Plagioclase Fractionation in Troctolitic Magma

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Troctolitic intrusive rocks poor in augite are common in certain Proterozoic anorthosite complexes and related rocks. The Lower Zone of the Kiglapait intrusion, Labrador, consists of \( \sim 1570 \) km\(^3\) troctolite today and possibly \( \sim 2900 \) km\(^3\) before erosion. In this augite-free Lower Zone, plagioclase fractionation is as low as 16\% An km\(^{-1}\) of cumulate thickness and averages 3\% An km\(^{-1}\). When augite crystallizes after 84\% of the magma has crystallized, the fractionation becomes as much as 17\% An km\(^{-1}\) of cumulate. Why such a difference? It is clear from first principles of phase equilibria that fractionation accelerates with saturation in augite, but not so clear that the difference should be so great. The answer is to be found in the silica-poor nature of troctolitic magma that is critically undersaturated in silica. This low-silica effect reduces the activity of the NaSi albite component relative to the CaAl anorthite component in the plagioclase, thereby favoring the An component of the liquid and crystals and weakening the fractionation process. As the normative augite component in the magma rises from the base of the Lower Zone to the base of the Upper Zone, the activity of silica also rises slightly and its consequent effect on plagioclase composition tends to diminish. Liquid fractionation paths derived from observed crystal paths, when plotted in the system Diopside-Anorthite-Albite, rise across the liquidus fractionation lines toward diopside and reach augite saturation near the 1 atm cotectic. They produce plagioclase compositions 10 mol \% higher in An than pure liquidus fractionation lines predict. The key criterion for the troctolitic fractionation of plagioclase composition is the absence of Ca-poor pyroxene from the rocks. Noritic magmas, by contrast, have higher activities of silica and more effective fractionation of plagioclase. A parallel fractionation of olivine is also retarded in the Lower Zone by the accumulation of ferric iron in the liquid until augite and titanomagnetite crystallize in the Upper Zone.

KEY WORD: plagioclase fractionation; troctolite melts; silica activity; layered intrusions; Kiglapait intrusion

INTRODUCTION

Troctolite is not an uncommon rock, depending on where you look. Troctolite of age 4.3 Ga is one of the oldest rocks on the Moon (Nyquist et al., 2012), and the freshest troctolite sample in captivity. Troctolite of age 1.3 Ga is the major component of the Kiglapait intrusion in Labrador (Morse, 1969). Other occurrences of troctolite abound in the Nain Plutonic Suite (Ryan, 1990; Morse, 2006), in the Sept Iles intrusion (Namur et al., 2010), in the Duluth Complex of Minnesota (Miller & Ripley, 1996) and at the base of the Skaergaard intrusion, East Greenland (Wager & Brown, 1967), among many others. Despite the moderate abundance of this simple rock composed mainly of plagioclase and olivine, the notion of troctolitic liquids has been occult in the imagination of many petrologists, for whom oceanic basalt is a reference point. However, there is much evidence in the field for the existence of troctolite melts, especially in the snowflake troctolite of the Hettasch intrusion (Berg, 1980) in which a very hot meltrctolite magma invaded a troctolite magma and was quenched to a remarkable variety of plagioclase textures derived from supercooling. Granitic magmas engulfing troctolite magma to form giant troctolite pillows in the Newark Island intrusion were vividly described by Wiebe (1988).

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The matter of troctolitic magmas comes particularly into focus in the Kiglapait intrusion (KI), where an estimated 84% of the intrusion volume is troctolite of the Lower Zone (Fig. 1). This large body (initially > 3500 km$^3$; Morse, 1969) is notable for its very small variation in plagioclase composition in the Lower Zone (Fig. 2), raising the question of multiple injections of fresh magma or some other effect of slow compositional evolution.

Fig. 1. Sketch map of the Kiglapait intrusion with sampling traverses. The traverse maps have been shown by Morse (1979b). The contours are those of volume per cent solidified (PCS) and are based on the strike of layering and the volumes of 13 cross-sections described in the original GSA Memoir (Morse, 1969). Plunge values of layering are shown in the western part of the synclinal axis; these show shallowing plunges that limit the probability that the steepness of layering has increased during subsidence: the layering seen must have been within 15° of the present dip. MOB, Main Ore Band at 93-5 PCS.
Fig. 2. Stratigraphic section of the Kiglapait intrusion, showing olivine and plagioclase composition trends superimposed; the crossover near 95+5 PCS should be noted. The vertical scale is logarithmic to show fine-scale changes in lithology over the last 300 m of stratigraphy (above 99+87 PCS). The subzones of the Upper Zone are indicated by letters a-f based on arrivals on the liquidus of augite (Aug⁺), titanomagnetite (Mt⁺), sulfide globules (Po⁺),apatite (Ap⁺), antiperthite, and mesoperthite. MOB, Main Ore Band at 93+5 PCS. Fₜ, fraction of liquid. The dashed excursion near 90 PCS represents the elevated Fo values interpreted as 'oxygen spikes' owing to the increasing components of Fe-Ti oxide minerals present in the system (Morse 1979a, 1980).
STATEMENT OF THE PROBLEM

A single, prolonged episode of magma chamber filling is assumed. Over the interval 0–40 PCS (volume per cent solidified) the model liquidus plagioclase composition in the basal Lower Zone of the Kiglapait intrusion varies only from An 67 to 64, a matter of 3 mol % over a stratigraphic thickness of ~1900 m and 40% by volume of the entire magmatic history (bold line in Fig. 3). Over the entire Lower Zone, a cumulative thickness of ~5 km, the variation is 2.9% An per km of cumulate deposited. In contrast, the (pre-augite) Skaergaard Lower Zone fractionates plagioclase at a rate of ~13-6 mol % An km⁻¹ (McBirney, 1996). The rational mind queries, what is going on here? The evolution of the Kiglapait liquid is evidently retarded. Is the cause exotic or intrinsic?

