

## **CHARACTERISTICS OF THE RAMAN SPECTRUM OF TURQUOISE FROM THE TEBINBULAK DEPOSIT (SULTANUIZDAG MOUNTAINS, UZBEKISTAN)**

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### **ABSTRACT**

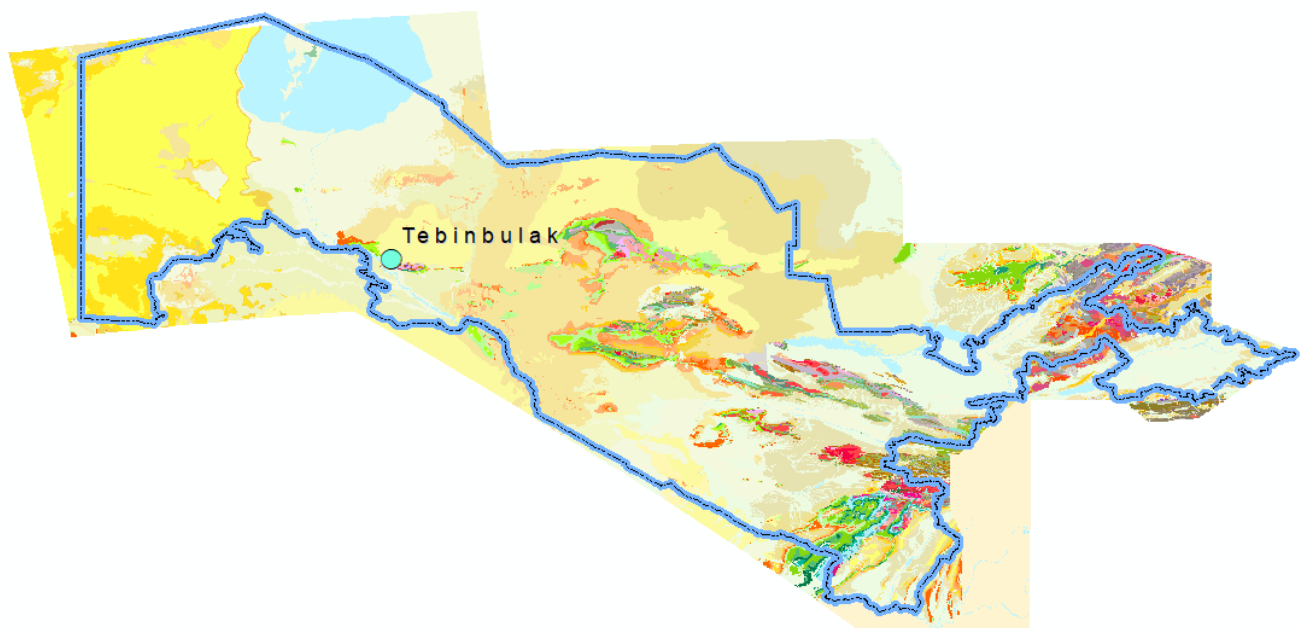
This article discusses a study using Raman spectroscopy to identify turquoise. A distinctive feature of this method is the indestructibility of the sample during the study. The obtained spectra of the samples were interpreted and correlated with the vibrational modes of the turquoise component elements.

**Keywords:** *Turquoise, Phosphate, Hydroxyl Ion, Raman spectrometry, Raman spectra*

### **INTRODUCTION**

Throughout the history of our civilization, no gem has been so loved and popular as turquoise. Turquoise was mined and used in jewelry back in Ancient Egypt, in the territory of Uzbekistan it began to be mined back in the Neolithic period (Gradiner, 1989). Due to the porosity of the stone, turquoise has been learned to refine since ancient times (Liddicoat, 1948). Most of the jewelry turquoise is subject to refinement, therefore the development of non-destructive methods of study is important to determine the refinements and imitations without the need to damage the stone (Moe *et al.*, 2007; Pavese *et al.*, 2005).

Currently, analytical devices are used to diagnose and determine gemological characteristics for obtaining and analyzing various spectra of stones: transmission, absorption, raman scattering and luminescence. Such technologies allow you to see the features of the structure, impurities, and also determine the country of origin, which is important for certification. One of the non-destructive methods is Raman spectrometry (Pristacz *et al.*, 2013).



