Linear partitioning in binary solutions: a review with a novel partitioning array

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ABSTRACT

Linear partitioning refers to a graphical plot of a partition ratio $D$ against a composition ratio $X_2$ given as the mole fraction of a refractory component 2. When this plot is linear from $D = 1.0$, $X_2 = 0.0$, its intercept at $X_2 = 1.0$ is a value on the $D$ scale here identified as the value of the exchange coefficient $K_D$. The plot is generated from phase compositions 1,2 in states $L_V$ or $L_S$ or $S_S$ depending on whether the system is a boiling mixture, a melting equilibrium, or a solid-solid equilibrium. The linear partitioning equation so generated is a mathematical description of a binary solution loop, and it has the form $y = ax + b$ where $y = D$, $a = K_D$, $x = X_2$, and $b = 1-x = 1-X_2$. In practice, the linearity is tested by regressing values of $D$ against $X_2$ to find the intercept $K_D$. If linearity occurs, the system is a binary solution loop; if it does not occur, the system is not a binary loop. Strict linearity is not always observed even in true binary solutions; in such cases the path to $K_D$ may be either segmented or moderately curved. Such is the case with the melting equilibria of both plagioclase and olivine, possibly a clue to the non-ideality of solution. Loop width is an inverse function of $K_D$, and can vary with pressure as in the case of plagioclase in troctolites and gabbros.

Systems with two loops joined at a common minimum or maximum are called
azeotropes and all of them show linear partitioning. Sanidine crystalline solutions form a classic example of such behavior. When the system An-Ab is revisited to repeat the Bowen thermodynamic calculation from the latent heats of fusion with modern data, the array shows a single modest curvature. The monoclinic pyroxene pairs augite and pigeonite form a binary loop; augite - orthopyroxene does not. The olivine compositions of rocks in the Kiglapait intrusion follow a linear partitioning line with $K_D = 0.26$ for data above fifty percent crystallized (50 PCS). All the rocks below 50 PCS occupy a new trend in the linear partitioning diagram. This trend is anchored at $D = 0.0, X_2^S = 1.0$ and runs to the calculated liquid composition at its intercept with the $D = 1.0$ upper bound. The new trend is the graphical solution to the ambient liquid composition given the crystal composition and the value of $K_D$. Its origin involves at least three working hypotheses not yet fully explored.

Key words: Binary solutions, linear partitioning, phase equilibrium, plagioclase, olivine, augite, melting, crystallization.

**INTRODUCTION**

Linear partitioning in binary solutions is a device by which fractionation or reactive equilibrium processes can be explored mathematically and compared with natural or experimental results. Linearity occurs when a ratio of mole fractions is a linear function of composition in a binary solution. If this condition fails to occur, the object studied is not a binary solution. In this review the intent is to organize previous derivations and expositions into a concise collective whole with examples drawn from boiling mixtures, feldspars, pyroxenes and olivine. This exercise results in a geometrical solution to the problem of finding the liquid composition of a binary mixture when the crystal composition and crystal-liquid exchange coefficient are known or given. It is then possible to introduce a new and unforeseen application that defines a liquid composition but has plausible origins still being explored.

Abbreviations used in this paper are listed in Table 1.
GENERAL CONSIDERATIONS

The linear partitioning equation is the mathematical description of a binary solution loop. It is the simple equation $y = ax + b$ where $y$ is the partition coefficient, $a$ is the exchange coefficient, $x$ (in melting equilibria) is the refractory crystal composition, and $b = 1-x$. This equation first appeared in a discussion of olivine in the Kiglapait Intrusion (Morse, 1996) in which its chief purpose was to aid in the calculation of Rayleigh fractionation by iteration in small steps. This operation was accomplished by adjusting the partition coefficient at every step of the iteration using the current value of the exchange coefficient. For melting equilibria the linear partitioning equation takes the form

$$D = K_D \cdot X_2^S + X_1^S \quad (1)$$

where $D$ is the partition coefficient set $\leq 1.0$ and defined as $X_1^S/X_1^L$, $X$ is a mole fraction, $S$ is a solid crystalline solution, $L$ is liquid, component 1 is the low-temperature melting component and component 2 the corresponding high-temperature melting component. The exchange coefficient $K_D$ is the double ratio of moles $n$: $(n1/n2)^S$ so formed also as to be $\leq 1.0$. The equation is generally used by regressing values of $D$ against $X_2^S$ to test for unity at $X_2^S = 0$ and to find the intercept $K_D$ at $X_2^S = 1.0$.

This formulation, developed more fully below, was then subsequently tested against a variety of melting equilibria, boiling mixtures ($L-V$ equilibria), and solid-solid assemblages stimulated by the suggestion of garnet-chlorite or biotite-garnet Mg-Fe exchange within multi-component systems (Ramberg, 1952). The history after the olivine application is contained in papers by Morse (1997, 2000, 2001) and summarized in Morse (2013).

Some results of these explorations are listed in Table 2. They run from the standards of igneous petrology in the melting loops of olivine, plagioclase, alkali feldspars and pyroxenes, to systems with water, systems at pressure, solid-solid mantle equilibria such as magnesiowüstite, spinel, augite-olivine equilibria, chlorite-garnet and high-temperature biotite-garnet. Another
result in multi-component systems is the increase of $K_D$ with pressure for plagioclase crystallizing with pyroxene and olivine, to a value exceeding 1.0 at 15 kbar (Morse, 2013), a result that would suggest the presence of an azeotrope (a melting maximum) except that it is in fact the breakdown of plagioclase to spinel, garnet, and two aluminous pyroxenes (McIntosh, 2009).

For $L$-$V$ and $S$-$S$ equilibria the notation of linear partitioning needs to be changed to be more general in terms of components and ratios. This is done in Morse (2000) and need not concern us in the present mineralogical context. There are attendant thermodynamic considerations, developed in that paper as well; these are of secondary interest here.

**SYSTEMATICS OF LINEAR PARTITIONING**

**Notation**

The conventions of Beattie et al. (1993) are followed herein. Problems eternally arise because in some conventions the partition coefficient $D$ and the exchange coefficient $K_D$ have been interchanged, at least in name. The distinction can be important, because in the convention adopted here the partition coefficient can have a thermal dimension whereas the exchange coefficient is rigorously athermal. The partition coefficient is akin to the Nernst distribution coefficient and has often been called that in the older geochemical literature.