Among exotic causes might be the injection of new magma, or even better, a leading-edge fractionated magma that could cause the scatter to low An values. Such periodic reversals are well known and distinct on a small scale in many other troctolitic intrusions, particularly at Rum (Emeleus et al., 1996). The only small-scale study at Kiglapait so far found four paired reversals and returns in a 65 cm section, but the variations are not large (~1% An; Morse, 1969, p. 127). Because the lens-like layering in the intrusion generally extends for only a few hundreds of meters (Young, 1983), it is inferred that the section described is a local phenomenon, and intrinsic.

In the absence of more small- to medium-scale traverses, the case for significant new refreshments of magma above 10 or 20 PCS cannot be made. Given this stand-off, it is worthwhile to consider all possible intrinsic effects that could cause retardation of the mineral compositional evolution. If these can be shown to suffice, then the exotic scenario becomes moot, and unnecessary.

INTRINSIC EFFECTS

The effect of pressure

The inferred central magma depth of the intrusion is 8400 m (Morse, 1979) at PCS = 0. This depth decreases outward toward the limbs of the basin-shaped structure (Morse, 1969, 1979) so that the ambient pressure at the cumulative interface also decreases. The following discussion refers only to the central maximum pressure range from 5 to 2.8 kbar, giving only the maximum effects of pressure on plagioclase composition. Crystals of plagioclase at high pressure are closer in composition to their parent liquids than at lower pressures. This relationship is quantified in the direct variation of the exchange coefficient $K_D$ with pressure, as

$$K_D = 0.0516P + 0.2622 \quad (1)$$

where $P$ is in kbar (Morse, 2013, fig. 7). The systematics of linear partitioning bearing on equation (1) are reviewed in Supplementary Material Appendix 1 (supplementary data are available for downloading at http://www.petrology.oxfordjournals.org). As $K_D$ increases, the binary loop narrows to a limit of zero width at $K_D = 10$. Lower values of $K_D$ describe fatter loops. The effects of compression in a deep magma chamber can be highly variable and significant (Table 1). To first order a magma crystallizing plagioclase of composition An 67 at the roof, if transferred instantly and adiabatically to the floor, could be in equilibrium with plagioclase An 61, a drop of ~6.5 mol % (Fig. 4). Because the crystal–liquid tieties are shorter at depth, the magma fractionates more slowly at depth than at higher levels and lower pressures. This is the intrinsic pressure effect on fractionation; pressure damps the tendency for the liquid to evolve.

There are other features of interest in this context. Crystals may grow over time within the magma and encounter liquid motions leading to reverse, normal, and oscillatory zoning (Maaløe, 1976) to cause pre-cumulus zoning. This effect has been estimated to cause up to 4% An variation in the An range in the Kiglapait intrusion (Morse, 2012). If a low-pressure plagioclase crystal suddenly becomes taken down to the floor and survives, it

*Fig. 3. Kiglapait plagioclase compositions for 0–90 PCS. Each data point represents a bulk analysis for the sample. Causes of scatter are discussed in the text. Various paths can be modeled through or away from the data, according to varying multiphase Rayleigh fractionation processes (Morse, 2008). The main path (bold continuous line) is a model for the liquids at variable depth and pressures, 54–3.5 kbar, and hence a variable $K_D$. The uppermost, dotted curve would satisfy limiting cumulus compositions starting from An₆₀. The dashed line near the lower bound of the data represents another Rayleigh fractionation path without the pressure effects; it is of no concern in this study. Paths for the binary and depletion mode represent special fractionation effects not of interest here except to note that they may satisfy many of the low values at stratigraphic levels above 20 PCS (volume per cent solidified). Figure modified from fig. 13 of Morse (2008). The horizontal axis is the negative log of the fraction of liquid remaining; the PCS scale denotes the per cent of liquid solidified.*
Table 1: Pressure effect on plagioclase and liquid compositions*

<table>
<thead>
<tr>
<th>Line</th>
<th>PCS</th>
<th>P (kbar)</th>
<th>(K_D)</th>
<th>-log (F/L)</th>
<th>X An</th>
<th>XI</th>
<th>X An Liq</th>
<th>Difference</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Roof</td>
<td>2.8</td>
<td>0.409</td>
<td>n.a.</td>
<td>0.7</td>
<td>0.484</td>
<td>0.216</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Roof</td>
<td>2.8</td>
<td>0.409</td>
<td>n.a.</td>
<td>0.67</td>
<td>0.451</td>
<td>0.219</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Roof</td>
<td>2.8</td>
<td>0.409</td>
<td>n.a.</td>
<td>0.502</td>
<td>0.298</td>
<td>0.204</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>86</td>
<td>3.6</td>
<td>0.445</td>
<td>0.854</td>
<td>0.502</td>
<td>0.310</td>
<td>0.192</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>70</td>
<td>4.0</td>
<td>0.468</td>
<td>0.523</td>
<td>0.579</td>
<td>0.392</td>
<td>0.187</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>35</td>
<td>4.6</td>
<td>0.496</td>
<td>0.187</td>
<td>0.642</td>
<td>0.474</td>
<td>0.169</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>5.1</td>
<td>0.525</td>
<td>0</td>
<td>0.671</td>
<td>0.519</td>
<td>0.152</td>
<td></td>
</tr>
</tbody>
</table>

*Morse (2008, fig. 10). n.a., not applicable.

Fig. 4. Pressure effect on plagioclase–liquid tielines. The diagram shows crystal–liquid tielines at the roof and at four selected pressures corresponding to several PCS levels in the Lower Zone. The upward trend in decreasing \(X_{An}\) of the crystal compositions (x symbol) is taken from the plagioclase model, Fig. 1. The liquid compositions (ellipses) are calculated from the crystal compositions using the linear partitioning equation and the pressure variation of \(K_D\) taken as \(K_D = 0.0525 \times 10^{-0.2622} (\text{Morse, 2013})\). P is in kbar. The point of the diagram is to illustrate quantitatively the narrowing of the plagioclase loop with increasing pressure. Liquids descending directly from the roof would be in equilibrium with crystals \(0.22 - 0.53 = 0.063 \times X_{An}\) units closer than at the roof. Pressure–depth relations are developed from the modified PREM table of Stacey & Davis (2009). The emplacement pressure at the top of the UBZ is taken as 2.5 kbar based on the phase relations of the contact aureole (Berg & Docka, 1983).

will be richer in An than the local high-pressure crystals, and this might be the cause of local high-An crystals as suggested in Fig. 3, none of which exceeds the main trend by more than 4% An.