**Figure 1: The location of the Tebinbulak deposit**

### **Research Article**

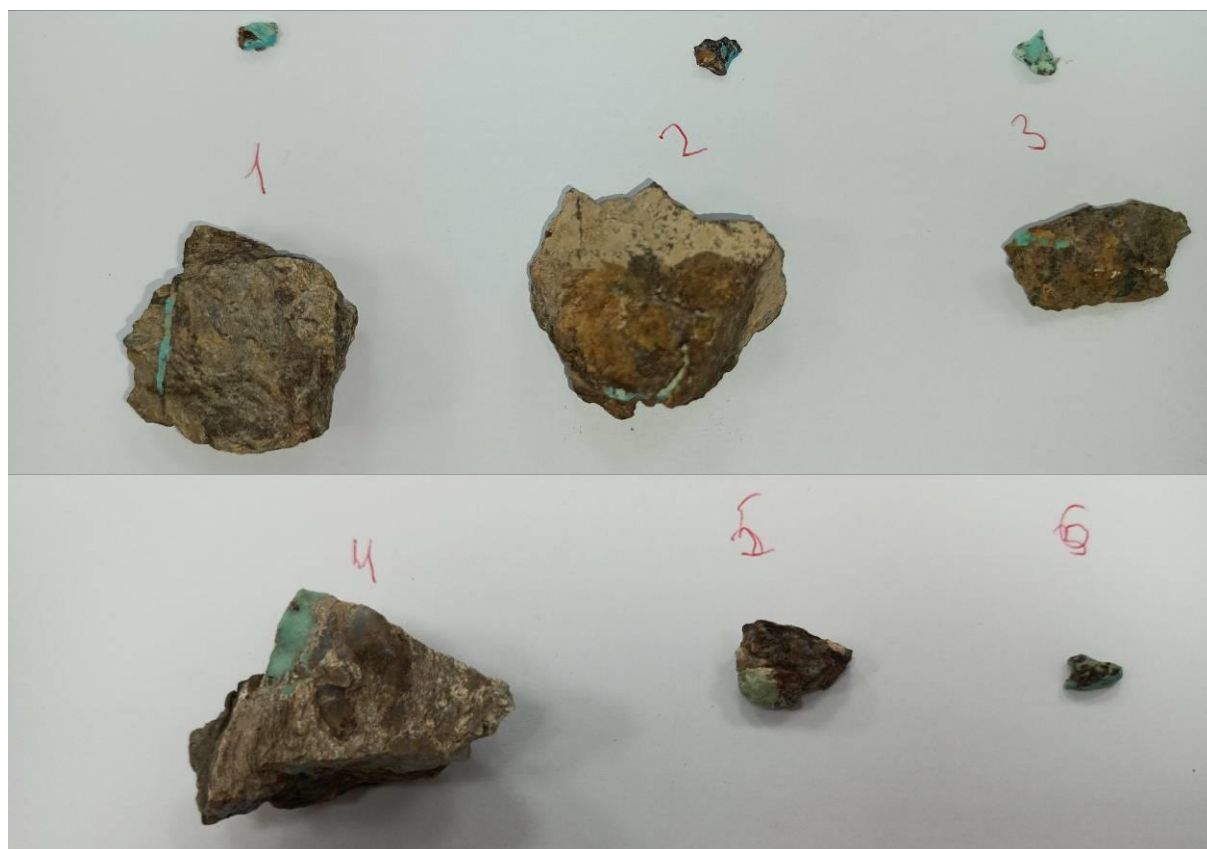
The main purpose of this article is to consider the Raman spectra of turquoise samples from the deposits of the Tebinbulak deposit and the correlation of spectral characteristics with molecular and crystalline structure.

The parameters of the turquoise unit cell were determined by Graham (Graham, 1948). The crystal structure was determined quantitatively by Giester. The crystal structure of turquoise consists of a  $\text{Cu}\Phi_6$  octahedron, where  $F=2 \text{ H}_2\text{O}$  and  $4 \text{ OH}^-$ , two  $\text{Al}\Phi_6$  octahedra with  $3 \text{ OH}^-$ ,  $1 \text{ H}_2\text{O}$  and  $2 \text{ O}_2^-$ , and one  $\text{Al}\Phi_6$  octahedron with  $4 \text{ O}_2^-$  and  $2 \text{ OH}^-$ , and two symmetrically different  $(\text{PO}_4)_3$ -tetrahedra (Kolitsch, Giester, 2000).

### **MATERIALS AND METHODS**

The studied turquoise samples were taken from the Tebinbulak 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  $160 \text{ cm}^-1$  -  $4000 \text{ cm}^-1$ , the resolution is  $4\text{-}6 \text{ cm}^-1$ . The intensity difference in the same spectral regions of different samples is explained by small differences in the orientation of the crystals.

