



The effect of H₂O on crystal-melt partitioning of trace elements

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Abstract—Many experimental data demonstrate distinct differences between crystal-liquid partition coefficients D_1 measured under high temperature, anhydrous conditions and those determined at lower temperatures in the presence of H₂O. In this study we develop a thermodynamic method of separating the effects of H₂O from those of temperature. We then apply the method to predict partitioning of REE between clinopyroxene, garnet and silicate melt over wide ranges of temperature, pressure and H₂O content.

Our initial inputs are the model of Wood and Blundy (1997) for REE partitioning between clinopyroxene and anhydrous melt and the melting temperatures of diopside on the join CaMgSi₂O₆-H₂O (Eggler and Rosenhauer, 1978). We then make the hypothesis that the effect of H₂O on the activity of REE clinopyroxene component (REEMgAlSiO₆) in the melt is the same as the measured effect on CaMgSi₂O₆ component. This leads to predictions of REE partition coefficients for clinopyroxene coexisting with hydrous melt at any P,T and H₂O content up to 45 weight %. The results agree with observed REE partition coefficients with a standard deviation which is the same as that for the anhydrous data. We conclude, therefore, that the 'H₂O-effect' may, in this case, be accurately predicted. We extend the approach to garnet by using the join Mg₃Al₂Si₃O₁₂-H₂O to estimate the effects of H₂O on all 'garnet-like' components in the melt. This enables calculation of garnet-melt REE partition coefficients for melts containing up to 25% H₂O.

The observation that H₂O influences major and trace component activities in a similar manner enables us to make some generalisations about the combined effects on partitioning of decreasing temperature and increasing water content of the melt. The relative enthalpies of fusion ΔH_f of major and trace components dictate whether trace element partition coefficients increase or decrease with H₂O addition:

$$\Delta H_f^{\text{trace}} > \Delta H_f^{\text{major}} \text{ gives increasing } D_{\text{trace}} \text{ with addition of H}_2\text{O and}$$

$$\Delta H_f^{\text{trace}} < \Delta H_f^{\text{major}} \text{ leads to decreasing } D_{\text{trace}} \text{ with addition of H}_2\text{O.}$$

Note that D_{trace} is strictly the ratio of mole fractions of charge-balanced components such as REEMgAlSiO₆ in solid to melt phases. In the cases considered here, however, D_{trace} closely approximates $D \left(= \frac{[\text{trace}]_{\text{solid}}}{[\text{trace}]_{\text{melt}}} \right)$ where [trace] refers to weight concentration. For clinopyroxene $\Delta H_f^{\text{REE}} < \Delta H_f^{\text{major}}$ and H₂O addition leads to substantial decreases in REE partition coefficients. For garnet, $\Delta H_f^{\text{REE}} \approx \Delta H_f^{\text{major}}$ and addition of H₂O results in little change in D_{REE} . The consequences are illustrated with respect to Yb contents of melts of spinel lherzolite. For partial melting under anhydrous conditions, Yb is relatively compatible in clinopyroxene and the Yb contents of the product melts remain close to 5 times source values at all F (fraction of equilibrium batch melting) between 0 and 0.25. Hydrous peridotite produces melts, because of low D_{Yb} , which are strongly enriched in Yb (up to at least 10 times source) and whose Yb concentrations depend strongly on F. This means that the low Yb concentrations observed in many island arc tholeiites cannot be due to the addition of water to fertile peridotite.

1. INTRODUCTION

Most magmatic processes take place in the presence of water, either as an important component dissolved in silicate melt or, more rarely, as a major species of a separate fluid phase. Since the work of Tuttle and Bowen (1958) and Shaw (1963) it has been known that, even at low concentrations, H₂O dissolved in melts has profound effects on crystallisation temperatures, phase equilibria and viscosity. In both granitic and basaltic compositions addition of 1% water to the melt depresses the liquidus by 50 to 80°C and in the latter case expands the stability field of olivine relative to orthopyroxene (e.g., Kushiro, 1972). Precise work in simple systems such as CaMgSi₂O₆-H₂O (Fig. 1), shows, however, that liquidus tem-

perature is generally a nonlinear function of water concentration and this has led to determination of the complex activity-composition relations in hydrous silicate melts (e.g., Burnham, 1975). The interactions between water and silicate melts, elucidated in experimental studies, are of profound petrological importance. In volcanic arcs, for example, water-rich fluids derived from dehydration of the subducted slab play a major role in reducing the solidus temperature of mantle peridotite and initiating partial melting at relatively low temperatures (Kushiro et al., 1968). Beneath midocean ridges, seismic data indicate that melt may be present at depths of 150 km (Toomey et al., 1998), an observation also consistent with a low solidus temperature due to the presence of trace amounts of water. In the crust, the presence of hydrous minerals such as micas and amphiboles has long been recognised as an important source of the water required to drive melting (Brown and Fyfe, 1970). In general, petrogenetic arguments for rocks derived from all of

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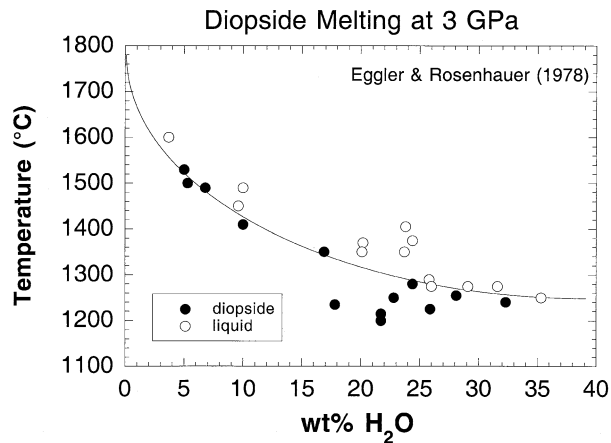


Fig. 1. The effect of H₂O on the melting of diopside at 3GPa. Data from Egger and Rosenhauer, 1978.

these tectonic environments are based on measured trace element and isotopic compositions combined with some simple assumptions about how the trace elements partition between crystals and melts. Experimentally, there have been a large number of determinations of crystal-liquid trace element partition coefficients D_i ($= [i]_{\text{xtl}}/[i]_{\text{liq}}$) in anhydrous systems, and all of the extant models of trace element partitioning focus on anhydrous processes. Experimental data in hydrous systems are much fewer, however. Despite the importance of water in igneous processes and advances in understanding of water solubility in melts and in the thermodynamic properties of the fluid at high pressure, there is no physicochemical understanding of the effects of water on trace element partition coefficients. The aim of this study was to develop a thermodynamic basis for predicting how water changes partition coefficients relative to anhydrous systems. The approach is novel, simple and can be applied universally to crust and mantle melting environments. In principle, our methodology can be extended to any anhydrous or hydrous mineral phase. We have chosen, however, to focus on clinopyroxene and garnet in recognition of the universal importance of these phases in mantle and crust melting, and because there are the greatest number of experimental data available for these phases.

