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AUGITE–OLIVINE EQUILIBRIA IN THE KIGLAPAIT INTRUSION, LABRADOR, CANADA

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ABSTRACT

The first appearance of abundant cumulus augite in the Kiglapait layered mafic body, on the coast of Labrador, defines the base of the Upper Zone at 84 PCS (percent solidified). The appearance of this phase is gradual, culminating in an impressive overproduction in the region around 90 PCS. This behavior can be rectified to yield an "errorless equivalent" cumulus arrival of augite at 81 PCS. The observed modal behavior was interpreted as evidence for a poorly stirred magma in which augite components were sequestered in the core of a convection cell. The compositional relations of augite and olivine offer some support for this hypothesis. These relations are best viewed in the context of linear partitioning in binary solutions extended to coexisting pairs of mineral species that share the same exchange reaction, here $FeMg_{-1}$. Hence, rather than a melting loop, the partitioning of Fe and Mg involves the two crystalline solutions augite and olivine. Here, the partition coefficient D is formulated as X_{Fe}^{Aug}/X_{Fe}^{Ol} (hence $D \leq 1.0$). A test of linear partitioning is applied: $D = X_{Mg}^{Aug}*K_D + X_{Fe}^{Aug}$, where K_D has its usual Roeder–Emslie meaning. For the subsolidus Kiglapait equilibria, a strong linear correlation is found ($r^2 = 0.995$) for PCS > 91.4, running from fictive $D = K_D = 0.32$ at the pure Mg end of the augite series to $D = 1.0$ at the pure Fe end of the augite series. For the stratigraphic interval 84–91 PCS, D is clustered well above the line at $D = 0.63$–0.68. This higher value of D suggests a metastable equilibrium on a narrower loop driven by an overstepping reaction. At high temperature modeled by QUILF, the same general relations hold, but all values of D are higher, and the linear array leads back to a significantly higher $K_D = 0.44$, as would be expected for higher-temperature interphase equilibria. Hence, linear partitioning can be used successfully to describe both liquidus and subsolidus interphase equilibria. With calibration, the fictive K_D can be correlated with T, from liquidus equilibria at the higher limit to intracrystalline cation diffusion blocking at the lower limit.

Keywords: linear partitioning, Kiglapait intrusion, subsolidus equilibria, binary solutions, augite, olivine, Labrador.

SOMMAIRE

Le premier signe de l'augite cumulative en abondance dans le massif stratiforme basique de Kiglapait, sur la côte du Labrador, marque la base de la Zone Supérieure à 84 PCS (pourcent de solidifié). L'apparition de cette phase est graduelle, menant à une surproduction impressionnante dans la région de 90 PCS. Ce comportement peut-être corrigé afin d'obtenir un point de saturation équivalent de l'augite cumulative à 81 PCS. La proportion modale observée a été interprétée comme résultat d'un magma stagnant dans lequel les composants de l'augite étaient piégés au centre d'une cellule de convection. Les compositions de l'augite et de l'olivine coexistantes étayent cette hypothèse. Leurs relations mutuelles sont évaluées avec avantage en utilisant le concept de la répartition linéaire dans un système de solutions binaires, ici appliqué aux paires de minéraux coexistants régis par la même réaction d'échange, $FeMg_{-1}$. Dans ce cas, à la place d'un intervalle de fusion, il s'agit de la répartition de Fe et Mg entre les deux solutions cristallines, augite et olivine. Le coefficient de partage D dans ce cas a la forme X_{Fe}^{Aug}/X_{Fe}^{Ol} ; donc, dans ce cas, les valeurs de D sont égales ou inférieures à 1.0. Il est possible de tester la validité de la répartition linéaire: $D = X_{Mg}^{Aug}*K_D + X_{Fe}^{Aug}$, le K_D ayant sa signification "Roeder–Emslie" normale. Pour les équilibres au stade subsolidus à Kiglapait, il y a une forte corrélation linéaire ($r^2 = 0.995$) pour les roches dont la valeur de PCS dépasse 91.4, allant d'un D virtuel = $K_D = 0.32$ pour le pôle magnésien de la série de l'augite jusqu'à $D = 1.0$ au pôle Fe de la série. Sur l'intervalle stratigraphique 84–91 PCS, les valeurs de D se regroupent nettement au dessus de la droite, à $D = 0.63$–0.68. Cette valeur de D plus élevée fait penser qu'il y a eu un équilibre métastable et un intervalle de compositions plus restreint à cause d'une réaction dépassant le point d'équilibre. A température élevée d'après l'équilibre QUILF, les mêmes relations générales s'appliquent, mais toutes les valeurs de D sont plus élevées, et la collection linéaire de points implique une valeur nettement plus élevée de K_D, 0.44, comme on pourrait s'y attendre pour les équilibres interphases à plus haute température. Il semble donc que le concept de répartition linéaire peut servir à décrire les équilibres entre phases sur le liquidus et dans le domaine subsolidus. Avec calibrage, la relation du K_D virtuel avec la température pourrait être établie entre les équilibres sur le liquidus à la limite supérieure jusqu'à la fermeture du système à la diffusion intracristalline des cations, au seuil inférieur.

