Fusion Curve Slope and Crystal/Liquid Buoyancy

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A general solution for the slope of a fusion curve is presented. It is not the Clausius-Clapeyron equation which is a special case for one-component systems. The connection between fusion curve slope and crystal/liquid buoyancy is obscure in multicomponent systems even though the slopes of fusion curves for any given composition are always well defined. The olivine flotation hypothesis at high pressure is poorly constrained by information derived from fusion curve analysis. Physical property measurements provide the best constraints on buoyancy questions.

INTRODUCTION

There has been much recent interest in the proposition put forward by Stolper et al. [1981] that basic silicate liquids are so compressible that they may become denser than the olivines and pyroxenes in the earth's mantle at pressures of 5-10 GPa. The possible implications of this inversion of normal density relations between magmatic liquids and coexisting crystals are quite important for the early differentiation of the earth or any other large terrestrial planet [Nisbet and Walker, 1982; Walker, 1983; Ohtani, 1985]. Negative buoyancy of liquid at high pressure would reduce the effectiveness of the normal magmatic degassing. The profound implications of the Stolper et al. [1981] conjecture require that it be tested as thoroughly as possible. Does olivine really float in the appropriate basic silicate liquid?

Density relations between crystals and liquid can be investigated by at least two broad approaches: physical property measurements and phase equilibrium determinations. Physical property measurements by shock wave [Rigden et al., 1984; Stolper et al., 1986], ultrasonic [Rivers, 1985] and static compression [Agee and Walker, 1986] techniques on silicate liquids have suggested that the Stolper et al. [1981] conjecture is incorrect. However, fusion curve analysis results have been more equivocal, in some cases supporting the concept [e.g., Ohtani, 1984; Takahashi, 1986; Scarfe and Takahashi, 1986], in some cases producing ambiguous results [Bottinga, 1985; Shaw, 1986], and in some cases leading the author to reject the concept [Herzberg, 1985, 1987b]. It is the purpose of this paper to examine the relationship between phase equilibrium constraints and physical properties in the context of the solution of the equations for the slope of fusion curves, presented here. To anticipate our conclusion, we find that some, but not all, of the apparent discrepancy between the physical property and phase equilibrium approach can be resolved by considering the effects on liquidus curves introduced by multicomponent systems. In short, multicomponent fusion curve analysis does not provide the clearest evidence on olivine buoyancy. Olivine should float in some high-pressure ultrabasic liquids, but this conclusion comes from physical property measurements not fusion curve analysis.

SINGLE COMPONENT SYSTEMS

In simple systems (i.e., the number of chemical components C = 1) there is a direct connection between the slope of a fusion curve and the sign of the volume change between crystal and liquid when the entropy of fusion is "well behaved." Good behavior will be assumed in all subsequent discussions, and means that liquid has higher entropy than coexisting crystals. In multicomponent systems this caveat will be amended to account for compositional effects. The connection between relative crystal and liquid volumes and fusion curve slope is given by the Clausius-Clapeyron equation of thermodynamics:

\[ \frac{dT}{dP} = \frac{\Delta V}{\Delta S} = \frac{1/V - 1/V_L}{1/S - 1/S_L} \]  

where \( \rho = 1/V \) is mass density and \( V \) the specific volume. Superscripts refer to phase, so the entropy of fusion is \( \Delta S = 1/V - 1/V_L \) which by our "well behaved" caveat is positive. Equation (1) then asserts that the \( (dT/dP)_{Z=L} \) slope of the fusion curve is positive if \( \Delta V \) is positive or \( V_L > V \). This condition is equivalent to \( p < p_L \). Crystals should sink in melts along positive-sloped fusion curves.

Figure 1 illustrates the melting relations of two crystals, \( \chi_1 \) and \( \chi_2 \), in a single component system. With increasing pressure the melting curve of \( \chi_1 \) flattens with \( (dT/dP)_{Z=1} \) at \( P_m \). The slope is then negative until \( \chi_2 \) becomes the stable crystal with increasing pressure. Relations such as this, with a maximum on the melting curve, are common in systems where the more flexible liquid structure anticipates the compressive change which causes the transformation of \( \chi_1 \) to \( \chi_2 \) as the stable crystal structure. At the maximum on the liquidus, \( P_m, \) \( x_{Li} = 1 \) and at higher pressures, \( \chi_1 \) should float in its coexisting liquid. For a liquidus curve to go through a maximum, the liquid must have the same specific volume as the crystal at the maximum. Thus phase equilibrium studies of fusion curves should have a bearing on crystal-liquid density relations. The slope of the curve gives the sign of the density difference. This analysis must be modified, however, in systems of more than one chemical component.

C=2 LIQUIDS

Equation (1) gives a solution for \( dT/dP \) for coexisting C=1 crystal and liquid. The two-phase, C=1 assemblage is univariant and solvable, but no \( dT/dP \) solution can be found for the coexistence of liquid and crystal when C=1 because it is not a univariant equilibrium. Nevertheless, a specific bulk composition does possess a unique liquidus fusion curve, marking the completion of fusion, for which a definite \( dT/dP \)
slop exists. Likewise, a specific bulk composition also has a
definite solidus curve marking the beginning of fusion. Along
the C>1 liquidus curve, the liquid has composition identical to
the bulk composition but the coexisting liquid need not have the
same composition. Likewise along the C>1 solidus curve, the
solid crystalline assemblage at the start of melting has
composition identical to the bulk composition but the coexisting
liquid need not have the same composition. (In the special case
where liquidus and solidus meet, the liquid has identical
composition to the solid assemblage for a system of any number
of components [Walker, 1986]).

To solve for liquidus dT/dP requires the recognition of
additional constraints on the problem for C>1. These
constraints are derived from the requirement that the liquid
composition is fixed (at the bulk composition, for instance).
Interested readers may find Spear et al. [1982] a useful review
of the solution method.

