Compositional effect on the pressure derivatives of bulk modulus of silicate melts

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ABSTRACT

Although the bulk moduli ($K_0$) of silicate melts have a relatively narrow range of values, the pressure derivatives of the isothermal bulk modulus ($K_T$) can assume a broad range of values and have an important influence on the compositional dependence of the melt compressibility at high pressure. Based on the melt density data from sink/float experiments at high pressures in the literature, we calculate $K_T$ using an isothermal equation of state (EOS) (e.g., Birch–Murnaghan EOS and Vinet EOS) with the previously determined values of room-pressure density ($\rho_0$) and room-pressure bulk modulus ($K_0$). The results show that best estimates of $K_T$ vary considerably from ~3 to ~7 for different compositions. $K_T$ is nearly independent of Mg # (molar Mg/(Mg+Fe)), but decreases with SiO$_2$ content. Hydrous melts have anomalously small $K_T$, leading to a high degree of compression at high pressures. For anhydrous melts, $K_T$ is ~7 for peridotitic melts, ~6 for picritic melts, ~5 for komatiitic melts, and ~4 for basaltic melts.

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1. Introduction

Melting of silicates in the deep interior of terrestrial planets has likely played an important role in the evolution and dynamics of the planets. Examples of deep melting include the deep magma oceans during the early accretion processes of the planets (Ohtani, 1985; Agee and Walker, 1988a), the dehydration-induced melt layer above the 410- km boundary proposed by Bercovici and Karato (2003) and possibly evidenced by seismological observations (e.g., Revenaugh and Sipkin, 1994; Song et al., 2004), and the partial melts at the bottom of the lower mantle suggested by the ultra-low velocity zone in the D* layer (Williams and Garnero, 1996; Stixrude and Karki, 2005). Equation of state (EOS) for silicate melts is critical to understand the processes of separation and migration of these deep melts, and hence to explore the geophysical and geochemical consequences of deep melting.

Deep melts may have a broad range of compositions. Effect of melt composition on density in the low pressure regime has been very well described by the ideal mixing model (e.g., Bottinga and Weill, 1970; Lange and Carmichael, 1987; Lange, 1997). However, this type of model cannot be directly extrapolated to high pressures because melts are highly compressible and the exact nature of compression at high pressures is not well known.

A common approach to study the density of materials at high pressures is to use an isothermal EOS such as the widely used Birch–Murnaghan EOS and the Vinet EOS. This type of EOS can be parameterized using the room-pressure density ($\rho_0$), room-pressure bulk modulus ($K_0$), and the pressure derivatives of the bulk modulus at room pressure ($K_T$, $K_{T0}$, ...). For the pressure range relevant to the Earth’s mantle, higher order parameters ($K_{Tm}$, ...) are often truncated leaving $\rho_0$, $K_0$, and $K_T$ as fitting parameters. Among them $\rho_0$ and $K_0$ are well constrained by room-pressure measurements. The compositional dependence of $\rho_0$ is successfully characterized by the ideal mixing model (e.g., Bottinga and Weill, 1970; Lange and Carmichael, 1987; Lange, 1997), and $K_0$ is relatively insensitive to composition except for alkaline elements (Rivers and Carmichael, 1987). Consequently, in most of mafic or ultramafic melts, the key parameters that control their densities at high pressures are $\rho_0$ and $K_T$.

However, the compositional dependence of $K_T$ has not been well documented. Using a melting-curve analysis, Lange (2003, 2007) proposed an inverse relationship between $K_T$ and $K_0$ at pressures less than 6 GPa. However, no explicit compositional dependence of $K_T$ at high pressures (>6 GPa) was well resolved by this approach. Rigden et al. (1988, 1989) predicted that $K_T$ is higher for melts with lower SiO$_2$ and Al$_2$O$_3$ contents based on the shock-wave studies of anorthite (An), diopside (Di), and An$_{34}$–Di$_{66}$. Recently Ai and Lange (2008) revised the results of Rigden et al. (1989) and confirmed that $K_T$ decreases with increasing Al$_2$O$_3$ content. However such compositional dependence has not been confirmed for a broader range of composition other than the An–Di system and komatite. $K_0$ was also constrained by melt density data at high pressures obtained from sink/float experiments (e.g., Agee, 1998; Ohtani and Maeda, 2001). However, most results of $K_0$ in these studies were obtained by the
fitting method in which all of the three parameters \((\rho_0, K_{\text{T}0}, K_T)\) or both \(K_{\text{T}0}\) and \(K_T\) are estimated by fitting the data to an equation of state. As we will show, such an approach is subject to large uncertainties in the estimated value of \(K_{\text{T}0}\) because of a strong trade-off among various inferred parameters.

