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## Quantitative modeling of trace element fractionation during incongruent dynamic melting

HAIBO ZOU<sup>1,\*</sup> and MARY R. REID<sup>1</sup>

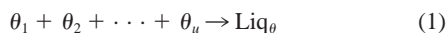
<sup>1</sup>Department of Earth and Space Sciences, University of California at Los Angeles, Los Angeles, California 90095-1567, USA

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**Abstract**—A recent significant achievement in trace element modeling is the development of the congruent (eutectic) dynamic melting (CDM) model where only melt is generated. However, melting reactions in the mantle and crust often produce not only melt but also minerals. By introducing melting reactions into the dynamic melting model, we present a series of equations for incongruent dynamic melting (IDM). We also compare IDM with incongruent batch melting (IBM) and CDM. The difference in calculation results between IDM and IBM is significant, particularly for incompatible elements in the residual melt and the total residue. The difference between IDM and CDM is noticeable when the fraction of the product minerals is significant and when the distribution coefficient of the product mineral is sufficiently different from those of the reaction minerals. More realistic but more complex IDM models are also derived to further account for the progressive changes in partition coefficients, the variations in the net fractional contribution of a phase to the total melt, and the consumption of a solid phase. Applications of IDM equations to model residual clinopyroxenes are illustrated. Distinctive rare earth element (REE) patterns with a middle REE hump in clinopyroxene can be produced by partial melting in garnet stability field. The IDM equations presented here are very useful in modeling partial melting of both the mantle and the crust. *Copyright © 2001 Elsevier Science Ltd*

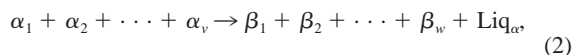
### 1. INTRODUCTION

During partial melting of the crust and the mantle, some minerals melt congruently and others melt incongruently. Melting of congruent minerals only produces melt, and such a process can be expressed as

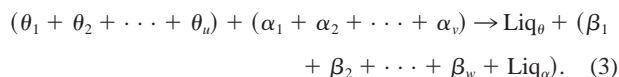


where  $\theta_1$ ,  $\theta_2$ , and  $\theta_u$  are minerals that melt congruently and  $\text{Liq}_\theta$  is the liquid formed by congruent melting. A dynamic melting model that takes into account the progressive extraction as the above melting proceeds is called congruent dynamic melting (CDM). Quantitative models for CDM have recently been developed by various authors (Langmuir et al., 1977; Maaløe, 1982; Maaløe and Johnson, 1986; Williams and Gill, 1989; Petersen and Hertogen, 1990; Sobolev and Shimizu, 1992; Ozawa and Shimizu, 1995; Albarede, 1995; Zou and Zindler, 1996; Shaw and Pereira, 1997; Zou, 1998; 2000).

By comparison, melting of incongruent minerals produces not only melt but also minerals, and such a melting reaction process can be expressed as



where  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_v$  represent the minerals that melt incongruently,  $\beta_1$ ,  $\beta_2$ , and  $\beta_w$  are product minerals, and  $\text{Liq}_\alpha$  is the liquid formed by melting reactions. In fact, a source rock often contains both congruent minerals and incongruent minerals, therefore, a general melting equation is



The minerals ( $\beta$ ) that are produced in the melting reaction can be the congruent minerals ( $\theta$ ) already present in the system or minerals that are new to the system. In contrast to CDM, an incongruent dynamic melting (IDM) model which takes into account the melting reactions in Eqn. 3 has not been investigated. Since incongruent melting is common in the process of mantle and crust melting (Zeck, 1970; Benito-Garcia and Lopez-Ruiz, 1992; Kinzler and Grove, 1992; Kinzler, 1997; Gudfinnsson and Presnall, 1996; Walter, 1998), the main aim of this paper is to quantify trace element fractionation during incongruent dynamic melting. We develop a simple model for incongruent dynamic melting with constant partition coefficients and constant net fractional contribution of a phase to the total melt. More complex models that account for the variations in partition coefficients, in net fractional contribution of a phase to the total melt, and in discontinuous changes of melting parameters (such as the consumption of a solid phase) are presented in the Appendix.

### 2. INCONGRUENT DYNAMIC MELTING

Let  $S_\theta^i$  and  $L_\theta$  be the consumed mass of a congruent mineral and the mass of the produced melt by congruent melting, respectively. Then, according to Eqn. 1, we have the total consumed mass of all congruent minerals as  $\sum_\theta S_\theta^i = L_\theta$ . Let  $S_\alpha^i$ ,  $S_\beta^i$ , and  $L_\alpha$  be the converted mass of an incongruent mineral, the produced mass of a mineral, and the mass of the produced melt, respectively, during incongruent melting, then, according to Eqn. 2, we have  $\sum_\alpha S_\alpha^i = \sum_\beta S_\beta^i + L_\alpha$ . The mass balance for Eqn. 3 is

$$\sum_\alpha S_\alpha^i + \sum_\theta S_\theta^i = \sum_\beta S_\beta^i + L_\alpha + L_\theta \quad (4)$$

For the general melting reaction in Eqn. 3, the degree of partial melting ( $F$ ) is the mass fraction of the total melt ( $L_\theta + L_\alpha$ ) relative to the initial amount of the source ( $M_0$ ), or,

\* Author to whom correspondence should be addressed (hzou@ess.ucla.edu).

$$F = (L_\theta + L_\alpha)/M_0. \quad (5)$$

In a dynamic melting model, the system consists of the extracted melt, the residual solid, and the residual liquid. For simplicity of derivation, we will treat the residual solid and the residual melt together as the total residue. If  $M_0$  is defined as the initial mass of the source and  $M_L$  the mass of the extracted melt, then  $(M_0 - M_L)$  is the mass of the total residue (residual melt + residual solid). Similarly, if  $m_0$  is defined to be the mass of the element in question in the initial solid and  $m_L$  the mass of the element in the extracted melt, then  $(m_0 - m_L)$  is the mass of the element in the total residue. Therefore, the concentration of the element in the total residue is  $C_{\text{res}} = (m_0 - m_L)/(M_0 - M_L)$ . Essentially, the effective distribution coefficient  $D_{\text{eff}}$  is the ratio of the concentration of the element in the total residue relative to its concentration in the last drop of the extracted melt. Since the concentration of the element in the last increment of the extracted melt is  $dm_L/dM_L$ , we have

$$D_{\text{eff}} = C_{\text{res}}/(dm_L/dM_L) = \left( \frac{m_0 - m_L}{M_0 - M_L} \right) / \left( \frac{dm_L}{dM_L} \right). \quad (6)$$

We define the mass fraction of the extracted melt relative to the initial source as  $X = M_L/M_0$ , the source concentration of the element as  $C_0 = m_0/M_0$ , and the average concentration in the extracted melt as  $\overline{C}_L = m_L/M_L$ . The effective distribution coefficient  $D_{\text{eff}}$  is related to the bulk distribution coefficient of the residual solid  $D_{\text{sf}}$  (Greenland, 1970) by

$$D_{\text{eff}} = \Phi + (1 - \Phi)D_{\text{sf}} \quad (7)$$

where  $\Phi$  is the mass fraction of the total residue that is residual melt. Combining Eqns. 6 and 7, and using the above definitions, we obtain

$$\frac{d(\overline{C}_L X)}{C_0 - \overline{C}_L X} = \frac{1}{\Phi + (1 - \Phi)D_{\text{sf}}} \frac{dX}{1 - X}. \quad (8)$$