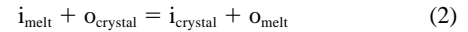
2. THERMODYNAMIC BACKGROUND

Nagasawa (1966) demonstrated that one of the most important factors governing trace element partitioning is the energy required to strain the crystal lattice when the host cation is replaced by a trace ion of greater or smaller ionic radius. Quantitative application of this 'lattice strain theory' to trace element partitioning in synthetic silicate systems was first made by Beattie (1994) and Blundy and Wood (1994). In the simplest form of the model (Brice, 1975), when an ion of radius r_i enters a lattice site, radius r_o , the work done (ΔG_{strain}) is given by:

$$\Delta G_{\text{strain}} = 4\pi EN_A \left(\frac{r_o}{2} (r_o - r_i)^2 - \frac{1}{3} (r_o - r_i)^3 \right) \quad (1)$$

where E is the Young's Modulus of the site and N_A is Avogadro's Number. For a liquid, the Modulus of Rigidity and

Young's Modulus are both zero, so there is no equivalent work done in substituting i into the melt. The partition coefficient of i , D_i ($= \frac{[i]_{\text{crystal}}}{[i]_{\text{melt}}}$) can therefore be related to D_o , the partition coefficient of an ion (o) of the same charge, but of radius r_o , which enters the lattice without strain, by considering the exchange reaction:



Since there is no strain involved in removing i from the melt and replacing it by o , then, if i and o are the same charge and enter the same sites in the melt, their activity coefficients, according to this theory, should be the same. In that case the partition coefficient D_i depends only on D_o and the strain energy, ΔG_{strain} (Brice, 1975):

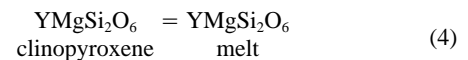
$$D_i = D_o \exp \left(\frac{-4\pi EN_A \left(\frac{r_o}{2} (r_o - r_i)^2 - \frac{1}{3} (r_o - r_i)^3 \right)}{RT} \right) \quad (3)$$

Eqn. 3 gives the near-parabolic dependence of D_i on cation radius r_i observed in natural systems (Onuma et al., 1968) and demonstrated recently in a number of experimental studies (Beattie, 1994; Wood and Blundy, 1997, Blundy et al., 1998; van Westrenen et al., 1999, for example).

Application of Eqn. 3 to experimentally determined partition coefficients D_i enables, at fixed pressure, temperature and major element composition, calculation of D_o for ions of a given charge provided r_o and E are known. Conversely, D_o may be used to calculate D_i for ions of the same charge but different radii. Wood and Blundy (1997) and van Westrenen et al. (2001) have shown that r_o values for the clinopyroxene M2 site and the (large) garnet X site are approximately predictable from crystallographic data and exhibit the anticipated dependencies on bulk composition. Apparent values of Young's Modulus E , obtained from fitting Eqn. 3 to trace element partitioning data, generally depend on charge and polyhedral volume in reasonable and predictable ways (e.g., Blundy and Wood, 1994). These observations mean that, for trace cations substituting into clinopyroxene and garnet, values of D_o at the P,T, composition conditions of the experiment can be extracted from measured partition coefficients D_i . In general, as implied above, D_o values are different for ions of different charge and we have recently shown (Wood and Blundy, 2001) that, for ions replacing a cation of charge +2 (e.g., Ca²⁺) the order of relative compatibility should be $D_o^{2+} > D_o^{1+} \approx D_o^{3+} > D_o^{4+}$.

The problem now reduces to how one predicts D_o for the different charges under appropriate conditions.

Consider a hypothetical C2/c clinopyroxene YMgSi_2O_6 where Y^{2+} is a cation of radius r_o which fits exactly into the large M2 site without straining the structure. The partitioning of Y^{2+} between crystal and silicate melt should then be determined principally by the free energy of the fusion reaction:



The equilibrium constant K_o is given by the simple relationships:

$$\Delta G_4^o = G_{\text{YMgSi}_2\text{O}_6}^o_{\text{melt}} - G_{\text{YMgSi}_2\text{O}_6}^o_{\text{melt}} \quad (5)$$

$$K_o = \frac{a_{\text{YMgSi}_2\text{O}_6}^{\text{melt}}}{a_{\text{YMgSi}_2\text{O}_6}^{\text{cpx}}} = \exp\left(\frac{-\Delta G_4^0}{RT}\right) \quad (6)$$

where $a_{\text{YMgSi}_2\text{O}_6}^{\text{cpx}}$ and $a_{\text{YMgSi}_2\text{O}_6}^{\text{melt}}$ refer to the activity of the YMgSi_2O_6 component in the clinopyroxene and melt phases respectively. If activity-composition relationships for melt and pyroxene are available, it is relatively straightforward to relate K_o to the measured Nernst partition coefficient D_o .

Let us assume, for illustration, that the activities $a_{\text{YMgSi}_2\text{O}_6}^{\text{cpx}}$ and $a_{\text{YMgSi}_2\text{O}_6}^{\text{melt}}$ are linearly dependent on the atomic concentrations of Y in clinopyroxene and melt respectively. Then, introducing activity coefficients γ_i yields:

$$K_o = \frac{[\text{Y}]_{\text{melt}} \cdot \gamma_{\text{YMgSi}_2\text{O}_6}^{\text{melt}} \cdot \{\text{melt}\}}{[\text{Y}]_{\text{cpx}} \cdot \gamma_{\text{YMgSi}_2\text{O}_6}^{\text{cpx}} \cdot \{\text{cpx}\}} \quad (7)$$

where $[\text{Y}]_{\text{melt}}$ and $[\text{Y}]_{\text{cpx}}$ refer to the weight concentrations of Y in melt and clinopyroxene and $\{\text{melt}\}$ and $\{\text{cpx}\}$ refer to the mean molecular weights of melt and pyroxene phases respectively on a 6 oxygen basis. The ratio of the latter, required for the conversion from atomic to weight concentrations is usually, in anhydrous systems, within a few percent of 1.0, so can generally be ignored. Noting that the ratio of weight concentrations is the partition coefficient, D_o , we obtain the relationship between D_o and K_o :

$$K_o = \frac{\gamma_{\text{YMgSi}_2\text{O}_6}^{\text{melt}} \cdot \{\text{melt}\}}{D_o \cdot \gamma_{\text{YMgSi}_2\text{O}_6}^{\text{cpx}} \cdot \{\text{cpx}\}} \quad (8)$$

or:

$$RT \ln D_o = \Delta G_4^0 + RT \ln \left[\frac{\gamma_{\text{YMgSi}_2\text{O}_6}^{\text{melt}} \cdot \{\text{melt}\}}{\gamma_{\text{YMgSi}_2\text{O}_6}^{\text{cpx}} \cdot \{\text{cpx}\}} \right]$$

$$RT \ln D_o = \Delta H_f - T \Delta S_f + RT \ln \left[\frac{\gamma_{\text{YMgSi}_2\text{O}_6}^{\text{melt}} \cdot \{\text{melt}\}}{\gamma_{\text{YMgSi}_2\text{O}_6}^{\text{cpx}} \cdot \{\text{cpx}\}} \right] \quad (9)$$

where ΔH_f and ΔS_f refer, respectively, to the enthalpy and entropy changes of the melting reaction (4). ΔH_f and ΔS_f are normally both large and positive. Their effects on partition coefficients are illustrated schematically in Figure 2. Because ΔS_f is positive, decreasing temperature raises ΔG_4^0 thereby, at constant pressure and composition, increasing D_o . If water is added, at fixed temperature, its principal effect is to lower the activity and activity coefficient (γ) of YMgSi_2O_6 in the melt and hence lower D_o as shown in Figure 2. The important question from the geochemical standpoint is whether, while remaining on the liquidus, the combined effects of adding water and lowering temperature is to increase or decrease D values for trace elements. We will show below how this question may be answered in specific cases.