In this study, a different approach is applied to fit the isothermal EOS, which can significantly reduce the uncertainties in \(K_{\text{T}0}\). We then investigate the compositional dependence of \(K_{\text{T}0}\) and discuss its influence on the melt density under deep mantle conditions.

### 2. Methods for the estimation of \(K_{\text{T}0}\) and its uncertainties

#### 2.1. Some notes on the methods for estimation of \(K_{\text{T}0}\)

The density of materials as a function of pressure, temperature, and composition can be composed by an isothermal EOS,

\[
\rho(P, T, X) = \rho(P, \rho_0(T, X), K_{\text{T}0}(T, X), K_T(T, X), ...)
\]

where the room-pressure density \((\rho_0)\), the room-pressure bulk modulus \((K_{\text{T}0})\), and the pressure derivatives of bulk modulus at room pressure \((K_T, K_{\text{T}0}, ...)\) are temperature and compositional dependent parameters. Two isothermal equations of state are widely used: the Birch–Murnaghan EOS and the Vinet EOS. We will mainly use the Birch–Murnaghan EOS as an example of an isothermal EOS, but all the methods can be easily adapted to other isothermal equations of state such as the Vinet EOS. For the pressure range in the Earth’s mantle, the Birch–Murnaghan EOS is often truncated to the third order, which is given by Birch (1947):

\[
P = \frac{3}{2} K_{\text{T}0} \left[ \left( \frac{\rho}{\rho_0} \right)^{7/3} - \left( \frac{\rho}{\rho_0} \right)^{5/3} \right] \left[ 1 + \frac{3}{4} (K_{\text{T}0} - 4) \left( \frac{\rho}{\rho_0} \right)^{2/3} - 1 \right]
\]

with \(\rho_0, K_{\text{T}0}\), and \(K_T\) are the parameters that depend on composition. These parameters can be constrained by fitting the EOS to the melt density data determined by isothermal compression experiments. However, melt density data at high pressures are so limited that a direct fitting to the density–pressure curve cannot give all the parameters at the same time with reasonable uncertainties. This requires additional constraints from other independent measurements.

The compositional dependence of \(\rho_0\) as well as its temperature dependence can be calculated using the ideal mixing model (e.g., Lange and Carmichael, 1987; Lange, 1997; Ochs and Lange, 1997) in which the molar volume of a silicate melt is given by a linear combination of partial molar volumes of oxide components,

\[
V = \sum_i X_i \rho_i
\]

where \(X_i\) and \(\rho_i\) are the molar fraction and the molar volume of the \(i\)th component. To a first-order approximation, the temperature dependence can be incorporated as

\[
V = \sum_i X_i \left[ \rho_i \frac{\partial \rho_i}{\partial T}(T - T_{\text{ref}}) \right]
\]

where \(\rho_i / \partial T\) is the partial molar expansivity of the \(i\)th component and \(T_{\text{ref}}\) is the reference temperature. Then the room-pressure density at temperature \(T\) can be given by

\[
\rho_0(T, X) = \frac{V}{\sum_i X_i M_i}
\]

where \(M_i\) is the gram formula weight of the \(i\)th component. The partial molar quantities \(\rho_i\) and \(\rho_i / \partial T\) have been calibrated by many studies. In this study we use the results of Lange (1997) for melt components other than FeO and H2O. For FeO component the result from Lange and Carmichael (1987) is used, and for H2O the result from Ochs and Lange (1997) is used. Results of \(\rho_0\) for the melt compositions in this study are listed in Table 1.

In contrast to previous studies, we also calculate \(K_{\text{T}0}\) using the ideal mixing model of compressibility,

\[
\frac{\partial V}{\partial P} = -\sum_i X_i \frac{\partial \rho_i}{\partial P} + \frac{\partial^2 V}{\partial T \partial P}(T - T_{\text{ref}})
\]

Then \(K_{\text{T}0}\) is given by

\[
K_{\text{T}0} = -\left( \frac{\partial^2 V}{\partial T \partial P} \right)_0
\]

For components other than H2O, \(\rho_i / \partial T\) and \(\partial^2 V / \partial T \partial P\) are given by the results of Kress and Carmichael (1991), which are based on ultrasonic sound velocity studies of silicate melts (e.g., Rivers and Carmichael, 1987; Kress and Carmichael, 1991). For the H2O component, results based on density estimation at elevated pressure from Ochs and Lange (1997) are used. Results of calculated \(K_{\text{T}0}\) are also listed in Table 1.

