

**KUANNERSUITE-(Ce), Ba₆Na₂REE₂(PO₄)₆FCl, A NEW MEMBER
OF THE APATITE GROUP, FROM THE ILÍMAUSSAQ ALKALINE COMPLEX,
SOUTH GREENLAND: DESCRIPTION AND CRYSTAL CHEMISTRY***

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ABSTRACT

Kuannersuite-(Ce) is a new mineral species belonging to the apatite group. It was found in the Ilímaussaq alkaline complex, South Greenland, and occurs as light rose-colored hexagonal prismatic crystals, up to 1.5 mm long, with a white streak and a vitreous luster. Associated minerals include aegirine, analcime, beryllite, chkalovite, galena, gmelinite, gonnardite, lovdarite, nabesite, neptunite, pectolite, polyolithionite, pyrochlore, sphalerite and tugtupite. It is brittle with an uneven fracture, and poor {001} and {100} cleavages, and a Mohs hardness of 4½ – 5½. Although kuannersuite-(Ce) is trigonal and uniaxial negative with $\varepsilon = 1.669(1)$ and $\omega = 1.694(1)$, it has a $2V(\text{meas.})$ of 10 to 20°. The empirical formula based on results of electron-microprobe analyses and calculated with 26 anions is: $(\text{Ba}_{5.61}\text{Sr}_{0.15}\text{K}_{0.03})_{\Sigma 5.79}\text{Na}_{2.14}(\text{Ce}_{1.00}\text{Nd}_{0.43}\text{La}_{0.25}\text{Sm}_{0.05}\text{Th}_{0.02}\text{Pr}_{0.01})_{\Sigma 1.76}(\text{P}_{6.02}\text{Si}_{0.14})_{\Sigma 6.16}\text{O}_{23.72}(\text{F}_{1.70}\text{Cl}_{0.58})_{\Sigma 2.28}$ or, ideally, $\text{Ba}_6\text{Na}_2\text{REE}_2(\text{PO}_4)_6\text{FCl}$. The strongest X-ray-diffraction lines [d in Å (I)(hkl)] are: 2.969(100)(211,112), 2.867(60)(300), 1.965(80)(320,213). The crystal structure was refined ($R = 2.79\%$) in space group $P\bar{3}$, with a 9.9097(6) Å, c 7.4026(6) Å, V 629.42(7) Å³, $Z = 1$ and $D_{\text{calc.}} = 4.51(1)$ g/cm³. Ba, REE and Na are distributed over different structural sites with distinct atomic coordinations, whereas F and Cl occupy positions in two different octahedrally coordinated voids formed by Ba atoms, with distances typical for a regular six-fold coordination of these anions. Cl is incorporated only in the larger of the two coordination polyhedra. A comparative analysis of the crystal chemistry of kuannersuite-(Ce) and related Ba and Sr phases from the apatite family is reported.

Keywords: kuannersuite-(Ce), new mineral species, crystal structure, apatite group, crystal chemistry, Ilímaussaq alkaline complex, Greenland.

SOMMAIRE

La kuannersuite-(Ce) est une espèce minérale nouvelle, et membre du groupe de l'apatite. On l'a découverte dans les roches du complexe alcalin d'Ilímaussaq, dans le sud du Groenland, sous forme de prismes hexagonaux rose pâle atteignant une longueur de 1.5 mm, avec une rayure blanche et un éclat vitreux. Lui sont associés aegyrine, analcime, beryllite, chkalovite, galène, gmelinite, gonnardite, lovdarite, nabesite, neptunite, pectolite, polyolithionite, pyrochlore, sphalérite et tugtupite. Elle est cassante, avec une fracture inégale, et possède deux clivages de piètre qualité, {001} et {100}, et une dureté de Mohs de 4½ – 5½. Quoique la kuannersuite-(Ce) est trigonale et uniaxe négative, avec $\varepsilon = 1.669(1)$ et $\omega = 1.694(1)$, elle fait preuve d'un angle $2V(\text{mes.})$ de 10 à 20°. La formule empirique, fondée sur les résultats d'analyses à la microsonde électronique recalculés sur une base de 26 anions, est: $(\text{Ba}_{5.61}\text{Sr}_{0.15}\text{K}_{0.03})_{\Sigma 5.79}\text{Na}_{2.14}(\text{Ce}_{1.00}\text{Nd}_{0.43}\text{La}_{0.25}\text{Sm}_{0.05}\text{Th}_{0.02}\text{Pr}_{0.01})_{\Sigma 1.76}(\text{P}_{6.02}\text{Si}_{0.14})_{\Sigma 6.16}\text{O}_{23.72}(\text{F}_{1.70}\text{Cl}_{0.58})_{\Sigma 2.28}$ ou, en termes idéaux, $\text{Ba}_6\text{Na}_2\text{TR}_2(\text{PO}_4)_6\text{FCl}$. Les raies les plus intenses du spectre de diffraction [d en Å (I)(hkl)] sont: 2.969(100)(211,112), 2.867(60)(300), 1.965(80)(320,213). La structure cristalline a été affinée ($R = 2.79\%$) dans le groupe spatial $P\bar{3}$, avec a 9.9097(6) Å, c 7.4026(6) Å, V 629.42(7) Å³, $Z = 1$ et $D_{\text{calc.}} = 4.51(1)$ g/cm³. Le Ba, les terres rares (TR) et Na sont répartis sur des sites structuraux différents, ayant des coordinences distinctes, tandis que F et Cl occupent des positions à l'intérieur de deux lacunes différentes à coordinence octaédrique entourées par des atomes de Ba, les distances étant typiques d'un

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* Contribution to the mineralogy of Ilímaussaq, no. 121.

agencement octaédrique régulier de ces anions. Le Cl est admis dans le plus spacieux de ces deux polyèdres. Nous présentons les résultats d'une analyse comparative de la cristallographie de la kuannersuite-(Ce) et des phases à Ba et Sr de la famille de l'apatite.

(Traduit par la Rédaction)

Mots-clés: kuannersuite-(Ce), nouvelle espèce minérale, structure cristalline, groupe de l'apatite, cristallographie, complexe alcalin d'Ilímaussaq, Groenland.

INTRODUCTION

Kuannersuite-(Ce), a new mineral species of the apatite group having the composition $Ba_6Na_2REE_2(PO_4)_6FCl$, was found in cavities in albite veins that intersect augite syenite on the Kuannersuit Plateau (formerly Kvanefjeld) in the Ilímaussaq alkaline complex, South Greenland, by one of the authors (HF) during a mineralogical excursion in the summer of 1999. Only one sample with less than 10 crystals has been found. The mineral is named after the type locality and in accordance with the Levinson system for naming REE minerals (Levinson 1966). The aim of this study is to describe the physical and chemical properties of this new mineral species, its crystal structure and the relation with other members of the apatite group. The mineral and its name were approved by the Commission on New Minerals and Mineral Names (IMA #2002–013). The type material is kept in the collection of the Geological Museum, Copenhagen, Denmark under the number GM 2003.42, and at the Geological Faculty, Moscow State University, Moscow, Russia (II–1016).

COMPARISONS

The Ilímaussaq complex has on average a Ba concentration of 406 ppm (Bailey *et al.* 2001), generally comparable to the similar alkaline complexes Lovozero and Khibina, Kola Peninsula, Russia. According to new estimates (Arzamastsev *et al.* 2001), Lovozero and Khibina contain an average of 389 and 629 ppm Ba, respectively. Note, however, that previous estimates were approximately twice as high (Vlasov *et al.* 1966, Galakhov 1975). In the complexes, 21 and nine Ba minerals have already been identified, respectively (Khomyakov 1995, Pekov 2000), whereas kuannersuite-(Ce) is only the fifth Ba mineral to be found within Ilímaussaq (Matsubara *et al.* 2001, Petersen 2001). The average concentration of Sr is much lower at Ilímaussaq (~100 ppm) (Bailey *et al.* 2001) than at Lovozero and Khibina, which are estimated to contain averages of 855 and 1398 ppm, respectively (Arzamastsev *et al.* 2001). The difference in geochemistry of the complexes, combined with the fact that the augite syenite hosting the albite veins at Kuannersuit Plateau is enriched in Ba (2300–2600 ppm) compared to Sr (300–400 ppm) (Bailey *et al.* 2001) is probably one of the main reasons why kuannersuite-(Ce) has formed rather than belowite,

the Sr member of the apatite group known from evolved parageneses at the Lovozero and Khibina complexes.

