A ternary solid solution model of natural chlorites

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Structural formula of natural chlorites

- **Chlorite general formula**

$$\left(R^{2+}_{6-y-z}R^{3+}_{y}\square_{z}\right)_2\left(Si_{4-k}R^{3+}_{k}\right)_2O_{20}(OH)_{16}$$

- **Talc layer**

$$(R^{2+}_{6-y_2-z_2}R^{3+}_{y_2}\square_{z_2})(Si^{4+}_{4-k}R^{3+}_{k})O_{20}(OH)_4$$

- **Brucite sheet**

$$(R^{2+}_{6-y_1-z_1}R^{3+}_{y_2}\square_{z_1})(OH)_{12}$$

Structural chemistry of chlorites used in study

Low-Fe clinochlore (Mg-Chl)

$$(Al_{2.64}Cr^{3+}_{0.006}Fe^{3+}_{0.124}Fe^{2+}_{0.98}Mg_{7.94}Ni_{0.018}\square_{0.292})(Si_{5.72}Al_{2.28})O_{20}(OH)_{16}$$

Windsor Chlorite [Fe-Chl (W)]

$$(Al_{2.96}Fe^{3+}_{0.666}Fe^{2+}_{5.46}Mg_{2.38}Mn_{0.052}Zn_{0.014}\square_{0.468})(Si_{5.24}Al_{2.76})O_{20}(OH)_{16}$$

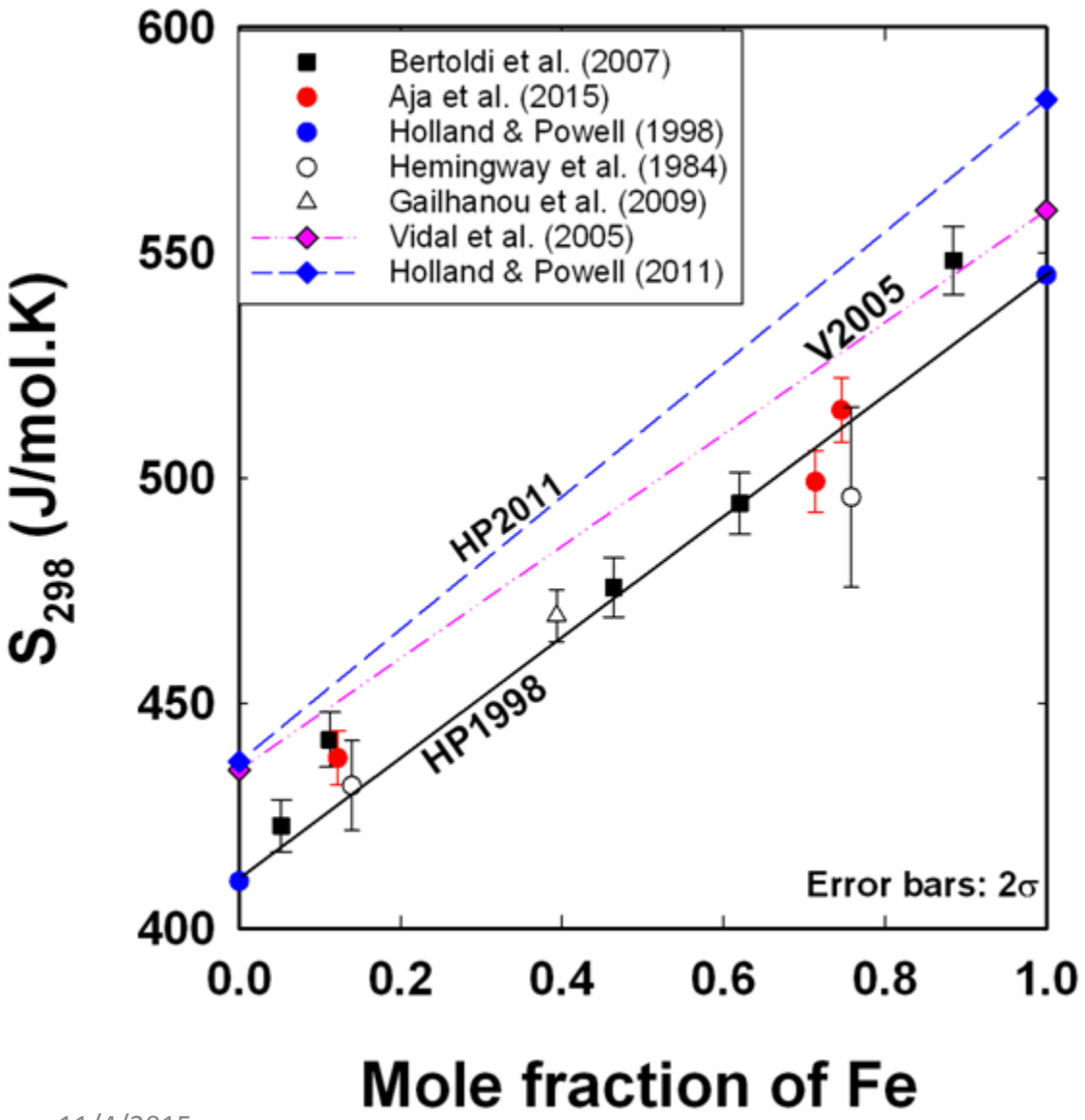
Michigan Chlorite [Fe-Chl(M)]

