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A modified iterative sandwich method for determination of near-solidus partial melt compositions. I. Theoretical considerations

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Abstract The sandwich technique for determining the composition of partial melts in equilibrium with mantle lithologies may be a particularly powerful method for determining melt compositions at the onset of melting if the method is applied iteratively. However, conventional iterative sandwich experiments, in which the liquid from a preceding experiment is used as the ''meat'' of the sandwich in the following experiment, may require many iterations before the melts produced can be directly relatable to the melting relations of the target bulk rock composition. A modified iterative sandwich experimental (MISE) technique is proposed that may circumvent many of the problems of more conventional techniques. Consideration of experimental uncertainties, including both random and systematic errors in determination of partial melt compositions as well as the influence of errors in estimates of the solidus temperature of the rock of interest, suggests that the MISE technique may produce robust results even when melt composition errors are significant and that errors in estimation of the solidus location are detectable and therefore avoidable.

Keywords Batch melting · Experimental petrology · Iterative sandwich experiments · Mantle peridotite · Partial melting

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Introduction

A long standing goal of experimental petrology is documentation of the compositions of small-degree melts of mantle lithologies. Simple experimental petrologic methods are well-suited for determination of large-degree partial melts of rocks, as these form large melt pools that are readily analyzed by microbeam methods. However, many natural environments produce small degree melts on the order of a few percent. For example, geochemical constraints suggest that melting in the source regions of many oceanic island basalts may be <5% (Clague and Frey 1982; Chauvel et al. 1992; Thomas et al. 1999; Frey et al. 2000). Partial melting in the deepest portions of basalt source regions induced by H_2O or CO_2 may produce even smaller melt fractions (Eggler 1976; Plank and Langmuir 1992; Hirth and Kohlstedt 1996; Karato and Jung 1998; Presnall et al. 2002; Asimow and Langmuir 2003; Dasgupta and Hirschmann 2006).

Determining the compositions of small degree partial melts (<10%) is a considerable experimental problem because of the difficulty in isolating pools of quenched melt that are sufficiently large to analyze by microbeam methods and that are not affected by quench crystallization. Several methods have been developed to meet this challenge, including sandwich experiments, melt traps, thermal segregation, and microdikes (Stolper 1980; Takahashi and

Kushiro 1983; Hirose and Kushiro 1993; Baker and Stolper 1994; Zhang and Herzberg 1994; Walter 1998; Laporte et al. 2004). Each has advantages and pitfalls.

Among these methods, the most commonly employed may be sandwich experiments. In their simplest form, sandwich experiments consist of a layer of assumed melt composition (the ''meat'') surrounded by two thicker layers of a rock composition such as peridotite (the ''bread'') (Fig. 1). Over the course of the experiment, the melt composition approaches equilibrium with the minerals in the rock by diffusive exchange. The relatively large region of melt in the ''meat'' may quench to a homogeneous domain suitable for microanalysis at the end of the experiment.

There are two principal pitfalls with the simple sandwich experiment methodology. First, the melt layer may not equilibrate completely with the minerals in the rock layer. This may occur either because the length scales for equilibration across the experimental charge are too large relative to the characteristic diffusion distances for the temperatures and durations of the experiment or because reaction between the ''meat'' and the ''bread'' may produce a skarn of reaction minerals that impedes complete exchange between the two domains. Second, addition of a significant amount of melt shifts the bulk composition of the charge, potentially producing mineral and melt compositions that are different from those expected during partial fusion of a natural rock and making it difficult or impossible to relate the resulting phase compositions to a specific fraction of melting of a particular magma source region.

The first of these pitfalls can be addressed by performing sandwich experiments iteratively, with the melt composition from each experiment being used as the initial ''meat'' of each succeeding experiment. This method has been employed for carbonated lherzolite (Wallace and Green 1988; Thibault 1992), as well as for nominally volatile-free spinel peridotite (Robinson et al. 1998). The iterative method does not require complete equilibration between the bread and the meat at each experimental step. So long as the two approach equilibrium during each iteration, a sufficient number of iterations will eventually produce an equilibrium melt. Also, the iterative approach partially addresses the second pitfall, because the melt composition eventually reaches the composition expected for the unadulterated source rock composition at its solidus (i.e., at a melt fraction, F, of zero). This is because repeated use of the same ''bread'' composition eventually buffers the melt composition to that in equilibrium with the unmelted minerals of the source rock.

Here we propose a novel method for determining near-solidus compositions of partial melts of rocks in magma source regions. Our procedure is based on the methodology of the iterative sandwich experiment, and is therefore a modified iterative sandwich experiment (MISE). Compared to the conventional iterative sandwich experiment, MISE can be shown to approach equilibration in a smaller number of experiments. Additionally, the MISE technique can be adapted to produce phase compositions that are unambiguously representative of finite melt fractions above the solidus. In this paper, we develop and discuss the methodology of MISE. In a companion contribution (Dasgupta and Hirschmann 2007), we apply the MISE technique to near-solidus partial melting of carbonated peridotite at 6.6 GPa. We begin by considering in greater detail the methodology and expected consequences of conventional iterative sandwich experimental (CISE) technique.