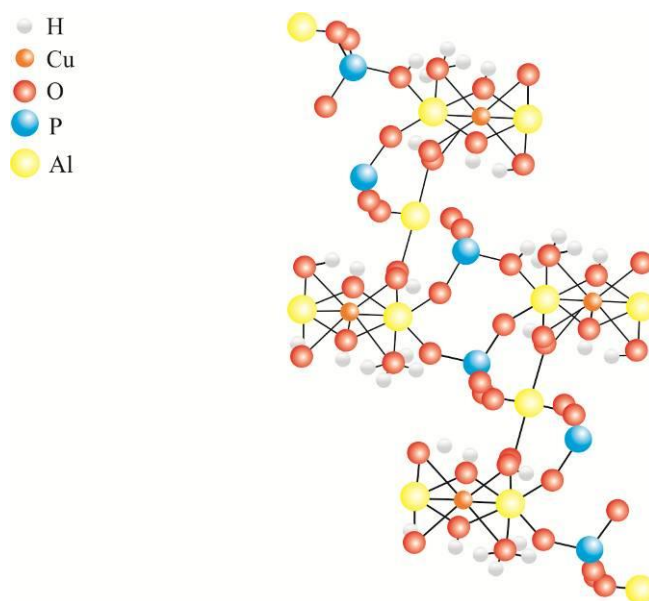
Spectrum processing (noise removal, correction) was performed in the original software of the EnSpectr GREEN spectrometer.



**Figure 2: Photos of samples from turquoise deposits of the Tebinbulak deposit**

### **RESULTS AND DISCUSSION**

The crystal structure of the turquoise mineral consists of one symmetrically different  $\text{CuO}_6$  octahedron, two structurally different  $\text{AlO}_6$  octahedra and two symmetrically different  $\text{PO}_4$  octahedra. They make up a dense three-dimensional structure, which is reinforced by a strong system of hydrogen bonds. The crystal structure includes two structurally nonequivalent water molecules and four structurally nonequivalent hydroxyl ions (Kolitsch, Giester, 2000) (Fig.3). The interpretation of the studied Raman spectrum is based on the materials of the publication Frost et al. (Frost *et al.*,2006) and Nakamoto (Nakamoto, 1986).



**Figure 3: The molecular structure of turquoise**

According to Nakamoto, octahedral units of  $XY_6$  are characterized by 6 normal vibrations, of which  $\nu_1$  ( $A_{1g}$ ),  $\nu_2$  ( $E_g$ ) and  $\nu_3$  ( $F_{1u}$ ) are stretching vibrations, and  $\nu_4$  ( $F_{1u}$ ) and  $\nu_5$  ( $F_{2g}$ ) are bending vibrations. The free anion  $(PO_4)_3^-$  has tetrahedral symmetry  $T_d$ , which is characterized by 9 normal vibrations characterized by four distinct modes of vibration:  $\nu_1$  ( $A_1$ ) symmetric tension oscillation,  $\nu_2$  ( $\delta$ ) ( $E$ ) – twice degenerate bending oscillation,  $\nu_3$  ( $F_2$ ) – thrice degenerate anti-symmetric tension oscillation, and  $\nu_4$  ( $\delta$ ) ( $F_2$ ) is a thrice degenerate bending oscillation.

All Raman spectra of the studied samples are shown in Figures 4-5. The spectrum represents the length of the vibrational modes and their relative intensity. In the spectrum, a fairly large part is occupied by areas with low and near-zero vibration intensity, therefore it makes sense to describe only areas with high intensity and characterizing the constituent parts of the mineral. The studied peaks of the intensity of the Raman shift are very close to the peaks of the spectra of reference samples from the international online database of spectra of minerals RRUFF (R50225, R50418 and R50554), as well as samples of Chinese turquoise (Chen *et al.*, 2009).

#### *The 4500 – 3500 $cm^{-1}$ spectral range*

For most of the samples, two peaks of high intensity are characteristic in this area. There is no information in the published literature about the intensity in this area of the spectrum. Presumably, both peaks may relate to the stretching fluctuations of  $\nu_1$  hydroxyl ions and water molecules.

#### *The 3500 – $cm^{-1}$ spectral range*

The peaks of the Raman spectrum at 3513(4), 3470 (samples #2, 6)  $cm^{-1}$  are associated with stretching fluctuations of OH and relate to symmetrically different hydroxyl  $OH^-$  bound hydrogen bonds. The peak of the Raman spectrum at 3298  $cm^{-1}$  (#4) is associated with stretching fluctuations of OH bound by a hydrogen bond symmetrically to different water molecules. The spectral region with a peak at 2405  $cm^{-1}$  (samples #4, 3) is associated with organic impurities.