$$(Al_{2.80}Fe^{3+}_{0.468}Fe^{2+}_{6.14}Mg_{2.34}Mn_{0.036}\square_{0.216})(Si_{5.72}Al_{2.28})O_{20}(OH)_{16}$$

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	$(Mg_4Al_2)(Si_2Al_2)O_{10}(OH)_8$
Chamosite	$(Fe_5Al)(Si_3Al)O_{10}(OH)_8$
Clinochlore	$(Mg_5Al)(Si_3Al)O_{10}(OH)_8$
Al-free chlorite	$Mg_6Si_4O_{10}(OH)_8$
Sudoite	$(Mg_2Al_3\square_1)(Si_3Al)O_{10}(OH)_8$

Excess entropy of chlorite solid solutions

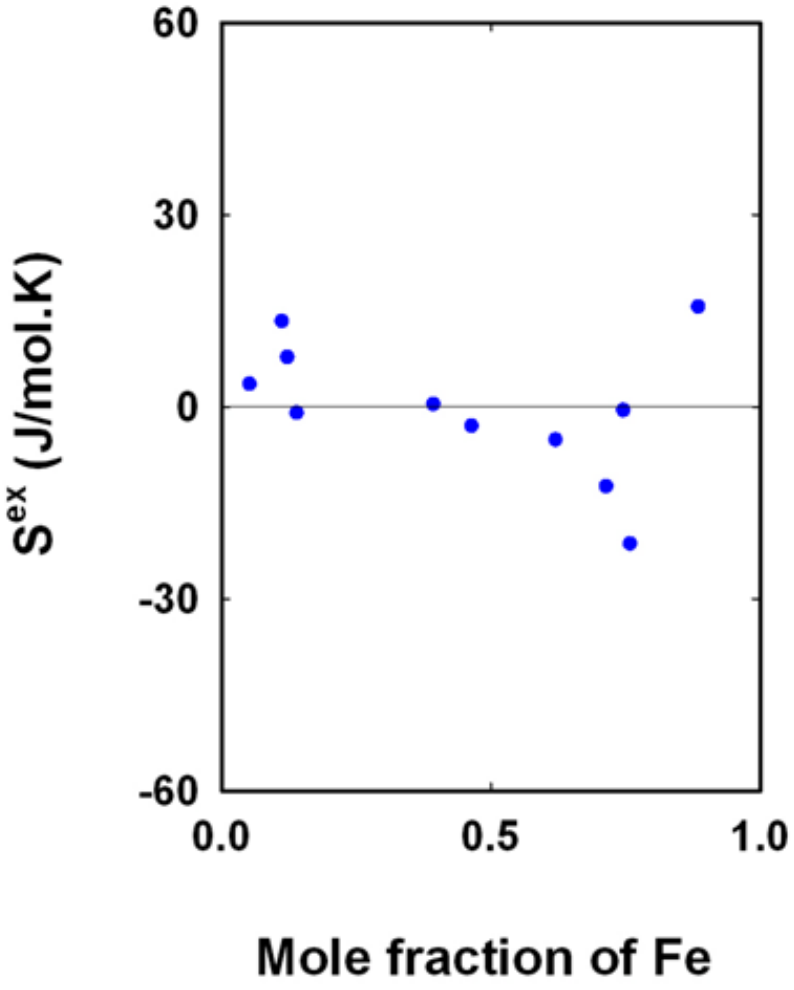
$$S^{ex} = S_{real} - S_{ideal}$$

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

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

S_i° 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)

