). Most of the works focused on the geological structure and age of the massif; the study of the material composition of chromium ores, platinoids and near-ore ultramafites of the large chromite deposit “Central” and small manifestations around it. The late hydrothermal mineralization occurring at the sites has been poorly studied.

When conducting field geological and mineralogical studies of empty dumps in 2019, for their use as additional minerals (raw materials) or collection raw materials,

overburden dumps were found to contain deposits of crushed stone-block material with the release of an unusual pink-purple serpentine. The maximum size of the samples with this material was 30x38cm. Due to the unusual color and previously undescribed similar secretions, this material was originally given the name rayizit after the place of discovery-the Rai-Iz massif. The purpose of this work was to study the mineralogy and gemology of this jewelry and ornamental material.

2 Factual Materials

Rayisite formations are represented by zonal crusts up to 1 cm thick. The color of the discharge varies from a faint pinkish-gray to a rich pink-purple (lavender) color (Fig. 1, 2). The gloss ranges from matte to glass. The material is brittle, the fracture is cancellous, and the hardness is variable 3.5–4.5 on the Mohs scale. Opaque, sometimes translucent. On paradise in some places a semitransparent mineral is growing, presumably an opal with a glassy luster and a hardness above 4.5–5.0 Mohs. Sometimes there is a scaly white-yellow discharge of serpentine on its surface. The mineral has a weak “alexandrite effect”. Rayisite is found mainly on breakaway cracks or tectonic cracks in weathered dunites from the overburden zone of the Tsentralnoye chromite deposit. Sometimes it fills cracks in dunites or fills space in tectonic breccias. Preparations for research were made from these samples.



Fig. 1. Photo of a rayisite sample taken under irradiation with a white light source (source D65)

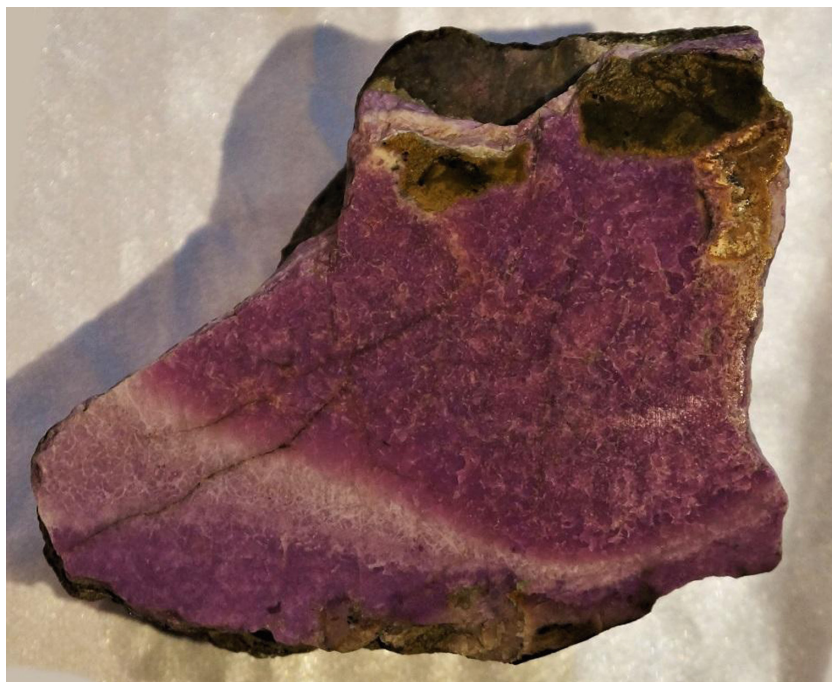


Fig. 2. Photo of a rayisite sample taken when irradiated with a yellow light source (source A)

3 Research Methods

The samples for determination of mineral composition were taken on an automatic powder diffractometer D2 Phaser (Bruker) (Co-anode, position-sensitive detector Lynx-eye), phase identification was carried out using the PDXL2 software package, semi-quantitative phase analysis was carried out using the TOPAS 4.2 software package by full-profile analysis. Local chemical analyses of rayisite were performed on a Camebax SX-50 microprobe, accelerating voltage 15 kV, probe current 1–2 nA, probe diameter 1–2 microns. The accuracy of the analyses was systematically controlled by natural and synthetic standards.

