Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Raman and infrared spectroscopic study of turquoise minerals

Jiří Čejka^{a,b}, Jiří Sejkora^a, Ivo Macek^a, Radana Malíková^a, Lina Wang^b, Ricardo Scholz^c, Yunfei Xi^b, Ray L. Frost^{b,*}

^a Department of Mineralogy and Petrology, National Museum, Cirkusová 1740, CZ-193 00 Praha 9, Czech Republic

^b School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia

^c Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35.400-00, Brazil

HIGHLIGHTS

- We have studied the Raman and infrared spectra of turquoise $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$.
- Observed Raman and infrared bands were assigned.
- Approximate O–H...O hydrogen bond lengths were calculated from the Raman and infrared spectra.
- No Raman and infrared bands attributable to $(\text{PO}_3\text{OH})^{2-}$ units were observed.

GRAPHICAL ABSTRACT

ARTICLE INFO

Article history:

Received 14 September 2014

Received in revised form 8 April 2015

Accepted 16 April 2015

Available online 21 April 2015

Keywords:

Turquoise

Phosphate

Hydroxyl ions

Raman spectroscopy

Infrared spectroscopy

ABSTRACT

Raman and infrared spectra of three well-defined turquoise samples, $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$, from Lavender Pit, Bisbee, Cochise county, Arizona; Kouroudaiko mine, Faleme river, Senegal and Lynch Station, Virginia were studied, interpreted and compared. Observed Raman and infrared bands were assigned to the stretching and bending vibrations of phosphate tetrahedra, water molecules and hydroxyl ions. Approximate O–H...O hydrogen bond lengths were inferred from the Raman and infrared spectra. No Raman and infrared bands attributable to the stretching and bending vibrations of $(\text{PO}_3\text{OH})^{2-}$ units were observed.

© 2015 Elsevier B.V. All rights reserved.

Introduction

The mineral turquoise is one of the oldest gem materials known. Its use in jewellery and for personal decoration can be traced back 70 centuries, to ancient Egypt [1,2]. Today, turquoise is popular in fine jewellery as well as in various cultures, most notably among Native Americans in the south-western United States [1,2]. The first orientation of turquoise studies allows archaeologists to investigate pre-Colombian turquoise trade structures in North America and

identify or authenticate the natural sources of turquoise worldwide [3–7]. Various physico-chemical characteristics of turquoise were studied together with questions of turquoise provenance especially with regard to its wealth of colors (blue, green in various shades) and further properties important for its use in jewellery [8–15]. The sources of high-quality gem turquoise are limited and because this material (due to porosity characteristic for massive aggregates) easily accepts many treatments, the majority of gem turquoise are adulterated [2,16,17]. Detection of the extent and character of these treatments, inclusive impregnation with polymers, is a very important job especially for use of non-destructive methods [18–21].

* Corresponding author.

E-mail address: r.frost@qut.edu.au (R.L. Frost).

Turquoise was one of the first gem materials to be simulated by synthetics like glass, plastic, pressed turquoise powder bonded by resin, colored gelmagnesite or howlite [22]. At the present time, synthetic turquoise is produced by the method of Gilson [23]. A set of analytical methods, such as PXRD and EDS analysis or ATR-IR, UV-VIS-NIR and Raman spectra are used for distinguishing these artificial replacements from natural turquoise [24]. Last, but not least, turquoise affected by extended exposure to sunlight and water weathered to chalky white minerals; this alteration processes are as yet, poorly understood [3–4].

Most of as yet published papers on turquoise (as mentioned above) are, however, usually, based only on one or several research methods; especially in the case of papers focused to infrared or Raman spectroscopy the data on chemical composition or values of unit-cell parameters of studied mineral phases are mostly missing. The main aim of this paper is to report the Raman and infrared spectra of three well-defined natural untreated turquoise samples from three different occurrences, and to relate the spectra to its molecular and crystal structure. Further aim of the paper is also to certify the possibility to use Raman data for the provenance of turquoise samples; this is the reason why three samples from various localities differing in morphology, color and details in chemical composition were studied. The paper follows the systematic research of the large group of oxyanions containing minerals [25–29], and especially their molecular structure using IR and Raman spectroscopy [30–35].

Background information

Triclinic mineral turquoise belongs to a turquoise group; general formula for minerals of this group may be written as $A_{0-1}B_6(PO_4)_4(OH)_8 \cdot 4H_2O$. Most common substituents at the A position are Cu^{2+} , Fe^{2+} , Zn^{2+} or vacancy; at the B position then Al^{3+} or Fe^{3+} [4,36–38].

Turquoise usually occurs as apple-green, bluish green, sky-blue or greenish gray fine granular, dense massive to cryptocrystalline aggregates, nodules, crusts or veinlets; small short columnar crystals are rare [1,39]. It has dozens of occurrences but only few produce commercial gem material or contain well-formed crystals [1,39]. Turquoise is uncommon supergene mineral formed in the oxidized zone (mainly in arid climates) of phosphorus-rich aluminous rocks (volcanic, phosphate-rich sediments, hydrothermal porphyry deposits, etc.) in the presence of Cu minerals [1,39].

