

CONTRIBUTIONS TO THE MINERALOGY OF NORWAY

No. 17. Cerianite from cleavelandite pegmatite dykes in Iveland

By

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In 1960 the well known and highly skilled collector of Iveland minerals Mr. Olaf Landsverk asked the senior author to examine a reddish brown mineral from Kåbuland¹, which he himself had not been able to identify.

An X-ray powder diagram gave a cubic pattern of the fluorite type with a spacing slightly different from that of fluorite. A spectrogram showed only rare earths, among which cerium dominated, as main components. There was thus not much doubt left that the mineral was cerianite, until then known from two localities only, one in North America and the other in South America.

In 1961 one of the authors (H. N.) in the company of Messrs. Olaf Landsverk and Orest Landsverk found the same mineral in another cleavelandite pegmatite dyke in Iveland on the farm Birkeland (Birkeland No. 3, Tunnelen. See H. Bjørlykke (1935)). A search for it in all the other known Iveland dykes of the cleavelandite type was unsuccessful.

Description

A. *Physical Properties.*

The Iveland cerianite occurs as more or less imperfectly developed, thick, tabular crystals of a maximum size of 2 centimeters. The crystals

¹ The specimen had been found in a cleavelandite bearing dyke 600 meters east of the Kåbuland farm by Mr. Orest Landsverk, his oldest son, who like his father is a very keen and knowledgeable collector. One of us (H. N.) visited the same quarry in 1961 accompanied by father and son, but only one more specimen could be located, which was a small and poor one at that.

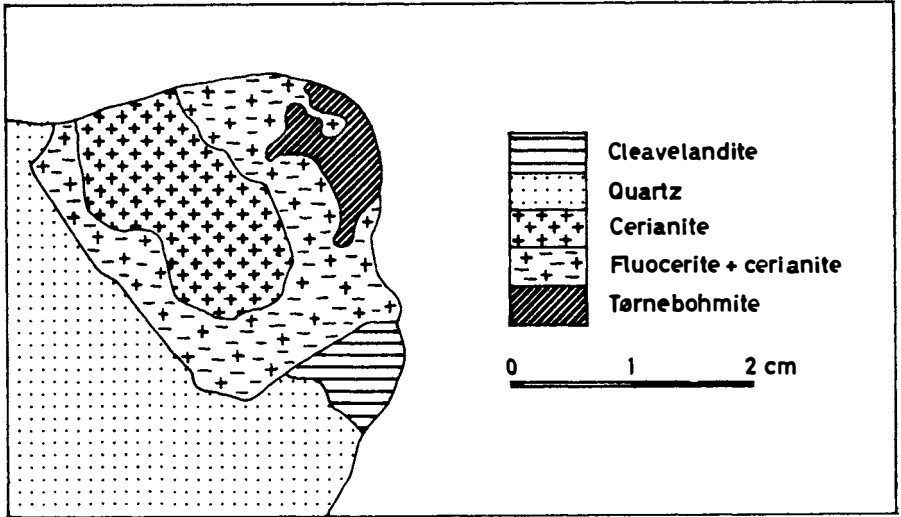


Fig. 1. Sketch illustrating the textural relationships of the several minerals in the largest cerianite specimen from Kåbuland farm.

are not cubic and even if they do not permit any exact measurements of diagnostic angles to be made, there can be no doubt that their outer shape is that of monazite. Hence, the cerianite is pseudomorphous after monazite.

The colour of the pseudomorphs varies from reddish brown to orange yellow, the outer parts tending to be more yellow while the interior is reddish brown. The interior parts are reasonably pure and fresh cerianite while X-ray diagrams reveal that the lighter material is a mixture of cerianite and fluocerite, $(\text{Ce, La, etc})\text{F}_3$. Obviously younger than these two minerals, bastnäsite occurs at the border of the pseudomorphs and in cavities. In the very border zone is found monazite which appears also to be younger than cerianite and fluocerite. Because of the textural relations of the monazite to the other minerals present it would seem unwarranted to regard it as relics of the original pseudomorphed monazite crystal. An olive green patch in the Kåbuland specimen proved to be törnebohmitte, a cerium-rich rare earth silicate with a formula near $(\text{R. E.})_3(\text{SiO}_4)_2(\text{F, OH})$. A drawing of this specimen is given as Fig. 1. On heating at 1275°C

törnebohmitte gives a composite X-ray pattern of quartz and cerianite with cell edge $a_0 = 5.425 \text{ \AA} \pm 0.005 \text{ \AA}$.