Consider the case for C=2 where both liquid and crystal are
binary solutions. We have Gibbs-Duhem equations for each
phase. For the liquid,
\[d\mu_1 + X_2 d(\mu_2 - \mu_1) = \frac{LV}{dP} - \frac{LS}{dT} \tag{3}\]
and for the crystal,
\[d\mu_1 + X_2 d(\mu_2 - \mu_1) = \frac{x_2 LV}{dP} - \frac{x_2 LS}{dT} \tag{4}\]

Superscripts refer to crystal (\(Z\)) and liquid (\(L\)), subscripts 1
and 2 refer to the components, and \(X_2\) refers to the mass fraction
of component 2. We now have two equations in four
unknowns: \(d\mu_1, d(\mu_2 - \mu_1), dP, \) and \(dT\). But we can also write
an expression for the total differential \(d(Ix_2-Ix_1)\) in either phase
as a function of \(dP, dT, \) and \(dX_2\). Doing this for the liquid
gives,
\[d(\mu_2 - \mu_1) = \frac{LV}{dP} - \frac{LS}{dT} + LXX dLX_2 \tag{5}\]
\(LV_1\) and \(LS_1\) are the partial specific volume and entropy
of component 1 in the liquid. \(LXX\) is the second derivative of Gibbs
energy of the liquid with respect to the independent composition
variable \(X_2\). The last term on the right-hand side of (5)
vanishes because \(dLX_2 = 0\) by the fixed liquid composition
constraint. We can further reduce the number of variables by
taking their ratio so that (5) becomes, for example,
\[\frac{d(\mu_2 - \mu_1)}{dP} = \frac{1}{LX_2} \left(\frac{LV}{LV} - \frac{LS}{LS} \right) \left(\frac{d}{dP} LX_2 \right) \tag{6}\]
The \(1X_2\) subscript on the partial derivative indicates that \(1X_2\)
is held constant. If we invoke the equilibrium condition between
liquid and crystal, we find that
\[\frac{dL\mu_1}{dP} = -\frac{dXX \mu_1}{dP} = \text{etc.}\]

so that we now have three equations and three unknowns which
can be solved:
\[\frac{dT}{dP} = \frac{LV - [LV - x_2 \nu_1 - x_2 \nu_2 - x_2 \nu_2]}{LS - [LS - x_2 \nu_1 - x_2 \nu_2 - x_2 \nu_2]} \tag{7}\]

This is the slope for a fixed liquid composition coexisting
with its equilibrium crystal, possibly of variable composition. If
the fixed liquid composition is the same as the system bulk
composition, then (7) is the slope of the liquidus. Equation (7)
is general and could be used to trace the slope of contours of
constant melt composition within a melting interval whether or
not it was the liquidus contour. We also note, for liquid and
crystals of the same composition \((LX_2 = x_2)\) that (1) is
recovered as a special case of (7).

Now that we have (7) and have found that it is not (1), what
does it mean? It would be (1) were it not for the product of
difference terms. We can make these terms less mysterious by
reference to Figure 2, which shows the volume relations of
crystal and liquid binary solutions as a function of composition
at fixed P and T. Both solutions increase in density with the
addition of component 2. The particular crystal and liquid in
equilibrium with each other at this P-T have compositions
marked \(X_2\) and \(X_2\). The tangent to the \(LV\) curve at \(X_2\) has
intercepts on the \(X_2=0\) and \(X_2=1\) sidelines which are the partial
specific volumes of the liquid, \(LV\) and \(LV\). The slope of this
tangent line is then \(LV - LV\). But this slope also
characterizes the ratio of sides -A/B of the small right triangle
with part of the tangent line as the hypotenuse. Because B is
\(X_2\), it follows that A is \(-LV - LV\). Thus A is the
product of the difference term in the numerator of (7). The
significance of this is that \(LV\) is the specific volume of the
open circle in Figure 2 and is the quantity in brackets in the
numerator of (7), to which we give the following symbol:
\[\frac{LV - [LV - x_2 - LV]}{LV - [LS - x_2 - LS]} \equiv LV_x \tag{8}\]

LV_x is the specific volume the liquid would have if it had the
same composition as the crystal with which it is in equilibrium.
It is the partial specific volume in the liquid of a component
which has the same composition as the equilibrium crystal.
Using this notation, (7) becomes,
\[\frac{dL\mu_1}{dP} = \frac{LV - [LV - x_2 - LV]}{LV - [LS - x_2 - LS]} \tag{6}\]

Fig. 1. T-P phase diagram for single-component system with two crystals
and one stable liquid.

Fig. 2. Specific volume - composition at fixed P.T for a binary system.
Liquid of composition \(X_2\) is in equilibrium with crystal of composition
\(X_2\). Open arrow C points down, indicating crystal sinking at this P.T.
Solid arrow D points up, indicating the slope of the \(dT/dP\) vs. \(X_2\) for
this \(X_2\) is positive. If \(X_2\) is the bulk composition, then the liquidus
slope is positive at this P.T.
The analogy to, but nonequivalence with, (1) is obvious. Use of the partial specific notation, referring to a component of variable composition coincident with the equilibrium crystal's, gives an equation of the form of the Clausius-Clapeyron for C=2.

But now the connection between liquidus slope and crystal buoyancy has been obscured. The liquidus slope is given by (9). The numerator of (9) and the liquidus slope are positive or negative depending on whether arrow D in Figure 2 points up or down. By contrast, crystal buoyancy depends upon the numerator on the right-hand side of (1) which indicates crystal sinking or flotation, depending on whether arrow C in Figure 2 points down or up. Arrows C and D are not the same, so the questions of buoyancy and liquidus slope are nonequivalent.

