

CARLGIESECKEITE-(Nd), $\text{NaNdCa}_3(\text{PO}_4)_3\text{F}$, A NEW BELOVITE-GROUP MINERAL SPECIES FROM THE ILÍMAUSSAQ ALKALINE COMPLEX, SOUTH GREENLAND

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ABSTRACT

Carlgieseckeite-(Nd), ideally $\text{NaNdCa}_3(\text{PO}_4)_3\text{F}$, a new mineral species of the belovite group of the apatite supergroup, was found at the Kuannersuit Plateau, Ilímaussaq alkaline complex, South Greenland. It is associated with albite, analcime and fluorapatite in cavities of an albite vein cross-cutting augite syenite. Carlgieseckeite-(Nd) forms hexagonal tabular crystals up to $0.25 \times 1 \times 1.3$ mm, and their parallel intergrowth up to 0.7×1.3 mm is found epitactically overgrown on prismatic crystals of fluorapatite. A phase with the idealized formula $\text{Na}_{1.5}\text{Nd}_{1.5}\text{Ca}_2(\text{PO}_4)_3\text{F}$ epitactically overgrows some crystals of carlgieseckeite-(Nd). Carlgieseckeite-(Nd) is transparent and shows a distinct color-change effect, from almost colorless with a greenish hue in daylight to pink in yellow electric light. The luster is vitreous. The Mohs hardness is *ca.* 5. The mineral is brittle with no observed cleavage and an uneven fracture. The calculated density is 3.91 g/cm^3 . Carlgieseckeite-(Nd) is optically negative, uniaxial [$\omega = 1.655(3)$, $\varepsilon = 1.632(2)$] or shows anomalous biaxiality [$\alpha 1.632(2)$, $\beta 1.654(3)$, $\gamma 1.656(3)$, $2V(\text{meas.}) 15(5)^\circ$]. The average chemical composition (electron-microprobe data) is: Na_2O 5.68, CaO 18.53, SrO 7.55, BaO 0.14, La_2O_3 1.32, Ce_2O_3 10.60, Pr_2O_3 2.62, Nd_2O_3 15.08, Sm_2O_3 2.89, Gd_2O_3 0.52, SiO_2 0.56, P_2O_5 32.72, F 2.80, Cl 0.06, $-\text{O}=(\text{FCl})_2$ -1.19 , total 99.88 wt.%. The empirical formula calculated on the basis of 13 O + F + Cl *apfu* is: $\text{Na}_{1.17}\text{Ca}_{2.11}\text{Sr}_{0.46}\text{Ba}_{0.01}\text{La}_{0.05}\text{Ce}_{0.41}\text{Pr}_{0.10}\text{Nd}_{0.57}\text{Sm}_{0.11}\text{Gd}_{0.02}\text{Si}_{0.06}\text{P}_{2.94}\text{O}_{12.05}\text{F}_{0.94}\text{Cl}_{0.01}$. Carlgieseckeite-(Nd) is trigonal, space group $P\bar{3}$, a 9.4553(1), c 6.9825(1) Å, V 540.62(1) Å³, $Z = 2$. The crystal structure was refined from X-ray-diffraction data (single crystal, $R = 0.0218$). Carlgieseckeite-(Nd) is the isostructural Ca- and Nd-dominant analogue of belovite-(Ce) and belovite-(La). The strongest lines of the powder X-ray pattern [d in Å (hkl)] are: 7.02(22)(001), 5.33(18)(101), 3.923(27)(111), 3.463(23)(002), 3.095(19)(210), 2.815(100)(211,112), 2.727(42)(300). The mineral is named in honor of Carl Ludwig Giesecke (1761–1833), a mineralogist and polar explorer, the pioneer researcher of the mineralogy of Greenland. The Levinson suffix modifier -(Nd) is appropriate to express the dominance of Nd over other REE in the mineral. The holotype material is deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow.

Keywords: carlgieseckeite-(Nd), new mineral species, rare-earth phosphate, belovite group, apatite supergroup, crystal structure, alkaline formation, Ilímaussaq, Greenland.

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INTRODUCTION

A new belovite-group fluorophosphate of calcium, sodium and rare-earth elements, *carlgieseckeite*-(Nd), has been found in the Ilímaussaq alkaline complex, South Greenland, Denmark. The new mineral species is named in honor and memory of Carl (or Karl, in original spelling) Ludwig Giesecke (1761–1833), a mineralogist and polar explorer who was the pioneer researcher in the mineralogy of Greenland. He carried out the first systematic studies at different mineral localities during his long expedition in Greenland from 1806 to 1813. In particular, he worked at Ilímaussaq in 1806, and collected abundant, scientifically valuable specimens from which arfvedsonite, eudialyte and sodalite were later described as new mineral species (Petersen & Secher 1993; see also Petersen & Johnsen 2005). The Levinson suffix -(Nd) is appropriate given the dominance of neodymium among the rare-earth elements in the mineral (Levinson 1966). The name of the new species is spelled карлгизекит-(Nd) in Cyrillic. Both the new mineral and its name have been approved by the IMA CNMNC (IMA 2010–036).