**ALGEBRAIC DERIVATION FOR MELTING OF CRYSSTALLINE SOLUTIONS**

Here we derive equation (1) for melting equilibria so as to clarify each step of the development. For a solid phase $S$ and liquid phase $L$ we define the partition coefficient $D$ set always to be $\leq 1.0$ and hence

$$D_{X_1}^{SL} = \frac{X_1^S}{X_1^L} \quad (2)$$
where the mole fraction $X_i$ is the normalized fraction of the low-melting component (1), i.e.

$$X_1 = \frac{n_1}{n_1 + n_2} \quad (3)$$

where $n$ is the number of moles and component (2) is the high-melting component. The notation may apply in other cases with different names, to units of mass, gram-atoms, or oxygen-normalized cations. Defining the exchange coefficient $K_D$ as

$$K_{D(n1/n2)}^{S/L} = \frac{(n_1 / n_2)^S}{(n_1 / n_2)^L} \quad (4)$$

and using this, we obtain

$$D_{X_1}^{S/L} = K_{D(n1/n2)}^{S/L} \cdot (1 - X_1^S) + X_1^S \quad (5)$$

$$= (K_D \cdot X_2^S) + X_1^S \quad (6)$$

which is the linear partitioning equation relating the partition coefficient to the exchange coefficient via the crystal compositions (Morse, 1996).

**Proof**

The above result is shown to be true as follows, using for petrologic interest a familiar case of olivine melting (Morse, 1997). Defining

$$K_D = \frac{\left(\frac{n_{Fe}}{n_{Mg}}\right)^S}{\left(\frac{n_{Fe}}{n_{Mg}}\right)^L} = \frac{\left(\frac{X_{Fe}^S}{X_{Mg}^S}\right)}{\left(\frac{X_{Fe}^L}{X_{Mg}^L}\right)} = \frac{X_{Fe}^S}{X_{Fe}^L} \cdot \left(\frac{1 - X_{Fa}^S}{1 - X_{Fa}^L}\right) \quad (7)$$
we have
\[ K_D (X_{Fa}^L) \cdot (1 - X_{Fa}^S) = X_{Fa}^S (1 - X_{Fa}^L) \] (8)

\[ K_D (X_{Fa}^L) - K_D X_{Fa}^L \cdot (X_{Fa}^S) = X_{Fa}^S - X_{Fa}^S X_{Fa}^L \] (9)

\[ K_D - K_D X_{Fa}^S = \frac{X_{Fa}^S}{X_{Fa}^L} - X_{Fa}^S \] (10)

and finally
\[ K_D (1 - X_{Fa}^S) = D - X_{Fa}^S \quad QED \] (11)

Discussion and an application

The geometric expression of this result is illustrated in Fig. 1. If the system is a true binary loop then the partitioning is strictly linear from (0,1) to the value of \( K_D \) at \( X_2^S = 1.0 \). This was found to be almost true for olivine as computed by Bradley (1962) from the data of Bowen and Schairer (1935), but the actual data points for Fe-rich olivines defined a slightly variable array above the linear approximation (Morse, 1997 Fig. 1). The result is that in the real case the implied value of \( K_D \) changes from 0.227 at pure Fo to 0.266 at pure Fa. Although this would seem to be a trivial difference, it is probably not erroneous. A more significant effect on olivine partitioning is the structure of the liquid, to be discussed.

Loop width and \( K_D \)

The exchange coefficient \( K_D \) carries the essential feature of the binary loop because its value relates inversely to the width of the loop. Thus a low value of \( K_D \) describes a wide or fat loop with a large distance between the solidus and liquidus, whereas a high value of \( K_D \) describes a
narrow loop. It helps to remember this relationship if note is taken that a $K_D$ of 1.0 means a loop with no width at all: a single line. This limit is actually achieved in azeotropes, systems with a maximum or minimum, as we shall see. And of course, the lower limit of $K_D = 0$ describes a rectangular box, hence no longer a loop. This loop-width feature of $K_D$ is quantified for an arbitrary special case in Fig. 2a. Figure 2b describes another feature of $K_D$, the pressure effect on natural plagioclase feldspar.

**APPLICATION TO BOILING MIXTURES**

In an earlier treatment (Morse, 2000) the formulation of equation (5) was expanded for boiling mixtures to erect a general notation for components $(i, j)$ in place of $(1,2)$ and states of matter $(L,V)$ for boiling mixtures. An example of a rigorously linear result is shown in Fig. 3 here. The cited paper also illustrated this notation in a reverse linear partitioning diagram, and one example of a boiling mixture was shown in three frames: one with $X_j$ in the liquid; one with $X_j$ in the vapor, and a third with a comparison of both $D_j^{-1}$ and $D_j$, plotted against the vapor composition. In that case the inverse formulation $D_j^{-1}$ is linear and the direct formulation $D_j$ is a concave-up curve. This reference also showed a pronounced failure of linear partitioning in a boiling mixture (CCL4 - Acetone at 0.600 bar), reproduced here as Fig. 4. In this case the strong curvature of the data require a distorted loop with a nearly isothermal tail. The reference also lists the outcome of examining 11 boiling mixtures among which five clearly failed to yield linear partitioning.

**Azeotropes**

An azeotrope is a pair of interconnected binary solutions melting (condensing) at a common point that is either a thermal (pressure) minimum or a maximum. Familiar examples in petrology are the alkali feldspars. The application of linear partitioning to azeotropes requires dual partitioning equations; the identities of components $i$ and $j$ are switched at the azeotropic point (AP). Each regression is carried out independently and each finds a unique value of the composition of the AP. These are averaged if required to find a joint solution, and the treatment
of regressions to find the intercepts at each end member is discussed in the referenced article.

Continuing the literature search in boiling mixtures, of six azeotropic mixtures examined, all were linear, including both \( T-X \) and \( P-X \) variations. Typical correlations found for azeotropes have a correlation coefficient \( R^2 > 0.99 \). Because of the common azeotropic point, all azeotropes are made of binary solution loops. This result leads us back to familiar silicate systems.

**ALKALI FELDSPARS: THE AZEOTROPIC SYSTEM Ab-Or**

Azeotropic systems are typically non-ideal mixtures. A major contribution to the science of mixing properties in crystalline solutions was made by Waldbaum (1969) on the system NaCl - KCl and by Waldbaum and Thompson (1969) on sanidine crystalline solutions in the system NaAlSi\(_3\)O\(_8\)-KAlSi\(_3\)O\(_8\), Albite-Orthoclase, Ab-Or. Because their solution models are so elegant, they make especially good examples of linear partitioning. Both systems were figured and described in Morse (2000); a new version of the Ab-Or system is shown here in Fig. 5, using all data from the original Table 2 of Waldbaum and Thompson (1969). Part A of the figure shows the \( T-X \) binary loop with a minimum, the azeotropic point AP at 1063 °C. The temperatures are uncorrected to Ab = L at 1100 °C (see the An-Ab system discussed below). The sanidine (Or component) limb is metastable with respect to leucite plus liquid, caused by the incongruent melting of Or (e.g., Morse, 1994). Part B of Fig. 5 is the linear partitioning diagram showing the separate treatments of the two limbs of the binary loop. Here the protocols described above are put to work: the identities of \( X_1 \) and \( X_2 \) (reverting to the previous notation) are switched at the AP and separate regressions are run on each. This interchange means that, for example in the Ab-rich limb, \( X_2 = Ab \) and \( X_1 = Or \); as always component (1) is the low-\( T \) component. For each limb the linear partitioning equation is modified so that \( D = K_D X_2^S + (a \cdot X_1^S) \) where \( a \) is a fitting parameter, with calculated values shown in the figure. The values of \( K_D \) are received in the regressions. As commonly found, the values at the extrema of composition are highly sensitive to rounding error and exact coincidence with the regressed limit is rare. In this example the last
data points are omitted from the regression, which has in both cases $R^2 = 0.999$.

