

REFINEMENT OF THE ATOMIC STRUCTURE OF BAOTITE AND THE ISOMORPHIC RELATIONSHIPS IN THIS MINERAL

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The positional and individual isotropic parameters of the basic atoms of baotite $\text{Ba}_4\text{Ti}_4(\text{Ti}_{0.48}\text{Nb}_{0.36}\text{Fe}_{0.16})_4\text{ClO}_{16}[\text{Si}_4\text{O}_{12}]$; $a = 19.99$; $c = 5.908 \text{ \AA}$; space group $I 4_1/a$; $Z = 4$ are refined by reference to 830 independent nonzero structure amplitudes, yielding an R factor of $\sim 4\%$. The three-dimensional set of intensities is obtained in a DAR-1 diffractometer using Cu radiation. The question as to the distribution of isomorphous impurities among the crystallographic positions in the structure is solved. The structural characteristics of this natural silicate, which contains a silicon-oxygen radical in the form of quadrupole $[\text{Si}_4\text{O}_{12}]$ rings, are considered.

The barium-titanium silicate baotite was discovered and described in 1959 [1]. A model of the atomic structure of the mineral based on the $I4_1/a$ Fedorov group was published in 1960 [2]. The experimental material for this solution was provided by the intensities of one equatorial Weissenberg photograph of the $hk0$ type, obtained in Mo radiation. The projection of the structure was plotted on the basis of an $M_4(x, y)$ Burger minimization function, while the z coordinates of the basis atoms were established from crystallochemical considerations. The quadrupole $[\text{Si}_4\text{O}_{12}]$ metasilicate rings were first reliably established in baotite. The Ti, Nb, and Fe atoms occupy two crystallographically-independent octahedra which overlap extremely accurately on the $\sigma(x, y)$ projection. This circumstance prevented the isomorphous relationships in this mineral from being determined on the basis of the experimental material used in [2].

Another paper devoted to a further structural determination of baotite appeared in 1963 [3]; this added very little to the results of [2]. Although the structural analysis in [3] was carried out on the basis of a unit cell coinciding with that obtained in [2], the authors of [3] asserted that the c period of

this cell was in fact a pseudoperiod, constituting one quarter of the true translation along the tetragonal axis. It was further suggested in [3] that the increase in the c period was due to the ordered arrangement of the Ti and Nb atoms in the structure.

The aim of this paper is to refine the crystal structure of baotite and solve the problem as to the isomorphous substitution of cations in this silicate.

EXPERIMENTAL MATERIAL

Baotite samples for the experiments were kindly presented by E. I. Semenov and analyzed chemically by T. A. Kapitonova and A. V. Bykova. The experimental diffraction material was obtained with a spherical baotite single crystal. The mean diameter of the sample was $0.184 \pm 0.004 \text{ mm}$ with a standard deviation of 3.2% from the spherical state. Using a DRON-1 diffractometer, we refined the parameters of the tetragonal baotite cell, obtaining $a = 19.99 \pm 0.01$, $c = 5.908 \pm 0.002 \text{ \AA}$, and established the angular range representing the mosaic structure of the sample in question, equal to 0.3° . In order to verify the proposition of [3] regarding the fourfold increase in the c spacing, we

took a complete rotation photograph of baotite along the tetragonal axis, using Mo radiation with a Zr filter. The exposure was continued until the $c = 5.908 \text{ \AA}$ spots appeared on the x-ray film. No additional reflections between the severely-overexposed layer lines due to the period $c = 5.908 \text{ \AA}$ appeared on this photograph. The crystal structure of baotite was in fact characterized by the bc cell indicated above and was unambiguously determined by the regular extinctions of the reflections of the tetragonal $I4_1/a$ space group.