OCCURRENCE AND PARAGENESIS

The Ilímaussaq alkaline complex, dated at 1161 ± 2 Ma (Waight *et al.* 2002), is one of the youngest alkaline complexes of the Gardar Province in the southwestern part of Greenland. It was formed during continental rifting in Proterozoic times. The Kuannersuit Plateau is situated in the northwestern part of the Ilímaussaq alkaline complex, and consists of alkaline rocks such as sodalite nepheline syenite, aegirine–arfvedsonite nepheline syenite, and augite syenite. The latter is intersected by a number of albite veins that exhibit complex mineralogy (Sørensen *et al.* 1971). The walls of cavities in the veins are covered with albite crystals on which hydrothermal minerals have crystallized, among them kuannersuite-(Ce). Associated minerals include aegirine, analcime, beryllite, chkalovite, galena, gmelinite, gonnardite, lovdarite, nabesite, neptunite, pectolite, polythionite, pyrochlore, sphalerite and tugtupite.

APPEARANCE, MORPHOLOGY, PHYSICAL AND OPTICAL PROPERTIES

Kuannersuite-(Ce) forms translucent light rose elongate hexagonal crystals up to 1.5 mm in length. They show poor cleavage along {001} and {100}. Because kuannersuite-(Ce) is among the latest-formed minerals in the cavities, the morphology of its crystals is influenced by the available voids between already existing minerals, and only {100} prism faces can typically be seen. The mineral has a white streak and a vitreous luster, and shows no fluorescence under ultraviolet light (long or short wave). It is brittle with an uneven fracture. The Mohs hardness is between $4\frac{1}{2}$ and $5\frac{1}{2}$, and the calculated density is $4.51(1)$ g/cm³. Owing to the small amount of material, it was not possible to determine the density experimentally.

According to the results of a X-ray-diffraction study (see below), kuannersuite-(Ce) is trigonal and is expected to be optically uniaxial. According to the measured properties, it is optically negative, with ϵ 1.669(1) and ω 1.694(1), but a low $2V$ of 10 to 20° was measured, suggesting that the mineral is biaxial. The origin of this discrepancy is not explained, but it should be

noted that the same effect was recorded for other minerals in the apatite group (Deer *et al.* 1992). The optical properties were investigated with the spindle-stage technique (Bloss 1981). The indices of refraction for $\lambda = 589$ nm were determined by the microrefractometer spindle stage technique, using smithsonite as refractometer crystal (Medenbach 1985), and by the $\lambda - T$ variation method. The dispersion is $r > v$. The indices of refraction are approximately 0.03 larger than those of belovite-(Ce), but the birefringence corresponds to that of belovite-(Ce) from Mt. Alluaiv, Lovozero (Pekov *et al.* 1995). The Gladstone–Dale compatibility index, $1 - (K_p/K_C)$, is -0.033 , *i.e.*, excellent (Mandarino 1981).

CHEMICAL COMPOSITION

Kuannersuite-(Ce) was analyzed with a Camebax electron microbeam instrument with an acceleration voltage of 15 kV, a beam current of 30 nA creating a $5 \times 5 \mu\text{m}$ beam. The following mineral and synthetic standards were used: diopside (Ca, Si), albite (Na), orthoclase (K), chlorapatite (P, Cl), synthetic SrSO_4 (Sr, S), synthetic BaSO_4 (Ba), synthetic ThO_2 (Th), synthetic MgF_2 (F), synthetic phosphates (La, Ce, Pr, Nd). The elements Mg, Mn, Fe, Al, Cr, V, Y, U, Ti, As and REE heavier than Sm were all below the detection limit. The average of three sets of analytical data is listed in Table 1 together with chemical data on belovite-(Ce), and the formula calculated on the basis of 26 anions. The grains analyzed did not show any zoning. K is grouped with Ba rather than Na because the K–O bond distance is closer to Ba–O than to Na–O, resulting in the following empirical formula $(\text{Ba}_{5.61}\text{Sr}_{0.15}\text{K}_{0.03})_{\Sigma 5.79} \text{Na}_{2.14}(\text{Ce}_{1.00}\text{Nd}_{0.43}\text{La}_{0.25}\text{Sm}_{0.05}\text{Th}_{0.02}\text{Pr}_{0.01})_{\Sigma 1.76} (\text{P}_{6.02}\text{Si}_{0.14})_{\Sigma 6.16} \text{O}_{23.72} (\text{F}_{1.70}\text{Cl}_{0.58})_{\Sigma 2.28} (Z = 1)$. In accordance with the crystal-structure refinement, the idealized formula can

be written as $\text{Ba}_6\text{Na}_2\text{REE}_2(\text{PO}_4)_6\text{FCl}$, to emphasize that Cl occupies only one of the two independent F sites.

X-RAY CRYSTALLOGRAPHY

Owing to the small amount of available material, it was only possible to collect an X-ray-diffraction pattern using a 114.6 mm Gandolfi camera with $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The observed powder-diffraction pattern is presented in Table 2, together with the calculated pattern derived from the crystal-structure data.

The structure of the mineral was solved from single-crystal data collected on a Bruker–AXS 4-circle diffractometer with a CCD detector (sealed Mo tube and graphite monochromator). For crystal orientation and data collection, the program SMART was used. The intensity data were integrated with the program SAINT+, and XPREP was used to perform an empirical absorption-correction and to prepare SHELX files (all Bruker–AXS programs). The structure was solved with SHELXS–97 by means of direct methods (Sheldrick 1997a), and refined with SHELXL–97 (Sheldrick 1997b). Scattering factors for neutral atoms were used. Crystal and measurement data are presented in Table 3. Tables of structure factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

CRYSTAL STRUCTURE

Intensity statistics and the absence of systematic extinctions suggest the space group $P\bar{3}$. The positions of all atoms except oxygen and fluorine were found by direct methods, whereas the latter were located by sub-

TABLE 1. CHEMICAL COMPOSITION OF KUANNERSUITE-(Ce) AND BELOVITE-(Ce)

	Kuannersuite-(Ce) from Ilímaussaq		Belovite-(Ce) from Lovozero ¹	
Na ₂ O wt.%	3.9(3)	Na <i>apfu</i>	2.14(16)	4.19(47)
K ₂ O	0.09(5)	K	0.03(2)	n.d.
CaO	0.03(3)	Ca	0	0.61(9)
SrO	0.9(2)	Sr	0.15(3)	38.1(18)
BaO	50.6(9)	Ba	5.61(10)	2.15(21)
La ₂ O ₃	2.4(6)	La	0.25(6)	6.67(24)
Ce ₂ O ₃	9.6(10)	Ce	1.00(10)	12.47(19)
Pr ₂ O ₃	0.12(5)	Pr	0.010(4)	n.d.
Nd ₂ O ₃	4.3(9)	Nd	0.43(9)	3.74(32)
Sm ₂ O ₃	0.3(3)	Sm	0.05(3)	n.d.
ThO ₂	0.3(2)	Th	0.02(1)	n.d.
SiO ₂	0.5(4)	Si	0.14(11)	0.9(15)
P ₂ O ₅	25.1(8)	P	6.02(19)	27.5(16)
SO ₃	0.04(4)	S	0	n.d.
F	1.9(2)	F	1.70(18)	2.39(26)
OH	1.2(2)	Cl	0.58(10)	0.93(1)
Cl	n.d.			0.1(1)
-O=(F,Cl) ₂	-1.10			-1.01
Total	100.38			97.86

n.d.: not detected. The calculation of atom proportions is based on a 26-anion formula. ¹Rakovan & Hughes (2000); composition expressed in wt.%.

