

Comments on ‘Mantle Melting and Melt Extraction Processes beneath Ocean Ridges: Evidence from Abyssal Peridotites’ by Yaoling Niu

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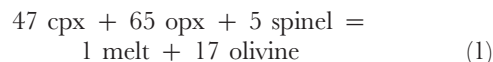
Phase equilibrium data for melting of lherzolite in simplified and natural systems are used to show that the ‘polybaric melting reaction’ for mid-ocean ridge basalt proposed by Niu (1997, Journal of Petrology 38, 1047–1074) is erroneous for two reasons. First, the modal abundances of minerals in abyssal peridotites that have equilibrated at low pressures and temperatures cannot be used to calculate high-pressure and -temperature melting reactions. This is because the observed low-temperature mineral modes do not faithfully reproduce the changing abundances of clinopyroxene and orthopyroxene as a function of temperature and pressure that occur at the conditions of melting. Using abyssal peridotite mineral modes to calculate melting reactions results in a severe overestimation in the amount of orthopyroxene, and an underestimation in the amount of clinopyroxene, that dissolves into the melt in polybaric, near-fractional melting paths. The magnitude of these errors can be quantitatively significant for trace element melting models. Second, experimental data show that the complexity of phase relations as a function of pressure and temperature leads to a rich variety of melting reactions in polybaric melting paths. A single ‘polybaric melting reaction’ is not realistic. Only high-pressure and -temperature phase relations can yield reliable melting reactions.

KEY WORDS: mantle melting reactions; abyssal peridotite; mid-ocean ridge basalt

INTRODUCTION

In a recent study (Niu, 1997), it was proposed that a single ‘polybaric melting reaction’ to produce mid-ocean

ridge basalt (MORB) from spinel lherzolite has the form



and that ‘this melting reaction provides so far the most realistic melting modes for trace element modeling’. However, this reaction, with orthopyroxene (opx) contributing more by weight than clinopyroxene (cpx) to the melt, is very different from melting reactions obtained for melting of spinel lherzolite on the basis of experimental data from both natural and simplified systems (e.g. Kinzler & Grove, 1992; Walter *et al.*, 1995; Kinzler, 1997). For example, experimental data show opx crystallizing from melt in a peritectic reaction over a range of high pressures in the spinel lherzolite field [see reaction (2) below].

Reaction (1) was calculated by Niu (1997) on the basis of the observed rate of change of mineral abundances in abyssal peridotites as a function of the degree of melt extraction as estimated from the MgO contents of the peridotites. That is, reactions were calculated from the slopes of linear regressions fitted to the observed modal variation for each mineral. Figure 1 shows the regressions as presented by Niu (1997). Here, it is shown on the basis of experimental data for melting of lherzolite in both the CaO–MgO–Al₂O₃–SiO₂–Na₂O system (CMASN; Walter & Presnall, 1994) and the natural system (Kinzler & Grove, 1992, 1993) that the method for calculating melting reactions employed by Niu is not valid because the observed abyssal peridotite mineral modes do not reproduce accurately the mineral modes

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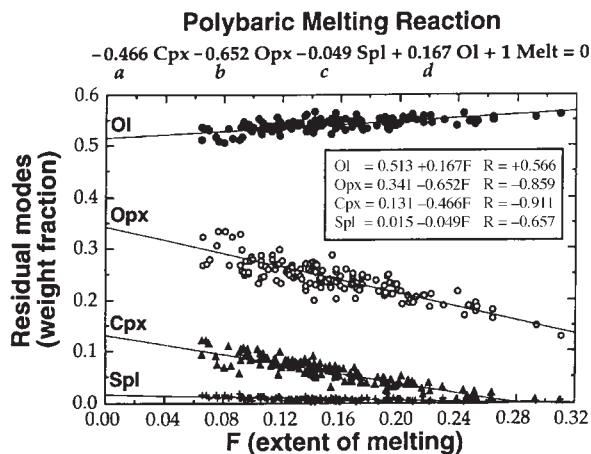


Fig. 1. Figure 12 from Niu (1997) showing the rate of change of residual modes as a function of extent of melting for abyssal peridotites. Mineral modes are from the literature [see Niu (1997) and references therein], and the extent of melting is estimated from the MgO contents of the bulk peridotites. The slopes of linear regressions fitted to the data yield the coefficients for the 'polybaric melting reaction'.