The three-dimensional set of integrated intensities was obtained in an automatic DAR-1 diffractometer [4]. We used earlier-published programs for calculating the adjusting angles of the diffractometer [5] and for the primary analysis of the experimental intensities [6]. The method of working with the DAR-1 was described in detail in [7]. The photographs were taken in $\text{CuK}\alpha$ radiation with a nickel filter, a BSV-11 tube, an accelerating voltage of 35 kV, and an anode current of 15 mA; the counter was of the scintillation type, and the integrated intensity was measured by the combined $\omega - \omega/2\omega$ method [8]. The spectral range of the radiation was taken as $\Delta\lambda = \Delta\lambda_{\text{K}\alpha_1 - \text{K}\alpha_2} + 5(\Delta\lambda_{\text{K}\alpha_1} + \Delta\lambda_{\text{K}\alpha_2})$, where $\Delta\lambda_{\text{K}\alpha_1 - \text{K}\alpha_2}$ is the resolution of the $\text{K}\alpha$ doublet, $\Delta\lambda_{\text{K}\alpha_1}$ and $\Delta\lambda_{\text{K}\alpha_2}$ being the half-widths of the doublet components. The measurements were carried out up to a total of 10,000 pulses, or until reaching a limiting number of crystal oscillations equal to four. The background was measured to the left and right; the total time of measuring the background was equal to the time of measuring the integrated intensity. Altogether 5000 reflections were obtained on layer lines $hk0$ to $hk6$; after averaging the equivalent reflection, this gave a set of 1166 independent reflections, including 830 differing from zero. The intensity was regarded as nonzero if it equalled more than three times the standard deviation. A correction for absorption in the spherical sample was introduced on the basis of the data in the International Tables [9] for $\mu R = 7.3$. The absorption coefficient of baotite was calculated from its chemical composition and mass-absorption coefficient taken from [9].

ISOMORPHISM IN BAOTITE

The complex chemical composition of the mineral found an adequate reflection in its structure. As indicated in [2], in the crystal structure of baotite even the Cl is individualized, although this element comprises only 2.2 at. % in the formula of the silicate. In 1960 the question as to the dis-

position of Ti, Nb, and Fe among the crystallographic positions remained open. For an independent region of the baotite unit cell, chemical analysis gives 1.48 Ti, 0.36 Nb, and 0.16 Fe. As emphasized earlier, our special check on the c spacing, carried out as accurately as possible, refuted the hypothesis as to the existence of the superstructure in baotite proposed in [3]. Within the framework of the $I4_1/a$ Fedorov group and a unit cell with $a = 19.99$, $c = 5.908 \text{ \AA}$, it simply remained to solve the problem as to the distribution of the isomorphic additives Nb and Fe with respect to the two crystallographically-independent octahedra. With this end in view, we carried out a preliminary refinement of the positional parameters of all the basic atoms of baotite for a uniform statistical occupation of the two positions in question by Ti, Nb, and Fe. It should be emphasized that in so doing we tried to locate the more contrasting additive Nb ($Z = 41$) on a background of the principal component, Ti ($Z = 22$), while a small amount of Fe ($Z = 26$), having an atomic number close to that of titanium, was added to the main isomorphic impurity. The results of our calculations of the R factors for fixed coordinates of the atoms and different assumptions as to the manner in which the Nb + Fe impurity entered into the Ti_1 and Ti_2 octahedra are presented in Fig. 1.

An analogous result indicating that the Nb only replaced Ti in the Ti_2 octahedron of baotite was obtained by another method. Using the method of least squares, in accordance with programs devised by the Mathematics Department of the Branch of the Institute of Chemical Physics of the Academy of Sciences of the USSR [10], we refined our estimates of the multiplicity of the atoms in the Ti_1 and Ti_2 positions. This process indicates that these positions were occupied by atoms with effective atomic (Mendeleev) numbers of $Z_{\text{eff}} = 21.6$ and 31.4. The calculated values correspond-