Equations 5 through 9 provide the thermodynamic basis for relating partition coefficients (D_i) to the thermodynamic properties of the melting reaction and to the mixing properties of the phases (γ_i). The main problem with the approach is that the activity coefficients γ_i are, apart from in a few simple cases, unknown. This does not, however, present an insuperable obstacle, provided components can be chosen in such a way that activity is a simple function of composition (e.g., Carmichael et

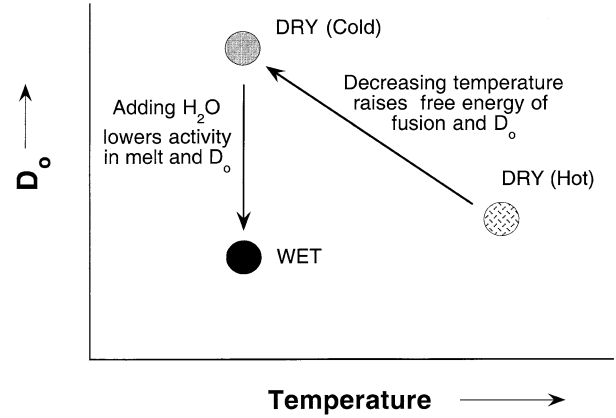
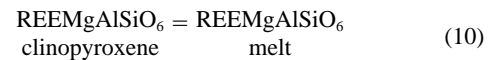


Fig. 2. Schematic illustration of the combined effects of increasing H_2O content of the melt and decreasing temperature on partition coefficients. Decreasing temperature raises D_o because the entropy of fusion (ΔS_f) is positive, while adding H_2O decreases D_o because it lowers the activities of all other components in the melt.

al., 1974 p.179). Blundy et al. (1995) showed, for example, that Eqn. 8 can be used to predict weight partition coefficients of Na between clinopyroxene and silicate melt from the measured thermodynamic properties of the jadeite ($\text{NaAlSi}_2\text{O}_6$) fusion reaction. In this case the activity of $\text{NaAlSi}_2\text{O}_6$ component in clinopyroxene and melt appears to be approximately equal to the atomic concentration of Na in the two phases (Blundy et al., 1995). A similar approach was used by Wood and Blundy (1997), in their attempt to parameterize the pressure, temperature and composition dependencies of D_o for rare earth elements entering clinopyroxene. The latter authors assumed that the REE partitioning could be treated in terms of a fusion reaction for the fictive component REEMgAlSiO_6 :



In equilibrium (10), 'REE' refers to a 3+ ion which fits, like ion o in Eqn. 2 without strain into the clinopyroxene M2 site. Activity-composition relations for the REE component are not, of course, known, so Wood and Blundy applied several different types of activity model to the large number of available partitioning data. They found, by trial and error, that the partitioning results closely obey simple mixing models for pyroxene and melt. The clinopyroxene was treated as if there is complete disorder on M2 and M1 sites but that the tetrahedral Al-Si substitution is locally coupled to the M sites (e.g., Wood and Banno, 1973) and contributes nothing to the partial molar entropy of mixing of the pyroxene. This gives, with ideal solution on each individual sublattice:

$$a_{\text{REEMgAlSiO}_6}^{\text{cpx}} = X_{\text{REE}}^{\text{M2}} \cdot X_{\text{Mg}}^{\text{M1}} \quad (11)$$

For the melt, we started with the hypothesis that it behaves approximately as an ideal mixture of the 6-oxygen components, $\text{CaMgSi}_2\text{O}_6$, $\text{CaFeSi}_2\text{O}_6$, $\text{NaAlSi}_2\text{O}_6$, KAlSi_2O_6 , $\text{CaAl}_2\text{SiO}_6$, $\text{CaTiAl}_2\text{O}_6$, $\text{Mg}_3\text{Si}_{1.5}\text{O}_6$, $\text{Fe}_3\text{Si}_{1.5}\text{O}_6$ and Si_3O_6 . These components enable complete compositional description (excluding minor elements such as Mn) of virtually all compositions with clinopyroxene on the liquidus. If we then assume that the

activity of $\text{NaAlSi}_2\text{O}_6$ (at the clinopyroxene liquidus) is equal to its mole fraction, we obtain very good agreement between clinopyroxene-melt partitioning of $\text{NaAlSi}_2\text{O}_6$ (97 data points) and the free energy of fusion of pure jadeite, as shown by Blundy et al. (1995). This means that, under the restricted range of pressures, temperatures and compositions which have clinopyroxene on the liquidus, the activity of $\text{NaAlSi}_2\text{O}_6$ component is very approximately equal to its mole fraction. For $\text{CaMgSi}_2\text{O}_6$ component the identical approach necessitates calculating the total fraction of $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$ in the 6-oxygen melt and multiplying that by $\left(\frac{\text{Mg}}{\text{Mg} + \text{Fe}}\right)$ in order to obtain the mole fraction of $\text{CaMgSi}_2\text{O}_6$:

$$a_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}} = X_{\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6}^{\text{melt}} \cdot \left(\frac{\text{Mg}}{\text{Mg} + \text{Fe}}\right)_{\text{melt}} \quad (12a)$$

The test of this model is, as for jadeite, that the free energy of fusion extracted from $\text{CaMgSi}_2\text{O}_6$ partitioning between clinopyroxene and melt in complex systems agrees well with the measured free energy of fusion of pure diopside (Wood and Blundy, 1997 Fig. 8). We do not claim that our simple molecular components in any way represent the true microscopic structure of the melt. We showed, however, that, for melts at the clinopyroxene liquidus, ideal mixing of 6-oxygen components provides a reasonable representation of activity for those components we are able to test. Extension of the approach to the REE implies that we should consider the two components REEMgAlSiO_6 and REEFeAlSiO_6 . The mole fraction of the former will then be equal to the total multiplied by:

$$a_{\text{REEMgAlSiO}_6}^{\text{melt}} = [\text{REE}] \cdot \left(\frac{\text{Mg}}{\text{Mg} + \text{Fe}}\right)_{\text{melt}} \quad (12b)$$

where [REE] refers to the atomic concentration of the REE in the melt on a 6-oxygen basis. Substituting (11) and (12b) into (6) and rearranging as in Eqn. 9 yields an equation which can be fitted as a function of pressure (in GPa) and temperature (K), with the following result:

$$\text{RT} \ln \left(\frac{D_o^{3+} \cdot X_{\text{Mg}}^{\text{M1}}}{\left(\frac{\text{Mg}}{\text{Mg} + \text{Fe}}\right)_{\text{melt}}} \right) = 88750 - 65.644T + 7050P - 770P^2 \quad (13)$$

where D_o^{3+} refers to the weight partition coefficient for the 3+ ion (normally an REE) which enters the Ca site in clinopyroxene without straining the lattice. The terms on the right hand side of Eqn. 13 are, in order, the 1bar enthalpy of fusion, entropy of fusion, volume of fusion and the pressure derivative of the volume of fusion. Eqn. 13 enables prediction of D_o for REE partitioning between anhydrous silicate melt and clinopyroxene at known pressure, temperature and major element composition (Wood and Blundy, 1997). The effect of H_2O will be discussed next.