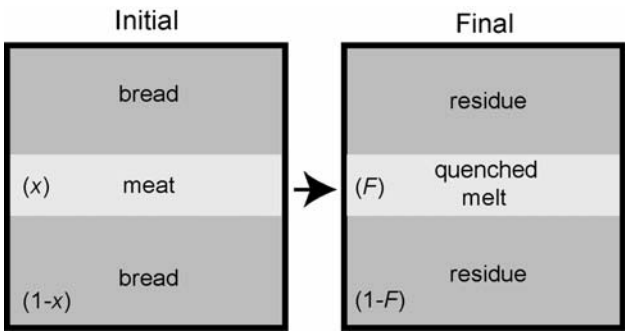


Fig. 1 Basic illustration of the sandwich technique. An initial melt composition (''meat'') is chosen and equilibrated with the bulk rock composition of interest (''bread''). The initial fractions of ''meat'' and ''bread'' are x and (1–x), respectively. Assuming that the ''meat'' equilibrates perfectly with the ''bread'' at the P and T of the experiment, the result will equilibrium between the melt and residual minerals, but it will not be directly relatable to the melting relations of pure ''bread'' because the bulk composition of the system has been modified by the ''meat''

Conventional iterative sandwich experiments (CISE)

We wish to determine the near-solidus partial melt composition of a particular rock such as peridotite or pyroxenite, for which the concentrations of elements i are given by C_i^0. A glossary of symbols and variables used in this paper is provided in Table 1. To do this, we execute a series of experiments in which a layer of silicate or carbonate melt (''meat'') is equilibrated with surrounding layers (''bread'') consisting of the rock composition of interest (Fig. 2). In the following text, the ''bread'' composition is also termed the ''target'' composition, as it has the bulk composition of the rock for which we wish to determine the near-solidus equilibrium partial melt. Unless, otherwise stated, the near-solidus melt is the incipient partial melt that would be produced at the solidus of the target composition at F equal to zero.

Table 1 Glossary of symbols used for variables and constants

n	Experimental iteration
x	Proportion of ''meat'' inserted into the experimental charge prior to each experiment.
F	Proportion of melt at the end of each experiment.
i	An oxide (e.g., SiO_2, TiO_2, Na_2O, etc.)
C_i^0	Concentration of the ith oxide in the ''bread'' inserted into the experimental charge and concentration of the ith oxide in the target composition for which the melting relations are sought
$C_i^{m,n}$	Concentration of the ith oxide in the ''meat'' inserted into the experimental charge prior to the nth experimental iteration.
$C_i^{T,n}$	Concentration of the ith oxide in the bulk composition of the experimental charge in the nth experimental iteration.
$C_i^{L,n}$	Concentration of the ith oxide in the liquid resulting from the nth experimental iteration.
$C_i^{R,n}$	Concentration of the ith oxide in the aggregate solids resulting from the nth experimental iteration.
$\overline{D}_i^n$	Bulk residue/liquid partition coefficient of the ith oxide resulting from the nth experimental iteration.
$T^0_{solidus}$	The solidus temperature of the target composition for which the melting relations are sought, at the pressure of the experiments.
F^n	The melt fraction resulting from the experiment during the nth iteration
F^0	The melt fraction that prevail at equilibrium for the unadulterated target composition at the temperature and pressure of the experimental iteration.
$\overline{D}_i^{estimated}$	The value of $\overline{D}_i^n$ that is determined from measurements of the liquid and mineral compositions resulting from the nth experimental iteration.
$\overline{D}_i^{true}$	The value of $\overline{D}_i^n$ that would prevail in the nth experimental iteration if perfect equilibrium were achieved and if there were no analytical errors.
r	A random number between –1 and 1 that is used to parameterize random uncertainties 2in determination of $\overline{D}_i^n$

At each experimental step, n, the initial fraction of ''meat'' is given by x and so the initial fraction of ''bread'' is $(1–x)$. The initial concentration of any element in the meat is given by $C_i^{m,n}$ and the concentration in the bulk experiment is given by

$$C_i^{T,n} = xC_i^{m,n} + (1-x)C_i^0. \quad (1)$$

Note that the composition of the ''meat'', $C_i^{m,n}$, and the bulk experiment, $C_i^{T,n}$, change with each iteration, but the composition of the ''bread'' C_i^0 is always that of the target rock composition for which the melting relations are being determined. An experiment is conducted at a given temperature and pressure that is known by independent means to be characteristic of the solidus of the target composition, $T^0_{solidus}$, i.e., that of the ''bread''.

Assuming that the ''bread'' and ''meat'' equilibrate over the course of the experiment, the resulting concentration of each element in the melt is given by the batch melting equation

$$C_i^{L,n} = \frac{C_i^{T,n}}{(F^n - F^n\overline{D}_i^n + \overline{D}_i^n)}, \quad (2)$$

where F^n and $\overline{D}_i^n$ are the melt fraction and the applicable bulk rock/melt partition coefficient in the resulting experiment, respectively. Note that F^n refers to the melt fraction in the actual experiment during the nth iteration, whereas F^0 refers to the melt fraction that would prevail at equilibrium for the unadulterated target composition under these conditions (i.e., in the present case, $F^0 = 0$). The remaining minerals constitute the residue of the experiment, which have an aggregate composition given by

$$C_i^{R,n} = \frac{C_i^{T,n} - FC_i^{L,n}}{(1-F^n)}. \quad (3)$$

The bulk rock/melt partition coefficient, which is given by

$$\overline{D}_i^n = \frac{C_i^{R,n}}{C_i^{L,n}}, \quad (4)$$

may be determined empirically from the experiment by measuring concentrations of the elements in quenched melt and the minerals in the residue, as well as the relative proportions of the phases, which may be determined by a suitable method such as mass balance or image analysis.