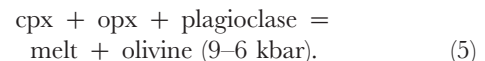
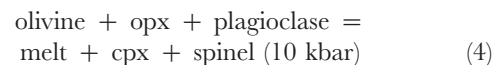
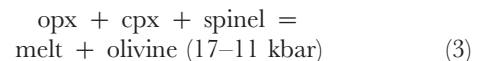
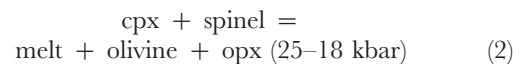
at the conditions of melting. Moreover, the concept of a single 'polybaric melting reaction' is inappropriate because of the complex variation of melting reactions that must occur in a polybaric melting path.

SYNTHETIC MELTING MODELS

I use phase equilibrium data from the CMASN system for melting of spinel and plagioclase lherzolite (Walter & Presnall, 1994) to calculate melting reactions and residual mineral modes for polybaric near-fractional melting. The CMASN system is ideal for calculating the stoichiometry of melting reactions because: (1) melting of four-phase lherzolite is isobarically univariant; (2) all phase compositions are known along isobaric melting curves, permitting precise calculation of melt and mineral modes as a function of pressure, temperature, and melting rate; (3) melting paths are uniquely determined for any bulk composition that lies within the composition space defined by a spinel or plagioclase lherzolite assemblage [see Walter & Presnall (1994) for details]. These attributes permit the precise calculation of melt and mineral modes for polybaric near-fractional melting of a progressively depleted source [see Walter *et al.* (1995)], the probable mechanism by which MORBs are generated (e.g. Klein & Langmuir, 1987; Johnson *et al.*, 1990).

Figure 2 shows residual mineral modes as a function of degree of melt depletion for polybaric melting of model lherzolite from 25 to 6 kbar. In this model, 1% melt is extracted at 1 kbar pressure increments, and the initially fertile source [i.e. model lherzolite A of Walter & Presnall (1994)] is sequentially depleted. [The sequence of melting

reactions that occur along a polybaric melting path will depend on melt production rate, dF/dP , as well as pressure and temperature. The melt production rate chosen here, 1% per kbar of decompression, is in the range of estimates made by previous workers for melting at oceanic ridges (e.g. Iwamori *et al.*, 1995), although in detail this rate will probably not be constant throughout the melting interval (Asimow *et al.*, 1997; Yang *et al.*, 1998). The arguments presented here are not sensitive to the exact choice of this value for modeling a polybaric near-fractional melting process.] Mineral modes for the sequentially depleted residues are calculated by mass balance from phase compositions at the pressures and temperatures of melt extraction. Melting reactions are calculated at each pressure from changes in the mass proportions of phases for a melt increment of 0–1%, that is, from the solidus to the degree of melting at which melt is extracted [see Walter *et al.* (1995)]. Four melting reactions occur along this melting path, each with variable stoichiometry as a function of pressure and temperature, rather than a single polybaric reaction as proposed by Niu (1997). These are:



Quantitative reaction stoichiometries are given in Table 1. It should be noted that at high pressures in the spinel lherzolite field, opx crystallizes during melting in a peritectic reaction [reaction (2)]. Over the remainder of the melting path in the spinel lherzolite field, opx dissolves during melting [reaction (3)], but at a rate much less than that for cpx. During melting of plagioclase + spinel lherzolite [reaction (4)] and plagioclase lherzolite [reaction (5)], plagioclase replaces cpx as the primary mineral contributing to the melt, and opx dissolves into the melt at a slightly higher rate than cpx. In contrast, the 'polybaric melting reaction' of Niu (1997) shows opx decreasing continuously with increasing melt depletion, and it dissolves into the melt at a higher rate than all other coexisting minerals.