$$X_{amesite} = [Al^{IV}/O_{10}(OH)_8 - 1]$$

$$X_{chamosite} = (X_{Fe})(1-X_{amesite})$$

$$X_{clinochlore} = 1 – (X_{amesite} + X_{chamosite})$$

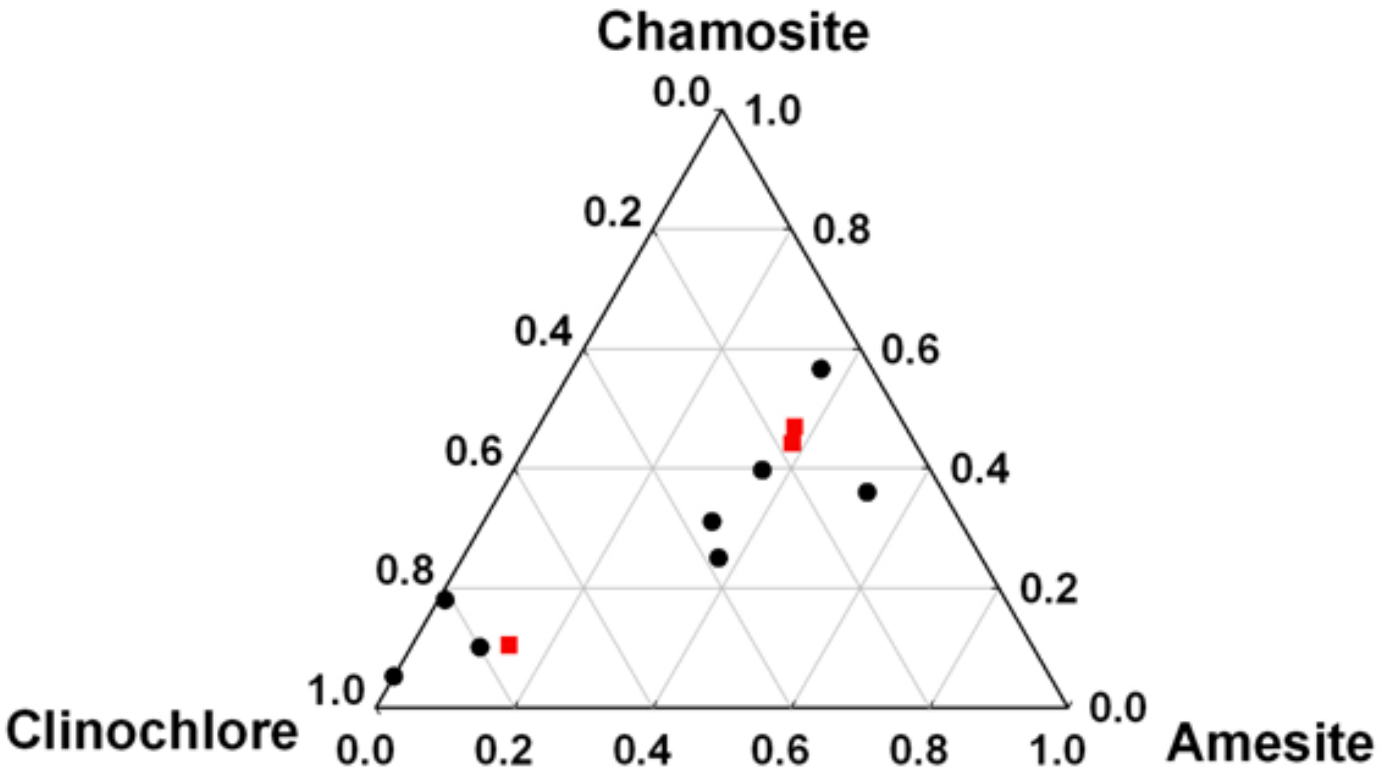
Al-poor chlorite solid solution (Al-free chlorite – chamosite –clinochlore)

$$X_{Al\text{-}free\ chlorite} = [1 - Al^{IV}/O_{10}(OH)_8]$$

$$X_{chamosite} = (X_{Fe})(1-X_{Al\text{-}free\ chlorite})$$

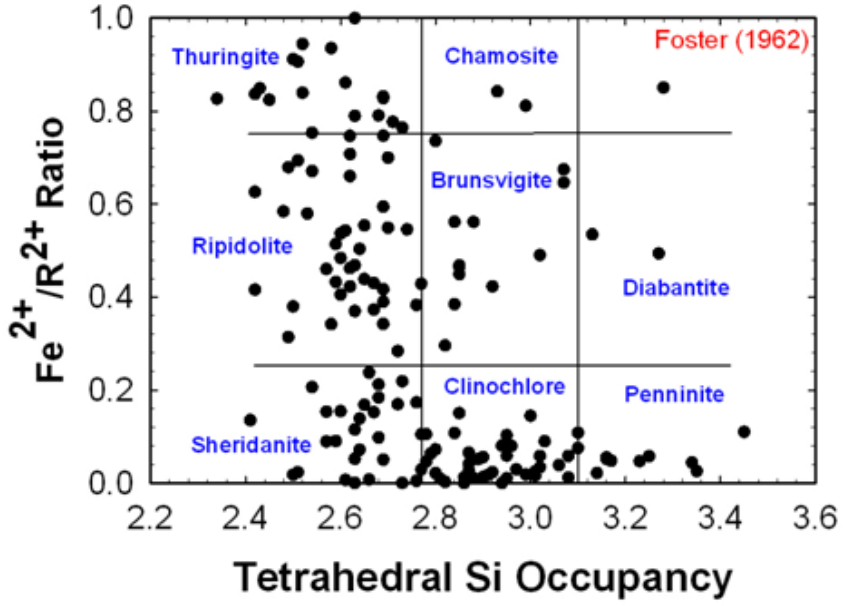
$$X_{clinochlore} = 1 – (X_{Al\text{-}free\ chlorite} + X_{chamosite})$$