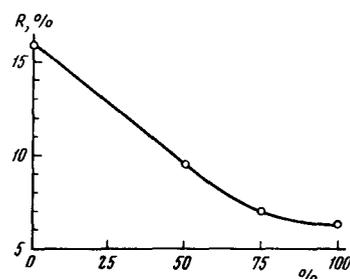


Fig. 1. Dependence of the R factor on the amount of Nb + Fe impurity in the Ti_2 octahedron. As 100% we take 0.36 Nb + 0.16 Fe, belonging to the independent part of the unit cell.

ing to the entry of all the Nb + Fe impurity into the Ti_2 position equal 22.0 (Ti) and 29.5 (0.48 Ti + 0.36 Nb + 0.16 Fe). Thus the fully-developed chemical formula of baotite should be written $Ba_4Ti_4 \cdot (Ti_{0.48}Nb_{0.36}Fe_{0.16})_4ClO_{16} [Si_4O_{12}]$.

REFINEMENT OF THE POSITIONAL AND THERMAL PARAMETERS OF THE STRUCTURE

The refinement was carried out by the method of least squares, using the programs of [10]. For the Ti_2 position we used the effective atomic curve of $f_{eff} = 0.48 f_{Ti} + 0.36 f_{Nb} + 0.16 f_{Fe}$. Initially the refinement was carried out with respect to a set of experimental structure amplitudes with trivial weighting factors $w = 1$ for $|F_e| \neq 0$ and $w = 0$ for the remaining amplitudes. In this way refinement of the factor used for reducing the amplitudes to the absolute scale k , the general isotropic temperature factor B , and the 33 positional parameters of all the basic atoms of baotite led to $R = 4.12\%$. Subsequent refinement of the 12 individual isotropic thermal factors of the atoms (including Cl, the coordinates of which were rigidly fixed by symmetry) reduced R to 3.75%. The reduction of the R factor from 4.12 to 3.75% by the inclusion of 12 new parameters is, according to Hamilton [11], significant with a probability (reliability) factor of over 0.995.

Then all the stages of refinement were repeated, using the individual experimental weighting

factors w_{hkl} for the structure amplitudes [6]. The refinement of k , B , and all the coordinate parameters led to $R = 4.22\%$ (the R factor was calculated as in the first case, i.e., from all the $|F_e| \neq 0$ without allowing for the weights). The introduction of the individual thermal parameters of the atoms reduced R to 4.01%. In the case of baotite the programs of [10] enable us to carry out a simultaneous refinement of all the coordinate and thermal parameters of the structure. A refinement of this kind was in fact carried out; the results of the three different procedures are shown in Table 1 for comparison. For economy of space the table shows the results for one atom of each sort only, while the changes in the distances are exemplified by the case of Si-O.

Analysis of Table 1 leads to two conclusions. The introduction of the experimental weights w_{hkl} increased the R factor (calculated without allowing for the weighting factors!), but the errors in the coordinates of the atoms diminished, while the sum of the deviations of the Si-O distances from the mean contracted by a factor of almost two. Thus refinement by the method of least squares, using the experimental weights, has a clear advantage over the $w = 1$ or 0 weighting scheme. Our second comment concerns the successive and simultaneous refinement of the coordinates and individual isotropic parameters of the thermal vibrations of the atoms. In the present case there

TABLE 1. Comparison of Various Procedures for Refining the Crystal Structure of Baotite

