Insights into the crystal chemistry of the serandite-schizolite-pectolite series

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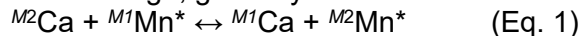
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Summary

A complete solid solution exchange, given by

$$^{M2}Ca + {}^{M1}Mn^* \leftrightarrow {}^{M1}Ca + {}^{M2}Mn^* \qquad \text{(Eq. 1)}$$

where ($Mn^* = Mn^{2+} + Fe^{2+} + <Mg + <Al + <Ti^{4+}$) relates the wollastonite group minerals serandite {Na} [$^{[M1]}Mn^{[M2]}Mn)Si_3O_8(OH)$], schizolite {Na} [$^{[M1]}Ca^{[M2]}Mn)Si_3O_8(OH)$] and pectolite {Na} [$^{[M1]}Ca^{[M2]}Ca)Si_3O_8(OH)$]. Here, a detailed investigation of crystal chemical variations across the series is presented, using data from 16 literature sources as well as 6 new crystal structure refinements (1 pectolite, 4 schizolite and 1 serandite), all originating from igneous (save one hydrothermal) localities worldwide. For crystals refined here, $<R_1>$ is 2.02(1), and all H atoms are located.

It has been well-documented (*e.g.*, Rozhdestvenskaya & Vasilieva 2014; Nagashima *et al*. 2018) that across the series, Ca and Mn* order preferentially at the *M1* and *M2* octahedral sites, respectively. Modeling the site-population distributions, using Eq. 1, shows that site-occupancies closely follow a two-site distribution coefficient, $K = 20.0(5)$, indicating order-disorder equilibrium, consistent with the long time elapsed since crystallization (youngest, Late Cretaceous). Application of the symmetric formalism model of Holland & Powell (1996) shows mixing to be nearly ideal with activity coefficients of unity and $\Delta H^{ex} = -1.77$ kcal for Eq. 1.

The observed variations in octahedral bond lengths, $<M1 - \Phi>$ and $<M2 - \Phi>$, as a function of $\sum$Ca *apfu* are linear, incongruent with the nonlinear nature of $K(\sum Ca)$. To investigate this, systematic variations of distortion and structural strain in M1- and M2-octahedra were examined, calculated by the formulae of Robinson *et al*. (1971) and the Kirchhoff network equations, respectively. Comparison of these parameters shows a cooperative and predicable variation across the series, with distortion and strain occurring at maximum values for compositions nearing those of ideal schizolite. With K being known, species differentiation across the series may be done with reasonable confidence on the basis of bulk compositional data only, *i.e.* without refinement of Ca and Mn* ordering: corresponding to $0 \leq \sum Ca$ *apfu* < 0.55

$(^{M1,M2}\text{Ca} < {}^{M1,M2}\text{Mn*})$ for serandite; $0.55 < \sum\text{Ca}$ *apfu* < 1.45 (and $^{M1}\text{Ca} > {}^{M1}\text{Mn*}$) for schizolite; and $1.55 < \sum\text{Ca}$ *apfu* ≤ 2 $(^{M1,\,M2}\text{Ca} > {}^{M1,\,M2}\text{Mn*})$ for pectolite.

References: Holland & Powell (1996) *Am. Mineral*. 81 : 1425-1437; Nagashima *et al*. *Eur. J. Mineral*. 30 : 451-463; Robinson *et al*. (1971) *Science*. 172 : 567-570; Rozhdestvenskaya & Vasilieva (2014) *J. Strc. Chem*. 55 : 1268-1276.