The pressure difference decreases with stratigraphic height as the cumulate surface rises to lower pressure. It also decreases from the center of the chamber to the margins, which is where we see and sample all the rocks at the present erosion level. However, any pre-cumulus or complexly zoned crystals may contribute to local variety anywhere. Perhaps this is the effect of wandering crystals.

**Effect of trapped liquid**

The resident melt trapped in a cumulate presumably has partition coefficients equal to 10 for all components, hence it has no capacity to cause the parent magma to evolve. The residual porosity has been calculated for single rocks in the KI from the range of An content in plagioclase (Morse, 2012). It ranges erratically from 35% to zero in the range from zero to 40 PCS and can therefore cause the local orthocumulates and mesocumulates to reduce their bulk plagioclase composition by \(\sim 6\) to \(\sim 2\) mol % An in that range. This effect tends to damp the fractionation process by sequestration. Trapped liquid solidification has been discussed by Morse (2013).

**Modal effect of olivine**

The systematics of multiphase Rayleigh fractionation reveals that a fractionation curve can become steepened when a given phase component is scarce, having nothing to do with chemistry (Morse, 2008). This effect causes the ‘depletion mode’ curve shown in Fig. 3. That effect is brought into play to some extent when the local cumulate is richer in olivine than the Ol:Pl cotectic ratio of about 25:75 in oxygen units (Morse, 2013). This may account for some rocks with low An in plagioclase over the range 10–40 PCS, or even in the olivine-rich basal Lower Zone at \(<10\) PCS. Here the olivine compositions and abundance tend to be high even where the plagioclase compositions are low in An, a condition fostering depletion in An owing to modal scarcity of plagioclase. Where both Fo and An are low together, recharge with fractionated magma may be inferred (there are five examples in the range 0–20 PCS).

**Magmatic characteristics**

Experimental studies of the inferred parent magma composition, designed to mimic the evolution of the Lower Zone to its eventual saturation with augite (Morse et al., 2004), show that the path from very little augite component to saturation can indeed be very long, with about 83% of the primary melt crystallizing as troctolite. That result is to some extent embedded in the experimental design. Nevertheless, the estimated bulk composition of the intrusion is very similar to that of the chilled margin.
A Relevant Formalism

Apart from the issues of pressure and competition from olivine discussed above, we seek a more fundamental cause of weak evolution of plagioclase composition in troctolites. Issues involving the augite component will not work, as discussed below. Instead, an intrinsic property of the system, the low activity of silica, will do the trick. If the silica activity is low, the NaSi component, Ab, of plagioclase, is rendered less effective and instead the role of An is enhanced. These terms will be given more formal development in the ensuing treatment.

Silica Activity in Magmas

From observation, the concept of the activity of silica in magmas is not frequently encountered in the current petrological literature. Its history may therefore usefully be mentioned in a contribution such as this, in which the burden of the argument revolves around silica activity. The ‘critical plane of silica undersaturation’ was a description by Yoder & Tilley (1962) of the Albite–Orthoclase (Ab–Or) join in Bowen’s (1937) ‘ Petrogenesis of Residual System’, the ternary system Nepheline–Leucite–Silica (Schairer, 1950). Liquids below this line were deemed ‘critically undersaturated’ because the crystallization of feldspar would drive the residual liquid to eventual saturation with a feldspathoid. Liquids above this Ab–Or line, in contrast, would evolve toward saturation with quartz or another form of pure silica. From these principles it is clear that the feldspar join is a thermal maximum in the residua system.

This nomenclature is conceptually useful in dividing intrinsically undersaturated liquids from those that are capable of becoming saturated with a silica phase. But it is only a generalized concept with some attached ambiguity. In what dimension is Ab–Or a ‘plane’? (It is actually a section through a Gaussian negative surface, a saddle-shaped temperature–composition surface.) Exactly how silica-undersaturated is this divide? And how shall we numerically express its relationship to actual silica saturation? The answer lies in the quantitative calculation of silica activity, most notably brought into the light of a magmatic discussion by Carmichael et al. (1970) and then made the foundation of all magmatic petrology by Carmichael et al. (1974) in their classic and revolutionary textbook on Igneous Petrology.

Despite its enduring utility in discussing magmas and their evolution, the numerical value of the silica activity associated with different magma types is rather sensitive to the thermodynamic parameters used in the calculations. One result of this sensitivity was that in the actual parameters used by Carmichael et al. (1974), a stable equilibrium was found to exist between forsterite (Fo) and quartz (Q), an assemblage contrary to experience because it is known to be unstable with respect to the orthopyroxene enstatite (En). Accordingly, Morse (1979a) applied free energies from the newer literature for En and Fo and used a new value for the entropy of orthopyroxene based on the mineral–liquid assemblages found in Makaopuhi Lava Lake in Hawaii, in order to write a new equation for the activity of silica.

From this practical approach it was then possible also to show that there exists an activity ratio for oxygen/silica, thereby linking oxygen fugacity (itself an activity) and silica activity in such a way that the one could be calculated from the other. In this result, tholeiitic magmas plotted just above the fayalite–magnetite–quartz (FMQ) buffer. Troctolitic magmas, however, were found to lie on the wustite–magnetite (WM) buffer, substantially below the FMQ buffer (Morse, 1980, fig. 10). They then fractionated to slightly less-reduced compositions until titanomagnetite forms, after which the oxygen fugacity runs at a constant distance between FMQ (~40%) and WM (~60%).

