

# DISTRIBUTION PATTERNS OF RARE EARTH ELEMENTS IN CERIANITE

BY

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**Abstract.** Geochemical fractionation of the larger rare earth elements tends to follow simple trends, and, as a result, the relative abundance of these elements in the majority of rocks and minerals can be plotted as a smooth curve. An exception to this general rule is predictable in the case of the mineral cerianite, which can be expected to contain anomalously high concentrations of cerium (present in the quadrivalent state). The present paper demonstrates that this expected anomaly does *not* occur in the cerianite found in an Iveland pegmatite, and the significance of this fact is discussed.

## Introduction

In spite of the very great similarity in the physical and chemical properties of the elements of the rare earth series, geochemical fractionation within the series commonly occurs during igneous and metamorphic processes. It is apparently related, directly or indirectly, to the small but steady decrease in ionic radius which occurs with increasing atomic number (known as the lanthanide contraction).

Fractionation is very strong among the larger elements, and over the range La to Tb the degree of fractionation commonly varies steadily with atomic number. This regular trend can be expressed graphically by plots of the type shown in Fig. 1, where each analysis appears as a relatively smooth curve.<sup>1</sup> The trend is apparent both in whole rock analyses (JENSEN & BRUNFELT 1965) and in mineral analyses (NEUMANN *et al.* 1966).

<sup>1</sup> Plots are limited to the range La-Gd since analytical data for Tb is seldom available.

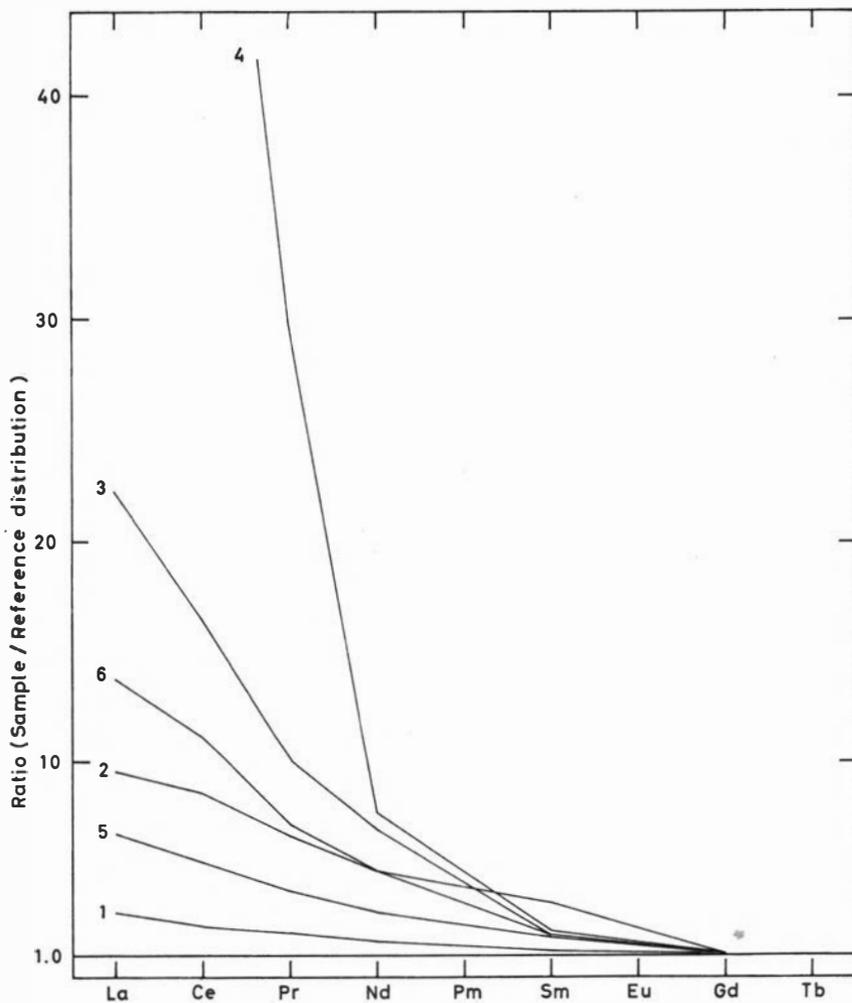


Fig. 1. Rare earth distribution curves of six mineral and rock samples: 1. CALCITE, E. Sayan carbonatite (VAINSHTEIN *et al.* 1961). 2. MONAZITE, N. Carolina quartz monzonite pegmatite (MURATA *et al.* 1957). 3. LOPARITE, Lovozero alkalic massif (BALASHOV & TURANSKAYA 1960). 4. DAVIDITE, Tuftan pegmatite (NEUMANN & SVERDRUP 1960). 5. GRANODIORITE, Susamyr batholith (LEONOVA & BALASHOV 1963). 6. LUJAVRITE, Lovozero alkalic massif (BALASHOV & TURANSKAYA 1961).