**Effect of a third component**

Simple binary solutions are ideal systems for rigorous understanding of the geometric and physical principles underlying their behavior. In many cases, the addition of a third component would not have a profound effect on the binary equilibria. For example, the addition of quartz to the system Ab-Or cited above does not by itself change the fundamentally azeotropic nature of the binary loop, because silica is common to both binary components in similar ways. On the other hand, the addition of a new component contained in only one of the binary pairs is likely to have a significant effect. Such is the effect of adding a Ca-pyroxene to plagioclase. This classic example of the system Di-An-Ab due to Bowen (1915) furnishes yet another linear partition of interest for the information it yields. The ternary diagram in Fig. 6a (inset) reminds us of the single cotectic running through the ternary with diopside crystallizing on one side and plagioclase on the other side.

Readers may recall that the liquid in the plagioclase field runs sharply toward the cotectic, but when that is reached, the liquid makes a hard turn towards Ab and runs directly away from both of the Ca-rich phases on the Di-An sideline. Accordingly, the fractionation toward Ab speeds up greatly when the liquid is multiply-saturated. But we diverge from the task at hand. The main feature of Fig. 6a is the $T-X$ plot showing the steepening toward the Ab end and in particular the incomplete termination near Ab. This occurs because when the liquid reaches the sideline Ab-Di it leaves the ternary plane into multicomponent space involving all components of all three phases liquid, pyroxene, and plagioclase. The details need not concern us here, but of some interest is the composition of the plagioclase when the liquid reaches the sideline.

Bowen’s tools and his fine-grained crystals were not well suited to this determination. Figure 6b contains the answer. Bowen’s original three-phase triangle determinations yield the points marked with filled black rectangles. These eight points were found through a series of subtle and
canny experiments involving several bulk compositions and the beginning of melting. In two
experiments using electron microprobe determinations by Kushiro (1973), shown as filled
triangles, one lies exactly on Bowen’s line and another well off the line despite a long run time.
The line is the linear regression on all but two points, yielding a value of $K_D = 0.26$. The upper end
of the correlation misses the upper corner and instead lands at $D = 0.975$. From the partitioning
equation the limiting plagioclase composition is An 9, and that is where the $T-X$ diagram places it.
The loop is not strictly binary, but its treatment with linear partitioning brings out a useful
quantification of its imperfection. Of major interest is the value of $K_D = 0.26$ given by the
regression, because this gives us a best 1-atm value for plagioclase - liquid partitioning in a
pyroxene - saturated system, corresponding to the nature of many mafic igneous rock types
including norite and gabbro. This value serves as the anchor for the effect of pressure on the value
of $K_D$ in pyroxene-saturated plagioclase previously mentioned and as shown in figures 5 and 7 of
Morse (2013).

In summary, the addition of a third component can change the partitioning of a binary loop
and needs to be considered when seeking information about the behavior of liquids in natural
systems.

**IDEALITY IN BINARY SOLUTIONS**

Ideal solutions evidently display linear partitioning. Non-ideal solutions might not be
expected to do so. Nevertheless, as the Ab-Or system has dramatically shown, linear partitioning
can occur even in an azeotrope for which the substantial mixing energies were famously calculated
from thermodynamic principles.

A system at equilibrium has a locally minimized Gibbs free energy related to the exchange
coefficient and the activity coefficient by

$$\ln K_D = -\frac{\Delta G^o}{RT} - \ln K_\gamma$$  \(\text{(12)}\)
where $\gamma$ is the activity coefficient and $K\gamma$ is the ratio of activities in one phase divided by the ratio of activities in the other phase when there is a simple equilibrium of the form $a = b$. For the case $K\gamma = 1.0$, the solution is said to be ideal, but alternatively their ratio is fortuitously equal to 1.0. In the case of the azeotropes (for which $K_D$ is a constant for each individual side), a practical result must be the assumption that the activity coefficient is fortuitously equal to 1.0. In this case, the linearity of the partition coefficient against composition says nothing whatever about the individual activities of the conjoined binary solutions.

The plagioclase feldspar system is expected to be non-ideal from the behavior of Al$^{3+}$ in An and Ab and the disorder of AlSi in anorthite (e.g., Mysen and Richet, 2005). In an earlier treatment (Morse, 1997) it was shown that for Bowen’s (1913) system An-Ab the partitioning was not linear, but curved, concave-up, with an intercept at $K_D = 0.282$. It was also shown that the departure from linearity became less at high pressure. We may now revisit this problem with a brief review of Bowen’s analysis of the data, in which possibilities arise for retrieving fundamental information from linear partitioning.

**MELTING IN THE SYSTEM AN-AB AT 1-ATM**

**Introduction**

It is now a century plus two years since Bowen (1913) published “The melting phenomena of the plagioclase feldspars,” a treatise that is surely the rock-bottom foundation of all modern igneous petrology. In this document, Bowen not only determined the liquidus and solidus curves and temperatures of the plagioclase loop, but also used thermodynamics to analyze the result. In this exercise, he proceeded not merely to assume the provisional enthalpies of fusion of An and Ab, but ultimately to *extract* one of these values from the experimental array. He then conducted an error analysis (Bowen’s Table V) by changing each value of the enthalpy of fusion by 10% and recalculating the implied temperature for each of the liquidus and solidus. In this exercise he showed that the result of the 10% variation was “well beyond the limits of error of the temperature measurements.”
In passing, it is worth our notice to cite two of Bowen’s classic statements, as follows:

“van Laar derives a more rigid relation which contains factors for the heats of mixing in both phases, but in its application he finds it necessary to neglect these and the equations then reduce substantially to the form given above” (page 590)

And again from p. 590:

“If the calculated mean molal latent heat of melting of anorthite is divided by the formula weight, the result is 29000 ÷ 278 = 104.2. Åkerman and Vogt have found by direct measurement that the latent heat of melting of anorthite is 105 cal. per gram, which agrees well with the calculated value. The extraordinary agreement is, of course, in part pure accident.”

NB: “in part”

Bowen’s Figure 8 shows the calculated liquidus and solidus curves for plagioclase along with the experimental data. All the points lie on the lines except three solidus points close to the Ab endmember, which lie at lower temperatures than observed.