Projection of some Fe-Mg chlorite compositions onto the ternary system

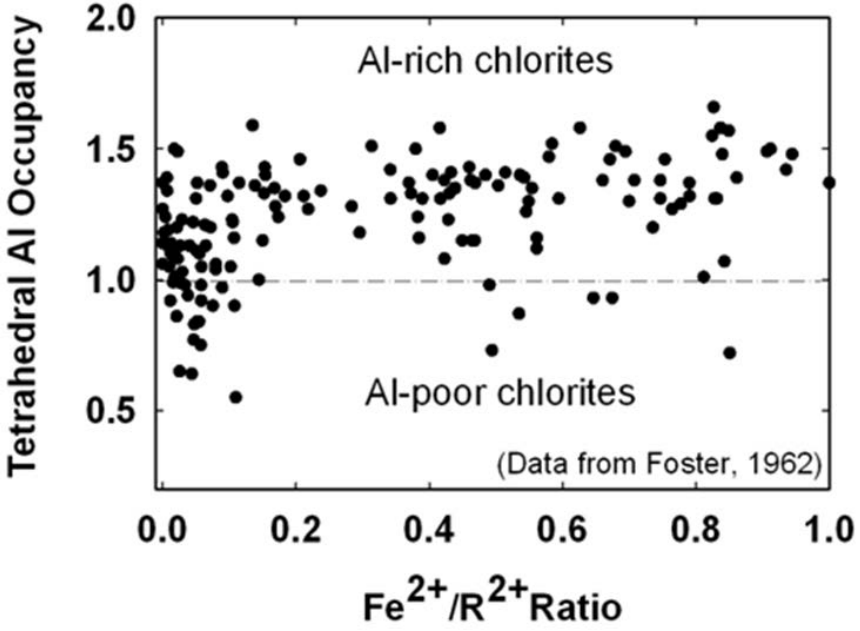


- **Calorimetrically investigated chlorites**
- Red squares: Aja et al. (2015)
- Solid circles (Hemingway et al., 1984; Bertoldi et al., 2007; Gailhanou et al., 2009)

Compositions of some natural Fe-Mg chlorites (Foster, 1962)