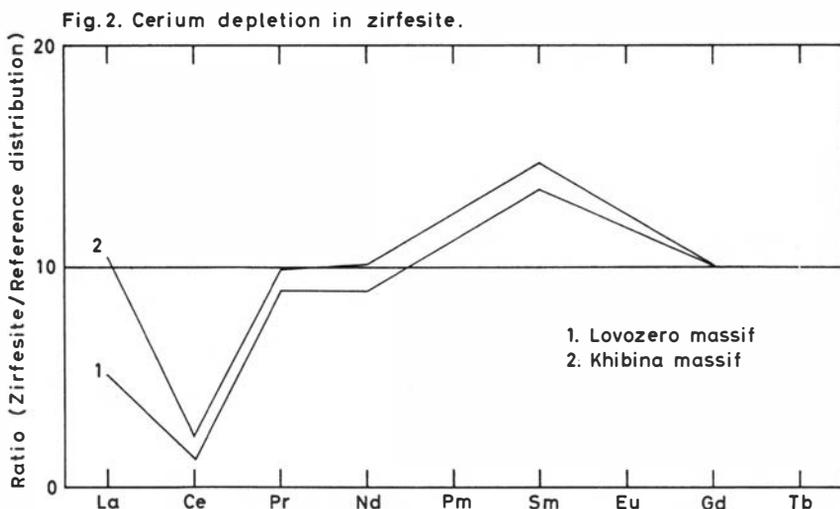
In these graphs, primary differences in the total abundance of individual rare earth elements have been eliminated by ratioing each analysis element by element with a terrestrial reference distribution (an average of three basaltic rocks), while differences in the concentration of rare earths as a group have been eliminated by normalizing each analysis to  $Gd = 1.00$ . A general discussion of plotting methods and a full account of the calculation of the reference distribution is given in JENSEN & BRUNFELT (1965).

### Oxidation state of cerium and europium

The simple pattern of fractionation can, however, be marred. All rare earth elements commonly show preference for the 3+ oxidation state, but two (cerium and europium) are known to exist in another oxidation state under conditions which can be reproduced in a natural environment (cerium as  $Ce^{4+}$  under oxidizing conditions, and europium as  $Eu^{2+}$  under reducing conditions). When such a change of valency state occurs, these elements naturally cease to follow the regular trend of fractionation.

Difficulties in determining the two elements with high precision have previously hindered studies of the extent and nature of anomalous cerium and europium fractionation in geochemical samples. Strongly anomalous europium, however, has been found by TOWELL *et al.* (1965) in rocks of the California Batholith and is recently reported by BRUNFELT & STEINNES (in press) in the standard granodiorite issued by the U. S. Geological Survey. It would thus appear that reduction of europium to the divalent state can be achieved fairly readily in an igneous environment.

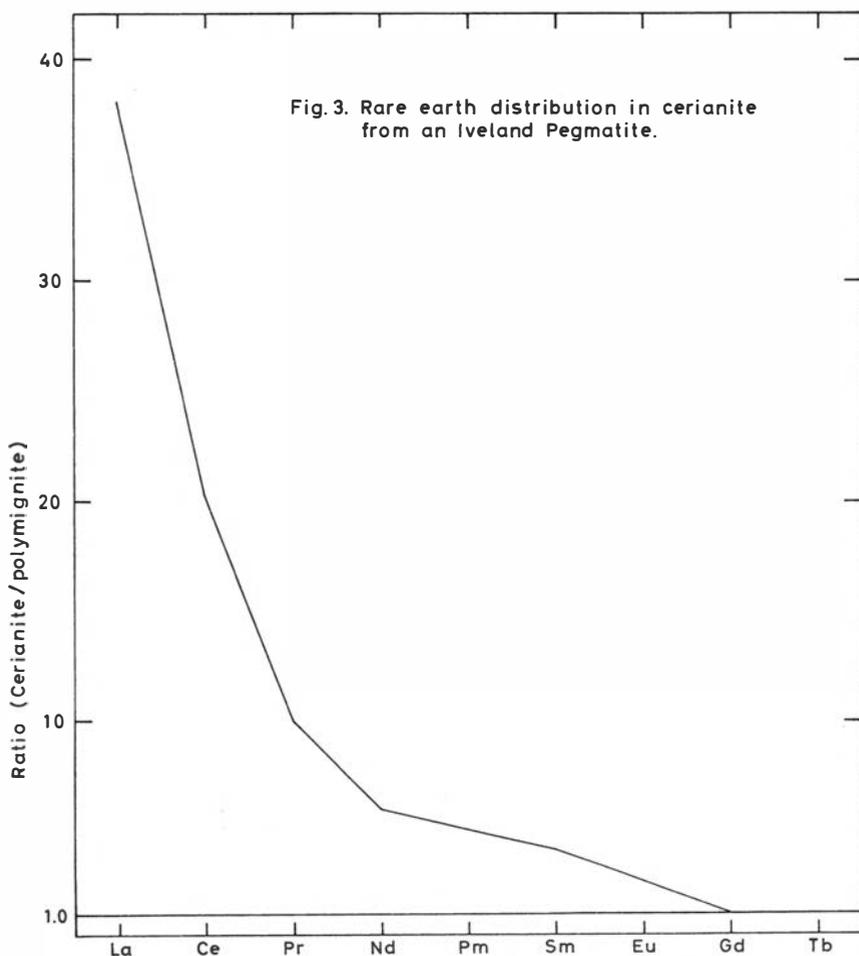
Cases of anomalous fractionation of cerium will probably be less common, since it is unlikely that an oxidizing environment sufficiently extreme to give rise to quadrivalent cerium will often be achieved during *igneous* or *metamorphic* processes. However, BALASHOV *et al.* (1965) reported cerium depletion in zircon (Zr, Fe silicate) formed from eudialyte by weathering (Fig. 2) and MINEYEV *et al.* (1962) reported Ce depletion in weathered allanite. It may be that the oxidation conditions prevailing in a *zone of weathering* are quite often sufficiently extreme to produce stable ceric ions.



