

# CERIANITE $\text{CeO}_2$ : A NEW RARE-EARTH OXIDE MINERAL

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## ABSTRACT

The discovery of a cubic ( $Fm\bar{3}m$ ) mineral with cell-edge  $5.42 \pm 0.01 \text{ \AA}$  and composition  $(\text{Ce, Th})\text{O}_2$  with Ce:Th about 16:1 indicates a three-way isomorphous series among cerium, thorium and uranium dioxide minerals.

## INTRODUCTION

Late in August 1954, the author observed a few minute translucent dark greenish-amber radioactive octahedrons in a mineral separate from a sample of carbonate rock. The sample had been submitted for study from mineral claims of the Dominion Gulf Company in Lackner Township, Sudbury Mining District, Ontario, by Dr. E. G. Robinson of our Company. A group mounted directly as a powder sample in an  $x$ -ray powder camera gave a diffraction pattern sufficiently well-populated with spots to define a cubic ( $Fm\bar{3}m$ ) lattice with cell-edge  $5.42 \pm 0.01 \text{ \AA}$ . As this cell-edge lies within the range 5.40–5.47  $\text{ \AA}$  quoted for pitchblende-uraninite (Brooker & Nuffield, 1952), either fluorite or mineral uranium dioxide or both were at first suspected. However, the clear translucency of the crystals as opposed to the usual opacity of uraninites, and their radioactivity, demanded more conclusive evidence for such an identification.

Immediate information available included qualitative optical emission and fluorescent  $x$ -ray spectrographic analyses on rock and mineral bulk samples from the immediate area. In general, thorium, cerium and other rare-earths predominated quantitatively over uranium. Search of the cubic cell-edge tables of Frevel (1942) published in Parrish, Ekstein & Irwin (1953), showed that artificial cerium dioxide had the nearest cell-edge (5.40  $\text{ \AA}$ ) among the required fluorite structure types. Fluorite itself had to be discarded as a possibility because of the radioactivity, and because its specific gravity, 3.18 is below that of the heavy liquid used in the original separation. Mineral cerium dioxide with some thorium or uranium in solid solution was the remaining possibility. The name "cerianite" was therefore tentatively assigned to the mineral by analogy with thorianite and uraninite. More crystals were immediately sought for confirmatory element analysis.

## DESCRIPTION OF LOCALITY

Additional samples and information on the occurrence were kindly supplied by Dr. Robinson and by Mr. G. E. Parsons, Dominion Gulf Company, who had also collected in the area. Their attention had been

drawn by an increase in radioactivity over a partly-exposed narrow dike-form zone of impure sugary carbonate rock in a nephelinized hybrid gneiss. This increased radioactivity appeared to be related to brownish, silicate-rich, pod-shaped inclusions a foot or so in long dimension scattered throughout the carbonate rock. These may represent partly absorbed inclusions of wallrock. The latter is described as a medium to dark gray crudely banded gneissic rock, locally comprising a nepheline syenite intrusive facies, and a nephelinized granulitic facies of more mafic constitution. The granulitic rocks seem to represent a highly metamorphosed and metasomatized mixed volcanic and sedimentary series. The carbonate rock may be either a rheomorphic derivative of the sedimentary series, or a sövite dike similar to those of Alnö area, Sweden (von Eckerman, 1948).

The original sample in which the first crystals of cerianite were discovered was taken across the contact of one of the silicate-rich inclusions with the carbonate rock, and included portions of both rock types. A well-defined contact, discernible within a few millimetres, was evident between a light gray crystalline carbonate rock with grain-size up to 2-3 millimetres, and a slightly coarser, dark gray to brownish gray more silicate-rich phase. The latter material, a hybrid of carbonate, nepheline and feldspar, owed its brownish tinge to 10%-20% by volume of a translucent brown tremolitic amphibole in fine to coarse prisms, occasionally reaching about one centimetre in length. Both phases contained approximately 10% total by volume of magnetite and ilmenite as subhedral to euhedral crystals up to 1 or 2 millimetres in size. Accessory transparent white prisms of apatite up to 200 microns in length were more numerous in the carbonate-rich phase.

#### ISOLATION OF CERIANITE

A further sample, weighing about one pound, of the material submitted by Mr. Parsons was selected for separation. More silicate-rich than the original, it showed a deeper brown colour, and apparently represented an inclusion nearly completely absorbed in the carbonate rock. The sample was carefully crushed to  $-\frac{1}{4}$  inch, and leached overnight in a large volume of cold 1:10 HCl, to remove soluble carbonate. The residue, amounting to about 40% of the original sample, was further crushed with frequent screening to secure a large volume of material in the size-range of the original crystals recovered,  $-80+150$  mesh. This fraction was then separated into heavy and light portions using diiodomethane of gravity 3.21. The heavy portion was passed through the Franz isodynamic separator at the highest magnetic flux available. The final non-magnetic residue contained about half a gram of translucent white

apatite, minor gray nepheline, and pinkish albite and microcline, as well as about one milligram of dark greenish-amber octahedral crystals similar to the original material isolated and described.