For simplicity, we assume that F^n is equal to x, meaning that it is the same as the initial proportion of ''meat'' and that it is the same for each experiment. We further assume that the value of $\overline{D}_i^n$ can be determined precisely and that it does not change in subsequent iterations, i.e. that $\overline{D}_i^1 = \overline{D}_i^2 = \overline{D}_i$. These assumptions may not apply in real

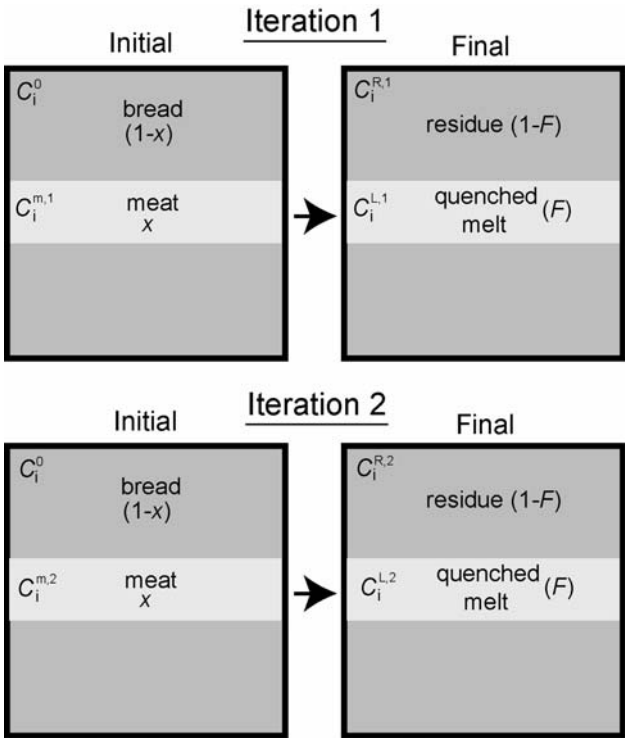


Fig. 2 The iterative sandwich technique to determine the near-solidus ($F = 0$) partial melt composition of a target rock composition. An initial sandwich iteration ($n = 1$) is performed using the target composition as the ''bread''. Concentrations of each element, i, in the bread are given by C_i^0 and elemental concentrations in the ''meat'' in the initial experiment, $C_i^{m,1}$, are arbitrary, though they may be selected to be a reasonable guess as to the near-solidus melt composition. In successive iterations ($n = 2,3,4...$), the composition of the ''meat'', $C_i^{m,n}$, is determined from the results of the preceding iteration. In conventional iterative sandwich experiments (CISE), $C_i^{m,n}$ is the same as the melt composition from the previous experiment, $C_i^{L,n-1}$. In modified iterative sandwich experimental (*MISE*), $C_i^{m,n}$ are determined from $C_i^0/\overline{D}_i$, where values of $\overline{D}_i$ are the bulk mineral/melt partition coefficients determined in the preceding iteration

experiments and below we will assess the impact of more realistic assumptions on experimental outcomes. For the moment, it is sufficient to note that achieving the desired result will be most straightforward and take the fewest number of iterations if these assumptions are applicable.

Each subsequent experiment is performed exactly as the previous one, except that the composition of the ''meat'', $C_i^{m,n}$ is taken from the liquid produced by the previous iteration, $C_i^{L,n-1}$. If this process is repeated indefinitely, the concentration of any element will approach $C_i^0/\overline{D}_i$. In other words, the equilibrium liquid composition depends only on the concentration of the element in the ''bread'' in the sandwich and the bulk mineral/melt partition coefficient. This is illustrated in Fig. 3, in which initial bread compositions are assumed to have either zero or 1.5 times the value of $C_i^0/\overline{D}_i$. Two different bread/meat proportions are considered, one with 15% ''meat'' (Fig. 3a) and the other with 30% ''meat'' (Fig. 3b). The concentration of all elements in the liquid, $C_i^{L,n}$ irrespective of their applicable value of $\overline{D}_i$, converge to $C_i^0/\overline{D}_i$, and therefore values of $C_i^{L,n}/\left(C_i^0/\overline{D}_i\right)$ converge to unity. Note that $C_i^0/\overline{D}_i$ is the concentration of a liquid produced at the solidus ($F^0 = 0$) of the ''bread'' bulk composition, which demonstrates the assertion in the Introduction: The iterative sandwich method converges to the composition of the zero melt fraction liquid composition of the lithology of interest.

Liquids in CISE experiments approach $C_i^0/\overline{D}_i$ because repeated introduction of the same solid ''bread'' forces the liquids to equilibrate with an effectively infinite reservoir of the target composition at its solidus. Therefore, a second feature of convergence to the equilibrium phase compositions at the solidus of a rock is reflected in the mineral compositions. If, at the end of an experiment, the liquid present has the true equilibrium composition that would be generated by infinitesimal partial melting of the ''bread'', then the compositions of the coexisting minerals should be those present at the solidus of the ''bread'' bulk composition at that pressure. The latter can be determined independently from experiments on the unadulterated bread just below the solidus at the pressure of interest. Thus, monitoring the compositions of minerals resulting from iterative sandwich experiments provides an additional check on the success of the experimental method.

As illustrated in Fig. 3, the number of iterations for an element to converge to the concentration expected at the solidus of the ''bread'' depends on the proportion of ''meat'' added at each experiment (x) and on the bulk rock/liquid partition coefficient of the element. More rapid convergence for low values of x favor experiments performed with small proportions of ''meat'', but the proportions cannot be too small and still produce the desired large pools of analyzable melt that are unaffected by quench modification. A compromise must be sought between more rapid convergence and more easily analyzable melt pools.