TABLE 2. X-RAY DIFFRACTION PATTERN FOR KUANNERSUITE-(Ce)

<i>l</i>	<i>h</i>	<i>k</i>	<i>l</i> _(obs)	<i>d</i> _(meas)	<i>d</i> _(calc)	<i>I</i> _(calc)	<i>hkl</i>	<i>l</i> _(obs)	<i>d</i> _(meas)	<i>d</i> _(calc)	<i>I</i> _(calc)	<i>hkl</i>	
				8.582	16	100							
			80	7.403	48	001		1.965	{	1.969	14	320	
				5.605	94	101		1.903	{	1.904	31	213	
				4.291	38	200			{	1.873	21	410	
40	4.077		60	4.118	100	111		1.863	{	1.868	11	303	
40	3.693			3.712	20	201			{	1.856	23	402	
20	3.389			3.399	29	102		1.811	{	1.816	20	411	
20	3.243			3.244	45	210		40	1.608	{	1.607	9	214
100	2.969	{		2.971	53	211		20	1.554	{	1.554	4	304
		{		2.965	38	112			{	1.541	3	510	
60	2.867		20	2.861	46	300		20	1.537	{	1.539	9	323
				2.668	22	031			{	1.509	3	511	
			40	2.468	13	003		40	1.510	{	1.508	6	332
20	2.380			2.380	18	130			{	1.461	3	314	
			20	2.349	22	221		20	1.459	{	1.459	3	105
20	2.259	{		2.266	20	311		40	1.351	{	1.351	9	251
		{		2.263	19	302		20	1.337	{	1.334	6	602
40	2.212			2.209	31	113			{	1.318	3	342	
20	2.113		20	2.139	6	203		20	1.318	{	1.316	10	414
				2.061	10	401			{	1.289	5	611	
40	2.058	{		2.059	29	222		20	1.288	{	1.288	10	522
20	2.002			2.002	35	312							

The theoretical diagram was calculated using the program LAZY PULVERIX of Yvon *et al.* (1977).

sequent refinement of the structure using difference-Fourier synthesis. The structure was refined to $R = 2.79\%$ and found to be closely related to that of apatite, with a generalized structural formula $Me(1)_2Me(2)_3(PO_4)_3(OH,F,Cl)$. In apatite, Ca occupies two distinct sites. The $Me(1)$ sites are surrounded by 9 atoms of oxygen in vertices of tri-capped trigonal prisms that share bases and form columns parallel to the c axis. The $Me(2)$ sites are grouped in triangles around columns of monovalent anions that run parallel to the c axis (Elliott 1994). On the outer parts, the coordinations of $Me(2)$ sites are completed by six oxygen atoms. Owing to a lower symmetry, the cation positions in the columns of trigonal prisms in kuannersuite-(Ce) [corresponding to $Me(1)$] fall on two independent sites that alternate inside the same column. The two sites are preferentially occupied by light REE (dominated by Ce) and Na, respectively (Table 4, Fig. 1). A discussion of their coordination characteristics follows. Barium occupies preferentially the $Me(2)$ site (Figs. 2, 3). Selected bond-lengths and angles in kuannersuite-(Ce) and two related structures are listed in Table 5. Attempts were made to refine the three different cation positions as mixed Ba +

Na + REE sites, but owing to a very small degree of substitution in these sites, no decisive quantitative result could be obtained. They were therefore assigned each one of the atomic species Ce, Na, and Ba, respectively, according to their approximate numbers of electrons and coordination characteristics. To detect any substitution, the occupancies of the three cations were not constrained during the refinement. Because the results suggest that any cation mixing at the three sites is at or below the detection limit of the method, the REE site was assigned $59\%Ce + 26\%Nd + 15\%La$ at the last stage of refinement in accordance with proportions of the main REE obtained in the electron-microprobe analysis, whereas the Na and Ba sites were assigned full occupancies.

The F position in anion columns is represented in kuannersuite-(Ce) by two independent sites at or close to centers of symmetry, and Cl is found to substitute only in the former site. An attempt to make the atomic displacement factors for the latter site (F1) anisotropic resulted in an unstable refinement. Accordingly, this site was the only one refined with an isotropic displacement factor at the last stage of refinement.

TABLE 3. CRYSTAL DATA AND MEASUREMENT DATA FOR KUANNERSUITE-(Ce)

Size (mm)	0.126 x 0.135 x 0.135	Exposure time (s)/frame	10
a (Å)	9.9097(6)	Crystal to detector distance (mm)	38.5
c (Å)	7.4026(6)	$2\theta_{max}$ (°)	69.6
Vol. (Å ³)	629.42(7)	Reflections collected	8620
Space group	$P\bar{3}$ (147)	Unique reflections	1750
Z	1	Observed reflections ($F_o > 4\sigma F_o$)	1539
μ (mm ⁻¹)	13.34	R_{int} (%)	4.89
Extinction coefficient	0.0017(2)	wR2 (%)	5.65
Radiation	MoK α /graphite	R1 for $F_o > 4\sigma F_o$ (%)	2.79
No. of frames	2240	R1 for all data (%)	3.48
Step size (°)	0.25	Goof for all data	1.224

$$R1 = \Sigma (F_o - F_c) / \Sigma F_o, w = 1 / (\sigma^2(F_o^2) + (0.0142 \times P)^2 + 1.97 \times P) \text{ where } P = (\max. (F_o^2, 0) + 2F_c^2)^3,$$

$$wR2 = [(\Sigma w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}.$$

TABLE 4. COORDINATES, SITE-OCCUPANCY FACTOR, ANISOTROPIC DISPLACEMENT PARAMETERS AND BOND-VALENCE SUM FOR KUANNERSUITE-(Ce)

Site	x	y	z	sof	U eq.	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	BVS ¹
Ba	0.26020(3)	0.02440(3)	0.23296(3)	0.981(5)	0.01277(8)	0.0163(1)	0.0117(1)	0.0104(1)	-0.00074(7)	-0.00062(8)	0.00718(9)	2.218 ²
REE	$\frac{1}{2}$	$\frac{1}{2}$	0.47754(5)	1	0.0086(1)	0.0087(1)	0.0087(1)	0.0085(2)	0	0	0.00438(6)	3.023
Na	$\frac{1}{2}$	$\frac{1}{2}$	0.0159(4)	1.17(2)	0.0213(8)	0.024(1)	0.024(1)	0.014(1)	0	0	0.0125(5)	0.836
P	0.3809(1)	0.4123(1)	0.2619(1)	1	0.0096(2)	0.0097(4)	0.0100(4)	0.0098(4)	-0.0003(3)	-0.0005(3)	0.0054(3)	4.799
O1	0.5072(4)	0.3668(4)	0.2841(4)	1	0.0185(6)	0.019(1)	0.024(2)	0.018(1)	-0.002(1)	-0.003(1)	0.016(1)	1.816
O2	0.1318(3)	0.5455(3)	0.2190(4)	1	0.0155(6)	0.013(1)	0.014(1)	0.021(1)	-0.002(1)	0.0007(11)	0.008(1)	2.059
O3	0.2851(4)	0.3867(4)	0.4371(4)	1	0.0175(6)	0.020(1)	0.020(1)	0.011(1)	0.002(1)	0.003(1)	0.010(1)	1.942
O4	0.2676(4)	0.3096(4)	0.1150(4)	1	0.0192(6)	0.014(1)	0.024(2)	0.016(1)	-0.009(1)	-0.006(1)	0.008(1)	2.131
F1	0	0	0.035(1)	1	0.027(2)							0.963
F2	0	0	$\frac{1}{2}$	0.41(1)	0.015(1)	0.013(1)	0.013(1)	0.020(2)	0	0	0.0066(6)	
Cl	0	0	$\frac{1}{2}$	0.59(1)	0.015(1)	0.013(1)	0.013(1)	0.020(2)	0	0	0.0066(6)	1.170 ²

The anisotropic displacement factor is defined as: $\exp(-2\pi^2 [h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \dots + 2hka^*b^*(U_{12})])$.