(Traduit par la Rédaction)

Mots-clés: répartition linéaire, massif intrusif de Kiglapait, équilibre subsolidus, solutions binaires, augite, olivine, Labrador.

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INTRODUCTION

The Kiglapait Intrusion is a large, 1.3-Ga-old strongly differentiated, layered mafic body exposed on the coast of Labrador, near latitude 57° North. Its layered series is dominated by a thick, troctolitic Lower Zone (LZ), which eventually gives way to an Upper Zone (UZ) whose lower bound is defined by the appearance of augite. This pyroxene is at first highly magnesian, but over the span of the UZ it varies, along with olivine, to the Mg-free end of the augite series and coexisting fayalite. The covariation of these two crystalline solutions is the principal subject of this paper. Recent summary descriptions of the Kiglapait Intrusion can be found in a study of olivine by Morse (1996), in two MS theses on the experimental investigation of the liquid line of descent (Sporleder 1998, Peterson 1999), and in a comprehensive review of troctolitic magmas and sulfide deposits by Scoates & Mitchell (2000).

A secondary but nearly co-equal subject of this paper is the treatment of augite–olivine Fe–Mg equilibria in terms of linear partitioning in binary solutions. This principle was introduced in terms of melting equilibria (Morse 1996, 1997), then extended to intercrystalline equilibria in the Earth's transition zone (Morse 1998), and later applied to distillation of boiling mixtures, volcanism, and lower mantle equilibria (Morse 2000). The emphasis here is once again on intercrystalline equilibria, using linear partitioning as a tool for testing hypotheses on the origin of anomalous partitioning between augite and olivine, as well as for demonstrating a rather elegant non-anomalous partitioning behavior at both subsolidus and magmatic temperatures.

BRIEF REVIEW AND PREVIEW

The key to the principle of linear partitioning is that it is anchored to the exchange coefficient K_D, which many petrologists first learned to apply in practice through the seminal study on olivine–liquid equilibria by Roeder & Emslie (1970). It is this link to the fertile career of Pete Roeder that I wish to celebrate in this brief note. Few papers in petrology can have had the impact of that succinct and elegant 1970 paper. In defense of this statement, I offer the following quote from a famous geochemist: "Well, if the olivines and liquids aren't Roeder–Emslie then I don't believe it," (Stan Hart, *circa* 1980). In due course, the compositions of olivine and liquid at Kiglapait were found to be "Roeder–Emslie"; the problem lay in the liquid compositions determined by summation (Morse 1996).

In what follows, I return to the field setting and a review of the compositional variation in these mafic minerals as a function of height in the stratigraphic section of the Kiglapait Intrusion. I then introduce linear partitioning as applied to intercrystalline equilibria, with some examples from the metamorphic literature. Then the application to the field data is discussed, leading to the conclusions of the paper.

STRATIGRAPHIC MINERALOGY

Cumulus olivine and augite appear sequentially in any up-stratigraphic traverse through the Kiglapait Intrusion. The field relations involving these two minerals require some review in order to afford a clear basis for understanding their compositional relations. Olivine is present throughout the stratigraphy (Morse 1979a, b), including the inverted Upper Border Zone (UBZ; Morse & Allison 1986, Morse 1995). Augite appears much higher than olivine in the stratigraphic section of the layered series, or in the more evolved rocks of the UBZ. Stratigraphic position in the intrusion is referred to a volumetric measure of the observed and inferred lithological boundaries, and represented as volume percent solidified (PCS; Morse 1969).