In modern terms, the activities of oxygen and silica in magmas are most usefully calculated from multiple mafic mineral compositions in the QUILF equilibria of Andersen et al. (1993), assuming the presence of all relevant mafic minerals. But it should be emphasized that calculations of phase equilibria can be usefully made even in compositional–thermal spaces that are not physically saturated with all relevant phases: these are metastable equilibria. An example will be shown in the development that follows.

Silica Saturation in Magmas

A chemical system is said to be saturated in silica if a crystalline phase of silica is present at equilibrium. At relatively low temperature and low pressure, 1 atm to ≤1.43 kbar, that phase is generally tridymite; at higher temperatures it is cristobalite, and otherwise at plutonic magmatic conditions high (β) quartz. Systems deficient in silica may contain silica-poor phases such as nepheline or leucite; in petrological parlance such systems are considered ‘undersaturated’ in silica. Systems containing...
neither normative quartz nor a feldspathoidal signature have been called ‘critically undersaturated’. Troctolitic magmas fractionating to syenite are an example. Tholeiitic magmas that fractionate to rhyolite or granite may become saturated in silica.

Complex multicomponent systems can be defined by a few pertinent reactions leading to a determination of intensive parameters such as the chemical potential, or more specifically the activity, of silica and oxygen. The chemical potential \( \mu_i \) is defined as the partial molar free energy per mole of a component \( i \). The activity \( a_i \) of a component \( i \) is related to the mole fraction \( X_i \) of that component by

\[
a_i = X_i \gamma_i
\]

where \( \gamma_i \) is the activity coefficient, to be determined empirically. Ideal solutions are defined as those for which \( \gamma_i = 1 \). The activity is related to the chemical potential by

\[
\mu_i = \mu_i^0 + RT \ln a_i
\]

where \( \mu_i^0 \) is the chemical potential at some standard state (such as the pure component \( i \) at the temperature and pressure of interest), \( R \) is the ideal gas constant, and \( T \) is the temperature in degrees Kelvin.

The presence of quartz or its polymorphs in equilibrium with a silicate melt defines the activity of silica as \( a^{\text{SiO}_2} = 10 \) in the system. A carbonatite magma may have \( a^{\text{SiO}_2} = 0 \), and a granite magma crystallizing quartz will have \( a^{\text{SiO}_2} = 10 \). All phases at equilibrium in such a system will also have \( a^{\text{SiO}_2} = 10 \). The presence of magnesian olivine suggests \( a_{\text{SiO}_2} < 10 \) but the presence of fayalite permits \( a_{\text{SiO}_2} = 10 \). Therefore, the activity of silica in a mafic melt will be expected to increase toward 10 as the ferrous iron ratio increases. In the Skaergaard intrusion, that tendency occurs when pigeonite ceases to be a cumulus phase at a coexisting olivine composition of \( \sim\text{Fo}_{10} \). Calculations then yield a value of \( a_{\text{SiO}_2} = 0.9 \) (Morse, 1994), or nine-tenths of the way to silica saturation.

**Kiglapait petrography**

The Kiglapait magma was critically undersaturated to the extent that it never crystallized either quartz or a feldspathoid at the liquidus. Its final product was a high-temperature syenite with feldspars at the ternary minimum. Most of the rocks contain normative hypersthene (NE) and after the crystallization of major Fe–Ti oxides near 94 PCS a few calculated liquids contain normative NE (Fig. 5). The normative NE is accommodated in feldspar and augite components. Unlike tholeiitic magmas, the Kiglapait liquid did not encounter an olivine hiatus, conventionally ascribed to the oxidation accompanying the arrival of cumulus magnetite and leading to the breakdown of iron-rich olivine to magnetite plus silica (Morse et al., 1980). Instead, in the Kiglapait intrusion, olivine remained present at the liquidus but became locally more magnesian near the Main Ore Band, leading to ‘oxygen spikes’ in some rocks (Morse, 1979b). These spikes result from the oxidation of the magma that decreases the activity of ferrous iron, hence favoring the Mg end-member. The absence of Ca-poor pyroxene in the Kiglapait cumulates is diagnostic of the difference between troctolitic and tholeiitic magma types, and is a major signal of low silica activity.

That said, traces of Ca-poor pyroxene do occur locally in troctolites as reaction rims on olivine, revealing the minor presence of trapped liquid. They also occur in small (millimeter- to centimeter-scale) pockets where enough liquid has been trapped to form oxysymplectites (e.g. Morse, 1969, plate 34; Morse, 1980). These strictly local intergrowths (rarely more than one, and usually zero, per thin section) consist of magnetite and hypersthene, partially invading crystals of olivine that have reacted with trapped liquid. Although fundamentally caused by the oxidation of olivine with release of silica to form hypersthene, the bulk analyses of the phases also show the introduction of Fe, Ti, Al, and Si as well as oxygen, so the symplectites result from a late, local magmatic reaction above the solidus. The process eventually runs out of oxygen and stops consuming olivine. The persistence of unaltered olivine exterior to the oxysymplectites defines a low activity of silica and oxygen in the rock generally.
These intergrowths, local vestiges of trapped liquid, are highly concentrated in the evolved components of magnetite, silica, and oxygen that are ordinarily encountered in crystals only near 90 PCS. They do not represent the ambient magma of the Lower Zone. Nevertheless, they furnish an opportunity to reveal the chemical reactions that are pertinent to the issues of plagioclase fractionation encountered here. A silication reaction that leads to an understanding of silica activity is the EFS reaction:

\[
\text{MgSiO}_3 = \text{MgSi}_{0.5}\text{O}_2 + 0.5\text{SiO}_2.
\]

Enstatite Forsterite Silica

A redox reaction that also locks the silica activity is the ‘FMQ’ reaction:

\[
6\text{FeSi}_{0.5}\text{O}_2 + \text{O}_2 = 2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2.
\]

Fayalite Oxygen Magnetite Quartz

Reaction constants used for these equations were developed by Morse (1979a) and summarized by Morse (1980), for a pressure of 4 kbar. Quartz was used as the reference state for these calculations. Reactions and their constants from Morse (1980) may be found in the Supplementary Material to this paper.

