

# Structural Features of a New Naturally Occurring Representative of the Fluoroapatite–Deloneite Series

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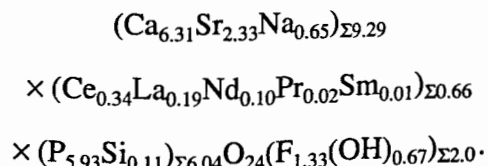
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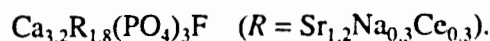
**Abstract**—A complete X-ray structure analysis of a new naturally occurring representative of the apatite group,  $\text{Ca}_{3.2}\text{R}_{1.8}(\text{PO}_4)_3\text{F}$  ( $\text{R} = \text{Sr}_{1.2}\text{Na}_{0.3}\text{Ce}_{0.3}$ ), from the Khibini massif was carried out (an automated Enraf–Nonius diffractometer, 637 reflections,  $R_{\text{hkl}} = 2.9\%$ ). The parameters of the hexagonal unit cell are  $a = 9.485$ ,  $c = 7.000$  Å;  $V = 545.4$  Å<sup>3</sup>; sp. gr.  $P6_3$ ;  $Z = 2$ . *R*-apatite is chemically and structurally related to strontium apatite, belovite, and deloneite and differs from these minerals in composition, the distribution of isomorphous elements over structural positions, and symmetry.

Minerals and synthetic compounds of the general formula  $\text{A}_{10}(\text{TO}_4)_6\text{X}_2$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$ , rare earth elements,  $\text{Na}, \text{Mn}, \text{Cd}, \text{Fe}, \text{K}$ , or  $\text{Li}$ ;  $\text{T} = \text{P}, \text{Si}, \text{Ge}, \text{As}, \text{Cr}, \text{N}, \text{V}$ , or  $\text{S}$ ;  $\text{X} = \text{F}, \text{Cl}, \text{OH}, \text{O}, \text{Br}, \text{I}$ , or  $\text{CO}_3$ ) and of the apatite structural type form a large group, which is studied extensively in connection with its biological, industrial, and ecological applications. Because isomorphous components are miscible over a wide range, many of these compounds are of very complex composition; however, most of these compounds are characterized by a low degree of cation and anion ordering. A newly found representative of this family is of interest for the study of structural ordering in apatite substantially enriched with isomorphous impurities.

The new mineral, which we arbitrarily named *R*-apatite ( $\text{R} = \text{Sr}, \text{Na}$ , and  $\text{Ce}$ ),<sup>1</sup> was found in hyperagpaitic pegmatites of the Khibini alkaline massif (the Kola Peninsula) [1]. This mineral occurs as transparent pale yellow prismatic crystals up to 5 mm in size or as aggregates of these crystals in epitaxial concretions with other apatite-like minerals, namely, with deloneite and belovite. The new mineral is optically uniaxial and negative,  $n_e = 1.637$ ,  $n_o = 1.649$ . The chemical composition of the mineral, which was established by microprobe analysis, is converted to the following empirical formula:



The simplified formula for  $z = 2$  is as follows:



X-ray structure analysis of the mineral was carried out with the diffraction data set collected within a hemisphere of the reciprocal space from the crystal with dimensions of  $0.2 \times 0.3 \times 0.25$  mm on an automated Enraf–Nonius diffractometer ( $\text{MoK}_\alpha$  radiation, graphite monochromator, 3191 reflections with  $I > 2\sigma(I)$ ,  $\sin \theta/\lambda < 0.8$  Å<sup>−1</sup>). After averaging symmetrically equivalent reflections within the Laue class  $6/m$  (the  $R_{\text{av}}$  factor of averaging over 582 groups of equivalent reflections was 6.2%; when an absorption correction was applied, the *R* factor was reduced to 3.1%), 637 independent reflections with  $|F| > 3\sigma(F)$  were obtained. The parameters of the hexagonal unit cell were determined and refined on the same diffractometer:  $a = 9.485(3)$ ,  $c = 7.000(3)$  Å;  $V = 545.4(6)$  Å<sup>3</sup>;  $\rho_{\text{exp}} = 3.60$ ;  $\rho_{\text{calc}} = 3.57$  g/cm<sup>3</sup>. All calculations were performed using the AREN program package [2].