¹ The bond-valence sums are calculated with parameters from Brese & O'Keefe (1991).

² BVS is calculated in accordance with the occupancy factors for F2 and Cl.

ORDERING SCHEME

The decrease in symmetry from $P6_3/m$ for fluorapatite to $P\bar{3}$ for kuannersuite-(Ce) is due to the splitting of the $Me(1)$ site in fluorapatite into the two independent cation sites occupied by Na and REE, respectively. The same decrease in symmetry to space group $P\bar{3}$ has also been found for belovite-(Ce) and belovite-(La) (Klevtsova & Borisov 1964, Nadezhina *et al.* 1987, Pekov *et al.* 1995, 1996, Kabalov *et al.* 1997, Rakovan & Hughes 2000). In a study of three synthetic barium-dominant fluorapatite compositions, Mathew *et al.* (1979) found $Ba_{10}(PO_4)_6F_2$ to have the space group $P6_3/m$, which was also found by Hata *et al.* (1979) for $Ba_{10}(PO_4)_6Cl_2$, whereas with increasing Na + REE replacement, a lowering of symmetry to $P\bar{6}$ in $Ba_6La_2Na_2(PO_4)_6F_2$, and to $P\bar{3}$ in $Ba_4Nd_3Na_3(PO_4)_6F_2$ occurred.

As there is only about 5% difference in the number of electrons between Ba and the mixture of dominant REE (La, Ce and Nd) present in kuannersuite-(Ce), the main problem in the structure analysis with conventional X-ray diffraction is the assignment of these atomic species to specific structural sites, and the question of their mutual substitution. The chemical analysis gives a Ba:Na:REE proportion very close to 3:1:1, which corresponds to the proportion of multiplicities of the three large cation sites. In the Sr-dominated analogue belovite, where there is a large difference in atomic numbers between Ce, Sr, and Na, an easier attribution of species to different sites was possible, and it showed a very high preference of Sr for the $Me(2)$ and Ce and Na for each of the independent $Me(1)$ sites (Nadezhina *et al.* 1987, Rakovan & Hughes 2000).

The assignments are further supported by results of the structure refinement. The chemical analysis suggests a small surplus of light cations (both Na, and P + Si) and a small deficit of heavy cations (Ba + Sr + K and REE) as compared to an idealized formula. However, it should be noted that the differences from ideal values are of the order of the standard deviation of analyses. For a comparison with the structure refinement, the number of electrons per site as obtained in the latter can be compared to the one obtained from the empirical formula. The values from an unconstrained refinement are 54.9(3), 58.7(3), and 13.0(2) electrons for $Me(2)$, and the two $Me(1)$ sites respectively, or 329(2), 117.4(6), and 26.0(4) electrons, respectively, per formula unit. Corresponding values calculated from the chemical analysis are 319(7), 102(19), and 23(2) electrons, respectively. It is evident that owing to a large number of elements that contribute to the REE site, and are present only in very small amounts, and a small number of electron-microprobe analyses, the estimated standard deviations are especially large for this site. There is therefore insufficient information from the microprobe results to judge whether the low number of electrons indicates vacancies at the Ba and REE sites, or are just due to a low accuracy. Owing to the method,

and a large number of reflections measured, the results of the structural refinement have lower estimated standard deviations. They could, however, be biased by a strong correlation between the occupancy factors, and atom-displacement factors. If no vacancies are supposed at Ba and REE sites, and the proportion of elements at each of them is made the same as that obtained by chemical analysis, the calculated electrons per formula unit are 332, and 118 respectively, very close to the structure values. The latter could suggest a very small substitution of Na in the Ba site, and *vice versa*, but in any case show that it does not exceed 5 at.%.

As a conclusion, the differences between the results of the chemical and the structural analyses are relatively small and show that the distribution of Na, Ba (+Sr), and REE in kuannersuite-(Ce) is highly ordered, as is also observed for belovite-(Ce) and belovite-(La) (Klevtsova & Borisov 1964, Nadezhina *et al.* 1987, Pekov *et al.* 1995, 1996, Kabalov *et al.* 1997, Rakovan & Hughes 2000).

Surpluses of P + Si and F + Cl compared to an idealized apatite-type formula are also suggested by the results of chemical analyses. But they are again of the order of the standard deviation. Furthermore, a surplus of halogens can be caused by diffusion under the electron beam (Stormer *et al.* 1993). The contents of Cl obtained by chemical analysis and structural analysis are in good agreement and suggest that Cl plays a significant role in the structure of kuannersuite-(Ce).

COORDINATION NUMBERS
AND ANALYSIS OF COORDINATION POLYHEDRA

As kuannersuite-(Ce) represents a natural member of the apatite family containing one of the largest cations, it is interesting to investigate the properties of its atomic coordinations in more detail. They are compared below with corresponding coordinations in closely related structures: four synthetic Ba-members of the apatite family $Ba_{10}(PO_4)_6F_2$, $Ba_6La_2Na_2(PO_4)_6F_2$, $Ba_4Nd_3Na_3(PO_4)_6F_2$ (Mathew *et al.* 1979) and $Ba_{10}(PO_4)_6Cl_2$ (Hata *et al.* 1979), and natural belovite $Sr_6REE_2Na_2(PO_4)_6F_2$ (Nadezhina *et al.* 1987, Kabalov *et al.* 1997, Rakovan & Hughes 2000). The coordination characteristics are quantified using the centroid approach of Balić-Žunić & Makovicky (1996) and Makovicky & Balić-Žunić (1998). The quantitative characteristics of the coordination polyhedra in various compared structures can be seen in Tables 6, 7 and 8.

The coordination of the cations

The atom coordinations at $Me(2)$ sites in the structures compared are presented in Figure 3. Barium in kuannersuite-(Ce) is situated in a cavity formed by 9 O, 1 F, and 1 Cl atoms. The attachment of F and Cl corresponds to that found in $Ba_4Nd_3Na_3(PO_4)_6F_2$, at the $M2$ site in $Ba_6La_2Na_2(PO_4)_6F_2$, and at the Ba2 site in Ba_{10}