An important problem with this method is that the number of iterations required to converge may be unmanageably large. Elements with bulk partition coefficients smaller than 0.1 can require ten or more iterations to reach a steady state (Fig. 3). Slower convergence for larger values of x and smaller values of $\overline{D}_i$ is expected because more of the element of interest is in the liquid, and reaction with greater proportions of ''bread'' is required to buffer the melt to equilibrium with the peridotitic mineral assemblage. In some cases, this may be of great importance to accurate characterization of near-solidus phase equilibria. For example, during partial melting of spinel lherzolite the bulk partition coefficient of Na_2O is ~0.03–0.04 (Baker and Stolper 1994; Robinson et al. 1998; Pickering and Johnston 2000; Schwab and Johnston 2001) and the Na_2O concentration in

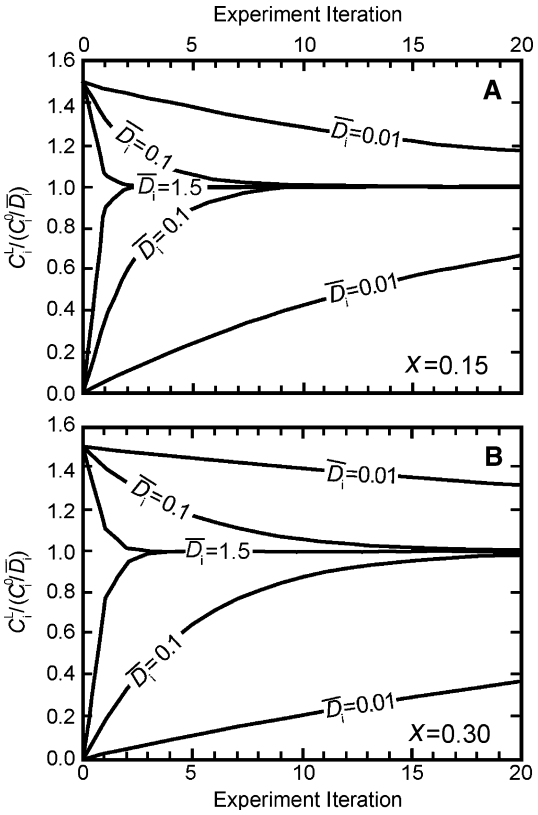


Fig. 3 Hypothetical composition of melt layer after each conventional iterative sandwich experiment (CISE). Concentrations of each element, *i*, in the liquid, $C_i^{L,n}$, after each iteration, *n*, are normalized to $C_i^0/\overline{D}_i$, the bulk composition divided by the partition coefficient for the element, which is the concentration expected at 0 % melting ($F^0 = 0$). Values of $C_i^{L,n}/\left(C_i^0/\overline{D}_i\right)$ converge to unity as *n* increases, showing that elemental concentrations in the liquid approach $C_i^0/\overline{D}_i$. However, the rate of convergence is slow for elements that are incompatible in the solid residue. **a, b** show simulations for CISE iterations in which the initial proportion of ''meat'' is 0.15 and 0.3, respectively. Larger values of *x* lead to slower convergence for incompatible elements

near-solidus melts has profound influence on other aspects of melt composition (Hirschmann et al. 1998, 1999).

Clearly the CISE technique is capable of producing liquids that share some of the compositional features of near-solidus liquids. However, we emphasize that the simulation in Fig. 3 applies only to the idealized assumptions that each iteration achieves perfect equilibration, that the melt fraction produced at each experiment and that the partition coefficient for each element remains constant between iterations. More realistic assumptions may inhibit the approach to equilibrium near-solidus liquid compositions.

Modified iterative sandwich experiments (MISE)

The slow convergence of CISE experiments (Fig. 3) can be overcome because the concentration of elements at convergence is predictable from values of C_i^0 and $\overline{D}_i$. Thus, an improved iterative procedure is to use the first experiment to determine provisional values of mineral/partition coefficient, $\overline{D}_i$, for major and minor elements of interest and then to estimate concentrations in the near-solidus liquid simply from $C_i^0/\overline{D}_i$. This relation derives from the batch melting equation (e.g., Eq. 2) when the melt fraction, *F*, is zero.

If perfect equilibrium were achieved in each experiment and if $\overline{D}_i$ did not vary between iterations, this MISE technique could produce the sought-after near-solidus melt from the second iteration, even for highly incompatible elements. However, an individual experiment may only approach equilibrium and in practice values of $\overline{D}_i$ determined in an initial sandwich experiment may not be characteristic of near-solidus partial melting of the unadulterated target lithology. Realistically, this means that more than two iterations will likely be required to constrain the actual near-solidus liquid composition.

Measured partition coefficients may differ between iterations owing to random analytical errors as well as owing to systematic biases. Systematic biases may arise owing to incomplete equilibration during an experiment or if the partition coefficient applicable to the sandwich experiment differs from that applicable to the partial melt of the unadulterated rock. This latter situation may occur for one of three reasons: (a) mineral/melt partition coefficients may vary with the composition of the liquid (Gaetani 2004; Schmidt et al. 2006), which may not be the same in the experiment and at the solidus of the target composition. (b) Mineral/melt partition coefficients may vary with mineral compositions (e.g., Wood and Blundy 1997), which also may not be the same. (c) Finally, reaction between ''bread'' and ''meat'' may alter the relative proportions of minerals in the residue and thereby influence the bulk partition coefficients.

Incomplete equilibration and shifts in partition coefficients between experiments should increase the number of iterations required to determine the composition of near-solidus partial melts. A key consideration, however, is that the magnitude of these systematic influences is proportional to the mismatch between the ''meat'' composition and the final composition characteristic of the near-solidus melt. As the mismatch between these compositions diminishes, the measured partition coefficients and the proportion of minerals in the residue approach those of the near-solidus condition. Also, the influence of imperfect equilibration diminishes as the initial mineral and melt compositions approach equilibrium. Thus, we expect that the influence of systematic impediments to be damped with successive iterations, and that the target composition can be determined with confidence in a relatively small number of iterations.

The influence of mineral mode on bulk partition coefficients may be significant if the mode of minerals at the

end of an experiment is significantly different from the mineral modes expected at the solidus of the target rock composition. For example, if the initial estimate of melt composition has CaO or Al_2O_3 concentrations much different from the equilibrium near-solidus melt compositions, reaction between the melt and the ''bread'' could increase or decrease the proportion of clinopyroxene or garnet in the residue. This problem can be minimized if the bulk $\overline{D}_i$'s used to calculate the ''meat'' composition for the next experiment are derived from the mode of minerals present at the solidus of the target rock composition, determined independently, rather than the mode of minerals present during each iterative experiment. As the ''meat'' composition approaches that of the target equilibrium melt composition, the differences in modes between experimental residues and the target rock just below its solidus become negligible.