### Quadrivalent cerium in cerianite

The rare mineral cerianite is essentially ceric oxide with some trivalent rare earth ions held in solid solution. Only three occurrences of the mineral have so far been reported. At the first two — Lachner Township, Sudbury District, Ontario (GRAHAM 1955) and Morro de Ferro on Pocos de Caldas plateau, Minas Gerais, Brazil (FRONDEL & MARVIN 1959) — the mineral is nearly pure  $\text{CeO}_2$  and clearly indicates an environment of cerium enrichment. The third, at Iveland, differs from the other occurrences in containing only 50–56%  $\text{CeO}_2$  and 30–36% of other rare earth elements (NEUMANN & BERGSTÖL 1963). It was originally assumed that this mineral was also enriched in cerium, but to a lesser degree than the first two reported occurrences. Plotting to the system used in Fig. 1, however, revealed the surprising fact that, in spite of the quadrivalent state of the cerium, there has been no anomalous enrichment of cerium in this mineral (Fig. 3).<sup>2</sup>

<sup>2</sup> In order to eliminate minor irregularities due to analytical difficulties with the La standardization, the data are ratioed to another mineral analysis made in the same laboratory. The plot is approximately comparable with those of Figs. 1 and 2, since this mineral has a rare earth element distribution very similar to that of the normal reference distribution.



The cerianite occurs as pseudomorphs after monazite in a pegmatite and shows mineralogical relationships which indicate a complex crystallization history. It is suggested by Neumann and Bergstöl that the following processes have taken place; first, oxidation and removal of all  $\text{PO}_4^{3-}$  ions, resulting in the total replacement of monazite by cerianite; second, onset of reducing conditions accompanied by the addition of silica plus fluoride, carbonate, and hydroxyl ions, which converted some of the cerianite to fluocerite and caused bastnäsite, törnebohmitite, and monazite to form at the boundaries of the pseudomorph. They report anomalously low cerium in the fluocerite.

### Significance of the cerianite pattern

The relative abundance of rare earths in a mineral formed by replacement will be determined by three factors: 1) relative abundance in the original mineral, 2) the chemical conditions of replacement which may promote or inhibit ionic movement and fractionation, and 3) the selectivity of the replacing mineral phase.

A number of analyses of rare earth minerals which have suffered partial replacement (VAINSHTEIN *et al.* 1956 and MURATA *et al.* 1957) indicate that the relative abundance curve of the rare earths in an alteration product can be substantially different from that of the original mineral. However, to date there is little evidence to indicate whether the controlling factor in this fractionation is commonly 2) or 3).

In the case of the Iveland cerianite the composition of the original mineral cannot be determined, since replacement is complete. It can, however, be assumed that any fractionation of the rare earths after oxidation would be bound to involve partition of trivalent and quadrivalent ions. Since this has not occurred, it must be assumed that either the rare earth elements moved as a group, or the total rare earth content of the monazite remained in position during oxidation and recrystallized as cerianite. In either case, the cerianite lattice must have taken up the trivalent rare earth elements without fractionation. As  $Ce^{4+}$  has an ionic radius smaller than that of Gd, it was originally assumed that strong fractionation of the larger rare earth elements would occur analogous to that shown to occur during the substitution of rare earths for Ca in an apatite lattice (NEUMANN *et al.* 1966). Failure to fractionate must be attributed to greater 'flexibility' of the cerianite lattice which, unlike apatite, is thus able to expand without strain to incorporate the larger rare earth ions.