According to the volume calibration as still used, the appearance in the stratigraphy (or "arrival" at the accumulating floor) of augite begins (or began) below 82 PCS with the mapped appearance of "2-cm pyroxene clots" (Morse 1969), *i.e.*, oikocrysts of augite that nucleated and crystallized at random centers from trapped liquid. The modal amount of these augite clots is too small to signify saturation of the main magma with augite. On traversing up the stratigraphy, one soon finds rare independent grains of augite in addition to the clots, and these are interpreted as cumulus grains that presumably nucleated from locally augite-saturated magma that was not yet, however, the main type of magma at the floor. At yet higher levels, the clots disappear, and the cumulus grains become more abundant until they achieve the status later found to represent full saturation of the magma with augite. At this level of modal abundance of augite representing full cumulus status, the base of the UZ is assigned at 84 PCS. The evolving sequence of augite textures and modes is illustrated in photographs of thin sections (Morse 1979b).

Modal abundances of all the cumulus minerals at Kiglapait are plotted against PCS in the petrographic summary by Morse (1979b). As shown there, and as recapitulated above, the gradual appearance or "slow arrival" shown by augite is also seen in the modal behavior of Fe–Ti oxides and immiscible sulfide droplets in the region near 90 PCS, but it is strikingly absent in the case of the arrival of apatite, which is instantaneous and intrusion-wide at 94 PCS. In all the slowly arriving phases, the cumulus arrival is arbitrarily assigned to the level of modal abundance considered normal. This normal level of abundance is inferred from the modal quantities higher in the stratigraphy, where the modal excursions have ceased.

In the case of augite, the following sequence of modal criteria was noted (Morse 1979b, Table 3): oikocrysts at 81.6 PCS, slope change in modal abundance also at 81.6 PCS, cumulus status at 84 PCS, half-height of abundance at 86 PCS, wholesale saturation at 86.5 PCS, peak abundance of 42% at 91 PCS, and equivalent equilibrium (or errorless) saturation at 81 PCS. This latter criterion bears further elucidation.

When a phase-saturation boundary is reached at stable equilibrium in a well-stirred fractionating system, the new fractionating product undergoes a discontinuous jump in abundance from zero to something. In magmatic terms, this discontinuity has been called a "rock hop" (Morse 1994). The modal behavior of augite, oxides, and sulfide is inconsistent with a discontinuous, wholesale saturation of the magma with the incoming phases, whereas the behavior of apatite is consistent therewith. The slow arrivals were therefore interpreted (Morse 1979b) as reflecting an incremental saturation of the main magma with the retarded phases. That process in turn was attributed to poor stirring of the crystallizing boundary-layer into the less active main body of the magma. The gradual modal variations were therefore regarded as evidence for a system in error because of poor communication across its whole volume. This interpretation, in turn, led to a strenuous objection to the fluid-dynamics school of generalized, wholesale magmatic turbulence, as earlier summarized in this Journal (Morse 1988).

The hypothesis of poor stirring was tested in one way by a purely geometrical exercise on the modal variation diagrams. The modal slopes representing the slow arrivals persist into the UZ stratigraphy beyond the assigned cumulus arrivals, thereby creating a region of "overproduction" of the mafic mineral in question. It therefore became a natural idea to equate the positive modal overproduction with the negative modal quantities lower down in the stratigraphy, as measured against the assumed equilibrium values. This exercise of equating areas on the stratigraphic diagrams resulted in the concept of the "errorless equivalent arrival" of each retarded cumulus phase. In this analysis, the idealized (discontinuous) saturation in augite of the equivalent, well-stirred system was pegged at 81 PCS, rather than at the UZ boundary, 84 PCS. The 81 PCS criterion represents the calculated stratigraphic level at which augite would have appeared in a well-stirred magma; the 84 PCS criterion represents the first persistent cumulus status actually recognized in the field.

The calculated liquid path based on volumetric modes for the Kiglapait LZ and nearby UZ was shown in a ternary Ol–Pl–Aug plot by Morse (1979b). The plot showed the LZ cotectic extending far into the augite field, to a maximum augite content of 42 modal percent at ~91 PCS. This extension was regarded as a metastable excursion of the crystallizing boundary-layer into the oversaturated magma that had not earlier participated in the production of augite. Such an excursion then represented the "other end" or consequence of the error. The 81 PCS point in that plot falls at an Ol/(Ol + Aug) ratio of 0.38. Experimental determination of the LZ liquid line of descent at 5 kbar in graphite (Sporleder 1998) showed the first crystallization of augite at the same Ol ratio. The lever rule applied to the array from augite saturation through the bulk composition to the troctolite sideline also identifies the augite saturation point as ~81 PCS. The original analysis of the "errorless equivalent arrival" therefore correctly predicts the experimental result within the experimental and conceptual uncertainty.