There are some other calibrations for the partial molar quantities in the ideal mixing model in addition to the results mentioned above. An updated calibration is given by the study of Ghiorso and Kress (2004), in which they included many recent experimental data on both melt density and sound velocity, although data for hydrous melts were not included. We will compare the calculated results based on different calibrations in the Discussion section, and choose the above calibrations to make the presentation clear.

Consequently, \(K_{\text{T}0}\) is the only parameter to be determined by using density data at high pressures. This type of approach was previously applied to calculate silicate solids by Bass et al. (1981), where the static compression data were combined with ultrasonic studies to constrain \(K_{\text{T}0}\) for several solid silicates. By a detailed error analysis, they showed that the uncertainties in \(K_{\text{T}0}\) given by this method were significantly reduced. For silicate melts, this approach was once applied to the MORB composition by Agee (1998), however, values of \(K_{\text{T}0}\) for the other melts in Agee (1998) were not constrained by the same approach.

This approach is better demonstrated by a normalized EOS. If we define the normalized density and pressure as

\[
\rho^* = \frac{\rho(T, P, X)}{\rho_0(T, X)}
\]

\[
P^* = \frac{P}{K_{\text{T}0}(T, X)}
\]

then, the normalized Birch–Murnaghan EOS is given by

\[
P^* = \frac{3}{2} \left[ (\rho^*)^{7/3} - (\rho^*)^{5/3} \right] \left[ 1 + \frac{3}{4} (K_{\text{T}0} - 4) \left( (\rho^*)^{2/3} - 1 \right) \right]
\]

where \(K_{\text{T}0}\) is the only fitting parameter left in this equation. We note that the shape of a normalized EOS solely depends on the values of \(K_{\text{T}0}\). After calculating the normalized density and pressure, \(K_{\text{T}0}\) is then obtained for each composition and temperature condition by solving Eq. (10).

#### 2.2. Uncertainties in \(K_{\text{T}0}\)

The uncertainties in \(K_{\text{T}0}\) determined by this approach can be analyzed by the propagation of errors through the normalized density and pressure. We follow the approach described in Bass et al. (1981) and Angel (2000). We only summarize the results of error propagation here. The detailed analysis is presented in Appendix A.

There are mainly four error sources that can contribute to the uncertainties in \(K_{\text{T}0}\): the uncertainties in pressure \((P)\), room-pressure density \((\rho_0)\), room-pressure bulk modulus \((K_{\text{T}0})\), and high-pressure density \((\rho)\). The uncertainties in pressure for the ex-situ high-pressure experiments come from the uncertainties in the pressure calibrations as well as the imperfect reproducibility in the experiments and may vary from lab to lab. A rough estimation of the relative uncertainty...
Table 1
Compilation of experimental data and EOS parameters

<table>
<thead>
<tr>
<th>Composition (wt.%)</th>
<th>Peridotitic</th>
<th>Picritic</th>
<th>Komatiitic</th>
<th>Basaltic</th>
<th>Hydrous basaltic</th>
<th>Hydrous ultramafic</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>44.5</td>
<td>41.2</td>
<td>42.1</td>
<td>42.1</td>
<td>45.1</td>
<td>46.2</td>
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<tr>
<td>Al₂O₃</td>
<td>3.6</td>
<td>3.7</td>
<td>6.5</td>
<td>6.5</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>FeO</td>
<td>8.1</td>
<td>15.1</td>
<td>16.0</td>
<td>16.0</td>
<td>10.4</td>
<td>10.4</td>
</tr>
<tr>
<td>MgO</td>
<td>30.2</td>
<td>33.0</td>
<td>30.2</td>
<td>30.2</td>
<td>38.4</td>
<td>38.4</td>
</tr>
<tr>
<td>CaO</td>
<td>3.4</td>
<td>7.0</td>
<td>5.3</td>
<td>5.3</td>
<td>3.4</td>
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</tr>
<tr>
<td>Na₂O</td>
<td>3.1</td>
<td>2.7</td>
<td>2.7</td>
<td>2.7</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>H₂O</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mg #</td>
<td>0.90</td>
<td>0.80</td>
<td>0.77</td>
<td>0.77</td>
<td>0.87</td>
<td>0.87</td>
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<td>Experimental conditions and results</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Pressure (GPa)</td>
<td>8.2</td>
<td>16.3</td>
<td>16</td>
<td>7.4</td>
<td>13.5</td>
<td>20.5</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>2273</td>
<td>2543</td>
<td>2603</td>
<td>2163</td>
<td>2303</td>
<td>2633</td>
</tr>
<tr>
<td>ρ (g/cm³)</td>
<td>3.21</td>
<td>3.56</td>
<td>3.56</td>
<td>3.31</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ρ₀ (g/cm³)</td>
<td>2.643 ± 0.001</td>
<td>2.663 ± 0.023</td>
<td>2.640 ± 0.025</td>
<td>2.760 ± 0.015</td>
<td>2.656 ± 0.014</td>
<td>2.751 ± 0.019</td>
</tr>
<tr>
<td>KT₀ (GPa)</td>
<td>23.4 ± 3.6</td>
<td>19.6 ± 3.1</td>
<td>20.3 ± 3.3</td>
<td>22.5 ± 2.3</td>
<td>22.7 ± 3.5</td>
<td>20.8 ± 4.3</td>
</tr>
<tr>
<td>KT₀'(B-M)</td>
<td>6.2 ± 2.2</td>
<td>7.8 ± 1.9</td>
<td>6.9 ± 1.7</td>
<td>6.7 ± 1.2</td>
<td>7.0 ± 1.9</td>
<td>6.7 ± 1.8</td>
</tr>
<tr>
<td>KT₀'(Vinet)</td>
<td>6.2 ± 2.2</td>
<td>7.8 ± 1.9</td>
<td>6.9 ± 1.7</td>
<td>6.7 ± 1.2</td>
<td>7.0 ± 1.9</td>
<td>6.7 ± 1.8</td>
</tr>
</tbody>
</table>

