

Compositional variation of turquoise-group minerals from the historical collection of the Real Museo Mineralogico of the University of Naples

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ABSTRACT

Five turquoise samples, belonging to the XVII century historical collection of the Real Museo Mineralogico (University of Naples Federico II), were investigated by a multi-methodological approach based on powder X-ray diffraction, electron microprobe analysis in wavelength-dispersive spectroscopy mode, back-scattered electron images from scanning electron microscopy in energy-dispersive spectroscopy mode, laser ablation inductively coupled plasma mass spectrometry, Fourier transform infrared and Raman spectroscopy.

The samples originate from Sinai (Egypt), Santa Fè S. Miguel (New Mexico), Saxony (Germany), Montebbras Creuse (France) and Nishapur (Khorassan, Iran) and display different mineralogical compositions and various mineral associations. The study has shown the presence of: (1) four minerals of the turquoise group: turquoise, faustite, chalcocite and planerite; (2) other phosphates from different groups: wavellite, crandallite, goyazite, gorceixite, variscite, metavariscite, fluorapatite; and (3) other minerals: voltaite, adularia and quartz.

The present investigation is intended to show the mineralogical and geochemical variability of the samples with particular attention to the mineralogical parageneses, textural analyses and trace-element concentrations.

KEYWORDS: turquoise-group minerals, alteration, electron microprobe analysis, powder X-ray diffraction, *QualX2.0*, FTIR, Raman.

Introduction

THE turquoise group includes natural hydrated phosphates for which the general formula can be

indicated as $A_{0-1}B_6(PO_4)_4(OH)_8 \cdot 4H_2O$, with Cu^{2+} , Fe^{2+} , Zn^{2+} and (rarely) Ca^{2+} occupying the *A* position, and Al^{3+} , in some cases replaced by Fe^{3+} , at the *B* position. Such variability in composition produces a wide range of colours. Foord and Taggart (1998) suggested that differences in the Cu/Fe ratio are responsible for differences in the colour of the samples, stating that blue turquoise displays

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Cu at the *A* position and Al at the *B* position, whereas chalcociderite (green turquoise) essentially contains Fe^{3+} at the *B* position. However, care must be taken in the definition of the turquoise-group minerals according to their colours, as stated recently by Hyršl (2011), who reports a new variety of variscite, discovered in Peru, which was initially thought to be 'green turquoise', for the particular colour, but was identified subsequently as variscite by X-ray diffraction (XRD).

According to Foord and Taggart (1998), the turquoise group of minerals consists of at least five end-members, isotypic within triclinic $\text{P}\bar{1}$ space group: aheylite $\text{Fe}^{2+}\text{Al}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4(\text{H}_2\text{O})$, chalcociderite $\text{CuFe}_6^{3+}(\text{PO}_4)_4(\text{OH})_8 \cdot 4(\text{H}_2\text{O})$, faustite $(\text{Zn,Cu})\text{Al}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4(\text{H}_2\text{O})$, planerite $\square\text{Al}_6(\text{PO}_4)_2(\text{PO}_3\text{OH})_2(\text{OH})_8 \cdot 4(\text{H}_2\text{O})$ and turquoise $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4(\text{H}_2\text{O})$. In addition, the substitution of Al by Fe^{3+} results in the solid-solution turquoise–chalcociderite series: $\text{Cu}(\text{Al,Fe}^{3+})_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$.

Turquoise-group minerals are usually found as massive or micro-crystalline aggregates, and there is thus a lack of an exhaustive bibliography of structure determinations from single-crystal XRD data (Cid-Dresdner, 1965; Giuseppetti *et al.*, 1989; Kolitsch and Giester, 2000).

Recent studies have highlighted that, when affected by near-surface conditions and extended exposure to sunlight and meteoric (rain) water, turquoise weathers to chalky-white clay minerals (Abdu *et al.*, 2011). The alteration process precludes the correct identification of the precursor phase. Such processes require further investigation (Hull *et al.*, 2008). Abdu *et al.* (2011) reported a study on altered turquoise, showing variable cation deficiencies at the *A* and *B* sites. This investigation highlights the presence of Ca replacing Cu at the *A* site, and Si replacing P at the *B* site. These replacements are accompanied by a reduction in the H_2O contents, although the crystal structure of turquoise is maintained, as verified by XRD. Foord and Taggart (1998) claimed that Ca replaces Cu at the *A* site and that there exists a Ca-dominant phase, named 'coeruleolactite', suggesting further that the *A*-site deficiency in turquoise, accompanied by an excess of H_2O , leads to the formation of planerite. The turquoise-group minerals have been also studied by Fourier transform infrared (FTIR) and Raman vibrational spectroscopy techniques. These are suitable tools for studies of hydrated minerals because of their sensitivity to the hydroxyl-group vibrational spectroscopies as they can distinguish easily between OH and H_2O groups; this being

essential in many cases as a support technique for XRD and compositional analysis, both for single crystals as well as for powder materials (Frost *et al.*, 2006; Reddy *et al.*, 2006; Abdu *et al.*, 2011; Malcherek *et al.*, 2014; Cejka *et al.*, 2015).

The present research takes place within the context of a general survey on natural phosphate which some of the authors have been undertaking (Rossi *et al.*, 2011; Capitelli *et al.*, 2011; 2012; 2014a,b; Ventruti *et al.*, 2016). In particular, the objectives of this investigation is to present a detailed characterization of minerals from the turquoise group, evaluating their provenance, various mineralogical arrangements, and different compositions. In addition, it contributes to the knowledge of the alteration processes of turquoise-group minerals.

Samples

The samples labelled 'turquoise' used in the present investigation and shown in Fig. 1, belong to the collection of the 'Real Museo Mineralogico, Centro Musei delle Scienze Naturali e Fisiche', University of Naples Federico II (Naples, Italy). They originate from historical mine sites and entered the collections of the Museum between 1790 and 1872. Due to a lack of a recent bibliography for these historical mines, descriptions of the mineralogy and features of turquoise minerals found are from publications from the early 1900s (Lacroix, 1910; Pogue, 1916).

Sample E5683 (inventory number), named in this work as 'TUR 1', is a rock with horizontal layers. Turquoise is found in small clusters between the layers; it shows blue-green and light blue colours (Fig. 1) and is from the Sinai Peninsula, Egypt. Sample E7666, labelled 'TUR 2', is a sheet 2 mm thick, with blue-green, white-beige and egg-white colours (Fig. 1), is from Santa Fè, S. Miguel and Los Cerrillos counties in New Mexico, USA. Sample E1675, labelled as 'TUR 3', from Messbach Saxony, Germany, is a layered rock where the turquoise extends in continuous horizontal layers. The turquoise is characterized by apple-green and light-green colours (Fig. 1). Sample E7272, labelled 'TUR 4' from Montebrias Creuse, France, consists of essentially white microcrystalline amblygonite, while the turquoise is only visible locally with blue and pale-blue colours (Fig. 1).

Sample E1670, labelled 'TUR 5', comes from Nishapur, Khorasan, Iran, and shows typical blue and pale-blue turquoise colours. The sample is



FIG. 1. Images of the turquoises studied. TUR 1 (Sinai, Egypt); TUR 2 (Santa Fè S. Miguel, New Mexico); TUR 3 (Saxony, Germany); TUR 4 (Montebras Creuse, France); and TUR 5 (Nischapur, Khorassan, Iran).

composed of small, rounded fragments in which the turquoise is dominant (Fig. 1).

Geological setting

The TUR 1 sample is probably derived from the ancient mines of Wady Maghareh or Serabit el Khadem in the Sinai peninsula, where the oldest turquoise mines in the world are located.

The Wady Maghareh lies in sandstone, derived from nearby mountains of granite that rise up (Basement rocks). On the valley slopes of the turquoise deposits there are outcrops of the El Hashash Formation (pinkish Carboniferous sandstone with numerous cross laminations and ripple marks, thin shale and siltstone; El Aassy *et al.*, 2011) and Magharet El Miah Formation (in particular siltstone with sandstone intercalations; El Aassy *et al.*, 2011). The adjacent hills are capped by a basalt flow of Tertiary age (El Aassy *et al.*, 2011; Pogue, 1916). The turquoise occurs in veins, pockets and patches near the top of the lower sandstone member and in the pinkish sandstone. The mineral is very unevenly distributed, and the productive area is confined within narrow limits,

due to a fault on the north and the steep dip of the beds to the west (Pogue, 1916).

The geology of Serabit is similar to that at Maghareh, consisting of the Cambro-Ordovician formation of Abu Hamata (glauconitic fine- to very-fine-grained sandstone, siltstone and shale with copper mineralization) and Serabit El Khadim (pink sandstone, coarsely laminated, kaolinized with conglomerate interbeds; El Aassy *et al.*, 2011). The turquoise occupies joints traversing a bed of sandstone and is principally confined to a productive stratum below a thin dolostone layer (Um Bogma formation; El Aassy *et al.*, 2011) capping the formation (Pogue, 1916).

Within the Wadi Naseib area, in the Um Bogma formation there are Mn deposits with Fe, Ba, Cu and Zn minerals (El Sharkawi *et al.*, 1990; Magaritz and Brenner, 1979), and a gibbsite deposit associated with Fe, Pb, Zn, S, Si and K mineralization (Segev, 1984). El Reedy *et al.* (1988) and El Aassy *et al.* (2011) report the presence of uranium and thorium ($105 < U < 5083$ ppm, $Th < 330$ ppm; El Reedy *et al.*, 1988) in Um Bogma and El Hashash formations.

The TUR 2 sample comes from Los Cerrillos, New Mexico (USA) old mining districts (Pogue, 1916, Disbrow and Stoll, 1957). In this locality the

turquoise occurred in veins, horizontal layers, fractures, and nodules with kaolinite. In some cases turquoises are associated with a limonitic horizon (derived from pyrite alteration) with inclusions of quartz (Pogue, 1916). Disbrow and Stoll (1957) highlight that the Cerrillos mining district has produced Zn, Pb, Cu, Ag and Au from one group of deposits, and turquoise from another one. Quartz, ankerite, calcite, siderite, baryte, opal and chalcedony are the most prominent gangue minerals (Disbrow and Stoll, 1957). Bournonite and stibnite have also been reported (Northrop, 1944).

In Europe, the presence of 'turquoise' was reported in Saxony, near Oelsnitz and Zwickau districts. Pogue (1916) described it as a 'thin green coating on a dark rock' as the TUR 3 sample shows well in Fig. 1. In southern Saxony many metals were extracted from heterogeneous mineralizations of pyrite, galena, chalcopryrite, sphalerite and arsenopyrite. Stockmann *et al.* (2012) report the presence of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, S and Zn heavy metals. Such mineralization from the Erzgebirge district, spatially coincide with the Erzgebirge–Fichtelgebirge Anticlinorium in the fold framework of the Bohemian Massif. The Erzgebirge–Fichtelgebirge Anticlinorium is dissected by numerous fault zones, diverse in orientation, size, depth, and time of activity. In the second half of the 19th Century, the extraction of uranium started along the faults where the different mineralizations are located (Meinrath *et al.*, 2003; Velichkin and Vlasov, 2011).

The northeastern part of the Erzgebirge–Fichtelgebirge Anticlinorium consists of the Neoproterozoic biotite and two-mica gneisses, schists, and granite gneisses, but also Cambrian crystalline schists. The southwestern part of the FEA consists of the Ordovician quartz-sericite and albite-quartz sericite phyllite-like slates. Over most of the territory of the FEA, the metamorphic rocks are intruded by granites of the Erzgebirge Batholith, ~7000 km² in area (Štemprok, 1993). The emplacement of granites was accompanied by aplite, granite porphyry, and lamprophyre dykes.