We need to express  $D_{\text{sf}}$  as a function of  $X$  in order to solve this differential equation. The bulk distribution coefficient of the residual solid is (Shaw, 1970)

$$D_{\text{sf}} = \sum x^i K^i, \quad (9)$$

where  $x^i$  is the mass fraction of mineral  $i$  in the solid and  $K^i$  is the mineral/melt distribution coefficient of mineral  $i$ . The change of  $x^i$  during incongruent partial melting according to mass balance for mineral  $i$  is given by Benito-Garcia and Lopez-Ruiz (1992) as

$$x^i(1 - F) = x_0^i - q^i F, \quad (10a)$$

where  $x_0^i$  is the mass fraction of mineral  $i$  in the source and

$$q^i = \frac{p_\theta^i + p_\alpha^i - t^i \sum_\alpha p_\alpha^i}{1 - (1 - t^i) \sum_\alpha p_\alpha^i}. \quad (10b)$$

$p_\theta^i$  and  $p_\alpha^i$  are the fractional contribution of mineral  $i$  to the melting through incongruent reaction and congruent melting, respectively;  $t^i$  and  $t^i$  are mass fractions of incongruent minerals converted to melt and mineral  $i$ , respectively.  $\sum_\alpha p_\alpha^i$  is the

sum of  $p_\alpha^i$  for all incongruent minerals. It should be emphasized here that the term  $q^i$  is essentially the net fractional contribution of phase  $i$  to the total melt or  $(S_\theta^i + S_\alpha^i - S_\beta^i)/(L_\theta + L_\alpha)$  (see Eqn. 4 for notations). Detailed explanations of this statement and concise definitions of each parameter and term in Eqn. 10 are given in the Appendix to facilitate a better understanding of the incongruent melting process. Substituting Eqn. 10 into Eqn. 9 and assuming a constant distribution coefficient ( $K^i = K_0^i$ ), we have

$$D_{\text{sf}} = \frac{1}{1 - F} \left[ D_0 - \frac{P_0 - \left( \sum_\alpha p_\alpha^i \right) \left( \sum_\beta t^i K_0^i \right)}{1 - (1 - t^i) \left( \sum_\alpha p_\alpha^i \right)} F \right], \quad (11)$$

where  $D_0 = \sum x_0^i K_0^i$  and  $P_0 = \sum (p_\theta^i + p_\alpha^i) K_0^i$ . Note that for congruent melting, we have  $\sum_\alpha p_\alpha^i = 0$ , all  $t^i = 0$ , and  $t^i = 1$ . In this case, Eqn. 11 reduces to the familiar equation of Shaw (1970):

$$D_{\text{sf}} = \frac{D_0 - P_0 F}{1 - F}. \quad (12)$$

The relationship between the degree of partial melting and the fraction of extracted melt relative to the initial solid is (Zou, 1998)

$$F = \Phi + (1 - \Phi)X. \quad (13)$$

Combining Eqns. 8, 11, and 13, we obtain the differential equation for incongruent dynamic melting (IDM):

$$\frac{d(\overline{C}_L X)}{C_0 - \overline{C}_L X} = \frac{dX}{[D_0 + \Phi(1 - Q_0)] - [Q_0 + \Phi(1 - Q_0)]X}, \quad (14)$$

where

$$Q_0 = \frac{P_0 - \left( \sum_\alpha p_\alpha^i \right) \left( \sum_\beta t^i K_0^i \right)}{1 - (1 - t^i) \left( \sum_\alpha p_\alpha^i \right)}. \quad (15)$$

The solution to Eqn. 14 for the extracted melt is

$$\overline{C}_L = \frac{C_0}{X} \left\{ 1 - \left[ 1 - \frac{Q_0 + \Phi(1 - Q_0)}{D_0 + \Phi(1 - Q_0)} X \right]^{1/[\Phi + (1 - \Phi)Q_0]} \right\}. \quad (16)$$

Consequently, the concentration in the residual melt is

$$C_f = \frac{\partial(X\overline{C}_L)}{\partial X} = \frac{C_0}{D_0 + \Phi(1 - Q_0)} \left[ 1 - \frac{Q_0 + \Phi(1 - Q_0)}{D_0 + \Phi(1 - Q_0)} X \right]^{1/[\Phi + (1 - \Phi)Q_0] - 1}. \quad (17)$$

The concentration in the residual solid is

$$C_s = C_f D_{\text{sf}} \quad (18)$$

where  $D_{s/f}$  is given by Eqn. 11.

The concentration in the total residue can be obtained by

$$C_{\text{res}} = C_f D_{\text{eff}} = \frac{C_0}{1-X} \left[ 1 - \frac{Q_0 + \Phi(1-Q_0)}{D_0 + \Phi(1-Q_0)} X \right]^{1/[\Phi+(1-\Phi)Q_0]} \quad (19)$$

Equations 16–19 satisfy the following mass balance requirement:

$$\overline{C_L} X + [C_f \Phi + C_s(1-\Phi)](1-X) = C_0. \quad (20)$$

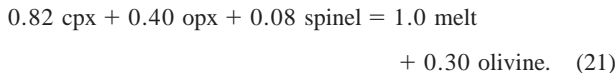
It is also noted that, if  $\sum_{\alpha} p_{\alpha}^i = 0$ , all  $t^i = 0$  and  $t^j = 1$ , which is the case for congruent melting, then  $Q_0 = P_0$ , and Eqns. 16–19 reduce to the set of equations for congruent dynamic melting in Zou (1998) which were obtained from a different approach.

### 3. APPLICATIONS AND DISCUSSION

#### 3.1. Comparison of IDM with Incongruent Batch Melting

Schilling and Winchester (1967) and Gast (1968) developed models for modal batch melting. Shaw (1970) first introduced the case of varying mineral proportions during eutectic melting by modeling nonmodal batch melting. To treat melting reactions, Hertogen and Gijbels (1976), Benito-Garcia and Lopez-Ruiz (1992), and Maaløe (1994) proposed equations for the incongruent batch melting (IBM). The IBM equations of Hertogen and Gijbels (1976) are only suitable for the case where there is one incongruent mineral, for example, the melting of parasitic hornblende in a hydrous spinel lherzolite. In order to compare the results of the IDM model derived here with those of IBM, we will use Eqns. 23 and 24 in Benito-Garcia and Lopez-Ruiz (1992) to model IBM with multiple incongruent minerals.

We modeled the variations in a rare earth element Nd, and a high field strength element Zr, in solids and liquids as a function of the degree of melting of spinel peridotite. At 10 kbar, melting of a spinel peridotite has the following melting reaction in mass units (Kinzler and Grove, 1992)



A step-by-step calculation for Nd is shown in the Appendix and the results for both Nd and Zr are shown in Fig. 1. Differences in concentrations produced by IDM and IBM are evident for the extracted melt, the residual melt, and the total residue (Fig. 1). The differences are particularly significant for the residual melt and the total residue, especially when  $X$  is large. It would be difficult, for example, to deplete incompatible elements like Nd and Zr in the residual melt and the total residue to a significant amount by batch melting using a reasonable  $X$ . Thus, the compositions of melting residues may be highly sensitive to differences between IDM and IBM.

