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 ($\Delta G_{298.1}^\circ$, $\Delta G_{T,i}^\circ$, $S_{298.1}^\circ$, 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. $\Delta G_{298.1}^\circ$ 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, $C_p^\circ$ 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 ($S^s$, $G^s$) 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 ferrugineous sediments.

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

INTRODUCTION

Chlorites are phyllosilicates in which adjacent 2:1 talc layers are linked by an octahedral brucite sheet; their general structural formula

$$R_{x+y}^{2+}R_y^{3+}\Delta_{z/2}(Si_{4-k}Al^k_{k})_{2/3}O_{20}(OH)_{16}$$

consists of alternating talc layer

$$R_{x+y}^{2+}R_y^{3+}\Delta_{z/2}(Si_{4-k}Al^k_{k})_{2/3}O_{20}(OH)_{16}$$

and brucite sheet

$$R_{x+y}^{2+}R_y^{3+}\Delta_{z/2}(Si_{4-k}Al^k_{k})_{2/3}O_{20}(OH)_{16}$$

along the c crystallographic direction (Bailey 1988; Zazzi et al. 2006). The extent of substitution ofivalent cations ($R^{2+}$) in the octahedral and tetrahedral sheets are represented by $y$ (the sum of $y_1$ and $y_2$) and $k$, respectively; the total octahedral vacancy ($z$) is the sum of the vacancies in both octahedral sheets ($z_1$ and $z_2$) and $y$ is the sum of $y_1$ and $y_2$. Defined atomic site occupancies have been reported in the form (M1,M2)(M3,M4)(T1,T2) O$_{20}$(OH)$_{16}$; for instance, the structural formula of an ordered triclinic clinochlore was reported (Smyth et al. 1997), on a half unit-cell basis, as (Mg$_{0.964}$Fe$_{0.034}$)$_{M1}$(Mg$_{0.962}$Fe$_{0.038}$)$_{M2}$(Mg$_{0.989}$ Fe$_{0.011}$)$_{C1}$($Al_{0.851}Fe^{3+}_{0.149}$)$_{C2}$($Cr_{0.004}Ti_{0.006}$)$_{T1}$($Si_{2.006}Al_{1.02}$)$_{T2}$O$_{10}$(OH)$_{16}$.

T1 and T2 describe the distinct tetrahedral sites found in the talc layer whereas the distinct octahedral sites of the talc layer are denoted as M1 and M2. M3 and M4 are the octahedral sites located in the brucite sheet though there are half as many M4 as M3 sites per layer. The two tetrahedral sites are somewhat homologous given their identical volume and average metal-oxygen bond distance and show little ordering of Al and Si between T1 and T2. The M3 and M4 octahedral sites differ significantly in octahedral volume, distortion, and mean cation-oxygen bond distance. Considerable cation ordering occurs in the brucite sheet with the preference of trivalent cations for the M4 site and virtually no Fe in the M3 site (Smyth et al. 1997). Furthermore, evidence for cation ordering in the octahedral sites of the talc layer is equivocal; the preference of Al for the M1 site was inferred by Welch et al. (1995) based on $^{27}$Al and $^{29}$Si MAS NMR and was attributed to Al avoidance in the talc tetrahedral sheet; by contrast, the distinction between the tetrahedral sites was not confirmed in the crystallographic study of Smyth et al. (1997).

Petrogenetically, chlorites constitute a major minerals group found in a wide variety of geological environments. Authigenic chlorites are common in siliciclastic petroleum reservoirs where they may occur as pore-filling and/or grain-coating chlorites.