The unit-cell parameters of turquoise were determined by Graham [40], the first solution of its crystal structure was published by Cid-Dresdner [41]. Recently, the crystal structure of turquoise refined by Kolitsch and Giester [42]. Turquoise contains in its crystal structure $Cu\Phi_6$ octahedra, with $\Phi = 2 H_2O$ and $4 OH^-$, two $Al\Phi_6$ octahedra with $3 OH^-$, $1 H_2O$ and $2 O^{2-}$ and one $Al\Phi_6$ octahedron with $4 O^{2-}$ and $2 OH^-$, and two symmetrically distinct $(PO_4)^{3-}$ tetrahedra [41,42]. No $(PO_3OH)^{2-}$ units were observed in its crystal structure [4,41,42]. Only in the case of planerite, $Al_6(PO_4)_2(PO_3OH)_2 \cdot 4H_2O$, the charge balance should be maintained by the protonation, connected with Cu-site occupancy decrease [36]. However, according to Kolitsch and Giester [42], the charge balance might be also achieved by introducing additional Cu^{2+} or other cations in the partially occupied site at $(1/2, 0, 1/2)$.

Experimental

Minerals

The studied samples of the mineral turquoise originated from three different occurrences: Lavender Pit, Bisbee, Cochise county, Arizona (labeled as A) – little greenish cryptocrystalline aggregates

Fig. 1. Cryptocrystalline aggregates of turquoise, Lavender Pit, Bisbee, Cochise county, Arizona. Photo J. Sejkora, FOV 2 cm.

Fig. 2. Light greenish blue globular aggregates of turquoise in association with tiny transparent senegalite crystals, Kouroudaiko mine, Faleme river, Senegal. Photo J. Sejkora, FOV 3 cm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Groups of transparent dark sky-blue well-formed turquoise crystals up to 2 mm in size on quartz gangue, Lynch Station, Virginia. Photo J. Sejkora, FOV 1 cm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

up to some cm in size (Fig. 1); Kouroudaiko mine, Faleme river, Senegal (labeled as S) – light greenish blue globular aggregates up to 3 mm in size in association with tiny transparent senegalite crystals (Fig. 2); Lynch Station, Virginia (labeled as V) – rich groups of transparent dark sky-blue well-formed crystals up to 2 mm in size on quartz gangue (Fig. 3).

Table 1
Unit-cell parameters of turquoise samples (for triclinic space group *P*-1).

	Virginia	Senegal	Arizona	[42]	[38]
<i>a</i> [Å]	7.411 (3)	7.411 (5)	7.410 (5)	7.410(1)	7.426(8)
<i>b</i> [Å]	7.632 (3)	7.635 (6)	7.635 (6)	7.633(1)	7.634(8)
<i>c</i> [Å]	9.905 (4)	9.904 (7)	9.901 (7)	9.904(1)	9.91(1)
α [°]	68.43 (3)	68.46 (5)	68.43 (5)	68.42(1)	68.67(8)
β [°]	69.65 (2)	69.64 (5)	69.63 (5)	69.65(1)	69.70(8)
γ [°]	65.05 (3)	65.03 (5)	65.05 (5)	65.01(1)	65.01(8)
<i>V</i> [Å ³]	459.9 (3)	460.0 (7)	459.7 (6)	460.3(1)	461.5(9)

Table 2
Chemical composition of studied turquoise samples (wt.%).

	Virginia	Senegal	Arizona	Ideal
CaO	0.04	0.00	0.00	
FeO*	0.92	0.42	0.83	
BaO	0.37	0.21	0.00	
CuO	9.76	6.17	8.61	9.78
ZnO	0.12	0.24	0.13	
Al ₂ O ₃	35.37	37.92	37.33	37.60
Fe ₂ O ₃	1.56	0.12	0.00	
SiO ₂	0.00	0.00	0.09	
P ₂ O ₅	33.75	35.27	34.09	34.90
H ₂ O**	17.52	17.90	17.62	17.72
Total	99.41	98.25	98.69	100.00
Ca ²⁺	0.006	0.000	0.000	
Fe ²⁺	0.108	0.047	0.095	
Ba ²⁺	0.020	0.011	0.000	
Cu ²⁺	1.032	0.625	0.898	
Zn ²⁺	0.013	0.023	0.013	
Σ Me ²⁺	1.178	0.706	1.006	
□	0.000	0.294	0.000	
Al ³⁺	5.835	5.987	6.078	
Fe ³⁺	0.165	0.013	0.000	
Σ Me ³⁺	6.000	6.000	6.078	
(SiO ₄)	0.000	0.000	0.012	
(PO ₄)	4.000	3.706	3.988	
(PO ₃ OH)	0.000	0.294	0.000	
Σ T	4.000	4.000	4.000	
OH	8.356	7.706	8.236	
H ₂ O	4.00	4.00	4.00	

FeO* and Fe₂O₃ contents were calculated on the basis of Me²⁺/Me³⁺ cations; H₂O** content was calculated on the basis of charge balance and ideal content of 4 H₂O molecules.