Atoms, parameters, and distances	Successive refinement of x , y , z , and B		Combined refinement of x , y , z , and B	
	weighting scheme with $w = 1$ or 0	experimental weighting factors w_{hkl}		
Ba	x	0.02941 ± 0.00007	0.02946 ± 0.00002	0.02947 ± 0.00002
	y	0.09739 ± 0.00007	0.09737 ± 0.00002	0.09736 ± 0.00002
	z	0.62129 ± 0.00012	0.62138 ± 0.00006	0.62140 ± 0.00006
	B	0.35	0.42 ± 0.01	0.42 ± 0.02
Ti_1	x	0.21270 ± 0.00007	0.21264 ± 0.00005	0.21269 ± 0.00004
	y	0.10798 ± 0.00007	0.10787 ± 0.00005	0.10794 ± 0.00004
	z	0.8699 ± 0.0004	0.8698 ± 0.0002	0.8699 ± 0.0002
	B	0.32	0.34 ± 0.02	0.33 ± 0.01
Si	x	0.09291 ± 0.00012	0.09288 ± 0.00007	0.09292 ± 0.00006
	y	0.18531 ± 0.00012	0.18533 ± 0.00007	0.18541 ± 0.00006
	z	0.1249 ± 0.0005	0.1244 ± 0.0003	0.1243 ± 0.0003
	B	0.15	0.28 ± 0.02	0.27 ± 0.05
O_1	x	0.0168 ± 0.0003	0.0168 ± 0.0002	0.0168 ± 0.0002
	y	0.1561 ± 0.0003	0.1568 ± 0.0002	0.1567 ± 0.0002
	z	0.1334 ± 0.0013	0.1349 ± 0.0008	0.1349 ± 0.0008
	B	0.79	0.60 ± 0.05	0.67 ± 0.05
Si-O ₁	1.631 Å	1.624 ± 0.012 Å	1.627 Å	
Si-O ₂	1.596 Å	1.609 ± 0.013 Å	1.602 Å	
Si-O ₃	1.632 Å	1.626 ± 0.013 Å	1.629 Å	
Si-O _{1'}	1.629 Å	1.630 ± 0.013 Å	1.629 Å	
R factor	3.75%	4.01%	3.95%	

was no serious difference in the results. The additional simultaneous refinement of all the baotite parameters reduced the R factor from 4.01 to 3.95%; statistical verification [11] showed that this reduction was not significant.

As final values for the parameters of the crystal structure of baotite, we took the results of our refinement of these based on the set of structure amplitudes with the experimental weighting factors. The coordinates and individual isotropic parameters of the thermal vibrations of the atoms are shown in Table 2.

CRYSTAL STRUCTURE OF BAOTITE

In the 1960 edition of "Crystal Chemistry" [12], in the table of the bridge silicon-oxygen radicals, there is a note placed near the quadrupole $[\text{Si}_4\text{O}_{12}]$ ring to the effect that there are no reliable examples of silicates with this kind of radical, although an analogous phosphate ring was established in the $\text{Al}_4[\text{P}_3\text{O}_{12}]_3$ structure as far back as 1937 [13]. The claim made by Ito and Takeuchi in 1952 regarding the structure of axinite [14], which according to these authors contained a $[\text{Si}_4\text{O}_{12}]$ radical, requires considerable checking.

The hypothesis of Strunz [15] regarding the existence of $[\text{Si}_4\text{O}_{12}]$ in neptunite when studying the structure of the latter was refuted in [16]. Thus baotite proved to be the first silicate in which the ring radical $[\text{Si}_4\text{O}_{12}]$ had been reliably established [2]. Later an analogous quadrupole ring was found in kainosite [17].

In baotite the $[\text{Si}_4\text{O}_{12}]$ rings are threaded on four-fold inversion axes and lie in planes perpendicular to these; the planes pass through at a level corresponding to one of the systems of inversion points of the axes. A second system of inversion points of each of the 4 axes is occupied by the Cl atoms. The deviation of the Si atoms from

the planes indicated is less than 0.004 \AA ; the O_1 atoms joining the tetrahedra into the rings lie no more than 0.06 \AA from these planes; the $\text{Si}-\text{O}_1-\text{Si}$ angle equals $159^\circ 09'$. Practically the $[\text{Si}_4\text{O}_{12}]$ rings of baotite may be regarded as having maximum 4/mmm symmetry, although strictly they only obey 4. In the geometry of the Si tetrahedron one notes the anomalous length of the O_2-O_3 edge parallel to the c axis, which reaches a value of 2.75 \AA , almost equal to the average edge of the Ti octahedra of baotite (2.80 \AA). The enlarged edges of the Si tetrahedra link the tips of the successive Ti and (Ti, Nb, Fe) octahedra, which are connected by common horizontal edges into columns extending along the c axis. The crystal structure of baotite is shown in two projections in Figs. 2 and 3. Particularly clear is the plane of the structure (Fig. 2), in which the end projections of the square stems formed by the infinite columns of octahedra are plainly distinguished. This structural detail of baotite corresponds to the principal motif of rutile