To compare the results of polybaric melting models with observed abyssal peridotite modes, Niu used the CIPW norm to transform model residue compositions into normative mineral modes. Niu showed that a reasonably meaningful comparison can be made in this way [see fig. 5 of Niu (1997)], and this is because the endmember normative mineral components have

Table 1: Melting reactions and rock modes for polybaric near-fractional melting of spinel lherzolite in CMAS_N (weight units)*†

	melt	fo	opx	cpx	sp	pl
Initial rock mode‡	—	53.8	14.3	29.2	2.7	—
24 kbar, 1485.9°C, 2% melt§						
reaction¶	100	7.3	31.8	-125.4	-13.7	—
rock mode	—	54.9	16.0	26.6	2.5	—
22 kbar, 1466.8°C, 4% melt						
reaction	100	9.7	20.8	-116.6	-14.0	—
rock mode	—	56.0	18.2	23.5	2.3	—
20 kbar, 1446.9°C, 6% melt						
reaction	100	12.3	10.1	-108.3	-14.1	—
rock mode	—	57.2	19.9	20.7	2.2	—
18 kbar, 1425.8°C, 8% melt						
reaction	100	14.9	0.1	-101.0	-14.1	—
rock mode	—	58.5	21.2	18.3	2.0	—
16 kbar, 1403.0°C, 10% melt						
reaction	100	17.8	-8.9	-94.8	-14.1	—
rock mode	—	60.0	22.1	16.1	1.8	—
14 kbar, 1374.1°C, 12% melt						
reaction	100	25.1	-23.1	-87.6	-14.4	—
rock mode	—	61.7	22.3	14.4	1.7	—
12 kbar, 1342.7°C, 14% melt						
reaction	100	32.2	-38.4	-77.9	-15.9	—
rock mode	—	63.3	22.4	12.7	1.7	—
10 kbar, 1307.5°C, 16% melt						
reaction	100	-26.0	-10.0	6.0	10.0	-80.0
rock mode	—	64.2	22.9	11.4	1.5	0.01
8 kbar, 1292.0°C, 18% melt						
reaction	100	9.5	-37.0	-28.8	—	-43.7
rock mode	—	70.8	20.1	2.8	—	6.4
6 kbar, 1272.4°C, 20% melt						
reaction	100	13.5	-41.2	-26.6	—	-45.7
rock mode	—	73.1	19.1	0.2	—	7.6

*Melting reactions are calculated from changes in mass proportion using the method described by Walter *et al.* (1995). In the polybaric melting model, reactions were calculated at 1 kbar pressure increments for a melting interval of 0–1%, and the bulk composition was sequentially depleted. However, reactions are shown at 2 kbar increments for brevity. The rock modes are calculated on a melt-free basis by mass balance of coexisting mineral compositions with the bulk composition at the conditions of melt extraction.

†The computer software used to calculate these reactions, and which can be used to calculate melting reactions for a wide range of lherzolite melting paths, is available from the author upon request.

‡Rock mode at the 25 kbar solidus (1492.3°C).

§Pressure and temperature of melt extraction, and total accumulated melt percent.

¶For mineral phases, a negative coefficient means that the phase dissolves into the melt, whereas a positive coefficient means that the phase crystallizes from melt (e.g. the reaction at 24 kbar is: 100 melt + 7.3 fo + 31.8 opx = 125.4 cpx + 13.7 sp).

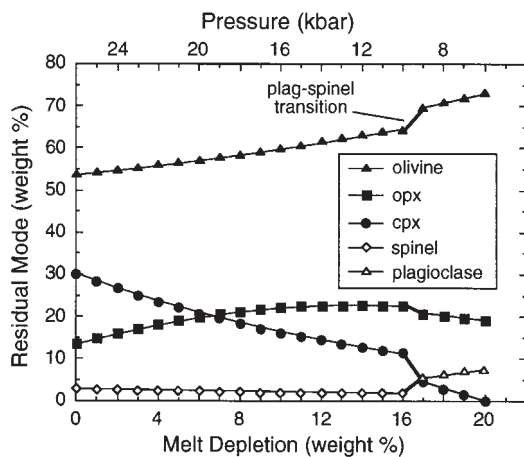


Fig. 2. Residual mineral modes vs degree of melt depletion for polybaric, near-fractional melting of model lherzolite from 25 to 6 kbar using phase equilibrium data from the CMASN system (Walter & Presnall, 1994). One percent melt is extracted at each pressure, and the bulk composition is sequentially depleted. Mineral modes are calculated by mass balance from the phase compositions that occur at the conditions of melting.

