# THE RAMAN STUDY ON RHODONITE MINERAL AND ITS WEATHERING PRODUCT FROM THE ACHCHITAU DEPOSIT (SULTANUIZDAG MOUNTAINS, UZBEKISTAN)

### \* L.R. Sadikova and D. Nurtaev

Institute of Geology and Geophysics named after H.M. Abdullaev (Tashkent, Uzbekistan) \*Author for Correspondence: rang.tosh@rambler.ru

#### ABSTRACT

This article discusses the results of a study of rhodonite samples taken at the Achchitau occurence, as well as a sample of an aggregate of rhodochrosite, manganosite and quartz. The obtained spectra of the samples were interpreted and correlated with the vibrational modes of the elements composing these minerals.

Keywords: Rhodonite, Weathering, Manganosite, Raman Spectrometry, Raman Spectra

#### INTRODUCTION

The Achchitau rhodonite deposit is located in the central part of the Sultanuizdag range and is administratively located on the territory of the Kegeyli district of Karakalpakstan.

The area of the deposit (0.05 sq.km.) is composed of sedimentary-metamorphic deposits of the fifth pack of the Jamansai formation of the Lower Devonian ( $D_1ds_5$ ), represented by quartz and chlorite-amphibole shales and marbles, intruded by a gabbro-diorite stock ( $C_2$ ).

The deposit is located on the northeastern wing of the Tebinbulak syncline, complicated by higher-order folding, one of which is an asymmetric anticlinal fold, the axis of which is oriented in a submeridian direction with the rocks falling in the western wing at angles of 50-65°, and the eastern one at angles of 30-35°. Discontinuous faults have an interplastic character such as overflows with zones of crushing and silicification of rocks developed along them.

Two rhodonite-bearing quartz-manganese zones have been identified within the deposit, having a seamlike shape and traced in the submeridian direction up to 90-100 m with a thickness of up to 2-3m. The body length ranges from 12 m to 38 m, and the thickness is 0.3m to 2m. The body is composed in the peripheral parts of quartz-pyrolusite rock of a fine-grained structure with a massive and mottled texture caused by 5 cm-sized separations of rhodonite and tephroite in the largest dimension in the central part of the body. The rhodonite separations have an elongated shape, oriented in accordance with the general prostration of the body. The length of such separations varies widely from 10-15 cm to 1-1.5m. The saturation of the body with rhodonite is uneven and ranges from a few percent to 32%, averaging 21.9%. Its greatest concentration is noted in the central part of the body, the least - on its flanks.

Rhodonite deposits essentially consist of rhodonite (up to 80%), quartz (10-40%), pyrolusite (0-10%), psilomelan (0-15%), rhodochrosite (2-10%), and tephroite (0-20%). Their color ranges from pale pink to deep crimson. The most brightly colored rhodonite clusters predominate in the central part of the body. Quartz in the clusters is present in two generations - syngenetic with rhodonite - in the form of fine-grained bands oriented parallel to shale and in the form of secant fine-grained veins and nests. Fine-grained rhodochrosite develops in rhodonite in the form of spots, nests and veins. Patches and numerous veins of pyrolusite and psilomelan are observed in the rhodonite, which do not affect the decorative effect of the stone, and in some cases even enhance it. The hardness of rhodonite is 6 (Mohs), the volume weight varies from 3.14 g/cm<sup>3</sup> to 3.66 g/cm<sup>3</sup>, averaging 3.4 g/cm<sup>3</sup>. The samples selected during the development were studied by the non-destructive method of Raman spectrometry.



Figure 1: The location of the Achchitau deposit

The main purpose of this article is to study the Raman spectra of rhodonite samples from the Achchitau deposit and the correlation of spectral characteristics with molecular structure.

## MATERIALS AND METHODS

The studied samples of rhodonite were taken from the Achchitau deposit (Fig.1). Photos of the samples are shown in Figure 2. The samples were studied using the EnSpectr R532 Raman spectrometer equipped with a 532nm laser, filter and CCD detector (3648 pixels). The spectral range is 160 cm - 4000 cm<sup>-</sup>, the resolution is 4-6 cm<sup>-</sup>. The intensity difference in the same spectral regions of different samples is explained by small differences in the orientation of the crystals.