Batch melting equations particularly fail to account for the extremely low concentrations of incompatible elements measured in residual clinopyroxene of abyssal peridotites (Johnson et al., 1990) and melt inclusions (Sobolev and Shimizu, 1993; Gurenko and Chaussidon, 1995; Shimizu, 1998). The batch melting equation has been used to model near-fractional melt-

ing processes by setting the degree of melting equal to a small value and carrying out an incremental calculation, in which the source concentration and the bulk distribution coefficients are recalculated between each step. This approach, however, often assumes complete extraction of a small amount of melt from the residue in every step. The IDM thus provides a more straightforward and realistic method for determining the trace element characteristics of trapped melt and residual solid.

#### 3.2. Applications to Melting in Mantle and Crust

Although partial melting of spinel peridotite mantle at the pressure range of 4–6 kbar may be at a cotectic-type boundary (i.e., congruent melting) (Grove et al., 1990), melts produced at higher and lower pressures in the mantle are generated along peritectic-type boundaries (i.e., incongruent melting) (Kinzler and Grove, 1992; Gudfinnsson and Presnall, 1996; Kinzler, 1997). For example, clinopyroxene (cpx) + orthopyroxene (opx) + spinel (sp) are consumed to produce liquid + olivine (ol) at 10–17 kbar (Kinzler and Grove, 1992). During partial melting of garnet (gt) peridotite mantle at >30 kbar, cpx + ol + gt are consumed to produce liquid + opx (Gudfinnsson and Presnall, 1996; Walter, 1998). Thus, the IDM equations provide a more realistic model for melting under these conditions, especially for the solid and liquid residues.

The IDM equations derived here can be employed to model trace element concentrations in residual cpx during mantle melting. Assuming isolation of trapped melt from further reaction with cpx, trace element concentration in residual cpx can be obtained by

$$C_{\text{cpx}} = D_{\text{cpx}} C_f \quad (22)$$

where  $C_f$  is given by Eqn. 17 for IDM. The above assumption can be generally satisfied if the amount of trapped melt is small and if we measure the center of cpx grains. We then use Eqn. 22 to model primary cpx in abyssal peridotite from Vulcan FZ and Atlantis II FZ (Johnson et al., 1990) and in ophiolitic peridotites from Internal Ligurides (Italy) and Mt. Maggiore (Corsica) (Rampone et al., 1997) generated by partial melting in the spinel stability field. The melting reaction Eqn. 21 is used in the calculation. Cpx from these abyssal peridotites and ophiolitic peridotites can be modeled as that in equilibrium with residual melt after extraction of 3–9% partial melt from a slightly depleted spinel lherzolite mantle (Fig. 2A). These results are in reasonably good agreement with previous estimates (Johnson et al., 1990; Rampone et al., 1997). We can also model the cpx as the product of congruent dynamic melting by combining Eqn. 22 with Eqn. 33 for  $C_f$  from Zou (1998). Results for incongruent and congruent dynamic melting of spinel peridotites are similar due to the fact that the calculated  $Q_0$  for IDM is similar to  $P_0$  for CDM in this case (Fig. 2). The difference between IDM and CDM lies in the parameters  $Q_0$  and  $P_0$ . The extent of difference in results for IDM and CDM depends on the specific reaction coefficients, trace elements, and subsystems (e.g., extracted melt, residual melt, the residual solid) in question and has to be evaluated on a case-by-case basis. According to Eqn. 15, it is clear that if the contribution to the melt from incongruent minerals is small ( $\sum_{\alpha} p_{\alpha}^i \rightarrow 0$ ), or if the partition coefficients of the product minerals are negligible ( $\sum_{\beta} t^i K^i \rightarrow 0$ ) and melt dominates the reaction

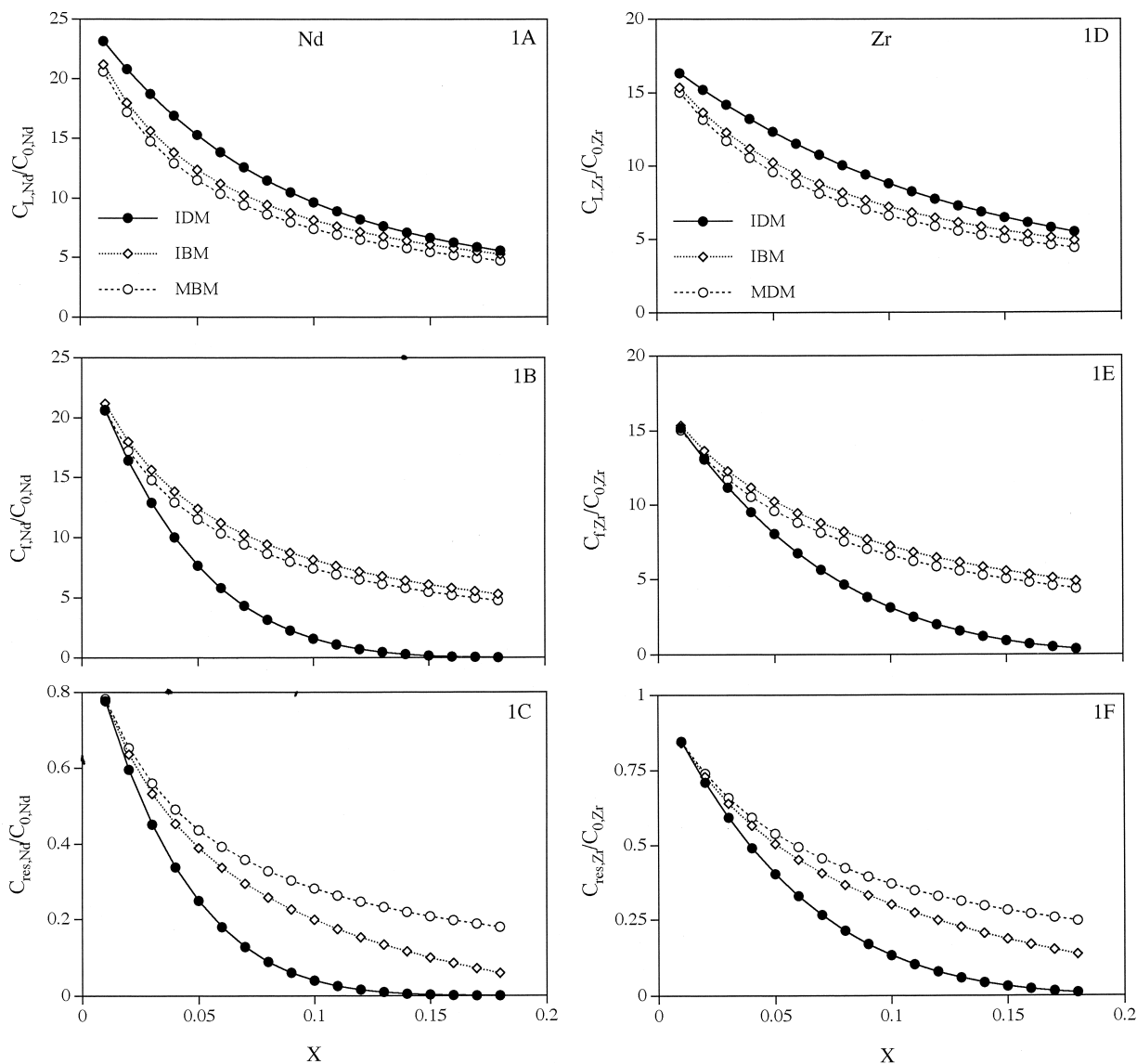


Fig. 1. Comparison of IDM with IBM for Nd (A)–(C) and Zr (D)–(F) during partial melting of a spinel peridotite at 10 kbar. Distribution coefficients are from Table 1 of Johnson et al. (1990). MBM represents modal batch melting and is also plotted here for comparison.

product ( $t' \rightarrow 1$ ), then  $Q_0 \rightarrow P_0$ . In this case, the results from IDM and CDM are similar.