The hypothesis of poorly stirred and sequestered magma was also used to explain the contrasting behavior of apatite. The overproduction of Fe–Ti oxide minerals is strikingly evident in the field (and from the air!) in the upward-increasing frequency, density, and thickness of oxide-rich layers. These culminate in the submeter-thick "Main Ore Band" (MOB) at 93.5 PCS, above which the frequency of oxide-rich layers drops sharply to zero. The succession of oxide deposits culminating in the MOB appears to represent a quantitative flushing out of excess oxide components from the magma. Such dense mineral deposits, ultimately devoid of any silicate phases whatever, must have sunk with great speed through the magma. It is therefore to be expected that they signify the end of poor stirring, and represent at least one episode of wholesale, perhaps violent turbulence.

And then apatite first arrived at the floor, at 94 PCS, a few hundred meters above the MOB disturbance, and it did so instantaneously, consistent with wholesale saturation of the well-stirred main magma.

The entire stratigraphic evolution of the early Upper Zone is, then, hypothesized with some supporting evidence to represent a transition from crystallization controlled by a relatively segregated boundary-layer, through a crisis brought on by oversaturation of a major body of magma in dense mafic components, to a stable, durable late stage of routine crystallization and accumulation. It is in the context of this hypothesis that the Fe–Mg exchange relationship between augite and olivine is to be examined.

COMPOSITIONAL RELATIONS

Olivine compositions determined by electron microprobe are given in Morse (1996) in stratigraphic order. Augite analyses were made by wet chemistry by Ken-Ichiro Aoki, and the results are as yet unpublished. The augite trend in the pyroxene quadrilateral lies near Wo_{40} throughout its length, as shown in Morse (1994, Fig. 17.11). For both minerals, the compositional parameters of interest here are X_{Mg} and X_{Fe}, in which the Mg and Fe end members are projected from all other components. The complete dataset contains 23 analyzed coexisting pairs (Table 1). Their stratigraphic relations are shown in Figure 1.

Three sample tielines are shown in Figure 1 to illustrate that the two mineral compositions are at first relatively close together (*e.g.*, the short tieline at 84.5 PCS),

TABLE 1. COMPOSITIONAL DATA FOR AUGITE AND OLIVINE IN THE UPPER ZONE, KIGLAPAIT INTRUSION

Sample #	PCS	F(L)	En(AUG)	Fo(OL)	Fs	Fa	D=Fs/Fa
KI 3363	84.5	0.155	0.734	0.594	0.266	0.406	0.655
KI 3364	85.8	0.142	0.714	0.569	0.286	0.431	0.664
KI 3367	87.0	0.130	0.716	0.580	0.284	0.420	0.676
KI 3368	87.6	0.124	0.717	0.570	0.283	0.430	0.658
KI 3369	89.3	0.107	0.688	0.510	0.312	0.490	0.637
KI 3371	91.0	0.090	0.683	0.520	0.317	0.480	0.660
KI 4032	91.4	0.086	0.691	0.508	0.309	0.492	0.628
KI 3351	94.9	0.051	0.564	0.304	0.436	0.696	0.626
KI 3249	96.4	0.036	0.608	0.348	0.392	0.652	0.601
KI 4066	(UBZ)		0.536	0.250	0.464	0.750	0.619
KI 3247	96.6	0.034	0.492	0.220	0.508	0.780	0.651
KI 3377	97.0	0.030	0.417	0.181	0.583	0.819	0.712
KI 3003	98.0	0.020	0.397	0.143	0.603	0.857	0.704
KI 3379	98.6	0.014	0.296	0.114	0.704	0.886	0.795
KI 4120	99.55	0.0045	0.191	0.053	0.809	0.947	0.854
KI 4119	99.60	0.0040	0.191	0.059	0.809	0.941	0.860
KI 4080	99.92	0.0008	0.102	0.029	0.898	0.971	0.925
KI 4061	99.94	0.0006	0.171	0.052	0.829	0.948	0.874
KI 4081	99.94	0.0006	0.064	0.013	0.936	0.987	0.948
KI 4076	99.98	0.0002	0.029	0.005	0.971	0.995	0.976
KI 3381	99.98	0.0002	0.069	0.016	0.931	0.984	0.946
KI 4077	99.985	0.00015	0.002	0	0.998	1	0.998
KI 4078	99.985	0.00015	0.010	0	0.99	1	0.990

Note: PCS, percent solidified; F(L), fraction liquid.