Assuming, based on Wilson's statistics, that the structure of the mineral is acentric and is, apparently, similar to the structure of Sr-apatite (sp. gr.  $P6_3$ ) [3], we used the structure of Sr-apatite as the initial model in the refinement by the least squares method in the approximation that the positions of large cations are occupied by Ca atoms. A high value of the *R* factor and the character of the thermal parameters indicated that it was necessary to use combined atomic scattering curves both for one position on the threefold axis and for general positions. The best cation distribution is characterized by an *R* factor of 5.9% with reasonable values of the thermal parameters. An absorption correction, which was applied with the use of the DIFABS program [4], reduced  $R_{\text{hkl}}$  to 4.6%; an anisotropic

<sup>1</sup> A suggestion to recognize *R*-apatite as a new mineral species was submitted to Commission on New Minerals and Mineral Names of the International Mineralogical Association.

**Table 1.** Coordinates and thermal parameters of atoms in the structure of *R*-apatite

| Atom             | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>B</i> <sub>eq</sub> , Å <sup>2</sup> |
|------------------|------------|------------|------------|-----------------------------------------|
| P                | 0.6305(1)  | 0.0290(1)  | 0.2448(6)  | 0.44(3)                                 |
| A <sub>I</sub> * | 0.3333     | 0.6667     | -0.0042(1) | 0.85(5)                                 |
| A <sub>I</sub> ' | 0.3333     | 0.6667     | 0.4987(4)  | 0.90(8)                                 |
| A <sub>II</sub>  | 0.0128(1)  | 0.2519(1)  | 0.2496(4)  | 0.69(2)                                 |
| O(1)             | 0.324(1)   | 0.254(1)   | 0.420(1)   | 1.7(1)                                  |
| O(2)             | 0.156(4)   | 0.671(5)   | 0.244(1)   | 1.3(1)                                  |
| O(3)             | 0.536(5)   | 0.121(5)   | 0.263(2)   | 1.2(1)                                  |
| O(4)             | 0.355(1)   | 0.263(1)   | 0.068(1)   | 1.0(1)                                  |
| F, OH            | 0          | 0          | 0.276(3)   | 2.8(2)                                  |

\* A<sub>I</sub> = Sr<sub>0.5</sub>Na<sub>0.3</sub>Ca<sub>0.2</sub>; A<sub>I</sub>' = Ca; A<sub>II</sub> = Ca<sub>0.7</sub>Sr<sub>0.2</sub>Ce<sub>0.1</sub>.

refinement taking into account the extinction ( $E = 0.0000233$ ) reduced the *R* factor to 2.9%.

An attempt to refine the structure in the centrosymmetric group resulted in less reasonable characteristics, namely, in a higher value of the *R* factor (by ~1.5%) and in an increased thermal parameter of the F-anion.

Coordinates of the basis atoms and equivalent temperature factors are given in Table 1; interatomic distances are listed in Table 2; the local valence balance according to Brown [5] taking into account the contributions of all components of the composition is given in Table 3.

The well-known apatite structural type is characterized by the presence of A polyhedra of two different types (seven-vertex and nine-vertex polyhedra); these polyhedra share vertices, edges, and faces to form the

three-dimensional framework. The P tetrahedra occupy cavities of the framework, whereas extraradical X anions are located on the 6(3) axes of the coordinates. The symmetry of apatites of monocationic composition is, generally, described by the centrosymmetric sp. gr. *P6<sub>3</sub>/m*. The lowering of the symmetry may be caused by the displacement of X anions from special positions on the symmetry plane *m* when the sizes of these anions do not correspond to the sizes of large cations [6]. The flexible framework of apatite allows varied cationic and anionic isomorphism; the framework may deform along the *a* and *c* axes as the composition changes, which is often accompanied by a lowering of the symmetry down to monoclinic [7]. In polycationic apatites, the ordering of isomorphous impurities both in cation positions (including tetrahedral positions) and in positions of extraradical anions is, apparently, the major factor lowering the symmetry of the structure.