The Raman spectra of the light were recorded using the inVia Qontor confocal Raman spectrometer (Renishaw, UK) on the basis of the laboratory module of the Institute of Geology and Oil and Gas Technologies of Kazan Federal University. The spectra were taken at room temperature in the wavenumber range of 100–4500 cm^{-1} , mode control and data processing were performed in the Wire 5.3 program. A laser with a wavelength of 532 nm (laser power of 100 MW) was used.

Optical absorption spectra were recorded on a standardized MSFU-K spectrophotometer in the wavelength range of 350–800 nm with a step of 1 nm. For the objective measurement and description of the color of the rayisite samples, the method of calculating the chromaticity coordinates according to the international colorimetric system CIE Lab was used. Colorimetric parameters were calculated using a specialized program

“Spectrum”, the type of observer “MKO 1964”, and using two light sources-A (incandescent lamp) and D65 (the color of the cold northern sky). All experimental studies were conducted at room temperature.

4 Research Results

Because of the X-ray diffraction study, it was found that the main mass of rayisite consists of antigorite and dolomite, with an admixture of other carbonates and chromium spinelide (Popov et al., 2019). The main minerals composing the release of rayisite are carbonate (dolomite and calcite) and serpentine. Moreover, the carbonate predominates quantitatively, composing in many places up to about 60–70% of the rock volume. The carbonate forms xenomorphic, sometimes porous, aggregates up to 0.1 mm in size, between which there is a thin-scaled homogeneous mass of serpentine. Due to this close fusion of the two minerals, a dense and draining rock is formed, which is well amenable to mechanical processing.

Dolomite forms two types of formations: its own homogeneous interlayers and aggregate accretions with serpentine. The carbonate interlayers frame the rhayisite and are stacked in a parallel-pole-like aggregate. In the interbeds among the carbonate, inclusions of manganese hydroxides, calcite and serpentine (close to antihorite) are noted. According to the microprobe analysis, the carbonate belongs to almost pure dolomite. Of the impurities, it contains extremely low amounts of MnO (up to 0.2 wt.%) and BaO (up to 0.1 wt.%). At the same time, the carbonate from the accretions with serpentine is characterized by greater contamination, although it also belongs to quite pure dolomite. Of the impurities in the carbonate, MnO (up to 0.6 wt.%), SrO (up to 0.3 wt.%), FeO (up to 0.2 wt.%) and silica (up to 0.1 wt.%). No mineral inclusions other than serpentine are found in the carbonate aggregate.

Calcite forms xenomorphic clusters and individual individuals, up to 0.1 mm in size, in layers of homogeneous dolomite. Traces of plastic deformation and polysynthetic twinning are observed in the mineral. Calcite is well distinguished by its light color in the BSE mode against the background of dark gray dolomite. According to microprobe analysis, it is close to the ideal composition of calcite and contains a small amount of MgO from impurities (up to 0.6 wt.%) and SrO (up to 0.1 wt.%).

Serpentine in the dolomite layers forms xenomorphic fragments, up to 0.1–0.2 mm in size, consisting of a thin-flaked aggregate. Without the analyzer, the unit looks brownish. According to the microprobe analysis, it is defined as antigorite and contains FeO impurities (up to 1.4 wt.%) and CaO (up to 0.24% by weight). These fragments, apparently, are fragmented layers of homogeneous serpentine, which also occur at the contact with rayisite. Interestingly, the serpentines own veins are very similar in composition to the secondary serpentine from the host serpentinite. There, the secondary serpentine encases and dissects the budinated fragments of the primary serpentinite. Among themselves, serpentines differ in composition, so the primary serpentine contains up to 1 wt.% Al₂O₃ and up to 4.3 wt.% FeO, and secondary-non-alumina and low-iron FeO (up to 1 wt.%).