From this sort of construction it is clear that a diverting number of additional possible relationships between crystal buoyancy and liquidus slope may be discovered. Figure 3 shows some of them. These diagrams are at fixed P-T and say nothing about how these relationships change, for instance, with increasing pressure. They hold at this P-T whether or not conditions change at some other P-T and whether or not the fusion curve sustains a maximum or a minimum. Figures 3b, 3c, and 3d show that liquidus crystals can float regardless of the liquidus slope. Figure 3d is particularly interesting in that it shows that crystals can float even though the density of liquid would be decreased by crystallization of the floating solid. Thus we feel that Shaw's [1986] prescription that "crystal flotation on the liquidus is possible ... only if liquid density increases as crystallization of the floating solid proceeds" is incorrect because Figure 3d shows a counterexample. We emphasize that fusion curve slope is a poor guide to both partial specific quantities and buoyancy relations. It is easy to be misled into connecting buoyancy too directly with fusion curve slope or with the relative values of partial specific quantities. Likewise for each additional component we add, C_i, the Gibbs-Duhem equations each get an additional LXi' d(gi - gl) term and variable which can be neutralized by the judicious application of a d(X_i = 0) total differential expression with the constraint of constant liquid composition. The general solution is,

\[
\frac{\partial T}{\partial P} \bigg|_{LX_2, LX_3, X=L, C=3} = \frac{LX_2, LX_3 \frac{\partial T}{\partial P} \bigg|_{LX_2, LX_3}}{(LX_2 - LX_3)(LX_3 - LX_1)}
\]

Now there are four equations and four unknowns for C=3, which have the solution,

\[
LX_2, LX_3, X=L, C=3 = \frac{LX_2, LX_3 \frac{\partial T}{\partial P} \bigg|_{LX_2, LX_3}}{(LX_2 - LX_3)(LX_3 - LX_1)}
\]

LX_2, LX_3, X=L, C=3 = \frac{LX_2, LX_3 \frac{\partial T}{\partial P} \bigg|_{LX_2, LX_3}}{(LX_2 - LX_3)(LX_3 - LX_1)}
\]

as previously presented by Walker and Agee [1986].

For each additional component we add, C_i, the Gibbs-Duhem equations each get an additional LXi' d(u_i - u_j) term and variable which can be neutralized by the judicious application of a d(X_i = 0) total differential expression with the constraint of constant liquid composition. The general solution is,

\[
\frac{\partial T}{\partial P} \bigg|_{LX_1, X=L} = \frac{LX_1 - \sum \frac{\partial T}{\partial P} \bigg|_{LX_1, X=L}}{(LX_1 - \sum i \frac{\partial T}{\partial P} \bigg|_{LX_1, X=L}}
\]

as previously presented by Walker and Agee [1986].

The quantity in brackets in (13) for C=2 has an exactly analogous meaning to the quantity in brackets in (7) and (8) for C=2. It can be shown after some manipulation that the bracketed quantity reduces to the expression \( \sum X_i \), which is equivalent to \( LX_1 \), the partial specific volume of a component in the liquid which has the composition of the coexisting equilibrium crystal. Therefore (9) is a perfectly general result with the proviso that we note all LXi are held constant, not simply LX_2, in the \( \partial T/\partial P \) partial derivative. Consequently, the conclusions about the nonequivalence of crystal buoyancy and liquidus slope and related pitfalls drawn above for C=2 on the basis of (9) also apply to a system of any number of components.

**Solidus Curves**

Analysis of the slope of solidus fusion curves is more complex than for the liquidus. Furthermore it is less relevant to the issue of whether particular crystals will float or sink in a liquid. It might be thought to be relevant to the issue of whether
an incipient partial melt of a crystalline aggregate will be buoyant or not with respect to the residual crystal aggregate. However, as with liquidus slopes, the connection between buoyancy and slope of phase equilibrium curves is obscured when C > 1.

Some of the complexity in generalizing relations for solidus slopes arises because solidi of several sorts, with different variance, are possible. First consider the case where the solid assemblage in a particular bulk composition of an i-component system is composed of a single i-component solid solution. If melting begins without a reaction to form a second crystalline phase, then the variance and analysis are the same as for the liquidus slope. The solution for the solidus slope of the form of (9) follows immediately:

\[
\frac{\partial T}{\partial p} \bigg|_{x_i = x, x = L} = \frac{L_V - \sum_i L_{X_i} x_{X_i}}{L_S - \sum_i L_{X_i} x_{S_i}}
\]

\[\text{(14)}\]

L_V is the partial specific volume in the crystal of a component having the (variable) composition of the coexisting liquid. This sort of solidus occurs along the lower limb of a melting loop, for instance between Fe and Mg olivine compositions. Equation (14) gives the P-T slope of initial melting of a particular composition on this loop. If the fixed L_X's are not the bulk composition's, then (14) gives the slope of a crystal isopleth in the melting interval.

A different sort of solidus occurs in a system with eutectic or peritectic melting. This solidus is truly a univariant curve along which the initial melting of any number of bulk compositions occurs. Its slope can be found without recourse to special conditions of fixed composition because there are enough Gibbs-Duhem equations, one of them for each crystalline phase and one more for the liquid, to solve for C + 1 independent variable ratios. Using Cramer's rule,

\[
\frac{\partial T}{\partial p} \bigg|_{x_1 = \ldots = x_C = L} = \frac{L_V - \sum_i L_{X_i} x_{X_i}}{L_S - \sum_i L_{X_i} x_{S_i}}
\]

\[\text{(15)}\]

Equation (15) describes a univariant equilibrium in composition space of dimensionality C whereas (14) describes a C-variant equilibrium. They are different equations describing fundamentally different equilibria of different variance. The possibility of liquidus slope with variance less than C does not occur, so in this respect, solidus fusion curves are more diverse in type. However (14) and (15) have more resemblance than is obvious from their statements above. The numerator of (15) can be expanded by the second column as,

\[
\sum_{i=1}^{C} u_i \cdot x_{Vi} - u_0 \cdot L_V
\]

The denominator can be written in the same form. Dividing numerator and denominator by \(-u_0\) (the determinant of L_X's with no row substitutions of L_X's) gives for the numerator,

\[
L_V - \sum_{i=1}^{C} \frac{u_i}{u_0} x_{Vi}
\]

The meaning of \(u_i/u_0\) can be found from examination of a set of equations, one of which is

\[
f_{X_1} + f_{X_2} + \ldots + f_{X_C} = 1
\]

\[\text{(17)}\]

and C-1 of which are:

\[
x_1 X_2 \cdot f_{X_1} + x_2 X_2 \cdot f_{X_2} + \ldots + x_c X_c \cdot f_{X_c} = L_{X_2}
\]

\[
\ldots
\]

\[\text{(18)}\]