The oxysymplectite reaction is represented by equation (3) run backwards to make orthopyroxene (hypersthene) and the redox reaction dissolves the Fa component of the olivine to make magnetite plus quartz in equation (4) run forward.

When the condensed phases coexist in equilibrium at \( P \) and \( T \) they define the state of the system in terms of silica and oxygen activities, and if liquid is present it also shares those activities. Therefore the crystal equilibria also define the crystal + liquid state of equilibrium. The equations can be used to evaluate the intensive parameters of the magma at equilibrium with only olivine and plagioclase, as happens in the entire Kiglapait Lower Zone from 0 to 84 PCS.

**Application to liquidus equilibria**

For the EFS reaction (3) we can write the equilibrium constant \( K \) for a given temperature and pressure as

\[
\log K = \log a_{\text{MgSi}_{0.5}\text{O}_2} + 0.5\log a_{\text{SiO}_2} - \log a_{\text{MgSiO}_3}.
\]

Rearranging and multiplying to eliminate the fraction, we have

\[
\log a_{\text{SiO}_2} = 2\log a_{\text{MgSiO}_3} - 2\log a_{\text{MgSi}_{0.5}\text{O}_2} + 2\log K.
\]

Log \( K \) is equal to \(-\Delta G_e/RT\) where \( \Delta G_e \) is the Gibbs free energy change for the reaction. Empirical constants for log \( K \) in the form \( A/T + B + C(P - 1)/T \) are given in table 6 of Morse (1980), reproduced here in the Supplementary Material. Because this reaction involves the presence of orthopyroxene it furnishes only a maximum estimate of the silica activity for the Kiglapait troctolites, and that result must be adjusted downwards from the FMQ results to estimate the actual activity of silica.

Similar relations are also developed for the oxygen activity called the fugacity, \( f_{\text{O}_2} \), in the Supplementary Material. From this process the oxygen fugacity is obtained using mineral compositions and temperatures as input.

For the FMQ reaction [equation (4)] we write

\[
\log K = 2\log a_{\text{Fe}_3\text{O}_4} + 3\log a_{\text{SiO}_2} - 6\log a_{\text{FeSiO}_3} - \log \text{O}_2
\]

and when the appropriate constants are applied (see Supplementary Material) we have a solution for the last term, the log of the oxygen fugacity. When this was determined for the Kiglapait oxide minerals it was also possible, using the mineral compositions, to isolate the activity of silica from the above equation (Morse, 1980). This result in turn required correction to a value 0.1 lower in the log scale of silica activity relative to the EFS result.

Upper Zone rocks with Ti-magnetite furnish a direct estimate of silica activity through the QUILF equilibria (Andersen et al., 1993):

\[
\text{SiO}_2 + \text{Fe}_2\text{TiO}_4 = 2\text{Fe}_3\text{O}_4 + \text{FeTiO}_3.
\]

Quartz Ulvöspinel Fayalite Ilmenite

**Application to the Kiglapait Lower Zone**

To calculate silica activity in the natural rocks we require a description of the olivine compositional trend (Fig. 6). The data are scattered for many reasons, including probable addition of fresh, fractionated magma in the region 0–20 PCS and the abundant crystallization of plagioclase in felsic layers (‘plag effect’) that drives the olivine composition to lower values simply because it is scarce (Morse, 2008). A ‘trapped liquid path’ is shown as a dotted line for the Lower Zone, and this is calculated from observed residual porosity values (Morse, 2012) that cause the Fo values to decrease by reaction with trapped liquid. The upper path (continuous line) in this figure is drawn to represent a plausible trend of liquidus compositions. It is this path that will yield the silica activity in the main body of the magma (see Supplementary Material for the equation).

A labor-saving device was constructed (Morse, 1979a) by contouring the compositions of liquidus olivine against the Kelvin temperature and silica activity referred to quartz at 5 kbar. A portion of this \( T-X\)–activity space is shown here as Fig. 7. The contours are linear on \( T/K \) and derived from the EFS reaction. Using an algorithm relating nominal orthopyroxene compositions to olivine compositions, \( X_{\text{en}} \approx 0.85X_{\text{fo}} + 0.15 \), the observed olivine compositions are translated directly to the silica activities.
of the inferred pyroxene compositions that would coexist with the observed olivines. Temperatures were taken from the 5 kbar experimental study of Morse et al. (2004) covering the entire Lower Zone to saturation with augite at 84 PCS. The results are shown in Fig. 7 as open circles from 0 to 90 PCS.

From the study of Fe–Ti oxide minerals (Morse, 1980) it was found that at 93.5 PCS the silica activity obtained from the FMQ equilibria was lower than that for OPX saturation by 0.1 units in the log scale. The plotted array of points was therefore lowered by that amount to give the ambient silica activity for the LZ troctolites. The result is shown by the lower bold line in Fig. 7, with labels showing points of interest in the PCS scale. The evolution of silica activity is flat to 60 PCS and then climbs by a value of ~0.04 log units to augite saturation at 84 PCS. It then declines modestly to 87.5 PCS within the Upper Zone, at which point the modal augite proportion is about 30 vol. %, greater than its cotectic proportion (Morse, 1979c). This metastable excursion of the magma into the augite field reaches its maximum augite production of 42.5% at 90 PCS.

Although the graphical method of evaluating this record of silica activity is based on old and probably outmoded reaction constants, the general nature of the result is adequate to show an interesting change in the trend, peaking at 84 PCS. This inflection can only result from the steepening (and tightening) of the olivine compositional array toward a lower Fo value that in itself responds to the new coexistence with augite (Fig. 6).

