

DISTRIBUTION PATTERNS OF RARE EARTH ELEMENTS IN CERIUM RICH MINERALS

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Abstract. Evidence is presented which suggests that certain cerium-rich minerals (in particular allanite and monazite) commonly take up the larger rare earth elements with little (if any) fractionation, and that apatite shows a fixed degree of selectivity.

Introduction

Geochemical fractionation of the larger rare earth elements (La to Gd) tends to follow simple trends. As a result, the relative abundance of these elements in almost any rock or mineral can be plotted as a smooth curve (JENSEN & BRUNFELT 1965).

Analysis of the curves obtained by plotting much of the available data of rare earth abundances in geological samples to this system (JENSEN & BRUNFELT 1965, NEUMANN *et al.* 1966) has led to the following conclusions:

1) The take up of elements in the range La to Gd is strongly selective in many rock-forming minerals, and follows a pattern which is predictable in terms of the ionic radii of the elements involved. It is this crystallochemical fractionation which is probably responsible for the steady enrichment of a melt in the larger rare earths — a trend frequently observed in the early stages of magmatic differentiation.

2) A reverse trend, also involving strong fractionation of the rare earths, but with progressive relative depletion of the larger ions, takes place when an environment is enriched in volatiles, alkalis, and rare earth elements. It is not known whether this is another case of crystallochemical control (selective removal of the larger rare earths when

'cerium' rich¹ minerals such as allanite and monazite begin to crystallize), or whether it is some other form of chemical fractionation, e.g. due to differing degrees of rare earth complexing in a melt, or differing degrees of ionic migration across a geochemical gradient.

It is commonly assumed that a mineral which is 'cerium' rich is also 'cerium' selective, but this is a *non sequitur*. When rare earth rich minerals begin to form, the melt is commonly enriched in the larger rare earths (as a result of the strong fractionation by earlier formed rock-forming minerals). Crystallization without fractionation would thus equally well produce minerals which are strongly enriched in the larger rare earth elements. The object of this paper is to examine some of the evidence available from localities where the degree of selectivity may be directly assessed in order to test the hypothesis, based primarily on theoretical considerations, that a number of the rare earth rich minerals are *not* strongly selective in their take up of the larger rare earth elements. Such localities are not, however, easy to find. Rare earth rich minerals commonly crystallize when the melt is rich in volatiles (often in a pegmatitic environment). Therefore, it is not possible to assume with a reasonable degree of certainty that the rock in which they occur has crystallized as a 'closed system'. Much of the supporting evidence in this paper is drawn from the somewhat specialized cases of *in situ* replacement of one rare earth rich mineral by another.

Theoretical considerations

The question of selective take up of rare earth elements during crystallization has already been examined in some detail in the case of rock forming minerals (NEUMANN *et al.* 1966). Many of the observed patterns in rock forming minerals can be readily explained, if it is assumed that the ionic radius of the element which most commonly occupies a given lattice position is close to the optimum value for that position. It is clear, for instance, that if such is the case, it will be

¹ Minerals containing a high proportion of the larger rare earths are commonly referred to as 'cerium' rich, since, in terms of total abundance, cerium is the element which predominates. Use of the term does not imply anomalous fractionation of cerium. The relative abundance curves for these minerals still show maxima at lanthanum.

progressively more difficult for the larger rare earth ions to occupy the relatively small sites commonly filled by Fe, Mg, and Ca, and their incorporation will place the lattice under strain. Hence the ferromagnesian and calcian rock forming minerals commonly fractionate the larger rare earths strongly and take up only a small proportion of the rare earth ions available in the melt.

Certain rare earth rich minerals incorporate rare earths by substitution in the same way as rock forming minerals. Allanite, for example, is essentially an epidote structure in which certain of the Ca ions are replaced by rare earths, but it differs from the majority of rock forming minerals: a) in being capable of taking up relatively large quantities of rare earths, and b) in frequently containing a high percentage of the larger rare earth ions. This can be explained if it is assumed that the allanite structure is not so 'rigid' as structures in the majority of rock forming minerals, i.e. there is not one optimum ionic radius for ions entering the Ca lattice position, but a range of acceptable values. The lattice is thus capable of taking up larger ions in the Ca positions without strain, and not only accepts a relatively high percentage of the larger rare earths, but does so without appreciable fractionation. If this is true, then the relative abundance of larger rare earths in allanite will be determined entirely by their relative abundance in the environment at the time of allanite crystallization.