The influence of imperfect determinations of partition coefficients on the MISE method can be investigated by calculating the results of MISE iterations but introducing random and systematic errors in $\overline{D}_i$'s. Note that systematic errors in $\overline{D}_i$'s also approximate the behavior of imperfect equilibrium. For example, if perfect equilibration should lead a particular element in the melt to diminish to a particular concentration, $C_i^{L,n}$, but at the end of an experimental step the element instead has a concentration $> C_i^{L,n}$, the resulting bulk $\overline{D}_i^n$ observed in that experiment is systematically lower than the equilibrium value.

In Fig. 4 we investigate three different cases of the influence of experimental imperfections on the MISE method: In case A, there are random errors of ±20% in the estimates of $\overline{D}_i$ s, as might be appropriate for a case where only analytical errors impede the method:

$$\overline{D}_i^{\text{estimated}} = \overline{D}_i^{\text{true}} + 0.2r\overline{D}_i^{\text{true}} \quad (5)$$

where r is a random number between –1 and 1. Cases B and C include random errors of up to ±20% and, respectively, systematic overestimates and underestimates of $\overline{D}$ s equal to 40% of the difference between the initial (meat) and equilibrium composition. In other words, the estimated bulk partition coefficient, $\overline{D}_i^{\text{estimated}}$, will be greater or less than the true equilibrium partition coefficient, $\overline{D}_i^{\text{true}}$, by 40% if the initial ''meat'' composition is off by 100%:

$$\overline{D}_i^{\text{estimated}} = \overline{D}_i^{\text{true}} + 0.4\overline{D}_i^{\text{true}} \frac{\left(C_i^{\text{m,n}} - C_i^{L,n}\right)}{C_i^{L,n}} + 0.2r\overline{D}_i^{\text{true}}. \quad (6)$$

For Case A, where there are only random analytical errors, the number of iterations required to achieve a steady state composition does not increase from the nominal value of two, but the number of iterations required to characterize

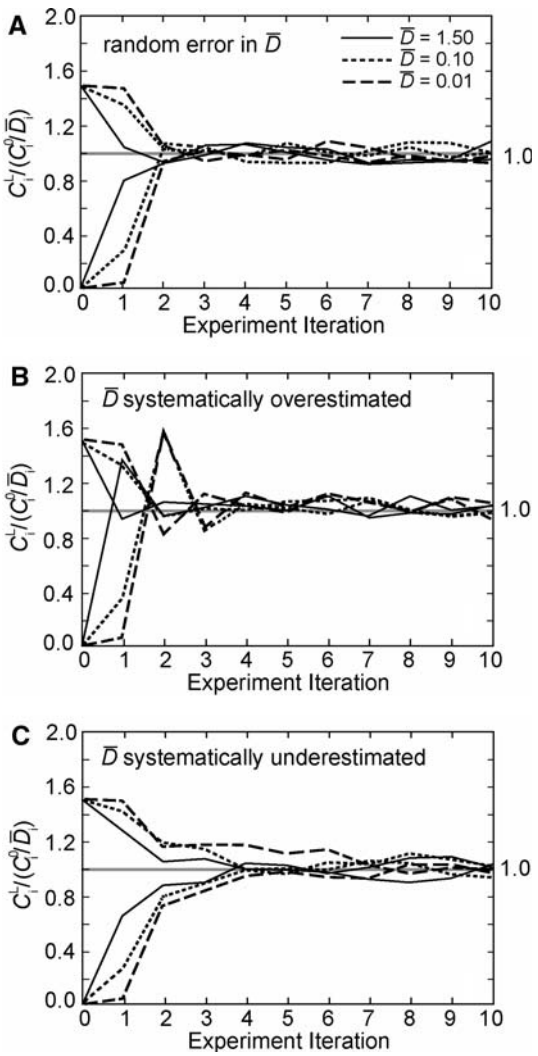


Fig. 4 Monte Carlo simulations of MISE where there are errors in estimates of $\overline{D}$ from each experiment: **a** includes a 20% random error (**b**) and (**c**) include a 20% random error plus a systematic overestimate and underestimate, respectively, that is proportional to the difference between the observed liquid and the true equilibrium liquid such that the estimated $\overline{D}$ will be wrong by 40% if the initial ''meat'' composition is off by 100%; (i.e., $\pm 0.4\overline{D}_i(C_i^L - C_i^{L-\text{equil}})/C_i^{L-\text{equil}}$). Each panel shows three simulations beginning with concentrations that are too high and 3 that are too low. In all cases, the results oscillate about the true equilibrium value after 3–4 iterations. However, more iterations may be required to achieve a good statistical average of equilibrium composition. Calculations performed with for $x = 0.2$; i.e., 20% ''meat'' and 80% ''bread''

that steady state composition with reasonable certainty increases to some larger number, as an average of several measurements is necessary to overcome the statistical fluctuations (Fig. 4). For cases B and C, the number of iterations required to characterize the steady state increases from the theoretical limit (2) to somewhere between 3 and 4 (Fig. 4). But owing to the combined effects of random and systematic errors, 4–6 iterations may be required to

firmly establish that equilibrium has been achieved. A practical illustration of this effect for partial melting of carbonated peridotite is demonstrated in the companion paper (Dasgupta and Hirschmann 2007).