**Stratigraphic results**

To put this result into context, the entire history of silica activity in the intrusion is shown in Fig. 8, modified from fig. 16 of Morse & Ross (2004). The data for the Lower Zone and early Upper Zone are taken from Fig. 7 where they are scaled downward from the EFS reaction. Here the trend is reversed along with the temperature scale. It is connected at 90 PCS to the array determined for the Upper Zone. The LZ–UZ boundary is marked with a vertical dashed line labeled ‘AUG+’.

In the UZ array the original estimates from the FMQ reaction (Morse, 1980) are shown as open rectangles. New estimates from QUILF, kindly provided by D. H. Lindsley (personal communication, 2004), are based on a significantly larger assemblage of equilibria among fictive quartz, ulvöspinel, ilmenite, liquid, and fayalite.
suggests a range toward a lower value. pigeonite is not an early liquidus phase; accordingly, a small arrow EFS fig. 1a of Morse (1979)

Band arises from the sudden deposition of Fe^Ti oxide and is strengthened by the QUILF result. The triangle above the MOB gives the open rectangles and lower, dotted line, but the subsequent calculations from QUILF (black rectangles) supersede the earlier results. The sharp increase in silica activity beyond the Main Ore Band arises from the sudden deposition of Fe-Ti oxide minerals, mostly titanomagnetite, and the resulting silication of the main magma body. Figure modified from fig. 16 of Morse & Ross (2004). The polygon labeled ‘MLL’ shows the silica activity for the tholeiitic Makaopuhi lava lake (Wright & Weiblen, 1967) at an olivine composition of Fo49, corresponding to 91 PCS in the Kiglapait intrusion. The MLL liquid is reported to have the phases Ol, Opx, and Mt at 1293°C. The dotted line at 0.15 on the y-axis labeled ‘Skd’ is a recalculation for the base of the Skaergaard intrusion as an example. Let us consider the low-silica effect, using comparisons with the tholeiitic Makaopuhi Lava Lake, a natural experiment analyzed by Morse et al. (1993), and is enhanced.

The polygon labeled ‘MLL’ shows the silica activity for the tholeiitic Makaopuhi lava lake (Wright & Weiblen, 1967) at an olivine composition of Fo49, corresponding to 91 PCS in the Kiglapait intrusion. The MLL liquid is reported to have the phases Ol, Opx, and Mt at 1293°C. The dotted line at 0.15 on the y-axis labeled ‘Skd’ is a recalculation for the base of the Skaergaard intrusion using $T = 1368^\circ$C and olivine Fo72 (Thy et al., 2009, 2013) and the EFS fig. 1a of Morse (1993a) for conditions at 1 atm, tridymite base, and pigeonite at the liquidus. This is a maximum value because pigeonite is not an early liquids phase; accordingly, a small arrow suggests a range toward a lower value.

Near the Main Ore Band the mineralogy is dominated by the peak production of augite and depletion of olivine in the rocks (Morse, 1979c). The Main Ore Band itself shows a wide range of silica activity, shown by the vertical line at 93.5 PCS. The estimated early UZ trend bisects this line and is strengthened by the QUILF result. The sharp increase in silica activity beyond the Main Ore Band arises from the sudden deposition of Fe-Ti oxide minerals, mostly titanomagnetite, and the resulting silication of the main magma body.

Figure 8 also shows a pentagon symbol at 0.05 on the log scale (0.9 on the activity scale) labeled MLL for Makaopuhi Lava Lake, a natural experiment analyzed by Morse (1979a) from several data sources. The x-axis location of this point is taken from the olivine composition (Fo49) applied to the Kiglapait PCS scale. This sample is quartz-tholeiitic, and is of high silica activity for its olivine composition; it lies on the FMQ buffer. The sample of melt with olivine, orthopyroxene, and magnetite was taken at 1293°C, very hot!

Also shown in Fig. 8 is a horizontal dashed line (‘Skd’) near 0.15 in the log scale, representing the calculated initial silica activity for the Skaergaard intrusion (Morse et al., 1980). The magma represented here is an olivine tholeiite with an olivine hiatus from ~Fo53 to Fo40 with pigeonite as the low-Ca pyroxene. In this intrusion the mean plagioclase composition varies as ~16% An km$^{-1}$, not inhibited by low silica activity. The Kiglapait Lower Zone was, in sharp contrast, at a much lower silica activity, ~0.27 on the log scale.

**APPLICATION TO PLAGIOCLASE FRACTIONATION**

If a system of melt and crystals is sufficiently rich in silica the activity of the NaAlSi$_3$O$_8$ albite component is maximum and, all other things being equal, crystallization will proceed with maximal enrichment of Ab and depletion of An. If, however, the silica activity is low, the activity of albite itself may become low as in the following reaction:

$$NaAlSi$_3$O$_8 - 2SiO_2 = NaAlSiO_4$$

which we may write with rearrangement

$$2\log a_{SiO_2} = \log a_{NaAlSiO_4} - \log a_{NaAlSiO_3} + \log K$$

and thereby the activity of silica available to plagioclase is diminished by loss to nepheline. With this loss, the enrichment in Ab is retarded and the relative activity of anorthite is enhanced.

At what point does the silica activity become critically low for this to happen? To a first approximation it is synchronous with the absence of orthopyroxene or pigeonite among the cumulus crystals. It is ensured in the absence of intercumulus crystals of orthopyroxene except where local as in reaction rims or intergrowths.

Other petrographic measures can help to identify the low-silica effect, using comparisons with the tholeiitic Skaergaard intrusion as an example. Let us consider the mean value of 3% An km$^{-1}$ of cumulate for the Kiglapait Lower Zone, versus several measures for the Skaergaard...
intrusion as follows (McBirney, 1996): 14% An km\(^{-1}\) for the first 1000 m (the Lower Zone) and for the interval LZb alone, 8.3% An km\(^{-1}\), even where augite was crystallizing and magnetite arriving. It may be recalled that the Skaergaard intrusion has an olivine hiatus where oxygen and silica activities are high enough to destabilize Mg-olivine until the liquid evolves enough to stabilize Fe-olivine (e.g. Morse, 1994). The Kiglapait intrusion lacks this hiatus, but instead generates Mg-rich olivine by oxidation when magnetite crystallizes. Therefore the intrinsic silica activity is lower in the Kiglapait system. The LZ and early UZ path shown in Fig. 8 defines the silica activity trend over this interval, and it is clearly much lower than that at Skaergaard, even when augite crystallizes.