The situation is very different for modeling residual cpx formed during partial melting in the garnet stability field. Figure 3A shows that, for the same degree of partial melting, IDM can produce more pronounced Ce depletion in cpx than CDM does. In addition, model REE patterns calculated with IDM develop more pronounced MREE humps at similar degrees of melting than those produced by CDM.

Thus, partial melting of garnet peridotite mantle can produce distinctive cpx patterns where there is depletion in both light REE (LREE) and heavy REE (HREE) with maximum values occurring in the middle REE (MREE) region (Fig. 3). In fact, clear MREE humps in the REE patterns of cpx have been reported from garnet lherzolite xenoliths in Nushan alkali basalts (Xu et al., 2000). Assuming an LREE enriched garnet

lherzolite source similar to that in Table 2 of Zou and Zindler (1996) or Table 3 of Zou et al. (2000), the Nushan cpx can be modeled by about 3% partial melting. Cpx with MREE humps has also been documented in spinel peridotite xenoliths from Hannuoba basalts (Song and Frey, 1989), which indicates a garnet peridotite source. This is consistent with their whole-rock REE patterns which exhibit a wide range in LREE abundance and relatively constant HREE abundance, as expected for whole-rock residues from different degrees of partial melting of a garnet peridotite source (e.g., Frey, 1984). Consequently, a significant MREE hump in the cpx REE pattern coupled with a smooth LREE-depleted whole-rock pattern strongly reflects extraction of melt when the peridotites were in the garnet stability field. The lack of garnet in this kind of spinel peridotites may indicate recrystallization to garnet-free assemblage at lower pressure conditions (Loubet et al., 1975). Late stage

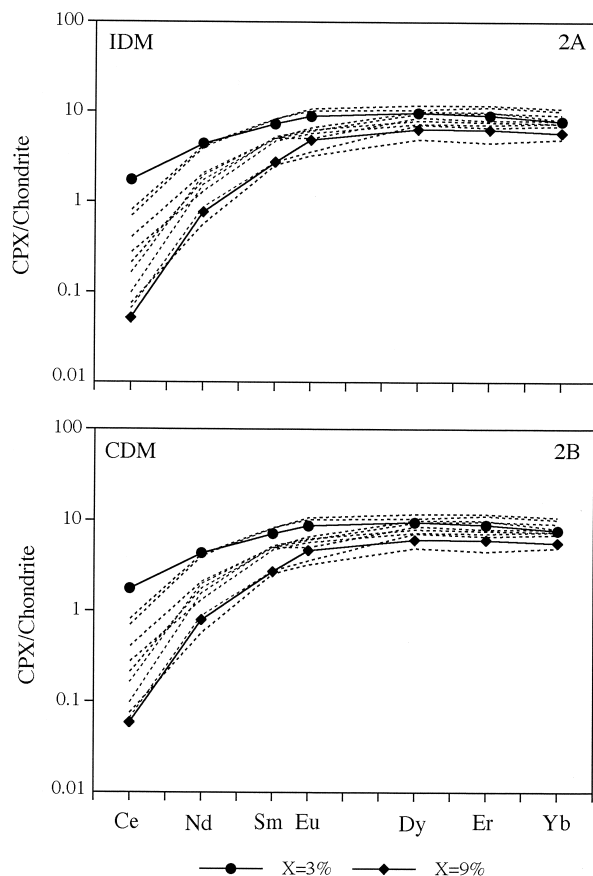
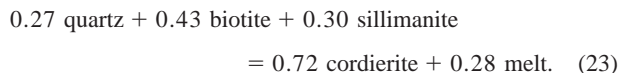


Fig. 2. Modeling of residual cpx in abyssal peridotites and ophiolitic peridotites by (A) IDM and (B) CDM in a spinel stability field. Partition coefficients, source mineral proportions and starting bulk compositions for spinel peridotites are from Table A1, A2, and A3 in Johnson et al. (1990). Melting reaction Eqn. 21 is used for IDM and the melting proportions in Table A2 in Johnson et al. (1990) for spinel peridotites are employed for CDM.

formation of spinel from garnet may increase the HREE content and thus reduce the extent of MREE hump in cpx; however, since the content of garnet will in general decrease quickly after the initial stage of melting, this effect is generally not very significant.

As for crustal melting, metapelitic rocks often melt incongruently. For example, melting of biotite–sillimanite–quartz gneisses produces not only melt but also cordierite (Zeck, 1970; Benito-Garcia and Lopez-Ruiz, 1992). Modeling of crustal melting often has to use incongruent melting equations. We take the following melting reactions (in mass units) in a biotite–sillimanite–quartz gneiss as an example (Zeck, 1970; Benito-Garcia and Lopez-Ruiz, 1992),



During incongruent dynamic melting, Th can change from an incompatible element into a compatible element since Th is compatible in cordierite (Fig. 4A). In contrast, Rb can change from a compatible element into an incompatible element because Rb is incompatible in cordierite [Fig. 4E]. In this extreme

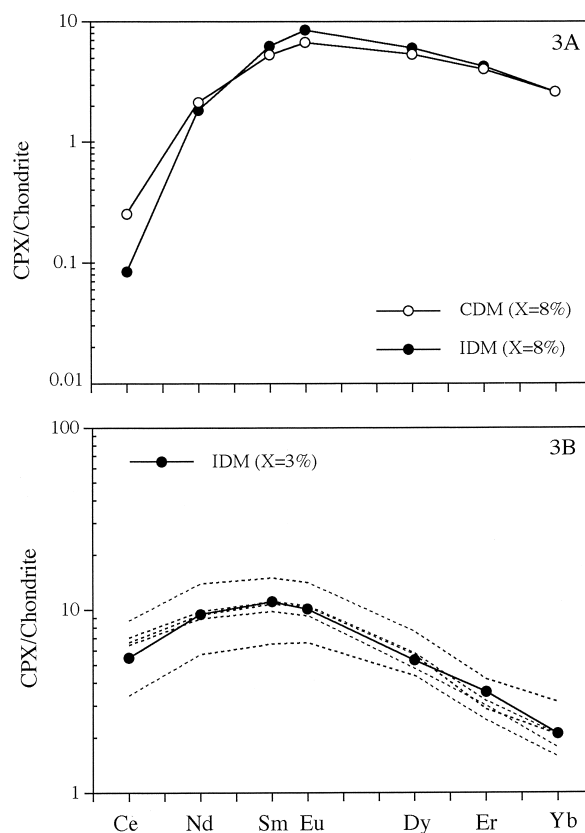


Fig. 3. (A) Comparison of modeling results for residual cpx produced in garnet stability field by IDM and CDM; (B) Modeling of residual cpx from mantle xenoliths from Nushan alkali basalts. Partition coefficients and source mineral proportions are from Table A1 and A2, respectively, in Johnson et al. (1990). Source starting compositions are estimated from Table 2 of Zou and Zindler (1996). Melting reaction in garnet stability field for IDM is  $0.06 \text{ ol} + 0.71 \text{ cpx} + 0.23 \text{ gt} = 0.52 \text{ melt} + 0.48 \text{ opx}$ . The high  $p_{\text{cpx}}$  set in Table A2 of Johnson et al. (1990) is used for melting proportions during CDM. Distribution coefficients are from Table 1 of Johnson et al. (1990).

case, there is a noticeable difference in the products of IDM and CDM (Fig. 4). This difference is particularly evident in the residual melt.