Sample TUR 4, from Montebbras Creuse, France, is associated with amblygonite. This locality is also well known for the presence of turquoise within alterations of a granitic dome, characterized by the presence of amblygonite, montebbrasite, morinite (Lacroix, 1910), and apatite, topaz, cassiterite and niobo-tantalite (Dudoignon *et al.*, 1988). In the second half of the 19th century this locality was exploited by the Limoges industry for feldspar and tin, and successively, in the 20th century for lithium (Gravier, 2006).

The occurrence of turquoise is in the tin lodes traversing granite and aplite (Bart, 1948). Lacroix (1901, 1910) in his description of the Montebbras turquoise, states that it results from the alteration of amblygonite with which the mineral is associated intimately. It is also associated with cassiterite, very rarely wolframite, and commonly wavellite, in quartzose vein-stuffs. The copper, according to Lacroix (1901, 1910), has been furnished by small quantities of a sulfide in the cassiterite. Pirard *et al.* (2007) report that phosphate minerals from Montebbras show the occurrence of three mineralization stages. The magmatic stage, with crystallization of primary minerals and F and Li enrichment, the metasomatic stage, with Na and Ca enrichment, and finally low-temperature hydrothermal and meteoric processes. The turquoise growth is correlated with the hydrothermal stage.

Crandallite-group minerals are also very common (Dill, 2001). Below 150°C, variscite appears in vein assemblages also containing kaolinite and gorceixite. Oxidation and alteration of more minerals at this stage forms varlamoffite, cassiterite and stannoidite. Copper from this latter mineral reacts with phosphates to form turquoise.

Sample TUR 5 from near the small village of Maden, 36 miles from Nishapur, Khorosan province, Iran, where many ancient and famous turquoise mines are located. The region surrounding the mines consists of nummulitic limestones and sandstones of Tertiary age, resting upon clay slates and enclosing immense beds of gypsum and rock salt. The strata are intruded by porphyritic trachyte and a diabasic rock, and are locally metamorphosed by them. Both the trachyte and the basic intrusive brecciated phases, and the trachyte contains needles of apatite. The turquoise occurs both in a decomposed phase of the trachyte and in its corresponding breccia. In the trachyte, it forms an extensive system of small veins, from 2–6 mm thick. It fills small clefts and crevices irregularly distributed through the rock and locally replaces feldspar crystals. In the breccia, it is confined to the spaces between the fragments. In nearly all places it is accompanied by limonite or yellow ochre, which partly, or entirely, encloses the turquoise. The alluvium near the foot of the hills carries roughly-rounded pieces of turquoise derived through the processes of weathering from the original veins (Pogue, 1916).

Analytical methods

For each sample under investigation, the analyses (textural, compositional and Raman spectroscopy) were carried out on three different fragments.

Textural analysis

Textural analyses were undertaken on samples by collecting back-scattered images (BSE) using a scanning electron microscope (SEM) JEOL-JSM 5310 (CISAG-University of Naples Federico II), operating at 15 kV and equipped with energy dispersive X-Ray spectroscopy (EDS); data were processed with INCA version 4.08 (Oxford Instruments, 2006).

Electron microprobe analysis

Quantitative compositional analyses of the major and minor elements, were performed by means of electron microprobe analysis in wavelength-dispersive mode (EMPA-WDS) by using a Cameca SX50 (IGAG-CNR, Rome), with the following operating conditions: 15 kV and 20 kV (for Zn and Cu, respectively), 15 nA specimen current and a beam diameter of 10 μm . The natural and synthetic standards used were (crystal, peak): apatite for P (PET, $K\alpha$) and Ca (PET, $K\alpha$); GaAs for As (TAP, $L\alpha$); rutile for Ti (PET, $K\alpha$); baryte for S (PET, $K\alpha$); wollastonite for Si (TAP, $K\alpha$); jadeite for Na (TAP, $K\alpha$); magnetite for Fe (LIF, $K\alpha$); periclase for Mg (TAP, $K\alpha$); orthoclase for K (PET, $K\alpha$); celestine for Sr (PET, $L\alpha$); corundum for Al (TAP, $K\alpha$); rhodonite for Mn (LIF, $K\alpha$); MgF_2 for F (PC1, $K\alpha$); KCl for Cl (PET, $K\alpha$); and Zn metallic for Zn (LIF, $K\alpha$). Data were corrected using the 'PAP' program (Pouchou and Pichoir, 1991); analytical measurements are affected by a relative uncertainty of 1% for major elements, 5% for minor elements and 7–10% for fluorine. For each fragment ten analytical points for turquoise minerals and associated minerals were determined. For all minerals the crystal-chemical formulae were calculated on a cation basis. In particular, for turquoise, the Fe_2O_3 and FeO contents were calculated, from total Fe, with the B site ($\text{Fe}^{3+} + \text{Al}^{3+}$) = 6.

Laser ablation ICP-MS

Quantitative compositional analyses of trace elements were performed by using laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) (IGG-CNR, Pavia), with a magnetic sector double focusing mass spectrometer equipped with a plasma source type ELEMENT I (ThermoFinnigan) and a laser microprobe developed at the Memorial University of Newfoundland (Canada) with a wavelength of 266 or 213 nm. The mass spectrometer is a Model Element II ICP for

torch (CD-2), magnet and magnetic field controller (option 'fast scanning'). A spot size of 20 μm and NIST 612 were used. Tiepolo *et al.* (2003) demonstrated that the ELEMENT sector field mass spectrometer, coupled with a 266 nm laser source, allows trace-element determination on geological samples with a precision and accuracy generally better than 10%. For each fragment five analytical points for turquoise minerals and associated phosphates were determined.

Powder X-ray diffraction

For each turquoise sample, powder X-ray diffraction (PXRD) data were collected at room temperature using an automated Rigaku RINT2500 diffractometer (50 kV, 200 mA) equipped with the silicon strip Rigaku D/teX Ultra detector (IC-CNR, Bari). An asymmetrical Johansson Ge crystal was used to select the monochromatic $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). The angular range $6\text{--}120^\circ$ (2θ) was scanned with a step size of 0.02° (2θ) and counting time of 3 s/step. The measurements were executed in transmission mode, by introducing the samples in special glass capillaries, 0.5 mm in diameter, and mounted on the axis of the diffractometer. In order to reduce the effect of possible preferred orientation, the capillaries were rotated during measurements to improve the randomization of the orientations of the individual crystallites. Phase(s) identification of polycrystalline turquoise mixtures was carried out by using the fourth generation computer program *QualX2.0* (Altomare *et al.*, 2015), equipped with the PDF database (International Centre for Diffraction Data, 2014) and the freely available POW_COD database. *QualX2.0* searches for the phase(s) belonging to the database best matching the experimental pattern, via a search/match approach using the list of experimental values of interplanar d -spacings (derived from the diffraction angles) and the peak intensities. The qualitative phase analysis results from *QualX2.0*, for all the samples investigated, are reported in the supplementary materials (Fig. 1S). All the supplementary material (Figs 1S–3S) has been deposited with the Principal Editor of *Mineralogical Magazine* and is available from http://www.minersoc.org/pages/e_journals/dep_mat_mm.html

Raman spectroscopy

Raman spectra were obtained by using a confocal Raman microscope (Jasco, NRS-3100). The

647 nm line of a water-cooled Kr⁺ laser (Innova 300, Coherent), was injected into an integrated Olympus microscope and focused to a spot diameter of $\sim 1\ \mu\text{m}$ by a 100x objective with a final 2–10 mW power at the sample. A holographic notch filter was used to reject the excitation laser line. Raman back-scattering was collected at 180°, using a 0.1 mm slit and a diffraction lattice of 1200 groove/mm, corresponding to an average spectral resolution of $4\ \text{cm}^{-1}$. It takes five accumulations (60 s each) to collect a complete data set by a Peltier-cooled 1024×128 pixel CCD photon detector (Andor DU401BVI). Wavelength calibration has been performed by using cyclohexane as a standard. All samples were analysed in three different points, and to check for reproducibility and spatial heterogeneity each spectra took six acquisitions of 30 s.

Fourier transform infrared spectroscopy

Powder FTIR spectra were collected at Università Roma Tre, on a Nicolet iS50 FTIR spectrometer equipped with a DTGS detector and a KBr beamsplitter; the nominal resolution was $4\ \text{cm}^{-1}$ and 64 scans were averaged for both sample and background. The samples were prepared as a KBr disk by mixing ~ 1 mg of powder sample in 150 mg of KBr.

Results

Mineralogical investigation: morphology, diffraction and crystal-chemical data

TUR 1

Powder X-ray diffraction qualitative analysis for phase identification, highlights the presence of faustite, turquoise, crandallite and quartz in sample TUR 1; the EMPA-WDS data show the presence of goyazite. The PXRD data are in good agreement with Erd *et al.* (1953) for faustite; with Cid-Dresdner (1965) for turquoise; and with Blanchard *et al.* (1972) for crandallite. Textural analysis highlights the presence of areas filled essentially by blue-green faustite (Fig. 2a), and locally also by turquoise, goyazite, and quartz (Figs 2b,c).

Compositional analysis of faustite (F1, Table 1a) shows significant amounts of Cu, occupying the A site at 33%; this is a higher value with respect to that found in the sample coming from Copper King mine, Eureka County, Nevada (Erd *et al.*, 1953) (Table 2). In particular, the Zn/Cu ratio is 1.80 vs.

4.68, while values for P, Al and Fe³⁺ are comparable. Faustite (F2, Table 1a) was found, in the analysed fragments, characterized by high Si (1.14 apfu) and Ca (0.12 apfu) contents.

The turquoise (T, Table 1a) has the A site occupied by Cu at 59% and relatively high contents of Ca (0.13 apfu), Sr (0.082 apfu) and Ba (0.043 apfu), whereas the P site is occupied by Si at 41%. Such data were also obtained for turquoises from Wadi Maghara, Sinai (Si = 0.59, Ca = 0.57, Cu = 0.34 apfu; sample 9, Table 2a; Pogue, 1916).

In good agreement with Sejkora *et al.* (2006), the compositional analyses of goyazite (G, Table 1a), in which the A site is occupied by 60% Sr, shows the significant presence of crandallite Ca (0.204 apfu) and gorceixite Ba (0.039 apfu) molecules. In addition, there are high levels of S occupying the P site of 15%.

The trace-element contents of turquoise and goyazite (T and G, Table 3) are comparable, however they are different from those of faustite, as shown in Fig. 3, where Ti is plotted vs. Zr, Cr, Mn and V. The latter are commonly used as compositional discriminants given their particular resistance to low-temperature alteration and weathering (Shortland *et al.*, 2007; Pearce and Cann, 1973). In addition the turquoise and goyazite show high contents of U: 287 and 399 ppm, respectively. Besides, faustite is richer in light rare-earth elements (LREE) (Table 4), and also the trend of REE normalized to chondrite (Fig. 4, Table 4) varies with respect to those of turquoise and goyazite, which are comparable to each other.

TUR 2

Sample TUR 2 is composed of turquoise and Fe-rich turquoise (dominant, with blue-green colour), Fe-rich variscite and metavariscite, with voltaite (egg-white colour) and adularia (white-beige colour). The qualitative phase analysis shows the presence of: (1) turquoise and Fe-rich turquoise, in agreement, respectively, with Foord and Taggart (1998) and Cid-Dresdner and Villarroel (1972); (2) Fe-rich variscite in agreement with Onac *et al.* (2004); and (3) metavariscite in agreement with Kniep *et al.* (1977) and Blanchard (1981). The EDS-BSE analyses show turquoise at the core of the sample, Fe-rich variscite at the rim with variable thickness (Fig. 5a) and, locally, voltaite and adularia (Fig. 5b).