At the same time, serpentine in accretions with dolomite, i.e. in rhayisite, is characterized by an increased chromium content from 1.8 to 2.1 wt.% Cr₂O₃, a constant stable impurity of CaO, up to 0.3 wt.% and, interestingly, is extremely low-iron content. Given

that no chromophore minerals, such as stichtite, clinochlor, or amesite, characteristic of chromite deposits, have been found in the rhayisite, it is safe to say that the pink color of the rock is given by the chromium-containing serpentine. Interestingly, the position of silicon in the serpentine is completely filled and the entry of chromium is possible only in the position of magnesium, which leads to deformation of the structure and, most likely, caused an unusual color of the mineral.

Manganese hydroxides in the layers of homogeneous dolomite form dendritic aggregates with a size of no more than 10–15 microns in elongation. It was not possible to determine the mineral in detail, but most likely it belongs to asbolan, since it contains a significant impurity of NiO (up to 4.6 wt.%). In addition, in rayisite, there are grains of chrome spinelide, which are surrounded by serpentine edges. According to the microprobe analysis, the mineral belongs to chromite with a high content of magnetite mineral. Moreover, the grains have a weak zoning.

Figure 3 shows the Raman spectrum of an antigorite sample from a rayisite sample. The identification of all pronounced peaks showed that the studied variety of serpentine, which forms the basis of rayisite, belongs to the antihorite. Note that the most characteristic line that corresponds to the anti-meteorite is the line at 1098 cm^{-1} (Orlov, Orlov et al., 2007).

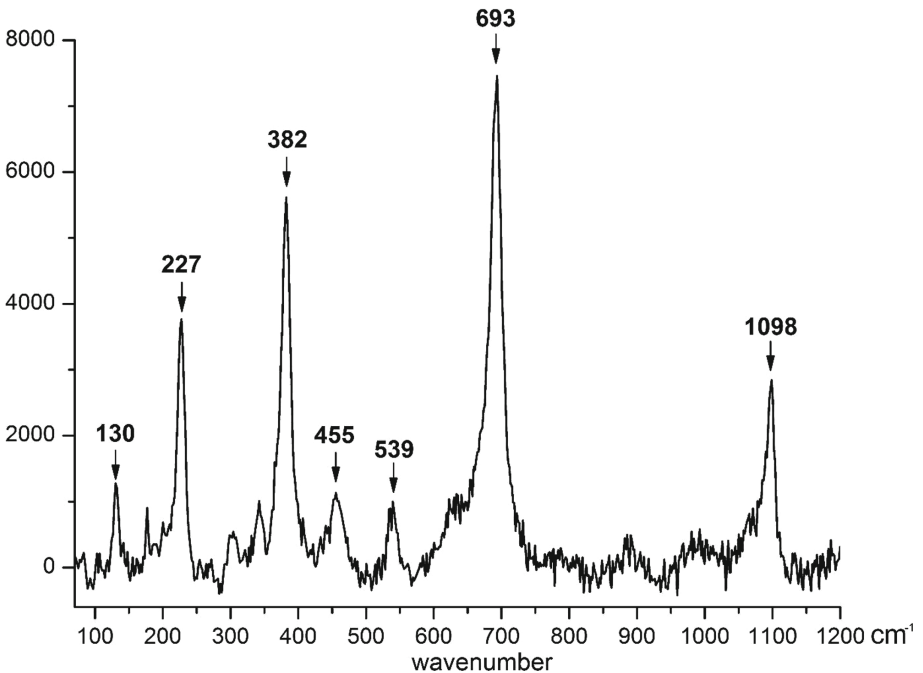


Fig. 3. Raman spectrum of antigorite from a rayisite sample

The study of the optical absorption spectrum of rayisite showed that two wide bands with centers at 392 nm and 552 nm (Fig. 4) form it. The configuration and energy values of the optical absorption bands allowed us to attribute these bands to the ions of trivalent

chromium, which is contained in rayisite in an increased content and, accordingly, to the transitions between spin quartets ${}^4A_2 \rightarrow {}^4T_1$ (Y-band) и ${}^4A_2 \rightarrow {}^4T_2$ (U- band) (Platonov, 1984; Sviridov, Sviridov et al., 1976).