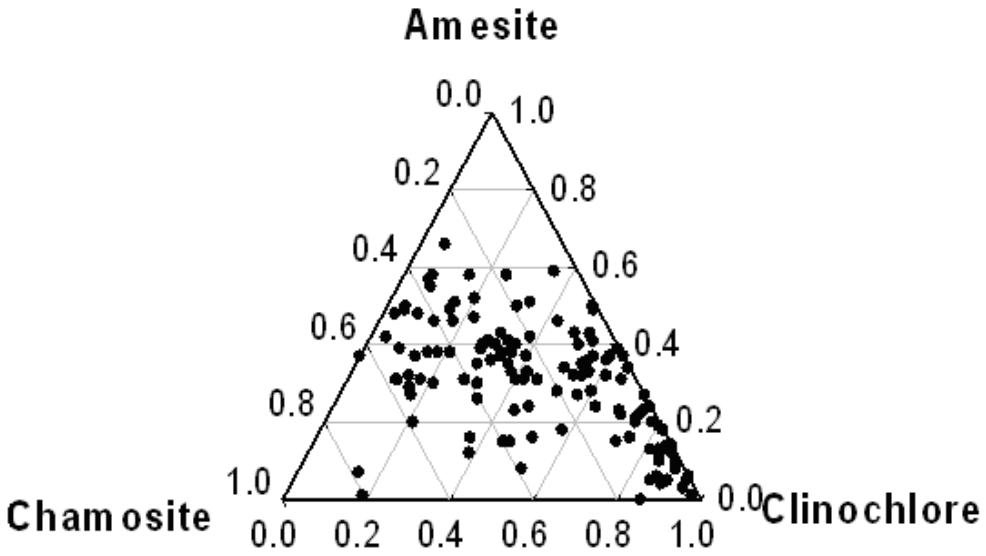


a) Foster (1962) chemography

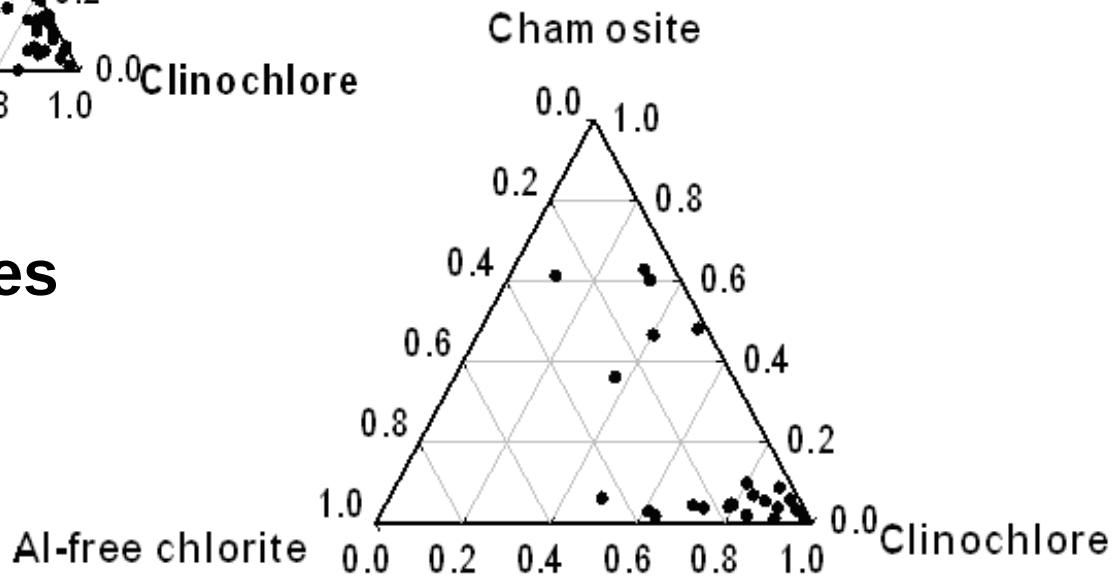


b) Chamosite – clinochlore series

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

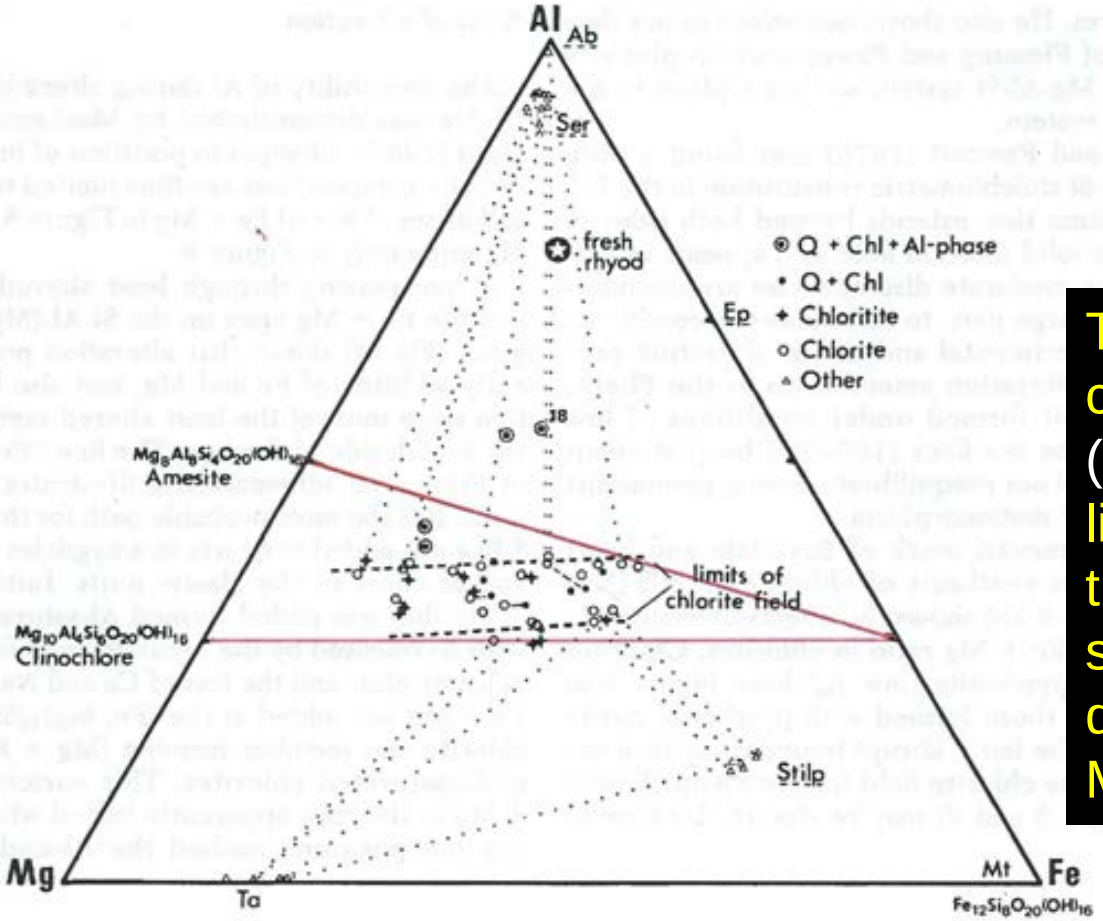
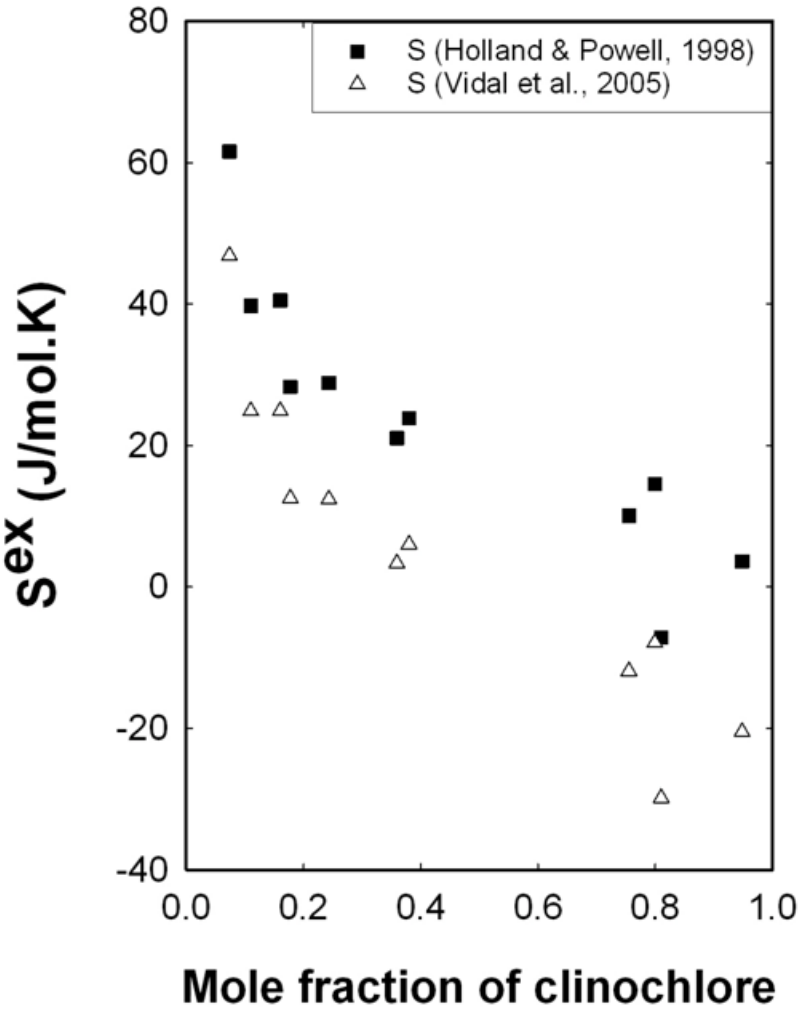


FIG. 9. Al-Fe-Mg plot of chlorite data (average compositions). The