Present work

The current exercise to find a modern working diagram for plagioclase is basically that of Bowen (1913). The history of the albite melting point is interesting. With much struggle, Bowen concluded that this end member melted at 1100 ± 2 °C. This result was later changed to 1118 °C by Schairer and Bowen (1956), and then returned to 1100 °C by Anovitz and Blencoe (1999; see discussion by Lange, 2003). The melting point of An (1553 °C instead of Bowen’s 1550 °C) is taken from Osborn (1942). The liquidus and solidus curves were first recalculated from the latent heats of fusion using Bowen’s value for \( \Delta H_f (\text{An}) = 121.3 \text{ kJ} \) and the value for \( \Delta H_f (\text{Ab}) = 59.28 \text{ kJ} \)
kJ (compared to Bowén’s 53.3 kJ) from Robie et al. (1978). The liquidus curve (Fig. 7a) so calculated fits Bowén’s data almost exactly. The solidus curve is continuous (Fig. 7a) instead of the former straight line at high values of An followed by a curve to the Ab end point (e.g., Morse, 1994 p. 63).

There is an objection to the use of modern data for the latent heats of fusion when they were determined on glass (quenched melt) which is frozen in at the glass transition. In consequence, the heat of fusion calculated from solution calorimetry of glasses, as done in the recent literature including Robie et al. (1978), is not the $\Delta H$ of melting (e.g., Richet and Bottinga, 1986). There is, however, a purely empirical approach in which we may test the results of new data inputs against the experimental $T$-$X$ data of Bowén (1913). This procedure reflects the original use of the phase diagram from which Bowén extracted at least one of the heats of fusion, as discussed above.

Still using Bowén’s $\Delta H_f$ (An) = 121.3 kJ, the partitioning plot is linear in two segments joined at An$_{60}$ (dotted line in Fig. 7b) and a $K_D$ value of 0.3. However, using instead an updated value $\Delta H_f$ (An) = 134.6 kJ (Navrotsky et al. 1980), the partitioning line becomes a single curve with $K_D$ = 0.276, as shown by the heavy solid line in Fig. 7b. As also shown in the figure, the data near the An end of the array are typically scattered because an error of only 0.001 in $X_{An}$ has a large effect on the result. This marriage of old and new data continues the Bowén principle of testing for a thermodynamic quantity by fitting to the experimental data. In this comparison there is no empirical evidence for rejecting the 1980 result, despite its origin from glass. As a result, we have a reasonable interim model for plagioclase alone to compare with more complex bulk compositions.

**Solid-solid equilibria: a pyroxene solvus**

The system Wo-En-Fs furnishes in its lower half the familiar pyroxene quadrilateral bounded by the Mg-Fe solutions Diopside-Hedenbergite at the top ($X_{Wo} = 0.5$) and Enstatite-Ferrosilite at the bottom ($X_{Wo} = 0$). This diagram features a three-dimensional solvus whose limbs separate Ca-rich augites from Ca-poor pigeonites accompanied by even Ca-poorer
orthopyroxenes. The solvus has the form of an eastward-plunging anticline that becomes narrower with pressure as the temperatures rise (Lindsley, 1983). Two partitioning plots taken graphically from Fig. 9a of Lindsley (1983) are shown in Fig. 8. In the upper panel the augite-pigeonite pairs show an ideal linear partitioning relationship with a value of $K_D = 0.74$ received from the regression, and an exact intercept at $D = 1.0$. This result is not unsurprising for the two structurally-similar monoclinic crystal species. Using the same original diagram we find that the augite-orthopyroxene partitioning (Fig. 8b) is erratic – that is, the data points are randomly distributed without slope and a rough estimate of $D = K_D = 0.94$. For these two mixed-crystallographic phases there is no binary solution loop and the relationships are not athermal. They are not well-related to temperature either. Examples of the pyroxene solvus at higher pressures, 5 to 15 kbar, are also furnished in the Lindsley (1983) address, but are derived from the 1-atm solvus and are not reviewed here except to say that the augite-pigeonite pairs also give linear partitioning results at pressure.

**EXTENSION TO MULTI-COMPONENT SYSTEMS**

At Figure 2 it was mentioned that linear plagioclase partitioning could be studied within such multi-component systems as anorthosite and gabbro. Experimental studies by Morse et al. (2004), McIntosh (2009), and Fram and Longhi (1992) all involved bulk compositions made up of natural mineral components. The liquid compositions for binary solutions within multi-component systems are obtained from the normative calculation of mineral components in quenched glass for which the composition is determined by electron probe. The norm calculations are commonly made in oxygen units and corrected for pyroxene compositions as found in nature rather than, for example, on the Di-Hd join at 50% wollastonite. Further details are reported by Morse et al. (2004). Extension to a global range of bulk compositions is reported in the study of large databases by Morse (2013), in which the problems and pitfalls of liquid calculations are discussed at some length. In what follows, the linear partitioning principle is extended to a suite of natural olivine compositions.
KIGLAPAIT OLIVINE STUDIES

Here we begin with a review of olivine compositions in the entire intrusion (Morse, 1979a; 1996). Liquid compositions are then introduced from earlier-published estimates. Partitioning of augite against liquid and against olivine is reviewed with linear plots. The choice of exchange coefficient values is reviewed in the light of liquid structure as represented by NBO/T indices (where NBO is the sum of non-bridging oxygens and T is the number of tetrahedral cations: Mysen et al., 1982). Then the linear partitioning plots for olivine - liquid are examined. This exercise reveals a novel second linear array that identifies the liquid composition and might be used to deduce a previously existing liquid composition.

Stratigraphic relationships

Olivine compositions in the Kiglapait intrusion are plotted in stratigraphic context, Fig. 9, along with key arrivals of new phases augite, Fe-Ti oxide minerals, and apatite. The X axis is stratigraphic and runs from the base of the intrusion at the left to the top at the right. The PCS scale represents the volume percent solidified as calculated from cross sections (Morse, 1969). The logarithmic scale is based on the fraction of remaining liquid $F_L$, equal to 1-(PCS/100). It is used to display quantities in detail that would be simply a blur at linear scale.

The initial trend in the Lower Zone is limited in variation from Fo$_{71}$ to about Fo$_{61}$. As shown also in Fig. 8 of Morse (2008) the expectation for cotectic olivine + plagioclase would be fractionation to Fo$_{40}$ at 65 PCS. The retardation of the natural olivine variation in the Lower Zone can be attributed in considerable part to the evolving ferric iron component of the magma, which reduces the activity of the ferrous end-member fayalite. Much of the other scatter to high-Fo values, as found for example after 99.9 PCS, can also be attributed to the contact of olivine with grains of magnetite. Of note in the figure is the cluster of Fo-rich olivines labeled “Oxygen spikes” in the stratigraphic region after the Fe-Ti oxide minerals become important. The cause of the oxygen spikes was discussed in Morse (1979a,b) and particularly in Morse (1980) where the oxygen and silica activities of the magma were described in some detail. In that contribution,
reversed rims on olivine grains among the titanomagnetite grains of the Main Ore Band were reported in Figure 4, ranging from Fo$_{58.8}$ to as high as Fo$_{66}$. A jump in $f_{O_2}$ from well below FMQ to well above FMQ at the top of the Main Ore Band was shown in figure 10 of that paper. This oxidation effect on local olivine compositions can be seen as a low-$f_{O_2}$ counterpart to the olivine hiatus in the Skaergaard intrusion, where the loss of olivine can be ascribed to a locally high silica activity that de-stabilizes Mg-olivine until the magma eventually evolves to a more iron-rich composition that stabilizes Fe-olivine (e.g., Morse et al. 1980).