The specific gravity of the cerianite from Kåbuland is 6.033 and of that from Birkeland 5.89, determined on material prepared for chemical analyses. The values are low due to the fact that it was quite impossible to produce material for analysis free from appreciable amounts of fluocerite. Also, a probable incipient metamictization tends to lower the specific gravity.

All the above mentioned minerals were identified by their characteristic X-ray powder patterns. As far as the authors are aware not only cerianite, but also törnebohmitte and fluocerite are new to Norway.

B. X-ray Data.

All the cerianite found in Iveland so far appears to be metamict to some extent. Unheated it gives an X-ray powder pattern with rather weak lines, which, however, are distinct enough for identification purposes and for determination of unit cell sizes. By heating in air to 1000°C and especially to 1275°C the cerianite patterns become clear and distinct, with lines of very satisfactory sharpness and definition.

Unit cell dimensions: —

Kåbuland (analyzed material)

Unheated $a_0 = 5.470 \text{ \AA} \pm 0.005 \text{ \AA}$ ²

Heated 1000°C $a_0 = 5.480 \text{ \AA} \pm 0.005 \text{ \AA}$ (+ weak lines : $a_0 = 5.515 \text{ \AA} \pm 0.005 \text{ \AA}$)

Heated, 1275°C $a_0 = 5.495 \text{ \AA} \pm 0.003 \text{ \AA}$

Birkeland (analyzed material)

Unheated $a_0 = 5.482 \text{ \AA} \pm 0.005 \text{ \AA}$

Heated, 1275°C $a_0 = 5.505 \text{ \AA} \pm 0.003 \text{ \AA}$

² Fluocerite is present in too small quantities to give lines on a usual powder film. By long exposures with a Guinier focussing camera very faint lines of fluocerite are just discernible.

The intergrowth of fluocerite and cerianite near the border of the pseudomorphed crystal drawn in Fig. 1 gives, when x-rayed, the pattern of fluocerite together with the pattern of a cerianite with $a_0 \sim 5.43 \text{ \AA}$.

The cerianite lines are much weaker than the fluocerite lines, and are not sufficiently well defined to permit very accurate measurements. The figure given is probably not wrong by more than $\pm 0.01 \text{ \AA}$, however. When heated to 1000°C this intergrowth will give two different cerianite patterns, one with strong lines of a cerianite with $a_0 = 5.522 \text{ \AA} \pm 0.005 \text{ \AA}$ and one with weak lines of the cerianite with $a_0 = 5.430 \text{ \AA} \pm 0.005 \text{ \AA}$. By heating to 1275°C it gives one very clear pattern only of a cerianite with $a_0 = 5.503 \text{ \AA} \pm 0.003 \text{ \AA}$.

These heating experiments indicate that fluocerite when heated in air will be oxidized and form a CeO_2 structure at a temperature below 1000°C . To confirm this pure synthetic CeF_3 was heated to 1000°C and 1275°C for 24 hours, and gave in both cases the characteristic CeO_2 pattern. Pure CeO_2 has a cell edge of $a_0 = 5.396 \text{ \AA}$ (ZINTL (1939) (for a list of later measurements see Frondel, C. (1958))

Furthermore, the fact that two cerianites are found at 1000°C differing in cell size, can only be explained by a difference in chemical compositions, and it seems reasonable to assume an original difference in the distribution of the individual rare earth elements in fluocerite on the one side and cerianite on the other. Quantitative data are not easily obtained, but some information is given by an X-ray fluorescence spectrogram of a part of the fluocerite-cerianite intergrowth giving exceptionally heavy lines of fluocerite on a powder diagram. It is strongly indicated that there is a pronounced enrichment of La, Pr, Nd and Sm in fluocerite, i.e. elements with ionic radii larger as well as smaller than that of cerium. To put it more simply, cerium is the one and only element which is strongly enriched in cerianite as compared to fluocerite. The reason is obviously that cerium is so much more easily oxidized to the quadrivalent state than any other member of the rare earth family. The other rare earth elements present in cerianite are in fact not oxidized to the quadrivalent state at all, but are trivalent strangers, straining the CeO_2 host structure by their demand for vacant anion positions.

C. *Chemical Composition.*

Samples from Kåbuland as well as from Birkeland were prepared for analysis. After grinding to varying degrees they were run through a Frantz isodynamic separator a large number of times and also

repeatedly treated by heavy liquids. In spite of these various efforts it was quite impossible to produce samples of satisfactory purity as an appreciable amount of fluocerite always remained with the cerianite. Other impurities were easily removed.

Table 1.
Analysis of cerianite.