Recalculated compositions, based on Fe_{tot}, confirmed the presence of Fe³⁺ (T2, Table 1a), but only locally. The compositional trends for both

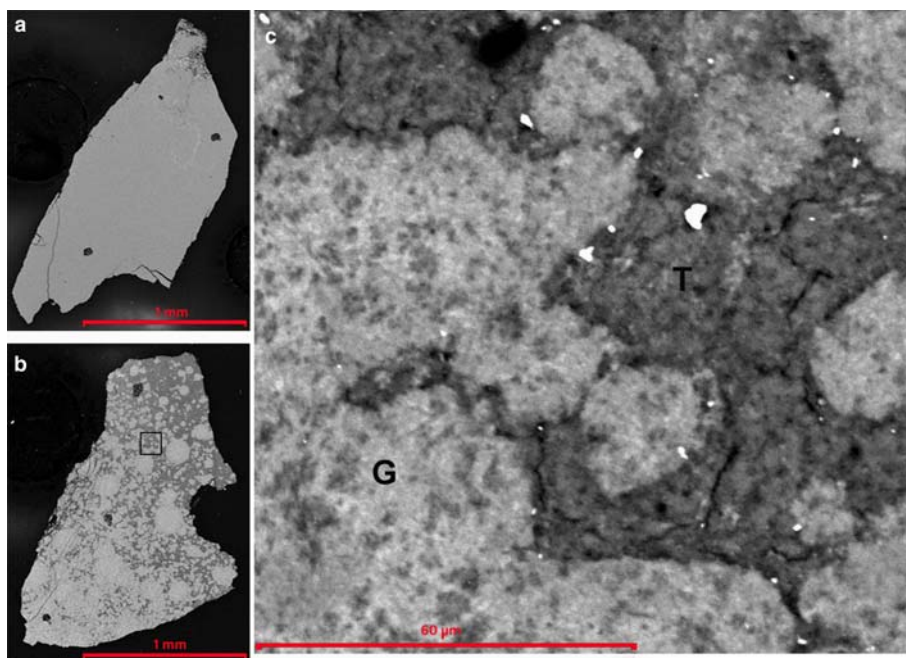


FIG. 2. BSE images of TUR 1: (a) homogeneous fragment made up of faustite; (b) fragment with strong compositional variability; (c) detail of the fragment in (b), made up of turquoise (T) and goyazite (G). Scale bars: (a) and (b) 1 mm; (c) 60 μm .

turquoises (T1 and Fe-rich T2, Table 1a), are comparable with samples from Los Cerrillos-New Mexico (Table 2, samples 3, 11, 12 and 13, respectively).

The recalculated Fe^{3+} content in variscite is comparable with that of the samples from Everdosa Portugal: P (1.029 apfu); Al (0.930 apfu); Fe^{3+} (0.030 apfu) (Calas *et al.*, 2005); and from Cioclovina cave, Romania: P (0.947 apfu); Al $^{3+}$ (0.965 apfu); and Fe^{3+} (0.012 apfu) (Onac *et al.*, 2004). Voltaite presents a peculiar composition (Table 1a) in comparison with the sample from Smolnik, Czech Republic (Anthony *et al.*, 1990; Mereiter, 1972). In all the phases analysed significant amounts of Ti (Table 1a) were determined.

The LA-ICP-MS analyses were carried out only on turquoise and variscite, in which the contents of trace elements are generally comparable (T and V, Table 3; Fig. 3). These data highlight the high Ba contents for turquoise and variscite, respectively, of 801 and 678 ppm, and high As contents, of 449 and 555 ppm. The REE patterns of turquoise and variscite are very similar, even if the turquoise seems slightly enriched in comparison with variscite (Fig. 4, Table 4).

TUR 3

The EMPA for TUR 3 indicated the presence of chalcociderite and variscite, the latter confirmed by PXRD qualitative analysis.

The sample is quite homogeneous as evidenced by BSE imagery (Fig. 6a,b). Chalcociderite is located at the rim (Fig. 6c), while at the core there is variscite that locally shows a higher content of Fe^{3+} . The recalculated Fe^{3+} content of chalcociderite is higher, and Al, Cu and P lower, than that found in samples from Schneckenste, Germany (Table 2b); in addition, there are high contents of Ca, Cr and V (Table 1b).

The variscite composition is quite similar to that of samples from Portugal, Romania and New Mexico (TUR 2), but with higher contents of Fe^{3+} , and significant contents of Cr and V, as known in variscite from Sardinia (Italy) [(P 1.011, Al 0.896, Fe^{3+} 0.041, Cr 0.005 and V 0.008 apfu) Calas *et al.*, 2005]. Chalcociderite and variscite show small differences in trace-element content (Fig. 3) and non-negligible amounts, respectively, of: As (1259 and 679 ppm), U (460 and 391 ppm) and Pb (229 and 94 ppm) (Table 3). Their REE-normalized trends are quite similar (Fig. 4, Table 4).

TABLE 1A. Representative composition (wt.%) and unit formula (apfu) for turquoise-group minerals and other related minerals.

Mineral	TUR 1 Sinai, Egypt				TUR 2 Los Cerrillos New Mexico				
	F1	F2	T	G	T1	T2	V	Vo	A
P ₂ O ₅	34.714	32.388	20.091	25.376	34.180	34.203	46.088	2.169	0.102
SO ₃	0.147	0.601	0.203	5.090	0.528	0.787	0.193	45.175	n.d
SiO ₂	0.122	8.675	12.177	n.d	0.008	0.015	0.004	0.130	63.101
Al ₂ O ₃	37.070	33.356	36.292	31.473	35.685	34.363	30.887	2.828	18.435
^a Fe ₂ O ₃	0.108	0.143	0.244	n.d	2.216	4.515	1.422	11.552	n.d
CuO	3.211	3.081	6.437	0.634	7.177	7.196	0.400	0.632	n.d
ZnO	5.922	5.232	0.422	0.483	0.108	0.090	0.005	0.232	0.840
FeO	-	-	-	n.d	0.325	-	-	15.135	0.760
TiO ₂	n.d	n.d	n.d	n.d	1.077	0.861	0.675	0.106	0.322
MnO	n.d	n.d	n.d	n.d	0.038	0.056	0.016	0.043	n.d
MgO	0.170	0.334	0.134	0.284	0.002	0.009	0.010	0.549	0.064
CaO	0.195	0.852	0.898	2.447	0.046	0.039	0.025	0.147	0.078
SrO	n.d	n.d	1.025	13.226	0.466	1.050	1.082	0.082	1.043
Na ₂ O	0.038	n.d	0.320	0.267	0.035	0.027	0.037	1.211	1.103
K ₂ O	0.037	0.304	0.284	0.118	0.071	0.083	0.035	3.500	14.126
^b BaO	0.249	-	0.808	1.618	n.d	n.d	n.d	n.d	n.d
F	0.014	0.005	n.d	0.284	n.d	n.d	n.d	n.d	n.d
^c H ₂ O ⁺	18.004	15.032	20.664	18.702	16.705	18.039	19.121	16.509	-
(F,Cl)/O	0.006	0.002	-	0.120	-	-	-	-	-
Tot.	99.994	99.998	100.00	99.88	100.00	100.00	100.00	100.00	99.97
		11		6		11	2	23	2
Cu	0.330(40)	0.31(22)	0.664(87)	0.038(12)	0.744(75)	0.743(53)	0.008(4)	0.159(43)	-
Zn	0.595(42)	0.51(14)	0.043(10)	0.028(10)	0.011(15)	0.009(9)	-	0.057(53)	0.029(5)
Fe ²⁺	-	-	-	-	0.037(21)	-	-	4.21((25)	0.030(21)
Ti	-	-	0.007(7)	-	0.111(34)	0.088(16)	0.013(9)	0.026(38)	0.011(5)
Mn	-	-	-	-	0.004(4)	0.007(8)	-	0.012(17)	-
Mg	0.034(4)	0.065(46)	0.027(4)	0.034(1)	-	0.002(3)	-	0.272(1)	0.004(1)
Ca	0.028(3)	0.12(12)	0.13(10)	0.208(3)	0.007(5)	0.006(4)	0.001(1)	0.052(19)	0.004(1)
Sr	-	-	0.081(20)	0.612(68)	0.037(40)	0.083(15)	0.016(2)	0.016(8)	0.028(4)
Na	0.010(3)	-	0.085(40)	0.041(30)	0.009(2)	0.007(18)	0.002(2)	0.78(13)	0.100(5)
K	0.006(2)	0.051(63)	0.049(7)	0.012(16)	0.012(7)	0.014(7)	0.001(1)	1.49(11)	0.839(15)
Ba	0.013(10)	-	0.043(25)	0.051(40)	-	-	-	-	-
Al	5.943(33)	5.15(31)	5.843(91)	2.958(41)	5.771(70)	5.54(17)	0.930(16)	1.109(61)	1.01(18)
Fe ³⁺	0.011(7)	0.014(10)	0.025(8)	-	0.229(54)	0.46(14)	0.027(5)	2.89(54)	-
P	3.997(20)	3.59(45)	2.32(50)	1.713(68)	3.971(38)	3.958(42)	0.997(14)	0.611(54)	0.004(1)
S	0.015(2)	0.059(60)	0.021(16)	0.305(68)	0.054(12)	0.081(21)	0.004(3)	11.28(16)	-
Si	0.017(6)	1.14(57)	1.66(59)	-	0.001(2)	0.002(4)	-	0.043(1)	2.939(71)
F	0.006	0.002	-	0.072	-	-	-	-	-
^d OH	16.335	13.139	18.830	9.949	15.230	16.512	3.260	36.625	-
<i>A</i>	1.017	1.046	1.124	1.024	0.974	0.960	0.041	7.070 ^c	1.045
<i>B</i>	5.954	5.165	5.869	2.958	6.000	6.000	0.958	4.000 ^f	-
<i>T</i>	4.029	4.789	4.008	2.018	4.026	4.040	1.001	11.994 ^g	3.955
<i>X</i>	16.341	13.140	18.830	10.020	15.230	16.512	3.260	41.973	-

F = faustite; T = turquoise; G = goyazite; V = variscite; Vo = voltaite; A = adularia; n.d = not detected.

Structural formulae (apfu) normalized to cations (CAT).

^a Calculated with B_{site} = 6; ^b calculated by LA-ICP-MS data; ^c calculated by difference to 100. ^d OH + H₂O. ^e A_{site} = K + Na (2.266 apfu) + bivalent cations (4.805 apfu); ^f B_{site} = Al + Fe³⁺; ^g T_{site} = S + Si + P. Standard deviation given in parentheses.

TURQUOISE-GROUP MINERALS AND ASSOCIATED PHASES

TABLE 1B. Representative compositions (wt.%) and unit formula (apfu) for turquoise-group minerals and other related minerals.