**Liquid compositions for Kiglapait olivine partitioning**

Kiglapait olivines and their parent liquids were discussed in detail by Morse (1996) and Morse (2001). The result for the Kiglapait liquid compositions in $X_{Fe} =$ molecular Fe$^{2+}$/Fe$^{2+}+$Mg was listed in Table 2 of the 1996 paper. These compositions were generated from the linear partitioning equation assuming $K_D = 0.33$ for all of the Lower Zone, 0-84 PCS, and varying to 0.45 at the end of crystallization based on earlier literature data. These assumptions are re-visited below.

**Augite-Olivine relations**

The linear partitioning of Kiglapait augite with liquid is demonstrated in Fig. 10a from data calculated from the QUILF equilibria with olivine and liquid (Morse, 1996). The solid-solid plot of augite on olivine compositions is shown in Fig. 10b in which three points lie well above the linear partitioning line defined by the other six points. This result was ascribed (Morse, 2001) to metastable, supercooled compositions of augite that crystallized early from augite-oversaturated liquids and became too Fe-rich as a result. [It might be thought that the olivines were at fault instead, being too Mg-rich, but the Mg-rich ("Ox-spikes") olivine compositions were not used in the cited paper.]

**Liquid polymerization and olivine partitioning**

Experimental and theoretical investigation has shown that the partitioning of olivine and
silicate melts clearly depends on the polymerization of the melt. Among significant steps in the
evolution of this principle are studies by Kushiro and Walter (1998), Toplis (2004), and Mysen
(2007). The NBO/T data\(^2\) for experimental Kiglapait liquid compositions (Fig. 11) show a base
line near a value 0.8, increasing to > 1.0 near the augite + oxide mineral maximum, and with a
long gap to ~1.0 in the Upper Zone. Very mafic samples have high values of NBO/T, as seen in
three cases at 95 and ~99.9 PCS. All other liquid samples plot among those for the rocks, so the
paucity of data for liquids between 93 and 99.7 PCS is of little concern. This range in NBO/T lies
essentially at the crest of Mysen’s (2007) figure 7 where the values of \(K_D\) range from ~0.23 to
0.35, with a mean of 0.27. A formal calculation with a best fit to the experimental data can be
made as follows. Using a best fit for the experimental data represented by the gray filled circles in
Fig. 11, we have a stratigraphic variation of NBO/T, as follows. For \(x = \) the stratigraphic measure
“\(-\log F_L\)”, NBO/T (experimental) = \(-0.0614x^2 + 0.2811x + 0.6452\). From this and the diagram of
\(K_D\) v. NBO/T of Mysen’s (2007) figure 7 we solve for \(K_D\) as follows: For \(x = \) NBO/T, \(K_D = 0.01x^3 - 0.1053x^2 + 0.2118x + 0.155\). The values of \(K_D\) vary from 0.25 to 0.27, with a mean of 0.26.
These values are significantly lower than previously assumed to be \(\geq 0.33\).

From these results we can now generate a new estimate of the liquid composition in
equilibrium with the observed olivine compositions in the Kiglapait intrusion. The result is shown
in Fig. 12.

**LINEAR PARTITIONING OF OLIVINE IN THE KIGLAPAIT INTRUSION**

**Region 50 PCS to the end of crystallization**

The partitioning result for the whole intrusion is shown in Fig. 13, where the derived criterion
of the mean value of \(K_D = 0.26\) is identified by a horizontal line. The data for all stratigraphic
levels above 50 PCS are shown as black filled circles. The data are partly from the Lower Zone,
50-84 PCS, and the rest are from the Upper Zone, >84 PCS. The previously noted “oxygen

\(^2\)Calculations of NBO/T for this contribution were made in a spreadsheet kindly furnished by B. O. Mysen.
spikes” from Fig. 9 are clearly revealed in this linear partitioning plot. The scatter of data about
the nominal trend line is to a lesser extent due to the small variation of $K_D$ values $\pm 0.01$ from the
mean of 0.26, and to greater extent due to local variations in crystal nucleation and growth, and the
subsequent effects of trapped liquid.

Lower Zone 0-50 PCS

The data plotted in gray filled circles occupy a completely different trend in the linear partitioning
diagram. The trend originates precisely at the origin (1, 0). The crystal compositions are
measured and therefore unquestioned. These samples do not plot as expected for reasons
discussed below. This array is the graphical solution to the problem of finding the liquid
composition at the $y = 1.0$ intercept, given the crystal composition and the value of $K_D$. The novel
array has the equation $y = -ax + a$, where $a > 1.0$ is a function of slope, as shown near the base of
Fig. 13.

Interpretations of the novel array

It is essential here to recapitulate the origin of the partitioning arrays and particularly the new
array. The crystal compositions are measured in grain mounts and represent secure input data. The
liquid compositions are calculated from the crystal compositions using the linear partitioning
equation and the experimental values of NBO/T and $K_D$. It is of interest that the upper intercept
value of the new array at $D = 1.0$ does reliably represent the liquid composition in equilibrium
with the nominal maximum crystal composition at Fo$_{71}$. This fact demonstrates internal
consistency, given the value of $K_D$ used. It is also to be noted that the lower values of $K_D$ now
used, based on the experimental NBO/T, are lower than the Roeder-Emslie result and they
consequently describe a fatter loop than that shown in Fig. 1a (but not as fat as that in Fig. 1b).

There are at least three plausible origins for the new array. It could represent equilibrium
crystallization in which cumulus olivine crystals have reacted with intercumulus (trapped) liquid
having the composition of the main magma. Or it could represent partial quenching of magma in a chilled margin in which liquids were to variable extent supercooled to the solidus. Or it could represent a mistaken assumption that the liquid producing the new array was that of the main magma, whereas it was in fact a magma with a more evolved composition.

These multiple working hypotheses can be tested in various ways. The first is to test the evidence from plagioclase. The next is to test the stratigraphic relationships of the samples in the array. Another is to find a calculation of some assumed quantity that makes the new array disappear. All three of these tests are in progress, and the final result will be reported in a separate contribution. It can be anticipated that some degree of each cause could play a role, but that one central principle will be dominant. The equilibrium crystallization hypothesis is mostly falsified by the plagioclase data and the lack of correlation with measured trapped liquid volumes. The extent of the array to half the entire volume of the Kiglapait magma makes the quenching notion seem unlikely. It remains to test and document the extent and effect of the liquid composition, and to find the least ambiguous result.