3. EFFECT OF H_2O ON TRACE ELEMENT PARTITIONING INTO CLINOPYROXENE

Consider the consequences of assuming that H_2O has no effect on REE partition coefficients for clinopyroxene. Quali-

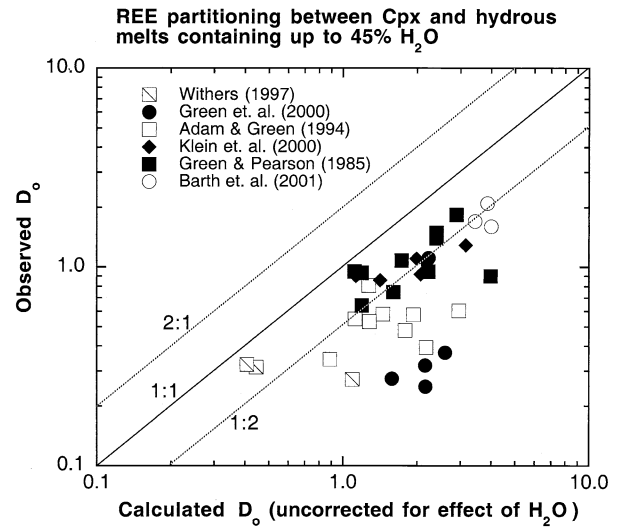


Fig. 3. Calculated and observed D_o values for REE partitioning between clinopyroxene and hydrous silicate melts. If the effect of H_2O is ignored, anhydrous data predict partition coefficients which are frequently an order of magnitude too high.

tatively, we anticipate that the decreasing liquidus temperature caused by H_2O addition should lead to increasing estimated partition coefficients unless the effect of H_2O on γ_i is accounted for. Fig. 3 shows a comparison of observed and predicted (H_2O -free) D_o values for REE partitioning between clinopyroxene and hydrous silicate melt. The data shown come from those experiments for which a sufficient number of partition coefficients of REE (and Y) were measured in order for D_o to be determined by fitting of the Brice Eqn. 3 to the results. Melts contain up to 45% H_2O and it can be clearly seen that partition coefficients are overestimated by, in the most hydrous cases, an order of magnitude if the effect of H_2O on the activity coefficient of the REEMgAlSiO_6 component is ignored. The correction to γ_i required by the addition of H_2O may, of course, be calculated directly from the errors in predicted partition coefficients. A more instructive approach is, however, to begin by considering the well-known effect of H_2O on the activity coefficient of $\text{CaMgSi}_2\text{O}_6$ component in silicate melts. Figure 1 shows the depression of the diopside liquidus caused by the addition of H_2O at 3 GPa, as determined by Eggler and Rosenhauer (1978). The data of Figure 1 are converted into activity-composition relations for the $\text{CaMgSi}_2\text{O}_6$ - H_2O join by considering the enthalpy of the reaction:



Assuming that the H_2O content of the clinopyroxene is negligible, the activity of $\text{CaMgSi}_2\text{O}_6$ component in the melt, at temperature T_1 and pressure P is given by:

$$\ln a_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}} = \frac{-1}{\text{RT}} \left[(\Delta H_{T_f}^o + \int_{T_f}^{T_1} \Delta C_p dT) - T \left(\Delta S_{T_f}^o + \int_{T_f}^{T_1} \frac{\Delta C_p}{T} dT \right) + \int_1^P \Delta V^o dP \right] \quad (15)$$

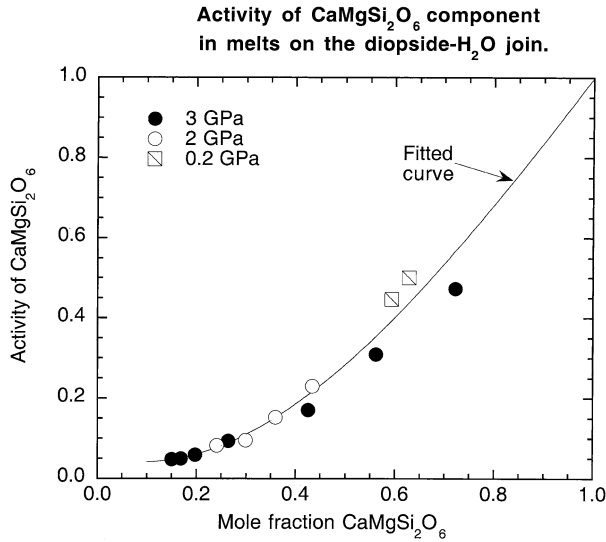


Fig. 4. Activity of $\text{CaMgSi}_2\text{O}_6$ component in $\text{CaMgSi}_2\text{O}_6$ - H_2O melts at high pressure. Data from Eggler and Rosenhauer (1978). Fitted curve is not forced through the origin for reasons discussed in the text.

where $\Delta H_{T_i}^\circ$ and $\Delta S_{T_i}^\circ$ are the enthalpy and entropy of melting of diopside at the 1 bar melting temperature, 1665K, ΔC_p is the heat capacity difference between liquid and solid phases and ΔV° is the volume difference. To calculate activities using Eqn. 15, C_p data were taken from Richet and Bottinga (1984) and Richet and Fiquet (1991) while $\Delta H_{T_i}^\circ$ and $\Delta S_{T_i}^\circ$ were taken from Lange et al. (1991). Finally, ΔV° as a function of pressure and temperature was determined from the volume, expansivity and compressibility data tabulated by Lange and Carmichael (1990), Sumino and Anderson (1982) and Finger and Ohashi (1976). These data enable calculation of $a_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}}$ and hence $\gamma_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}}$ in $\text{CaMgSi}_2\text{O}_6$ - H_2O melts at 0.2, 2 and 3 GPa from the experimental results of Eggler and Rosenhauer (1978) (see Fig. 1). Figure 4 shows activities calculated in this manner and a polynomial fitted through the data:

$$a_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}} = 0.0563 - 0.3208 X_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}} + 1.8452 (X_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}})^2 - 0.5807 (X_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}})^3 \quad (16)$$

In Eqn. 16 the mole fraction of diopside component $X_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}}$ was calculated by treating the 2 melt components as $\text{CaMgSi}_2\text{O}_6$ (6-oxygen unit) and H_2O (1-oxygen unit). It should be noted that the marked flattening of the diopside liquidus at high mole fractions of H_2O (Fig. 1) implies that $\left(\frac{\partial a_{\text{CaMgSi}_2\text{O}_6}}{\partial X_{\text{H}_2\text{O}}}\right)$ becomes small at $X_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}}$ values of ~ 0.15 . To reproduce this observation we fitted the polynomial by adding 'dummy' points at $X_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}}$ of 0.08 and did not force the fit through the origin. It was, however, forced through $a_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}}$ of 1.0 at $X_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}}$ of 1.0. For these reasons Eqn. 16 only applies for H_2O contents ≤ 50 weight%. Applying the definition of activity coefficient $\gamma_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}}$:

$$\gamma_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}} = \frac{a_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}}}{X_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}}} \quad (17a)$$

and noting that $X_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}}$ is equal to $(1 - X_{\text{H}_2\text{O}}^{\text{melt}})$ we obtain:

$$\gamma_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}} = -0.3208 + \frac{0.0563}{(1 - X_{\text{H}_2\text{O}}^{\text{melt}})} + 1.8452 \cdot (1 - X_{\text{H}_2\text{O}}^{\text{melt}}) - 0.5807 (1 - X_{\text{H}_2\text{O}}^{\text{melt}})^2 \quad (17b)$$