However, in the northern Upper Zone sector of the intrusion where Fe–Ti oxide minerals are more conspicuous, calculated silica activities at \(\sim 91\) PCS do rise locally to the same level as at Skaergaard (Fig. 8). This effect appears to be a precursor of the rapid rise in silica activity after the deposition of the Main Ore Band. In any case, it does not affect our understanding of conditions in the Lower Zone (0–84 PCS) where the slow evolution of plagioclase composition occurs.

An augite effect

The augite component of the magma has an opposite effect to that of low silica activity. The CaAl component of the pyroxene in effect steals from that available to plagioclase and by lowering the An activity it promotes the evolution toward Ab. The experimental normative augite content in the LZ melt rises from 5% to 25% at saturation with augite crystals (Morse et al., 2004; see Supplementary Material). Therefore the retardation of plagioclase compositional evolution by low silica activity is increasingly opposed by the decreasing activity of CaAl in the plagioclase component of the melt. Yet the low silica effect wins out, until augite actually crystallizes, when the tables are turned and the CaAl component is extracted from the melt by both solid phases at once. When augite does first crystallize, it does so in small amounts, and the mode rises in the rocks continually from a few per cent at 84 PCS to a maximum overshoot of 42% in the volume mode at \(\sim 90\) PCS (Morse, 1979e). It then has a very strong effect on the rapid evolution of plagioclase.

**Analysis of the crystallization paths**

**Normative issues**

The normative plagioclase composition of Kiglapait rocks for the region 0–90 PCS is compared with that of separated feldspars in Fig. 9. The rocks have persistently higher normative An than the actual plagioclase crystals that occur within them. The excess An in the oxygen norm amounts to about 6% at 0 PCS, 4% at 30 PCS, and diminishes to 2% at 90 PCS. One reason for this excess is that the norm convention takes all the Al (after orthoclase and albite have been formed) to form An to make anorthite. Instead, a considerable amount of the resident Al resides in the pyroxene component, along with a small amount of the Ab component NaSi. However, the amount of augite component in the early LZ rocks is minor, so the augite contribution to excess Al becomes important only at higher values of PCS. That the difference between norms and separated plagioclase crystals decreases with fractionation progress shows that the Al in augite is not a major contributor to the difference. The norm routine inflates the An content of the plagioclase by at least the amounts shown above. Accordingly, for purposes of modeling, the differences shown in Fig. 9 are applied as corrections to the normative plagioclase compositions, as shown in Table 2.

**Projection to the system Diopside–Anorthite–Albite**

**Conversion of data**

This ternary system (Fig. 10) is well suited to an examination of the paths of natural systems along with theoretical liquid fractionation paths. The latter are rigorously derived as tangents to the plagioclase—liquid legs of three-phase triangles at the cotectic with the constraint that all paths in the plagioclase field originate at the An corner (Presnall, 1969; Morse, 1994). Here these paths are shown in grayscale for a fixed value of \(K_D = 0.468\) (Table 1),
consistent with an assumed average Lower Zone pressure of 4 kbar [equation (1)].

Two liquid paths for the Kiglapait Lower Zone are shown in the figure. The continuous curve is calculated from the normative augite content of the summation liquid and the normative plagioclase composition adjusted for the differences shown in Fig. 7. The input data are given in Table 2. The curve runs dramatically toward Di across the liquid fractionation paths, simply showing that the observed data for the intrusion run rapidly toward saturation with augite but slowly in terms of plagioclase evolution.

To avoid the compromised model An content of the summation liquids it is desirable to plot liquid compositions that are derived solely from the actual plagioclase compositions as represented by the bold line in Fig. 3. Still using the normative augite contents, the dashed curve in Fig. 10 labeled \( K_D \) loop was generated from the last three columns in Table 2, and these in turn from the linear partitioning equation in Appendix 1 (Supplementary Material). This path also climbs dramatically toward augite saturation and nearly mimics the summation path, but is located 1–10% lower in An content.

### Analysis of the results

There are several notable features to Fig. 10. First, the pure fractionation path (dotted on the grayscale curve) leads to the cotectic with a plagioclase composition of An 40, as shown by the three-phase triangle. This end point compares with the plagioclase composition of An 50 at equilibrium with the last liquid in the \( K_D \) loop path (Table 2). Hence the natural crystallization path is far less advanced than in a pure fractionation process, and at a much higher augite to feldspar ratio (33% augite instead of 20%). The mean augite to feldspar ratio in the Kiglapait liquids never drops as low as 20% [Morse, 1981].

Second, the \( K_D \) loop path also crosses the liquidus fractionation lines at a considerable angle, with a final fictive crystal composition of An 42 that would be defined by the final tangent to the path. Instead, the actual crystal composition is An 50 (Table 2), so the path ignores the rules. It is also unlike an equilibrium crystallization path, for which the total solid composition would have to be An 56 given by a tie line from the last liquid through the starting composition.

Third, both the calculated paths show a small initial interval of pure fractionation along a liquidus fractionation line. This result is consistent with the low initial augite contents shown in Table 2; it also shows that the modeling is realistic.

Fourth, both paths terminate at saturation with augite near the 1 atm Di–An–Ab cotectic. This near-coincidence suggests that the pressure effect on the location of the field boundary is small, as the loop calculation was done for the pressure range 5–13 kbar. A similar indifference to pressure is also found with the experimental plagioclase–olivine cotectic, which does not move significantly with pressures up to 13 kbar [McIntosh, 2009]. This result puts the Aug–Plag cotectic ratio at 33% Aug for the Kiglapait composition at augite saturation.