Fig. 4a. Raman spectrum of turquoise sample from Arizona over the 100–4000 cm^{−1} spectral range. **Fig. 4b.** Raman spectrum of turquoise sample from Senegal over the 100–4000 cm^{−1} spectral range. **Fig. 4c.** Raman spectra of turquoise from Virginia over the 100–4000 cm^{−1} spectral range. **Fig. 4d.** Infrared spectra of turquoise from Arizona over the 500–4000 cm^{−1} spectral range.

Carefully hand-picked samples were used for X-ray powder diffraction experiments. To minimize the complicated shape of background, the samples studied were placed on a flat low-background silicon wafer. Powder XRD measurements were carried out with CuK α radiation at a Bruker D8 Advance diffractometer (40 kV, 40 mA) in the range 4–70° 2 θ in the step-scan mode 0.01°/8 s. The position and intensities of reflections were

Fig. 4e. Infrared spectra of turquoise from Senegal over the 500–4000 cm⁻¹ spectral range.

Fig. 4f. Infrared spectra of turquoise from Virginia over the 500–4000 cm⁻¹ spectral range.

calculated using the Pearson VII profile shape function in the ZDS program package [43]. The measured patterns were indexed using unit-cell parameters and space group proposed by Kolitsch and Giester [42]. The unit-cell parameters refined from measured powder XRD using the program of Burnham [44] are compared with published data in the Table 1.

All turquoise samples were quantitatively analyzed by Cameca SX 100 electron microprobe system in wavelength dispersion mode for chemical composition (Table 2). Studied sample was mounted into the epoxide resin and polished. The polished surface was coated with carbon layer 250 Å. An acceleration voltage of 15 kV, a specimen current of 10 nA, and a beam diameter of 5 μm were used. Well-defined natural and synthetic compounds were used as standards. The raw intensities were converted to the concentrations using automatic PAP matrix correction software package. On the basis of $P + Si = 4 \text{ apfu}$, empirical formula of turquoise from Arizona may be expressed as $(\text{Cu}_{0.90}\text{Fe}_{0.10}\text{Zn}_{0.01})_{\Sigma 1.01}\text{Al}_{6.08}[(\text{PO}_4)_{3.99}(\text{SiO}_4)_{0.01}]_{\Sigma 4.00}(\text{OH})_{8.24} \cdot 4\text{H}_2\text{O}$; from Senegal as $(\text{Cu}_{0.63}^{0.29}\text{Fe}_{0.05}\text{Zn}_{0.02}\text{Ba}_{0.01})_{\Sigma 1.00}(\text{Al}_{5.99}\text{Fe}_{0.01})_{\Sigma 6.00}[(\text{PO}_4)_{3.71}(\text{PO}_3\text{OH})_{0.29}]_{\Sigma 4.00}(\text{OH})_{7.71} \cdot 4\text{H}_2\text{O}$ and from Virginia as $(\text{Cu}_{1.03}\text{Fe}_{0.11}\text{Ba}_{0.02}\text{Zn}_{0.01}\text{Ca}_{0.01})_{\Sigma 1.18}(\text{Al}_{5.84}\text{Fe}_{0.16})_{\Sigma 6.00}(\text{PO}_4)_{4.00}(\text{OH})_{8.36} \cdot 4\text{H}_2\text{O}$.

Raman and infrared spectroscopy

Fragments of aggregates and crystals of turquoise were placed on a polished metal surface on the stage of an Olympus BHS microscope, which is equipped with 10×, 20×, and 50× objectives.

Table 3
Tentative assignment of turquoise spectra.