Our model for REE partitioning in anhydrous systems relied on the approximation that $\text{CaMgSi}_2\text{O}_6$ and REEMgAlSiO_6 components exhibit Raoult's Law behaviour in the melt. Let us, therefore make the simplest extension to this model, that H_2O dissolved in the melt has the same effect on the activity of REEMgAlSiO_6 component as on that of $\text{CaMgSi}_2\text{O}_6$ component. With this assumption we have:

$$\gamma_{\text{REEMgAlSiO}_6}^{\text{melt}} = \gamma_{\text{CaMgSi}_2\text{O}_6}^{\text{melt}} \quad (18a)$$

and

$$a_{\text{REEMgAlSiO}_6}^{\text{hydrous}} = X_{\text{REEMgAlSiO}_6}^{\text{anh}} \cdot \gamma_{\text{REEMgAlSiO}_6}^{\text{melt}} \cdot (1 - X_{\text{H}_2\text{O}}) \quad (18b)$$

In Eqn. 18 the superscripts *hydrous* and *anh* refer to activities in silicate melts of the same bulk composition (water-free) under hydrous and anhydrous conditions. The next step is to correct the value of D_0^{3+} calculated from Eqn. 13 under anhydrous conditions by adding water content and activity coefficient terms. This yields:

$$D_0^{3+} \cdot \gamma_{\text{REEMgAlSiO}_6}^{\text{melt}} \cdot (1 - X_{\text{H}_2\text{O}}) \frac{100}{(100 - \text{wt}\% \text{H}_2\text{O}^{\text{melt}})} = D_0^{\text{hydrous}} \quad (19)$$

where D_0^{hydrous} refers to the predicted value of D_0 for 3+ ions when the melt is hydrous. Note that in Eqn. 19 two corrections involving H_2O are required on the left hand side. The first comes from Eqn. 18 and is a correction to the activity. The second, involving weight % H_2O takes account of the fact that the weight D_0^{hydrous} is measured on a melt containing H_2O , while D_0^{3+} (weight) is calculated for the equivalent anhydrous melt.

In general, H_2O contents of experimental products are not measured quantitatively by ion microprobe or by FTIR spectroscopy but estimated by difference of electron microprobe total from 100 weight%. Since our experience is that this approach tends to overestimate water contents of melts, we have instead computed melt H_2O from the water content of the bulk composition and the estimated modal proportion of glass. Where the experimentalist provided no estimate of the latter, we used a value obtained by least-squares fitting of phase compositions to the bulk composition of the capsule. Typically this approach yields lower water contents than the method based on microprobe totals and errors are on the order of 10 to 15% relative.

Figure 5 shows the same observed D_0 values for clinopyroxene-hydrous melt partitioning as those shown in Figure 3. This time, however, the calculated D_0 values were corrected using Eqn. 19. Qualitatively, the agreement appears to be very good. The standard deviation of calculated $\text{RTln}D_0$ values from those measured is, for these 36 hydrous experiments, 3335 $\text{J}\cdot\text{mol}^{-1}$ and as such is smaller than the scatter of a much larger number (481) of anhydrous data points about the predicted values (Wood and Blundy, 1997). In the latter case, some of the scatter may have been due to the presence of H_2O in high-

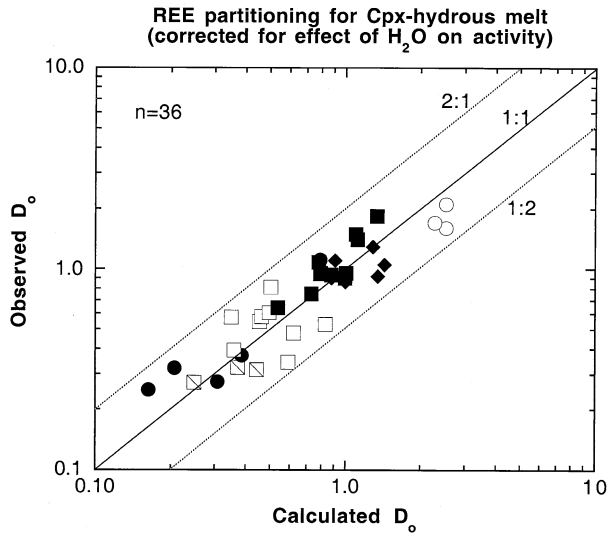
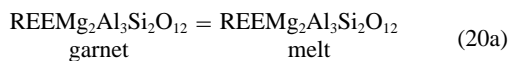


Fig. 5. Calculated and observed D_o values for REE partitioning between clinopyroxene and hydrous silicate melts. In this case the calculated values were corrected for the effect of H_2O using Eqn. 19. Experimental data as in Fig. 3.

pressure, nominally-anhydrous experiments. An H_2O -content of the melt of 0.5% introduces, for example an error in $RT \ln D_o$ of $1250 \text{ J} \cdot \text{mol}^{-1}$. We conclude, therefore that, when corrected for H_2O using Eqn. 19, hydrous data are as well predicted by Eqn. 13 as anhydrous data. Furthermore and even more important, these results indicate that the effect of H_2O on the minor REEMgAlSiO_6 component is very similar to the effect of H_2O on the major $\text{CaMgSi}_2\text{O}_6$ component in the melt. If this observation is generally applicable to trace element partitioning, it provides immediate constraints on the relative effects of H_2O and temperature on partitioning, effects which, being highly correlated, have historically been impossible to separate.

4. GARNET-MELT PARTITIONING OF REE

The approach embodied in Eqn. 13, in which partition coefficients are related to the free energy of fusion of a fictive, in this case clinopyroxene, component, has been found to be applicable to other solid phases. Van Westrenen et al. (2001), for example found that the partitioning of REE between garnet and melt could be treated in an analogous way. These authors considered the melting of a fictive $\text{REEMg}_2\text{Al}_3\text{Si}_2\text{O}_{12}$ component, where 'REE' refers to a rare earth element which enters the garnet X site without straining the lattice:



They assumed that the activity of the REE component in garnet is given by:

$$a_{\text{REEMg}_2\text{Al}_3\text{Si}_2\text{O}_{12}}^{\text{gt}} = X_{\text{REE}}^{\text{gt}} \cdot (X_{\text{Mg}}^{\text{gt}} \cdot \gamma_{\text{Mg}}^{\text{gt}})^2 \quad (20b)$$

where $X_{\text{REE}}^{\text{gt}}$ and $X_{\text{Mg}}^{\text{gt}}$ refer, respectively to the atomic fractions of REE and Mg on the garnet X-site and $\gamma_{\text{Mg}}^{\text{gt}}$ is the activity coefficient of Mg, normally greater than 1.0 because of non-ideal Mg-Ca interactions (Newton et al., 1977). The liquid

phase was assumed to mix as 12-oxygen units with similar entropy of mixing to the garnet, yielding:

$$a_{\text{REEMg}_2\text{Al}_3\text{Si}_2\text{O}_{12}}^{\text{melt}} = X_{\text{REE}}^{\text{melt}} \cdot (X_{\text{Mg}}^{\text{melt}})^2 \quad (20c)$$

where $X_{\text{REE}}^{\text{melt}}$ and $X_{\text{Mg}}^{\text{melt}}$ refer to one third the number of atoms of REE and Mg/12 oxygens in the liquid i.e., treating the liquid as if it had garnet stoichiometry. Note that, as in the case of clinopyroxene, we do not claim that this activity expression provides any insight about melt structure, simply that, at the garnet liquidus, it appears to correct for most of the compositional dependence of D_o^{3+} for garnet. Substituting these relationships into the equilibrium constant for reaction (20a) gives:

$$\frac{1}{K_o} = \frac{a_{\text{REEMg}_2\text{Al}_3\text{Si}_2\text{O}_{12}}^{\text{gt}}}{a_{\text{REEMg}_2\text{Al}_3\text{Si}_2\text{O}_{12}}^{\text{melt}}} = D_o^{3+} (D_{\text{Mg}} \cdot \gamma_{\text{Mg}}^{\text{gt}})^2 \cdot \frac{\{garnet\}}{\{melt\}} \quad (20d)$$

where D values are solid/liquid partition coefficients. Van Westrenen et al. ignored, for simplicity, the molecular weights of garnet and melt ($\{garnet\}$ and $\{melt\}$) and fitted measured garnet-anhydrous melt weight partition coefficients using an equation of the same form as (13), to give:

$$RT \ln [D_o^{3+} (D_{\text{Mg}} \cdot \gamma_{\text{Mg}}^{\text{gt}})^2] = 418000 - 226T + 10400P \quad (21)$$

Van Westrenen et al. (2001) calculated activity coefficients for garnet, $\gamma_{\text{Mg}}^{\text{gt}}$ by assuming that the solid phase behaves as a ternary regular solution of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ components. They adopted interaction parameters, on a single atom basis, of $19 \text{ kJ/gm} \cdot \text{atom}$ for W_{CaMg} and 0 for W_{FeMg} and W_{FeCa} . They then found that Eqn. 21 reproduces experimentally-measured REE partitioning data, over the temperature range 1703 to 1913K to within $\sim 15\%$ (1σ).

Following the same methodology as for clinopyroxene, one should use data on the depression of the liquidus in the pyrope- H_2O system as a means of determining activity-composition relationships for hydrous melts and determine whether or not these can be used to predict the dependence of D_o^{3+} on H_2O -content. In this case, however, the experimental constraints are not so good. The temperature range of the anhydrous data is small and well removed from that of the hydrous data, 1703 to 1913K as opposed to 1173 to 1473K. This means that any error in the temperature dependence (ΔS_p) of the partitioning data derived from the anhydrous data becomes greatly magnified when applied to low temperature hydrous data. For comparison, the temperature ranges of hydrous (1173 to 1760K) and anhydrous (1323 to 2050K) clinopyroxene data are much broader and have extensive overlap. Furthermore, in contrast to $\text{CaMgSi}_2\text{O}_6$ - H_2O , phase equilibria on the join $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - H_2O are very poorly known. The only data available are 4 points on the pyrope liquidus at 3 GPa determined by Wood (1976). We therefore used a more conservative approach for garnet-melt partitioning than that described above for clinopyroxene. Instead of directly testing the hypothesis that the effect of H_2O can be predicted, we determined whether or not the hydrous and anhydrous data are consistent with the hypothesis that the effect of H_2O on activities of major and trace components is the same. This involves applying an activity model and

re-fitting the hydrous and anhydrous data together as described below.

The results of Wood (1976) on the join $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}\text{-H}_2\text{O}$ were converted to activity at 3 GPa by using the 1 bar enthalpy and entropy of fusion of pyrope from Téqui et al. (1991) and adding volume terms derived by fitting the high pressure anhydrous melting curve of pyrope. This gives:

$$\begin{aligned} & -RT \ln a_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{melt}} \\ & = \Delta G_f = (-18031 + 165.59T) - T(69.546 + 0.18039T \\ & \quad - 2.421e^{-5}T^2) + 2911P - 15.39P^2 \quad (22a) \end{aligned}$$

The activity data were then fitted with a polynomial to yield:

$$\begin{aligned} \gamma_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{melt}} & = [0.0007 + 1.433(1 - X_{\text{H}_2\text{O}}) \\ & \quad - 1.7716(1 - X_{\text{H}_2\text{O}})^2 + 1.3379(1 - X_{\text{H}_2\text{O}})^3] \quad (22b) \end{aligned}$$

This expression refers to $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ mixing with H_2O (i.e., a 12 oxygen garnet with a 1 oxygen water) and applies only for H_2O contents less than 24 weight%. We took the anhydrous data fitted by van Westrenen et al. (2001) to Eqn. 21, added hydrous data, predominantly from Green et al. (2000), Klein et al. (2000) and Barth et al. (2001) and assumed that the activity coefficient of $\text{REEMg}_2\text{Al}_3\text{Si}_2\text{O}_{12}$ component in the melt depends on water in the same way as does that of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$:

$$\gamma_{\text{REEMg}_2\text{Al}_3\text{Si}_2\text{O}_{12}}^{\text{melt}} = \gamma_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{melt}} \quad (22c)$$

We then used measured values of D_o^{hydrous} and $D_{\text{Mg}}^{\text{hydrous}}$ to compute an apparent value of the product in brackets in Eqn. 21:

$$D_o^{3+} \cdot D_{\text{Mg}}^2 = \frac{D_o^{\text{hydrous}} \cdot (D_{\text{Mg}}^{\text{hydrous}})^2}{\gamma_{\text{REEMg}_2\text{Al}_3\text{Si}_2\text{O}_{12}}^{\text{melt}} \cdot (1 - X_{\text{H}_2\text{O}}) \frac{100^3}{(100 - \text{wt}\% \text{H}_2\text{O}^{\text{melt}})^3}} \quad (23)$$

Note that there are two terms involving H_2O in the denominator of Eqn. 23. The $(1 - X_{\text{H}_2\text{O}})$ term corrects the activity of $\text{REEMg}_2\text{Al}_3\text{Si}_2\text{O}_{12}$ component for mole fraction of water and the term in weight % H_2O accounts for the conversion from anhydrous to hydrous weight D values. The latter is cubed because both the REE and the Mg partition coefficients in the hydrous system have to be corrected for water content to calculate the apparent anhydrous values.