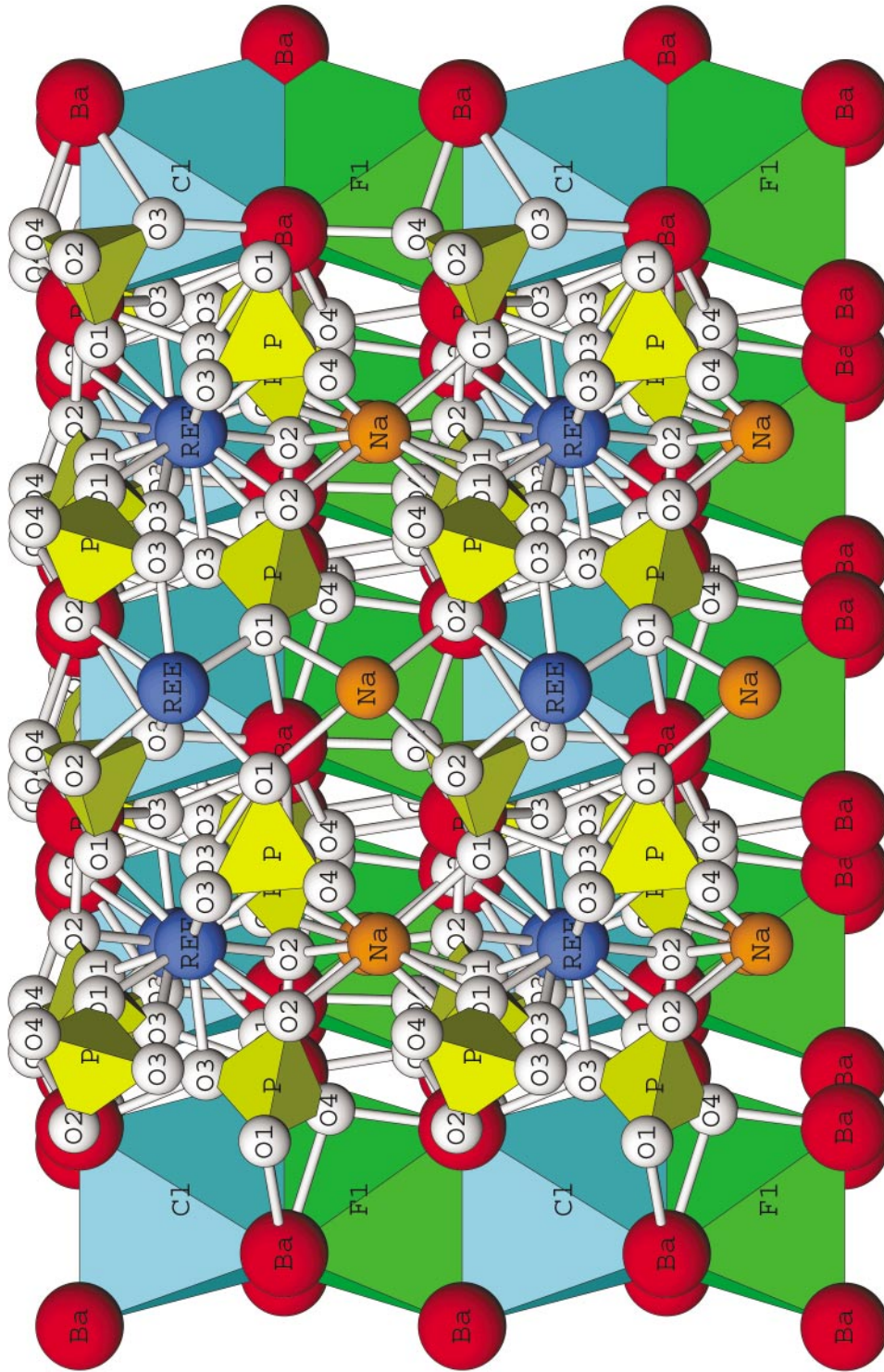


FIG. 1. The structure of kuannersuite-(Ce) seen perpendicular to the *c* axis showing the splitting of the *Me*(1) site into two independent sites occupied by Na and REE, and the placement of Cl in the same layer as REE.

$(\text{PO}_4)_6\text{Cl}_2$, where the two anions both lie at relatively large distances (2.8–3.3 Å) from the Ba. One of the F atoms is in a statistically split position [F1 in kuannersuite-(Ce), F2 in $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$ and $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$]. The Ba2 site in $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$, the M1 site in $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$, and the Sr site in belovite have one close F atom or OH group (2.4–2.5 Å). In the former two, it is in a statistically split position. In $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$ and belovite, there is an additional anion at the same side of the cation at a much greater distance (3.0–3.3 Å). In $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$, it is the statistically split F2 site, whereas in belovite-(Ce), a minor substitution of Cl for F is found to occupy such

a site (Rakovan & Hughes 2000). From Figure 3, one can see that the $\langle \text{Me}-\text{O} \rangle$ distances show very limited variations, suggesting that the oxygen part of the coordination is relatively uniform in all of the structures. A quantitative comparison is presented in Table 6, where the characteristics of the coordination polyhedra are calculated taking into account only the nine O atoms. The calculated parameters are: the average bond-distance ($\langle d \rangle$), the radius of the sphere fitted to the positions of oxygen (r_s), the volume of the coordination polyhedron (V_p), the eccentricity or the deviation of *Me* from the center of the sphere (Δ/r_s), the sphericity or the extent of deviation of oxygen atoms from the surface of

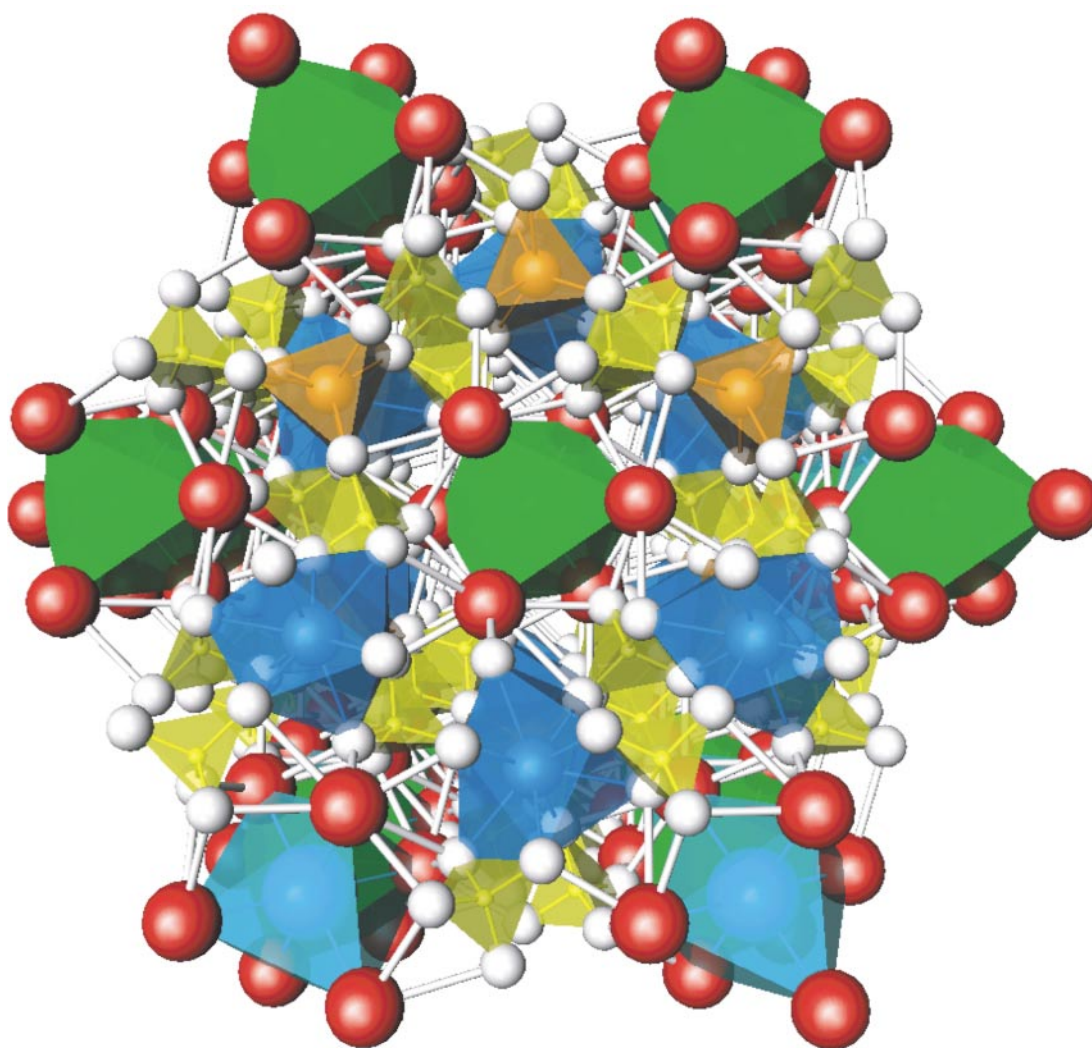


FIG. 2. A perspective view of the structure of kuannersuite-(Ce) parallel to the *c* axis. The same color code for the polyhedra as in Figure 1 is used. To emphasize the alternation of the cation and monovalent anion in the columns along the *c* axis, the bottom half of the figure is at a level *c*/2 lower than the top part.

the sphere (SPH), and the volume deformation of the polyhedron (v) (Balić-Zunić & Makovicky 1996, Makovicky & Balić-Zunić 1998). As can be seen from Table 6, the main difference is observed between the Ba–O and Sr–O distances. Whereas the radius of the fitted sphere and polyhedron volume in the case of Ba are 3.00 Å and 40.2 Å³ on average, the values for Sr are 2.84 Å and 35.4 Å³. This finding clearly illustrates the influence of cation size on the coordination polyhedron. The values of cation eccentricity, sphericity of the oxygen coordination surrounding the cation, and the volume distortion of the polyhedron (a discrepancy from the value expected for a maximum-volume tri-capped trigonal prism) suggest little or no difference between the two cation species. It can be seen that the size of the cavity in kuannersuite-(Ce) corresponds ideally to the average for the calculated Ba positions. Of the other five structures summarized in Table 6, the three with the supposedly pure or almost pure Ba content give larger values, whereas the two where about one-third of the Ba is considered to be replaced by REE or REE + Na show V_p , r_s and $\langle d \rangle$ values lower than in kuannersuite-(Ce). If these values can be considered representative, we can

conclude that the Ba site in kuannersuite-(Ce) hosts only minor quantities (up to 10–20%) of the smaller cations (Sr, REE, or Na).