Mineral	TUR 3 Messbach Saxony-Germany		TUR 4 Montebras Creuse-France			
	Ch	V	T	P	V	W
P ₂ O ₅	27.584	44.704	34.296	36.048	46.194	33.072
SO ₃	0.466	0.052	0.007	0.030	0.018	n.d
SiO ₂	0.086	0.015	0.008	0.020	0.025	0.016
^b V ₂ O ₅	0.722	0.556	n.d	n.d	n.d	n.d
Al ₂ O ₃	6.529	29.755	36.816	37.183	31.661	36.266
^a Fe ₂ O ₃	38.309	2.053	0.107	0.033	0.064	n.d
^b Cr ₂ O ₃	0.313	0.236	n.d	n.d	n.d	n.d
CuO	2.098	0.118	8.283	3.915	0.265	0.345
ZnO	0.082	0.029	0.030	0.058	0.015	0.010
FeO	2.127	-	-	-	-	n.d
TiO ₂	0.030	0.056	0.316	0.294	0.168	0.156
MnO	0.142	0.038	0.004	n.d	0.047	0.032
MgO	0.230	0.010	0.001	n.d	0.025	0.034
CaO	1.472	0.044	0.206	0.271	0.034	0.209
SrO	0.646	1.155	0.035	0.027	0.015	0.006
Na ₂ O	0.127	0.018	0.196	0.704	1.025	0.247
K ₂ O	0.176	0.032	0.026	0.089	0.021	0.030
F	-	-	0.163	0.150	0.182	3.186
^c H ₂ O ⁺	18.859	21.130	19.505	18.979	19.729	26.391
(F,Cl)/O	-	-	0.069	0.063	0.077	1.341
Tot.	100.000	100.000	99.931	97.737	99.411	98.659
	11	2	11	10	2	5
Cu	0.259(12)	0.002(3)	0.864(41)	0.37(12)	0.005(5)	0.018(76)
Zn	0.010(21)	0.001(3)	0.003(4)	0.005(9)	-	0.001(2)
Fe ²⁺	0.29(35)	-	-	-	-	-
Ti	0.004(3)	0.001(1)	0.033(1)	0.028(5)	0.003(1)	0.008(2)
Mn	0.020(4)	0.001(1)	-	-	0.001(1)	0.002(2)
Mg	0.056(13)	-	-	-	0.001(1)	0.004(1)
Ca	0.26(9)	0.001(1)	0.030(2)	0.036(13)	0.001(1)	0.015(41)
Sr	0.061(26)	0.018(1)	0.003(2)	0.002(1)	-	-
Na	0.040(35)	0.001(1)	0.052(10)	0.172(25)	0.050(9)	0.033(7)
K	0.037(8)	0.001(2)	0.005(4)	0.014(2)	0.001(1)	0.003(3)
Al	1.26(73)	0.923(13)	5.989(46)	5.518(45)	0.945(4)	2.970(38)
Fe ³⁺	4.71(45)	0.04(14)	0.011(2)	0.003(1)	0.001(2)	-
Cr	0.030(25)	0.004(4)	-	-	-	-
P	3.82(33)	0.996(7)	4.008(62)	3.84(19)	0.990(6)	1.945(32)
S	0.057(45)	0.001(1)	0.001(3)	0.003(1)	-	-
Si	0.014(17)	-	0.001(2)	0.002(2)	0.001(1)	0.001(1)
V	0.078(35)	0.010(7)	-	-	-	-
F	-	-	0.071(8)	0.06(12)	0.015(5)	0.70(12)
^d OH	20.562	3.709	17.958	15.942	3.332	12.231
<i>A</i>	1.034	0.026	0.990	0.630	0.063	0.084
<i>B</i>	6.000	0.967	6.000	5.522	0.946	2.970
<i>T</i>	3.966	1.007	4.009	3.848	0.991	1.946
<i>X</i>	20.562	3.709	18.029	16.001	3.347	12.931

Ch = chalcociderite; V = variscite; T = turquoise; P = planerite; W = wavellite; n.d = not detected. Structural formulae (apfu) normalized to cations (CAT). ^a Calculated with $B_{\text{site}} = 6$; ^b calculated by LA-ICP-MS data; ^c calculated by difference to 100. ^d OH + H₂O. Standard deviation given in parentheses.

TABLE 1C. Representative compositions (wt.%) and unit formula (apfu) for turquoise-group minerals and other related minerals.

Mineral	TUR 5 Nishapur Khorassan-Iran				
	T	P1	P2	Cr	FAP
P ₂ O ₅	35.283	35.793	35.900	29.930	41.040
SO ₃	0.269	0.166	0.198	0.197	2.080
SiO ₂	0.317	0.066	0.552	n.d	n.d
^b V ₂ O ₅	n.d	n.d	n.d	n.d	n.d
Al ₂ O ₃	37.180	36.009	36.614	32.920	0.280
^a Fe ₂ O ₃	0.701	1.409	1.152	0.286	-
^b Cr ₂ O ₃	n.d	n.d	n.d	n.d	n.d
CuO	7.175	3.809	0.928	0.245	n.d
ZnO	0.113	0.228	0.216	0.095	n.d
FeO	0.790	-	-	-	-
TiO ₂	n.d	0.042	0.065	0.079	0.111
MnO	0.013	0.053	0.024	0.064	0.075
MgO	0.009	0.483	0.791	0.344	0.22
CaO	0.092	0.482	0.650	6.532	52.00
SrO	n.d	0.716	0.753	10.860	1.21
Na ₂ O	0.100	0.066	0.129	0.087	0.524
K ₂ O	0.066	0.036	0.034	0.036	0.009
F	n.d	n.d	n.d	n.d	3.70
^c H ₂ O ⁺	17.892	20.642	21.994	18.324	-
(F,Cl)/O	-	-	-	-	1.558
Tot.	100.000	100.000	100.000	100.000	99.69
	11		10	6	10
Cu	0.733(42)	0.365(51)	0.089(39)	0.014(14)	-
Zn	0.011(21)	0.021(16)	0.020(7)	0.005(10)	-
Fe ²⁺	0.089(38)	-	-	-	-
Ti	-	0.004(4)	0.006(6)	0.005(4)	0.014(7)
Mn	0.001(3)	0.006(5)	0.003(3)	0.004(3)	0.011(5)
Mg	0.002(3)	0.091(41)	0.150(52)	0.039(35)	0.055(10)
Ca	0.013(10)	0.065(16)	0.088(92)	0.53(13)	9.411(89)
Sr	-	0.053(40)	0.056(40)	0.48(12)	0.119(20)
Na	0.026	0.016(22)	0.032(68)	0.013(14)	0.172(35)
K	0.011(6)	0.006(4)	0.005(3)	0.004(3)	0.002(1)
Al	5.929(80)	5.376(80)	5.49(13)	2.952(96)	0.056(20)
Fe ³⁺	0.071(14)	0.134(18)	0.110(27)	0.016(10)	-
Cr	-	-	-	-	-
P	4.041(69)	3.839(57)	3.865(83)	1.93(13)	5.895(79)
S	0.027(10)	0.016(10)	0.019(14)	0.011(15)	0.265(24)
Si	0.043(41)	0.008(10)	0.070(56)	-	-
V	-	-	-	-	-
F	-	-	-	-	1.985(19)
^d OH	16.147	17.443	18.655	9.299	0.015
<i>A</i>	0.888	0.627	0.394	1.093	9.665
<i>B</i>	6.000	5.511	5.597	2.968	0.056
<i>T</i>	4.084	3.863	3.935	1.928	5.895
<i>X</i>	16.137	17.443	18.655	9.299	2.000

T = turquoise; P = planerite; Cr = crandallite; FAP = fluorapatite; n.d = not detected. Structural formulae (apfu) normalized to cations (CAT). ^a Calculated with $B_{\text{site}} = 6$; ^b calculated by LA-ICP-MS data; ^c calculated by difference to 100. ^d OH + H₂O. Standard deviation given in parentheses.

TABLE 2. Representative composition in unit atomic formula (apfu) of turquoise-group minerals from bibliographic data.

Turquoise												Chalcosiderite	Planerite			Faustite
Pogue (1916)		Reddy <i>et al.</i> (2006)		Pogue (1916)		Cid Dresdner and Villarroel (1972)	Pogue (1916)		Reddy <i>et al.</i> (2006)		Cid Dresdner and Villarroel (1972)	Foord and Taggart (1998)			Erd <i>et al.</i> (1953)	
Sinai, Egypt	Wadi Maghara, Sinai, Egypt	Nishapur, Iran	Nishapur, Iran	Nishapur, Iran		Los Cerrillos, New Mexico	Los Cerrillos, New Mexico		Arizona, USA	Schneckenstein, Saxony, Germany	Mt. Tscherrmov, Gumeshevsk, Urals	Syssert District, Urals	Dug Hill, Arkansas, USA	Copper King mine, Eureka County, Nevada, USA		
Cu	8	9	2	4	5	14	3	11	12	13	1	-	14	18	21	-
Zn	0.49	0.34	0.68	0.79	0.49	0.45	0.79	0.66	0.79	0.67	0.84	0.78	0.34	0.04	0.31	0.17
Fe ²⁺	-	-	-	-	-	-	-	-	-	-	-	-	0.02	0.01	-	0.79
Mn	-	-	-	-	0.23	0.44	0.08	-	-	-	-	-	-	-	0.02	-
Mg	-	0.03	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ca	-	0.57	-	-	-	-	-	0.02	0.06	-	-	0.14	-	-	-	-
K	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Al	6.96	6.15	6.04	5.83	5.84	5.75	5.38	6.43	6.03	6.06	6.16	1.86	5.95	5.98	5.89	5.77
Fe ³⁺	0.12	-	0.03	0.17	-	-	0.45	-	0.25	0.42	0.16	3.89	0.05	0.02	0.09	0.18
P	3.43	3.25	4.25	4.21	3.43	2.88	3.98	3.73	3.86	3.29	3.85	4.33	4.06	4.11	4.01	4.09
S	-	0.07	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Si	-	0.59	-	-	0.02	0.49	0.31	0.16	0.02	0.57	-	-	-	-	-	-
OH	20.11	18.66	16.54	16.37	15.89	14.35	17.60	18.23	18.13	16.73	-	13.81	17.36	15.92	17.46	17.37
A	0.49	0.94	0.68	0.79	0.72	0.88	0.88	0.68	0.84	0.67	0.84	0.92	0.36	0.05	0.33	0.96
B	7.08	6.15	6.07	6.00	5.84	5.75	5.83	6.43	6.28	6.47	6.32	5.76	6.00	6.00	5.98	5.95
T	3.43	3.91	4.25	4.21	3.45	3.37	4.29	3.89	3.88	3.86	3.85	4.33	4.06	4.11	4.01	4.09

TABLE 3. Trace-element composition (ppm) of turquoise samples.