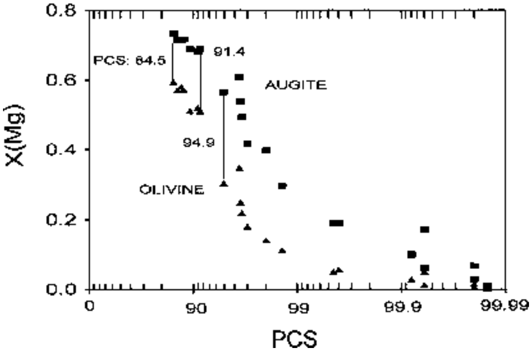

FIG. 1. Composition of pairs of augite and olivine in the Upper Zone of the Kiglapait Intrusion, plotted in terms of X_{Mg} against stratigraphic height, represented as volume percent solidified (PCS). Three sample tielines are drawn for reference at the indicated values of PCS.

then diverge to longer tielines, then converge again, finally to tielines of zero length at the Fe end members. The initial lengthening of the tielines would appear at first glance to be an unremarkable feature of a normal binary solution-loop, in which the tielines diminish to zero length at both extreme ends of the loop. However, by use of linear partitioning, one can show that the initial tielines are anomalously short for their composition range.

Of particular interest in Figure 1 is the scatter in mineral compositions at equivalent or nearby stratigraphic levels. There is a strong tendency, later to be shown more dramatically, for the values of X_{Mg} in the two minerals to vary sympathetically. This result shows that the compositional scatter is common to the rock itself, and not to modal variations and re-equilibration. Such stratigraphic compositional scatter is found in all Kiglapait minerals to some degree. It is partly due to the fact that samples from all over the intrusion are plotted against a common volume-scale, whereas fractionation actually proceeded at different rates in different radial segments of the intrusion, as measured against stratigraphic markers like the MOB and apatite arrival. The scatter may also be increased by local effects, such as foundering of UBZ roof cumulates, and other dynamic phenomena.

The mineral pairs shown in Figure 1 are those found in the natural rocks, and are therefore subsolidus pairs that have equilibrated to some extent during cooling. The amount of re-equilibration is a function of relative modal abundance of augite and olivine as well as relative closure temperature of intercrystalline diffusion for the two minerals. The equivalent compositions at the assumed high temperatures of the liquidus were calculated from QUILF (Andersen *et al.* 1993) for selected stratigraphic levels by Morse (1996, Table 2). The high-temperature pairs so calculated are shown in Figure 2, for comparison with Figure 1. Here, the variation of tielines is more orderly, but the early pairs are still anomalous, as will be shown.

LINEAR PARTITIONING

The principle of linear partitioning can be used fruitfully to examine the partitioning relations between augite and olivine at Kiglapait, and to test the hypotheses on the origin of the "slow arrivals" and subsequent overproduction of the three dense mafic cumulus phases. The principle was used in the earlier study of Kiglapait oli-

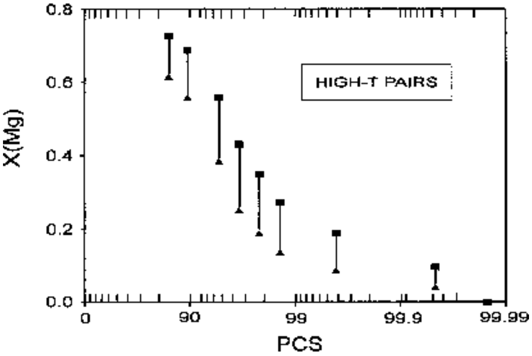

FIG. 2. Augite–olivine pairs as recalculated at high temperature by the QUILF routine of Andersen *et al.* (1993) and published in Table 2 of Morse (1996).

vine (Morse 1996, a paper dedicated to Pete Roeder and Ron Emslie) to simplify the stepwise calculation of olivine fractionation by the Rayleigh distillation equation.

Linear partitioning in binary solutions occurs when the partition coefficient for the mole (atom, mass) fraction of one component in two phases is linear against the composition of the numerator phase. The intercepts of this linear array are 1.0 at one end member of the solution pair, and the value of the exchange coefficient K_D at the other end. I use the terminology of Beattie *et al.* (1993) for the partition and exchange coefficients. The mole fraction is conventionally taken as

$$X_i = n_i/(n_i + n_j) \qquad (1)$$

where *i* and *j* are the endmember components of the binary solution, and *n* is the number of atoms. The partition coefficient is formed as

$$D_i \frac{X_i^m}{X_i^p} \qquad (2)$$

where *m* and *p* are the two phases of the binary solution. The linear partitioning relation is given (Morse 1997) by

$$D_i = K_D \bullet X_j^m + X_i^m \qquad (3)$$

where K_D is the familiar exchange-coefficient

$$K_D \frac{\left(n_i / n_j\right)^m}{\left(n_i / n_j\right)^p} \qquad (4)$$

Where linearity is observed, it signifies that K_D is constant, and *vice versa*. K_D is an inverse function of loop width, ranging from nil width at $K_D = 1.0$ to infinite width at $K_D = 0$.