In a combined substitution of Ba with Na + REE, a preference of the latter two for the *Me*(1) type structural site is observed, followed by a separation of this site into two distinct symmetry-independent sites (Mathew *et al.* 1979). The geometry of the coordination of this site is a tri-capped trigonal prism formed by nine atoms of oxygen. When the single Ba-occupied coordination in Ba₁₀(PO₄)₆F₂ and Ba₁₀(PO₄)₆Cl₂ is compared to REE- and Na-occupied sites in the other structures, the following can be concluded: both REE and Na are characterized by smaller cation sizes, as illustrated by smaller radii of fitted spheres and smaller volumes of the polyhedra. In the case of REE, the site is characterized by a high regularity (only 3 to 5% volume distortion compared to the largest-volume tri-capped trigonal prism) (Table 7). The coordination is even more regular than in the case of Ba. Where the same type of coordination is considered for Na (coordination number 9), a distinctly lower regularity is observed, characterized by both a higher volume-distortion (7–11%) and a lower sphericity (Table 8). As observed by Rakovan & Hughes (2000) for belowite-(Ce), it is more appropriate to consider Na as being 6- rather than 9-coordinated, because the three capping atoms have significantly greater distances to Na than the closest six. When a bond-valence calculation is performed, their summary contribution is only about 5% of the valence of the site in both belowite and kuannersuite. Indeed, when the coordination characteristics based only on the closest six oxygen atoms are calculated (Table 8), they show much more consistent values for Na-dominated sites, which confirms that the positions of the next three oxygen atoms are not influenced by bonding to Na. As suggested by radii of fitted spheres, the sizes of REE (CN9) and Na (CN6) correspond well, so it must be more the distribution of valence electrons and bonds rather than a difference in size that dictates their mutual ordering and a separation of *Me*(1)-type coordinations into two non-equivalent sites.

The presence of Na, Ba or even Sr in a REE-dominated site increases its size and volume distortion, and decreases its sphericity (Table 7). All this is in accordance with the above quoted observations for the Ba- and Na-dominated coordinations. The REE site in kuannersuite-(Ce), according to these characteristics, seems to be an almost pure REE site. It is closely comparable to the supposedly pure Nd site in Ba₄Nd₃Na₃(PO₄)₆F₂, or to the *REE* site in belowite-(Ce), but it differs significantly from the sites occupied by Ba, or those where a larger degree of replacement of REE by Na is expected (Table 7).

The incorporation of REE or Ba in a Na-dominated site is best monitored if a case of CN9 is considered. A decrease in size, a lowering of volume distortion, and an increase in sphericity can be observed. A lowering

TABLE 5. UNIT-CELL PARAMETERS (Å), INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR KUANNERSUITE-(Ce) AND RELATED STRUCTURES

	Kuannersuite-(Ce)	Ba ₄ Nd ₃ Na ₃ (PO ₄) ₆ F ₂ ¹	Belowite-(Ce) ²
<i>a</i>	9.9097(6)	9.786(2)	9.659(2)
<i>c</i>	7.4026(6)	7.281(1)	7.182(2)
Vol.:	629.42(7)	603.8(3)	580.2(3)
<i>Me</i> (2) - O2	2.659(3)	2.651(7)	2.532(4)
<i>Me</i> (2) - O3	2.676(3)	2.632(6)	2.525(3)
<i>Me</i> (2) - O3	3.057(3)	2.923(7)	2.805(3)
<i>Me</i> (2) - O4	2.924(3)	2.933(7)	3.027(3)
<i>Me</i> (2) - O1	3.057(3)	3.035(6)	2.802(3)
<i>Me</i> (2) - O4	2.611(3)	2.576(6)	2.491(3)
<i>Me</i> (2) - O4	2.749(3)	2.713(7)	2.585(3)
<i>Me</i> (2) - F1	2.867(5)	2.786(22)	2.411(1)
<i>Me</i> (2) - F2	3.1609(3)	2.934(4)	3.0227(4)
Mean:	2.862	2.798	2.689
<i>REE</i> - O1[x3]	2.499(3)	2.460(7)	2.483(3)
<i>REE</i> - O2[x3]	2.587(3)	2.533(6)	2.560(3)
<i>REE</i> - O3[x3]	2.586(3)	2.574(6)	2.638(4)
Mean:	2.557	2.522	2.560
Na - O1[x3]	2.659(4)	2.566(8)	2.537(3)
Na - O2[x3]	2.461(4)	2.482(7)	2.451(3)
Na - O4[x3]	3.402(4)	3.327(8)	3.207(4)
Mean:	2.841	2.792	2.732
+	2.560	2.524	2.494
P - O1	1.536(3)	1.533(8)	1.536(3)
P - O2	1.532(3)	1.528(5)	1.531(3)
P - O3	1.551(3)	1.543(7)	1.557(3)
P - O4	1.528(3)	1.529(7)	1.515(3)
Mean:	1.537	1.533	1.535
O1 - P - O2	110.6(2)	110.7(4)	111.1(2)
O1 - P - O3	112.5(2)	113.5(4)	111.6(2)
O1 - P - O4	108.3(2)	108.4(4)	108.9(2)
O2 - P - O3	105.3(2)	104.5(3)	106.0(2)
O2 - P - O4	112.3(2)	112.7(4)	112.5(2)
O3 - P - O4	107.5(2)	107.1(4)	106.7(2)
Mean:	109.4	109.5	109.5

(+) Mean calculated without the <Na–O4> distance.

In the first two columns, *Me*(2) represents Ba; it represents Sr in the last.

¹ Mathew *et al.* (1979). ² Rakovan & Hughes (2000).

of size in the case of Ba-for-Na substitution might seem strange if a pure Ba site has a significantly larger size (Table 6). However, in a mixed site, the lowering of size from a pure Na site, if a CN9 is considered, is a consequence of the onset of bonding to the last three oxygen atoms, which, as a consequence, approach the central atom. If only a case of CN6 is considered, then no irregularities are observed, and a constant increase in size is observed from the pure Na site in $\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2$

to the mixed Ba–Na site in $\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$ to the pure Ba-site in $\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2$ and $\text{Ba}_{10}(\text{PO}_4)_6\text{Cl}_2$ (Tables 6, 8).

The coordination of the anions

The two monovalent-anion sites in kuannersuite-(Ce) are octahedrally coordinated by Ba atoms. Fluorine fully occupies one of these sites, whereas the

TABLE 6. CHARACTERISTICS OF THE COORDINATION OF Ba IN KUANNERSUITE-(Ce) AND RELATED COORDINATIONS IN OTHER Ba-DOMINANT APATITE-GROUP PHASES AND BELOVITE

Structure	Supposed average content at site	<d>	r_s	V_p	Δ/r_s	SPH	v
Kuannersuite-(Ce)	Ba	2.98	2.98	39.73	0.139	0.897	0.267
$\text{Ba}_{10}(\text{PO}_4)_6\text{Cl}_2^1$	Ba	3.08	3.06	42.26	0.131	0.886	0.279
$\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2^2$	Ba	3.04	3.01	41.65	0.111	0.894	0.255
$\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$, M1 ²	2/3Ba+1/3La	2.95	2.93	37.28	0.088	0.896	0.277
$\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$, M2 ²	90%Ba+10%Na	3.04	3.06	41.10	0.134	0.931	0.301
$\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2^2$	2/3Ba+1/6Nd+1/6Na	2.95	2.93	37.86	0.125	0.897	0.269
Belovite-(Ce) ³	85%Sr+6%Ce+5%Na+2%Ba+2%Nd	2.87	2.84	35.48	0.135	0.877	0.244
Belovite-(Ce) ⁴	93%Sr+3%Ce+2%Ca+2%□	2.87	2.84	35.53	0.132	0.875	0.246
Belovite-(La) ⁵	92%Sr+4%Ba+2%Ca+2%□	2.87	2.85	35.16	0.102	0.867	0.260

¹ Hata *et al.* (1979). ² Mathew *et al.* (1979). ³ Rakovan & Hughes (2000). ⁴ Nadezhina *et al.* (1987).