Trace elements	TUR 1			TUR 2		TUR 3		TUR 4				TUR 5		
	F	T	G	T	V	Ch	V	T	P	V	W	T	P1	P2
Li	70.15	103.08	98.46	2.08	2.33	1.61	0.58	690.90	990.37	703.64	231.01	336.96	565.44	456.48
Be	44.35	29.17	37.14	4.93	8.11	30.55	47.48	141.87	119.89	22.49	5.21	20.22	1.73	1.02
B	26.63	68.02	71.09	14.88	6.29	14.67	14.58	2.03	2.41	4.08	2.17	28.73	28.73	31.43
^a Mg	-	-	-	5.79	5.42	-	-	-	45.49	-	-	-	-	-
Sc	3.53	26.44	135.65	85.17	36.86	2.63	2.13	0.73	0.89	1.93	2.08	16.07	0.47	0.40
^a Ti	35.28	67.41	146.92	-	-	-	-	-	-	-	-	2.65	-	-
^a V	0.81	14.75	14.06	29.70	27.72	-	-	0.44	0.32	0.16	0.16	0.19	31.08	29.76
^a Cr	5.95	88.56	116.81	40.47	37.72	-	-	1.93	2.92	2.32	4.12	1.62	371.61	372.11
Mn	21.22	0.53	0.39	0.80	0.78	18.81	9.74	150.35	160.25	33.30	59.47	12.78	0.26	0.19
^a Fe	-	-	58.59	-	-	-	-	-	-	-	67.60	-	-	-
Co	171.01	3.80	3.20	0.71	0.38	0.73	0.34	0.13	0.06	0.03	0.03	13.61	11.73	10.96
Ni	14.27	40.95	39.10	0.13	0.14	6.85	3.57	0.19	0.14	0.15	0.47	0.16	2.52	2.91
Ga	2.80	7.73	8.63	44.71	59.53	20.92	20.84	30.56	25.21	18.20	8.74	3.77	2.53	2.40
Ge	0.45	6.38	2.19	0.38	0.45	1.17	0.57	0.44	0.37	0.49	0.59	0.42	0.42	0.38
As	9.56	12.15	15.41	449.38	555.28	1259	678.66	126.34	104.54	39.94	57.28	78.20	28.59	30.07
Rb	1.31	2.19	0.80	6.02	4.89	1.47	0.95	5.59	4.85	2.16	2.81	1.84	0.58	0.78
^a Sr	-	-	-	-	-	-	-	94.23	-	-	-	90.17	-	-
Y	1.59	0.85	3.01	3.54	1.41	28.13	47.55	2.49	3.07	1.43	1.02	1.35	2.03	2.25
Zr	1.57	0.54	2.54	1.38	1.08	0.93	0.34	2.65	3.76	2.22	3.30	0.68	2.99	5.85
Nb	0.27	0.19	0.44	1.83	1.17	0.1140	0.0593	73.75	173.05	25.67	95.84	0.07	0.01	0.01
Mo	0.08	0.89	4.10	1.07	0.97	78.61	51.291	0.03	n.d	0.03	n.d	0.19	0.55	0.68
Ag	1.01	1.16	2.81	0.05	0.11	117.33	3.94	0.41	0.44	0.81	1.69	0.08	0.08	0.04
Cd	0.51	0.40	1.94	0.13	0.11	0.99	0.961	0.65	0.56	0.08	0.34	0.19	0.77	1.03
In	0.13	1.26	1.77	6.44	5.49	0.26	0.12	1.17	0.69	0.31	0.52	1.07	0.09	0.12
Sb	0.08	0.08	0.05	14.28	11.58	36.66	28.5400	31.56	26.76	1.95	2.39	0.31	5.06	4.97
Cs	0.01	0.52	0.17	0.11	0.14	0.36	0.07	0.36	0.76	1.34	3.99	0.03	n.d	n.d
^a Ba	-	-	-	801.50	678.07	147.67	73.80	195.71	167.82	8.51	9.05	951.22	446.85	302.62
Ta	0.01	0.02	0.00	0.03	0.02	0.04	0.01	1035	8467	377.02	940.26	0.03	0.00	0.00
W	0.01	0.03	0.05	0.08	0.03	0.30	0.14	52.33	62.01	5.93	51.91	0.01	0.01	0.02
Au	0.02	0.02	0.04	0.01	0.00	0.52	0.09	1.06	2.25	0.49	1.31	0.06	0.00	0.00
Tl	0.33	0.23	0.27	0.38	0.40	0.41	0.27	4.99	5.76	16.22	0.58	0.09	0.18	0.19
Pb	14.39	1.67	1.85	7.85	5.58	228.61	94.36	0.78	0.68	0.22	0.11	25.16	4.28	3.57
Bi	0.01	0.00	0.01	0.45	0.13	0.96	0.52	0.31	0.32	0.64	0.13	0.01	0.00	0.01
Th	0.18	0.01	0.01	0.70	0.42	0.09	0.08	0.04	0.04	0.01	0.01	0.01	0.08	0.09
U	11.77	286.75	398.60	16.75	11.12	460.19	391.35	169.97	170.46	125.57	66.01	22.83	49.20	51.35

^a omitted values are reported in Tables 1a and 1b as minor elements. F = faustite; T = turquoise; G = goyazite; V = variscite; Ch = chalcosiderite; P = planerite; W = wavellite; n.d = not detected

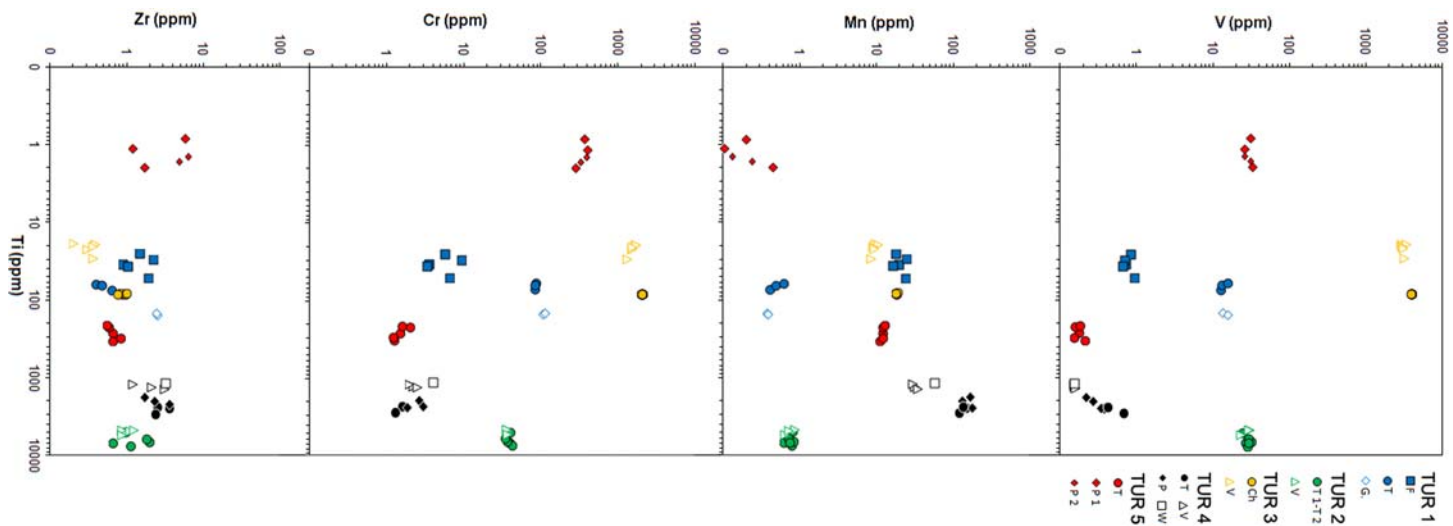


FIG. 3. Trace elements (Ti/V, Ti/Mn, Ti/Cr and Ti/Zr) selected as discriminants for the turquoises investigated.

TABLE 4. REE contents (ppm) of turquoise samples.

REE	TUR 1			TUR 2		TUR 3		TUR 4				TUR 5		
	F	T	G	T	V	Ch	V	T	P	V	W	T	P1	P2
La	1.09	0.03	0.01	0.02	0.06	1.03	0.25	0.01	0.05	0.01	0.94	-	0.04	0.03
Ce	7.65	0.11	0.09	0.35	0.45	2.54	1.79	0.05	0.41	0.34	0.79	0.01	0.12	0.14
Nd	4.58	0.23	0.58	1.42	0.41	6.04	9.84	0.10	0.55	0.08	1.09	0.19	1.09	1.61
Sm	1.02	0.21	0.41	0.94	0.26	5.31	7.92	0.05	0.15	0.04	0.07	0.20	0.88	1.15
Eu	0.21	0.06	0.19	0.46	0.18	1.56	2.86	0.02	0.02	0.01	0.01	0.06	0.25	0.36
Gd	0.90	0.38	1.38	2.20	0.67	3.95	10.48	0.08	0.15	0.16	-	0.30	1.10	1.64
Tb	0.15	0.08	0.21	0.34	0.11	0.83	1.72	0.03	0.02	0.02	0.024	0.04	0.15	0.23
Dy	0.66	0.41	1.03	1.92	0.72	7.16	10.63	0.26	0.30	0.18	0.06	0.23	0.87	1.17
Er	0.13	0.07	0.31	0.65	0.26	3.83	6.03	0.25	0.31	0.06	0.03	0.07	0.29	0.42
Yb	0.16	0.05	0.17	0.40	0.11	8.49	13.96	0.26	0.30	0.07	0.10	0.05	0.24	0.26
Lu	0.02	0.02	0.01	0.04	0.01	1.66	2.19	0.04	0.04	0.03	0.03	0.01	0.02	0.03

F = faustite; T = turquoise; G = goyazite; V = variscite; Ch = chalcosiderite; P = planerite; W = wavellite

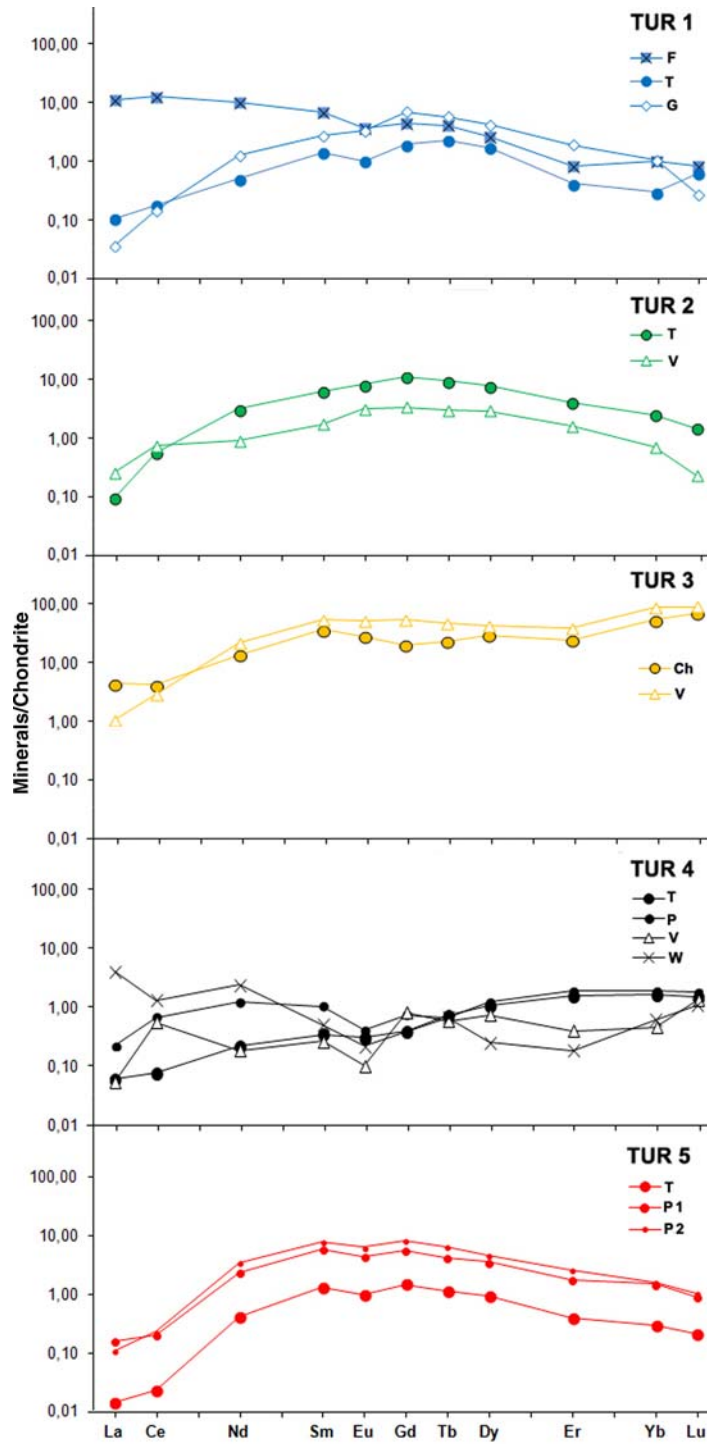


FIG. 4. Distribution patterns of REE normalized to chondrite (McDonough and Sun, 1995).