**Implications**

The study of linear partitioning and its systematics leads to new questions and answers about old rocks – the ones we see that crystallized in the past. It is a tool that allows the observer to calculate a magma composition from the crystal composition. Although mathematical and simple, it leads into serious considerations about unknown mixing properties of melts and crystals. It presents the following dilemma. In azeotropic systems such as Albite-Orthoclase where two loops meet in a conjugate minimum, we know very well the non-ideality of the solutions (solid and liquid). And yet the linear partitioning arrays are rigorously straight. So linear partitioning in such cases reveals nothing about the non-ideality of the liquid. Without the azeotropic constraint, some systems also show rigorously straight linearity, whilst other systems require curved or segmented partitioning arrays. The plagioclase feldspars are a case in point: they clearly form a true binary loop, but give curved partitioning. Better enthalpy data than used here are required, but the true meaning of the curve must be a target for future enlightenment about the interaction of the mixing
properties of solutions. The one should predict the other. These are classic systems known and
studied for 102 years and yet still full of secrets. The novel partitioning array could have
important consequences for understanding the history of mafic intrusions.

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**Figure captions**

Fig. 1. (a) Components of a linear partitioning diagram using the olivine melting series Fo-Fa as an example. Symbols: $D$, partition coefficient; $X$, mole fraction; $K_D$, exchange coefficient with value from Roeder and Emslie (1970); (S), solid; (L), liquid; Fa, fayalite (Fe end member); Fo, forsterite (Mg end member). (b) With the value of $K_D$ changed to 0.2, for values of NBO/T equal to either 0.2 or 2.4, from a concave-down relationship of $K_D$ with NBO/T illustrated by Mysen (2007). This figure illustrates the inverse relationship between $K_D$ and loop width.

Fig. 2. Characteristics of binary loops related to linear partitioning. Symbols: An, anorthite content in percent = 100 $X_{An}$, $X_2 = X_{An}$. (a) Variation of loop width with for varying values of $K_D$ with a fixed crystal composition of An$_{60}$. The curve is calculated from a spreadsheet that generates $T$-$X$ loops for differing values of $K_D$. (b) The pressure effect on natural plagioclase feldspar. Fram and Longhi (1992) found that a natural anorthosite showed an increase of $K_D$ with pressure up to 27 kbar, and a gabbroic composition showed a steeper correlation. With the work of Morse et al. (2004) and McIntosh (2009) the combined data show a strong pressure effect yielding the relationship shown in the figure. See also Fig. 7 of Morse (2013) for more details.

Fig. 3. Linear partitioning diagram for the boiling mixture Methylcyclohexane (“MCH”) - CCl4 with data taken from Weishaupt (1975). The ordinate is the partition coefficient for the mole fraction of CCl4 in the liquid (L) divided by that in the vapor (V).

Fig. 4. Linear partitioning diagram for the boiling mixture CCl4-Acetone. The data curve fails the linear test. Inset: $T$-$X$ loop for the system.

Fig. 5. The azeotropic melting diagram for sanidine crystalline solutions, the system Ab-Or. A. The $T$-$X$ diagram; AP = the azeotropic point. The Or-rich liquidus is metastable with respect to leucite plus liquid because of the incongruent melting of sanidine. The temperatures are
uncorrected for the adjustment to 1100 °C for albite melting (Anovitz & Blencoe, 1999). The
binary loops are plotted from the data in Table 2 of Waldbaum and Thompson (1969). B. the
linear partitioning diagram constructed from regressions on the same table, along with the
isotherms. The individual AP intercepts of the regression are listed near the top of the diagram,
and their average is given as the AP at $X_{Or} = 0.331$. The regressions are described by the two
equations with adjustments as described in the text.

Fig. 6. The system Di-An-Ab. A. The $T$-$X$ loop calculated from the linear regression shown in
(B). The inset shows the ternary phase diagram with cotectic. B. The linear regression, re-plotted
from Morse (1997).

Fig. 7. The system An-Ab. A. The $T$-$X$ diagram recalculated in Bowen’s method from the new
enthalpies of fusion as described in the text. B. The linear partitioning result. The dotted array
with a kink at An$_{60}$ is calculated using the original latent heat $\Delta H_f$ (An) from Bowen. The solid
curve is the result of using a newer value of that enthalpy, from Navrotsky et al. (1980), with the
second-order polynomial fit shown. The similarity between the two curves recalls Bowen’s error
analysis, in which errors in latent heat can result in excessive errors in temperature.

Fig. 8. Two pairs of solutions from the pyroxene quadrangle (Lindsley, 1983). A. Augite-
Pigeonite with an exact received intercept at 1.00 and a $K_D$ value of 0.74. B. Augite-
Orthopyroxene, with no linear partitioning.

Fig. 9. Kiglapait olivine compositions in stratigraphic context. The “oxygen spikes” refer to
stratigraphically abnormal Mg-rich samples associated with titanomagnetite crystals that reflect
enhanced ferric iron in the melt, thereby depleting the local activity of the ferrous component in
the olivine. This matter is discussed at some length in the text. Symbols: MOB, Main Ore Band;
Aug, augite; Ox, titanomagnetite; Ap, apatite; PCS, volume percent solidified; $F(L)$ fraction of
system present as liquid.
Fig. 10. Kiglapait augite-olivine-liquid relations in linear partitioning diagrams, calculated from olivine compositions and QUILF equilibria. (a) Augite-liquid partitioning with $K_D = 0.19$ (Morse and Ross, 2004). (b) Augite-olivine equilibria simplified from Morse (2001) showing the off-line results for early augites interpreted in the cited study as being metastable.

Fig. 11. Calculated ratios of non-bridging oxygens divided by tetrahedral cations (NBO/T; e.g., Mysen and Richet, 2005) for Kiglapait whole rocks (solid black diamonds) and experimental liquids (quenched melts, in grayscale,) for the Lower Zone (Morse et al. 2004) and the uppermost Upper Zone (Peterson, 1999). Note that feldspar-rich, hence more polymerized, compositions (in the Lower Zone and above 95 PCS) have low values of NBO/T, whereas feldspar-poor compositions rich in mafic minerals have higher values. Whole-rock analyses are from Morse (1981). The curve for the whole-rocks accurately reflects the arrival and over-production of augite and Fe-Ti oxide minerals in the region 85-95 PCS (modal data from Morse, 1979b). The sag after 95 PCS reflects a local increase and maximum in the amount of normative feldspar, as does the tail-end of the data at the end of crystallization. Two high values near 99.9 PCS are low-silica, mafic compositions with only 40-44 % normative feldspar and 57-60 % normative augite + olivine. Otherwise, most of the liquid compositions are similar to the whole-rock compositions. Abbreviation: OG, olivine gabbro. The data for the liquids help to define the more appropriate value of $K_D$ for olivine-liquid equilibria.

Fig. 12. Estimated $X_Fe$ compositions of Kiglapait liquids, derived from Fig. 11, transformed as described in the text. The stratigraphically varying value of $K_D$ is applied to the crystal compositions to find the value of $X_Fe^L$ from the linear partitioning equation.

