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The turquoise-chalcosiderite-planerite solid-solution series in samples from Chala deposit, Eastern Rhodopes

Тюркоаз-халкосидерит-планеритова серия от твърди разтвори в образци от находище Чала, Източни Родопи

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Introduction

The turquoise group, as redefined by Foord and Taggart (1998), consists of 6 members: planerite, turquoise, faustite, aheylite, chalcosiderite and an unnamed Fe^{2+}–Fe^{3+} analogue with the general formula $A_{0-1}B_6(PO_4)_{4-x}(PO_3OH)_x(OH)_8 \cdot 4H_2O$, where $x = 0-2$. Blue turquoise has Cu^{2+} at the A position and Al^{3+} at the B position, whereas green chalcosiderite largely contains Fe^{3+} at the B position. Planerite is characterized by a dominant A-site vacancy with ideal formula $\square_1Al_6(PO_4)_2(PO_3OH)_2(OH)_8 \cdot 4H_2O$ (Foord, Taggart, 1998). Faustite is the rare Zn analogue of turquoise (Erd et al., 1953). Aheylite is characterized by having Fe^{2+} dominant in the A position (Foord, Taggart, 1998). Complete solid solution exists between the six end-members. The minerals of the turquoise group are isostructural and crystallize in triclinic system, space group $P\bar{1}$ (Cid-Dresdner, 1965; Giuseppetti et al., 1989; Foord, Taggart, 1998; Kolitsch, Giester, 2000). The turquoise structure contains four octahedral positions (Cu, Al1(Fe2A), Al2(Fe2B), Al3(Fe1)) and two tetrahedral (P1, P2) positions (Cid-Dresdner, 1965; Giuseppetti et al., 1989).

In Bulgaria, turquoise was first described in the NE part of the Spahievo ore field, Eastern Rhodopes (Kunov et al., 1977, 1978, 1986). Turquoise occurs in altered andesitic rocks and in quartz veins. Other minerals of the turquoise group from the Spahievo ore field are cuprofaustite (Kunov et al., 1982) and alumochalcosiderite (Kunov et al., 1986). Later tur-quoise was also reported from the Obichnik deposit, Zvezdel-Pcheloyad ore field, Eastern Rhodopes (Kunov, Mandova, 1997).

The present study aims to show the crystal chemistry of green mineral from the turquoise group from Chala deposit (Spahievo ore field) with particular attention to planerite end-member that was approved by the IMA CNMMN as a revalidated mineral in 1984. The present article reports also mineralogical association, morphology, and some structural data of the samples under investigation.

Materials and methods

Two turquoise samples used in this study are deposited in the mineral collection of the Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences. The mineral specimens, donated by Ruslan Aleksandrov, have been found in the supergene zone of Chala deposit belonging to Spahievo ore field, Eastern Rhodopes.

Step-scan X-ray powder diffraction data were collected on D2 Phaser–Bruker AXS Bragg-Brentano diffractometer with $CuK\alpha$ radiation operated at 30 kV and 10 mA, over a range of 3–70 2θ with a step size of 0.015 2θ and a counting time of 10 s/step. The primary powder XRD data standardization and calculation of the unit cell parameters of the mineral were performed with the PDI package (Macicek, 1988), which provides indexation and unit cell parameters refinement by least squares algorithm.

SEM and backscattered electron images (BSEI) and electron microprobe analyses were done on scanning electron microscope (SEM) JEOL 6390 equipped with an energy-dispersive X-ray (EDX) analyzer Oxford INCA Energy 350 (at acceleration voltage of 20 kV).

Results and discussion

Turquoise is found as secondary mineral on the surface of the deposit in quartz veins crossing altered andesitic rocks. Its color is dark green (Fig. 1a). According to X-ray diffraction data it is associated with wavellite (Fig. 1b) and both minerals form lenses and fracture fillings in massive quartz. SEM and BSEI (Fig. 1c–f) show the good crystallinity of these minerals. Turquoise is observed as aggregates of steep pinacoidal crystals (up to 100 μm) on earlier formed wavellite (Fig. 1c–e). Wavellite individuals up to 150 μm long reveal prismatic habitus. Crystals also form dense intergrowths of subparallel prisms normal to vein walls (Fig. 1e) and are shaped by the {010}, (110), and {101} forms (Fig. 1f). The chemical composition of wavellite shows the presence of fluorwavellite component (F from 1.09 to 3.36 wt%).