Solving these equations for \(f_{X_i}\) shows that,

\[
f_{X_i} = \frac{u_i}{u_0}
\]

\[\text{(19)}\]

But from (17) and (18), \(f_{X_i}\) can be identified as the fraction of crystalline phase \(X_i\) which would be found in the bulk composition if the bulk composition were the same as the initial melt at the solidus. Equation (15) can be rewritten in terms of these new variables as,

\[
\frac{\partial T}{\partial p} \bigg|_{x_1 = \ldots = x_C} = \frac{L_V - \sum_i c f_{X_i} x_{Vi}}{L_S - \sum_i c f_{X_i} x_{Si}} = L_V - x_{Vi}
\]

\[\text{(20)}\]

In the second equality the terms \(x_{Vi}\) and \(x_{Si}\) do not refer to the properties of any particular crystal but to the bulk crystalline aggregate if this \(X\) has the same composition as the incipient solidus liquid. The fractions \(f_{X_i}\) which are used to weight the crystalline phase abundances to arrive at this composition may be positive, or some may be negative in the case of peritectic relationships. Thus both (14) and (15) reduce, as does (13), to an equation of the form of (9) with appropriate compositional partial and phase subscripts juggled to fit the particular case. These equations all resemble the Clausius-Clapeyron equation (1) but are not the same, especially in the context of slope versus buoyancy relations. Fusion curve slope and crystal/liquid buoyancy relations are not straightforward in multicomponent systems, as they are when the Clausius-Clapeyron equation applies.

Equations (14) and (15) illustrate the limiting cases of variance for solidus curves. Solidi of variance between the limits of C and 1 also exist. For example, a ternary system having a solid assemblage comprised of only two ternary solutions would have its initial melting behavior described neither by (14) or (15). However, it is possible with appropriate phase and component bookkeeping to show that for any solidus curve,
where the $X$ superscript again refers to the solid of however many phases (between 1 and C) are present at the solidus. Thus the form of (9) is general for all fusion curves.

Some conclusions which will be useful in our investigation of the relation between slope and buoyancy can be drawn from these various equations. Figure 4 illustrates the quantities in solidus equation (14) for a system of C=2. It is analogous to Figure 2 for illustrating the quantities in the liquidus equation. The solid arrow indicates solidus slope, whereas the open arrow indicates crystal buoyancy. They are not equivalent, and the reader is again referred to the constructions of Figure 3 to reinforce the lack of direct connection between buoyancy and slope.

Figure 5 complements (15) and illustrates the cases of eutectic and peritectic solidi in terms of $S$, $V$, and $X^2$. Consider Figures 5a and 5b for the eutectic which shows the values of $V$, $S$, and $X^2$ for two crystalline phases $X_1$ and $X_2$ and a liquid with composition between $X^1X^2$ and $X^2X^2$. Note in 5b that $LSX^1SX^2$ is consistent with our "well-behaved" entropy caveat for melting. In Figure 5a we find, however, that $2LV^V-2LV^S$. Thus the issue of whether the eutectic liquid is upward, downward, or flat with respect to its residual crystal aggregate is in principle indeterminant unless the proportion of phases is known. If the crystals are mostly $X_1$ then the liquid is buoyant; if they are mostly $X_2$ then the liquid is not. This indeterminancy underlines a generic contrast melting. (Note that this is not synonymous with the statement that the entropy of the liquid is greater than that of the crystals.)

This is most easily seen when (15) is rewritten in the form of (20). The determinant in the numerator of (15) is equivalent to the difference in volumes represented by the black arrows in Figures 5a and 5c connecting the liquid and the solid phases when they are taken in the proportions necessary to make the solid aggregate have the same composition as the liquid at the solidus. The determinant in the denominator of (15) has an analogous interpretation for entropy. Whether these arrows point up or down is arbitrary, but if we choose to place the tail on the solid and the point on the liquid, then these arrows give the sign of the change for a melting reaction. In this convention an arrow pointing up indicates a positive entropy or volume of melting. (Note that this is not synonymous with the statement that the entropy of the liquid is greater than that of the solid coexist with liquid of composition $X^2$. Although the entropy of the liquid is lower than that of the crystals in Figure 5d, the entropy determinant is well-behaved. Thus even though liquid in Figure 5c is denser than either crystal $X_1$ or $X_2$, the solidus slope is still positive because the solid slope arrow points up.

Fig. 5. Volume - entropy - composition diagrams for univariant solidi of eutectic and peritectic types in a binary system. Crystals of compositions $X^1X^2$ and $X^2X^2$ coexist with liquid of composition $X^2$. Although the entropy of the liquid is lower than that of the crystals in Figure 5d, the entropy determinant is well-behaved. Thus even though liquid in Figure 5c is denser than either crystal $X_1$ or $X_2$, the solidus slope is still positive because the solid slope arrow points up.

