
INTRODUCTION An understanding of major mineral/melt equilibria is important if we are to understand processes of lunar igneous differentiation, particularly if we are to model igneous processes quantitatively. Such information is also of use in deciding if experimental products are in equilibrium and for probing the nature of anhydrous silicate melts. Studies of olivine/melt equilibria have been reported by Roeder and Emslie [1] and others, while studies of plagioclase/melt equilibria have been reported by Kudo and Weill [2] and Drake [3]. A systematic study of pyroxene/melt equilibria has not been reported, however. As a result we have decided to undertake an experimental investigation of pyroxene/melt equilibria. Before embarking on this experimental study we have conducted a literature search for all available experimental data on pyroxenes and coexisting quenched melts. This Abstract reports our synthesis of these data.

THERMODYNAMICS OF PYROXENE/MELT EQUILIBRIA In order to understand pyroxene/melt equilibria it is necessary to evaluate the activities of the components of pyroxene and of the melt. The general formula for a pyroxene is 
\[(M_2)(M_1)T_0_6\] where \(M_2=Na, Ca, Mg, Fe; M_1=Mg, Fe, Al; \) and \(T=Si, Al.\) In order to estimate the activity of, say, \(CaMgSi_2O_6\) in pyroxene, we could make the simplest assumption of ideal mixing on each distinct site and no coupling of \(Al\) distribution between the \(M_1\) and \(T\) site, in which case 
\[a_{CaMgSi_2O_6} = x_{Ca}^{M_2} x_{M_1}^{M_1} (x_{Si}^T)^2.\]

Even so straightforward a model as this one is difficult to apply to experimental products, however, because in general we lack information concerning site occupancies by different cations. The evaluation of the activities of melt-components is still more difficult, in part because it is not clear which chemical units constitute "melt-components." Although these complex problems eventually must be addressed, we shall circumvent them for now, taking as our cue the success of the simple thermodynamic approach utilized by Roeder and Emslie [1] in evaluating activities in the olivine-liquid system. These authors modeled the activities of olivine-forming melt-components in terms of simple oxides which mix ideally with one another. Olivine was implicitly assumed to be an ideal solution of \(MgSiO_3\) and \(FeSiO_3.\) We shall begin with the simple-oxide-ideal-solution assumption for the melt. For the pyroxenes we shall assume an ideal solution of \(Na, Ca, Mg, Fe, \) and \(Al\) on the "\(M\)" site of \(MTO_3\) (i.e., no distinction between the \(M_1\) and \(M_2\) sites) with \(Al\) coupled to \(Na\) in the \(M\) site and excess \(Al\) in coupled substitution between the \(M\) and \(T\) site.

Thus, 
\[a_{MgSiO_3} = x_{M}^{M} = Mg/(Na+Ca+Mg+Fe+1/2Al),\] etc. In future work we shall introduce models in which cations are distributed between the \(M_1\) and \(M_2\) sites.

PRELIMINARY SYNTHESIS OF PUBLISHED EXPERIMENTAL DATA Several of the published experimental studies utilized in this work were specifically conducted in order to obtain a close approach to equilibrium. In other studies which were undertaken with different goals, a close approach to equilibrium cannot necessarily be assumed. This caveat should be recalled when reviewing the results discussed below.

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PYROXENE-MELT EQUILIBRIA

Nielsen and Drake

A straightforward method of discussing pyroxene-melt equilibria is in terms of an equilibrium relation between a pyroxene endmember and its constituent oxides in the melt. The success of the simple thermodynamic model utilized by Roeder and Emslie [1] for olivine-melt equilibrium encourages us to anticipate similar success in relating the enstatite- and ferrosilite-components of pyroxene to their respective oxide melt-components, at least for orthopyroxene. Indeed, Figure 1 illustrates that for the equilibrium $\text{MgO}(1) + \text{SiO}_2(1) \rightarrow \text{MgSiO}_3(\text{px})$ for orthopyroxene, a plot of $\ln K$ versus $1/T$ does indeed result in a linear trend. More surprisingly, the equivalent equilibrium for clinopyroxene also results in a linear trend which appears to be offset slightly from, but overlaps with, the orthopyroxene trend. A similar although more poorly defined pair of trends is observed for the equilibrium $\text{FeO}(1) + \text{SiO}_2(1) \rightarrow \text{FeSiO}_3(\text{px})$. This poorer correlation of $\ln K$ with $1/T$ is reflected in the plot of $\ln K$ versus $1/T$ (Fig. 2) for the exchange reaction $\text{MgO}(1) + \text{FeSiO}_3(\text{px}) \rightarrow \text{FeO}(1) + \text{MgSiO}_3(\text{px})$. Nevertheless, in view of the caveat given above, and the simple thermodynamic models, this correlation is surprisingly good. Again orthopyroxene and clinopyroxene appear to be slightly offset from one another although there is considerable overlap. This offset is enhanced if the simple-oxide-ideal-solution melt model is abandoned, and a more complex Temkin solution approach is utilized (see, for example, Drake [3]) as is illustrated in Figure 3 for the equilibrium relation $\text{FeO}(1) + \text{MgO}(1) + 2\text{SiO}_2(1) \rightarrow \text{FeSiO}_3(\text{px}) + \text{MgSiO}_3(\text{px})$.

A possible geothermometer for low-alkali basaltic rocks is obtained if one plots $\ln K$ versus $1/T$ for the equilibrium of the three pyroxene endmembers with their simple oxide melt-components. The equilibrium relationship $\text{CaO}(1) + \text{MgO}(1) + \text{FeO}(1) + 3\text{SiO}_2(1) \rightarrow \text{CaSiO}_3(\text{px}) + \text{MgSiO}_3(\text{px}) + \text{FeSiO}_3(\text{px})$ is shown in Figure 4. In this diagram we see that orthopyroxene and clinopyroxene again define two separate, distinct trends. Data are from experiments on synthetic lunar samples, lunar analogs, and compositions in the Fe-doped albite-anorthite-diopside system. Using the experimental data as unknowns and the regression lines as geothermometers we obtain "precisions" of $\pm 13^\circ C$ (1o) for orthopyroxenes and $\pm 22^\circ C$ for clinopyroxenes. The clinopyroxene geothermometer breaks down for very alkali-rich compositions such as those close to the albite-diopside join in the albite-anorthite-diopside system, a consequence of our very simple thermodynamic models for pyroxenes and melt. We stress that these results represent a progress report and will be refined with more sophisticated thermodynamic models for the activities of pyroxene- and melt-components. Nevertheless this preliminary synthesis of published experimental data strongly suggests that a study of pyroxene-melt equilibria will lead to an understanding of the variation of pyroxene composition during igneous differentiation, and to the development of useful geothermometers. This work is supported by NASA grant NGR 03-002-388.

PYROXENE-MELT EQUILIBRIA

Nielsen and Drake


FIGURES 1-4. Data from references [4-10]. See text for other information. Symbols: Figures 1, 2, 4 - o, orthopyroxene; x, clinopyroxene. Figure 3 - x, orthopyroxene; o, clinopyroxene.

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