Pitfalls in cases of extreme compositional dependence to partition coefficients

There are potential pitfalls to the iterative sandwich technique if there is an extreme compositional dependence to the partition coefficients, such that large differences in $\overline{D}$'s are produced by modest differences in mineral or melt compositions. From a thermodynamic point of view, such large effects are unlikely, as they imply large departures from Henry's law derived from extraordinary non-ideal mixing between the element of interest and other components in the liquid or minerals. One exceptional circumstance where such effects may occur is if the near-solidus liquid composition is close to a miscibility gap, in which case large changes in $\overline{D}_i$ can occur with only small changes in thermodynamic activity. Although extreme compositional dependences are not likely to be encountered in most circumstances, for completeness we review briefly the consequences should such dependences be relevant in a particular instance.

If there is an extreme compositional dependence on partition coefficients, the consequences depend on whether partition coefficients increase or decrease as the concentration of the element in the melt changes and on the differences between the initial melt composition in the experiment compared to the true equilibrium composition. There are three possible effects of such extreme dependences:

1. If enhanced element concentration in the liquid produces a partition coefficient that is significantly larger than the equilibrium value, observed values of $C^{L,n}{}_i$ and $\overline{D}_i^n$ will oscillate wildly from one iteration to the next, making it difficult to assess whether equilibrium is achieved. Numerical tests show that such oscillations may occur if a 100% increase in concentration of an element in the liquid causes the observed value of $\overline{D}_i^n$ to increase by more than 100%. This effect, which would be the same whether the initial concentrations of the element of interest are above or below the actual equilibrium concentrations, should be easily detectable.
2. If the concentration of an element in the liquid is initially greater than the equilibrium concentration and if enhanced element concentrations in the liquid produce partition coefficients that are significantly smaller than the equilibrium value, the observed values of $C^{L,n}{}_i$ and $\overline{D}_i^n$ may diverge to arbitrarily large, and small values, respectively. After several experiments, the partition coefficient approaches zero, producing extremely large predicted element concentrations in the liquid. Numerical tests show that such effects may prevent convergence of iterative experiments if a 100% increase in concentration of an element in the liquid causes the observed value of $\overline{D}_i^n$ to decrease by more than ~70%. This effect is probably implausible from the point of view of phase equilibria, but in any event, should be easily detectable and therefore avoided.
3. If the concentration of an element in the liquid is initially lower than the equilibrium concentration and if diminished element concentrations in the liquid produce partition coefficients that are significantly larger than the equilibrium value, then observed values of $C^{L,n}{}_i$ and $\overline{D}_i^n$ may converge to values that are smaller and larger than the true equilibrium values at the solidus of target bulk composition. Numerical tests show that such effects may occur if a 100% decrease in concentration of an element in the liquid causes the observed value of $\overline{D}_i^n$ to increase by more than 70% and will always occur if 100% decrease in element concentration causes the value of $\overline{D}_i^n$ to increase by more than 100%. We are not aware of any petrologically relevant system that behaves in this extreme fashion, but if such dependences were encountered, they could plausibly lead to an erroneous conclusion regarding the near-solidus partial melt composition. However, this possibility may easily be tested by conducting an experiment with an initial ''meat'' composition with a high concentration of the element of interest. Also, it will likely be evident from examination of experimental results, which should show a large dependence between liquid composition and partition coefficients.

Effect of changes in melt fraction

Thus far we have assumed that the melt fraction at the end of an experiment, F^n, is the same as the proportion of ''meat'' introduced into the experiment, x. Clearly, this may not be the case in real experiments. Melt fractions at the end of experiments may be greater than or less than x if the meat composition is more or less fertile than the equilibrium melt at the target temperature, which will cause reactions between the ''meat'' and ''bread'' to produce or consume melt. The magnitude of variations in F^n depends in part on the character of the petrologic system. For example, reaction between ''bread'' and ''meat'' can have greater effect on melt fraction if the ''meat'' is a silicate melt than if it is carbonatitic.

Variations in melt fraction owing to the fertility of the ''meat'' in a given iteration or owing to small random pressure and temperature uncertainties are not likely to

have significant effect on convergence to the accurate near-solidus liquid. So long as the mineral/melt partition coefficients derived from the experiment are close to those prevailing at the solidus of the target bulk composition and provided that the temperature of the experiment is a reasonable approximation of the solidus of the ''bread'' bulk composition. Application of these partition coefficients to the subsequent iteration should produce a ''meat'' composition that is closer to the target near-solidus liquid and therefore with the appropriate fertility to produce melt fractions closer to x in subsequent iterations. Therefore changes in melt fraction owing to this effect should be reduced in successive iterations.

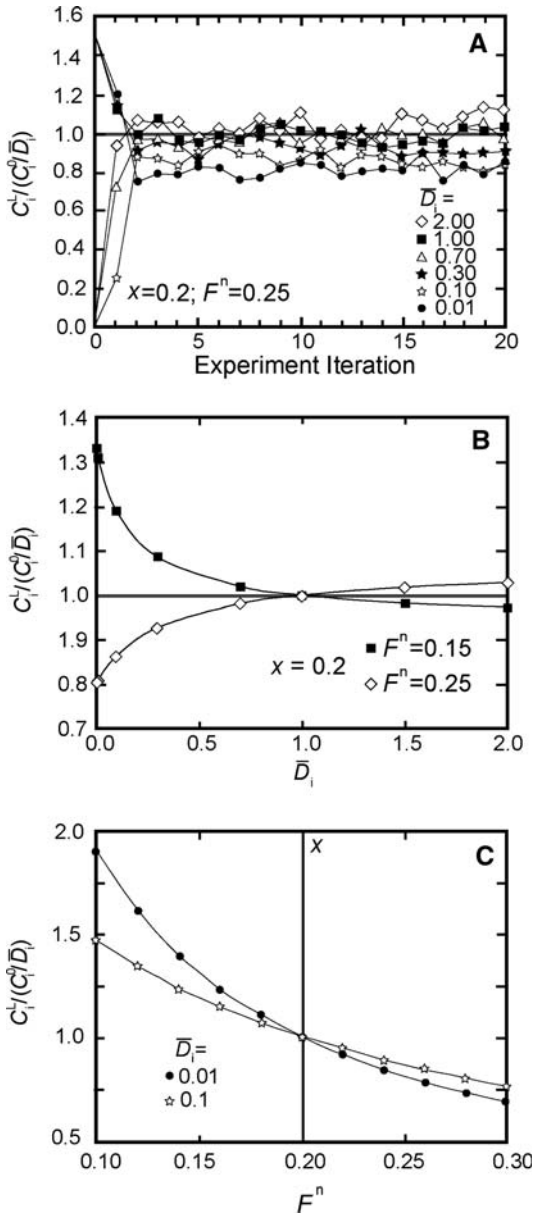
Melt fractions also may differ from x if the target rock composition is not at its solidus at the temperature and pressure of the experiment. This may occur if the solidus temperature is not known accurately or owing to experimental uncertainties in temperature or pressure. Unlike changes in melt fraction owing simply to reaction between bread and meat, those caused by temperature differences between the experiment and the true solidus of the ''bread'' may not be easily corrected by simply by compositional iteration. This scenario is discussed in greater detail in the next section.