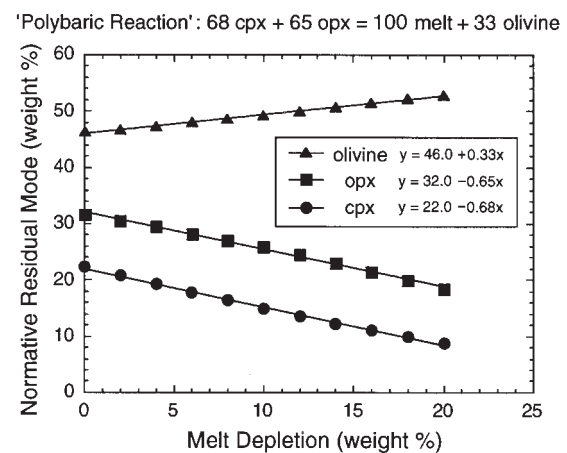


Fig. 3. Normative residual modes vs degree of melt depletion for the polybaric melting model shown in Fig. 2. Mineral modes are calculated from the CIPW norm, and a polybaric melting reaction is calculated from linear regressions fitted to the data. The 'polybaric melting reaction' is very similar to the reaction calculated by Niu (1997) for abyssal peridotites, but is very different from the melting reactions calculated from the phase relations (see Table 1).

compositions that are similar to the mineral compositions in abyssal peridotites. For comparative purposes, I have adopted this procedure and have applied it to the CMASN melting model shown in Fig. 2, and the results are shown in Fig. 3. In the construction of Fig. 3, normative mineral modes were calculated at each pressure step for each sequentially depleted bulk composition. Linear regressions were fitted to the modal trends as a function of degree of melt depletion to calculate a 'polybaric melting reaction'. A comparison of Fig. 3 with Table 1 and Fig. 2 shows that the method employed by Niu does not reproduce either the correct stoichiometry nor the rich variety of melting reactions known to occur from the phase relations. It does, however, produce a reaction in which opx dissolves into the melt at a rate nearly equal to that of cpx, very similar to the reaction calculated by Niu from both abyssal peridotite modes and polybaric melting models [e.g. reaction (1)].

Why cannot abyssal peridotite modal mineralogy be used to calculate the correct melting reactions? The answer is that the proportions of opx and cpx in peridotite are very sensitive to temperature and pressure. Figure 4a shows the compositions of cpx and opx, as projected onto the diopside–enstatite join in the system CMASN, as a function of temperature and pressure at the solidus of fertile lherzolite from 25 to 6 kbar (i.e. no melt extraction). With a rise in temperature, cpx becomes progressively more enriched in enstatite component, whereas opx has an essentially constant composition (e.g. Lindsley, 1980). Figure 4b shows the effect of the change in cpx composition on the modal proportions of cpx and opx. At low temperatures and pressures, in the plagioclase

lherzolite field, opx is more than three times as abundant as cpx in lherzolitic compositions. This is in part due to the presence of plagioclase as a coexisting Ca-rich aluminous phase. However, for spinel lherzolite Fig. 4b shows that the change in cpx composition alone causes a significant change in the cpx:opx ratio. For example, at about 13 kbar and 1350°C the cpx:opx ratio is about 1:1, whereas, at 25 kbar and 1500°C cpx is more than twice as abundant as opx. Indeed, experiments show that opx is no longer stable at the solidus of some natural fertile lherzolite compositions at pressures above ~35 kbar (Takahashi, 1986; Walter, 1998); that is, all the opx component is dissolved into cpx. Bertka & Holloway (1993) recognized that these high-temperature cpxs are pigeonitic, and Longhi & Bertka (1996) have called them 'supercritical cpx'. Whichever terminology you prefer, the net effect on mineral proportions is that *cpx increases substantially in the peridotite mineral mode at the expense of opx with rise in temperature and increase in pressure.*

To illustrate that abyssal peridotites have finally equilibrated at much lower temperatures than must have existed at the conditions of melt extraction, the compositions of coexisting cpx and opx in abyssal peridotites from the SW Indian Ocean (Dick, 1989) are plotted in Fig. 4a. The compositions of average cpx from four fracture zones are used to fix temperature and pressure estimates. It should be noted that this is not a unique result, and I do not wish to imply that these abyssal peridotites necessarily re-equilibrated at these exact low-pressure solidus conditions. However, the cpx compositions do indicate low-pressure and -temperature equilibration. If the two-pyroxene thermometer of Nickel *et*