⁵ Kabalov *et al.* (1997). Only the closest nine atoms of oxygen are included in the calculations.

TABLE 7. CHARACTERISTICS OF THE COORDINATION OF THE REE IN KUANNERSUITE-(Ce) AND RELATED COORDINATIONS IN OTHER Ba-DOMINANT APATITE-GROUP PHASES AND BELOVITE

Structure	Supposed average content at site	<d>	r_s	V_p	Δ/r_s	SPH	v
Kuannersuite-(Ce)	59%Ce+26%Nd+15%La	2.56	2.56	33.22	0.025	0.992	0.028
$\text{Ba}_{10}(\text{PO}_4)_6\text{Cl}_2^1$	Ba	2.82	2.82	43.59	0.041	0.955	0.052
$\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2^2$	Ba	2.83	2.83	43.38	0.016	0.943	0.061
$\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$, M3 ²	50%La+50%Na	2.66	2.66	36.92	0.067	0.955	0.047
$\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2^2$	Nd	2.52	2.52	31.86	0.022	0.986	0.028
Belovite-(Ce) ³	38%Ce+31%La+22%Sr+9%Ba	2.56	2.56	33.10	0.025	0.979	0.035
Belovite-(Ce) ⁴	73%Ce+18%Sr+9%□	2.59	2.59	34.28	0.023	0.972	0.039
Belovite-(La) ⁵	79%La+20%Na+1%□	2.66	2.66	36.54	0.015	0.965	0.049

¹ Hata *et al.* (1979). ² Mathew *et al.* (1979). ³ Rakovan & Hughes (2000). ⁴ Nadezhina *et al.* (1987).

⁵ Kabalov *et al.* (1997). Only the closest nine atoms of oxygen are included in the calculations.

TABLE 8. CHARACTERISTICS OF THE COORDINATION OF Na IN KUANNERSUITE-(Ce) AND RELATED COORDINATIONS IN OTHER Ba-DOMINANT APATITE-GROUP PHASES AND BELOVITE

Structure	Supposed average content at site	<d>	r_s	V_p	Δ/r_s	SPH	v
Kuannersuite-(Ce)	Na	2.84	2.83	41.46	0.040	0.847	0.111
$\text{Ba}_{10}(\text{PO}_4)_6\text{Cl}_2^1$	Ba	2.82	2.82	43.59	0.041	0.955	0.052
$\text{Ba}_{10}(\text{PO}_4)_6\text{F}_2^2$	Ba	2.83	2.83	43.38	0.016	0.943	0.061
$\text{Ba}_6\text{La}_2\text{Na}_2(\text{PO}_4)_6\text{F}_2$, M4 ²	64.5%Ba+35.5%Na	2.71	2.71	37.70	0.005	0.920	0.071
$\text{Ba}_4\text{Nd}_3\text{Na}_3(\text{PO}_4)_6\text{F}_2^2$	Na	2.79	2.78	39.52	0.056	0.855	0.104
Belovite-(Ce) ³	84%Na+12%Nd+4%□	2.73	2.73	37.57	0.043	0.868	0.094
Belovite-(Ce) ⁴	50%Na+25%Ca+20%Ce+5%□	2.72	2.72	37.70	0.019	0.883	0.086
Belovite-(La) ⁵	78%Na+22%La	2.72	2.71	37.72	0.071	0.900	0.077
<i>Kuannersuite-(Ce)</i>	<i>Na</i>	<i>2.56</i>	<i>2.56</i>	<i>16.83</i>	<i>0.053</i>	<i>1.000</i>	<i>0.247</i>
<i>Ba₁₀(PO₄)₆Cl₂¹</i>	<i>Ba</i>	<i>2.74</i>	<i>2.74</i>	<i>22.59</i>	<i>0.003</i>	<i>1.000</i>	<i>0.174</i>
<i>Ba₁₀(PO₄)₆F₂²</i>	<i>Ba</i>	<i>2.72</i>	<i>2.72</i>	<i>21.97</i>	<i>0.004</i>	<i>1.000</i>	<i>0.181</i>
<i>Ba₆La₂Na₂(PO₄)₆F₂, M4²</i>	<i>64.5%Ba+35.5%Na</i>	<i>2.57</i>	<i>2.57</i>	<i>16.55</i>	<i>0.027</i>	<i>1.000</i>	<i>0.265</i>
<i>Ba₄Nd₃Na₃(PO₄)₆F₂²</i>	<i>Na</i>	<i>2.52</i>	<i>2.52</i>	<i>16.10</i>	<i>0.023</i>	<i>1.000</i>	<i>0.249</i>
<i>Belovite-(Ce)³</i>	<i>84%Na+12%Nd+4%□</i>	<i>2.49</i>	<i>2.49</i>	<i>16.70</i>	<i>0.024</i>	<i>1.000</i>	<i>0.192</i>
<i>Belovite-(Ce)⁴</i>	<i>50%Na+25%Ca+20%Ce+5%□</i>	<i>2.51</i>	<i>2.51</i>	<i>17.27</i>	<i>0.036</i>	<i>1.000</i>	<i>0.183</i>
<i>Belovite-(La)⁵</i>	<i>78%Na+22%La</i>	<i>2.53</i>	<i>2.53</i>	<i>18.43</i>	<i>0.034</i>	<i>1.000</i>	<i>0.150</i>

¹ Hata *et al.* (1979). ² Mathew *et al.* (1979). ³ Rakovan & Hughes (2000). ⁴ Nadezhina *et al.* (1987).

⁵ Kabalov *et al.* (1997). Only the closest nine and six (in italics) atoms of oxygen are included in the calculations.