a Agee and Walker (1993).
b Suzuki et al. (1998).
c Suzuki and Ohtani (2003).
f Sakamaki et al. (2006).
g Matsukage et al. (2005).
(defined as \( \sigma_P \), where \( \sigma_P \) is the standard deviation of \( P \)) would be around 5% (corresponds to a deviation of 0.5 GPa at 10 GPa (e.g., Matsukage et al., 2005; Sakamaki et al., 2006). The relative uncertainties in \( \rho \) determined from sink/float method are estimated to be about 1% (e.g., Matsukage et al., 2005; Sakamaki et al., 2006). The uncertainties in calculating \( \rho_0 \) and \( K_T \) can be obtained by propagating the errors in the calibrated partial molar quantities, which were given in the aforementioned literature. For each melt composition, these uncertainties are calculated and listed in Table 1. The uncertainties in \( \rho_0 \) are in the range of 0.1–1.1%; the uncertainties in \( K_T \) are in the range of 1% to 21%. In general, when an extrapolation to a higher temperature is needed, the uncertainties are larger. These propagated uncertainties are consistent with the reported average uncertainties: 0.4% for \( \rho_0 \) of the FeO-bearing dry silicate melts (Lange, 1994), and about 0.6% for hydrous melts (Ochs and Lange, 1997, 1999). For \( K_T \), the average uncertainties are estimated to be about 4% in Lange and Carmichael (1987) (uncertainties should be smaller for Kress and Carmichael (1991), which is used in this study, due to the better treatment of the oxidation states of iron in the melts) for dry melts. However, the extrapolation to high temperatures gives relatively large uncertainties since the temperature dependence of \( K_T \) is poorly constrained.

Based on the formulation of error propagation derived in Appendix A, the uncertainties in \( K_T \) can be estimated given the above error sources. Fig. 1 shows the relative uncertainties in \( K_T \) for fitting a hypothetical data point at various pressures to the Birch–Murnaghan EOS, assuming constant input errors in \( P \), \( \rho \), \( \rho_0 \), and \( K_T \) are 5%, 1%, 1%, and 10%, respectively. This diagram shows that given fixed relative uncertainties in all error sources, a fitting to a data point at relatively high pressures can provide a smaller uncertainty in \( K_T \) than the fitting to a data point at low pressures. This is because the data point at high pressure provides a larger pressure span so that the pressure derivatives are better constrained. Therefore for the purpose of this paper we prefer to use sink/float data determined at pressures higher than 6 GPa, which give a relative uncertainty in \( K_T \) around 15–30%.

3. Data set

As mentioned in the previous section, melt density data at high pressures are used to constrain \( K_T \). In this study, all melt density data are from sink/float experiments. These include Agee and Walker (1988b, 1993), Suzuki et al. (1995), Agee (1998), Suzuki et al. (1998), Ohtani and Maeda (2001), and Suzuki and Ohtani (2003) for dry melt compositions and Matsukage et al. (2005) and Sakamaki et al. (2006) for hydrous melt compositions. In sink/float experiments, the melt density can be bracketed by those of the density markers sinking or floating in each experiment. The experimental data used in this study are listed in Table 1. The experimental conditions fall in a temperature range of 1673 K–2773 K and a pressure range of 6–22 GPa. The melt compositions vary from peridotites to komatiites and to basalts; from anhydrous melts to hydrous melts. The Mg # (defined as molar ratio Mg/(Mg+Fe)) varies from 0.6 to 0.9. SiO\(_2\) content is from 41 wt.% to 52 wt.% (or 37 mol% to 54 mol%) for dry melts. H\(_2\)O content is 5 wt.% in the hydrous ultramafic melts studied in Matsukage et al. (2005) and either 2 wt.% or 8 wt.% in hydrous MORB studied in Sakamaki et al. (2006).