In the case of minerals where cerium earths are an essential part of the structure (e.g. monazite $(\text{Ce, La})\text{PO}_4$), it can be postulated that the optimum ionic radius for the rare earth position in the lattice is close to that of the most abundant cerium earths, i.e. La and Ce. In which case it can be expected that fractionation will be minimal among the larger rare earths and will increase steadily towards the Lu end of the series. Since this is a case of substitution of ions which are smaller than the optimum for the lattice, fractionation, even in the case of a relatively 'rigid' lattice, may well be negligible over the first half of the series (La to Gd). Since rare earth elements smaller than Dy are virtually absent from monazite, it may be that in this mineral the smallest ions which can fill the La, Ce positions without strain to the lattice are of the size of Gd or Tb and that beyond this limit selectivity is *very* strong.

Plotting Method

The plotting method used in this paper was first described by JENSEN & BRUNFELT 1965. Primary differences in the total abundance of the individual rare earth elements are eliminated by ratioing each analysis element by element with a reference distribution, while differences in the concentration of rare earths as a group are eliminated by normalizing each analysis to $Gd = 1.00$. Since the object in this paper is to examine the degree of rare earth selectivity exhibited by certain minerals, plots have been ratioed, not to a common reference distribution, but to the distribution which, in each case, is thought to have been that of the environment at the time of crystallization of the mineral.

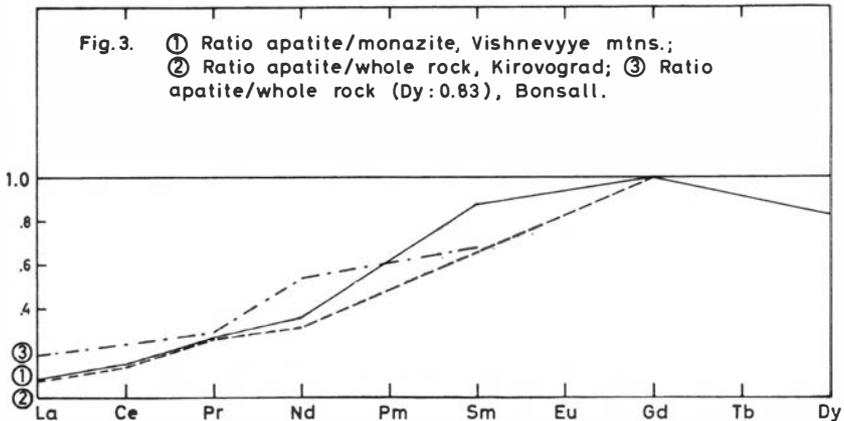
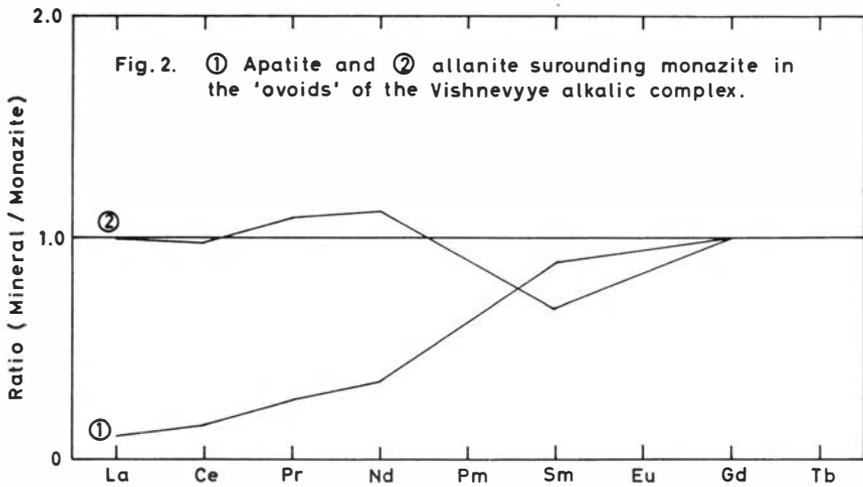
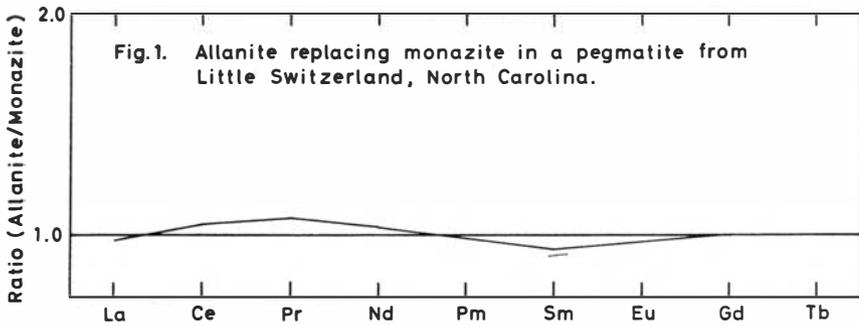
Distribution patterns in selected minerals