The X-ray data of turquoise and planerite are very similar, but according to Foord and Taggart (1998) there are some significant intensity differences of certain reflections: e.g. d(010) at about 9.0 Å. In true planerite, the A-site is empty and there is no d(010) diffraction line present. Turquoise with a
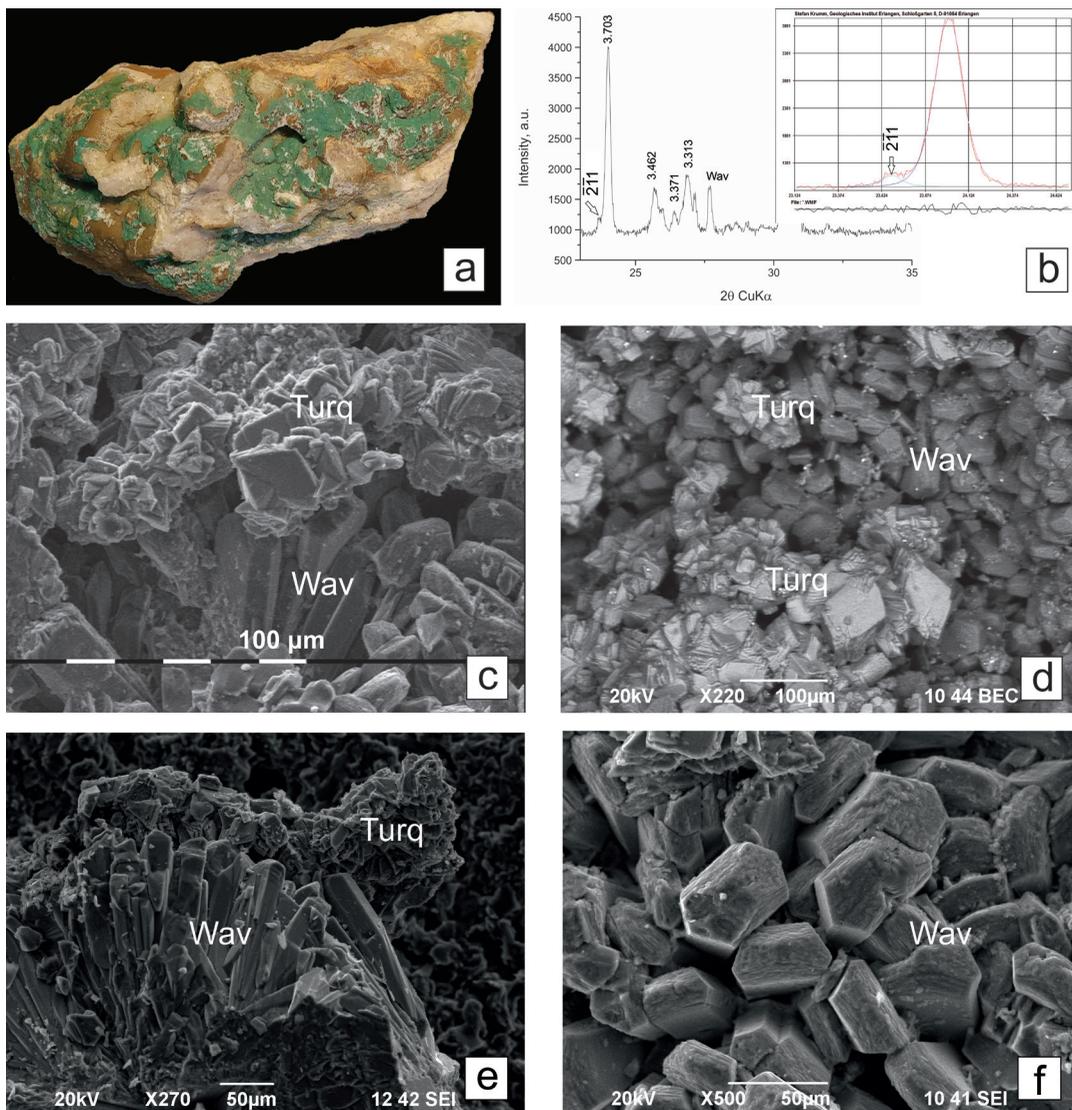