The effect of temperature

In their simplest form, iterative sandwich methods are designed to determine the composition of a partial melt at the precise solidus of the target bulk rock composition. This partial melt can only coexist with the solidus mineral assemblage at the unique solidus temperature of the target rock, because equilibrium between peridotitic minerals and their partial melts depends on temperature. Therefore, prior to conducting MISE experiments it is necessary to have a reasonable estimate of the solidus based on careful experiments conducted with the bulk rock composition of interest. However, in practice, it may be difficult to accurately constrain the precise solidus of a rock, and so it is important to consider the consequences of conducting MISE experiments either above or below the solidus temperature.

If conventional iterative sandwich experiments or MISE are performed at a temperature other than the solidus of the target composition, T^0_{solidus}, two effects are expected. First, resulting mineral/melt partition coefficients may be different from those expected at T^0_{solidus}. For example, owing to the temperature dependence of olivine/liquid partition coefficients for FeO and MgO (Roeder and Emslie 1970; Putirka 2005), the resulting liquid could have different concentrations of these oxides. Second, and more importantly, the resulting melt fraction (F^n) will be systematically different from x, the initial fraction of ''meat''. If $T > T^0_{\text{solidus}}$, the proportion of liquid will increase relative to the proportion of ''meat'' at the outset of the experiment ($F^n > x$) because the target composition, taken in isolation, would have a finite melt fraction ($F^0 > 0$) at this temperature. Alternatively an iterative sandwich experiment may be performed at a temperature below the actual solidus of the ''bread''. At this temperature, the true solidus liquid is not stable, but a more fertile liquid may be stable if it is enriched in fluxing components such as alkalis or volatiles. Such a liquid may be produced by partial crystallization of the ''meat'' composition, possibly combined with reaction between the ''meat'' and the ''bread''. Importantly, the proportion of liquid resulting from such an experiment will be smaller than the initial fraction of ''meat''; i.e., $F^n < x$. Thus, if iterative sandwich methods are applied at a temperature different from T^0_{solidus}, the partition coefficients derived from these experiments will fail to predict the composition of the solidus liquid, and the resulting melt fraction will not have the composition of the partial melt at the ($F^0 = 0$) solidus.

Clearly, iterative experiments performed at $T \neq T^0_{\text{solidus}}$ will not converge to the equilibrium near-solidus melt composition of the target bulk composition, though the magnitude of the mismatch will be small if T is close to T^0_{solidus}. The question that arises is whether the practitioner who attempts such a procedure will be aware of the error or whether he/she may mistakenly conclude that the experiments reveal an accurate estimate of the near-solidus liquid composition. The effects of the first problem, differing partition coefficients, may be small. For example if T is 20°C above T^0_{solidus}, then the known temperature-dependence of MgO and FeO* in equilibrium with olivine of a given composition (Roeder and Emslie 1970; Beattie 1993; Sugawara 2000; Putirka 2005) can be used to anticipate that MgO and FeO* concentrations in the liquid will be ~ 4% (relative) higher than the true near-solidus value. On the other hand, the second problem—the difference between x and F when $T \neq T^0_{\text{solidus}}$—will produce systematic increases ($T > T^0_{\text{solidus}}$) or decreases ($T < T^0_{\text{solidus}}$) in melt fraction at each iteration and will lead to a steady-state melt composition that diverges from $C^0_i/\overline{D}_i$ and does so more strongly for values of $\overline{D}_i$ far from unity (Fig. 5). Thus, if the MISE technique is conducted far from T^0_{solidus}, the problem will be evident from a systematic relationship between resulting values of $C^{L,n}_i/\left(C^0_i/\overline{D}_i\right)$ and $\overline{D}_i$. Also, the resulting minerals should have compositions different from those expected to be in equilibrium at the true solidus of the ''bread''. For example, if $T < T^0_{\text{solidus}}$, reaction of the too-alkali rich melt with the ''bread'' should produce pyroxenes with Na_2O concentrations greater than those present at the solidus of the ''bread''. Thus, spurious results from the MISE technique performed unintentionally at $T \neq T^0_{\text{solidus}}$ should be readily identifiable and hence avoidable.