#### *The 2000 – 1000 $cm^{-1}$ spectral range*

The peaks of the Raman spectrum at 1158  $cm^{-1}$  (all samples) refer to separate thrice degenerate  $\nu_3$  antisymmetric vibrations of the stretching of the  $(PO_4)_3^-$  molecule.

The peak of the highest intensity is observed in all samples at 1039  $cm^{-1}$  (all samples), is associated with a  $\nu_1$  symmetric vibration of the stretching of the  $(PO_4)_3^-$  molecule and is characteristic of all phosphate minerals of the turquoise group.

#### *The 1000 – 800 $cm^{-1}$ spectral range*

Two groups of intensity peaks at 966 (#1), and at 811 (all samples)  $cm^{-1}$  can be associated with bending fluctuations of the  $\delta$  Al-OH and  $\delta$  Cu-OH chains.

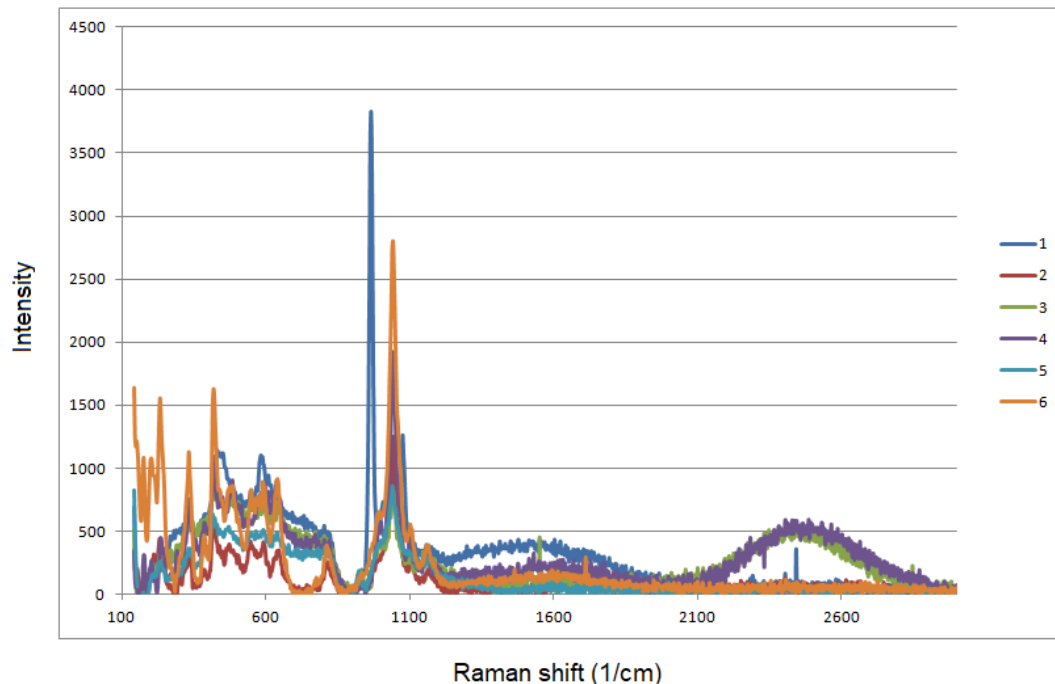
#### *The 800 – 100 $cm^{-1}$ spectral range*