chlorite field is outlined by tielines to Al-rich and Al-poor minerals. Amesite and clinochlore are shown for reference. Abbreviations and symbols as in Figure 8. Rhyod = rhyodacite.

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).

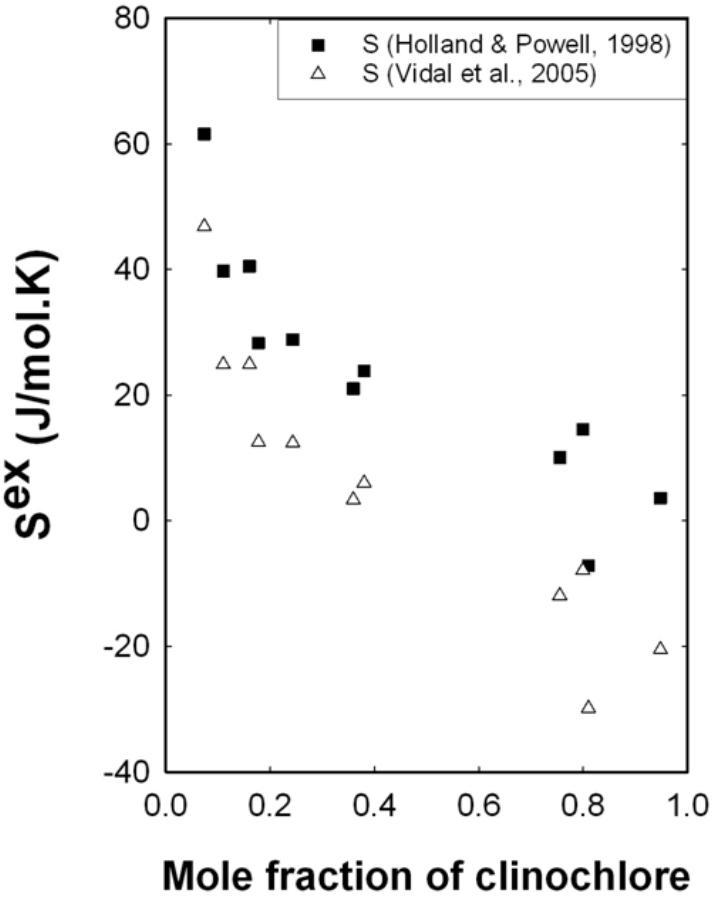
Adapted from Kranidiotis & Maclean (1987) Econ. Geol. 52, 1898-1911