This data set includes most available melt density data from sink/float methods. However, there are a few exceptions. The data for fayalite composition of Agee (1992) are not included due to the low pressure conditions and possible complication of the oxidation state of Fe component. The results of Smith and Agee (1997) for a picritic melt are not included because these data were obtained at relatively low pressure conditions (less than 5 GPa), which result in larger uncertainties in \( K_T \) when using our method (see Fig. 1). Data from Circione and Agee (1996) are not used because the melt contains a significant amount of TiO\(_2\), which is not the focus of our current study.

4. Results

All the melt density data we have compiled are analyzed by the fitting method described in the Methods section. Results of fitted values and uncertainties of \( K_T \) for the whole data set are calculated and listed in Table 1. Contrary to silicate solids, whose \( K_T \) fall in a relatively small range of 4–6, \( K_T \) varies from 3 to 7 for the melt compositions studied here. The relative uncertainties in \( K_T \) are within 7–40% (mostly around 15–30%) for these melts, and the absolute uncertainties fall in the range of 0.2–2.2. Given these results, we can study the compositional effect on \( K_T \)

4.1. Effect of temperature on \( K_T \)

As discussed in the Methods section, \( K_T \) is a function of temperature and composition in the isothermal EOS. To study the compositional effect on \( K_T \) temperature effect must be examined first. However, for the temperature variation in the Earth’s mantle, which is about 400–500 K across the depth range of 1000 km, the temperature effect is likely very small. This is illustrated in Fig. 2, where we plot the fitted values of \( K_T \) for a few melt compositions at different temperatures: MA at 2163 K and 2603 K, PHN1611 at 2303 K and 2633 K, MORB 2473 K and 2773 K, and komatite at 2073 K and 2173 K. The differences in \( K_T \) at different temperatures are less than 0.5, which is smaller than the uncertainties in \( K_T \). On the contrary, the
difference in $K_{T0}'$ due to different compositions could be as large as 3, which is distinguishably larger than the uncertainties in $K_{T0}'$. This means that the temperature effect is negligible compared to the compositional effect. Therefore, we will neglect the temperature effect on $K_{T0}'$ hereafter and directly compare the results of $K_{T0}'$ at different temperatures without any corrections.

4.2. Effect of FeO, MgO and SiO$_2$

Deep melts could have a wide range of components, which makes the study of compositional effect complicated. However, unlike transport properties, which may highly depend on the behavior of a trace amount of minor components, density of silicate melts is mainly determined by major components like SiO$_2$, Al$_2$O$_3$, FeO, MgO, CaO, and maybe in some cases H$_2$O. Other components like Na$_2$O, K$_2$O, CO$_2$ are less important (although could be important when their amounts are large), and will not be discussed in this paper. Among these components, SiO$_2$, FeO, and MgO are the most interesting components due to their high abundances in deep mantle melts. Besides there are other reasons which make these components important: FeO component has a much higher “density” (defined by the ratio of molar mass to partial molar volume) than other components so additional FeO can significantly increase melt density as shown by Matsukage et al. (2005); Although SiO$_2$ is not particularly dense or light compared to other components, it may have a very distinct compression behavior due to its ability to change coordination (e.g., Stixrude and Karaki, 2005). We will also discuss some effect of water, which is important due to its very small “density” and highly compressible nature compared to other components.

We plot the results of $K_{T0}'$ for all the peridotitic melts as a function of Mg # in Fig. 3a. There is only a small difference in SiO$_2$ content for these peridotites (see Table 1). However, the difference in FeO/MgO content is relatively large. The Mg # ranges from 0.77 to 0.90. The results show that $K_{T0}'$ is nearly independent of Mg #. Similar results for hydrous ultramafic melt compositions are also shown in Fig. 3a, in which case $K_{T0}'$ does not vary with the Mg # when the SiO$_2$, H$_2$O, and Al$_2$O$_3$ contents remain nearly the same.

