On the Fe–Ti solubility in sillimanite coexisting with ilmenite and rutile

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More than 30 years have passed since the pioneering researches (Grew, 1980; Yokoi, 1983; Grambling and Williams, 1985) that Fe_2O_3 content in sillimanite increases with temperature but decreases with pressure depending on the coexisting Fe_2O_3-buffer minerals including hematite, magnetite and ilmenite. It has not yet been successful in the quantification of the Fe_2O_3 solubility in sillimanite from the theoretical and experimental points of view. Here, I would like to report the thermodymanic formulation on the Fe–Ti solubility in sillimanite in the SiO_2–TiO_2–Al_2O_3–Fe_2O_3–FeO system.

Due to the ionic radii constraints (Table 1), Fe^{3+} substitutes for octahedral Al^{3+} as $Fe^{3+} \rightleftharpoons Al^{3+}$ in sillimanite (Figure 1). Moreover, Ti^{4+} also substitutes for the octahedral Al^{3+} ac-

Table 1. Ionic radii of Fe, Al, Ti, Si (Shanon Prewitt 1969)

Ion	CN[*]	r (pm)[**]
Si^{4+}	IV	26.0
Al^{3+}	IV	39.0
Al^{3+}	VI	53.0
Fe^{2+}	VI	77.0
Fe^{3+}	VI	64.5
Ti^{4+}	VI	60.5

[*]coordination number.
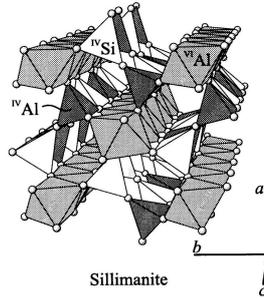[**]ionic radii in picometre (1 pm$= 1 \times 10^{-12}$ m.

Figure 1. Structure of sillimanite (Nesse 2000)

companying divalent cation Fe^{2+} by $Fe^{2+}Ti^{4+} \rightleftharpoons Al^{3+}Al^{3+}$. Therefore, sillimanite forms the solid solution $Al(AlSi)O_5$–$Fe^{3+}(AlSi)O_5$–$(Fe_{0.5}^{2+}Ti_{0.5})(AlSi)O_5$[*1].

Paired subsituttions $Fe^{2+}Ti^{4+} \rightleftharpoons Fe^{3+}Fe^{3+}$ and $Fe^{2+}Ti^{4+} \rightleftharpoons Al^{3+}Al^{3+}$ would occur within ilmenite (Figure 2). Then the ilmenite is described by the $Fe^{2+}TiO_3$–$Fe_2^{3+}O_3$–Al_2O_3 solid solution. Due to the charge balance rule, Ti^{4+} of rutile (Figure 3) generally substitutes for the hexa-, penta-, tri-, divalent cations (R^{6+}, R^{5+}, R^{3+}, R^{2+}) as $3Ti^{4+} \rightleftharpoons 2R^{3+} + R^{6+}$, $3Ti^{4+} \rightleftharpoons 2R^{5+} + Fe^{2+}$, $2Ti^{4+} \rightleftharpoons R^{6+} + Fe^{2+}$, $2Ti^{4+} \rightleftharpoons R^{5+} + Fe^{3+}$ and $2Ti^{4+} + \square \rightleftharpoons 2R^{3+} + R^{2+}$ (Bowles et al 2011). Here, $\square$ indicates the vacancy. In the present system it is sufficient to consider only the paired substitution $2Ti^{4+} + \square \rightleftharpoons 2Fe^{3+} + Fe^{2+}$ and $2Ti^{4+} + \square \rightleftharpoons 2Al^{3+} + Fe^{2+}$. Therefore, the end components of rutile are $TiTi\square O_4$, $Fe_2^{3+}Fe^{2+}O_4$ and $Al_2Fe^{2+}O_4$.