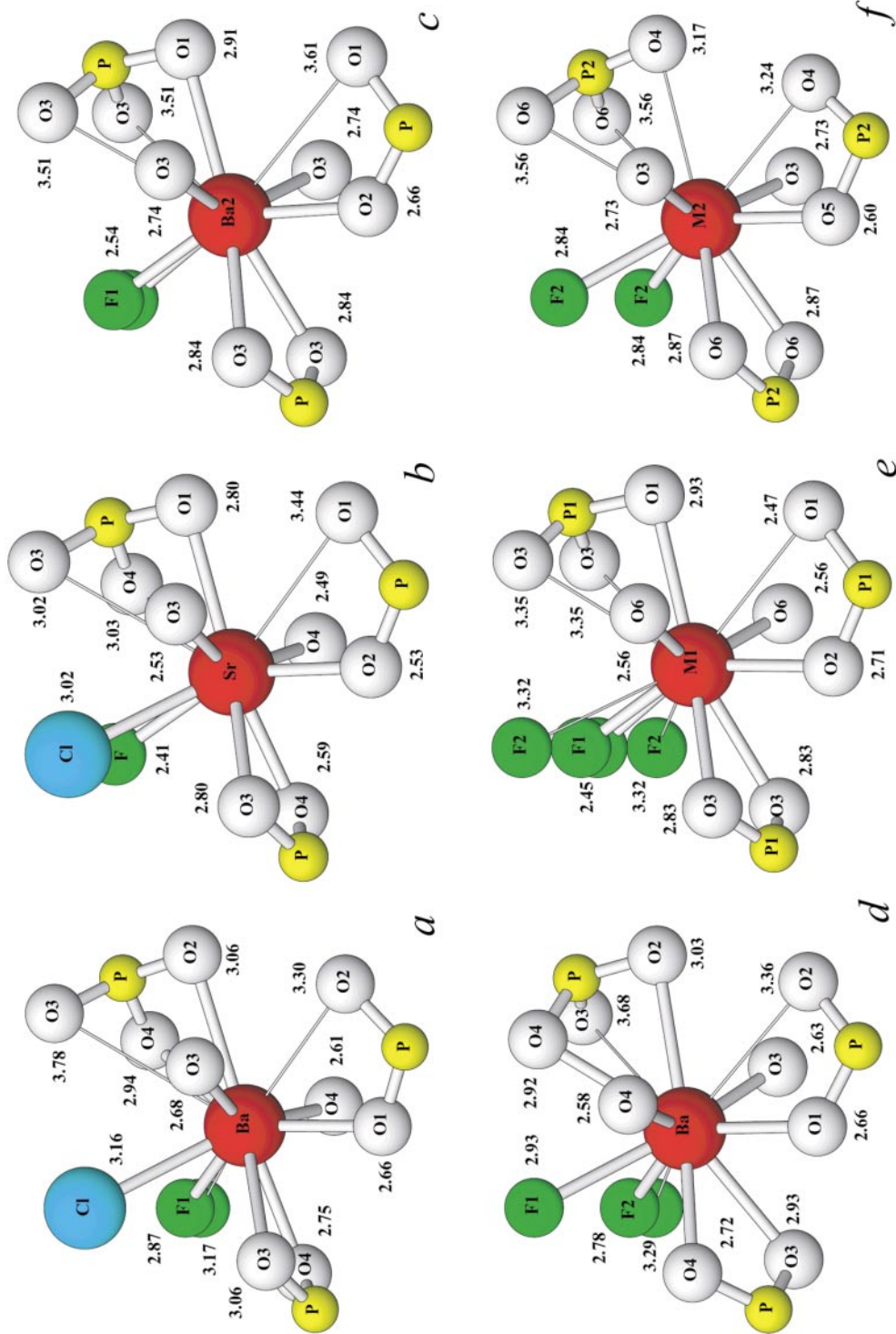


FIG. 3. Comparison of the Ba and Sr coordination for (a) kuannersuite-(Ce), (b) belovite-(Ce) (Rakovan & Hughes 2000), (c) $Ba_4Nd_3Na_3(PO_3)_6F_2$, (d) $Ba_4Nd_3Na_3(PO_3)_6F_2$, (e) and (f) $Ba_6La_2Na_2(PO_4)_6F_2$ (all four: Mathew *et al.* 1979).

proportion of Cl slightly exceeds that of F in the other. The Cl atoms are situated at the same level (along the *c* axis) as the REE atoms (Fig. 1). Such an ordering is evidently connected to the characteristics of trigonal-prismatic cation coordinations (REE and Na). The capping atoms of these coordination polyhedra are O3 and O4 atoms, forming the subvertical edge of a [PO₄] polyhedron (Fig. 1). The two oxygen sites are symmetry-equivalent, and the edge they form is parallel to the *c* axis in a higher-symmetry apatite structure, which has mirror planes perpendicular to the *c* axis. In the kuannersuite structure, however, this symmetry is lost, and the [PO₄] polyhedron edge is only subparallel to the *c* axis. The O3 atoms, which are the capping atoms of the REE coordination polyhedron, are shifted closer to the central atom and at the same time farther away from the positions of Cl atoms (Figs. 1, 2). This shift is achieved by an inclination of the O3–O4 edges of [PO₄] polyhedra relative to the *c* axis. As a consequence, O4 atoms, which cap the trigonal-prismatic coordination polyhedra occupied by Na, have moved away from the central atoms of these coordination polyhedra and closer to the positions of F atoms. The distances between the adjacent Ba-triangles along the *c* axis are also different along the two levels. Those at the level of REE atoms are 3.95 Å long, and those at the level of Na atoms, only 3.45 Å. The changes in the position of O3 and O4, compared to a higher-symmetry apatite-type structure, favors the ordering of the larger octahedrally coordinated anion at the level of REE atoms. The expected Ba–F and Ba–Cl bond lengths with a valence of 1/6, calculated using the bond-valence formula of Brown & Altermatt (1985) and parameters of Brese & O’Keeffe (1991), are 2.85 and 3.35 Å, respectively. The distance of Ba atoms from the center of an F-occupied coordination polyhedra is 3.01 Å, which is much longer than the ideal Ba–F distance. This site is statistically split, bringing the F atom at the appropriate distance of 2.87 Å from the Ba atoms (Table 5, Fig. 3). The F atoms probably oscillate between the two positions on the two opposite sides of the center of coordination. The distance of Ba atoms to the center of the other type of polyhedron, occupied statistically by Cl and F atoms, is 3.16 Å, which corresponds well with the average value (3.15 Å) obtained from the ideal distances to Cl and F summed with weights proportional to their occupancies.

STRUCTURAL COMPARISON OF KUANNERSUITE-(Ce) AND RELATED PHOSPHATES

The main difference between kuannersuite-(Ce) and belovite, apart from the main large cation, is the coordination of F. In belovite, as in the fluorapatite-type structure, F is found in a near-planar coordination with three cations, and thus lies close to the plane of Sr atoms, and not close to the centers of octahedrally coordinated voids. The F coordination is not perfectly planar; in such a case, the Sr–F distance would be too short for the rela-

tively large Sr atom. In belovite-(Ce) (Rakovan & Hughes 2000), the Sr–F distance is 2.41 Å, *i.e.*, very close to 2.43 Å, which is expected for a bond with a bond valence of 1/3. As observed by Rakovan & Hughes (2000), even small amounts of Cl substituting for F in belovite occupy the centers of octahedrally coordinated voids in this case, at the same level as REE atoms. It is interesting that in Ba₁₀(PO₄)₆F₂, F atoms occupy the same (near-) planar triangular coordination as in fluorapatite and belovite (Mathew *et al.* 1979). However, the coupled substitution of REE and Na for Ba changes this preference, and in Ba₆La₂Na₂(PO₄)₆F₂, one of the F coordinations is close to planar-trigonal, and the other to octahedral, whereas in Ba₄Nd₃Na₃(PO₄)₆F₂, the coordination of both F sites is equivalent to that in kuannersuite-(Ce), *i.e.*, octahedral. In terms of cation stoichiometry, kuannersuite-(Ce) is equivalent to Ba₆La₂Na₂(PO₄)₆F₂, with a Ba:REE:Na proportion of 3:1:1. If the findings of Mathew *et al.* (1979) for this structure are correct, then it is a combined effect of the relative sizes of the mono-, di- and trivalent cations and the size of the anion that determines the ultimate symmetry of the apatite-type structure. In the case of Ba₆La₂Na₂(PO₄)₆F₂, the extent of REE + Na substituting for Ba is not enough to achieve the *P*³ symmetry and the structural features found in kuannersuite-(Ce). A higher proportion of REE + Na, as in Ba₄Nd₃Na₃(PO₄)₆F₂, results in a structure of the kuannersuite type even with F as the only monovalent anion. However, if a significant proportion of Cl substitutes for F [as in kuannersuite-(Ce)], this type of structure is stabilized even at the 3:1:1 proportion of major cations. The data for the Ba₆La₂Na₂(PO₄)₆F₂ structure are not as reliable as for the other aforementioned phosphates, because it was refined to a relatively high *R*-factor with unusually high atom-displacement factors, and the possibility of a twinned *P*³ structure simulating the *P*⁶ symmetry was not considered (Mathew *et al.* 1979). Therefore the concluding part of the above discussion should be considered a hypothesis rather than conclusion.

ACKNOWLEDGEMENTS

We thank the referees, A. Chakhmouradian and J. Rakovan, as well as Associate Editor A.E. Lalonde for their highly valuable suggestions. Drs. J.A. Mandarino and R.F. Martin are also thanked for useful comments. Dr. J. Bailey has significantly improved the English of the manuscript.

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Received April 3, 2003, revised manuscript accepted January 25, 2004.