General Fusion Curve Slope

Whether fusion curve slopes are positive or negative or flat may be found in the graphical construction of arrows from solid to liquid of equivalent composition for two-component systems. In Figure 2 this means draw an arrow from the crystal composition to the tangent to the $LV$ curve at $(LV_{X_2})$. In Figure 4 this means an arrow from the tangent to the $LV$ curve (at $LV_{X_1}$) to
Having belabored the gaps between buoyancy and slope, we now perversely examine the obscured relations which do exist. Shown as binary between the composition of the crystal and that of the liquid, the "entropy crossovers" are more likely to be a danger. These quantities are shown in Figure 5, indicating that the density of the liquid is smaller than that of either crystal yet be lower than the X1 to X2 curves and their bearing on the Stolper et al. (1981) conjecture. Questions of buoyancy and slope can then be evaluated by the methods presented above. This analysis would not be of much concern if either the high-pressure physical property measurements or equations of state of liquid were well known. Then buoyancy could be directly evaluated without reference to fusion curves. Because the high-pressure data base and equations of state of liquids are poorly known, the fusion curve analysis is of interest as an indirect constraint on the buoyancy problem. We now examine the situation for liquidus slope without reference to volume considerations. Liquid and crystal densities at 1 atmosphere are reasonably well known. For example the partial molar volumes for silicate liquid components can be used to calculate the specific volumes of a komatiite liquid and liquid olivine of Fo93, at the liquidus temperature [Bottinga and Weill, 1970; P. A. Lange and T. E. Carns, personal communication of Na2O-K2O-CaO-MgO-FeO-Fe2O3-Al2O3-TiO2-SiO2; Na2O-K2O-CaO-MgO-FeO-Fe2O3-Al2O3-TiO2-SiO2 liquids: New measurements and derived partial molar properties, submitted to Geochimica et Cosmochimica Acta, 1987] we assume ideal Murnaghan equation of state with correction for thermal expansion along the liquidus. Fo93 olivine volumes are from Hazen (1977). Numerical details of the liquidus and the compression measurements are from C. Agee and D. Walker (manuscript submitted to J. Geophys. Res., 1987). Thermal expansion taken as 8 x 10^-6/°C for all liquids.

**Fig. 6** (a) Specific volume – composition diagram for liquid and liquidus crystal in a system of arbitrary number of components at P=0 and liquidus temperature. Numerical values correspond to those in the experimental study of C. Agee and D. Walker (manuscript submitted to J. Geophys. Res., 1987) for komatiite liquid and liquid olivine of Fo93. (b) Volumes of Figure 6a as an isothermal function of P for the simple equation of state written in the floating box. Values of the bulk modulus K are given on each curve. The curve crossing at P=0 delineates the transition to floating liquidus olivine with high pressure. The curve crossing at P=0 delineates the transition to negative liquidus slope. (c) Volumes of Figure 6a as a function of P and T (along the liquidus of komatiite). The komatiite liquid volume comes from static compression measurements to 6 GPa. A data point from Agee and Walker is shown with error bars. The Fo93 liquid volumes come from use of the listed parameters in a third-order Birch–Murnaghan equation of state with corrections for thermal expansion along the liquidus. Fo93 olivine volumes are from Hazen (1977). Numerical details of the liquidus and the compression measurements are from C. Agee and D. Walker (manuscript submitted to J. Geophys. Res., 1987). Thermal expansion taken as 8 x 10^-6/°C for all liquids.

**Discussion**

The foregoing analysis is independent of the particular equation of state which the substances obey. No assumptions about the compressibility, its derivatives, thermal expansion, and its derivatives, etc., need enter the determination of buoyancy or fusion curve slope. All that is needed are the volumes, entropies, and their compositional derivatives, not their P,T derivatives. Unfortunately, volumes and entropies are not tabulated for all the necessary compositionally varying substances at the P and T of interest. Therefore recourse to an equation of state is necessary to supply extrapolated or interpolated values of V(P,T), etc., from measured reference states V(Po,To).

Questions of buoyancy and slope can then be evaluated by the methods presented above. This analysis would not be of much concern if either the high-pressure physical property measurements or equations of state of liquid were well known. Then buoyancy could be directly evaluated without reference to fusion curves. Because the high-pressure data base and equations of state of liquids are poorly known, the fusion curve analysis is of interest as an indirect constraint on the buoyancy problem. We now examine the situation for liquidus curves and their bearing on the Stolper et al. (1981) conjecture that geologically interesting olivines can float in geologically interesting silicate liquids.

Liquid and crystal densities at 1 atmosphere are reasonably well known. For example the partial molar volumes for silicate liquid components can be used to calculate the specific volumes of a komatiite liquid and liquid olivine of Fo93, at the liquidus temperature [Bottinga and Weill, 1970; P. A. Lange and T. E. Carns, personal communication of Na2O-K2O-CaO-MgO-FeO-Fe2O3-Al2O3-TiO2-SiO2; Na2O-K2O-CaO-MgO-FeO-Fe2O3-Al2O3-TiO2-SiO2 liquids: New measurements and derived partial molar properties, submitted to Geochimica et Cosmochimica Acta, 1987] we assume ideal Murnaghan equation of state with correction for thermal expansion along the liquidus. Fo93 olivine volumes are from Hazen (1977). Numerical details of the liquidus and the compression measurements are from C. Agee and D. Walker (manuscript submitted to J. Geophys. Res., 1987). Thermal expansion taken as 8 x 10^-6/°C for all liquids.
of the liquid even though the whole system clearly is not binary. This is permissible at one P and T where there are only two compositions of interest: the crystal's and the liquid's. This diagram could not be used to rigorously examine the effects of crystallization but suffices for the analysis of buoyancy and slope at this P, T. By our previous analysis we can see that these volumes indicate Fo93 olivine should sink in komatiite at its 1-atm, positively sloped liquidus. This agrees with experimental observations.

How do these relations change with pressure? In Figure 6b we have applied a simple-minded isothermal equation of state to the \( V_0 \) values of Figure 6a. Values of the bulk modulus, K, liquidus slope parameters for that case, are shown on the figure. Since we are only looking at this question as an interpretation of data, it makes no sense to consider two sets of shock wave data or their mixtures. Figure 6c gives projected volume curves which intersect each other with increasing pressure. Two of these intersections are of interest for buoyancy and slope, the third is somewhat less interesting. The intersection at \( P_B \) of the solid-beaded \( V \) curve with the diamond \( V \) curve defines the density crossover. At \( P_S \) the intersection of the \( LV_{Fo93} \) open beaded curve with the \( X \) curve reflects the rollover of the liquidus from positive sloped at lower pressure to negative sloped at higher pressure. The intersection at lower pressure of the two beaded curves represents a change in sign of \( \left(\partial P / \partial T\right)_V < 0 \); otherwise it has no significance.