Allanite

MURATA *et al.* (1957) recorded an example of allanite (in a pegmatite at Little Switzerland, N. Carolina) replacing monazite without fractionating the larger rare earth elements. Since a big reduction in total percentage of rare earths accompanied the replacement (a reduction of two-thirds if the replacement is assumed to have been constant volume), it is clear that rare earth ionic migration occurred relatively freely in this environment. The lack of fractionation must be regarded as very strong evidence in favour of lack of selectivity in the replacing mineral (Fig. 1).

Data in a paper by YES'KOVA & GANZEYEV (1964) also support the suggestion that allanite frequently incorporates the larger rare earths without appreciable fractionation. They report examples from the alkalic complex of the Vishnevyye mountains, in which a reaction rim of allanite around a) bastnäsite and britholite and b) monazite has, in each case, the same rare earth distribution pattern as the original mineral. This is particularly striking in the second case, where an inner zone of apatite, between the monazite and allanite, has a very different pattern (Fig. 2).

The suggestion that the lack of selectivity of allanite is not a question of condition of formation, but due primarily to structural



properties, is supported by the instance just cited of apatite and allanite crystallizing together. These minerals have apparently formed under identical conditions. In both cases, rare earths occupy Ca lattice positions, and yet their rare earth distribution patterns are very different (Fig. 2). The only factor which can cause this difference is mineral structure. Since there is little difference in the co-ordination number of Ca in these two minerals, the variation cannot be explained by unequal change in the effective ionic radii of calcium and rare earth ions with change in co-ordination number (KHOMYAKOV 1963). It seems much more likely that it is related to the 'rigidity' or 'flexibility' of the structure, i.e. its ability for isomorphous substitution.

In a previous paper, it was shown that the range of rare earth distributions found in allanites is as great, or greater, than that shown by the complete range of igneous rocks (NEUMANN *et al.* 1966). Evidence which, although not in itself conclusive, again points to lack of selectivity in this mineral.

MURATA *et al.* (1957) have reported one case of allanite which was apparently strongly enriched in the larger rare earth elements relative to the minerals which it replaced. Mineralogical relationships in this example, however, are complex, and the allanite is not only replacing several vein minerals, but also aplitic wall rock.

The sum total of evidence seems to be strongly in favour of a non-selective incorporation of larger rare earth elements in the allanite lattice.

Cerianite

It has been shown (JENSEN 1967) that cerianite (essentially CeO_2), which occurs as pseudomorphs after monazite in a pegmatite at Iveland, has incorporated the larger trivalent rare earths in relatively large quantities without fractionation. Since quadrivalent cerium has an ionic radius close to that of gadolinium, it is necessary to postulate here also a less 'rigid' lattice capable of expansion without undue strain. Because of the nature of the replacement, it may be that the cerianite (unlike the allanite) was 'under pressure' to accept the total rare earth content of the original monazite, and may not incorporate the larger rare earth elements without fractionation when formed in an environment of relatively free ionic migration.