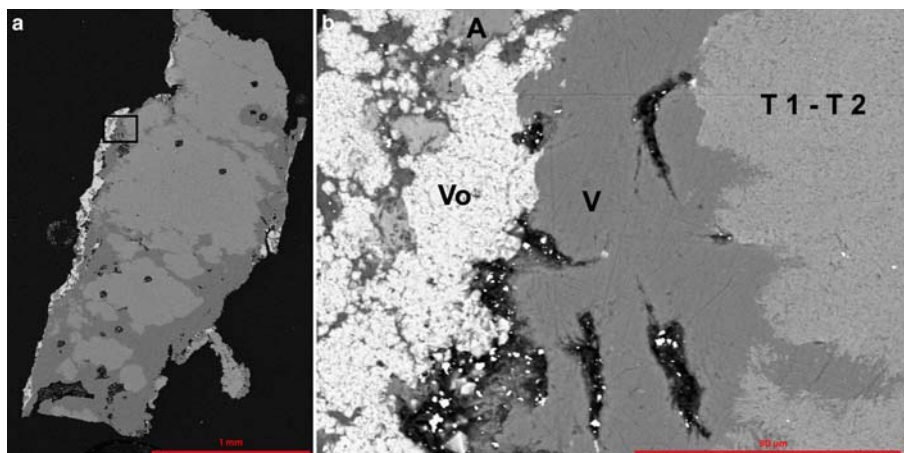


FIG. 5. BSE images of TUR 2: (a) fragment 1 with strong compositional variability; (b) detail of left side of the fragment, with evidence of turquoise assembly between turquoises (T 1 and T 2) and variscite (V), over voltaite (Vo) and adularia (A). Scale: (a) 1 mm; (b) 80 μm .

TUR 4

Powder XRD qualitative analysis of TUR 4 shows the presence of turquoise, planerite, variscite and wavellite, which are confirmed by EMPA results. The EDS-BSE data highlights the mineralogical variability showing a mixture of turquoise, variscite and wavellite (Fig. 7).

Because of the lack of bibliographic data for turquoise from Montebbras Creuse, the TUR 4 composition was compared with that of turquoise from Arizona, USA (Reddy *et al.*, 2006; Table 2), characterized by similar geological features. The compositional and diffraction analyses of planerite are in good agreement with those of Foord and Taggart (1998) (Table 2; sample 14 from Urals), even though there are significant amounts of Na (0.172 apfu) in Montebbras planerite.

Compositional data for the variscite are comparable to those from the literature (Knip *et al.*, 1977) except for the low content of Fe^{3+} (0.001 apfu). In wavellite there are Cu and Ca contents which are quite different from previous data (Capitelli *et al.*, 2014b). In all phases there are detectable amounts of fluorine (Table 1b): 0.071 apfu in turquoise (T), 0.060 apfu in planerite (P), 0.015 apfu in variscite (V) and 0.700 apfu in wavellite (W). Values of Ti, Zr, La, Cr, Mn and V are similar for turquoise and planerite, and quite different from those of variscite and wavellite (Fig. 3).

With respect to the trace-element data, there are significant contents of Ta and Li (Table 3), but also detectable amounts of U, Ba, Mn, As and Nb. The content of these elements is higher in turquoise and

planerite with respect to other minerals. In particular we observed 8467 ppm of Ta and 990 ppm of Li in planerite. The *REE*-normalized trends are very different, with the exception of heavy *REE*, which are similar for turquoise and planerite, and for variscite and wavellite (Fig. 4, Table 4).

TUR 5

In sample TUR 5 the PXRD qualitative analysis confirms the presence of turquoise, Cu-rich planerite, planerite and quartz; while the compositional analyses also highlight the presence of fluorapatite and crandallite.

The homogeneity of samples can be seen from EDS-BSE analysis (Figs 8a,b) but, locally, underlines the presence of minerals that form concentric rims, with the following sequence: apatite is surrounded firstly by crandallite, next by planerite, and lastly by turquoise (Fig. 8c). Quartz is also scattered throughout the sample.

The compositional data for this turquoise does not show extensive differences in comparison with turquoise from the Nishapur area (samples 2 and 4 in Table 2), except for the Fe^{2+} contents. Compositional analysis confirms the presence of two types of planerite, one richer in Cu with 0.365 apfu (P1, Table 1b) and the other (P2, Table 1c) richer in Ca with 0.088 apfu and Si with 0.070 apfu, which is similar to samples from Arkansas, USA (Table 2) and the Sysstert District, Urals (Table 2). There are no bibliographic data for planerite from Nishapur. The crandallite

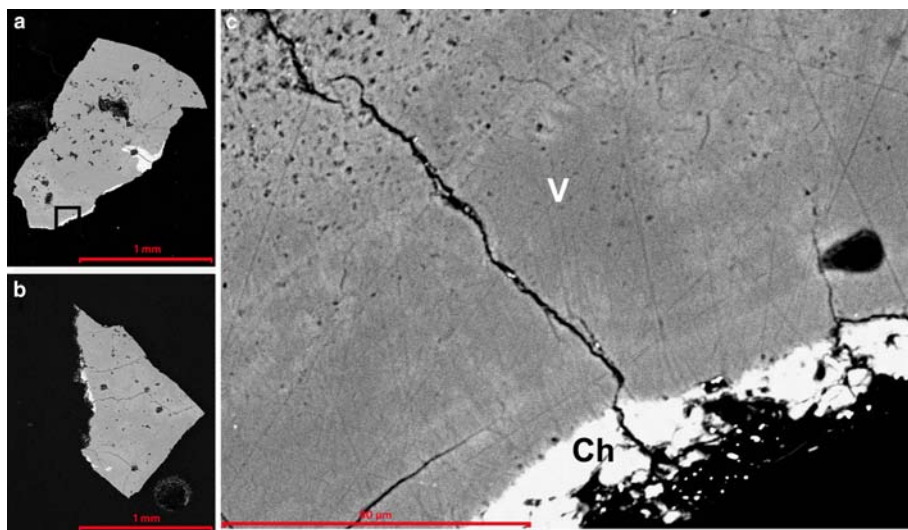


FIG. 6. BSE images of TUR 3: (a) fragment 1; (b) fragment 2. In both fragments the presence of chalcosiderite (marginal side of the sample, white colour) is visible. (c) Detail of fragment 1, with presence of chalcosiderite (Ch) and variscite (V). Scale: (a) and (b) 1 mm; (c) 80 μm .

composition, in terms of Sr, is comparable with analyses reported by Sejkora *et al.* (2006).

Turquoise and planerite show a very different content of Ti, Zr, La, Cr, Mn and V (Fig. 3), there are also present detectable amounts of Li (565, 456 and 337 ppm), and Ba (447, 303 and 951 ppm) in Cu-rich planerite (P1), planerite (P2) and turquoise (T), respectively. The *REE*-normalized trends are quite similar (Fig. 4, Table 4), even though the planerite minerals are richer in *REE*.

Raman microspectroscopy data

Raman spectra of the five turquoises were recorded in the spectral range from 4000–200 cm^{-1} , which can provide wavenumbers related to the stretching (symmetric ν_1 and antisymmetric ν_3) and bending vibrations (ν_2 and ν_4) of phosphate tetrahedra, water molecules and hydroxyl ions, ν_{OH} in turquoise (Frost *et al.*, 2006). Two relevant regions are shown in Figs 9a and b. The spectral window of 900–1200 cm^{-1} is the region of phosphate stretching bands (Fig. 9a), whereas the high-wavenumber window 3700–3300 cm^{-1} (Fig. 9b) contains the water and hydroxyl OH stretching bands. Raman spectra for the five turquoises reveal significant differences, both in the low- and high-wavenumber regions. The low-wavenumber regions have been compared with the limited Raman literature on

turquoise (Čejka *et al.*, 2015 and therein) and with the mineral database RRUFF (Downs and Hall-Wallace, 2003) for possible band assignments.

TUR 1 is a mixture of at least two/three components in comparable abundance: gorceixite (the strongest band at 967 cm^{-1}), faustite and turquoise (bands at 1025, 1037 and 1080 cm^{-1} and a shoulder at 1109 cm^{-1}). For the strong band below 1000 cm^{-1} , goyazite cannot be ruled out.

TUR 2 is composed mostly of turquoise (major band at 1045 cm^{-1} , with a minor band at 1110 cm^{-1}). Multiple Raman measurements detected no bands associated with variscite. Some yellowish regions of the sample revealed additional components (304, 361, 456, 581, 630, 1014, 1110 and 1161 cm^{-1} , Supplementary material, Fig. 2S), tentatively assigned to an iron sulfate (Jentzsch *et al.*, 2013), possibly copiapite (Kong *et al.*, 2011). No band above 1200 cm^{-1} (typical of voltaite) was observed in the punctual (few μm^2 spots) Raman measurements performed.

TUR 3 is composed mostly of variscite (two bands at 1024 and 1057 cm^{-1}), though chalcosiderite cannot be ruled out (Frost *et al.*, 2006). In TUR 3 black spots, corresponding to D and G bands (1353 and 1605 cm^{-1}) of charcoal (Alfè *et al.*, 2012) were also visible (Supplementary material; Fig. 3S).

TUR 4 is inhomogeneous, variably exhibiting variscite (1024 cm^{-1}) and wavellite / turquoise (1037 and 1098 cm^{-1}) features.

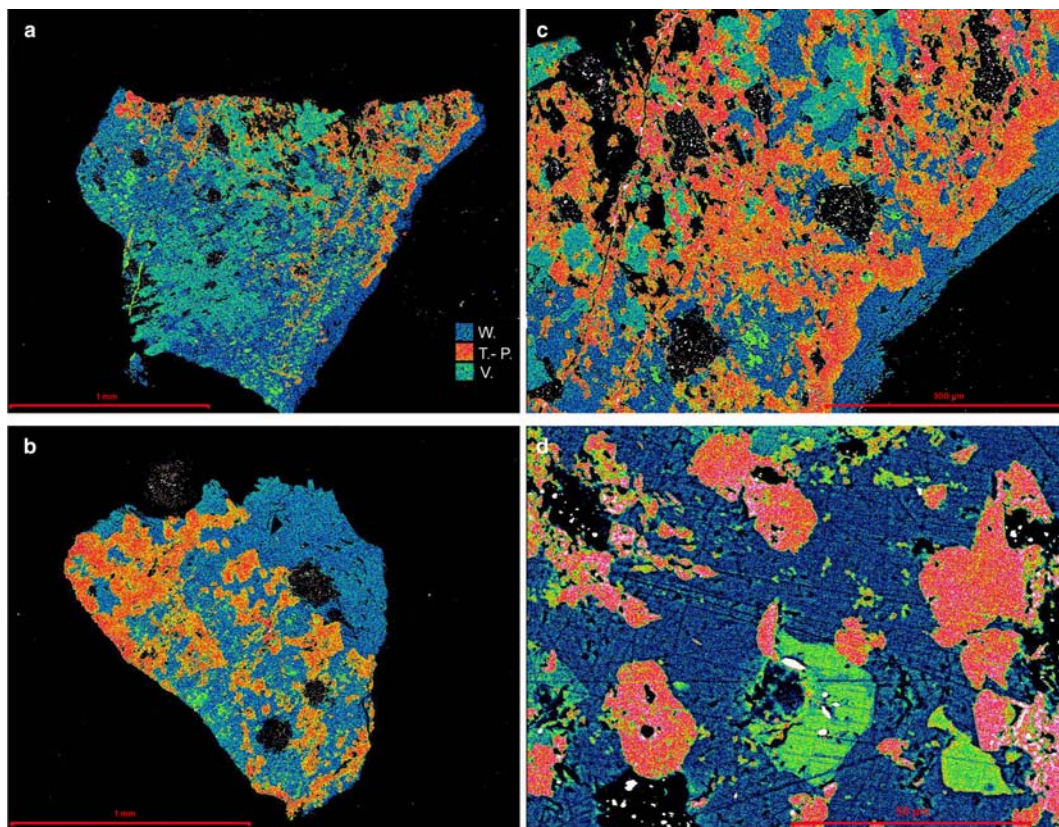


FIG. 7. False colour BSE images of TUR 4: colours highlight the compositional variability of two of the three analysed fragments. (a) and (b) represent two fragments of TUR 4, with largest compositional variability. (c) and (d) details of the two fragments with evidence of genetic relations among different phases: wavellite (W), turquoise (T), planerite (P) and variscite (V). Scale: (a) and (b) 1 mm; (c) 300 µm; (d) 50 µm.