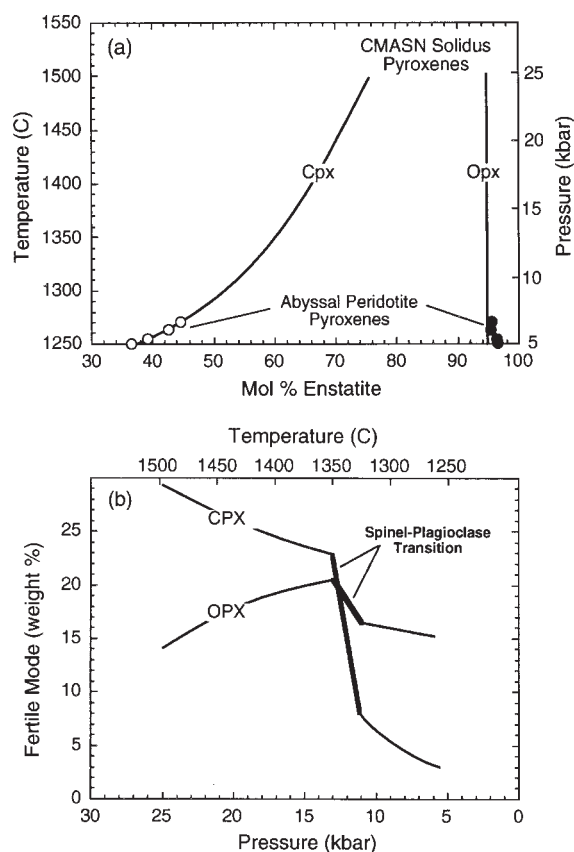


Fig. 4. (a) Temperature (°C) and pressure (kbar) vs mol % enstatite for coexisting pyroxenes at the solidus of fertile lherzolite based on data from the CMASN system (Walter & Presnall, 1994). Cpx becomes progressively enriched in enstatite component with rise in temperature and increase in pressure. Shown as open and filled circles, respectively, are averaged coexisting cpx and opx compositions from four fracture zones in the SW Indian Ocean (Dick, 1989). These compositions indicate low temperatures and pressures of equilibration. (b) The effect of changing cpx composition, as shown in (a), on the modal proportions of cpx and opx at the solidus of fertile lherzolite. The abundance of cpx increases at the expense of opx with rise in temperature and increase in pressure. The spinel-plagioclase lherzolite transition also has an important effect on pyroxene modal abundances, as plagioclase forms in a reaction of the form $\text{opx} + \text{cpx} + \text{spinel} = \text{olivine} + \text{plagioclase}$.

al. (1985) is used, and assuming a pressure of equilibration between 3 and 10 kbar, temperatures from about 1215 to 1265°C are calculated for the coexisting pyroxene compositions. Thus, cpx compositions observed in abyssal peridotites are very enstatite poor compared with the cpx compositions expected in the melting interval at high temperatures and pressures.

The change in mineral proportions along the solidus of lherzolite has a profound effect on melting reactions, as can be seen from Table 1. The low-temperature modes of abyssal peridotites fail to account for these changes, and this leads to an inaccurate assessment of mineral modes in the melting interval because much of the

enstatite component dissolved into cpx at high temperatures exists as opx at low temperatures. When this misrepresentation of mineral modes is perpetuated into the calculation of a melting reaction, the result is an overestimation in the amount of opx, and an underestimation in the amount of cpx, that dissolves into the melt. Most importantly for melting at oceanic ridges, at high pressures and temperatures in the spinel lherzolite stability field peritectic reaction (2) given above becomes important [see also Kinzler (1997)].