Apatite

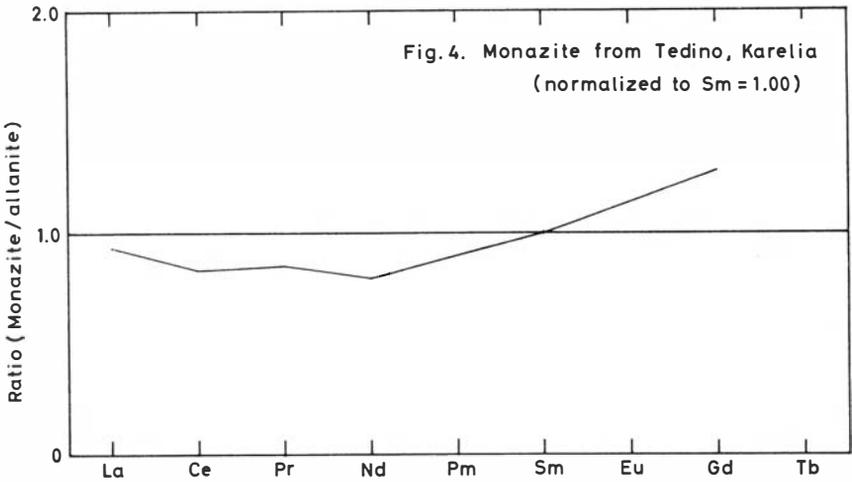
Since it is virtually certain that the relative abundance of available rare earths at the time of crystallization of the Vishnevyye apatite was that shown by the monazite and allanite which formed before and after (p. 12), it is possible to determine, with a fairly high degree of certainty, the selectivity of the apatite structure under these particular conditions. An attempt to determine the degree of selectivity of apatite was made previously using data from the Bonsall tonalite and the Kirovograd granite (NEUMANN *et al.* 1966). In spite of a) the incompleteness of the data, which necessitated normalizing to Dy in some cases and Gd in others, and b) the need for major assumptions concerning the composition of the magma at the time of apatite crystallization, the degree of selectivity shown by these earlier plots is very similar to that of the Vishnevyye apatite (Fig. 3). This is particularly surprising in view of the major differences in environment and the very variable composition of the minerals which form the apatite group. If it can be established by further studies that apatite invariably fractionates the larger rare earths to the same degree, then this provides a means of determining the rare earth distribution of an environment (at a given stage of crystallization) which is independent of any assumptions concerning a 'closed system' for that environment. Since apatite is of such widespread occurrence, this could be very valuable.

Monazite

The monazite group of minerals apparently include a complete solid solution series from $(La, Ce)PO_4$ to $CaTh(PO_4)_2$. Therefore, the monazite lattice is unlikely to have difficulty in accepting rare earth ions with ionic radii between those of Ce and Ca, i.e. Pr to Eu.

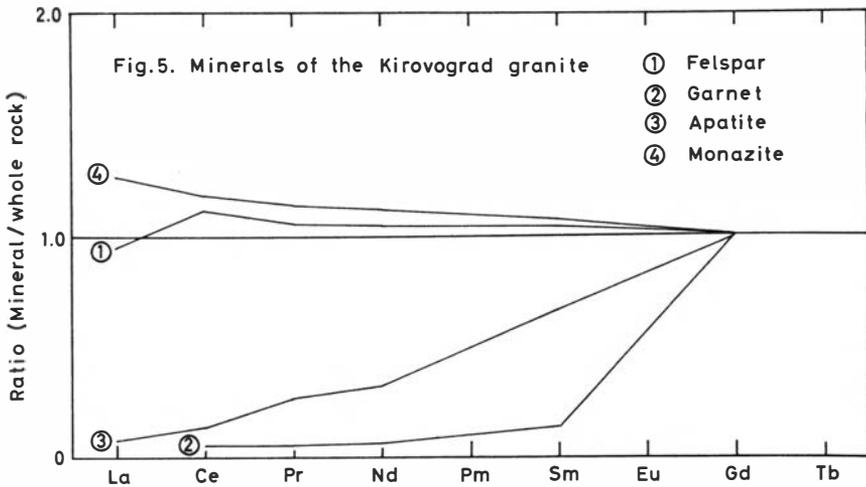
VAINSHTEIN *et al.* (1956) analysed a monazite from a pegmatite vein at Tedino, Karelia, and the allanite which it was replacing. The monazite data, ratioed to the allanite, are plotted in Fig. 4. The plot is very nearly horizontal and close to the base line if normalized to any element other than Gd (suggesting that Gd is anomalous and that virtually no fractionation of the larger rare earths has occurred during this replacement).