We then fitted hydrous and anhydrous data together with the following result:

$$\begin{aligned} RT \ln [D_o^{3+} (D_{\text{Mg}} \cdot \gamma_{\text{Mg}}^{\text{gt}})^2] & = 318390 - 198.2T \\ & + 34320P - 2470P^2 \quad (24) \end{aligned}$$

where P is, as before, in GPa and $\gamma_{\text{Mg}}^{\text{gt}}$ was calculated using the parameters given above. The quality of the fit can be observed in Fig. 6 which is a plot of the left hand side of Eqn. 24 for each experiment (corrected to 0.1 MPa by subtracting the pressure terms) against the experimental temperature. The ordinate therefore corresponds to an apparent 1 bar free energy of fusion, for which the best-fit line is 318390 to 198.2T. Comparison with Eqn. 21 shows that the combined data set gives

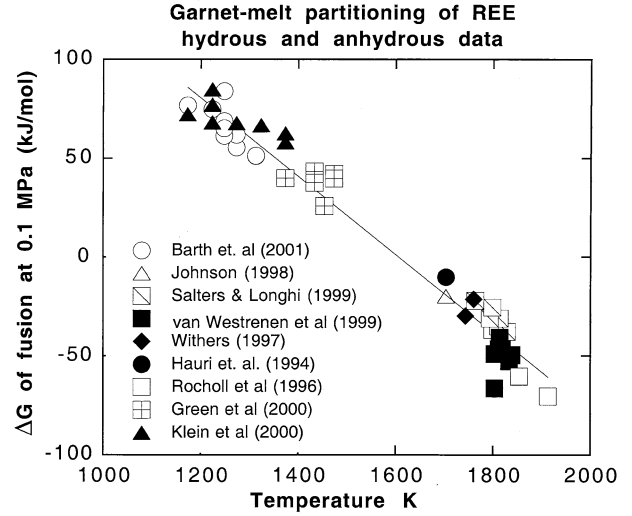


Fig. 6. The apparent free energy of fusion of $\text{REEMg}_2\text{Al}_3\text{Si}_2\text{O}_{12}$ garnet at 0.1 MPa as calculated from individual garnet-melt partitioning experiments. Experimental data were corrected to D_o for the best-fit REE using the methods of van Westrenen et al. (2001) and hydrous results were further corrected using Eqn. 23. Low temperature data (<1500K) are for hydrous melts while higher temperature experiments are anhydrous apart from 1 point of Withers (1997). The best fit line is 318390 to 198.2 J (see text).

rather lower values of ΔH_f and ΔS_f than the anhydrous data alone. Because of the narrow temperature range of the latter (1703 to 1913K), however, the melting properties are not well-constrained. Our new fit, including hydrous data at temperatures down to 1173K, reproduces the anhydrous data almost as well as the original fit. The average deviation of predicted as compared to observed values of D_o for the REE is only 3% worse for the anhydrous data with Eqn. 24 than with Eqn. 21. We consider this to be negligible with respect to the other uncertainties in partition coefficients.

Figure 7 illustrates the size of the correction to D_o required by the water contents of the hydrous melts (2 to 25 wt.%) If H_2O is ignored, then Eqn. 24 routinely overestimates REE partition coefficients by 2 to 3 orders of magnitude. If the H_2O -correction is applied, however (Fig. 7b) the agreement between calculated and observed D_o for the hydrous data is as good as that for the anhydrous data. In this case, errors in H_2O content of 1 weight% or in temperature of 50° would lead, as shown in Figure 7b to significant error in calculated values of D_o . It appears, however that the simple correction derived from the $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}\text{-H}_2\text{O}$ join enables hydrous and anhydrous data to be brought into agreement with one another. In this case we have shown not that the H_2O -effect can be predicted, but that the data are consistent with the hypothesis that the effect of H_2O on the activities of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and $\text{REEMg}_2\text{Al}_3\text{Si}_2\text{O}_{12}$ components is the same.

5. GENERAL EFFECT OF H_2O ON PARTITIONING

We have shown that the effects of water on the activities of major and minor components in silicate melts are, in two well-studied cases, approximately the same. This observation

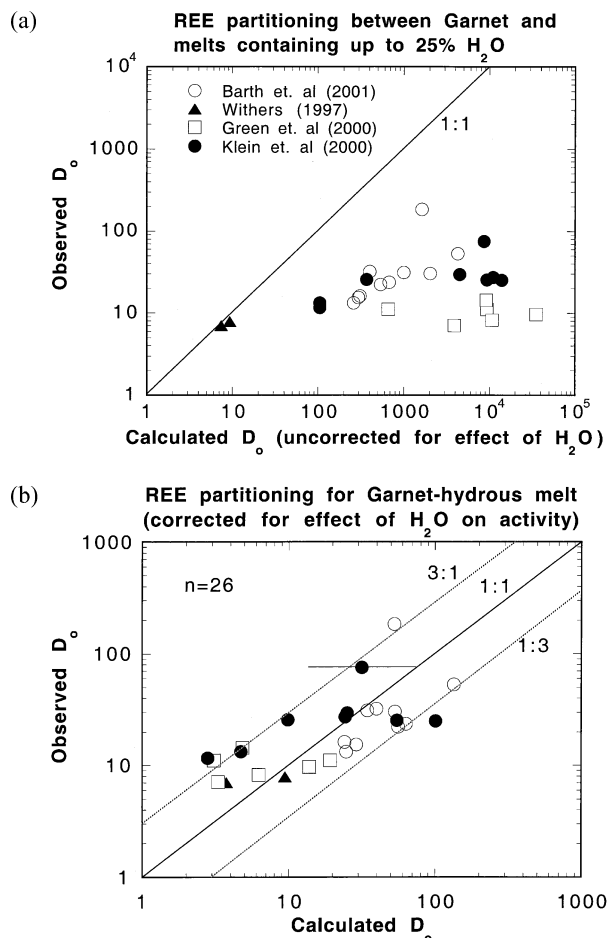


Fig. 7. Calculated and observed D_o values for REE partitioning between garnet and hydrous silicate melt. (a) If no correction is made for the effect of H_2O in the melt, calculated D values may be 3 orders of magnitude too high (b) Correction for the effect of H_2O using Eqn. 23 produces good agreement between observed and predicted D values. Horizontal error bar is indicative and represents ± 1 wt % H_2O in melt or $\pm 50^\circ$ approximately.

leads to a generalisation of the H_2O effect shown schematically in Figure 2. For the phase to remain on the liquidus as water is added to the melt, the effect of H_2O on the activity of the major component in the crystal must be *exactly* compensated by the temperature effect shown in Figure 2. Since both major and trace components in the melt are similarly affected by H_2O , then the overall effect of H_2O and temperature on trace element partitioning depends on whether or not the temperature effect on partitioning is greater for the trace component or for the major component. In the case of the major component the two effects exactly counterbalance one another. So, for the trace partition coefficient to increase with addition of water, its temperature effect must be greater than that of the major component. Applying Eqn. 15 to trace and major components it is fairly easy to show that if the enthalpy of fusion of the trace component is greater than that of the major component, addition of water leads to increasing D values i.e.,

$$\Delta H_f^{\text{trace}} > \Delta H_f^{\text{major}} \text{ gives increasing } D_{\text{trace}}$$

with addition of H_2O and

$$\Delta H_f^{\text{trace}} < \Delta H_f^{\text{major}} \text{ leads to decreasing } D_{\text{trace}}$$

with addition of H_2O .

(25)

In the case of clinopyroxene the enthalpy of fusion of trace $REEMgAlSiO_6$ is, at 88.75 kJ (Eqn. 19), much less than the value for diopside, the major component, of 137.7 kJ (Lange et al., 1991). This means that reduction of temperature and addition of H_2O leads to a strong decrease in the partition coefficients of the REE. The implications of this will be explored further below. For garnet, the $REEMg_2Al_3Si_2O_{12}$ component has an apparent enthalpy of fusion of 318 kJ (Eqn. 24). The enthalpy of fusion of pyrope, the major garnet component is strongly temperature dependent, with values close to 300 kJ per mole being appropriate for the temperature range of the anhydrous partitioning experiments. The combined temperature and water effect is therefore much smaller than for clinopyroxene and, at most, would lead to a very slight increase in REE partition coefficients as water is added.