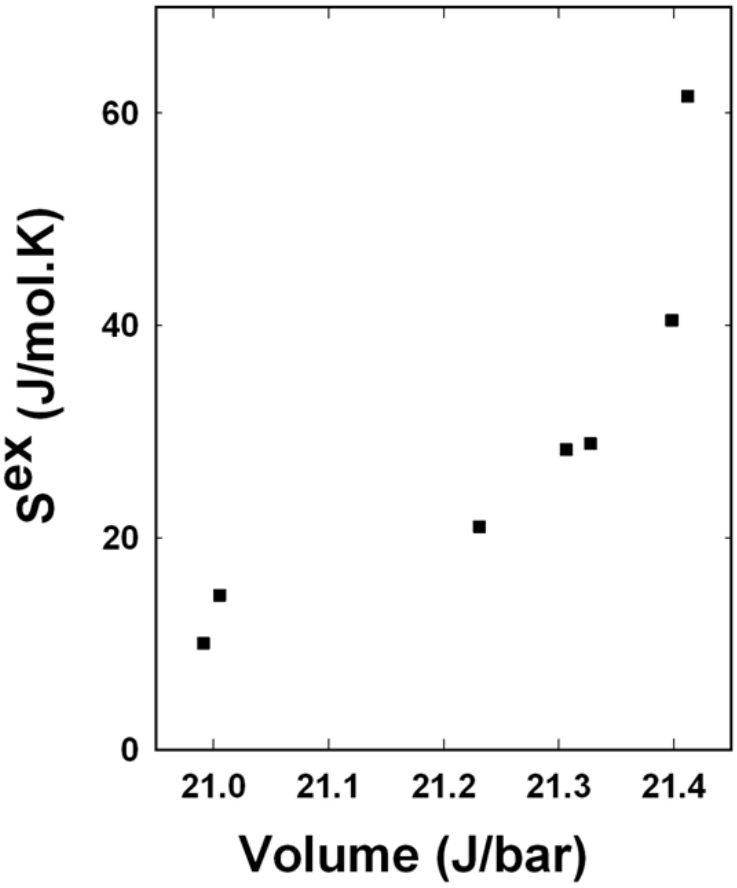
Excess entropy of mixing of natural chlorites in the amesite – chamosite –clinochlore system.



Calorimetric entropy (J/mol.K)		
Chlorite	HP1998	V2005
Amesite	390.00	403.20
Chamosite	545.00	559.40
Clinochlore	410.50	435.15

