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

SANG SOO LEE,1 STEPHEN GUGGENHEIM,1,* M. DARBY DYAR,2 AND CHARLES V. GUIDOTTI3,†

1Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, Illinois 60607, U.S.A.
2Department of Earth and Environment, Mount Holyoke College, South Hadley, Massachusetts 01075, U.S.A.
3Department of Geological Sciences, University of Maine, Orono, Maine 04401-5711, U.S.A.

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/[(Al + Mg + Fe) = 0.362 to 0.416, where Al 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 Fe3+ 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 Al3+ substitution in the M1 sites. Electrostatic restrictions occur for R2+ → R3+ substitutions in the M2 sites of the 2:1 layer. These restrictions produce an Al saturation in chlorite at Al/[(Al + 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

INTRODUCTION

Chlorite, [R2+(x+y)+ Alx+3y+ a \[Si4+y+ Alx]O10 (OH)2 where R2+(x+y)+ = (Mg + Fe2+) and = vacancy, is a common phyllosilicate constituent of calc-silicate, pelitic, mafic, and ultramafic rocks, and it is stable over a range of low- to medium-grade metamorphic conditions. Chlorite incorporates medium-size octahedral cations, primarily Mg, Fe2+, Fe3+, Al3+, and occasionally Cr, Mn, Ni, V, Cu, Zn, and Li. Various studies have suggested that the unit-cell parameters of chlorite vary linearly with chemical composition (Shirozu 1958; Bailey 1972; Jenkins and Chernosky 1986; Roots 1994; Baker and Holland 1996). However, because of the many possible chemical constituents that may enter the structure and the many possible sites for chemical substitutions (four unique octahedral sites and two unique tetrahedral sites for the IIb polytype, common to higher-temperature assemblages), determining the effect of substituting elements on unit-cell dimensions may be problematic (e.g., see Eggleton and Bailey 1967; Shirozu and Higashi 1976; Bailey 1988). Using synthetic chlorite is one way to minimize the chemical variations because the composition of the chlorite can be controlled by changing the bulk chemistry and by maintaining careful control of the experiments to ensure the appropriate oxygen fugacity. However, Jenkins and Chernosky (1986) showed that the length of the c axis of synthetic Mg- and Al-rich chlorite is sensitive to the presence of co-existing phases, presumably because of elemental (Mg, Al) partitioning between coexisting phases. Therefore, it is difficult to obtain consistent unit-cell parameters for chlorite at a given bulk composition from synthesis work.

The interlayer M4 site in the chlorite structure exhibits large thermal expansion (Nelson and Guggenheim 1993) but contains the smaller trivalent cations (Phillips et al. 1980). Nelson and Guggenheim suggested that the interlayer M3 site does not accept trivalent cations readily because of the high charge of these cations and M3-M3 and M3-M4 repulsions. Furthermore, any Fe3+ iron in M4 cannot easily oxidize to Fe3+ at elevated