Equilibria among sillimanite, ilmenite and rutile in the SiO_2–TiO_2–Al_2O_3–Fe_2O_3–FeO system can be described by

Figure 2. Ilmenite structure (Bowles et al 2011)

the following chemical reactions:

$$\underset{\text{Ilm}}{Fe_2^{3+}O_3} + \underset{\text{Sil}}{2Al(AlSi)O_5} \rightleftharpoons \underset{\text{Ilm}}{Al_2O_3} + \underset{\text{Sil}}{2Fe^{3+}(AlSi)O_5} \quad (1)$$

$$\underset{\text{Ilm}}{Fe^{2+}TiO_3} + \underset{\text{Sil}}{2Al(AlSi)O_5} \rightleftharpoons \underset{\text{Ilm}}{Al_2O_3} + \underset{\text{Sil}}{2(Fe_{0.5}^{2+}Ti_{0.5})(AlSi)O_5} \quad (2)$$

$$\underset{\text{Ilm solid solution}}{Fe^{2+}TiO_3 + Fe_2^{3+}O_3} \rightleftharpoons \underset{\text{Rt solid solution}}{Fe_2^{3+}Fe^{2+}O_4 + \frac{1}{2}TiTi\square O_4} \quad (3)$$
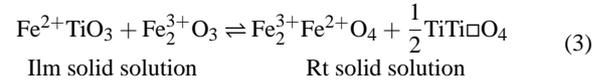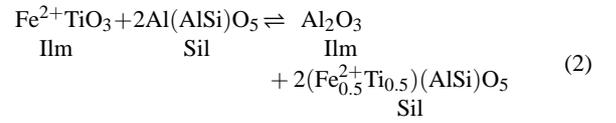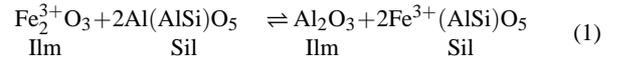
The Gibbs' free energy changes of reactions (1), (2) and (3) at the standard state are given by

$$-\Delta G_1^o = RT \ln \frac{X_{Al_2O_3}^{Ilm} \left(X_{Fe^{3+}(AlSi)O_5}^{Sil}\right)^2}{X_{Fe_2^{3+}O_3}^{Ilm} \left(X_{Al(AlSi)O_5}^{Sil}\right)^2} + RT \ln K_1^\gamma \quad (4)$$

$$-\Delta G_2^o = RT \ln \frac{X_{Al_2O_3}^{Ilm} \left(X_{(Fe_{0.5}^{2+}Ti_{0.5})(AlSi)O_5}^{Sil}\right)^2}{X_{Fe^{2+}TiO_3}^{Ilm} \left(X_{Al(AlSi)O_5}^{Sil}\right)^2} + RT \ln K_2^\gamma \quad (5)$$

$$-\Delta G_3^o = RT \ln \frac{X_{Fe_2^{3+}Fe^{2+}O_4}^{Rt} \left(X_{TiTi\square O_4}^{Rt}\right)^{0.5}}{X_{Fe^{2+}TiO_3}^{Ilm} X_{Fe_2^{3+}O_3}^{Ilm}} + RT \ln K_3^\gamma \quad (6)$$

where X, R and T are the mole fraction of the component related with reactions (1)–(3), gas constant and temperature in Kelvin, respectively. The excess term $RT \ln K_i^\gamma$ arises from the the non-ideal mixing of the phase and will be discussed in detail at the meeting.

References

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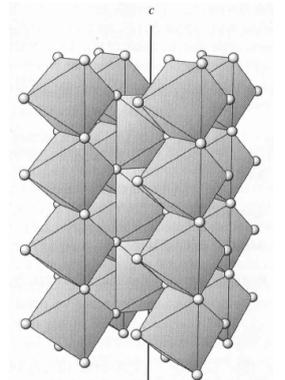Figure 3. Rutile (Nesse 2000)

[*1] Coordination numbers IV and VI are omitted here. The (AlSi) indicates tetrahedral cations. Octahedral cations are on the left side of (AlSi).