Raman			Infrared			Tentative assignment
A	S	V	A	S	V	
3544	3527			3607		ν OH stretch of (OH) ⁻
3502	3506	3499	3509	3506	3505	
3473	3471	3473	3465	3464	3465	
3450	3453	3451	3451	3450	3451	
				3447		ν OH stretch of water molecules
3397	3419	3410	3431		3417	
3279	3290	3273	3269	3276	3288	
3077	3092	3085	3075	3072	3058	
			3067	3051		δ H ₂ O bend
	1632		1646	1654	1622	
1609	1614		1595	1587		overtones of combination bands
			1474	1467	1513	
1173	1184	1185	1195	1194	1192	ν ₃ (PO ₄) ³⁻ antisymmetric stretch
1160	1161	1162	1158	1143	1142	
1105	1104	1105	1103	1104	1110	
			1084	1082	1092	
1065	1064	1065	1055	1056		ν ₁ (PO ₄) ³⁻ symmetric stretch
1042	1041	1042			1042	
	1031	1020	1034	1035		δ Al-OH and/or δ Cu-OH
1004			1011	1002	1008	
985	991	985	990		991	
931	935	942	964	948	956	
	836	889	899	897	897	libration modes of H ₂ O
815	815	811	835	835	835	
			785	786	784	
			727	722	723	
	663					ν ₄ (PO ₄) ³⁻ bend and/or Al-(O,OH) bend and/or Cu-O stretch
643	642	644				
		629				
		611				
593	592	593				ν ₂ (PO ₄) ³⁻ bend and/or Cu-O stretch and bend
571	571	571				
550	548	551				
506	511	511				
		498				Cu-(O,OH,H ₂ O) and Al-(O,OH,H ₂ O) stretch and bend vibrations (?)
485	483	486				
471	469	469				
457	460	449				
438	437	437				lattice vibrations and/or O-Cu-O bend and/or O-Al-O bend
426	423	425				
417	417	417				
		408				
387	385	385				lattice vibrations and/or O-Cu-O bend and/or O-Al-O bend
		367				
337	335	339				
321	320	319				
303	301	303				lattice vibrations and/or O-Cu-O bend and/or O-Al-O bend
276	277					
260	259	259				
		252				lattice vibrations and/or O-Cu-O bend and/or O-Al-O bend
245	244	246				
233	231	233				
219	218	218				
211	210	212				lattice vibrations and/or O-Cu-O bend and/or O-Al-O bend
200	196	202				
176	175	177				
155	152	156				

The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He–Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm⁻¹ and a precision of ±1 cm⁻¹ in the range between 200 and 4000 cm⁻¹. Repeated acquisition on the crystals using the highest magnification (50×) were accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer. Previous studies by the authors provide more

Fig. 5a. Raman spectrum of turquoise from Arizona over the 2600–3800 cm^{-1} spectral range.

Fig. 5d. Infrared spectrum of turquoise from Arizona over the 2600–3800 cm^{-1} range.

Fig. 5b. Raman spectrum of turquoise from Senegal over the 2600–3800 cm^{-1} spectral range.

Fig. 5e. Infrared spectrum of turquoise from Senegal over the 2600–3800 cm^{-1} range.

Fig. 5c. Raman spectrum of turquoise from Virginia over the 2600–3800 cm^{-1} spectral range.

Fig. 5f. Infrared spectrum of turquoise from Virginia over the 2600–3800 cm^{-1} range.

details of the experimental technique. Alignment of all samples in a similar orientation has been attempted and achieved. However, differences in intensity may be observed due to minor differences in the crystal orientation.

Infrared spectra was recorded by micro diffuse reflectance method (DRIFTS) on a Nicolet Magna 760 FTIR spectrometer (range 4000–600 cm^{-1} , resolution 4 cm^{-1} , 128 scans, 2 level zero-filtering, Happ-Genzel apodization), equipped with Spectra Tech InspectIR

micro FTIR accessory. Sample of amount less than 0.050 mg was mixed without using pressure with KBr. Samples were immediately recorded together with the same KBr as a reference.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be

selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian–Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Lorentzian–Gaussian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Results and discussion

Crystal symmetry and vibrational spectra of turquoise

Turquoise, $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$, is triclinic, space group $P-1 - C_i^1$, $Z = 1$. The structure consists of distorted CuO_6 polyhedra, AlO_6 octahedra and PO_4 tetrahedra. By edge- and corner-sharing of these polyhedra a fairly dense three-dimensional framework is formed which is further strengthened by a system of hydrogen bonds [42].

In the crystal structure of turquoise there are one symmetrically distinct CuO_6 octahedron, three structurally distinct AlO_6 octahedra, two symmetrically distinct PO_4 tetrahedra, two structurally unequivalent water molecules and four structurally unequivalent OH units [41,42]. Tentative interpretation of infrared and Raman spectra of turquoise studied is based on factor group analysis of phosphates and water in turquoise published by Frost et al. [13] and publications by Nakamoto [45], Čejka et al. [35], Keller [46–49], Pechkovskii et al. [50], Goldsmith and Ross [51], Devamani and Alagar [52], Aguirre et al. [53], Frost et al. [13,54] and Reddy et al. [14].