Fifth, the summation path is offset 1–10 mol % higher in An content than the \( K_D \) loop path, despite having been moderately adjusted for the difference between the norms of rocks and the actual plagioclase compositions, as seen in Fig. 9. This result can only mean that the summation liquid is intrinsically more An-rich than the equilibrium liquid defined by the \( K_D \) loop, and that not all of its richness in An resides in the augite component.

Sixth, as always the case in this system, there is a drastic change in the liquid direction and the rate of plagioclase evolution at the cotectic, when the liquid runs directly away from the Di–An sideline. This is reflected in the Kiglapait plagioclase trend (Fig. 11).

Finally, the two paths differ by one degree of freedom: they share the same augite content of the liquid, but the summation path is subject to closure assumptions and possible conceptual error, whereas the \( K_D \) loop rigorously finds the plagioclase liquid composition at equilibrium with the actual crystallizing plagioclase, according to the principles of the linear partitioning equation found by experiment (Morse et al., 2004). Still, the fact that the two paths show the same behavior in crossing the fractionation lines and becoming steeper with augite content shows
an intrinsic correlation of An with augite in the natural fractionation process.

**REVIEW AND CONCLUSIONS**

**The nature of troctolites**

The clue to this unaccustomed effect lies in two main compositional truths about troctolitic magmas. First, they are not basalts, which have been defined as rocks composed of augite plus plagioclase. And second, they are subject to liquid constraints on crystal fractionation that do not occur in basalts. Troctolitic magma is a high-temperature magma type, which, over a range of ~40°C, contains only two main crystallizing phases, olivine and plagioclase, before becoming saturated with augite (Morse et al., 2004). According to Table 2, this range corresponds to a variation in the liquid composition of 20 mol % An and in the crystal composition of 17 mol %.

At the same time the fraction of augite relative to augite + feldspar in the melt increases dramatically to ~30% in the experiments of Morse et al. (2004) and ~31% (referred to 84 PCS) in the summation liquids of Table 2. The experiments were intended to find the equilibrium condition, whereas the summation liquids are affected by the ‘slow arrival’ and overproduction of augite (Morse, 1979c). That the two paths are similar in shape is encouraging.

The entire stratigraphic array of plagioclase compositions in the intrusion is shown with a trend line (called ‘actual’) in Fig. 11. The expected path from pure fractional crystallization (Fig. 10) is shown dotted, and the difference at 84 PCS is 10 mol % An, as before. The shallower trend continues until 91 PCS, slightly beyond where the augite content of the metastable liquid path becomes maximum at 89 PCS (Morse, 1979c). Now the effect of augite crystallization is to steepen dramatically the curve of plagioclase
composition, as on the cotectic in the system Di–An–Ab. This steepening ceases at 96 PCS, precisely where the excess modal augite curve rejoins the normal curve in fig. 12 of Morse (1979c). The steep curve fractionates plagioclase at a rate of 17 mol % An km⁻¹. The ensuing trend over the last 1446 m fractionates at a rate of 13.8 mol % An km⁻¹.

The nature of norites

The alternative companion to troctolite is the silicated rock called norite, composed of hypersthene and plagioclase. A norite magma has the silica activity of the EFS reaction. That result is similar to the upper array in Fig. 7 for the following reason. Even though there may be no olivine present, the olivine grid is linked to the related orthopyroxene composition by the algorithm mentioned above. Olivine is then the proxy for Opx. Its use would only have to be adjusted with respect to the observed pyroxene composition. The present solution for troctolite would be appropriate if the observed pyroxene were appropriately more magnesian than the olivine plotted. Details can be ignored if we only wish to make the point: Opx saturation is essentially equivalent to tholeiitic silica activity, similar to the Skærgaard estimate.

Norite plays a large role in the Nain anorthosite. Troctolitic rocks occur east of the ‘Olivine line’ of Morse (2006). They include major troctolitic intrusions but also dark-facies anorthosite. These olivine-bearing anorthosites are dark because they have dark gray plagioclase and that is because the feldspars have many exsolved rods and blades of Fe–Ti oxide minerals. These in turn are favored by the low silica and oxygen activities that supply ferrous iron to the feldspar. To the west of the olivine line, the anorthosites are mostly noritic, mostly older, and paler because of fewer inclusions owing to higher oxygen fugacity. The color of the rocks betrays their origin. The dark troctolitic facies comes more directly from the mantle source. The pale noritic facies has seen more crustal influence (Morse, 2006).

Differentiation trends in troctolite

Olivine fractionation

The principle of fractionation influenced by the activity of some component in the liquid extends to olivine. In this case the retarding component within the troctolitic Lower Zone is ferric iron, which is conserved in the liquid until augite and then titanomagnetite crystallize at 84 and 88.6 PCS, respectively. Ferric iron then becomes overproduced at the ‘Main Ore Band’ at 93.5 PCS (e.g. Morse, 1979b, 1979c). In this stratigraphic region are found at least eight samples with anomalously high Mg ratios, called ‘oxygen spikes’ by Morse (1979b). These examples provide evidence that the increase in oxygen fugacity and of ferric iron occurs at the expense of ferrous iron, so that the activity of the fayalite component is depressed and that of the forsterite component enhanced as in the FMQ equation (4). Accordingly, the evolution of olivine in a troctolitic magma is retarded with respect to that in an augite-bearing magma, as illustrated in the sharp steepening of the olivine composition curve in the Kiglapait Upper Zone (fig. 10 of Morse (1979b)).

Plagioclase fractionation

The total combined effects on the retardation of plagioclase compositions in the Kiglapait Lower Zone are those from pressure, trapped liquid, presence of olivine, and the low silica activity in the melt. The results shown in Fig. 10 suggest a low-silica effect of 10 mol % An relative to a pure fractionation path. The critical signature of low silica activity in troctolites is the absence of Ca-poor pyroxene in the cumulate rocks.

The question has been raised as to whether noritic magmas can be shown to fractionate plagioclase faster than troctolitic ones. Unfortunately, existing noritic examples with stratigraphic sequences comparable with the Kiglapait troctolite are not known to this writer.

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