Volume correlation of S^{ex}



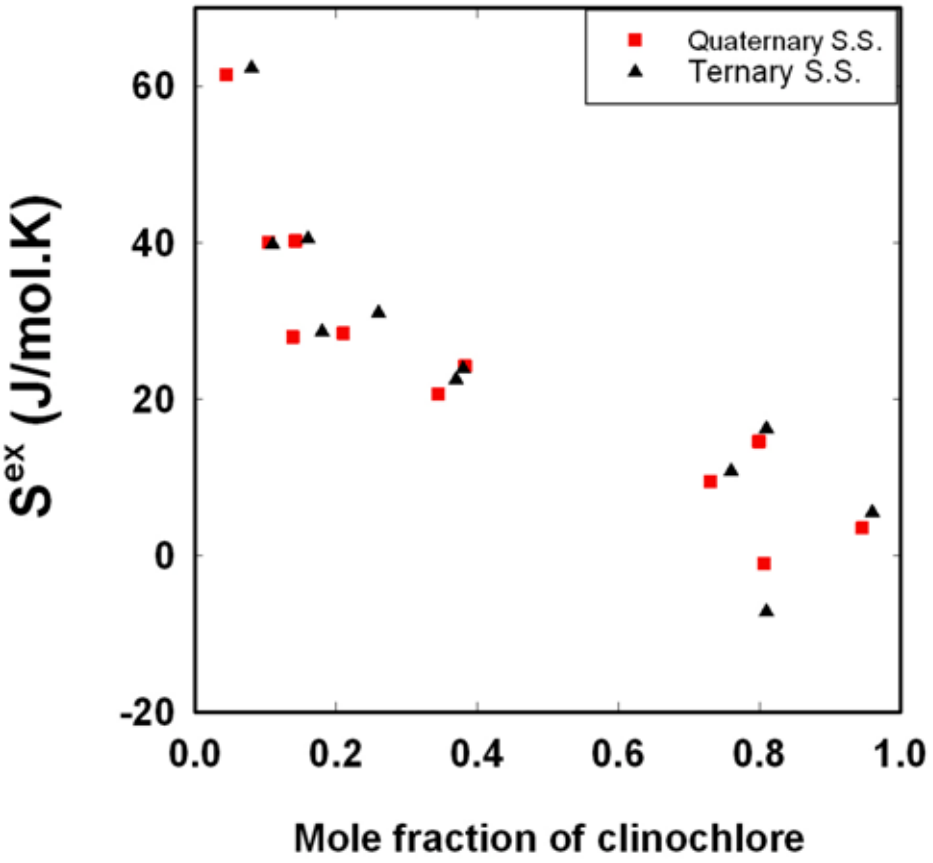


$$\Delta S^{ex} = (\Delta V_i + \Delta K_i)$$ [Benisek & Dachs, 2102]

ΔV_i differences in molar volumes of endmember phases

ΔK_i differences in compressibilities of endmember phases.

Estimating effect of octahedral vacancy



Sudoite	$(Mg_2Al_3\square_1)(Si_3Al)O_{10}(OH)_8$
Chamosite	$(Fe_5Al)(Si_3Al)O_{10}(OH)_8$
Clinochlore	$(Mg_5Al)(Si_3Al)O_{10}(OH)_8$
Amesite	$(Mg_4Al_2)(Si_2Al_2)O_{10}(OH)_8$

Amesite-chamosite-clinochlore solid solution

Xclinochlore = 1 – (Xamesite + Xchamosite)

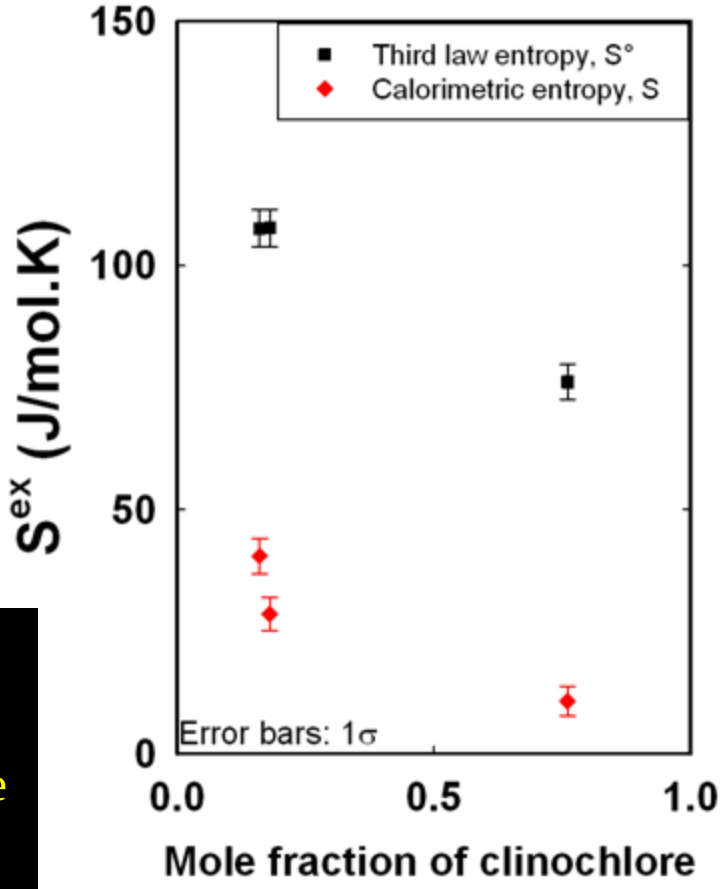
Amesite-chamosite-clinochlore-sudoite solid solution

Xclinochlore = 1 – (Xamesite + Xchamosite + Xsudoite)

Configurational entropy effects on S^{ex}

$$S^\circ = \int_0^{298.15} \frac{Cp}{T} dT + \Delta S_p + \Delta S_{conf}$$

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



ΔS_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}.