Unlike the dependence on the composition of divalent cations, $K_{T0}'$ has a strong dependence on SiO$_2$ content, which is illustrated in Fig. 3b. $K_{T0}'$ decreases from ~7 to ~4 for dry melts when SiO$_2$ content increases from 37 mol% to 54 mol%. That is, if we have more SiO$_2$ in a melt, the bulk modulus of the melts will not increase very fast with increasing pressure, which could make the melt relatively more compressible than the SiO$_2$-poor melt at high pressure. This observation confirms the similar prediction by Rigden et al. (1989), which was based on the results of An–Di system. Note that for natural melts compositions with higher SiO$_2$ content, the Al$_2$O$_3$ contents are also higher. For example, MORB has ~10 mol% Al$_2$O$_3$, while peridotites only have ~2 mol% Al$_2$O$_3$. Therefore it is important to separate the effects of SiO$_2$ and Al$_2$O$_3$. Ai and Lange (2008) conducted ultrasonic measurements for CaO–MgO–Al$_2$O$_3$–SiO$_2$ melts and revised the values of $K_{T0}'$ of Rigden et al. (1989). Their results show that $K_{T0}'$ decreases from 6.8 to 4.7 when Al$_2$O$_3$ content increases from 0 to 25 mol%. If the effect of Al$_2$O$_3$ on decreasing $K_{T0}'$ can be assumed universal for all silicate liquids that we have studied, then the effect of Al$_2$O$_3$ can be subtracted. This is shown in Fig. 3b, in which the dashed line shows the corrected effect of SiO$_2$ on $K_{T0}'$. Therefore for the compositions in this study effect of SiO$_2$ on $K_{T0}'$ is likely greater than that of Al$_2$O$_3$ due to the larger concentrations of SiO$_2$.

If this trend of $K_{T0}'$ with SiO$_2$ content can be extrapolated to the SiO$_2$ end-member, then a very small $K_{T0}'$ (~0 by extrapolating the dashed line in Fig. 3b) would be obtained. This unusual behavior of the SiO$_2$ component seems to be supported by some other studies, although controversy still exists. Based on an experimental determination of partial molar volume of SiO$_2$ in silicate liquids at high pressures, Gaetani et al. (1998) obtained a very small $K_{T0}'$ of ~−2 for the SiO$_2$ component in rhyolite liquid. Although a different calculation by Lange (2003) showed that $K_{T0}'$ is ~10 for the SiO$_2$ component.
are more compressible at high pressures.

Miller et al. (1991) and Rigden et al. (1989) obtained $K'_T$ for peridotitic melts. The result for the hydrous ultramafine melt (Sakamaki et al., 2006) are shown in Fig. 3c. Even for melts with low SiO$_2$ content, $K'_T$ could still be very small if enough water is added to the system. This means that a hydrous melt is more compressible at high pressures than the corresponding dry melt. However, currently available data are only for a limited range of compositions and the details of the influence of water are not well constrained.

4.3. Effect of H$_2$O

Effect of water on $K'_T$ is very significant. Results from hydrous ultramafic melts (Matsukage et al., 2005) and hydrous basaltic melts (Sakamaki et al., 2006) are shown in Fig. 3c. Even for melts with low SiO$_2$ content, $K'_T$ could still be very small if enough water is added to the system. This means that a hydrous melt is more compressible at high pressures than the corresponding dry melt. However, currently available data are only for a limited range of compositions and the details of the influence of water are not well constrained.

4.4. Results of $K'_T$ for some geologically important melts

According to the preceding analysis, SiO$_2$ content is the most important factor for the calculation of $K'_T$ whereas the Mg # of the melt is not as important. Consequently, it is reasonable to neglect the effect of Mg # and constrain the $K'_T$ only based on SiO$_2$ contents for several geologically interesting melts, including peridotites, picrites, komatiites, and basalts. Again the melt density data for dry melts in Table 1 are used. Dry melt compositions are divided into groups based on SiO$_2$ content. A weighted least-squares fitting to the normalized EOS (Eq. (10)) is used to obtain $K'_T$. The results of $K'_T$ for different compositional groups are shown in Table 2. Fig. 4 shows compression curves with different $K'_T$ for a few geologically interesting melts are previously determined using sink/float data (Agee, 1998; Ohtani and Maeda, 2001). These results are compared to the results of this study in Table 2. Ohtani and Maeda (2001) determined $K'_T$ for MORB, picrite, and peridotite using different calibrations are compared in Fig. 5. Three different calculations are shown: (1) $K'_T$ from Lange (1997) and Kress (1991), which is same as in Fig. 3b; (2) $K'_T$ from Lange (1997) and Kress and Carmichael (1991), which is same as in Fig. 3b; (3) both $K'_T$ from Ghiorso and Kress (2004). Fig. 5 shows that all three calculations give similar although different results on $K'_T$ and the relationship between $K'_T$ and SiO$_2$ content remains the same. Consequently a different choice of calibrations would not change our conclusions on the composition dependence of $K'_T$.