Hand-picking yielded slightly under a milligram of apparently pure crystals. Twice this amount had been recovered in the first operation on about half the weight of original sample. Thus, three milligrams represented the total material available for analysis and further study. Two milligrams approximately were submitted to Mr. D. A. Moddle, the Provincial Assayer for Ontario. Through his courtesy, a special quantitative spectrochemical analysis was carried out by Mr. Wiley O. Taylor of the Provincial Assay Laboratory. The method used was a variation of that employed by K. J. Murata of the U. S. Geological Survey, involving controlled dilutions of the sample. The results of this analysis appear in Table 1.

TABLE 1. SPECTROCHEMICAL ANALYSIS

Oxide	Weight per cent
CeO <sub>2</sub> .....	80 ± 20
ThO <sub>2</sub> .....	5.1 ± 0.5
Nb <sub>2</sub> O <sub>5</sub> .....	1.8 ± 0.2
La <sub>2</sub> O <sub>3</sub> .....	1.5 ± 0.2
Y <sub>2</sub> O <sub>3</sub> .....	1.2 ± 0.2
Yb <sub>2</sub> O <sub>3</sub> .....	1.1 ± 0.1
Ta <sub>2</sub> O <sub>5</sub> .....	0.6 ± 0.05
ZrO <sub>2</sub> .....	0.6 ± 0.05
U <sub>3</sub> O <sub>8</sub> .....	N.D.

## DISCUSSION OF RESULTS

Although the accuracy of the analysis for the major constituent is not high, the great excess of Ce over the other elements found, and the position of its range bracketing the theoretical content of Ce in CeO<sub>2</sub> (81%), are confirmatory evidence for the identity of the mineral. The presence of 5% Th accounts for the radioactivity as well as the slight increase in cell-edge from 5.40 to 5.42 Å. As cerium also forms an oxy-fluoride with similar crystallography and cell-size, a spot test for fluorine was performed. The result was negative.

During the literature search for possible previous mention of a cerium dioxide mineral, several analyses of thorianites and uraninites were noted in which cerium figures as a minor or trace constituent. Three of these quoted in Dana's Seventh Edition are from localities where more cerium-rich minerals are also reported. It is probable that close study of these

and other similar localities will result in the establishment of a three-way isomorphous series among uranium, thorium and cerium oxide minerals. Elsewhere in this issue appears evidence for at least a part of the uraninite-thorianite series; the appreciable thorium in the analysis above is an indication of a thorianite-cerianite series.

The metallogenetic implications of the occurrence are interesting because of the presence of fluorine and chlorine in apatite and minor fluorite in the region. Magnetite-apatite-ilmenite-pyrochlore deposits are associated with the complex nepheline syenite intrusive. A hypothesis of origin of similar deposits, advanced by several geologists in various forms (e.g., von Eckerman, 1948), postulates transfer in, and deposition from, a high-temperature halide-rich fluid, with localization control by both structure and change of chemical environment.

A possible analogous origin for the cerianite suggests itself. Removal of chlorine, fluorine and phosphorous from such a halide-rich fluid by reaction with calcareous sediments to form apatite and fluorite may have allowed crystallization of cerium as oxide instead of the more usual monazite, perovskite (knopite), complex carbonate, or cerian pyrochlore. The process is visualized as taking place at temperatures and pressures comparable to those of the granulitic facies developed in the surrounding rocks. An alternative explanation, also attractive, is formation of cerianite as a skarn mineral from pre-existing bastnaesite, or other rare-earth carbonate, under contact metamorphic conditions induced by the neighbouring intrusive syenite plug.

#### SUMMARY AND CONCLUSIONS

On the evidence adduced above, the existence in nature of a cerium dioxide mineral isostructural (and at least in part isomorphous) with thorianite and uraninite, is proposed. By analogy with the latter two minerals, the name "cerianite" should be appropriate for the pure end member. Application of compositional nomenclature to the mineral described above would place it as a thorian cerianite.

Characterization of minerals in this oxide group by cell-edge relationships alone appears fallacious. At least qualitative information on chemical composition should be available. The state of oxidation, i.e., incidence of "defect structures" in the uranian and cerian members of the group is a further complication which would appreciably affect cell-size.

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