◀ **Fig. 5** Consequences of performing MISE aimed at determining near-solidus melt compositions at a temperature different from the solidus of the target ''bread'' composition. **a** Simulation of iterative experiments with initial ''meat'' fraction, x, of 0.2 under circumstances where $T > T^0_{\text{solidus}}$ such that the resulting melt fraction F^n is always 0.25. Simulation also includes 20% random error in values of $\overline{D}_i$ at each iteration, similar to Fig. 4a. Note that liquid compositions do not all converge to $C_i^{L,n}/\left(C_i^0/\overline{D}_i\right) = 1$ (compare to Fig. 4a) and that their displacement from unity is greatest for smaller values of $\overline{D}_i$. **b** Dependence of $C_i^{L,n}/\left(C_i^0/\overline{D}_i\right)$ when n is large on $\overline{D}_i$ for increases or decreases in melt fraction compared to the proportion of ''meat''. For initial proportions of ''meat'', x, equal to 0.2, curves show results of simulations when the resulting melt fraction in each experiment, F^n, decreases to 0.15 or increases to 0.25. Elements with the smallest partition coefficient are most sensitive to these changes in melt fraction, and are therefore the strongest indicators of systematic shifts in melt fraction. **c** Effect of change in resulting melt fraction on $C_i^{L,n}/\left(C_i^0/\overline{D}_i\right)$ for elements with $\overline{D}_i = 0.1$ and 0.01, assuming an initial proportion of ''meat'', x, of 0.2 showing that highly incompatible elements can be sensitive to increases in melt fraction of just a few percent (relative)

Determining compositions of melt fractions above the solidus

Iterative sandwich techniques such as the MISE method produce melts that are in equilibrium at the solidus of the bulk composition of the ''bread'' lithology. Although such melts are of some theoretical interest, they have little practical importance to real Earth processes because their volumes are, by definition, infinitesimal. On the other hand, small finite melt fractions may be of considerable interest in Earth's mantle. Fortunately, the MISE method can be adapted to investigate compositions of liquids at small but finite extents of partial melting above the solidus.

Simple application of the MISE method to the zero melt fraction ($F = 0$) case works because the residue (bread) does not change composition by equilibration with the melt of interest. Therefore, the bulk composition of solids in equilibrium with the melt is the same as the bulk composition of the rock of interest, C_i^0, and it is only necessary to locate an appropriate melt composition that is in equilibrium with that residue. At finite melt fraction, the residue (bread) also shifts in composition during equilibration with the liquid of interest. Thus, for a given bulk composition C^0_i and melt fraction, F, the equilibrium melt and residue concentrations of element i are given by

$$C_i^L = (C_i^0/(F - F\overline{D}_i + \overline{D}_i);\ C_i^R = (\overline{D}_i C_i^0)/(F - F\overline{D}_i + \overline{D}_i), \quad (7a; 7b)$$

respectively. In theory, one could perform modified iterative experiments in which one varied both the initial ''meat'' and ''bread'' compositions according to partition coefficients, $\overline{D}_i$, determined from previous iterations, but synthesis of two new compositions for each iteration is laborious and unnecessary. Instead, the same 'bread'' can be used repeatedly, and the ''meat'' composition can be modified to account for changes in both the ''meat'' and ''bread'' during their approach to equilibrium.

An initial experiment provides a first approximation of an appropriate set of partition coefficients, $\overline{D}_i$, which allow calculation of $C_i^{L,1}$ and $C_i^{R,1}$ for the desired value of F from Eqs. 7a and 7b. For a sandwich experiment with a proportion of x ''meat'' (melt) and (1–x) ''bread'' (target rock), the second experiment can be constructed from the bulk composition of interest and an initial melt composition given by

$$C_i^{m,2} = \frac{xC_i^{L,1} + (1-x)(C_i^{R,1} - C_i^0)}{x}. \quad (8)$$

This procedure, applied iteratively, will produce the melt composition expected ($C_i^{L,n}$ as given in Eq. 7a) at the specified melt fraction of the bulk composition, C_i^0. Of course, the efficacy of this procedure depends on prior knowledge of the temperature at which the target melt fraction, F^0, is attained for the target bulk composition and the pressure of interest. However, as in the case of near-solidus MISE determinations, errors in assumed T–F relations should be evident from correlations between values of $C_i^{L,n}/(C_i^0/\overline{D}_i)$ and $\overline{D}_i$.

Robinson et al. (1998) performed iterative sandwich experiments to determine melt compositions at temperatures above the solidus of spinel peridotite at 1.5 GPa. These experiments were interpreted as documenting finite melt fractions between 1 and 20 wt%. However, the methodology employed by Robinson et al. (1998) differed in several respects from that advocated in the present work. First, they performed conventional iterative experiments, using the compositions of melts in sandwich experiments as the ''meat'' of succeeding iterations. Because they performed only 2–3 iterative cycles, this may not have produced melts characteristic of partial melts of the target lithology (Fig. 3). Second, Robinson et al. (1998) used the same target lithology as the ''bread'' for successive iterations, without taking into account the effects of melt extraction on depletion of the solid residua. Thus, with increasing melt fraction, the effective target composition investigated by Robinson et al. (1998) became more fertile. On the other hand, Robinson et al. (1998) performed some inverse experiments that showed that their resulting melt compositions were in equilibrium with spinel lherzolite residues. Their experiments may document reasonable approximations of equilibrium between silicate liquids and lherzolitic residua, but it is less certain whether they are indicative of the partial melting behavior of a specific bulk composition. There remains some uncertainty as to whether the melt fractions and melt compositions inferred by Robinson et al. (1998) are directly applicable to a well-constrained target bulk composition.

Concluding remarks

To our knowledge, the MISE technique is the only method that has the potential to determine the composition of near-solidus partial melts of natural (high variance) rocks at melt fractions well below 1%. Thus, although it is laborious, it may prove of considerable utility when compositions at very low melt fraction are of geologic importance. A demonstration of the efficacy of MISE to just such a case is presented in the companion paper (Dasgupta and Hirschmann 2007), in which near-solidus partial melts of carbonated peridotite is determined at 6.6 GPa. MISE may also be of use for determination of melt compositions at finite melt fractions, though the relative merits of MISE compared to already established melt-trap methods may vary, depending on the feasibility of trapping equilibrium melt compositions at the conditions and for the composition of interest.

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