Fig. 13. Linear partitioning plot of all Kiglapait olivine compositions, for which the liquid compositions are those from Fig. 12. The horizontal line identifies the mean value of the exchange coefficient as $K_D = 0.26$. The black data points reflect all data above 50 PCS, including points from the Lower Zone 50-84 PCS and all the data from the Upper Zone, defined as >84 PCS.
gray filled circles represent all the data from 0 to 50 PCS. These points define a novel array arising from the lower right corner of the diagram with the dotted line and equation shown. The upper intercept of this regression gives the value of the initial liquid composition assumed for the earliest crystals with Fo ~ 71. The origin of this array has three possible causes, as discussed in the text. The two most likely are an initial evolved magma and the effects of early trapped liquid.
Morse Figure 1

\[ D = K_D \times X_{F_0}^S + X_{F_a}^S \]

\[ D = \frac{X_{F_a}^S}{X_{F_a}^L} \]

Nominal Olivine

\[ K_D = 0.3 \]

Extreme Olivines

\[ K_D = 0.2 \]

For NBO/T = 0.2 or 2.4 (Mysen, 2007)
Morse Fig. 2

Loop Width on $K_D$, Crystal An 60

$-0.42x^3 + 1.13x^2 - 1.303x + 0.59$ (R$^2 = 1.0$) where $x = K_D$.

Loop width and $K_D$ on pressure

$K_D = 0.052P + 0.26$

Morse Fig. 2
Methylcyclohexane - CCl4 1.013 bar

\[ r^2 = 0.9996 \]

\[ KD = 0.514 \]

\[ D(i) = X_i(L)X_i(V) \]

\[ X_j(L) = \text{mole fraction MCH in Liquid} \]

Meth ccl4

Morse Fig. 3
CCL4 - ACETONE, P = 0.600 bar

\[ D(i) = \frac{X_i}{X_V} \]

DATA

LINEAR

KD \sim 0.14 \text{(LIMIT)}

Morse Fig. 4
Sanidine Crystalline Solutions
System Ab-Or
Waldbaum & Thompson 1969 Am Min
Temperatures uncorrected to Ab 1100

A

Azeotropic point at 0.331 ± 0.006, 1.011

B

\[ D = K_D \times X_{Ors} + 1.325 \times X_{AbS} \]

\[ D = K_D \times X_{AbS} + 2.425 \times X_{Ors} \]

\[ K_D = 0.417 \]

\[ K_D = 0.320 \]

Morse Fig. 5

Cite as Authors (Year) Title. American Mineralogist, in press. (DOI will not work until issue is live.) DOI: http://dx.doi.org/10.2138/am-201x-xx-xxxx

http://www.minsocam.org
System Di - An - Ab (Bowen, 1915)

Temperature, deg C

mol % An

0 20 40 60 80 100

0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

Kushiro, 1973

K = 0.26D

SYSTEM Di - An - Ab
Bowen, 1915
Di - saturated Plag. + Liq.

SS

D = K\textsubscript{D} \times X\textsubscript{AnS} + 0.975 \times X\textsubscript{AbS}

K\textsubscript{D} = 0.26

Morse Fig. 6
Morse Fig. 7

System An-Ab (Bowen, 1913) Mod. 2014

\[ y = 0.3076x^2 - 1.0379x + 1.0067 \]

\[ R^2 = 0.9997 \]

\[ K_D = 0.276 \]
Augite-Pigeonite 1-atm (Lindsley 1983)

\[ y = -0.26x + 1.00 \quad R^2 = 0.99 \]

\[ K_D = 0.74 \]

Augite - Orthopyroxene 1-atm (Lindsley 1983)

\[ y = 0.00x + 0.94 \quad R^2 = 0.01 \]

Morse Fig. 8
Kiglapait Olivine – all data

“Oxygen Spikes”

OL FO All 14

Morse Fig. 9
KI Augite-Olivine-Liquid Relations

\[ D(X_{Fe}), \text{Augite/Liquid} \]

\[ R^2 = 0.9955 \]

\[ K_D = 0.19 \]

A

Augite-Liquid

\[ y = -0.6367x + 0.9974 \]

\[ R^2 = 0.9972 \]

\[ K_D = 0.361 \]

B

Augite-Olivine

Morse Fig. 10
KI 3373
(mafic OG)

KI Whole Rocks
KI Exper. Glasses

Morse Fig. 11
Kiglapait XFe (Liq)
For KD 0.25-0.27

Morse Fig. 12
Morse Fig. 13

\[ y = -1.79x + 1.75 \quad R^2 = 0.99 \]

Kiglapait Olivines: All Data

Mean $K_D = 0.26$

All samples above 50 PCS

N = 61

"Oxygen Spikes"

Fo 42

LZ 0-50 PCS

N = 146

Morse Fig. 13
Table 1. Abbreviations used in the text

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ab</td>
<td>Albite</td>
</tr>
<tr>
<td>An</td>
<td>Anorthite</td>
</tr>
<tr>
<td>Aug</td>
<td>Augite</td>
</tr>
<tr>
<td>AUG</td>
<td>Oxygen-normative augite*</td>
</tr>
<tr>
<td>ΔHf</td>
<td>Latent heat (enthalpy) of fusion</td>
</tr>
<tr>
<td>D</td>
<td>Partition coefficient</td>
</tr>
<tr>
<td>Di</td>
<td>Diopside</td>
</tr>
<tr>
<td>Fa</td>
<td>Fayalite</td>
</tr>
<tr>
<td>FL</td>
<td>Volume fraction of system present as liquid</td>
</tr>
<tr>
<td>Fo</td>
<td>Forsterite</td>
</tr>
<tr>
<td>FSP</td>
<td>Oxygen-normative feldspar*</td>
</tr>
<tr>
<td>J</td>
<td>Joule</td>
</tr>
<tr>
<td>k</td>
<td>kilo-</td>
</tr>
<tr>
<td>K_D</td>
<td>Exchange coefficient</td>
</tr>
<tr>
<td>L</td>
<td>Liquid</td>
</tr>
<tr>
<td>LZ</td>
<td>Lower Zone</td>
</tr>
<tr>
<td>OL</td>
<td>Oxygen-normative olivine*</td>
</tr>
<tr>
<td>Opx</td>
<td>Orthopyroxene</td>
</tr>
<tr>
<td>Or</td>
<td>Orthoclase</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
</tr>
<tr>
<td>PCS</td>
<td>(volume) percent solidified in the Kiglapait intrusion</td>
</tr>
<tr>
<td>QUILF</td>
<td>Quartz-Ulvoiopinel-Ilmenite-Fayalite equilibria (Andersen et al. 1993)</td>
</tr>
<tr>
<td>S</td>
<td>Solid</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>UBZ</td>
<td>Upper Border Zone</td>
</tr>
<tr>
<td>UZ</td>
<td>Upper Zone</td>
</tr>
<tr>
<td>V</td>
<td>Vapor</td>
</tr>
<tr>
<td>X</td>
<td>Mole fraction</td>
</tr>
</tbody>
</table>