According to Nakamoto [45], octahedral units XY_6 exhibit six normal vibrations, from which ν_1 (A_{1g}) and ν_2 (E_g) stretching and ν_5 (F_{2g}) bending vibrations are Raman active, while only ν_3 (F_{1u}) stretching and ν_4 (F_{1u}) bending vibrations are infrared active. Symmetry lowering in the case of XY_4Z_2 may cause Raman and infrared activation of corresponding vibrations and also splitting of degenerate vibrations. Free $(\text{PO}_4)^{3-}$ anion exhibits tetrahedral T_d symmetry. In the case of a free ion of T_d symmetry, there are 9 normal vibrations characterized by four distinguishable modes of vibrations: ν_1 (A_1) symmetric stretching vibration, Raman active, ν_2 (δ) (E) doubly degenerate bending vibration, Raman active, ν_3 (F_2) triply degenerate antisymmetric stretching vibration, Raman and infrared active, ν_4 (δ) (F_2) triply degenerate bending vibration, Raman and infrared active. T_d symmetry lowering may cause infrared activation of the ν_1 and ν_2 vibrations and splitting of the doubly degenerate ν_2 and triply degenerate ν_3 and ν_4 vibrations [35].

Raman and infrared spectroscopy

Full range Raman and infrared spectra of the studied minerals from Arizona (A), Senegal (S) and Virginia (V) are given in Figs. 4a–f and their tentative assignments in Table 3. These spectra show the position of the bands and their relative intensities. It is obvious that there are large parts of the spectra where little or no intensity is observed. Therefore, the spectra are subdivided into sections according to the type of vibration is being investigated. In this way the precise position of the bands can be detailed. Observed wavenumbers of the Raman bands of the studied turquoise samples are close to the approximate wavenumbers inferred from the Raman spectra of RRUFF's three turquoise samples R50225, R50418 and R50554.

Raman and infrared spectral regions of ν OH stretching vibrations are presented in Figs. 5a–f. Raman bands at 3544, 3502, 3473 and 3450 cm^{-1} (A), 3527, 3506, 3471 and 3453 cm^{-1} (S) and 3499, 3473 and 3451 cm^{-1} (V) and infrared bands at 3509, 3465 and 3451 cm^{-1} (A), 3607, 3506, 3464, 3450 and 3447 cm^{-1}

Fig. 6a. Raman spectrum of turquoise from Arizona over the 1400–1800 cm^{-1} spectral range.

Fig. 6b. Raman spectrum of turquoise from Senegal over the 1400–1800 cm^{-1} spectral range.

Fig. 6c. Raman spectrum of turquoise from Virginia over the 1400–1800 cm^{-1} range.

(S) and 3505, 3465 and 3451 cm^{-1} (V) are assigned to the ν OH stretching vibrations and assigned to the hydrogen bonded, symmetrically distinct hydroxyls OH^- . Raman bands at 3397, 3279 and 3077 cm^{-1} (A), 3419, 3290 and 3092 cm^{-1} (S), 3410, 3273 and 3085 cm^{-1} (V), and infrared spectra at 3431, 3269, 3075 and 3067 cm^{-1} (A), 3276, 3072 and 3051 cm^{-1} (S) and 3417, 3288 and 3058 cm^{-1} (V) are attributed to the ν OH stretching vibrations of symmetrically distinct hydrogen bonded water molecules. Very

Fig. 6d. Infrared spectrum of turquoise from Arizona over the 1300–1800 cm^{-1} range.

Fig. 7a. Raman spectrum of turquoise from Arizona over the 800–1400 cm^{-1} range.

Fig. 6e. Infrared spectrum of turquoise from Senegal over the 1300–1800 cm^{-1} range.

Fig. 7b. Raman spectrum of turquoise from Senegal over the 800–1400 cm^{-1} range.

Fig. 6f. Infrared spectrum of turquoise from Virginia over the 1450–1750 cm^{-1} range.

Fig. 7c. Raman spectrum of turquoise from Virginia over the 800–1400 cm^{-1} range.

weak Raman and infrared bands at 2932, 2920 and 2934 cm^{-1} are probably connected with organic impurities.

Libowitzky's empirical relation [55] enables to infer from the wavenumbers of Raman and infrared bands of minerals assigned to the ν OH stretching vibrations approximate O–H...O hydrogen bond lengths. In the case of studied turquoise samples inferred hydrogen bond lengths vary from 2.98 to 2.67 Å. This agrees very

well with X-ray single crystal structure data 2.970–2.670 Å [41] and 3.020–2.685 Å [42].

Broad Raman bands at 1609 cm^{-1} (A), 1614 cm^{-1} (S) and 1632 cm^{-1} (V) and infrared bands at 1646 and 1595 cm^{-1} (A), 1654 and 1587 cm^{-1} (S) and 1622 cm^{-1} (V) are attributed to the ν_2 (δ) H_2O bending vibrations of the symmetrically distinct differently hydrogen bonded water molecules (Figs. 6a–f). Observed infrared bands at 1474 cm^{-1} (A), 1467 cm^{-1} (S) and 1513 cm^{-1} (V) are assigned to overtones or combination bands.

Fig. 7d. Infrared spectrum of turquoise from Arizona over the 500–1300 cm^{-1} range.

Fig. 8a. Raman spectrum of turquoise from Arizona over the 300–800 cm^{-1} range.