Several points are worth making. First, the intersection pressures \( P_B \) and \( P_S \) are different, so liquid rollover does not correspond to buoyancy change. Second, they could be the same only by accidental parameter choices. Third, \( P_S > P_B \) for those parameters. In the absence of evidence to the contrary, one might assume that both liquid curves should have the same compressibility, so that \( L \) and \( LV_{Fo93} \) should descend on similar noncrossing trajectories. If that were the case, then \( P_S < P_B \) would follow from the relatively well determined \( L \) and \( LV_{Fo93} \). But many authors have suggested that there is a compositional dependence to liquid compressibility. These suggestions have come from analysis of ultrasonic measurements by Rivers [1985] and from a variety of simple system mineral fusion curves analyzed by Ohtani [1984], Herzberg [1985], Bottigia [1985], and most forcefully by Herzberg [1987a]. These suggestions are marginally supported by shock wave [Stolper et al., 1986] density measurement although the extent and full characterization of the compositional effect remains controversial. If there is a consensus opinion among these suggestions, it is that olivine components contribute to incompressibility to normal basic and ultrabasic silicate liquids, whereas silica and aluminosilicate components increase liquid compressibility. For this reason we adopt the relative compressibilities shown on Figure 6b which lead to \( P_S < P_B \).

In defending the olivine flotation proposition, the question often arises as to why the liquid of the appropriate liquids do not mix. In view of the results shown by our previous analysis we can see that calculated from two different sets of shock wave and simple fusion curve parameters. Olivine volumes as a function of T and P are from Hazen [1977]. Evidently sophistication of equations does not clarify the situation. The upper beaded curve based on fusion curve compression parameters predicts no liquidus rollover at all. The lower starred curve based on the suggested parameters of Stolper et al. [1986] predicts \( P_S < P_B \). Enough latitude exists in suggested liquid olivine compression parameters to allow prediction of \( P_S \) either above or below \( P_B \). But if the parameters for the lower starred curve are correct, liquidus rollover should occur at pressures much lower than those reported. In fact these parameters would predict a liquidus maximum (and crystal flotation) at \( < 4 \) GPa for pure forsterite which is definitely not observed. This casts some doubt on whether this bulk modulus for fayalite olivine liquid [Rivers, 1985] really is a reliable guide to the compression parameters for forsteritic olivine liquids.

The resolution of these incompatible conclusions is not clear. We do not feel that it is possible or even necessary to choose between the correctness of the liquidus observations or the correctness of the compositional variation of the liquid compression parameters. (Both could be wrong although both could be right given present uncertainties.) We do restate one of our assumptions: ideal volume mixing. We need to know the partial specific volume of Fo93 in komatiite liquid, not the specific volume of liquid Fo93. They are the same for ideal mixing. Should volumes not mix ideally at high pressures, then the volumes of liquid olivines are irrelevant to both slope and buoyancy of komatiite liquid. The safest conclusion to draw from this is that fusion curve slope provides slim constraint on the buoyancy question.

**Conclusions**

A general solution to the fusion curve slope problems allows a simple graphical test for slope sign if \( V(T,X) \) relations are known at the P, T of interest. The analysis suggests a framework (V-P diagram) for testing the compatibility of various compression parameters with liquidus slope. The current high-pressure data set includes a rich inventory of possible contradictions, which we trust will be resolved by renewed investigation. The implication of this analysis is that renewed investigation of the buoyancy problem should proceed through high-pressure property measurements, not detailed fusion curve observations.

**Appendix: General Proof of**

\[
\left(\frac{\partial V}{\partial P}\right)_{\text{solidus}} = \left(\frac{\partial V}{\partial P}\right)_{X_{V}} \frac{V_{X} - V_{K}}{S_{X} - S_{K}}
\]

Consider a C component system with K + L phases at the solidus, where K phases are crystalline and L phase is liquid. K must be smaller than or equal to L because the variance in the system must be at least 1 so that T and P are not fixed and so that \( \partial T / \partial P \) can be evaluated. Therefore K ranges from 1 to C and variance in the system ranges from C to L.

The case in which K = 1 has been solved by equation (14), which is

\[
\left(\frac{\partial T}{\partial P}\right)_{\text{solidus}} = \left(\frac{\partial T}{\partial P}\right)_{X_{V}} \frac{V_{X} - V_{K}}{S_{X} - S_{K}} \frac{1}{C} \sum_{i=1}^{C} x_{i} V_{i}
\]

\[
= \sum_{i=1}^{C} \frac{x_{i} S_{i}}{S_{X}}
\]
where \( zV_i \) is the partial specific volume of the crystalline phase of a composition exactly the same as the coexisting liquid. The imaginary crystal composition is realized by varying the composition of the crystal which is a solid solution.

The case for \( K = C \) has been solved by equation (20), which is:

\[
\left( \frac{\partial T}{\partial P} \right)_{\text{solute}} = \frac{1}{1 - zV_L} \sum_{i=1}^{C} \xi_i \left( zV_j - zV_L \right)
\]

(AD2)

where \( zV \) is the partial specific volume of crystalline phase \( \chi_i \) and \( f_{i,j} \) the imaginary fraction of \( \chi_i \) which makes the composition of the imaginary crystal assemblage identical to liquid composition. We notice that the difference between equations (A1) and (A2) is that the imaginary crystal (or crystal assemblage) composition which is identical to liquid composition is made possible by varying the composition of the crystal itself in equation (A1) because there is only one crystalline phase of solid solution and by varying the fraction of each crystalline phase in equation (A2) because composition of each phase is fixed by phase relations. Therefore we propose the following form to be the general solution of \( \frac{\partial T}{\partial P} \):

\[
\left( \frac{\partial T}{\partial P} \right)_{\text{solute}} = \frac{1}{1 - zV_L} \sum_{i=1}^{C} \xi_i \left( zV_j - zV_L \right)
\]

(AD3)

where \( f_{i,j} \) is the imaginary fraction of phase \( \chi_i \) and \( zV_j \) is the imaginary fraction of the jth component in phase \( \chi_i \). \( zV_j \) and \( f_{i,j} \) together make the composition of the imaginary crystalline assemblage identical to that of liquid, that is, \( zV_j \) and \( f_{i,j} \) satisfy:

\[
\sum_{i=1}^{K} f_{i,j} \cdot zV_j = 1 \chi_j \quad \text{for } j = 1, 2, \cdots, C \quad \text{(A4)}
\]

\[
\sum_{i=1}^{K} f_{i,j} = 1 \quad \text{for } i = 1, 2, \cdots, K \quad \text{(A5)}
\]

\[
\sum_{i=1}^{K} \xi_i f_{i,j} = 1 \quad \text{(A6)}
\]

The use of \( zV_j \) is intended to distinguish the imaginary composition from the actual composition \( xV_p \). Because (A6) is true when both (A4) and (A5) are true, only (A4) and (A5) are independent.