In summary, this paper presents a series of equations for the incongruent dynamic partial melting. Comparison of IDM with IBM indicates that the results of the two melting processes are significantly different, particularly for incompatible elements in the residual melt and the total residue. The IBM does not adequately account for the incompatible trace element characteristics of residual melts and total residues produced by IDM. Comparison of IDM with CDM shows that the difference in calculation results are noticeable when the fraction of the product minerals is significant and when the distribution coefficient of the produced mineral is sufficiently different from those of the reaction minerals. Applications of IDM equations to mantle residues suggest that a significant MREE hump in cpx and a smooth LREE-depleted whole-rock pattern strongly indicate a garnet peridotite source. More realistic but more complex models that take into accounts variations in partition coefficients,  $q^i$ , and melting reactions are given in the Appen-

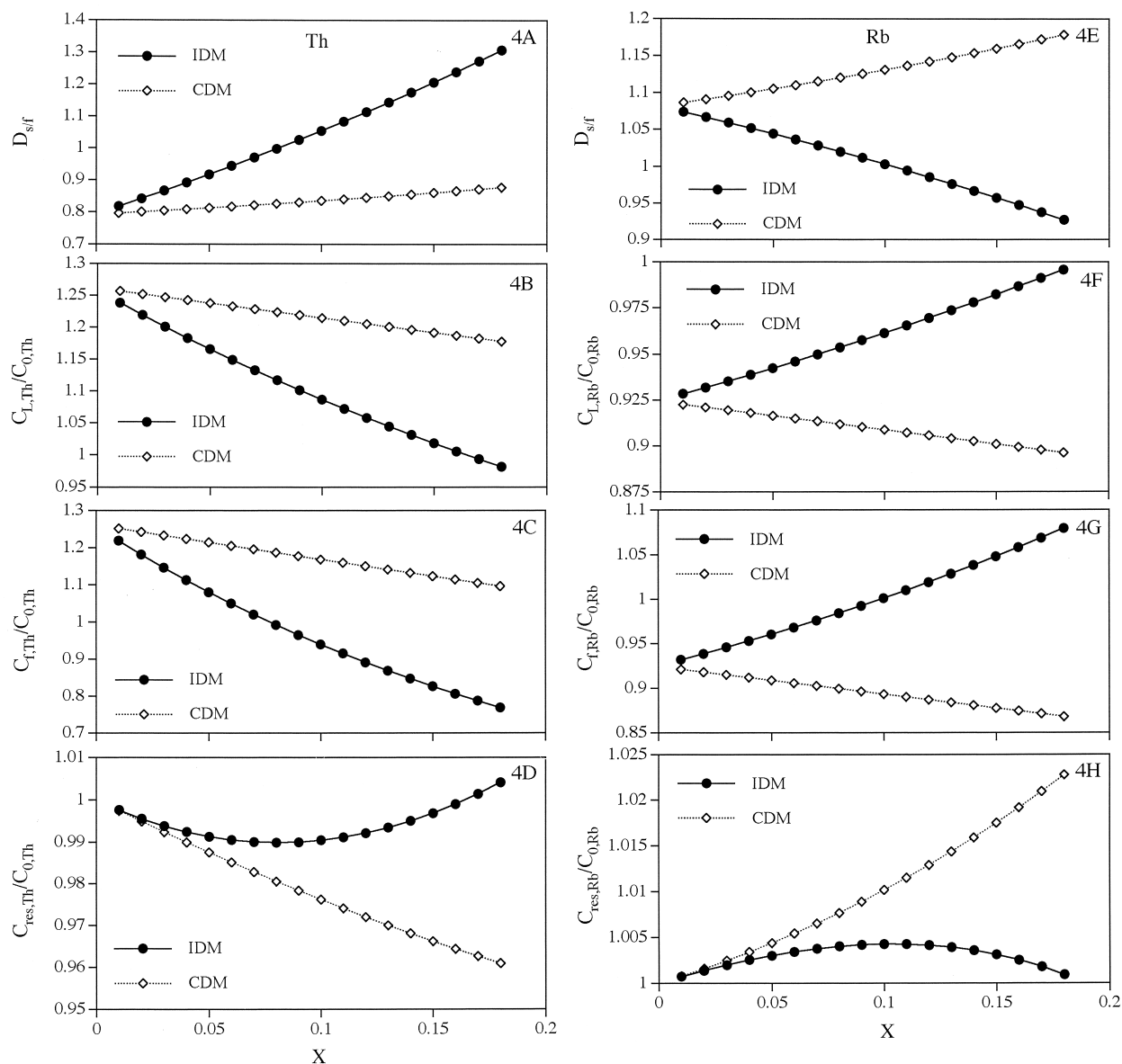


Fig. 4. Comparison of IDM and CDM for Th (A)–(D) and Rb (E)–(H) during partial melting of a biotite–sillimanite–quartz gneiss. Distribution coefficients are from Benito-Garcia and Lopez-Ruiz (1992). The source is assumed to have three minerals before melting reaction and the source mineral proportions are quartz: biotite: sillimanite = 0.175:0.525:0.30. The fraction of cordierite in reaction 23 is neglected for CDM.

dix. The IDM equations permit more realistic modeling of partial melting of both the mantle and the crust.

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## APPENDIX

### 1. The Change of Mineral Proportions During Nonmodal Melting

According to the definitions of  $S_\theta^i$ ,  $S_\alpha^i$ ,  $S_\beta^i$ ,  $L_\theta$ , and  $L_\alpha$  in Eqn. 3, the total mass of the converted minerals is  $(\sum_\theta S_\theta^i + \sum_\alpha S_\alpha^i)$ , and the total mass of the produced melt is  $(L_\theta + L_\alpha)$ . Therefore, the fractional contributions of phase  $i$  to the total mass of the converted minerals through congruent melting and incongruent melting are, respectively,

$$p_\theta^i = S_\theta^i / \left( \sum_\theta S_\theta^i + \sum_\alpha S_\alpha^i \right), \quad (\text{A1})$$

$$p_\alpha^i = S_\alpha^i / \left( \sum_\theta S_\theta^i + \sum_\alpha S_\alpha^i \right). \quad (\text{A2})$$

The mass fractions of incongruent minerals converted into melt or mineral  $i$  are, respectively,

$$t^i = L_\alpha / \left( \sum_\beta S_\beta^i + L_\alpha \right) = L_\alpha / \sum_\alpha S_\alpha^i, \quad (\text{A3})$$

$$t^i = S_\beta^i / \left( \sum_\beta S_\beta^i + L_\alpha \right) = S_\beta^i / \sum_\alpha S_\alpha^i. \quad (\text{A4})$$