Fig. 7e. Infrared spectrum of turquoise from Senegal over the 500–1300 cm^{-1} range.

Fig. 8b. Raman spectrum of turquoise from Senegal over the 300–800 cm^{-1} range.

Fig. 7f. Infrared spectrum of turquoise from Virginia over the 500–1300 cm^{-1} range.

Fig. 8c. Raman spectrum of turquoise from Virginia over the 300–800 cm^{-1} range.

The Raman spectra in the 800–1400 cm^{-1} spectral range and infrared spectra in the 500–1300 cm^{-1} spectral range are reported in Figs. 7a–f. Raman bands at 1173, 1160 and 1105 cm^{-1} (A), 1184, 1161 and 1104 cm^{-1} (S), and 1185, 1162 and 1105 cm^{-1} (V) and infrared bands and shoulders at 1195, 1158, 1103 and 1084 cm^{-1} (A), 1194, 1143, 1104 and 1082 cm^{-1} (S), and 1192, 1142, 1110 and 1092 cm^{-1} (V) are connected with split triply degenerate ν_3 (PO_4)^{3−} antisymmetric stretching vibrations.

Very intense Raman bands at 1042 cm^{-1} (A), 1041 cm^{-1} (S), 1042 cm^{-1} (V) and infrared bands at 1055 cm^{-1} (A), 1056 cm^{-1} (S), 1042 cm^{-1} (V) are assigned to the ν_1 (PO_4)^{3−} symmetric stretching vibrations. Raman bands at 1065 cm^{-1} (A), 1064 cm^{-1} (S) and 1065 cm^{-1} (V) are also related to the ν_1 (PO_4)^{3−} vibrations. Some of the Raman bands and shoulders at 1004, 985 and 931 cm^{-1} (A), 1031, 991, 935 cm^{-1} (S), 1020, 985, 942, 889 cm^{-1} (V) and infrared bands and shoulders 1034, 1011, 990, 964, 899 cm^{-1} (A), 1035, 1002, 948, 897 cm^{-1} (S), 1008, 991, 956, 897 cm^{-1} (V) may also be related to these vibrations, however more probably may be

Fig. 9a. Raman spectrum of turquoise from Arizona over the 100–300 cm^{-1} range.

Fig. 9c. Raman spectrum of turquoise from Virginia over the 100–300 cm^{-1} range.

Fig. 9b. Raman spectrum of turquoise from Senegal over the 100–300 cm^{-1} range.

attributed to the δ Al–OH and δ Cu–OH bending vibrations together with the Raman bands at 815 cm^{-1} (A), 836 and 815 cm^{-1} (S), 811 cm^{-1} (V) and infrared bands at 835 cm^{-1} (A), 835 cm^{-1} (S), 835 cm^{-1} (V), while the infrared bands at 785 and 727 cm^{-1} (A), 786 and 722 cm^{-1} (S), 784, 723 cm^{-1} (V) are assigned to the librational modes of water molecules.

Because the character of the Raman spectra of all three studied turquoise samples in the region from 1200 to 900 cm^{-1} is practically identical, it is very improbable that in the structure of the turquoise sample from Senegal could be present the $(\text{PO}_3\text{OH})^{2-}$ units, as expected from the mechanism of planerite substitution proposed by Foord and Taggart [36]. More distinctive is therefore the explanation of vacancy given by Kolitsch and Giester [42].

The Raman spectra of turquoise in the 300–800 cm^{-1} spectral range are displayed in Figs. 8a–c. Raman bands and shoulders at 643, 593, 571 and 550 cm^{-1} (A), 642, 592, 571 and 548 cm^{-1} (S), 663, 644, 629, 611, 593, 571 and 551 cm^{-1} (V) are assigned to the split out-of-plane triply degenerate ν_4 (δ) $(\text{PO}_4)^{3-}$ bending vibrations. Some of observed bands, however, may be also connected with the Al(O,OH) bending vibrations and Cu–O stretching vibrations. Coincidence (an overlap) of the mentioned vibrations is supposed. Raman bands and shoulders at 506, 485, 471, 457, 438, 426, 417 and 387 cm^{-1} (A), 511, 483, 469, 460, 437, 423, 417 and 385 cm^{-1} (S), 511, 498, 486, 469, 449, 437, 425, 417, 409 and 385 cm^{-1} (V) are related to the split doubly degenerate ν_2 (δ) $(\text{PO}_4)^{3-}$ bending vibrations. These bands may partly overlap with bands of Cu–O stretching vibrations and bending vibrations.

Raman bands at 337, 321 and 303 cm^{-1} (A), 335, 320 and 301 cm^{-1} (S), 367, 339, 319 and 303 cm^{-1} (V). – these bands may

probably be related to the stretching and bending vibrations of Cu–(O,OH,H₂O) and Al–(O,OH,H₂O). Raman bands observed in the region from 300 to 100 cm^{-1} (Figs. 9a–c) may be assigned to OCuO bending vibrations, OAlO bending vibrations and lattice vibrations.

