A ternary solid solution model of natural chlorites

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Structural formula of natural chlorites

• Chlorite general formula

$\left( R_{6-y-z}^{2+}R_{y}^{3+}\square_{z}\right)_{2}\left( Si_{4-k}R_{k}^{3+}\right)_{2}O_{20}(OH)_{16}$

• Talc layer

$\left( R_{6-y_2-z_2}^{2+}R_{y_2}^{3+}\square_{z_2}\right)\left( Si_{4-k}^{4+}R_{k}^{3+}\right)O_{20}(OH)_{4}$

• Brucite sheet

$\left( R_{6-y_1-z_1}^{2+}R_{y_2}^{3+}\square_{z_1}\right)(OH)_{12}$
Structural chemistry of chlorites used in study

Low-Fe clinochlore (Mg-Chl)
\[(\text{Al}_{2.64}\text{Cr}^{3+}_{0.006}\text{Fe}^{3+}_{0.124}\text{Fe}^{2+}_{0.98}\text{Mg}_{7.94}\text{Ni}_{0.018\Box_{0.292}})(\text{Si}_{5.72}\text{Al}_{2.28})\text{O}_{20}(\text{OH})_{16}\]

Windsor Chlorite [Fe-Chl (W)]
\[(\text{Al}_{2.96}\text{Fe}^{3+}_{0.666}\text{Fe}^{2+}_{5.46}\text{Mg}_{2.38}\text{Mn}_{0.052}\text{Zn}_{0.014\Box_{0.468}})(\text{Si}_{5.24}\text{Al}_{2.76})\text{O}_{20}(\text{OH})_{16}\]

Michigan Chlorite [Fe-Chl(M)]
\[(\text{Al}_{2.80}\text{Fe}^{3+}_{0.468}\text{Fe}^{2+}_{6.14}\text{Mg}_{2.34}\text{Mn}_{0.036\Box_{0.216}})(\text{Si}_{5.72}\text{Al}_{2.28})\text{O}_{20}(\text{OH})_{16}\]

Experimental Studies
a. Solution equilibration studies (Aja & Dyar, 2002)
b. Rietveld structure refinement (Aja et al., 2015, In press)
c. Calorimetric measurements (Aja et al., 2015, In press)
Variation of $S_{298}$ as a function of mole fraction of Fe in some natural chlorites.

Trend of available $S_{298}$ for natural non-stoichiometric chlorites render the accuracy of published $S_{298}$ for clinochlore and chamosite questionable.
Endmember chlorite compositions commonly used in solid solution models

Amesite: \((\text{Mg}_4\text{Al}_2)(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_8\)

Chamosite: \((\text{Fe}_5\text{Al})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8\)

Clinochlore: \((\text{Mg}_5\text{Al})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8\)

Al-free chlorite: \(\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8\)

Sudoite: \((\text{Mg}_2\text{Al}_{3\square\text{I}})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8\)
Excess entropy of chlorite solid solutions

\[ S^{\text{ex}} = S_{\text{real}} - S_{\text{ideal}} \]

\[ = S_{\text{Chl,measured}} - \left( \sum_i X_i S_i^\circ - R \sum_i X_i \ln X_i \right) \]

\( S_{\text{Chl,measured}} \) (or \( S_{\text{real}} \)) is the measured calorimetric entropy.

\( S_i^\circ \) and \( X_i \) are respectively the calorimetric entropy and mole fraction of the endmember components defining the solid solution.
Excess entropy of mixing ($S^{ex}$) in the chamosite – clinochlore pseudobinary system.

- Blues dots: natural chlorites whose $S_{298}$ are known from calorimetry.
- $S_{298}$ for clinochlore and chamosite from Holland and Powell (1998).
- Sinusoidal trend unusual for silicates.
- Chamosite – clinochlore join is apparently a pseudobinary solid solution.
Ternary models of chlorite solid solution

Al-rich chlorite solid solution (amesite – chamosite – clinochlore)

\[ X_{\text{amesite}} = \left[ \text{Al}^{IV}/\text{O}_{10}(\text{OH})_8 - 1 \right] \]
\[ X_{\text{chamosite}} = (X_{\text{Fe}})(1 - X_{\text{amesite}}) \]
\[ X_{\text{clinochlore}} = 1 - (X_{\text{amesite}} + X_{\text{chamosite}}) \]