Ramberg (*e.g.*, 1952) was among the first to represent intercrystalline metamorphic phase-equilibria as isobaric, *T–X* solution loops, most notably in his discussion of the equilibrium between chlorite and garnet (his Fig. 30). The modern version of this loop, as represented by the solution modeling of Spear (1995), is a wide loop with a low value of $K_D = 0.16$, as shown in Figure 3.

The partitioning of the biotite–garnet pair in the sillimanite zone was carefully studied and modeled using van Laar loops by Kretz (1990). Excluding one errant sample, the partitioning array for the 12 remaining sillimanite-bearing samples listed in Table 1 of Kretz is linear, with $r^2 = 0.995$ and $K_D = 0.250$, as shown in Figure 4.

A detailed consideration of van Laar loops, with calculated synthetic examples, was offered by Kretz (1991). All of the three nested loops shown in his Figure 1 show linear partitioning, and illustrate the inverse relation between loop width and K_D. This result is illustrated here in Figure 5, which shows one example of the linear fit, and a compilation of all the lines and their associated values of K_D.

Not all binary solutions show linear partitioning and constant K_D, but linear behavior is common among melting and metamorphic equilibria that are not strongly non-ideal, or that form binary maxima or minima (Morse 2000).

With this brief introduction to the principle of linear partitioning, I now return to an examination of the Kiglapait data for augite and olivine.

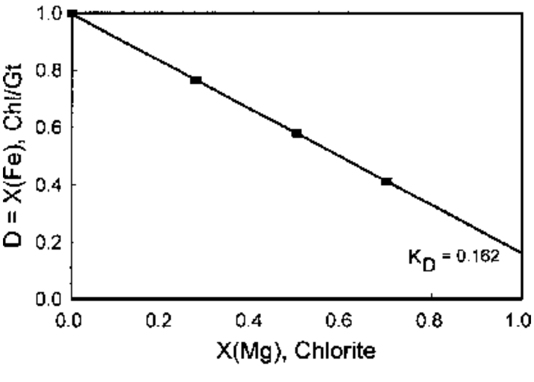

FIG. 3. Linear partitioning in model garnet–chlorite equilibria, as calculated by Spear (1995).

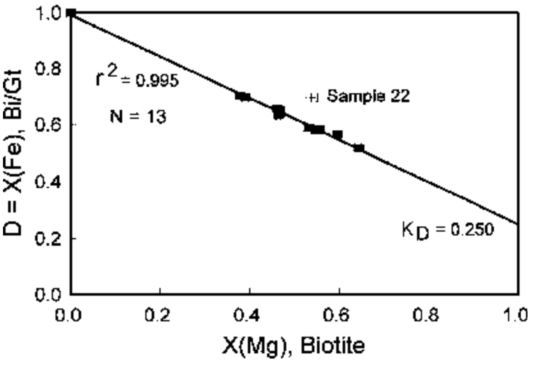

FIG. 4. Linear partitioning in 12 garnet–biotite pairs of Kretz (1990, Table 1) from the sillimanite zone. The theoretical end-point at unity was included in the regression. Sample 22 was considered anomalous by the original author and was omitted from the regression.

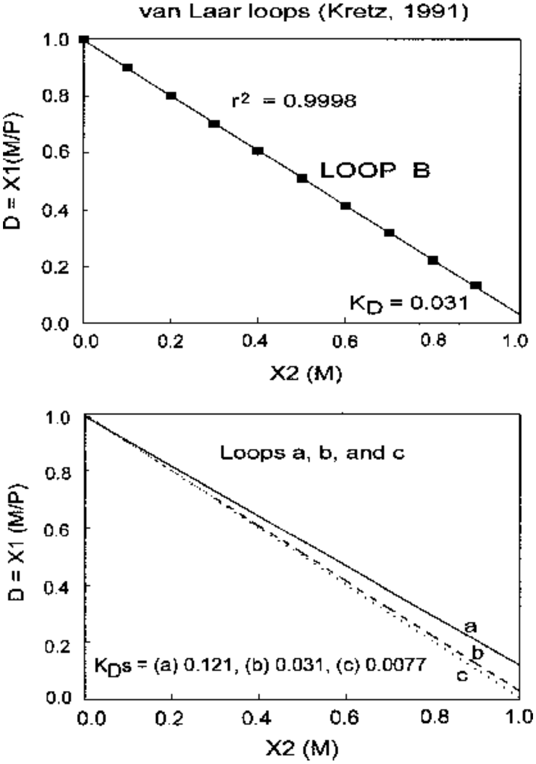

FIG. 5. Linear partitioning of the three synthetic van Laar loops of Kretz (1991, Fig. 1). Top figure: example of the regression on loop b. Bottom figure: lines and K_D values for all three loops.