TUR 5 is composed mostly of turquoise (a major band at 1037 cm^{-1} , and a minor band at 1095 cm^{-1}), though planerite and crandallite cannot be ruled out.

The high-wavenumber region (Fig. 9b) reflects the H_2O and OH vibrations in the minerals. Therefore, this region is expected to be a valuable for identification of modifications in the mineral hydration upon weathering. Spectra in Fig. 9b contain three different contributions from crystallization of H_2O : a sharp signal at $\sim 3570\text{ cm}^{-1}$, or bands at ~ 3468 and 3510 cm^{-1} . Analogously to the low-wavenumber region, TUR 4 exhibits a heterogeneity with a second component similar to the high-wavenumber feature of TUR 2 (data not shown). These high-wavenumber bands do not corresponds to those expected from the low-wavenumber assignment (with the exception of

variscite in TUR 3 and part of TUR 4), reflecting weathering-induced alteration.

FTIR data

Fourier transform infrared (FTIR) spectroscopy studies on turquoise-group minerals are relatively scarce. The only FTIR data to date are in Ross (1974), Reddy *et al.* (2006), Abdu *et al.* (2011), Chen *et al.* (2012) and Čejka *et al.* (2015). The crystal structure of turquoise-group minerals is characterized by the presence of hydroxyl groups and water molecules (Cid-Dresdner, 1965). This implies that in the FTIR spectra of these minerals, absorptions due to hydroxyl groups and H_2O molecules, are both observed.

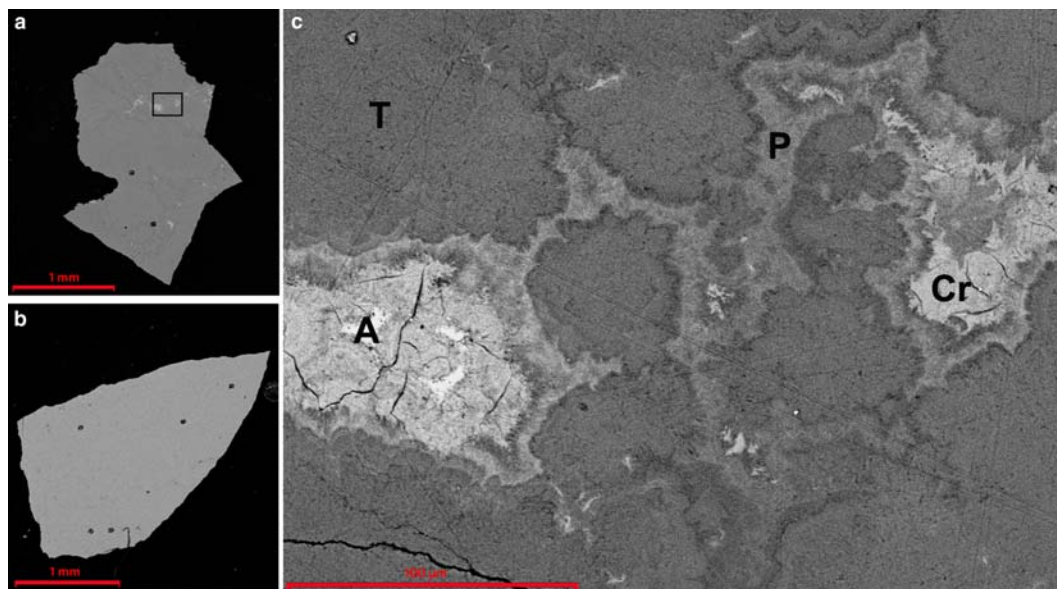


FIG. 8. BSE images of TUR 5: (a) fragment 1 with largest compositional variability; (b) representative fragment made up essentially by turquoise; (c) detail of fragment 1 with evidence of turquoise (T), planerite (P), crandallite (Cr) and apatite (A). Scale: (a) and (b) 1 mm; (c) 100 μm .

The FTIR spectra of the samples studied (Fig. 10a) show a very broad absorption extending from 3700 to 3000 cm^{-1} with several overlapping sharp components; these can be assigned to the stretching modes of OH groups and to the stretching modes and the bending overtone of the H_2O molecules. The absorption due to the bending mode of the H_2O molecules occurs from 1634 cm^{-1} to 1642 cm^{-1} . Ross (1974) reports H_2O and OH stretching absorptions at 3508, 3463, 3446, 3295 and 3090 cm^{-1} , while the bending of (H_2O) is at 1650 cm^{-1} . Reddy *et al.* (2006) and Chen *et al.* (2012) report stretching absorptions of OH and H_2O at ~ 3510 , 3463, 3290 and 3086 cm^{-1} , and the bending of H_2O at 1638 cm^{-1} . Frost *et al.* (2013) report, for the chalcosiderite phase, bands at 3458, 3506, 3507 and 3553 cm^{-1} for the OH stretching vibrations, and (broad) bands at 3030, 3098, 3201 and 3390 cm^{-1} for the water stretching vibrations. In this region the spectra of our samples (Fig. 10b), are quite different in number, width and position of the bands, as a function of their different mineralogical composition. According to Abdu *et al.* (2011) the sharp absorption at 3509, 3494, 3467 and 3448 cm^{-1} can be attributed to OH group components, which are well resolved in TUR 1 and TUR 5 and less so in TUR 2, TUR 4 and TUR 3. The band at 3584 cm^{-1} , occurring with increasing intensity, in TUR 2, TUR 4

and TUR 3 spectra, could be due to the increasing content of variscite in these samples (Ross, 1974; Chukanov, 2014).

The absorptions due to the ν_3 anti-symmetric vibrations of the phosphate group (PO_4)³⁻ are located between 1200–900 cm^{-1} and were recorded at ~ 1157 , 1107, 1058 and 1011 cm^{-1} by Chen *et al.* (2012) and by Ross (1974) at 1195, 1175, 1115, 1063 and 1016 cm^{-1} , while Frost *et al.* (2013) report values at 1196, 1153, 1107 and 1063 cm^{-1} in the chalcosiderite IR spectrum. These data are in good agreement with the data of TUR 1, TUR 2 and TUR 5 spectra (Fig. 10c) where the principal components are at (± 2 cm^{-1}): 1192, 1172, 1154, 1110, 1063 and 1011 cm^{-1} . However, TUR 3 and TUR 4 spectra are quite different with the principal components occurring at: 1153, 1087 (TUR 4), 1126 (TUR 3), 1064 and 1011 cm^{-1} .

In the region below 900 cm^{-1} there are absorptions due to coupled motions of the framework polyhedra and to the ν_4 phosphate bending modes from 615 to 460 cm^{-1} (Ross, 1974). From 830 to 780 cm^{-1} there are some very weak bands that can be assigned, according to Chen *et al.* (2012) and Ross (1974), to the bending vibration of OH groups.

Finally, at 1384 cm^{-1} there is a weak but very sharp band, which is of doubtful assignment. It cannot be an artifact from the KBr pellet, as

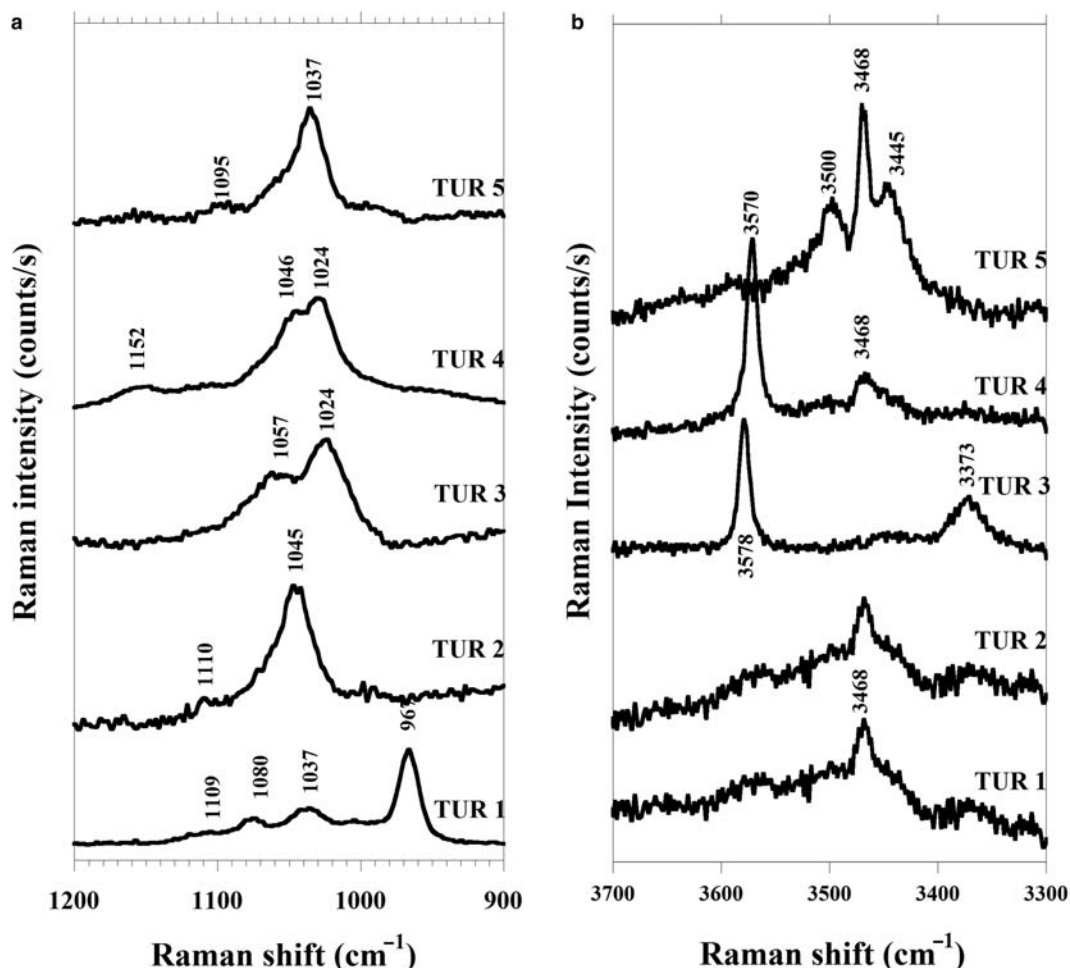


FIG. 9. (a) Raman spectrum in the low frequency region for the five samples investigated (647 nm, 2 mW at the sample). (b) Raman spectrum in the high frequency region for the five samples investigated (647 nm, 2 mW at the sample).

suggested by Abdu *et al.* (2011), because it occurs in other published turquoises and variscite IR spectra (Onac *et al.*, 2004; Chen *et al.*, 2012), Onac *et al.* (2004) observed that this peak could be ascribed to N-containing organic compounds.

In summary, the IR data show that there is a substantial difference for the five samples with TUR 1, TUR 2 and TUR 5 in one set, and TUR 3 and TUR 4 in another set.

Discussion

The five samples investigated originating from different localities, represent the end-member

phases of turquoise-group minerals, containing chalcocite, turquoise, planerite and faustite. They are interesting because of the presence of other Al phases such as crandallite, variscite, metavariscite and wavellite, and for other minerals typically associated with turquoises, such as adularia, quartz, magnetite and voltaite, mineralogical associations that have never been previously described.

In order try to characterize the paragenetic relation between the turquoise-group minerals and the associated phosphates and define the turquoise provenance, it is useful to investigate those elements (Ti, Zr, La, Cr, Mn and V) that show the greatest variation among the regions of provenance.