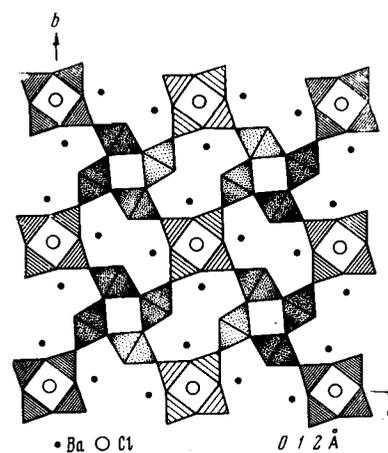


Fig. 2. Plane of the baotite structure.

TABLE 2. Coordinates and Individual Isotropic Thermal Factors of the Basic Atoms in the Baotite Structure (Origin of Coordinates in the Center of Symmetry)

Atoms	x/a	y/b	z/c	B
Ba	0.02847 ± 0.00002	0.09737 ± 0.00002	0.62138 ± 0.00006	0.42 ± 0.01
Ti	0.21264 ± 0.00005	0.10787 ± 0.00005	0.8699 ± 0.0002	0.34 ± 0.02
(Ti, Nb, Fe)	0.22174 ± 0.00003	0.11789 ± 0.00003	0.3728 ± 0.0002	0.39 ± 0.02
Si	0.09298 ± 0.00007	0.18533 ± 0.00007	0.1244 ± 0.0003	0.28 ± 0.02
O_1	0.0168 ± 0.0002	0.1568 ± 0.0002	0.1350 ± 0.0008	0.60 ± 0.05
O_2	0.1265 ± 0.0002	0.1593 ± 0.0002	0.8933 ± 0.0008	0.40 ± 0.05
O_3	0.1284 ± 0.0002	0.1617 ± 0.0002	0.3587 ± 0.0009	0.48 ± 0.05
O_4	0.1846 ± 0.0002	0.0530 ± 0.0002	0.1304 ± 0.0008	0.53 ± 0.05
O_5	0.1812 ± 0.0002	0.0547 ± 0.0002	0.6214 ± 0.0008	0.59 ± 0.05
O_6	0.2468 ± 0.0002	0.1684 ± 0.0002	0.1206 ± 0.0008	0.55 ± 0.05
O_7	0.2415 ± 0.0002	0.1703 ± 0.0002	0.6305 ± 0.0008	0.50 ± 0.05
Cl	0.0000	0.2500	0.6250	0.67 ± 0.04

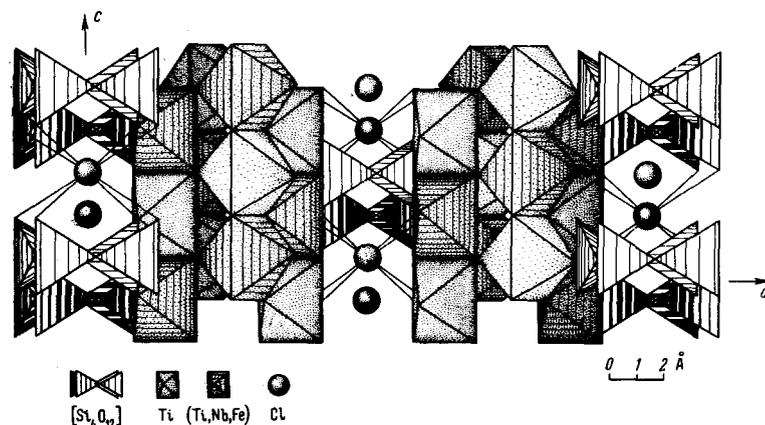


Fig. 3. Projection of the baotite structure along the b axis. Positions of the Ba atoms not shown.