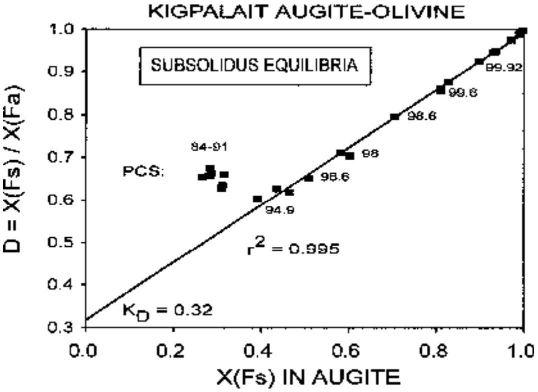

FIG. 6. Linear partitioning in Kiglapait augite–olivine pairs as they occur in the rocks today. The data are taken from Table 1. The pairs from lower stratigraphic levels, 84–91 PCS, lie distinctly off the linear array at a relatively high constant value of *D*.

APPLICATION TO KIGLAPAIT DATA

The data from Table 1 and Figure 1, representing the subsolidus compositions as found today in the Kiglapait rocks, are shown in the linear partitioning *D*–*X* plot of Figure 6. Two features of this array are especially noteworthy. The first is that all 15 of the sample pairs lying stratigraphically above 94 PCS form a very tight linear array with the high correlation-coefficient r^2 = 0.995, and consistent with an intercept value of K_D = 0.32. This linearity reflects the observation made earlier from the *X*–*h* plot of Figure 1, regarding the sympathetic variation of the olivine and augite compositions, which are therefore a property of the rock sample and not of partitioning differences. This conclusion is dramatically shown by the linearity in the *D*–*X* plot, whereas such a conclusion is obscure and qualitative in Figure 1.

The second feature of note in Figure 6 is that the early compositional pairs lie distinctly off the curve, at a nearly constant value of $D = 0.654 \pm 0.015$, well above the value of ~0.5 on the curve. This result strongly confirms the impression from the stratigraphic plot that the early tielines are anomalously short. The high value of *D* and the short tielines bespeak an equilibrium tendency toward converging compositions. Such a tendency is known to result from high temperatures, but the linear partitioning array on a quasi-ideal *T*–*X* loop is *independent* of temperature. A tendency toward *D* = 1.0 is also encountered in kinetically induced metastable equilibrium.

The question of the temperature effect can be readily addressed with Figure 7, a *D*–*X* transform of Figure 2 regarding the high-temperature pairs as modeled by QUILF. Here again one finds a strong correlation of the composition pairs higher in the stratigraphy, with a resulting value of K_D = 0.44. This value is significantly higher than the subsolidus value of 0.32 (Fig. 6), as expected from the general expectation that K_D is a positive function of temperature. But again, the early pairs lie well above the curve, a characteristic clearly inherited from the subsolidus pairs as found in the rocks today.

DISCUSSION

It is clear that no amount of thermal juggling will bring the anomalous values down onto the linear curve, which would require that the early temperatures be far lower than later ones. This notion is contradicted by the steady evolution of all the mineral compositions toward the low-temperature end members. An origin by metastable crystallization of anomalously Fe-rich augite, or anomalously Mg-rich olivine, would satisfy the observations. Olivine crystallized during the entire lifetime of the magma before the advent of augite near 84 PCS,

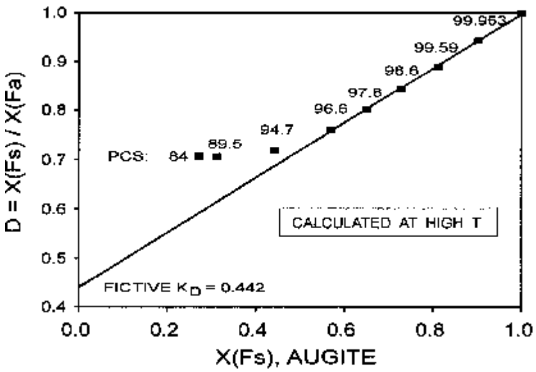

FIG. 7. Linear partitioning in augite–olivine pairs recalculated at high temperature using QUILF, as described in the text. Modeled pairs from the lower stratigraphic levels still lie off the curve, but the linear array shows a higher value of K_D than the subsolidus array, as expected for higher temperature.

