

## **Excess functions of chlorite solid solutions and neoformation of Fe-chlorites: Some implications of recent thermochemical measurements**

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### **ABSTRACT**

A full complement of standard state thermodynamic properties ( $\Delta_f G_{298.1}^\circ$ ,  $\Delta_a G_{T,i}^\circ$ ,  $S_{298.1}^\circ$ , and  $C_p^\circ$ ) has been determined for a magnesian chamosite [Fe-Chl(W)] and a ferroan clinochlore [Mg-Chl] investigated by calorimetry and low-temperature hydrothermal experiments; this makes these two samples the only natural chlorites whose complete set of thermochemical properties have been reported.  $\Delta_f G_{298.1}^\circ$  for Mg-Chl and Fe-Chl (W) have been determined to be  $-8161.76 \pm 32.50$  and  $-7278.97 \pm 21.50$  kJ/mol, respectively. Ternary molecular chlorite solid solution modeling approaches have been developed for Al-rich and Si-rich chlorites; unlike available atomic site-mixing chlorite solid-solution models, a molecular model obviates the need for the adoption of a *putative* structural chemistry. The calculated excess entropy of mixing in the ternary system exhibits a curvilinear dependence on composition and at 25 °C,  $G_{ss}^\circ$  vary from about  $-72$  to 413 kJ/mol implying a significant deviation from ideality. The effect of di-trioctahedral substitutions was evaluated by modeling the solid solutions in the quaternary amesite-chamosite-clinochlore-sudoite system for aluminous chlorites; excess functions ( $S^{ex}$ ,  $G^{ex}$ ) calculated for these quaternary and ternary solid solutions are *marginally* different, inherently validating the ternary model. The molecular solid solution model further unmasks significant deficiencies in the available database of standard state thermodynamic properties of chlorites. Finally, pursuant to the recent recognition that green rusts probably play significant roles in the cycling of iron through sedimentary sequences, the neoformation of authigenic iron chlorites from green rusts has been examined; green rusts will readily transform to berthierine and Fe-chlorites except under oxidizing conditions atypical of aquatic environments and ferruginous sediments.

**Keywords:** Ternary chlorite solid solutions, quaternary chlorite solid solutions, green rust chlorite precursor, excess thermodynamic properties