To give reassurance that the above results are not an artifact of the previous melting model, or of phase equilibrium data from an Fe-free system, the results of a variety of polybaric near-fractional melting models of spinel and plagioclase lherzolite are shown in Fig. 5. Figure 5a shows models from the CMASN system, and Fig. 5b shows models from the natural system (Kinzler & Grove, 1993). In both figures three models are shown, corresponding to between about 10 and 20% polybaric incremental melt extraction; values which are appropriate for MORB (e.g. Johnson *et al.*, 1990). Residual mineral modes were calculated from the residual bulk compositions for each model using the CIPW norm, and linear regressions were fitted to the modes as a function of degree of melt depletion. It should be noted that the two experimental data sets produce nearly identical results, and both show about an equal amount of opx and cpx contributing to melt in the 'polybaric melting reactions'. Indeed, these results are very similar to the result found by Niu (1997) for abyssal peridotites. However, phase relations show clearly that the actual melting reactions involve a significant amount of opx crystallization in the spinel lherzolite field. Thus, for the reasons discussed above, the melting reactions calculated from abyssal peridotite modes are clearly an artifact of the method. [It should be pointed out that the 'polybaric melting reaction' of Niu [reaction (1)] may describe adequately the average rate of depletion of specific low-temperature mineral components from an average fertile peridotite source of MORB. That is, from the reference point of the mineral compositions in abyssal peridotites the rate of depletion calculated by Niu is valid, although no chemical reaction with the stoichiometry of reaction (1) would ever have actually taken place anywhere in the mantle. Thus, given that the average fertile peridotite source for MORB is known, and using average mineral compositions from abyssal peridotites as component operators, Niu's reaction could be used to estimate the major element compositions of primary MORB melts at specified degrees of melting.]

The CMASN melting models also illustrate another fundamentally important point: that the concept of a single 'polybaric melting reaction' is not correct. Each residual composition represents the end-product of a complex series of melting reactions that change as a

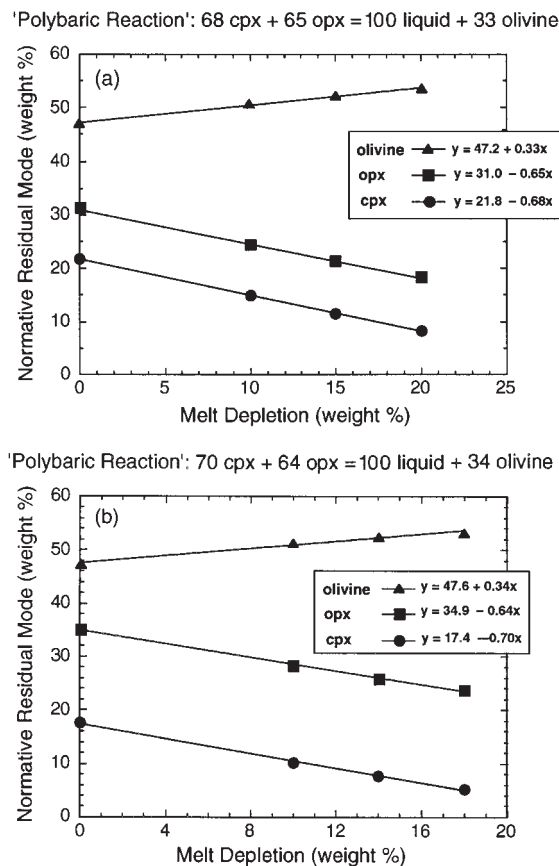


Fig. 5. Normative residual mode vs degree of melt depletion for a variety of polybaric near-fractional melting paths as calculated from data in the CMASN system [(a), this study] and the natural system [(b), models from Kinzler & Grove (1993)]. Normative mineral modes are calculated from the final residue compositions for each model. The three CMASN models range from 10 to 20% melting. Melting paths are 25–6, 20–6, and 15–6 kbar with 1% melt extracted at each pressure. Parameters for the models from the natural system can be found in table 3 of Kinzler & Grove (1993), but are nearly identical to those used in the CMASN models. Polybaric melting reactions are calculated from linear regressions to the model data points. The two data sets produce nearly identical reactions, and these reactions are very similar to reaction (1) given in the text as calculated by Niu (1997). However, phase relations show that the actual reactions are variable, and involve a significant amount of opx crystallization.

function of pressure, temperature, and bulk composition (see Table 1). It is impossible to determine these reactions from a single residue, or from a series of residues such as abyssal peridotites that have finally equilibrated at low pressures and temperatures. Tightly constrained high-pressure and -temperature phase relations must be used to constrain mantle melting reactions.