	Kåbuland	Birkeland
SiO ₂	1.89	1.56
Al ₂ O ₃	2.20	0.22
Y ₂ O ₃	0.10	0.10
La ₂ O ₃	15.10	20.80
CeO ₂	55.80	51.90
Pr ₂ O ₃	4.60	4.30
Nd ₂ O ₃	9.80	10.50
Sm ₂ O ₃	1.10	1.50
Gd ₂ O ₃	0.15	0.30
ThO ₂	1.80	1.60
CaO	1.67	1.05
MgO	0.05	0.23
F	6.59	6.41
H ₂ O	2.51	2.55
	103.36	103.02
-O ₂ for F	2.77	2.70
	100.59	100.32

The chemical analyses were carried out by Mr. B. Bruun at the Mineralogisk Geologisk Museum in Oslo. The rare earths (and Th) precipitates were analyzed by X-ray fluorescence spectrography; the Kåbuland sample by Mr. G. Faye in the laboratories of Norges geologiske undersøkelse and the Birkeland sample by one of the authors (S. B.). Results are given in Table 1, and the distribution of rare earths illustrated by Fig. 2.

The fluocerite contents of the analyzed cerianite samples are reflected in the high figures for fluorine (Table 1). Reasons are given above for assuming a difference in the distribution of rare earths in cerianite and fluocerite, and it is hard to say if the other elements

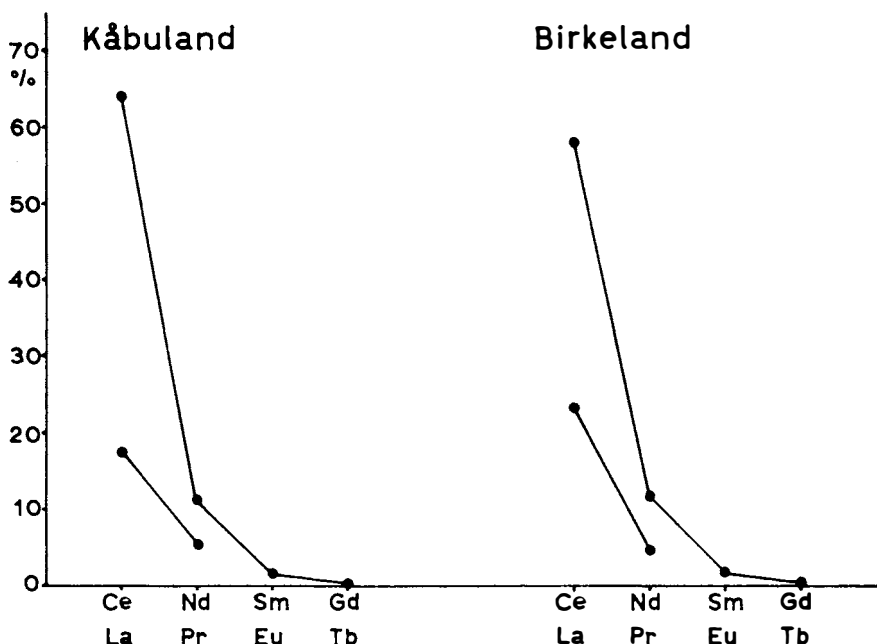


Fig. 2. Distribution of rare earths contained in cerianite from Kåbuland and Birkeland (Analysed material) Figures for individual elements in weight per cent of total rare earth oxide content.

reported in the analyses are present in one mineral or the other, or both.

The data of Table 1 are, therefore, not as valuable as could be desired, and restricted use should be made of them. The authors will refrain from a detailed discussion of the analyses, but it should be pointed out that there is a clear difference in chemical composition between formerly investigated cerianites and that from Iveland.

Cerianite was first described by GRAHAM (1955) from Lachner Township, Sudbury district, Ontario. The type locality cerianite has a cell edge $a_0 = 5.42 \text{ \AA} \pm 0.01 \text{ \AA}$, and a thorium content corresponding to $\text{CeO}_2 : \text{ThO}_2 = 16:1$. Four years later FRONDEL and MARVIN (1959) reported cerianite from Morro do Ferro on Pocos de Caldas plateau, Minas Gerais, Brazil, with cell edge $a_0 = 5.411 \text{ \AA} \pm 0.004 \text{ \AA}$.