Al-poor chlorite solid solution (Al-free chlorite – chamosite – clinochlore)

\[ X_{\text{Al-free chlorite}} = \left[ 1 - \text{Al}^{IV}/\text{O}_{10}(\text{OH})_8 \right] \]
\[ X_{\text{chamosite}} = (X_{\text{Fe}})(1 - X_{\text{Al-free chlorite}}) \]
\[ X_{\text{clinochlore}} = 1 - (X_{\text{Al-free chlorite}} + X_{\text{chamosite}}) \]
Projection of some Fe-Mg chlorite compositions onto the ternary system

- Calorimetrically investigated chlorites
- Red squares: Aja et al. (2015)
- Solid circles (Hemingway et al., 1984; Bertoldi et al., 2007; Gailhanou et al., 2009)
Compositions of some natural Fe-Mg chlorites (Foster, 1962)

a) Foster (1962) chemography

b) Chamosite – clinochlore series

Projections of natural Fe-Mg chlorite compositions onto ternary systems (data from Foster, 1962)

a) Al-rich chlorites

b) Al-poor chlorites
Applicability of the ternary model of chlorite solid solution

Adapted from Kranidiotis & Maclean (1987) Econ. Geol. 52, 1898-1911

The amesite-clinochlore-chamosite compositional field (red lines) fully define the limits of chlorite alteration from the Phelps Dodge massive sulfide deposit (Quebec) as determined by Kranidiotis & MacLean (1987).

Adapted from Kranidiotis & Maclean (1987) Econ. Geol. 52, 1898-1911

Excess entropy of mixing of natural chlorites in the amesite – chamosite – clinochlore system.

<table>
<thead>
<tr>
<th></th>
<th>HP1998</th>
<th>V2005</th>
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<tbody>
<tr>
<td>Chlorite</td>
<td>390.00</td>
<td>545.00</td>
</tr>
<tr>
<td>Amesite</td>
<td>403.20</td>
<td>559.40</td>
</tr>
<tr>
<td>Clinochlore</td>
<td>435.15</td>
<td>410.50</td>
</tr>
</tbody>
</table>

Calorimetric entropy (J/mol.K)
Volume correlation of $S^\text{ex}$

$$\Delta S^\text{ex} = (\Delta V_i + \Delta K_i) \ [\text{Benisek \& Dachs, 2102}]$$

$\Delta V_i$ differences in molar volumes of endmember phases
$\Delta K_i$ differences in compressibilities of endmember phases.
Estimating effect of octahedral vacancy

Amesite-chamosite-clinochlore solid solution

\[ X_{\text{clinochlore}} = 1 - (X_{\text{amesite}} + X_{\text{chamosite}}) \]

Amesite-chamosite-clinochlore-sudoite solid solution

\[ X_{\text{clinochlore}} = 1 - (X_{\text{amesite}} + X_{\text{chamosite}} + X_{\text{sudoite}}) \]
Configurational entropy effects on $S^e_x$

$$S^o = \int_0^{298.15} \frac{C_p}{T} dT + \Delta S_p + \Delta S_{\text{conf}}$$

$$S_{\text{conf}} = -R \sum_j m_j \sum_i X_{i,j} \ln X_{i,j}$$

$\Delta S_p$ attributed to magnetic spin ordering,
$R$ is the gas constant,
$m_j$ is the crystallographic multiplicity of atomic site $j$ divided by the number of formula units per cell,
$X_{i,j}$ is the atomic fraction of species $i$ on site $j$.

Source of structural & calorimetric data (Aja et al., 2015, In press)
Conclusions

• $S_{298}$ of non-stoichiometric natural Fe-Mg chlorites appears linearly dependent on $X_{Fe}$.

• $S^{ex}$ of molecular mixing of amesite-chamosite-clinochlore, to yield equivalent compositions to investigated chlorites, display curvilinear trends consistent with entropy-volume correlations.

• $S^{ex}$ of molecular mixing of chlorite endmembers are dominated by Fe-Mg exchange and Tschermak substitutions; the di-trioctahedral substitution (octahedral vacancy) has a marginal effect on $S^{ex}$. 