Conclusions

1. Raman and infrared spectra of three well defined turquoise samples were recorded.
2. Observed Raman and infrared bands are tentatively interpreted and assigned to the stretching and bending vibrations of $(\text{PO}_4)^{3-}$ tetrahedra and of vibrations of hydrogen bonded water molecules and hydroxyl ions. No Raman and infrared bands which could be unambiguously attributed to the stretching and bending vibrations $(\text{PO}_3\text{OH})^{2-}$ were observed.
3. Approximate O–H...O hydrogen bond lengths are inferred from observed Raman and infrared bands connected with the ν OH stretching vibrations of water molecules and hydroxyl ions.
4. Observed Raman and infrared spectra of studied turquoise samples are very similar and comparable. From the results may be inferred that Raman spectroscopy may be very well used to distinguish natural turquoise samples from possible imitations including impregnations of natural material. Vibrational spectra of natural turquoise samples from various localities possessing different morphology, colors etc. are very close. Vibrational spectroscopy cannot be therefore offer reliable data for the provenance determination of natural turquoise.

Acknowledgements

The financial and infra-structure support of the Discipline of Nanotechnology and Molecular Science, Science and Engineering Faculty of the Queensland University of Technology, is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation. This work was financially supported by the long-term project DKRVO 2014/02–2015/02 of the Ministry of Culture of the Czech Republic (National Museum, 00023272). The downloading of the Raman spectra of turquoise from the RRUFF web site is acknowledged.

References

- [1] O.T. Branson, *Turquoise, the Gem of the Centuries*, Treasure Chest Publication, Tucson, Arizona, 1975. 62 pp.
- [2] E. Fritsch, S.F. McClure, M. Ostrooumov, Y. Andres, T. Moses, J.I. Koivula, R.C. Kammerling, *Gems Gemol.* 35 (1999) 4–16.