QUANTITATIVE EFFECTS IN MELTING MODELS

Quantitative models for the behavior of trace elements during partial melting of the upper mantle are important

for deducing the conditions of origin of MORB and other basaltic magmas. The trace element modeling equation for equilibrium partial melting as presented by Shaw (1970), for example, has the general form

$$C_L = \frac{C_S}{D + F(1 - P)} \quad (6)$$

where C_L is the element concentration in the liquid, C_S is the concentration in the solid before melting, F is the melt fraction, D is the bulk partition coefficient and P is the bulk melting coefficient. This equation requires, as input, the mass proportions of coexisting minerals in the source in order to calculate the bulk partition coefficient (D), and the mass proportions in which these minerals contribute to the liquid in order to calculate the bulk melting coefficient (P). Thus, it is important to know both the rock modes and melting modes as a function of pressure, temperature and degree of melting.

Here, the results of a polybaric near-fractional melting model are used to assess the quantitative difference between using Niu's initial rock mode and 'polybaric melting reaction', and the reactions and rock modes calculated from phase equilibrium data in CMASN. Equation (6) was used to calculate the abundances of five rare earth elements (REE) in a polybaric incremental melting model of spinel lherzolite. These trace elements were chosen because their range of incompatibility in spinel lherzolite minerals varies from incompatible to mildly incompatible (see caption to Fig. 6 for details of the melting model). In Fig. 6 the abundances of elements in melts and residues, as calculated using the melting parameters from Niu (1997), are shown relative to abundances calculated using CMASN melting parameters. The general result is that for low degrees of melting, Niu's parameters give abundances in the melt at levels up to a factor of 1.8 greater than predicted using the CMASN parameters. At higher degrees of melting the differences become insignificant. For residues the opposite is true [see also Walter *et al.* (1995)]. At low degrees of melting differences are relatively insignificant, but at higher degrees of melting differences for some incompatible elements can be nearly a factor of ten. Whether these differences affect interpretations will depend on the specifics of a given model. The point here is that the 'polybaric melting reaction' presented by Niu (1997) is wrong on phase equilibrium grounds, and that it can lead to quantitatively significant errors in trace element melting models.

CONCLUSIONS

The 'polybaric melting reaction' for MORB proposed by Niu (1997), with opx dissolving into the melt at the highest rate during melting, is clearly an artifact of using

low-temperature abyssal peridotite mineral modes to calculate a melting reaction. Models for polybaric near-fractional melting of spinel and plagioclase lherzolite in the CMASN system show that opx actually crystallizes during melting over a substantial range of high pressures and temperatures in the spinel lherzolite field in a peritectic reaction, and that cpx (spinel lherzolite field) or plagioclase (plagioclase lherzolite field) dissolves into the melt at the highest rate. Moreover, polybaric melting involves a variety of melting reactions of variable stoichiometry rather than a single polybaric reaction. Thus, conclusion (2) of Niu (1997) is refuted by experimentally determined phase relations for melting of lherzolite.

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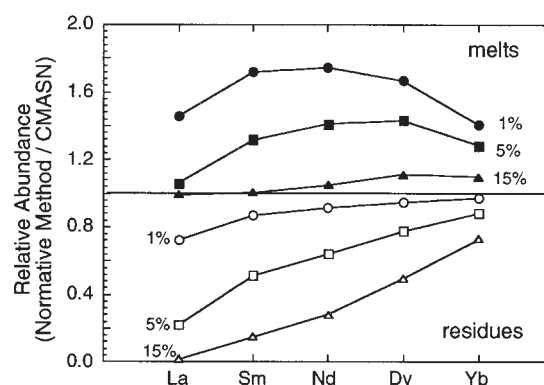


Fig. 6. Trace element abundances calculated for polybaric near-fractional melting of spinel lherzolite. The abundances calculated using the model melting parameters from Niu (1997) are shown relative to model abundances obtained using melting parameters from CMASN. Relative abundances are shown at 1%, 5% and 15% total melting for both melts and their residues. When using Niu's melting parameters, element abundances were calculated for 15 separate 1% melting increments. The initial mineral modes were taken from the γ -intercepts in Fig. 1, and the mineral modes were incremented using reaction (1). Bulk D and P values were calculated accordingly using the incremented mineral modes and the polybaric reaction. For the CMASN model, mineral modes and melting modes from 25 to 11 kbar are from the model shown in Fig. 2 and given in Table 1. Element abundances were calculated for 1% melting at each 1 kbar pressure increment. Mineral–melt partition coefficients are from Hauri & Hart (1995).

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