[18]. The difference lies in that, in rutile, all the octahedra are equivalent, while in baotite the c spacing is twice that of rutile and there are two independent octahedra.

As shown earlier, the isomorphic additives Nb and Fe provide a material representation of this crystallographic independence. All the Nb + Fe impurity passes solely into one of the two octahedra. Table 3 shows the main interatomic distances of the baotite structure. Whereas the Ti—O and (Ti, Nb, Fe)—O mean distances are very similar and equal to 1.983 and 1.987 Å, respectively, the mean square deviations of the cation—oxygen distances from these values differ by a factor of three, being 0.03 for the Ti octahedron and 0.09 Å for the (Ti, Nb, Fe) octahedron. The common horizontal edges of the octahedra are shortened to 2.61 (O₅—O₇) and 2.62 Å (O₄—O₆). The largest values of 2.90 and 3.01 Å characterize the vertical edges of the octahedra (parallel to the c axis).

The architectural characteristics of baotite are such that the two independent octahedra are situated in an almost equivalent manner with respect to all the structural details except the Ba atoms. It is the difference in the arrangement of the Ba atoms relative to these octahedra which is probably the cause of the isomorphic impurities passing only into the Ti₂ octahedron. It is also an important point that the leading component of the additive is Nb, the valence of which is higher than that of Ti. The Ti₁ octahedron has a common face with the Ba polyhedra and in addition to this two common edges (the corresponding Ti₁—Ba distances are 3.51, 3.90, and 3.95 Å), while the Ti₂ ≡ (Ti, Nb, Fe) octahedron only shares two edges with the Ba polyhedra (with Ti₂—Ba distances of 3.82 and 4.14 Å). Hence the

Ba cations prevent the replacement of Ti⁴⁺ by Nb⁵⁺ in the Ti₁ position to a greater degree (other conditions being equal) than the analogous replacement of titanium in the Ti₂ position. The proposed interpretation of the fact that the isomorphic substituent enters selectively into the Ti₂ octahedra only refers to Nb, the leading component of the additive. Moreover, our line of argument and considerations of local charge compensation suggest that there will be a greater probability of titanium being replaced by Fe³⁺ in the Ti₁ octahedra. The problem as to the accurate location of the small amount of Fe impurity has not been solved at the present stage, the atomic numbers of iron and titanium being too close together to allow this.

In considering the Ti octahedra of baotite, we should note the compactness of all six Ti—O distances. The structural solutions of lamprophyllite [19] and certain other Ti-containing silicates [20–22] compel us to regard a Ti octahedron with such close Ti—O distances as the exception rather than the rule. A possible reason for this discrepancy is the very high Ti content of baotite.

The Ba polyhedron has a uniformly-distributed set of cation—oxygen distances, from 2.74 to 3.27 Å. These are all shown in increasing order in Table 3. In the coordination polyhedron of Ba we should note the Cl atom, with a Ba—Cl distance of 3.11 Å, which is smaller than the corresponding sum of the ionic radii, 1.38 + 1.81 = 3.19 Å, while all the Ba—O distances are greater than (in one case equal to) the corresponding sum of the radii [12]. The Cl atom occupies the ample space between the translationally-identical [Si₄O₁₂] rings. In the equatorial plane drawn through the Cl atom perpendicular to the c axis there are four Ba atoms at the corners