The lowering of the symmetry to *P6<sub>3</sub>* in the structure of *R*-apatite studied is caused by the ordered distribution of Na, Sr, and Ce impurities in A polyhedra, located on the threefold axes. The displacement of the (F,OH)-extraradical anion from the position on the plane *m* to the general position is also a factor asymmetrizing this apatite. The ordering of the cation composition results in the fact that A polyhedra located at different heights along the *z*-axis differ in shape and size. The A<sub>I</sub>' polyhedron at *z* = 0.50 on the threefold axis [1/3 2/3 *z*] is a compact nine-vertex polyhedron with the Ca-O distances in the range 2.5–2.7 Å, whereas the mixed cation position A<sub>I</sub> at *z* = 0 (in Fig. 1, composite hatching indicates the corresponding polyhedron) is characterized by the coordination number of 6 + 3; the distances from the central cation to the six nearest O atoms vary within narrow limits from 2.397 to 2.431 Å, whereas the distances to the three remaining O atoms increase to 2.99 Å. With such a difference in distances, the inclusion of three distant oxygen atoms is decided based on the local valence balance, and, in this structure, such an inclusion is reasonable. The cation distri-

**Table 2.** Interatomic distances (Å) in the structure of *R*-apatite

| P tetrahedron                      | Nine-vertex polyhedron            |
|------------------------------------|-----------------------------------|
| P-O(4) 1.518(8)                    | A <sub>I</sub> -O(3) 2.397(9) × 3 |
| O(2) 1.538(3)                      | O(2) 2.431 (8) × 3                |
| O(3) 1.539(6)                      | O(1) 2.990(1) × 3                 |
| O(1) 1.550(9)                      | <2.606>                           |
| <1.525>                            |                                   |
| Nine-vertex polyhedron             | Seven-vertex polyhedron           |
| A <sub>I</sub> '-O(2) 2.460(8) × 3 | A <sub>II</sub> -F 2.337(1)       |
| O(3) 2.550(9) × 3                  | O(1) 2.390(9)                     |
| O(4) 2.728(6) × 3                  | O(4) 2.398 (8)                    |
| <2.579>                            | O(3) 2.441(4)                     |
|                                    | O(1) 2.538(7)                     |
|                                    | O(4) 2.607(8)                     |
|                                    | O(2) 2.697(3)                     |
|                                    | <2.487>                           |

**Table 3.** Local valence balance (according to Brown) in the structure of *R*-apatite

| Anion | Cation |                                                      |                   |                                                         | $V_i$ | $ \Delta _i$ |
|-------|--------|------------------------------------------------------|-------------------|---------------------------------------------------------|-------|--------------|
|       | P      | $A_I(\text{Sr}_{0.5}\text{Na}_{0.3}\text{Ca}_{0.2})$ | $A'_I(\text{Ca})$ | $A_{II}(\text{Ca}_{0.7}\text{Sr}_{0.2}\text{Ce}_{0.1})$ |       |              |
| O(1)  | 1.20   | 0.07                                                 |                   | 0.62                                                    | 1.89  | 0.11         |
| O(2)  | 1.24   | 0.33                                                 | 0.26              | 0.17                                                    | 2.00  | 0            |
| O(3)  | 1.23   | 0.35                                                 | 0.21              | 0.33                                                    | 2.12  | 0.12         |
| O(4)  | 1.31   |                                                      | 0.13              | 0.57                                                    | 2.01  | 0.01         |
| F     |        |                                                      |                   | 0.90                                                    | 0.90  | 0.10         |

Note:  $D = 3.8\%$ ;  $|\Delta|_{\max} = 6\%$ .

bution found is confirmed by the local valence balance (Table 3) and corresponds to the correlation between the average radii of cations located in positions  $A_I$ ,  $A'_I$ , and  $A_{II}$  with the average interatomic distances in their polyhedra.