GAVRILOVA & TURANSKAYA (1958) have analysed the Kirovograd monazite bearing granite and all of its main mineral constituents. The



early formed feldspar shows the same relative distribution pattern for the larger rare earths as the whole rock (Fig. 5), indicating: a) that feldspar crystallization occurred without fractionation of these elements and b) that virtually no selective removal of larger rare earths occurred at any stage during the crystallization of the rock. Crystallization as a 'closed system' is also indicated by the apatite/whole rock plot in Fig. 5, which (as explained in the previous section) shows the 'expected' degree of apatite selectivity. Selective take up of rare earths in apatite (and garnet) will cause steady enrichment of the melt in the larger rare earth elements, and it is to be expected that a non-selective mineral, crystallizing over the same period, will show some enrichment in the larger rare earths relative to the whole rock pattern — such as is seen in the monazite/whole rock plot in Fig. 5. The conclusion, therefore, is that the monazite here is either non-selective, or only very slightly selective in its take up of the larger rare earths.

In the Vishnevyye mountains alkalic complex (p. 12) the monazite, apatite, and allanite occur in 'ovoids' formed at a post-magmatic stage of crystallization of an igneous intrusion. Monazite forms the central core with an intermediate zone of apatite and a peripheral zone of allanite. Allanite replacing apatite should show an apatite rare earth element distribution, and it therefore seems likely that this is primarily a case of overgrowth rather than replacement. It is then neces-



sary to postulate that: a) monazite has crystallized, taking up the larger earth elements from the environment without fractionation, b) apatite crystallized from the same environment, fractionating the larger rare earth elements in its normal fashion, and c) allanite crystallized last, again without fractionation of the larger rare earths.¹

It has been shown previously that analyses of a large number of monazites show a range of rare earth element distributions as great as that of allanite (NEUMANN *et al.* 1966). This is again not conclusive evidence, but a further indication of lack of selectivity in this mineral.

It cannot be determined on this evidence, whether take up of the larger rare earth elements by monazite is slightly selective or completely non-selective. The difference is an important one, since a mineral which is slightly selective can, if it captures a sufficiently high proportion of the total rare earths available in a melt, have a very marked effect on the relative abundance of larger rare earths in the residuum. Therefore, it is not possible to rule out crystallochemical fractionation as a possible controlling mechanism in the 'reverse trend' of fractionation among the larger rare earths.

¹ If the same mode of formation is postulated for the bastnäsite, britholite, allanite 'ovoids' formed in the metamorphic aureole of the same complex, then we have some (admittedly tentative) evidence for lack of rare earth selectivity in bastnäsite and britholite.

Summary

1. On theoretical grounds, a fairly convincing case can be made for the suggestion that a number of rare earth rich minerals are not strongly selective in their take up of the larger rare earth elements.

2. In the few cases where published data yield any direct evidence of the rare earth distribution in an environment during formation of allanite and monazite, it would appear that these minerals have accepted the larger rare earth elements with very little, if any, fractionation.

3. There is reasonably strong evidence to suggest that this lack of fractionation is often not due to the conditions of formation, which varied widely in the cases examined, but is primarily a matter of control by the mineral lattice.

4. It seems likely that, with a little more data, it will be possible to establish a list of indicator minerals, which either do not fractionate the larger rare earths (such as allanite and monazite), or which fractionate them to a known fixed degree (such as apatite). These could be used to deduce the rare earth distribution in the melt at various stages during crystallization, which would clearly be of untold value for petrogenetic studies.

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