Based on the results of the interpretation of the optical absorption spectra, the chromaticity coordinates were calculated and the following variations of the main color parameters were obtained in rel. Units:

Source A parameter L varies from + 63,02 to + 75,14; parameter a-from + 15,89 to + 33,53; parameter b-from -3,67 to -9,49.

Source D65 parameter L varies from + 52,06 to + 76,02; parameter a-from + 1,79 to + 10,47; parameter b-from -6,53 to -13,51.

The structure of the antigorite consists of alternating layers of $MgO_2(OH)_4$ octahedra and SiO_4 tetrahedrons (Vengerov, 2017; Lyutoev 2003; Caterina, 2003). At the top of the tetrahedra are oxygen ions, and in the center are silicon ions, in the middle of the octahedra are magnesium ions, and at the top – oxygen ions and hydroxyl groups. Thus, the color of rayisite is associated with trivalent chromium, which isomorphically replaces the ions Mg^{2+} in the octahedral positions of the antigorite structure.

This color change is fully explained by the peculiarities of the rayisite spectrum. In this spectrum, there are two distinct broad bandwidths in the violet ($\lambda \leq 420$ nm) and red ($\lambda \geq 570$ nm) regions, as well as a weak band in the blue region. The mixing of purple, red and blue colors lead to the fact that when illuminated with white light, the antigorite in the sample has a rich purple hue, but in the absence of a purple component in the light source, the sample becomes bluish-purple. Thus, it should be assumed that the noble color and “alexandrite” effect of rayisite is given by chromium-containing anti-granite.

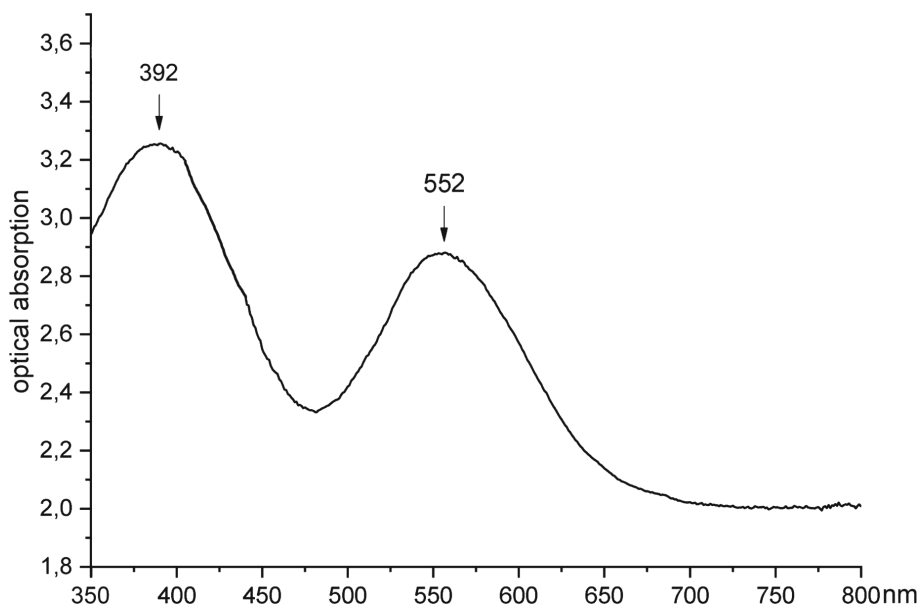


Fig. 4. Optical absorption spectrum of the rayisite sample

5 Conclusion

According to the results of the research, it was proved that the detected zonal crusts of pinkish-purple color are a mixture of the minerals serpentine, dolomite with small admixtures of talc and stichtite. In their composition, they differ significantly from those similar in color to stichtite, sugilite and charoite.

It is shown that the serpentine variety, which forms the basis of rayisite, belongs to the antihorite, and the color of the stone is given by an admixture of chromium, which replaces magnesium ions in the structure of the antihorite.

According to their decorative properties, these selections can be considered as a new jewelry and ornamental stone (Popov et al., 2019), and we can talk about the high decorative properties of the new jewelry and ornamental stone-rayizite, which will allow it to occupy its niche in the Russian and international jewelry market in the future.

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