TABLE 3. Interatomic Distances in the Baotite Structure¹

Si tetrahedron		Ba—O ₁ ' 3.12	O ₅ '—O ₆ 2.73 (Ba)
Si—O ₁ 1.62		Ba—O ₅ 3.15	O ₅ '—O ₇ 2.78 (Ba)
Si—O ₃ 1.61		Ba—O ₁ ' 3.27	
Si—O ₃ 1.63		Ti octahedron	
Si—O ₁ ' 1.63		Ti—O ₃ 2.01	(Ti, Nb, Fe) octahedron
O ₁ —O ₁ ' 2.68		Ti—O ₄ 1.97	(Ti, Nb, Fe)—O ₃ 2.06
O ₁ —O ₂ 2.62		Ti—O ₆ 2.03	(Ti, Nb, Fe)—O ₄ 2.07
O ₁ —O ₃ 2.58		Ti—O ₅ 1.92	(Ti, Nb, Fe)—O ₅ 2.10
O ₁ '—O ₂ 2.60		Ti—O ₇ 1.97	(Ti, Nb, Fe)—O ₆ 1.87
O ₁ '—O ₃ 2.64		Ti—O ₅ ' 2.00	(Ti, Nb, Fe)—O ₇ 1.89
O ₂ —O ₃ 2.75		O ₂ —O ₄ 2.80	(Ti, Nb, Fe)—O ₄ ' 1.93
Ba polyhedron		O ₂ —O ₅ 2.85 (Ba)	O ₃ —O ₄ 2.79
Ba—O ₇ 2.74		O ₂ —O ₆ 2.75	O ₃ —O ₅ 2.85 (Ba)
Ba—O ₆ 2.76		O ₂ —O ₇ 2.78 (Ba)	O ₃ —O ₆ 2.76
Ba—O ₂ 2.81		O ₄ —O ₅ 3.01	O ₃ —O ₇ 2.78 (Ba)
Ba—O ₇ 2.81		O ₄ —O ₆ 2.62 (Ti, Nb, Fe)	O ₄ —O ₅ 2.90
Ba—O ₃ 2.82		O ₅ —O ₇ 2.61 (Ti, Nb, Fe)	O ₄ —O ₆ 2.62 (Ti)
Ba—O ₅ 2.88		O ₆ —O ₇ 2.90 (Ba)	O ₅ —O ₇ 2.61 (Ti)
Ba—O ₂ ' 2.91		O ₅ '—O ₄ 2.83	O ₆ —O ₇ 3.01
Ba—Cl 3.11		O ₅ '—O ₅ 2.89	O ₄ '—O ₄ 2.80
			O ₄ '—O ₅ 2.86
			O ₄ '—O ₆ 2.80
			O ₄ '—O ₇ 2.84

¹Distances given in Å. If the edge of a polyhedron simultaneously enters as an edge into another polyhedron, the cation of the latter is shown in brackets.

of a regular square, having the Ba—Cl distances of 3.11 Å mentioned earlier. The sixteen distances from the Cl to the oxygen atoms of the upper and lower [Si₄O₁₂] rings are divided into symmetry-coupled groups of four Cl—O₁ (3.16), Cl—O₂ (3.49), Cl—O₃ (3.49), and Cl—O₄ (3.56 Å).

The structure of baotite may be characterized by a three-dimensional framework of infinite square stems or columns formed by the Ti octahedra and bridge metasilicate rings [Si₄O₁₂]. The channels in the framework extending along the c axis are filled with Ba cations. The very similar values of the individual parameters of the thermal vibrations for the oxygen atoms (Table 2) indicate homogeneity of the structure. However, the balance of the valence forces converging at the anions slightly distinguished the O₇ and particularly the O₆ from the others. Each of these enters into one Ti and one (Ti, Nb, Fe) octahedron and correspondingly into two and one Ba polyhedra, which gives valence-force sums of 1.75 and 1.55 instead of the 2 required for complete compensation. This fact indicates the possibility, in principle, that some of the oxygen, most probably in the O₆ and O₇ positions, may be statistically replaced by OH groups.

Our analysis of baotite clearly demonstrates the high structural sensitivity of the processes of isomorphic substitution in crystals. The breaking of the equivalence between the two Ti octahedra, attributable to the arrangement of the weakly-charged Ba cations, the closest of which lies at 3.51 Å from the Ti, proved to be sufficient to ensure the strictly selective absorption of the isomorphic Nb impurity by this mineral.

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