Consequently, we have

$$\sum_\theta p_\theta^i + \sum_\alpha p_\alpha^i = 1, \quad (\text{A5})$$

$$t^i + \sum_\beta t^i = 1. \quad (\text{A6})$$

Using Eqns. A1, A2, and A4, we obtain the mass fraction of net converted mineral  $i$  relative to the total converted mass as

$$(S_\theta^i + S_\alpha^i - S_\beta^i) / \left( \sum_\theta S_\theta^i + \sum_\alpha S_\alpha^i \right) = p_\alpha^i + p_\theta^i - t^i \sum_\alpha p_\alpha^i. \quad (\text{A7})$$

Using Eqns. 4, A2, A4, and A6, we get the mass fraction of total melt relative to the total converted mass as

$$\begin{aligned} (L_\theta + L_\alpha) / \left( \sum_\theta S_\theta^i + \sum_\alpha S_\alpha^i \right) &= 1 - \sum_\beta S_\beta^i / \left( \sum_\theta S_\theta^i + \sum_\alpha S_\alpha^i \right) \\ &= 1 - (1 - t^i) \sum_\alpha p_\alpha^i. \end{aligned} \quad (\text{A8})$$

Dividing Eqn. A7 by Eqn. A8, we obtain the mass fraction of net converted mineral  $i$  relative to the total produced melt

$$q^i = \frac{S_\theta^i + S_\alpha^i - S_\beta^i}{L_\theta + L_\alpha} = \frac{p_\theta^i + p_\alpha^i - t^i \sum_\alpha p_\alpha^i}{1 - (1 - t^i) \sum_\alpha p_\alpha^i}, \quad (\text{A9})$$

which can be interpreted as the actual fractional contribution of mineral  $i$  to the total melt. Multiplying Eqn. A9 by Eqn. 5 for the definition of the degree of partial melting ( $F$ ), we obtain the mass fraction of net converted mass for mineral  $i$  relative to the initial source amount ( $M_0$ ) as

$$x_c^i = \frac{S_\theta^i + S_\alpha^i - S_\beta^i}{M_0} = Fq^i = \frac{p_\theta^i + p_\alpha^i - t^i \sum_\alpha p_\alpha^i}{1 - (1-t^i) \sum_\alpha p_\alpha^i} F. \quad (\text{A10})$$

Mass balance of mineral  $i$  requires

$$x_0^i = x^i(1-F) + x_c^i. \quad (\text{A11})$$

Substituting Eqn. A10 into Eqn. A11 results in Eqn. 10 derived by Benito-Garcia and Lopez-Ruiz (1992) from a different approach. The step-by-step approach presented here is based on clear definitions and may help to better understand the parameters and terms related to the change of mineral proportions in the residual solid during incongruent melting.

## 2. A Calculation Example for Incongruent Dynamic Melting

We use melting reaction Eqn. 21 as an example. The reaction coefficients in Eqn. 21 are reported in mass units. Note that if the reaction coefficients are reported as molar units, then we have to transform them into mass units using the formula weight of each mineral. Since there is no congruent mineral for this example, we have  $\sum_\theta S_\theta^i = 0$ . The total converted mass is  $\sum_\theta S_\theta^i + \sum_\alpha S_\alpha^i = 0.82 + 0.40 + 0.08 = 1.30$ .

According to Eqns. A1–A6, we have

$$p_\theta^{\text{cpX}} = p_\theta^{\text{opX}} = p_\theta^{\text{sp}} = p_\theta^{\text{ol}} = 0,$$

$$p_\alpha^{\text{cpX}} = 0.82/1.30 = 0.63, p_\alpha^{\text{opX}} = 0.40/1.30 = 0.31,$$

$$p_\alpha^{\text{sp}} = 0.08/1.30 = 0.06, p_\alpha^{\text{ol}} = 0, \sum_\alpha p_\alpha^i = 1,$$

$$t^i = 1.0/(1.0 + 0.3) = 0.77, t^{\text{ol}} = 0.3/(1.0 + 0.3) = 0.23,$$

$$i^{\text{cpX}} = i^{\text{opX}} = i^{\text{sp}} = 0.$$

The distribution coefficients for Nd are  $K^{\text{cpX}} = 0.19$ ,  $K^{\text{opX}} = 0.01$ ,  $K^{\text{sp}} = 0.0008$ , and  $K^{\text{ol}} = 0.002$  (Table A1 of Johnson et al., 1990). Therefore

$$\sum_\beta t^i K^i = t^{\text{ol}} K^{\text{ol}} = 0.23 \times 0.002 = 0.00046.$$

If we assume the initial source mineral proportions are  $x_0^{\text{cpX}} = 0.18$ ,  $x_0^{\text{opX}} = 0.27$ ,  $x_0^{\text{ol}} = 0.52$ ,  $x_0^{\text{sp}} = 0.03$  (Kinzler, 1997), then we have

$$D_0 = \sum x_0^i K^i = x_0^{\text{cpX}} K^{\text{cpX}} + x_0^{\text{opX}} K^{\text{opX}} + x_0^{\text{sp}} K^{\text{sp}} + x_0^{\text{ol}} K^{\text{ol}} = 0.038,$$

$$P_0 = \sum (p_\theta^i + p_\alpha^i) K^i = p_\alpha^{\text{cpX}} K^{\text{cpX}} + p_\alpha^{\text{opX}} K^{\text{opX}} + p_\alpha^{\text{sp}} K^{\text{sp}} = 0.123.$$

Since  $\sum_\alpha p_\alpha^i = 1$  and only olivine is produced for this example, Eqn. 15 can be reduced to

$$Q_0 = (P_0 - t^{\text{ol}} K^{\text{ol}})/t^i = 0.159.$$

Note that even for this simple example without congruent minerals, we still can *not* calculate  $Q_0$  according to the following expression

$$Q_0 = P - t^{\text{ol}} K^{\text{ol}} = p^{\text{cpX}} K^{\text{cpX}} + p^{\text{opX}} K^{\text{opX}} + p^{\text{sp}} K^{\text{sp}} - t^{\text{ol}} K^{\text{ol}}$$

Substituting the parameters  $D_0$ ,  $P_0$ , and  $Q_0$  into Eqns. 16, 17, and 19, and assuming  $\Phi = 0.001$ , we can obtain Nd concentrations as a function of  $X$  [Figs. 1(A)–1(C)]. This example shows step-by-step calculation, and one can easily set up a spreadsheet to quickly calculate the results and to make figures.