Both cerianites reported earlier are nearly pure CeO_2 , while the cerianite from Iveland, Norway, has a CeO_2 content of 50–56 per

cent only, and 30–36 per cent of other rare earth oxides. Several years ago E. Zintl and V. Croatto (1939) demonstrated a solid solubility of La_2O_3 , which is itself hexagonal, in the cubic CeO_2 . By making synthetic mixtures of CeO_2 and La_2O_3 they found that a content of up to 44 mol per cent La_2O_3 left the cubic structure of CeO_2 unchanged apart from an increase in cell size with increasing La_2O_3 content. On very good evidence they could postulate vacant anion positions in the CeO_2 structure of their synthetic $\text{CeO}_2 - \text{La}_2\text{O}_3$ mix crystals.³

The Iveland cerianite, as distinct from those described earlier, is just such a mix crystal of CeO_2 with trivalent rare earth oxides as synthesized earlier by Zintl and Croatto. There would be precedence for giving a new name to the Iveland mineral because of the very marked difference in chemical composition. It may be convenient to use a number of names for mix crystal series of common minerals such as the plagioclases. The authors feel that it would serve no useful purpose, however, to introduce a new name in the present case, and suggest that the name cerianite be redefined to mean a cubic oxide with the fluorite type structure containing no less than 50 per cent CeO_2 .

Mode of formation

Not only the chemical composition but also the mode of occurrence of the cerianite from Iveland is different from that of the cerianites from Canada and from Brazil. The Canadian cerianite occurs as minute crystals in partly absorbed inclusions of wall rock in dykelike zones of carbonate rock which cut a nephelized hybrid gneiss. The Brazilian cerianite is a secondary mineral formed by weathering of allanite and bastnäsité under oxidising conditions. Both cerianites were found in alkaline provinces, while the Iveland cerianite occurs in perfectly normal granite pegmatites with no alkaline affinities whatever. Furthermore, it is clear that the cerianite does not belong to the major

³ It is rather interesting to notice that this very same crystal structure can also accomodate surplus anions in vacant lattice positions as in yttrifluorite $(\text{Ca}, \text{Y})\text{F}_{2-3}$, and to a lesser extent in U O_2 .

⁴ BJØRLYKKE (1935) in his paper on the Iveland pegmatites refers to these stages as the older magmatic stage and the younger hydrothermal-pneumatolytic stage, or also to magmatic dykes and hydrothermal-pneumatolytic dykes. The authors prefer the above non-genetic terms.

and older feldspar-mica-quartz stage, but to a later cleavelandite-amazonite-topaz-quartz stage of pegmatite formation.⁴

It has already been mentioned that the cerianite is a pseudomorph of monazite and has itself in turn been replaced by fluocerite, bastnäsité and törnbohmité, while a second generation monazite, deposited along the very border of the pseudomorphs, is the youngest mineral of the lot.

Chemically speaking, the sequence of events is as follows: Firstly, the phosphate of trivalent cerium with related rare earths crystallizes as well developed monazite crystals of usual habit. It is not known if this monazite belongs to the cleavelandite-amazonite-topaz paragenesis or if it is older. Secondly, trivalent cerium is oxidized to quadrivalent cerium which forms cerianite, CeO_2 with related trivalent rare earth oxides in solid solution, while PO_4^{3-} ions are removed. No trace of the original monazite has been found in any of the investigated pseudomorphs, not even in their cores, where, generally speaking, the chances are best for finding the original material of pseudomorphs. The oxidation is, therefore, hardly a mere *intermezzo*, but a process of some duration and consequence. Thirdly, quadrivalent cerium is reduced again to trivalent cerium which, together with related rare earths, combine with fluoride, carbonate and hydroxyl ions to form fluocerite and bastnäsité, and to a lesser extent with silica to form törnbohmité. The reducing medium obviously also carries the above mentioned ions, as well as silica. Most of the cerianite has survived this later reduction. Fourthly, a transfer of PO_4^{3-} ions has given rise to a subordinate replacement of the above minerals by monazite along the very borders of the pseudomorphs.

The greater stability of the quadrivalent ions of cerium as compared to that of other rare earths finds no manifestation in the geochemical behaviour of cerium. It is concluded that the cerous ion is the stable one during nearly all natural processes of mineral formation, while the ceric ion may or may not be stable in the oxidizing parts of the sedimentary cycle and possibly in the oxidation zone of mineral deposits near or above the ground water level. The ceric ion must be very rare and possibly non-existent during magmatic and metamorphic processes. To find the oxide of quadrivalent cerium as a mineral in the cleavelandite-amazonite-topaz paragenesis of granite pegmatites is, therefore, very remarkable indeed. It would seem to

warrant further investigations; oxidizing conditions severe enough to oxidize cerous cerium to ceric must have left other marks as well.

The questions which immediately arise are: what is the cause of such strong oxidation and what are the genetic implications of the process?

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