Fig. 1. *a*, hand specimen of dark green turquoise; *b*, X-ray diffraction data of studied sample No 1; *c*, SEM image of turquoise covering the earlier formed wavellite; *d*, BSEI of turquoise aggregates of pinacoidal crystals and prismatic wavellite; *e*, SEM image of subparallel elongated individuals of wavellite normal to vein walls coated by turquoise; *f*, wavellite prismatic crystals exhibit the forms {010}, (110), and {101}

filled A-site shows a well defined d(010) peak. Peak intensities and observed reflections for planerite are substantially different from those of turquoise. For example, the $\overline{2}1\overline{1}$ reflection is the most intense maximum for planerite and is not observed in turquoise. Another major difference is the presence of the $1\overline{1}1$ reflection in planerite that lacks in turquoise.

The obtained X-ray diffraction patterns of studied samples are close to those of the intermediate member of the turquoise-chalcosiderite solid-solution series described by Cid-Dresdner and Villarroel (1972). The four strongest lines in the region showed on Fig. 1b are (d_{obs} in Å): 3.703, 3.462, 3.371, 3.313. Line-profile analysis of broad and heavily overlapping X-ray reflections of turquoise and planerite was done with the program WinFit (Krumm, 1994). The $\overline{2}1\overline{1}$ reflection that is not observed for turquoise indicates the presence of planerite end-member in the studied samples (Fig. 1b). The unit cell parameters determined from a least-squares refinement are: $a = 7.685(4)$, $b = 10.094(8)$, $c = 7.497(4)$, $\alpha = 110.41(5)$, $\beta = 114.85(4)$, $\gamma = 68.39(4)$, $V = 477.5(5)$. According to Foord and Taggart (1998) chalcosiderite and the Fe^{2+}–Fe^{3+} analogue of turquoise both have similar volumes of about 502 A^3 while all of the other members of the group have volumes of about 460 A^3. The obtained structural parameters are comparable with that of the previously reported data by Foord and Taggart (1998): for turquoise-planerite – $a = 7.526$, $b = 9.946$, $c = 7.779$, $\alpha = 112.42$, $\beta = 116.56$, $\gamma = 68.54$, $V = 467.8$; for planerite – $a = 7.505$, $b = 9.723$, $c = 7.814$, $\alpha = 111.43$, $\beta = 115.56$, $\gamma = 68.69$, $V = 477.5(5)$. For chalcosiderite (ICDD #37-0446) they are: $a = 7.672$, $b = 10.199$, $c = 7.885$, $\alpha = 67.52$, $\beta = 69.17$, $\gamma = 64.88$, $V = 502.21$.

The chemical analyses are in good agreement with the obtained powder XRD data. Electron probe microanalyses (EPMA) reveal slight variations in the chemical compositions of the studied turquoise grains. The crystal chemical formulae are calculated on the basis of 24 (O,OH), H_2O was determined by difference. The compositions are characterized by significant deficiency of CuO 5.41–6.54 wt% (0.56–0.69 *apfu* at the A position). It is substantially less than the ideal amount of 1 *apfu*. Approximately 1/3 of the A-site is vacant in the studied mineral. Previously reported data for the turquoise group minerals by Kunov et al. (1977, 1978, 1982, 1986) from Spahievo ore field also shows A-site vacancy in the crystal chemical formulae. Al_2O_3 ranges from 26.46 to 30.34 wt% (4.38–4.95 *apfu* at the B position). The content of Fe_2O_3 is 9.86–14.27 wt% (1.03–1.51 *apfu* at the B position), P_2O_5 – 33.58–35.49 wt% (4.02–4.1 *apfu*), H_2O – 16.25–18.59 wt%. Small amounts of SiO_2 (up to 0.79), TiO_2 (up to 0.46), CaO (up to 0.65), BaO (up to 1.02), K_2O (up to 0.27) are determined

in some analyses. These oxides are common in natural turquoise (e.g., Sklavounos et al., 1992; Abdu et al., 2011). ZnO was not detected. Aluminium at the B-site was found to prevail over Fe^{3+} (Al:Fe = 5:1–4.5:1.5).

Chemical and XRD analyses have demonstrated that the studied mineral from the turquoise group is composed of a ternary solid solution between turquoise, chalcosiderite and planerite. The crystal chemistry of turquoise is important characteristic to authenticate the provenance regions for archaeological and gemological purposes.

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