

Investigations of brown-green, bi-coloured turquoise

H. Pristacz (1), M. Wildner (1), R. Skoda (2), F. Koller (1), and E. Libowitzky (1)

(1) Institute of Mineralogy and Crystallography, University Vienna, Austria (helmut.pristacz@univie.ac.at), (2) Institute of Earth Sciences, Masaryk University, Czech Republic

Polycrystalline turquoise samples with the general formula $X_{0-1}Y_6(PO_4)_{4-z}(PO_3OH)_z(OH)_8 \cdot 4H_2O$, with $X=Cu, Zn, Fe^{2+}$; $Y=Al, Fe^{3+}$ and $z=0-2$, have been studied by electron microprobe analysis (EMPA), powder X-ray diffraction (PXRD), infrared (IR) spectroscopy and ultraviolet-visible-near infrared (UV-VIS-NIR) spectroscopy.

One of the investigated samples shows two areas with different colours, i.e. a greenish and a brownish region. The green part contains a large amount of Si (10.5 wt% SiO_2 , according to the EMPA data), whereas the brown region shows only 2.8 wt% SiO_2 . Both areas show a negative correlation between P_2O_5 and SiO_2 , which may indicate that P is leached from the turquoise structure and replaced by Si (Abdu et al., 2011). The latter authors further attributed high Si and Ca contents of altered turquoise samples to the presence of kaolinite and calcium carbonate, identified by characteristic bands in IR spectra. The IR spectra of both, the green and brown, parts of the bi-coloured sample are very similar to those of pure turquoise, with additional bands at 3695 and 3622 cm^{-1} . As the OH stretching vibrations of kaolinite have been reported by Johansson et al. (1998) at 3695 (strong), 3674, 3668, 3653, 3648 and 3620 (strong) cm^{-1} , the presence of kaolinite is confirmed. Backscattered electron (BSE) images show a relatively homogenous texture in both areas, however, the brown part includes spots with higher Fe contents. A PXRD investigation indicates the additional presence of goethite and barite. Barite, however, is only enriched inside black veins in the turquoise sample.

Diffuse reflectance spectra of the sample were recorded in the UV-VIS-NIR spectral region (5000-32000 cm^{-1}). Spectra of the brownish turquoise include two broad absorption bands near 11500 and 15000 cm^{-1} and three broad absorption bands near 21000, 24000 and 27500 cm^{-1} . These bands can be assigned to octahedrally coordinated Fe^{3+} in iron oxides and oxide-hydroxides, as described by Sherman and Waite (1985). The two broad low-wavenumber bands appear also in the spectra of the green part of the turquoise sample and are very probably related to Cu^{2+} . In addition, the green area reveals narrow bands at 23200 and 23800 cm^{-1} . These characteristic bands can be attributed to the spin-forbidden field-independent ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}/{}^4E_g(G)$ transitions of d^5 configured Fe^{3+} in octahedral coordination (e.g. Spinolo et al., 2007) such as the Y site in turquoise.

References

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