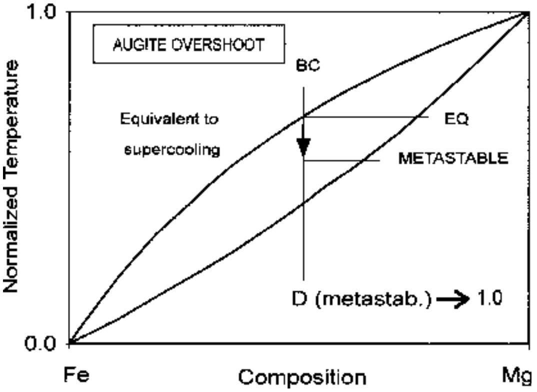

FIG. 8. Effect of metastable transit of the cosaturated L(Ol,Pl) composition into the Aug field. The result is equivalent to supercooling on a melting loop, and gives an anomalously Fe-rich composition of the crystals.

and its composition in the LZ and early UZ is well modeled by Rayleigh fractionation (Morse 1996). Moreover, metastability of pyroxene compositions is well known to be far more extreme, and more commonly observed in the plutonic setting, than that of olivine. It is therefore considered more likely that the early crystals of augite formed with anomalously Fe-rich compositions.

As discussed in the section on stratigraphic mineralogy, the modal data suggest a metastable overshoot of the augite saturation boundary, followed by an overproduction. Similar behavior is noted for Fe–Ti oxide minerals and sulfides (but not for apatite). Any transit of a liquid into the phase field of a third (or any added) crystalline phase must, in response to the evolution of the liquid consequent upon the crystallization of the previous crystalline solutions, result in supercooling relative to the condition of stable saturation in the new phase. Such a transit results in compositional supersaturation even on an isothermal path (Morse 1988).

Accordingly, it is possible to represent the delayed nucleation and overproduction of augite as equivalent to supercooling on a phase-transition loop (Fig. 8). In this analogy, the supercooling of a liquid BC of constant composition brings the solidus composition closer to the liquid, in this case making it more Fe-rich than at the condition of stable equilibrium. This is the case inferred from the linear partitioning evidence.

According to this interpretation, the olivine compositions represent the sustained equilibrium with the fractionating liquid, whereas the augite compositions, possibly nucleating in a physically different part of the S + L boundary-layer, represent a new, metastable equilibrium that eventually becomes restored to the stable condition, once the excess of augite component in the liquid is wiped out.

The actual physical location of the magma enriched in excess augite component is difficult to specify, other than to say it is not in the historically crystallizing boundary-layer. That magma fraction may have been resident or sequestered in an inactive part of the convection system, as originally considered (Morse 1979b). It might also have become involved with Fe-rich magma ponded at the base of the magma body from the draining of dense solute rejected from the LZ crystals (see discussion and references in Morse 1996). Such a scenario would furnish a compositional equivalent to the thermal metastability suggested above.

Any combination of the above considerations supports the original hypothesis on the slow arrival and overproduction of the three mafic cumulus phases in the Upper Zone of the Kiglapait Intrusion.

CONCLUSIONS

Treatment of the data by linear partitioning leaves little doubt that the augite–olivine loop is intrinsically linear. It also demonstrates clearly that the early-crystallizing pairs of Kiglapait olivine and augite are anomalous, whether considered as they sit in the rock today or as their high-temperature equivalents. The anomalous pairs show that the mineral compositions are too close together to represent equilibrium conditions. The best interpretation of the anomaly is to consider the augite crystals to be too Fe-rich for their position early in the stratigraphy. Such an inference supports, but does not exclusively demonstrate, the validity of the original interpretation of the slow arrival and later overproduction of augite.

The linear regressions in D–X space show that upon cooling, the augite–olivine pairs underwent subsolidus exchange from a nominal $K_D = 0.44$ at high temperature to 0.32 at a lower closure temperature. With the help of linear partitioning and adequate equations for diffusion involving the two phases, experimental equilibration of augite–olivine pairs should allow a good characterization of effective closure temperature *versus* K_D.

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