The breakdown of the cerianite lattice under reducing conditions involved a general movement of ions and partition of trivalent and quadrivalent rare earths then occurred (indicating that the movement took place prior to reduction of the ceric ions). Since the replacing fluocerite is relatively depleted in cerium, a complementary relative enrichment is probably to be found in the contemporaneous minerals formed at the margins of the pseudomorph (monazite, bastnäsite, and törnebohmite).

### Conclusions

This study provides another example of the potential value of rare earth data in determining the conditions of formation of a particular mineral association. Crystallization of the Iveland cerianite undoubtedly took place under somewhat specialized conditions, with less possibility of ionic migration than is normal in such an environment. It (somewhat unexpectedly) supplies further proof of the fact that some mineral structures can incorporate trivalent rare earths in relatively large quantities without appreciable fractionation, and it reinforces the author's opinion that non-selective take-up of the large rare earths is much more common among rare earth-rich minerals than is commonly recognized.

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### REFERENCES

- BALASHOV, YU. A., DORFMAN, M. D. & TURANSKAYA, N. V. 1965. Separation of cerium from rare earth elements during weathering of eudialyte. *Tr. Mineralogy Muzeya Akad. Nauk SSSR*, 16, 205-208
- BALASHOV, YU. A. & TURANSKAYA, N. V. 1960. Pattern of distribution of the rare earths in the rocks of the differentiated complex of the Lovozero alkalic massif and certain problems of the genesis of the complex. *Geochemistry* (English translation) 8, 845-859.
- BALASHOV, YU. A. & TURANSKAYA, N. V. 1961. Rare earths in the eudialyte complex of the Lovozero alkalic massif. *Geochemistry* (English translation) 12, 1213-1226.
- BRUNFELT, A. O. & STEINNES, E. (In press).
- FRONDEL, C. & MARVIN, U. B. 1959. Cerianite,  $\text{CeO}_2$ , from Pocos de Caldas, Brazil. *Am. Mineralogist* 44, 882-884.
- GRAHAM, A. R. 1955. Cerianite,  $\text{CeO}_2$ , a new rare-earth oxide mineral. *Am. Mineralogist* 40, 560-564.
- JENSEN, B. & BRUNFELT, A. O. 1965. Distribution patterns of rare earth elements in terrestrial rocks. *Norsk geol. Tidsskr.* 45, 249-283.

- LEONOVA, L. L. & BALASHOV, YU. A. 1963. Distribution of uranium, thorium and the rare earths in the granitoids of the Susamyr batholith (Central Tien-Shan). *Geochemistry* (English translation) *11*, 1047-1055.
- MINEYEV, D. A., MAKAROKHIN, B. A. & ZHABIN, A. G. 1962. On the behavior of lanthanides during alteration of rare earth minerals. *Geochemistry* (English translation) *7*, 684-693.
- MURATA, K. J., ROSE, H. J., JR., CARRON, M. K. & GLASS, J. J. 1957. Systematic variation of rare earth elements in cerium-earth minerals. *Geochim. et Cosmochim. Acta* *11*, 141-161.
- NEUMANN, H. & BERGSTÖL, S. 1963. Cerianite from cleavelandite pegmatite dykes in Iveland. *Norsk geol. Tidsskr.* *43*, 247-255.
- NEUMANN, H., JENSEN, B. B. & BRUNFELT, A. O. 1966. Distribution patterns of rare earth elements in minerals. *Norsk geol. Tidsskr.* *46*, 141-179.
- NEUMANN, H. & SVERDRUP, T. L. 1960. Davidite from Tuftan, Iveland. *Norsk geol. Tidsskr.* *40*, 277-288.
- TOWELL, D. G., WINCHESTER, J. W. & VOLFOVSKY SPIRN, R. 1965. Rare-Earth Distribution in some Rocks and Associated Minerals of the Batholith of Southern California. *Jour. geoph. Res.* *70*, 3485-3496.
- VAINSHTEIN, E. E., POZHARITSKAYA, L. K. & TURANSKAYA, N. V. 1961. Behaviour of the rare earths in the process of formation of carbonatites. *Geochemistry* (English translation) *11*, 1151-1154.
- VAINSHTEIN, E. E., TUGARINOV, A. I. & TURANSKAYA, N. V. 1956. Regularities in the distribution of rare-earths in certain minerals. *Geochemistry* (English translation) *2*, 159-178.

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