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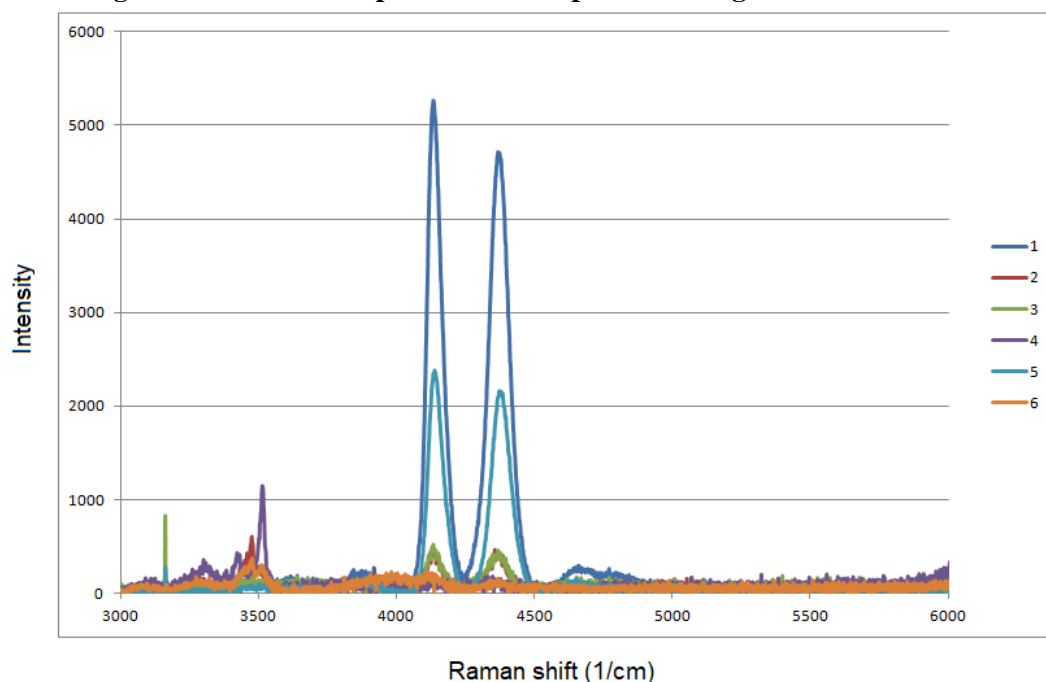
The head and shoulders of the intensity curve in the region of  $645-545\text{ cm}^{-1}$  (all samples) refer to separate thrice degenerate  $\nu_4 (\delta) (\text{PO}_4)_3^-$  bending vibrations. Some of these vertices may also relate to bending vibrations Al-(O,OH) and stretching vibrations Cu-O, possibly overlapping these vibrations.

The peaks of the Raman spectrum at  $418, 330\text{ cm}^{-1}$  refer to separate doubly degenerate bending oscillations of  $\nu_2 (\delta) (\text{PO}_4)_3^-$ , and are partially overlapped by bending and stretching oscillations of Cu-O and Al-O.

The peaks of the Raman spectrum in the range from  $330\text{ to }325\text{ cm}^{-1}$  may relate to bending and stretching fluctuations of Cu-(O, OH, H<sub>2</sub>O) and Al-(O, OH, H<sub>2</sub>O). Intensity peaks in the range from  $300\text{ to }100\text{ cm}^{-1}$  may refer to bending fluctuations of O-Cu-O and O-Al-O.



**Figure 4: The Raman spectrum of samples in the region of  $160-1500\text{ cm}^{-1}$**



**Figure 5: The Raman spectrum of samples in the region of  $3000-4000\text{ cm}^{-1}$**

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**CONCLUSION**

During the study, the Raman spectrum of turquoise samples from the Tebinbulak deposit was measured using the Enspectr R532 Raman spectrometer. Significant peaks in the intensity of the spectrograms were identified and associated with vibrations of ions and molecules that make up the turquoise mineral, reference literature data were used to correlate ranges and vibrations. The Raman spectrum of turquoise is similar to the reference spectra from the RRUFF database and the spectra of samples from Central Kyzylkum, with slight differences.

**REFERENCES**

- Chen QL, Qi LJ, Chen JZ (2009).** Raman spectrum study on turquoise. *Spectroscopy and Spectral Analysis*, **29**(2). 406–409 [in Chinese].
- Frost RL, Reddy BJ, Martens WN, Weier M (2006).** The molecular structure of the phosphate mineral turquoise – a Raman spectroscopic study. *Molecular Structure*. **788**, 224-231.
- Gardiner DJ (1989).** Practical Raman spectroscopy. *Springer-Verlag*, 157 p.
- Graham AR (1948).** XRay Study of Chalcocyanite and Turquoise. University of Toronto Studies, Geological Series. **52**, 39-53.
- Kolitsch U, Giester G (2000).** The crystal structure of faustite and its copper analogue turquoise. *Mineralogical Magazine*. **64**. 905-913.
- Liddicoat RT (1948).** Handbook of gem identification, 12th ed., Gemological Institute of America, Santa Monica, California. 364.
- Moe KS, Moses TM, Johnson P (2007).** Polymer-Impregnated Turquoise. *Gems & Gemology*. **43**, 149-151.
- Nakamoto K (1986).** Infrared and Raman spectra of inorganic coordination compounds, J. Wiley and Sons New York, 419 p.
- Pavese A, Prospero L, Dapiaggi M (2005).** Use of IR-spectroscopy and diffraction to discriminate between natural, synthetic and treated turquoise, and its imitations. *Australian Gemologist*. **22**, 366-371.
- Pristacz H, Wildner M, Hammer VM, Libowitzky E (2013).** Investigations of a synthetic turquoise. Corals-2013 (*Conference on Raman and luminescence spectroscopy in the earth sciences*) 81-82.