Using the indices accepted for strontium-apatite [3] and belovite [8], the crystal-chemical formula of *R*-apatite can be written in the following form:  $A_I A'_I A_{II} (\text{PO}_4)_3 (\text{F}, \text{OH})$ . Specifying the composition of  $A$  positions, this formula can be written as follows:  $(\text{Sr}_{0.5}\text{Na}_{0.3}\text{Ca}_{0.2})\text{Ca}(\text{Ca}_{0.7}\text{Sr}_{0.2}\text{Ce}_{0.1})_3 (\text{PO}_4)_3 (\text{F}_{0.7}\text{OH}_{0.3})$ . From this it follows that only one site in the structure of *R*-apatite is unaffected by isomorphism processes and remains the calcium site, whereas *R* impurities are distributed over other sites so that Na atoms are located on the threefold axes in large polyhedra with the number of vertices being  $(6 + 3)$ . Whereas compact seven-vertex polyhedra around the  $6_3$  axis are favored by rare-earth elements, Sr atoms are about evenly distributed among polyhedra of both types.

A comparison of *R*-apatite with belovite [8] and deloneite [9, 10] demonstrates that all three phosphates consist of identical sets of elements (Na, Ca, Sr, rare earth elements, P, O, and F) and belong to the same group of the apatite structural type. The general character of the X-ray powder diffraction patterns of these minerals are similar; these patterns differ mainly in the displacement of a portion of lines because of the difference in the unit cell parameters. However, these minerals differ in stoichiometry, symmetry, and structural and optical characteristics. Chemical differences between these three complex minerals can be expressed by the percent concentrations of six terminal members (minerals), which consist of rather simple sets of components; we represented these minerals as deloneite [*DI*,  $\text{NaCa}_3\text{Ce}(\text{PO}_4)_3\text{F}$ ], belovite [*BI*,  $\text{NaSr}_3\text{Ce}(\text{PO}_4)_3\text{F}$ ], britholite [*Br*,  $\text{Ca}_2\text{Ce}_3(\text{SiO}_4)_3\text{F}$ ], apatite [*Ap*,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ], strontium-apatite [*Sa*,  $\text{Sr}_5(\text{PO}_4)_3\text{F}$ ], and hypothetical Na,Ce-apatite [*NC*,  $\text{Na}_{2.5}\text{Ce}_{2.5}(\text{PO}_4)_3\text{F}$ ]. Formulas of the apatite-like minerals expressed in terms of these minerals are as follows:  $\text{DI}_{57}\text{BI}_{40}\text{Br}_3$  (Ce-deloneite),  $\text{BI}_{83}\text{DI}_{16}\text{Br}_1$  (Ce-belovite), and  $\text{Ap}_{62}\text{Sa}_{23}\text{NC}_{13}\text{Br}_2$  (*R*-apatite). Note

that the maximum (3%) and the minimum (1%) concentrations of the britholite mineral were found in deloneite and belovite, respectively, which correlates with the nonequivalence of tetrahedral sites in the structure of deloneite [8], whereas in two other phosphates, there is a unique sixfold P site.

The numbers of Na atoms and atoms of rare-earth elements in the empirical formulas of the minerals compared are virtually equal (1.95 and 2.17 in deloneite, 2.06 and 1.93 in belovite, and 0.65 and 0.66 in *R*-apatite), which indicates the occurrence of isomorphism according to the scheme  $\text{NaRE} \rightarrow 2\text{Ca}$ ; this isomorphism is typical of minerals of the apatite group. However, the replacement of Ca in structural fragments of these minerals proceeds in various ways, which is, apparently, associated with the specific features of physicochemical processes that affect the ordering. The *R*-apatite studied, which can be considered as a low-symmetry polymorph of fluoroapatite as well as an essentially calcium analogue of

