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Chemical composition, statistical analysis of the unit cell, and electrostatic modeling of the structure of Al-saturated chlorite from metamorphosed rocks

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ABSTRACT

Natural Al-saturated chlorite having a wide range of Mg:Fe ratios [Mg/(Mg + Fe) = 0.357 to 0.943] was studied to determine the effect of Mg-Fe substitution on the unit-cell parameters. With a nearly constant Al content [$Al_T/(Al_T + Mg + Fe) = 0.362$ to 0.416, where Al_T represents total Al contents in both tetrahedral and octahedral sites], the only major variable affecting the unit-cell dimensions of natural chlorite is the Mg:Fe ratio. The value of about 0.4 for the Al content represents apparent Al saturation for chlorites in metamorphosed rocks. Unit-cell parameters were determined by least-squares refinement from 39 chlorite samples obtained over a large range in metamorphic grades, from X-ray data derived from Gandolfi pattern simulations (via single crystals and a single-crystal diffractometer) from this study and from traditional powder diffractometer data from the literature. Nine of the samples were analyzed for their Fe^{3+} contents (= 0.147 to 0.304 atoms) by Mössbauer spectroscopy; chemical compositions were generally obtained by electron-microprobe analysis.

Statistical tests show that the change of the crystallographic *a* and *b* axes are linear over the range of Mg:Fe ratios studied, whereas the crystallographic *c* axis and the β angle have no significant relationship to these Mg:Fe ratios. Equations relating the effect of Mg:Fe ratio on *a* and *b* are: a (Å) = $-0.092\,x + 5.408$; $x = Mg/(Mg + Fe)$ and b (Å) = $-0.162\,x + 9.370$, respectively.

Electrostatic models involving Pauling's electrostatic valency principle for Al-saturated chlorite were determined assuming: (1) Al-Al avoidance for Al-substituted tetrahedra, (2) no vacancies, and (3) no Al^{3+} substitution in the M1 sites. Electrostatic restrictions occur for $R^{3+} \rightarrow R^{2+}$ substitutions in the M2 sites of the 2:1 layer. These restrictions produce an Al saturation in chlorite at $Al_T/(Al_T + Mg + Fe)$ ratios of near 0.4. This saturation limit requires that 37.5% of the tetrahedral sites (1.5 out of 4 sites) are occupied by Al, and the electrostatic charge (electrostatic valency units, e.v.u.) close to +1 e.v.u. is favored for the interlayer to offset the net negative charge on the 2:1 layer.

Keywords: Al-saturated chlorite, Gandolfi powder-pattern simulations, Mössbauer spectroscopy, Mg,Fe effects on chlorite unit cell, electrostatic modeling, layer charge