Note: *normative phases normalized to total AUG + FSP + OL
TABLE 2.  LIST OF LINEAR PARTITIONING RESULTS  

May 14, 2014

A. Binary Solutions  
Single Loop: Liquidus & Solidus

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>$K_D$</th>
<th>P</th>
<th>SOURCE</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fo-Fa Olivine</td>
<td>0.227</td>
<td>1-atm</td>
<td>Morse 1997 (Bowen &amp; Schairer)</td>
<td>Small curve</td>
</tr>
<tr>
<td>An-Ab Plagioclase</td>
<td>0.282</td>
<td>1-atm</td>
<td>Morse 1997 (Bowen)</td>
<td>NOT linear</td>
</tr>
<tr>
<td>-do-</td>
<td>0.285</td>
<td>1-atm</td>
<td>Morse 2000 (Bowen)</td>
<td>Two segments</td>
</tr>
<tr>
<td>-do-</td>
<td>0.22</td>
<td>5 kb</td>
<td>Morse 2000 (Nekvasil)</td>
<td>Barely 2 segments</td>
</tr>
<tr>
<td>-do-</td>
<td>0.252</td>
<td>10 kb</td>
<td>Morse 1997 (Lindsley)</td>
<td>Two segments</td>
</tr>
<tr>
<td>-do-</td>
<td>0.276</td>
<td>1-atm</td>
<td>This study</td>
<td>Single curve</td>
</tr>
<tr>
<td>An-Ab-H2O</td>
<td>0.05</td>
<td>5 kb</td>
<td>Morse 2000 (Nekvasil)</td>
<td>$R^2$ 0.9997</td>
</tr>
<tr>
<td>Di-An-Ab</td>
<td>0.26</td>
<td>1-atm</td>
<td>Morse 1997 (Bowen, Kushiro)</td>
<td>Intercept 0.975</td>
</tr>
<tr>
<td>Basaltic Olivine</td>
<td>0.33</td>
<td>1-atm</td>
<td>Morse 1997 (Hoover-Irvine)</td>
<td>Variable $K_D^*$</td>
</tr>
<tr>
<td>Augite - Olivine</td>
<td>0.32</td>
<td>1-atm</td>
<td>Morse 2001 (Selected range)</td>
<td>$R^2$ 0.995</td>
</tr>
</tbody>
</table>

B. Three-Phase Systems

(1) Two crystal species plus liquid (Two binary S-L solutions and one S-S(L) where () signifies the saturating phase).

Augite - Olivine - Liquid  
Based on Morse (1996; 2001)

Augite - Liquid (Ol)  
0.19  1-atm  This study  
$R^2$ 0.9995

Olivine - Liquid (Aug)  
0.335  1-atm  This study  
Variable $K_D^*$  
$R^2$ 0.996

Augite - Olivine (L)  
0.361  1-atm  This study  
$R^2$ 0.9972

(2) Two crystal species plus a third saturating phase: The pyroxene solvus (Lindsley, 1983).

Augite - Pigeonite  
0.74  1-atm  This study  
$R^2$ 0.990

Augite - Opx  
-NA--  1-atm  This study  
$R^2$ 0.01

C. Azeotropes in solid-liquid systems

(Binary solutions with a common invariant point between phases)

NaCl-KCl  
0.215, 0.395  1-atm  Morse 1997 (Waldbaum) Classic precision

Ab-Or wt %  
0.325, 0.417  1-atm  Morse 1997 (Waldbaum & Thompson) ditto

Ab-Or mol %  
0.320, 0.417  1-atm  This study (Waldbaum & Thompson) ditto

Ab-Or-H2O  
0.04, 0.12  5 kb  Morse 2000 (Morse 1970)

D. Two solid phases

Magnesiowüstite - spinel  
0.205  16-22 GPa, 1600 C  Morse 2000 (Matsuzaka)

Chlorite - Garnet  
0.162  Chlorite zone Morse 2001 (Spear)

Biotite - Garnet  
0.25  Sillimanite zone  Morse 2001 (Kretz)  
$R^2$ = 0.995

Synthetic van Laar loops  
0.121-0.0077  Morse 2001 (Kretz)  
$R^2$ ~ 1

Augite - Olivine as above
E. Boiling Mixtures

1. Simple liquid-vapor systems. All data from Weishaupt (1975).

Methylcyclohexane - CCl4 0.514 1-atm Morse 2000  \( R^2 0.9996 \)

CCl4 - Acetone Var. 0.600 bar Morse 2000 NOT LINEAR

Many others not linear, listed in Table 1 of Morse (2000).

2. Azeotropes

Methanol-Chloroform 0.336, 0.182 1-atm Morse 2000  \( R^2 >0.996 \)

Toluol - Isobutanol 0.352, 0.306 1-atm Morse 2000  \( R^2 >=0.9996 \)

Many others linear listed in Table 1 of Morse (2000).

\*D flattens out at low Mg- high Fa: See also this study
| 1996 Data PCS | X2S MAX -lgF(L) XMG(OL) X1S NBO/T KD X1L XFe (Liq) |
|---------------|-------------------------------------------------|---|---|---|---|---|---|
| 0 0.0458      | 0.740 0.260 0.645 0.251 0.584                   |
| 10 0.0969     | 0.734 0.266 0.658 0.252 0.590                   |
| 20 0.1549     | 0.719 0.281 0.687 0.254 0.606                   |
| 30 0.2218     | 0.710 0.290 0.705 0.255 0.615                   |
| 40 0.3010     | 0.700 0.300 0.724 0.257 0.625                   |
| 50 0.3979     | 0.687 0.313 0.747 0.259 0.638                   |
| 60 0.5229     | 0.672 0.328 0.775 0.261 0.652                   |
| 70 0.6990     | 0.650 0.350 0.812 0.263 0.672                   |
| 80 0.7959     | 0.610 0.390 0.830 0.264 0.708                   |
| 84 0.9788     | 0.540 0.460 0.862 0.266 0.762                   |
| 89.5 1.2757   | 0.374 0.626 0.904 0.268 0.862                   |
| 94.7 1.4685   | 0.222 0.778 0.926 0.269 0.929                   |
| 96.6 1.6576   | 0.153 0.847 0.942 0.269 0.954                   |
| 98.6 1.8539   | 0.112 0.888 0.955 0.270 0.967                   |
| 99.59 2.3872  | 0.075 0.925 0.966 0.270 0.979                   |
| 99.9 3.0000   | 0.050 0.950 0.936 0.269 0.986                   |
| 99.953 3.3279 | 0.036 0.964 0.901 0.268 0.990                   |
| 99.98 3.6999  | 0.015 0.985 0.845 0.265 0.996                   |
| 99.985 3.8239 | 1 0.822 0.264 1.000                             |
| 99.99 4 0     | 1 0.787 0.261 1.000                             |