Powder XRD and TEM study on structures, stacking faults, and interstratification in Cu-chlorite and Zn-chlorite (baileychlore)

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A partially altered Cu-bearing chlorite from a late-stage vein in the marble neighboring a skarn has been studied using X-ray powder diffraction, electron microprobe analysis, and transmission electron microscopy (TEM). The structural formula of the chlorite from un-weathered fresh areas is (Mg$_{3.153}$Cu$_{1.368}$Fe$_{0.222}$Mn$_{0.015}$K$_{0.019}$Ca$_{0.018}$Al$_{1.061}$)(Si$_{3.242}$Al$_{0.758}$)O$_{10}$(OH)$_8$. High-resolution TEM images and X-ray energy-dispersive analytical electron microscopy (AEM) analyses from the Cu-chlorite areas show that Cu occurs in structural positions within the chlorite, instead as inclusions of native Cu or Cu-sulfides. Unit-cell parameters of the Cu-chlorite are: $a=5.302$, $b=9.224$, $c=14.317$ Å, $\alpha=90.365^{\circ}$, $\beta=97.350^{\circ}$, $\gamma=90.075^{\circ}$. Rietveld analyses show that Cu and Zn prefer the octahedral sheets in T-O-T layers, instead of the brucite-like layers. Density functional theory (DFT) calculation also shows that Cu prefers the octahedral sheets in the T-O-T layer over the brucite-like layer.

Both Cu-chlorite (1Md) and baileychlore (1Ma) (in honor of Professor Sturges W. Bailey of the University of Wisconsin-Madison) display semi-random stacking. High-resolution TEM images show that small amount of tri-octahedral smectite occurs as isolated layers within Cu-chlorite and Zn-chlorite The smectite layers contains less Cu and Zn than the hosts of Cu-chlorite and Zn-chlorite. Small amount of Ca detected by EMPA and EDS are not from calcite, but from the interstratified smectite layers. Based on phase equilibrium calculations, it is more likely to crystallize Cu- and Zn-bearing chlorite minerals from S-free or S-depleted fluid at low temperature.