- [3] S. Hull, M. Fayek, F.J. Mathien, P. Shelley, K. Roler Durand, J. Archaeological Sci. 35 (2008) 1355–1369.
- [4] Y.A. Abdu, S.K. Hull, M. Fayek, F.C. Hawthorne, Am. Miner. 96 (2011) 1433–1442.
- [5] Q. Chen, L. Qi, J. Chen, Spectrosc. Spectral Anal. 29 (2009) 406–409.
- [6] L. She, Y. Qin, M. Feng, Z. Mao, C. Xu, F. Huang, Guang pu 28 (2008) 2107–2110.
- [7] Q. Chen, Z. Yin, L. Qi, Y. Xiong, Gems Gemol. 48 (2012) 198–204.
- [8] Q. Chen, L. Qi, J. Miner. Petrol. 27 (2007) 30–35.
- [9] Z. Jiang, D. Chen, W. Wang, W. Li, X. Cao, Q. Wu, Acta Miner. Sin. (1983) 198–206.
- [10] X.A. Li, Y.F. Wang, H.F. Zhang, Acta Miner. Sin. (1984) 78–83.
- [11] L.J. Luan, Z.X. Han, C.Y. Wang, Y.W. Zhang, Northwestern Geol. 37 (2004) 77–82.
- [12] H.F. Zhang, C.Y. Lin, Z.W. Ma, Z.G. Yang, Acta Miner. Sin. (1982) 254–261.
- [13] R.L. Frost, B.J. Reddy, W.N. Martens, M. Weier, J. Mol. Struct. 788 (2006) 224–231.
- [14] B.J. Reddy, R.L. Frost, M.L. Weier, W.N. Martens, J. Near Infrared Spectrosc. 14 (2006) 241–250.
- [15] H. Pristacz, M. Wildner, R. Škoda, F. Koller, E. Libowitzky, EMC2012 –European Mineralogical Conference, 1 (2012) 461.
- [16] B. Cerveille, La Rech. 163 (1985) 244–247.
- [17] R.T. Liddicoat Jr., Handbook of Gem Identification, 12th ed., Gemological Institute of America, Santa Monica, California, 1989.
- [18] Q. Chen, L. Qi, Y. Zhang, J. Gems Gemol. (2006) 9–12.
- [19] K.S. Moe, T.M. Moses, P. Johnson, Gems Gemol. 43 (2007) 149–151.
- [20] A. Pavese, L. Prosperi, M. Dapiaggi, Austr. Gemol. 22 (2005) 366–371.
- [21] J. Zhou, X. Yuan, J. Gems Gemol. (2008) 31–35.
- [22] D. Elwell, Man-made Gemstones, John Wiley Sons, New York, 1979.
- [23] J.D. Williams, D. Nassau, Gems Gemol. 15 (1976) 226–232.
- [24] H. Pristacz, M. Wildner, V.M.F. Hammer, E. Libowitzky, Corals-2013, Conference on Raman and Luminescence Spectroscopy in the Earth Sciences, 2013, 81–82.
- [25] J. Sejkora, T. Řídkošil, V. Šrein, N. Jb. Miner. Abh. 175 (1999) 105–124.
- [26] J. Sejkora, F.C. Hawthorne, M.A. Cooper, J.D. Grice, J. Vajdak, J.L. Jambor, Can. Miner. 47 (2009) 159–164.
- [27] J. Sejkora, J. Plášil, B. Bureš, Bull. Miner. Petrol. Odd. Nár. Muz. (Praha) 21 (2013) 143–156 (in Czech).
- [28] J. Sejkora, P. Škacha, V. Venclík, J. Plášil, Bull. Miner. Petrol. Odd. Nár. Muz. (Praha) 21 (2013) 113–130 (in Czech).
- [29] L. Vrtiška, J. Sejkora, H. Nováková, M. Vašinová Galiová, Bull. Miner. Petrol. Odd. Nár. Muz. (Praha) 21 (2013) 240–248 (in Czech).
- [30] R.L. Frost, J. Čejka, J. Sejkora, D. Ozdín, S. Bahfenne, E.C. Keefe, J. Raman Spectrosc. 40 (2009) 1907–1910.
- [31] J. Čejka, R.L. Frost, J. Sejkora, E.C. Keefe, J. Raman Spectrosc. 40 (2009) 1464–1468.
- [32] R.L. Frost, J. Sejkora, J. Čejka, E.C. Keefe, J. Raman Spectrosc. 40 (2009) 1546–1550.
- [33] R.L. Frost, S.J. Palmer, Y. Xi, J. Čejka, J. Sejkora, J. Plášil, Spectrochim. Acta A Mol. Biomol. Spectrosc. 103 (2013) 431–434.
- [34] J. Sejkora, J. Čejka, R. Malíková, A. López, Y. Xi, R.L. Frost, Spectrochim. Acta A130 (2014) 83–89.
- [35] J. Čejka, J. Sejkora, I. Macek, R.L. Frost, A. López, R. Scholz, Y. Xi, Spectrochim. Acta A126 (2014) 157–163.
- [36] E.E. Foord, J.E. Taggart Jr., Miner. Mag. 62 (1998) 93–111.
- [37] J. Sejkora, R. Škoda, P. Ondruš, J. Czech Geol. Soc. 51 (2006) 159–187.
- [38] J. Sejkora, J. Čícha, I. Jebavá, Bull. Miner. Petrol. Odd. Nár. Muz. (Praha) 19 (2011) 1–26 (in Czech).
- [39] J.W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols, Handbook of Mineralogy, Vol. 4, Arsenates, phosphates, vanadates, Mineral data publishing, Tucson, Arizona, 2000. 680 pp.
- [40] A.R. Graham, Univ. Toronto Stud. Geo. Ser. 52 (1948) 39–53.
- [41] H. Cid-Dresdner, Zeit. Kristal. 121 (1965) 87–113.
- [42] U. Kolitsch, G. Giester, Mineral. Mag. 64 (2000) 905–913.
- [43] P. Ondruš, ZDS – software for analysis of X-ray powder diffraction patterns. Version 6.01. User's guide, Prague, 1995.
- [44] C.W. Burnham, Carnegie Inst. Wash. Yearb. 61 (1962) 132–135.
- [45] K. Nakamoto, Infrared and Raman Spectra of Inorganic Coordination Compounds, J. Wiley and Sons, New York, 1986.
- [46] P. Keller, N. Jb. Miner. Mh. (H.11) (1971) 491–510.
- [47] P. Keller, N. Jb. Miner. Abh. 117 (1972) 217–252.
- [48] P. Keller, N. Jb. Miner. Abh. 119 (1973) 310–334.
- [49] P. Keller, N. Jb. Miner. Abh. 120 (1974) 229–269.
- [50] V.V. Pechkovskii, R. Ya. Mel'nikova, E.D. Dzyuba, T.I. Baranikova, M.V. Nikanovich, Atlas of Infrared Spectra of Phosphates. Orthophosphates, Nauka Moscow, 1981 (in Russian).
- [51] J.A. Goldsmith, S.D. Ross, Spectrochim. Acta A24 (1968) (1968) 2131–2137.
- [52] R.H.P. Devamani, M. Alagar, Nano Biomed. Eng. 5 (2013) 116–120.
- [53] J.M. Aguirre, A. Gutiérrez, O. Giraldo, J. Braz. Chem. Soc. 22 (2011) 546–551.
- [54] R.L. Frost, W.N. Martens, L. Rintoul, E. Mahmutagic, J.T. Klopogge, J. Raman Spectrosc. 33 (2002) 252–259.
- [55] E. Libowitzky, Monatsh. Chem. 130 (1999) 1047–1059.