## 3. IDM with Changing Distribution Coefficients

We may assume linear variations of distribution coefficients

$$K^i = K_0^i + aF. \quad (\text{A12})$$

Combining Eqn. A12 with Eqns. 7, 9, 10a, and 13, we have the effective distribution coefficients

$$D_{\text{eff}} = \frac{1}{1-X} (UX^2 + VX + W), \quad (\text{A13a})$$

where

$$U = -\left(\sum a^i q^i\right)(1-\Phi)^2, \quad (\text{A13b})$$

$$V = -\Phi - (Q_0 - \sum a^i x_0^i)(1-\Phi) - 2\Phi(1-\Phi)\left(\sum a^i q^i\right), \quad (\text{A13c})$$

and

$$W = \Phi + D_0 - \Phi(Q_0 - \sum a^i x_0^i) - \left(\sum a^i q^i\right)\Phi^2. \quad (\text{A13d})$$

$q^i$  and  $Q_0$  are given by Eqns. 10b and 15, respectively. And the governing Eqn. 8 becomes

$$\frac{d(\overline{XC}_L)}{C_0 - \overline{XC}_L} = \frac{dX}{UX^2 + VX + W}. \quad (\text{A14})$$

When, all  $a^i = 0$ , in other words,  $U = 0$ , then according to Eqns. A13c and A13d, we obtain  $V = -[Q_0 + \Phi(1 - Q_0)]$  and  $W = D_0 + \Phi(1 - Q_0)$ . Therefore, Eqn. A14 reduces to Eqn. 14 in the text.

When  $U \neq 0$ , the solutions to Eqn. A14 have the following three cases. If  $\Delta = V^2 - 4UW > 0$ , then

$$\overline{C}_L = \frac{C_0}{X} \left\{ 1 - \left| \frac{(2UX + V + h)(V - h)}{(2UX + V - h)(V + h)} \right|^{1/h} \right\}, \quad (\text{A15a})$$

$$C_f = \frac{d(\overline{XC}_L)}{dX} = C_0 \frac{V - h}{V + h} \frac{4U}{(2UX + V - h)^2} \left| \frac{(2UX + V + h)(V - h)}{(2UX + V - h)(V + h)} \right|^{(1/h)-1}, \quad (\text{A15b})$$

where  $h = \sqrt{V^2 - 4UW}$ ; if  $\Delta = 0$ , then

$$\overline{C}_L = \frac{C_0}{X} \left[ 1 - \exp\left(\frac{2}{2UX + V} - \frac{2}{V}\right) \right], \quad (\text{A16a})$$

$$C_f = \frac{4UC_0}{(2UX + V)^2} \exp\left(\frac{2}{2UX + V} - \frac{2}{V}\right) \quad (\text{A16b})$$

and if  $\Delta < 0$ , then

$$\overline{C}_L = \frac{C_0}{X} \left\{ 1 - \exp\left[\frac{2}{k} \left( \arctan \frac{V}{k} - \arctan \frac{2UX + V}{k} \right) \right] \right\}, \quad (\text{A17a})$$

$$C_f = \frac{4UC_0}{k^2} \frac{1}{1 + \left(\frac{2UX + V}{k}\right)^2} \exp\left[\frac{2}{k} \left( \arctan \frac{V}{k} - \arctan \frac{2UX + V}{k} \right) \right], \quad (\text{A17b})$$

where  $k = \sqrt{4UW - V^2}$ .

## 4. IDM with Changing Distribution Coefficients and Changing $q^i$

If  $q^i$  is also a function of  $F$ , then Eqn. A11 for mass conservation of phase  $i$  should be replaced by

$$x^i(1-F) = x_0^i - \int_0^F q^i dF. \quad (\text{A18})$$

We may assume linear variations in  $q^i$  during nonmodal melting



$$q^i = q_0^i + b^i F, \quad (\text{A19})$$

where  $b^i = (q^i(F_m) - q_0^i)/F_m$ ,  $F_m$  is the maximum degree of melting when one of the phases melt completely, and  $q^i(F_m)$  is the net fractional contribution to the melt when the degree of partial melting is  $F_m$ . Substituting Eqn. A19 into Eqn. A18, we have

$$x^i = \frac{x_0^i - Fq_0^i - 0.5b^i F^2}{1 - F}. \quad (\text{A20})$$

A combination of Eqn. A20 with Eqns. 9, 13, and A12 gives us

$$D_{sjf} = \sum \frac{x_0^i - q_0^i [\Phi + (1 - \Phi)X] - 0.5b^i [\Phi + (1 - \Phi)X]^2}{1 - [\Phi + (1 - \Phi)X]} \{K_0^i + a^i [\Phi + (1 - \Phi)X]\}. \quad (\text{A21})$$

According to Eqn. 7, the effective partition coefficient is

$$D_{\text{eff}} = \frac{1}{1 - X} (A_0 X^3 + A_1 X^2 + A_2 X + A_3), \quad (\text{A22a})$$

where

$$A_0 = -(\sum 0.5a^i b^i)(1 - \Phi)^3, \quad (\text{A22b})$$

$$A_1 = -\sum [a^i(q_0^i + b^i\Phi)](1 - \Phi)^2 - \sum [0.5b^i(K_0^i + a^i\Phi)](1 - \Phi)^2, \quad (\text{A22c})$$

$$A_2 = -\Phi + \sum [a^i(x_0^i - q_0^i\Phi - 0.5b^i\Phi^2)](1 - \Phi) - \sum [(q_0^i + b^i\Phi)(K_0^i + a^i\Phi)](1 - \Phi), \quad (\text{A22d})$$

$$A_3 = \Phi + \sum (K_0^i + a^i\Phi)(x_0^i - q_0^i\Phi - 0.5b^i\Phi^2). \quad (\text{A22e})$$

And the governing differential equation 8 is therefore

$$\frac{d(\overline{C}_L X)}{C_0 - \overline{C}_L X} = \frac{dX}{A_0 X^3 + A_1 X^2 + A_2 X + A_3}. \quad (\text{A23})$$

When all  $b^i = 0$ , then  $A_0 = 0$ , and  $A_1$ ,  $A_2$ , and  $A_3$  reduce to  $U$ ,  $V$ , and  $W$ , respectively, and Eqn. A23 collapses to Eqn. A14. When  $A_0 \neq 0$ , there are three cases and the solutions to Eqn. A23 depend on the discriminant of the cubic polynomial in the denominator of the right-hand side of Eqn. A23,

$$\Delta = A_0^2 A_3^2 - 6A_0 A_1 A_2 A_3 + 4A_0 A_2^3 + 4A_1^3 A_3 - 3A_1^2 A_2^2. \quad (\text{A24})$$

(1) If  $\Delta > 0$ , the cubic polynomial  $A_0 X^3 + A_1 X^2 + A_2 X + A_3$  has one real root  $r_1$  and two complex conjugate roots  $r_2$  and  $r_3$ , and Eqn. A23 can be rewritten as

$$\frac{d(\overline{C}_L X)}{C_0 - \overline{C}_L X} = u \frac{dX}{X - r_1} + v \frac{(2X + B) dX}{X^2 + BX + \eta} + w \frac{dX}{X^2 + BX + \eta}, \quad (\text{A25})$$

where  $X^2 + BX + \eta = (X - r_2)(X - r_3)$ , and  $r_1$ ,  $r_2$ , and  $r_3$  can be obtained using the Cardan (or Tartaglia's) method. The solution to Eqn. A25 is

$$\overline{C}_L = \frac{C_0}{X} \left( 1 - \left| \frac{r_1}{X - r_1} \right|^u \left| \frac{\eta}{X^2 + BX + \eta} \right|^v \exp \left[ \frac{2w}{\lambda} \left( \arctan \frac{B}{\lambda} - \arctan \frac{2X + B}{\lambda} \right) \right] \right), \quad (\text{A26})$$

where

$$\lambda = \sqrt{4\eta - B^2}.$$

(2) If  $\Delta = 0$ , the cubic polynomial has one single real root  $r_1$  and a double real root  $r_2$ , then

$$\frac{d(\overline{C}_L X)}{C_0 - \overline{C}_L X} = u \frac{dX}{X - r_1} + v \frac{dX}{X - r_2} + w \frac{dX}{(X - r_2)^2}, \quad (\text{A27})$$

where  $r_1$  and  $r_2$  can be obtained using the Cardan's method. The solution to Eqn. A27 is

$$\overline{C}_L = \frac{C_0}{X} \left( 1 - \left| \frac{r_1}{X - r_1} \right|^u \left| \frac{r_2}{X - r_2} \right|^v \exp \left[ \frac{wX}{r_2(X - r_2)} \right] \right). \quad (\text{A28})$$