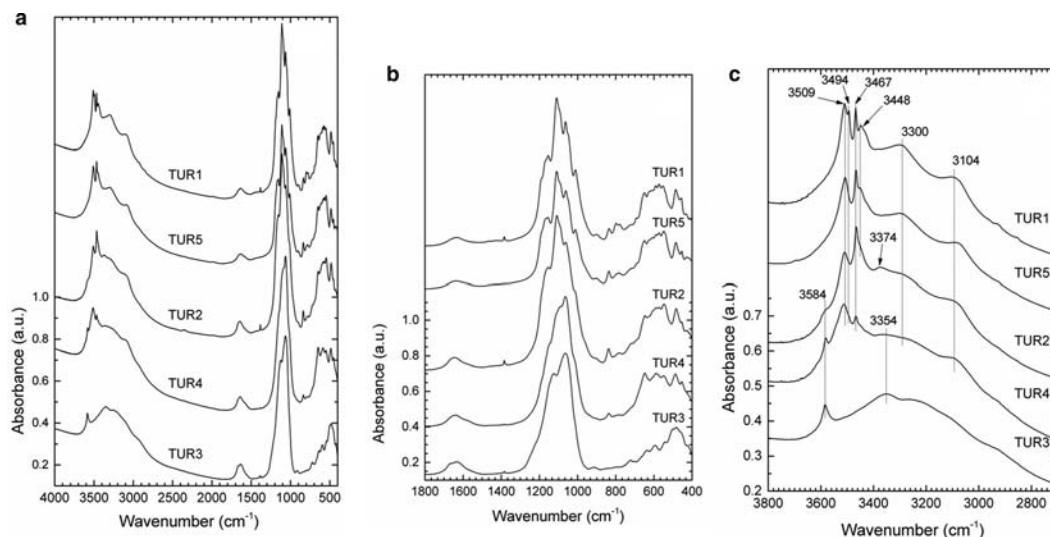


FIG. 10. FTIR spectra for turquoises investigated. (a) Spectra in the range 4000–400 cm^{-1} . (b) Detail of the OH/H₂O region. (c) Detail of the polyhedral region.

This is best observed with Ti, Zr, La and Cr, because of their regional variability, but also because they are refractory and non-volatile elements. Moreover they are commonly used as compositional discriminators in igneous geochemistry, being particularly robust during low-temperature alteration and weathering.

TUR 1

Sample TUR 1 is characterized by a noticeable compositional variability, and the compositional analyses of faustite (F1) are quite different from those previously reported (Erd *et al.*, 1953), due to the different provenance of the samples. The only data on ‘turquoises’ from Sinai, are reported by Pogue (1916) (sample 8, Table 2a). If we compare these data, we can observe a correspondence with samples from this work, especially for Cu contents. Keeping in mind that in 1916 faustite was not yet discovered, Pogue did not analyse for Zn. We noticed that for TUR1 the *A* site is only 49% occupied by Cu. This led us to presume that it is faustite, even if we cannot exclude that the low occupancy depends on the presence of structural vacancies, and so the presence of planerite was not found.

With regard to turquoise, the compositional data of this work are comparable with those of Wadi Maghara (sample 9, Table 2a; Pogue, 1916). Abdu *et al.* (2011) studied mixtures of turquoise–

chalcosiderites from Castillian Mine, Cerrillos Hills (New Mexico, USA). In a discussion on anomalies in Si and Ca values they hypothesize about the turquoise alterations, and noticed that altered samples show a negative correlation between P₂O₅ and (SiO₂ + SO₃), which may indicate that P is leached from the turquoise structure and replaced by Si and/or S during the alteration process. However, the samples have high Ca contents, correlated with Cu deficiency. It is unlikely that Ca replaces Cu at the *A* site, and the existence of a Ca-dominant *A*-site member of the turquoise group ‘coeruleolactite’ is doubted by Foord and Taggart (1998) and therefore it probably originates from microcrystalline impurities due to the presence of other minerals. Foord and Taggart (1998) further suggested that the *A*-site deficiency in turquoise, which is accompanied by an excess of H₂O, can be accounted for by protonation of the (PO₄)^{3−} groups to form planerite [□Al₆(PO₄)₂(PO₃OH)₂(OH)₈·4(H₂O)]. Abdu *et al.* (2011) has shown that the deficiency in *A* and *B* sites, is accompanied by lower H₂O contents, even if the crystal structure of turquoise is maintained, as verified by PXRD. With regards to our sample, the deficiency of Cu in the *A* site (0.709 apfu) and P in the *B* site in turquoise (T) implies an excess of H₂O in agreement with Foord and Taggart (1998). Therefore the presence of Ca, Na, Sr, Mg and Ba in turquoise (T) is attributed to microcrystalline impurities. In faustite 2 (F2), the presence of Ca in the *A* site and of Si in the *B* site is accompanied by

lower H₂O contents according to Abdu *et al.* (2011). In F2 the presence of Ca and Si is related to alteration processes on the basis of pre-existing data.

In TUR1 the presence of phases of high contents of Ba, Ca and Si is related to the geology of the area of origin. In particular the Um Bogma formation shows related mineralization (El Sharkawi *et al.*, 1990; Magaritz and Brenner 1979).

Analyses of REE and trace elements lead us to couple the turquoise with goyazite. These two minerals are characterized by high U contents in agreement with values from Um Bogma formations. Faustite differs considerably from the other phases, both for trace elements and REE; it is possible that, turquoise with correlated phases, and faustite come from different genetic processes.

TUR 2

The compositional data pertinent to TUR 2 are in agreement with Cid-Dresdner and Villarroel (1972) and Pogue (1916). The sample is characterized by the non-negligible presence of Fe³⁺ within the B site, and thus belongs to the turquoise–chalcosiderite series. Worthy of note is, unlike Abdu *et al.* (2011), the lack of chalcosiderite. This study has also highlighted that the other phases associated with turquoise (variscite and voltaite) are Fe-rich. In particular, PXRD data are comparable with Onac *et al.* (2004), who report an Fe-rich variscite. Raman analysis also records the presence of Fe sulfate (copiapite).

Diffraction analysis did not allow the detection of voltaite, adularia and copiapite, not only because such phases are rarely present, but also because their characteristic peaks completely overlap those of previously cited more abundant phases.

In effect, the presence of accessory minerals in this investigation are in good agreement with the mineralization cited above, as well as the Ba and As contents.

Considering the mineralogical and geochemical information, and also the textures of fragments under investigation, it is conceivable that the two minerals were formed by the same fluid, which first resulted in the formation of turquoise, and subsequently to variscite.

TUR 3

Sample TUR 3 consists essentially of variscite, and only locally of chalcosiderite, the presence of which was not ruled out by Raman spectroscopy.

Taking into account bibliographic data for chalcosiderite samples from different localities, it was noted that TUR 3 shows a distinctive composition, with the presence of Fe²⁺ (0.29 apfu), Cu (0.26 apfu) and Ca (0.26 apfu) in the A site. It is conceivably an aheylite–chalcosiderite mixture. Concerning the Ca contents, because of the lack of phases rich in Ca, there could be possible replacement within the A site.

The FTIR spectra also confirms such characteristics, highlighting some differences in comparison to previous data, which could be a possible marker of relevant structural modifications. Also the variscite varies from pre-existing data, showing some differences with respect to characteristic peaks probably due to a higher Fe³⁺ content. Regarding the macroscopic features of the sample, i.e. all the green colour, by taking into account data collected by different analytical methodologies, it is assumed that it is ascribable to variscite, which shows high Cr³⁺ and V⁴⁺ contents (Calas *et al.*, 2005; Odriozola *et al.*, 2010).

Concerning the presence of Fe, Cr, V, As, U in TUR 3, the data are in good agreement with the description of mineralization cited above and the particular geology of the sample provenance area would justify the presence of the minerals studied (chalcosiderite and variscite). In effect REE analysis and mineralogical study suggest that the two minerals are coeval and, given that variscite is a secondary mineral that forms by direct deposition of phosphatic groundwater descending along open fissures and reacting with Al-rich rocks (Larsen, 1942), it is possible that there is a similar formation process for chalcosiderite.

TUR 4

The investigation of sample TUR 4 was very limited, because of its particular textural features. Turquoise-group minerals found in this sample are turquoise and planerite which, due to the lack of published data, were compared with minerals from districts with similar geology. In this sample there is also variscite and wavellite distributed within all the fragments analysed, and easily detected by Raman spectroscopy. All the minerals described in TUR 4 are present in the mineralization of Montebbras Creuse and the presence of Li and Ta in these minerals is related to the geology of the provenance area.

On the basis of compositional, diffraction and texture data, TUR 4 is composed of one mineral

assemblage. In particular the trace-element contents, *REE* patterns, and the constant presence of F and Cu in all the crystalline phases, suggests that the first mineral that is formed is planerite, directly after, with enrichment of Cu, the turquoise crystallizes and finally wavellite and variscite form.

TUR 5

Sample TUR 5 is characterized by a varied and complex mineralogical composition: turquoise, Cu-rich planerite, planerite, crandallite and fluorapatite. In the diffraction study particular attention was given to the recognition of planerite, which according to Foord and Taggart (1998) can be recognized by characteristic peaks.

Raman analysis for TUR 5 pointed out the particular weathering processes suffered by the minerals, detectable in particular vibration modes of OH and H₂O groups such as in TUR 4, TUR 3 and TUR 1. The crystallization sequence by BSE analysis highlighted the anomalies in trace-element contents, and the *REE* patterns suggest that the system conditions aided planerite formation, and by indirect enrichment, the formation of Cu planerite and turquoise. In isolated cases the high Ca and Sr concentration allowed the formation of Sr-crandallite and fluorapatite, that, considering the particular geology of provenance areas, is justified.

Conclusion

The present investigation has focused on the crystal chemical, morphological and textural analysis of five samples from different geographical districts that contain minerals of the turquoise group, which have been identified as faustite (TUR 1), turquoise (TUR 1, TUR 2, TUR 4, TUR 5), turquoise–chalcosiderite series (TUR 2), chalcosiderite–aheylite series (TUR 3), planerite (TUR 5) and planerite–turquoise series (TUR 4, TUR 5) (Table 5).

Our data has permitted a better understanding of some features of these minerals and associated phases, and their paragenetic relations. From the crystal chemical point of view, we considered the faustite and turquoise in TUR 1, which has anomalous contents of Si, Ca and Ba, and a particular solid solution of chalcosiderite–aheylite in TUR 3. Other phases associated with the turquoise minerals in the present work are, in most cases, other phosphates such as variscite (TUR 2, TUR 3, TUR 4), crandallite–goyazite–

TABLE 5. Summary features of the samples studied.

Samples	TUR 1	TUR 2	TUR 3	TUR 4	TUR 5
Turquoise minerals	Faustite, turquoise	Turquoise, turquoise–chalcosiderite	Chalcosiderite–aheylite	Turquoise	Turquoise, planerite, planerite–turquoise
Associated phosphate	Goyazite–crandallite–gorceixite	Variscite	Variscite	Variscite, wavellite	Crandallite–goyazite, fluorapatite
Other minerals associated	Quartz and magnetite	Voltaite and adularia	-	Amblygonite	Quartz
Minor and trace elements of turquoise	Si, Ca, Ba, U	As, Ba	Si, Ca, As, U	Li, Ta	Li, Ba
Rocks containing turquoise	Sandstone, shale, siltstone	Kaolinite, limonitic rocks	Granite, gneiss, schists	Granite, aplite	Trachyte, biabasic rocks, limonitic rocks

gorceixite series (TUR 1, TUR 5), wavellite (TUR 4) and fluorapatite (TUR 5) (Table 5).

Minerals of the turquoise group contain trace elements, which are markers of petrological features (and genetic processes) of the rocks in which they are formed. Worthy of note in particular: in TUR 1 a different genesis for faustite and turquoise on the basis of U content; in TUR 2, TUR 3, TUR 4 and TUR 5 a petrological marker related to contents of As and Ba, As and U, Li and Ta, and Li and Ba, respectively.

According to textural features, minerals of the turquoise group and the other phosphates appear intimately admixed, forming in some cases chaotic mixtures, and in other cases dendritic morphologies.

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