PYROXENE/MELT EQUILIBRIA: AN UPDATE. Roger L. Nielsen and Michael J. Drake, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721.

INTRODUCTION

As part of our continuing research investigating major mineral/melt equilibria we have reported on our synthesis of pyroxene/melt equilibria [1,2] based on data available in the literature. The thermodynamic model for the melt utilized in this work is a modified version of the "network former-network modifier" model used by Drake [3] in his study of plagioclase/melt equilibria, which in turn was based on the work of Bottinga and Weill [4]. The thermodynamic properties of pyroxenes were approximated by ideal mixing on a single "M" site (i.e., no distinction between M1 and M2) with Al coupled to Na in the "M" site and excess Al distributed between the "M" and T site to maintain charge balance.

Using this approach we developed geothermometers for orthopyroxene/melt equilibria, clinopyroxene/melt equilibria, and orthopyroxene/clinopyroxene equilibria based on equilibrium relations (1) - (3):

\[
\begin{align*}
MgO(z) + FeO(z) + CaO(z) + 3SiO_2(z) & \rightarrow Mg^M Si^T O_3 (\text{opx or cpx}) \\
& + Fe^M Si^T O_3 (\text{opx or cpx}) + Ca^M Si^T O_3 (\text{opx or cpx}) \\
Mg^M Si^T O_3 (\text{opx}) + Fe^M Si^T O_3 (\text{opx}) + Ca^M Si^T O_3 (\text{opx}) & \rightarrow Mg^M Si^T O_3 (\text{cpx}) + Fe^M Si^T O_3 (\text{cpx}) \\
& + Ca^M Si^T O_3 (\text{cpx}) \\
\end{align*}
\]

Equilibrium relations (1) and (2) are illustrated in Figure 1. Equations for equilibrium relations (1) - (3) are:

\[
\begin{align*}
\Delta nK_{\text{opx/z}} & = 37800/T(K) - 26.25 (I) \\
\Delta nK_{\text{cpx/z}} & = 14600/T(K) - 9.52 (II); \Delta nK_{\text{cpx/px}} = 23200/T(K) + 16.73 (III).
\end{align*}
\]

Using the experimental data as unknowns and the regression lines as geothermometers we obtain "precisions" of approximately ±20°C (1σ). The two pyroxene geothermometer has been successfully applied to coexisting pyroxenes in eucrites, and results compare well with independent estimates of temperature (Hostetler and Drake [5]). The simple "M" site model for the pyroxenes, however, is not a thermodynamically defensible description of the mixing properties of the pyroxenes. In order to further examine pyroxene/melt equilibria and to investigate the reasons for the apparent success of the "M" site model, we have utilized the thermodynamic relations of Saxena [6] in order to calculate the distribution of Mg, Fe, and Ca between the M1 and M2 sites of orthopyroxene and clinopyroxene.

RESULTS USING SAXENA'S SITE DISTRIBUTION MODEL

Using Saxena's [6] site distribution model, we have examined the formation reaction:

\[
2MgO(z) + 2SiO_2(z) \rightarrow Mg^M Mg^M Si^T O_3 (\text{opx or cpx}) (4,5)
\]
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Equilibrium relations (4) and (5) are illustrated in Figure 2. This figure demonstrates that our models for the thermodynamic mixing properties of pyroxene and melt result in a tight distribution of our data points about the regression line for $\ln K$ versus $1/T$. It is instructive to compare Figure 2 with the equivalent Figure for formation reactions (4,5) using the "M" site model:

\[
\text{MgO}(\varepsilon) + \text{SiO}_2(\varepsilon) \rightleftharpoons \text{MgSiO}_3(\text{opx or cpx})
\]

(6,7)

Equilibrium relations (6) and (7) are illustrated in Figure 3. Equations for equilibrium relations (4) - (7) are:

$\ln K_{\text{opx}/\varepsilon} = 7180/T(K) - 2.78$ (IV);

$\ln K_{\text{cpx}/\varepsilon} = 22720/T(K) - 15.18$ (V);

$\ln K_{\text{cpx}/\varepsilon} = 6390/T(K) - 3.6$ (VII). We see that both models are comparable when they are evaluated in $\ln K$ versus $1/T$ space. This observation holds true for the equivalent formation reactions for hedenbergite and for diopside.

The formation reaction for diopside utilizing Saxena's [6] site distribution model is useful in geothermometry:

\[
\text{MgO}(\varepsilon) + \text{CaO}(\varepsilon) + 2\text{SiO}_2(\varepsilon) \rightleftharpoons \text{Ca}_2\text{MgSi}_2\text{O}_6(\text{opx or cpx})
\]

(8,9)

\[
\text{Ca}_2\text{Mg}_2\text{Si}_2\text{O}_6(\text{opx}) \rightleftharpoons \text{Ca}_2\text{Mg}_2\text{Si}_2\text{O}_6(\text{cpx})
\]

(10)

Equilibrium relations (8) and (9) are illustrated in Figure 4. Equations for equilibrium relations (8) - (10) are:

$\ln K_{\text{opx}/\varepsilon} = 38500/T(K) - 25.6$ (VIII);

$\ln K_{\text{cpx}/\varepsilon} = 11740/T(K) - 5.54$ (IX);

$\ln K_{\text{cpx}/\text{opx}} = 26760/T(K) - 20.1$ (X).

CONCLUSIONS

We have synthesized data available in the literature on pyroxene/melt equilibria, utilizing several models to describe the thermodynamic mixing properties of pyroxene and melt. This work has led to the development of several geothermometers. Geothermometers based on the thermodynamically-defensible M2-M1 sites mixing model for pyroxenes [6] are not more precise than those based on the empirical "M" site mixing model [2]. Which of the geothermometers should be used in practice depends upon the nature of the problem and the taste of the problem solver, and the authors express no preference. Finally, our synthesis has led to the development of equations which permit the calculation of the composition of a pyroxene crystallizing at known temperature from basaltic magmas of known composition with high (>10 wt.%Na_2O) or low alkali (lunar) contents [7].

REFERENCES


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