Spectrum processing (noise removal, correction) was performed in the original software of the EnSpectr GREEN spectrometer.

## **RESULTS AND DISCUSSION**

A tetrahedral SiO<sub>4</sub> molecule have four vibrational modes. These are the  $v_1$  symmetric stretching mode, the  $v_2$  doubly degenerate bend, the  $v_3$  triply degenerate antisymmetric stretching mode and the  $v_4$  triply degenerate bending mode. For tetrahedral SiO<sub>4</sub> units, the  $v_3$  and  $v_4$  modes will be infrared active and the  $v_1$  and  $v_2$  modes Raman active. If a cation causes the reduction in the tetrahedral symmetry, the degeneracy of the vibrational modes will be removed (Mills *et al.*, 2005; Gardiner, 1989).

The Raman spectra of samples are shown in Figure 3 and 4. The low wavenumber region of the Raman spectra of rhodonite is complex and consists of multiple sets of overlapping bands. Some of these peaks may be due to rotatory and translational modes. A second internal mode of the SiO<sub>4</sub> tetrahedra of *B*2g symmetry is observed at 245 and 267 cm<sup>-</sup>. These are also v2 bending modes. The intense peak is observed at 329 and 462 cm<sup>-</sup>. Other low intensity peaks are observed at 422, 501, 364 and 390 cm<sup>-</sup>.

These peaks are of A1g symmetry and v2 bending mode. The observation of multiple bands in this region shows the exact non-equivalence of the SiO4 tetrahedra. The observation of multiple bands shows loss of degeneracy of these tetrahedra.



Figure 2: Photos of samples from rhodonite deposits of the Achchitau deposit





An intense sharp Raman peak is observed at  $670 \text{ cm}^{-}$ , which belong to v4 bending mode. There are no additional small peaks near the intense bands like in other Raman reports on rhodonites.

Two peaks of high intensity are observed at around 974 and 1087 cm<sup>-</sup> and are assigned to the components of the v3 vibration and are considered to be a water librational mode which results from the replacement of  $O^{2-}$  ions by OH ions in the rhodonite structure. Evidence for the existence of water librational bands is confirmed by the presence of OH stretching bands in the spectral region from 3700 to 4200 cm<sup>-</sup> (not shown in the figure).

The most intense band is observed at 999 cm<sup>-</sup> and is assigned to the  $v_1$  symmetric stretching mode of the SiO<sub>4</sub> units. (Mills *et al.*, 2005; Farmer, 1974).

Macroscopically, the second sample differs from the first sample in a lighter color. Under a microscope and after a Raman study, it was discovered that this was not rhodonite, but an aggregate of rhodochrosite, manganosite and quartz formed during the degradation of rhodonite during weathering (Liddicoat, 1948). In the region of 200-800 cm<sup>-</sup> there are peaks of 289,481, 575 and 770 cm<sup>-</sup> characteristic of manganosite, 270 cm<sup>-</sup> for rhodochrosite, and a peak of 1029 cm<sup>-</sup> related to vibrations of the SiO<sub>4</sub> tetrahedra, related to quartz, manganosite and rhodochrosite are distinguished.



Figure 4: The Raman spectrum of the rhodochrosite, manganosite and quartz agreggate

## CONCLUSION

During the field work, rhodonite samples were taken from the Achchitau site. During the study, the Raman spectrum of rhodonite samples, and the quartz, manganosite and rhodochrosite aggregate were measured using the Enspectr R532 Raman spectrometer. Significant peaks in the intensity of the spectrograms were identified, which were associated with vibrations in the ions and molecules that make up these minerals, and data from the reference literature were used to correlate the ranges and fluctuations. The raman spectrum of turquoise is similar to the reference spectra from the RRUFF database.

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