We now proceed to prove the proposed solution.

1. Equations to solve \( \frac{\partial T}{\partial P}_{\text{solute}} \) are the following:

   (1) K + 1 Gibbs-Duhem equations:

   \[
   \sum_{i=1}^{K} f_{i,j} \cdot zV_j = 1 \chi_j \quad \text{for } j = 1, 2, \cdots, C
   \]

   \[
   \sum_{i=1}^{K} f_{i,j} = 1 \quad \text{for } i = 1, 2, \cdots, K
   \]

   \[
   \sum_{i=1}^{K} \xi_i f_{i,j} = 1
   \]

   [for liquid, 1 equation]

   \[
   \sum_{i=1}^{K} f_{i,j} \cdot zV_j = 1 \chi_j \quad \text{for } j = 1, 2, \cdots, C
   \]

   \[
   \sum_{i=1}^{K} f_{i,j} = 1 \quad \text{for } i = 1, 2, \cdots, K
   \]

   [for crystals, K equations]

   (2) K(C - 1) equations for \( \frac{\partial (\xi_i - \mu_i)}{\partial P} \) derived from total differential \( d(\xi_i - \mu_i) \) in phase \( \chi_i \):

   \[
   \frac{\partial (\xi_i - \mu_i)}{\partial P} = \left( xV_j - xV_L \right) \frac{\partial T}{\partial P}
   \]

2. Solution for \( \frac{\partial T}{\partial P}_{\text{solute}} \) is as follows: \( \frac{\partial T}{\partial P}_{\text{solute}} \) can be solved from the set of equations (A7) according to Cramer's rule as follows:

\[
\left( \frac{\partial T}{\partial P} \right)_{\text{solute}} = \frac{\text{det} A}{\text{det} A_{\text{v}}}
\]

(AD8)

where \( A_{\text{v}} \) is the coefficient matrix and \( |A_{\text{v}}| \) is the determinant of \( A_{\text{v}} \) and \( A_{\text{v}} \) is the matrix substituting the first column of \( A_{\text{v}} \) by the right-hand-side column of equations (A7). \( A_V \) and \( A_{\text{sv}} \) are similar except the first column where similar partial specific volume corresponds to partial specific entropy. Therefore, to simplify the right-hand side of equation (AD8), we need only to consider \( |A_{\text{v}}| \).

The matrix \( A_V \) is written in explicit form as follows:
We define $G$ to be a submatrix of $A_{V}$ by crossing out the first column of $A_{V}$ and note that $G$ is also the submatrix by crossing out the first column of $A_{S}$. We define $G_{m}$ to be a submatrix of $G$ by crossing out the $m$th row of $G$. Notice that $G_{m}$ is a square matrix. We define $g_{n}$ to be a column vector which is the $n$th column of $G$. We also define $a_{mn}$ to be an element of $G$ at the $m$th row and $n$th column. $a_{mn}$ can be expressed as follows:

\[
A_{mn} = \begin{cases} 
1 & n = 1, \quad 1 \leq m \leq K + 1 \\
0 & n = 1, \quad m > K + 1 \\
1 & 2 \leq n \leq C, \quad m = 1 \\
1 & 2 \leq n \leq C, \quad 2 \leq m \leq K + 1 \\
\delta_{m,n} & 2 \leq n \leq C, \quad K + 1 < m \leq KC + 1, \\
& \text{where} \quad k_{m,n} = K + 1 + (i-1)(C-1) + n - 1 \\
0 & 2 \leq n \leq C, \quad m > KC + 1 \\
0 & n > C, \quad m \leq K + 1 
\end{cases} \tag{A10}
\]

$|A_{V}|$ can be expanded by the first column as

\[
|A_{V}| = \frac{1}{G_{1}} \sum_{i=1}^{K} (-1)^{i} x_{V_{i}} |G_{i+1}| + \sum_{i=1}^{K} \sum_{j=2}^{C} (-1)^{m_{i,j} + 1} (x_{V_{j}} - x_{V_{i}}) |G_{m_{i,j}}| \tag{A11}
\]

where

\[
m_{i,j} = K + 1 + (i-1)(C-1) + j - 1 \tag{A12}
\]

Divide the above by $|G_{1}|$, then

\[
\frac{|A_{V}|}{|G_{1}|} = \frac{x_{V}}{x_{V_{imag}}} \tag{A13}
\]

where

\[
x_{V_{imag}} = -\frac{1}{G_{1}} \sum_{i=1}^{K} (-1)^{i} x_{V_{i}} |G_{i+1}| + \sum_{i=1}^{K} \sum_{j=2}^{C} (-1)^{m_{i,j} + 1} (x_{V_{j}} - x_{V_{i}}) |G_{m_{i,j}}| \tag{A14}
\]

Our task now is to prove

\[
x_{V_{imag}} = x_{V_{L}} \sum_{i=1}^{K} \sum_{j=1}^{C} x_{X_{j}} x_{V_{i}} \tag{A15}
\]

which leads to (from (A8))

\[
\left( \frac{\partial T}{\partial P} \right)_{solidus} = \frac{|A_{V}|}{|G_{1}|} = \frac{|A_{V}|}{|G_{1}|} = \frac{x_{V}}{x_{V_{imag}}} = \frac{x_{V}}{x_{V_{imag}}} \tag{A9}
\]
then we can interpret \( z\mathbf{V}_{\text{imag}} \) as \( z\mathbf{V}_L \), that is, we then would have proven the final form.