(3) If  $\Delta < 0$ , the cubic polynomial has three different real roots  $r_1$ ,  $r_2$ , and  $r_3$ , then

$$\frac{d(\overline{C}_L X)}{C_0 - \overline{C}_L X} = u \frac{dX}{X - r_1} + v \frac{dX}{X - r_2} + w \frac{dX}{X - r_3}, \quad (\text{A29})$$

where  $r_1$ ,  $r_2$ , and  $r_3$  can be obtained using the trigonometrical method for the cubic polynomial. The solution to Eqn. A29 is

$$\overline{C}_L = \frac{C_0}{X} \left( 1 - \left| \frac{r_1}{X - r_1} \right|^u \left| \frac{r_2}{X - r_2} \right|^v \left| \frac{r_3}{X - r_3} \right|^w \right). \quad (\text{A30})$$

## 5. IDM with Discontinuous Variations of Parameters

All the above IDM equations are suitable for continuous variations of parameters. If there are discontinuous changes in melting parameters, such as the consumption of a mineral, we have to combine the stepwise approach with the above IDM equations even though the stepwise approach is not the most elegant and definitive method.

The keys in the derivations for IDM with discontinuous changes are (1) to treat the residual melt and residual solid as a whole residue and (2) to use total residue at the end of a previous interval as the initial condition for the very next interval. In this case, we use the fraction of the extracted melt relative to initial source ( $X$ ) instead of the partial melting degree ( $F$ ) for simple derivations. An important concept is the fraction of the extracted melt in an intermediate interval  $j$  relative to the total residue at the end of its very previous interval  $j - 1$ . At the end of interval  $j$ , the fraction of the extracted melt in this interval relative to the original source is  $(X_j - X_{j-1})$ , and the total residue relative to the original source at the end of interval  $j - 1$  is  $(1 - X_{j-1})$ . Therefore, the fraction of extracted melt for interval  $j$  relative to the total residue at the end of interval  $j - 1$  is defined as

$$Z_j = \frac{X_j - X_{j-1}}{1 - X_{j-1}}. \quad (\text{A31})$$

When the total number of melting intervals is  $n$ , the concentration in the total extracted melt can be expressed as

$$\begin{aligned} \frac{\overline{C}_L}{C_0} &= \sum_{j=1}^n \frac{\overline{C}_L^j X_j - X_{j-1}}{C_0 X} \\ &= \frac{\overline{C}_L^1 X_1}{C_0 X} + \frac{\overline{C}_L^2 X_2 - X_1}{C_0 X} \dots + \frac{\overline{C}_L^j X_j - X_{j-1}}{C_0 X} + \dots \\ &\quad + \frac{\overline{C}_L^n X_n - X_{n-1}}{C_0 X}. \end{aligned} \quad (\text{A32})$$

Note that  $X_0 = 0$  and  $X_n = X$ .

The mass balance in any interval  $j$  requires

$$C_{\text{res}}^{j-1}(1 - X_{j-1}) = C_{\text{res}}^j(1 - X_j) + \overline{C}_L^j(X_j - X_{j-1}) \quad (\text{A33})$$

which we can rewrite as

$$C_{\text{res}}^j = \frac{C_{\text{res}}^{j-1}(1 - X_{j-1}) - \overline{C}_L^j(X_j - X_{j-1})}{1 - X_j}. \quad (\text{A34})$$

Note that  $C_{\text{res}}^0 = C_0$ . As an example, we show the explicit equations of the extracted melt for IDM with constant  $K^i$  and  $p^i$  for two melting intervals. In this case,  $n = 2$ ,  $X_0 = 0$ , and  $X_2 = X$ , then according to Eqns. A31, A32, and A34, we have

$$Z_1 = X_1, \quad (\text{A35})$$

$$Z_2 = \frac{X - X_1}{1 - X_1}, \quad (\text{A36})$$

$$\frac{\overline{C}_L}{C_0} = \frac{\overline{C}_L^1 X_1}{C_0 X} + \frac{\overline{C}_L^2 X - X_1}{C_0 X}, \quad (\text{A37})$$

$$C_{\text{res}}^1 = \frac{C_0 - \overline{C}_L^1 X_1}{1 - X_1}, \quad (\text{A38})$$

$$C_{\text{res}}^2 = \frac{C_{\text{res}}^1 (1 - X_1) - \overline{C}_L^2 (X_2 - X_1)}{1 - X_2}. \quad (\text{A39})$$

According to Eqn. 16, the concentration for the first interval in the extracted melt is

$$\overline{C}_L^1 = \frac{C_0}{X_1} \left\{ 1 - \left[ 1 - \frac{Q_1 + \Phi_1(1 - Q_1)}{D_0 + \Phi_1(1 - Q_1)} X_1 \right]^{1/[\Phi_1 + (1 - \Phi_1)Q_1]} \right\}. \quad (\text{A40})$$

The initial source concentration for the second interval ( $C_{\text{res}}^1$ ) is the concentration of the total residue at the end of the first interval.  $Z_2$  is the

fraction of the extracted melt for the second interval relative to the total residue at the end of the first interval. We can still use Eqn. 16 one more time to calculate the concentration in the extracted melt for the second interval,

$$\overline{C}_L^2 = \frac{C_{\text{res}}^1}{Z_2} \left\{ 1 - \left[ 1 - \frac{Q_2 + \Phi_2(1 - Q_2)}{D_1 + \Phi_2(1 - Q_2)} Z_2 \right]^{1/[\Phi_2 + (1 - \Phi_2)Q_2]} \right\}, \quad (\text{A41})$$

where  $Z_2$  and  $C_{\text{res}}^1$  are given by Eqns. A36 and A38, respectively.

The concentration in the total extracted melt is therefore

$$\frac{\overline{C}_L}{C_0} = \frac{\overline{C}_L^1 X_1}{C_0 X} + \frac{\overline{C}_L^2 X - X_1}{C_0 X} \quad (\text{A42})$$

$$= \frac{1}{X} \left\{ 1 - \left( 1 - \frac{\overline{C}_L^1}{C_0} X_1 \right) \left( 1 - \frac{Q_2 + \Phi_2(1 - Q_2)}{D_1 + \Phi_2(1 - Q_2)} Z_2 \right)^{1/[\Phi_2 + (1 - \Phi_2)Q_2]} \right\}.$$

The equations with more than two intervals, for example, the polybaric partial melting, can be obtained analogously by using Eqns. A31, A32, and A34 and the equations for IDM.