5. Discussion

5.1. Uncertainty again

As we have demonstrated in the Methods section, room-pressure properties play a very important role in anchoring the EOS of silicate melts. Here we discuss the uncertainties due to different calibrations of $p_0$ and $K'_T$. Results of $K'_T$ calculated using different calibrations are compared in Fig. 5. Three different calculations are shown: (1) $p_0$ and $K'_T$ from Lange (1997) and Kress (1991), which is same as in Fig. 3b; (2) $p_0$ and $K'_T$ from Lange (1997) and Kress and Carmichael (1991), which is same as in Fig. 3b; (3) both $p_0$ and $K'_T$ from Ghiorso and Kress (2004). Fig. 5 shows that all three calculations give similar although different results on $K'_T$ and the relationship between $K'_T$ and SiO$_2$ content remains the same. Consequently a different choice of calibrations would not change our conclusions on the composition dependence of $K'_T$.

5.2. Comparison to other studies

$K'_T$ for a few geologically interesting melts are previously determined using sink/float data (Agee, 1998; Ohtani and Maeda, 2001). These results are compared to the results of this study in Table 2. Ohtani and Maeda (2001) determined $K'_T$ for MORB, picrite, and peridotite using similar experimental data were used in these studies. For most melt compositions in Agee (1998) and Ohtani and Maeda (2001) except for the MORB melt in Agee (1998), $K'_T$ and $K''_T$ were constrained simultaneously by fitting to the isothermal EOS, which, as discussed in Bass et al. (1981) and this study, will lead to a trade-off between $K'_T$ and $K''_T$. In addition, when using sink/float results at different temperatures, the temperature effect on $K''_T$ was simply neglected in Agee (1998) and Ohtani and
Maeda (2001), although the temperature effect on density was corrected. As an exception, however, the result for MORB ($K'_{\text{MORB}}=4.4$) in Agee (1998) is similar to our result because similar methods were applied. $K_0$ for komatiite and MORB are also determined from shock-wave measurements (Rigden et al., 1988; Miller et al., 1991) (Table 2), which give similar although slightly larger $K_0$ than this study, if the difference between $K_0$ and $K_{\text{MORB}}$ is ignored (4.9 for komatiite compared to 4.5 in this study, and 4.85 for MORB compared to 4.3 in this study). Although in these studies the trade-off between $K_0$ and $K_{\text{MORB}}$ still exists, larger data sets (6–13 data points) and wider pressure ranges than those of typical sink/float experiments can ensure much smaller uncertainties in $K_0$.

5.3. Assumptions and limitations in this study

There are some limitations in our approach in the present study. (1) Using the third-order Birch–Murnaghan EOS for silicate melts is an assumption. We have also tested the Vinet EOS, which gives similar results in $K'_{\text{MORB}}$ (Table 1), and hence similar trends in the compositional dependences of $K_0$. (2) We assume that there is no phase transition in the silicate melts, i.e., no sharp change in the curvature of the compression curves, within the pressure range studied here. This has been verified for the An–Di system and komatiite by the shock-wave studies (Rigden et al., 1988, 1989; Miller et al., 1991), in which smooth compression curves were always observed. However, if there is indeed an abrupt change in the compression curve, then density data distributed over the whole pressure range are required to constrain the $K_0$ for each smooth segment of the curve. (3) The calculation of $K_{\text{MORB}}$ by an ideal mixing model is an assumption. The physical picture of mixing is not clear for melts so there is no reason to believe that the ideal mixing model is better than other models. However, Rivers and Carmichael (1987) and Ai and Lange (2008) applied different ideal mixing models (mixing linearly with mole fraction or volume fraction of the components, or even the linear mixing in sound speed) to the ultrasonic data and found out that the compressibility of melts predicted from these models are nearly identical. This suggests that $K_{\text{MORB}}$ of silicate melts is likely insensitive to mixing models. (4) For the composition range of study only the effects MgO, FeO, SiO$_2$, and H$_2$O could be resolved. However, other melt components could have complex behaviors of compression. Therefore special caution must be taken when the relationship of $K_{\text{MORB}}$ and SiO$_2$ content is extrapolated to the melt compositions which are very different from this study. For instance, a simple extrapolation may result in very small values of $K_{\text{MORB}}$ for KAlSi$_3$O$_8$ and NaAlSi$_3$O$_8$ melts, whereas high values of $K_{\text{MORB}}$ were shown by Lange (2003, 2007). (5) Finally we note that the data on hydrous melts are very sparse. Influence of water was studied only for a small range of water contents and of melt compositions.