Because definitions (A17) do not define \( f_x \) and \( zY_j \) separately, any set of \( f_x \) would be compatible with (A17). Now we define

\[
 f_{z_i} = (-1)^{i+1} \frac{|G_{i+1}|}{|G_i|}
\]

(A21)

then

\[
 f_{z_i} \sum_{j=1}^{c} zY_j = \sum_{j=1}^{c} f_{z_i} zY_j
\]

\[
 = - \frac{1}{|G_i|} \left\{ \left( (-1)^{i+1} zX_i |G_{i+1}| \right) - \sum_{j=2}^{c} (-1)^{m_{ij}+1} |G_{m_{ij}}| \right\}
\]

\[
 + \sum_{j=2}^{c} (-1)^{m_{ij}+1} |G_{m_{ij}}|
\]

\[
 = - (-1)^i \frac{|G_{i+1}|}{|G_i|}
\]

Therefore

\[
 \sum_{j=1}^{c} zY_j = 1
\]

(equation (A19) or equation (A5) is proven). Now we need only to prove equation (A18) (or equation (A4)).

Equation (A18) is equivalent to

\[
 -LX_j |G_i| = \sum_{i=1}^{K} \left\{ (-1)^j zX_i |G_{i+1}| \right\} + \sum_{j=2}^{c} (-1)^{m_{ij}+1} |G_{m_{ij}}|
\]

\[
 j = 2, 3, \cdots, C
\]

(A22a)

and

\[
 -LX_j |G_i| = \sum_{i=1}^{K} \left\{ (-1)^j zX_i |G_{i+1}| \right\} + \sum_{j=2}^{c} (-1)^{m_{ij}+1} |G_{m_{ij}}|
\]

\[
 (A22b)
\]

Let

\[
 \varphi_1 = \langle X_1 |G_i| \rangle + \sum_{i=1}^{K} \left\{ (-1)^j zX_i |G_{i+1}| \right\}
\]

\[
 = \sum_{i=1}^{K} \left\{ (-1)^j zX_i |G_{i+1}| \right\} + \sum_{j=2}^{c} (-1)^{m_{ij}+1} |G_{m_{ij}}|
\]

(A23a)

and

\[
 \varphi_j = \langle X_j |G_i| \rangle + \sum_{i=1}^{K} \left\{ (-1)^j zX_i |G_{i+1}| \right\} + \sum_{j=2}^{c} (-1)^{m_{ij}+1} |G_{m_{ij}}|
\]

\[
 j = 2, 3, \cdots, C
\]

(A23b)

Then equation (A18) is equivalent to

\[
 \varphi_j = 0 \quad \text{for} \quad j = 1, 2, \cdots, C
\]

(A24)

We first prove \( \varphi_j = 0 \) for \( j = 2, 3, \cdots, C \), then prove \( \varphi_j = 0 \). For \( j = 2, 3, \cdots, C \), we have (using (A10))

\[
 \varphi_j = a_{1j} |G_i| + \sum_{i=2}^{K} (-1)^{i+1} a_{ij} |G_i|
\]

\[
 + \sum_{i=1}^{K} (-1)^{m_{ij}+1} |G_{m_{ij}}|
\]

(A25)

Now consider

\[
 \sum_{m=K+2}^{K+C+1} (-1)^{m_{ij}+1} a_{mj} |G_m| = \sum_{m=K+2}^{K+C+1} (-1)^{m_{ij}+1} \delta_{jk} |G_m|
\]

(A26)

where

\[
 k_{ij} = (K + 1) + (i - 1)(C - 1) + j - 1 = m_{ij}
\]

for \( j = 2, 3, \cdots, C \) and \( i = 1, 2, \cdots, K \)

Therefore

\[
 \sum_{m=K+2}^{K+C+1} (-1)^{m_{ij}+1} a_{mj} |G_m| = \sum_{i=1}^{K} (-1)^{k_{ij}+1} a_{ij} |G_i|
\]

(A27)

Replacing the third term in (A25) by (A27), we get

\[
 \varphi_j = \sum_{i=1}^{K+C+1} (-1)^{i+1} a_{ij} |G_i| = \langle g_j |G \rangle
\]

(A28)

We now prove \( \varphi_j = 0 \). Using (A27), \( \varphi_j \) can be rewritten

\[
 \varphi_j = \langle X_j |G_i| \rangle + \sum_{m=K+2}^{K+C+1} (-1)^{m_{ij}+1} X_i |G_m|
\]

\[
 + \sum_{m=K+2}^{K+C+1} (-1)^{m_{ij}+1} |G_m| \left[ \sum_{j=2}^{c} (-a_{mj}) \right]
\]

(A29)

where \( \gamma \) is a column vector and its transpose is

\[
 \gamma^T = \left[ \begin{array}{cccc}
 \langle X_1, s_1X_1, \cdots, zX_1, \\
 -s_2X_1, \cdots, -s_{K+C+1}X_1,
\end{array} \right]
\]

(A30)

Examining (A9) and (A30), we notice that

\[
 \gamma = g_1 - \sum_{j=2}^{c} g_j
\]

(A30)

Therefore the first column of determinant \( \gamma |G| \) is a linear combination of the next \( C \) columns; therefore

\[
 \varphi_j = 0 \quad \text{for} \quad j = 2, 3, \cdots, C
\]

(A31)

Combining (A28) and (A31), we proved (A24), which is equivalent to (A4). This concludes our proof of

\[
 \frac{\partial \mathbf{V}}{\partial \mathbf{P}} \bigg|_{\text{solidus}} = \frac{1}{T_S} \mathbf{V}_L - \mathbf{V}_S
\]

Acknowledgements. We thank J. F. Hays for originally pointing out the inadequacies of the Clausius-Clapeyron equation. The manuscript has substantially benefited from the detailed review comments of J. Stout, D. C. Presnall, and an anonymous reviewer. This work was supported by grants from the National Science Foundation and Department of Energy although this support does not constitute an endorsement of the views expressed here. Lamont-Doherty Geological Observatory Contribution No. 4199.
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