6. EFFECT OF H_2O ON Yb IN PARTIAL MELTS OF SPINEL PERIDOTITE

The results described above allow us, for the first time to separate unambiguously the effects of water and temperature on partitioning of the REE into clinopyroxene and garnet. For illustration we will consider the effects of H_2O on the Yb contents of primary melts of spinel lherzolite mantle. For the anhydrous case we used partition coefficients calculated from the compositions of experimentally produced melts and crystals at 1.5 GPa (Robinson et al., 1998) in conjunction with Eqns. 13 and (3). Values of E and r_o for REE entering the clinopyroxene M2 site were obtained from the equations of Wood and Blundy (1997) and orthopyroxene was assigned a D_{Yb} 0.33 times the clinopyroxene value, consistent with recent experimental data (Salters and Longhi, 1999). Concentrations of Yb in batch anhydrous melts of MORB-pyrolite (Falloon and Green, 1987) were then computed for the non-modal melting case of Shaw (1970) using modal proportions at the solidus and the melting reaction from Robinson et al. (1998) and assuming that Yb does not enter olivine or spinel. Hydrous results at 1.5 GPa (Hall, 1999) were treated in the same manner. Figure 8 shows that anhydrous melting leads to Yb contents of the basaltic liquid which are between 4 and 5.5 times the source values for any degree of batch melting between 0 and 0.25. In contrast to these almost constant Yb concentrations for anhydrous melting, the hydrous case produces liquids strongly enriched in Yb relative to the source and for which Yb concentration is a strong function of F (Fig. 8). The reason for the difference is that, in the anhydrous case D_{Yb} for clinopyroxene is close to 1.0 and this exerts a buffering effect on the Yb content of the liquid. In the hydrous case, illustrated for 0.8% H_2O in the source, the near-solidus values of D_{Yb} , with $>15\%$ H_2O in the melt, are close to 0.1. In this case, Yb is an incompatible element and melt concentrations are high. As extents of melting increase and water contents of hydrous melts decrease, the curves for

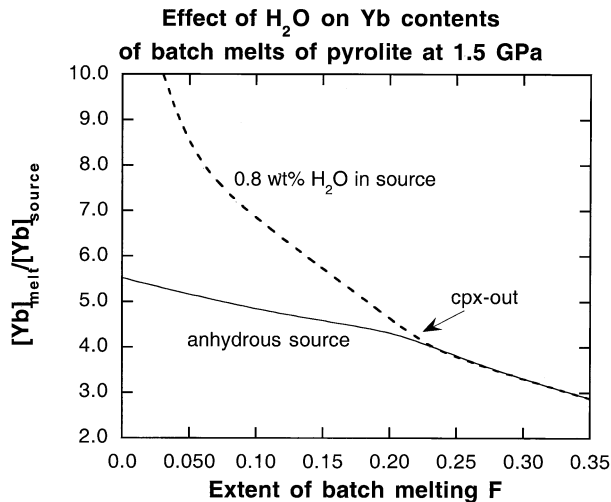


Fig. 8. The effect of H_2O on the Yb contents of melts produced during equilibrium partial melting of hydrous and anhydrous peridotite at 1.5 GPa. The melting reactions were taken from Robinson et al. (1998) for anhydrous peridotite and Hall (1999) for peridotite containing 0.8% H_2O . Partition coefficients for clinopyroxene were calculated from Eqns. 19 and (13) while those for orthopyroxene were fixed at 0.33 times the clinopyroxene values (see text).

hydrous and anhydrous cases converge, giving similar melt concentrations at F above 0.23.

An important implication of Figure 8 is that the observed low Yb contents, relative to N-MORB, of many supra-subduction zone (e.g., Ulmer, 2001) and back-arc basalts (e.g., Peate et al., 2001) is not a consequence of elevated H_2O contents of source regions. The latter must have lower Yb contents than the N-MORB source. They might, for example, have already been depleted by prior partial melting. Depletion of an anhydrous source by 50% of its Yb $\left(0.5 = F \left[\frac{[\text{Yb}]_{\text{melt}}}{[\text{Yb}]_{\text{source}}} - 0.5 \right] \right)$ would require an extent of batch melting, F , of ~ 0.12 . Calculated effects of fractional melting lead to virtually identical source depletions because Yb is relatively compatible under anhydrous conditions.

7. CONCLUSIONS

We have shown that the effect of H_2O on the activity of REEMgAlSiO_6 in silicate melts is approximately the same as its effect on the activity of the major component $\text{CaMgSi}_2\text{O}_6$. Since the mixing properties of $\text{CaMgSi}_2\text{O}_6\text{-H}_2\text{O}$ melts can be extracted from the liquidus temperature of diopside in this binary, we have been able to develop a quantitative method of predicting the effect of H_2O on the activity of REEMgAlSiO_6 component in silicate melts. Starting from the model of Wood and Blundy (1997) for REE partitioning between clinopyroxene and anhydrous melts, shifts in REEMgAlSiO_6 activity should factor directly into REE partition coefficients. Applying this theoretical adjustment to the Wood and Blundy (1997) model, we find that predicted REE partition coefficients for melts containing up to 45% H_2O agree with observed values with a standard deviation which is the same as for the anhydrous data. We conclude, therefore that the 'H₂O-effect' may

be accurately predicted for clinopyroxene-melt partitioning of the REE.

A similar approach to garnet-melt partitioning of REE is limited by the sparsity of liquidus data on the join $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}\text{-H}_2\text{O}$ and by the limited temperature range of the available partitioning data. Use of the latter indicates, however, that garnet-melt partitioning may also be treated by assuming that the effect of H_2O in the melt is the same for the minor REE component as for $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ component.

The observation that H_2O influences major and trace component activities in a similar manner has enabled us to make some generalisations about the combined effects on partitioning of decreasing temperature and increasing water content of the melt. The relative enthalpies of fusion ΔH_f of major and trace components dictate whether trace element partition coefficients increase or decrease with H_2O addition:

$$\Delta H_f^{\text{trace}} > \Delta H_f^{\text{major}} \text{ gives increasing } D_{\text{trace}}$$

with addition of H_2O and

$$\Delta H_f^{\text{trace}} < \Delta H_f^{\text{major}} \text{ leads to decreasing } D_{\text{trace}}$$

with addition of H_2O .

(26)

For clinopyroxene $\Delta H_f^{\text{REE}} < \Delta H_f^{\text{major}}$ and H_2O addition leads to substantial decreases in REE partition coefficients. The consequences are illustrated with respect to Yb. For partial melting of peridotite under anhydrous conditions, Yb is relatively compatible in clinopyroxene and the Yb contents of the product melts remain close to 5 times source values at all F between 0 and 0.25. Hydrous peridotites produce melts, because of low D_{Yb} , which are strongly enriched in Yb (up to at least 10 times source) and whose Yb concentrations depend strongly on F . The enrichment in melt Yb caused by H_2O addition implies that the low Yb contents of many island arc tholeiites is a consequence of their derivation from a previously-depleted source.

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