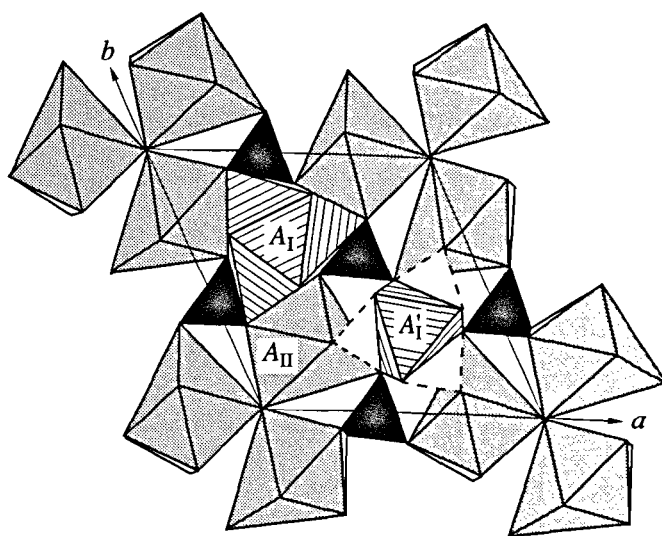


**Fig. 1.** Projection of the structure of *R*-apatite onto the (001) plane. Tetrahedra are black; the nine-vertex polyhedron and the polyhedron with the number of vertices of  $6 + 3$  are hatched with solid lines; seven-vertex polyhedra are hatched with dots

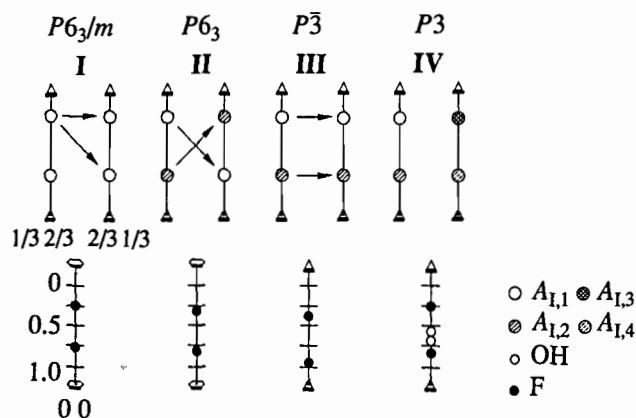


Fig. 2. Schematic representation of the sites of large cations and extraradical anions in hexagonal and trigonal structures of the apatite-like minerals: (I) fluoroapatite, (II) strontium-apatite and *R*-apatite, (III) belovite, and (IV) deloneite.

strontium-apatite, is closer in chemical composition to trigonal apatite-like minerals, namely, to belovite and deloneite. The structural characteristics of minerals of this series are schematically shown in Fig. 2. Schemes I, III, and IV correspond to the structural types of fluoroapatite, belovite, and deloneite, respectively; Scheme II corresponds to strontium-apatite and *R*-apatite. Adopting the notations accepted previously to describe the structure of deloneite [9, 10], we denoted the positions  $A_1$  and  $A'_1$  as  $A_{1,1}$  and  $A_{1,2}$ ; two other positions on a threefold axis, which do not occur within the framework of high symmetry, were denoted as  $A_{1,3}$  and  $A_{1,4}$ . When this uniform notation of structural positions is used, the characteristic features of the distribution of A cations and extraradical anions in the structures of this group are readily apparent in Fig. 2 in going from fluoroapatite ( $P6_3/m$ ), which generally contains small amounts of isomorphous impurities, to *R*-apatite ( $P6_3$ ), belovite ( $P\bar{3}$ ), and deloneite, which is the most ordered ( $P3$ ).

The fact that deloneite and belovite are found in epitaxial concretions with *R*-apatite provides evidence that the structure-dimensional correspondence of the minerals forming concretions is the most important factor of their cocrystallization. The lowering of the symmetry of these minerals as compared to the synthetic ana-

logues [11], which are close in composition and for which the centrosymmetrical sp. gr.  $P6_3/m$  was established, is caused by low temperatures of crystallization (these temperatures do not exceed the range 150–300°C), whereas for synthetic phosphates, the temperature of synthesis was 1100°C. The fact that the compositions of the naturally occurring compounds under consideration are not identical is, apparently, a factor that controls ordering processes and causes the existence of several minerals with different symmetry.

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