5.4. Compositional effect on the density of silicate melts

In a summary, we have found that the most important melts components that control melt density at high pressures are FeO, SiO$_2$, and H$_2$O. FeO is a very dense component, which will increase $\rho_0$ of the melts considerably, but has no significant effects on $K_0$ and $K_{\text{MORB}}$. SiO$_2$ can slightly decrease $\rho_0$ and maybe $K_0$ depending on temperature, but will make melts more compressible at high pressures due to its effect on $K_{\text{MORB}}$. H$_2$O has large effects on all the EOS parameters ($\rho_0$, $K_0$, $K_{\text{MORB}}$). It will decrease melt density significantly at low pressure. At high pressure, this reduction in density is partly compensated by the effect of H$_2$O on $K_{\text{MORB}}$ and $K_0$.

6. Conclusions

The pressure derivatives of bulk modulus of silicate melts for a range of compositions are determined from high-pressure density data using room-pressure density and bulk modulus of the melts. This method provides us with more robust estimates of $K_{\text{MORB}}$ compared to the estimates by previous authors. Results show that the pressure derivative of bulk modulus is independent of Mg #, but has a systematic trend with SiO$_2$ content. H$_2$O component can also reduce the pressure derivative of bulk modulus significantly. A basaltic melt is likely more compressible at high pressures than a peridotitic melt due to its higher SiO$_2$ content, that is, smaller $K'_{\text{MORB}}$. Similarly a hydrous melt is likely more compressible at high pressures than the corresponding dry melt.

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Appendix A. Error analysis

The procedure of error analysis in this work is mainly adapted from the analysis by Bass et al. (1981), which is based on the least-squares method. The Birch–Murnaghan EOS (Eq. (10)) can be linearized as

$$P^n = Q + aR$$

by defining

$$Q(p^n) = \frac{3}{2} \left[ (p^n)^n - (p^n)^2 \right]$$

$$R(p') = \frac{9}{8} \left[ (p')^3 - (p')^2 \right] \left[ (p')^2 - 1 \right] = \frac{3}{2} Q \left[ (p')^2 - 1 \right]$$

and

$$a = (K_{\text{MORB}}-4)$$

where $a$ is the parameter to fit. The weighted least-squares solution of $a$ is given by

$$a = \frac{\sum \frac{R_i}{\sigma_i^2} \sum \frac{R_i K_0}{\sigma_i^2 K_0}}{\sum \frac{1}{\sigma_i^2}}$$

where subscript $i$ represents the $i$th data point, and $\sigma_i$ is the total uncertainty of data point $i$. The summation is over the number of data points at high pressure. After some manipulation, $\sigma_i$ can be calculated by the propagation of errors from the error sources as

$$\sigma_i^2 = \frac{\sigma_i^2}{\rho_i} \left( \frac{\partial \rho_i}{\partial R_i} \right)^2 + \frac{\sigma_i^2}{K_0} \left( \frac{\partial K_0}{\partial R_i} \right)^2 + \frac{\sigma_i^2}{K_{\text{MORB}}} \left( \frac{\partial K_{\text{MORB}}}{\partial R_i} \right)^2$$

where based on the Eulerian finite strain theory (e.g., Anderson, 1995)

$$K_{0} = \rho_0 \left( \rho' \right)^2 \left\{ 1 + \frac{1}{2} \left[ 1 \left( \rho' \right) - \frac{\rho_0}{\rho_0} \right] \right\} = 5 - 3K_{\text{MORB}} - 27 \left( 1 - \left( \rho' \right)^2 \right)$$

Therefore the uncertainty in $K_{\text{MORB}}$ is

$$\sigma_{K_{\text{MORB}}} = \sigma^2 = \frac{\sigma^2}{\sum \frac{1}{\sigma_i^2}}$$

For the case with only one density data point at high pressure, the uncertainty in $K_{\text{MORB}}$ is simply given by

$$\sigma_{K_{\text{MORB}}} = \frac{1}{K_{\text{MORB}}} \left( \frac{\sigma_i^2}{\rho_i} \left( \frac{\partial \rho_i}{\partial R_i} \right)^2 + \frac{\sigma_i^2}{K_0} \left( \frac{\partial K_0}{\partial R_i} \right)^2 + \frac{\sigma_i^2}{K_{\text{MORB}}} \left( \frac{\partial K_{\text{MORB}}}{\partial R_i} \right)^2 \right)$$

References


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