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The turquoise-chalcosiderite $Cu(Al,Fe^{3+})_6(PO_4)_4(OH)_8 \cdot 4H_2O$ solid-solution series: A Mössbauer spectroscopy, XRD, EMPA, and FTIR study

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Abstract

Eight turquoise samples covering a wide range of compositions in the turquoise-chalcosiderite solid-solution series were analyzed by Mössbauer spectroscopy, X-ray diffraction (XRD), electron microprobe analysis (EMPA), and Fourier transform infrared (FTIR) spectroscopy. Two of the turquoise samples display evidence of alteration from weathering processes. The unit formulas were calculated on the basis of 24 (O,OH) anions and 11 cations using the results of EMPA, assuming all Fe as Fe^{3+}, as confirmed by Mössbauer spectroscopy. The altered turquoise samples show deficiencies in both cations and anion groups, indicated by EMPA, but they preserve the crystal structure of turquoise, as verified by XRD. They also show large amounts of Si and Ca in their microprobe data, due to the presence of kaolinite and Ca carbonate, respectively, which are identified by FTIR spectroscopy. The isomorphous substitution of Fe^{3+} for Al in the turquoise structure broadens and shifts the IR bands to lower frequencies, in particular the OH-stretching bands. The Mössbauer spectra, collected at room temperature, are fitted with two generalized Fe^{3+} sites, using a Voigt-based quadrupole-splitting distribution method, which are assigned to the M3 (smaller quadrupole splitting) on the one hand and M1 and M2 octahedral sites on the other hand. The Fe^{3+} distribution over the M3 and M1,2 sites, calculated from the Mössbauer relative areas and EMPA, indicates that Fe^{3+} prefers the larger M3 octahedron in the turquoise-chalcosiderite solid-solution series.

Keywords: Turquoise, chalcosiderite, alteration, Castillian Mine, Tyron Mine, Cornwall, electron microprobe analysis, FTIR, Mössbauer spectroscopy