We did not propose the name “gieseckeite-(Nd)” because the name “gieseckeite” has been in use for almost two hundred years. It was introduced by J. Sowerby in 1817 for a supposed new mineral species from the Igaliko Fjord, Greenland (Stromeyer 1819). Blum (1852) showed that “gieseckeite” of Sowerby is

not an individual mineral but a pseudomorph after nepheline, mainly consisting of muscovite. Thus, Giesecke’s name disappeared from the nomenclature of valid mineral species in 1852 and returns now. The holotype material of *carlgieseckeite*-(Nd) is deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow, with registration no. 3996/1.

Our purpose in this paper is to describe the physical and chemical attributes of *carlgieseckeite*-(Nd), including its crystal structure.

BACKGROUND INFORMATION

The belovite group was recently defined as a part of the apatite supergroup (Pasero *et al.* 2010). The general crystal-chemical formula of apatite-supergroup compounds is $^{IX}M_1^{VII}M_2^{IV}M_3^{IV}TO_4)_3X$ ($Z = 2$; the Roman-numeral superscripts indicate the ideal coordination numbers), in which species-defining constituents known in minerals are: $M = Ca^{2+}, Pb^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Na^+, REE^{3+}, Bi^{3+}$; $T = P^{5+}, As^{5+}, V^{5+}, Si^{4+}, S^{6+}, B^{3+}$; $X = F^-, Cl^-, (OH)^-$. The archetype structure of apatite is hexagonal with space group $P6_3/m$ (Hughes & Rakovan 2002). The belovite group includes hexagonal and trigonal phosphates with the $M1$ site split into the $M1$ and $M1'$ sites containing different prevailing (species-defining) cations. This group includes fluorcaphite $SrCaCa_3(PO_4)_3F$, fluorstrophite (formerly “strontium-apatite”) $SrCaSr_3(PO_4)_3F$,

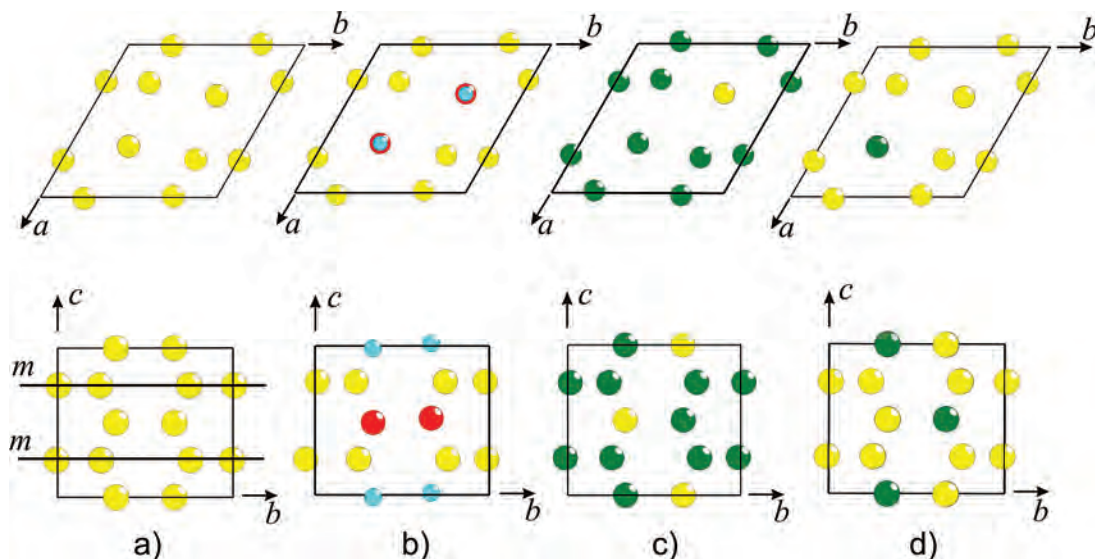


FIG. 1. Idealized schemes of the cation arrangements in: (a) fluorapatite ($P6_3/m$, after Hughes & Rakovan 2002); (b) *carlgieseckeite*-(Nd) [$P\bar{3}$, this work; belovite-group phases and kuannersuite-(Ce) have the same cation arrangement but with Sr and Ba, respectively, instead of Ca]; (c) fluorstrophite ($P6_3$, after Klevtsova 1964); (d) fluorcaphite ($P6_3$, after Rastsvetaeva & Khomyakov 1996a). The Ca-dominant sites: yellow circles, the Sr-dominant sites: green, the REE-dominant sites: red, the Na-dominant site: blue; m refers to mirror planes in the fluorapatite structure. The upper row shows $a - b$ projections, and the lower row, $b - c$ projections.

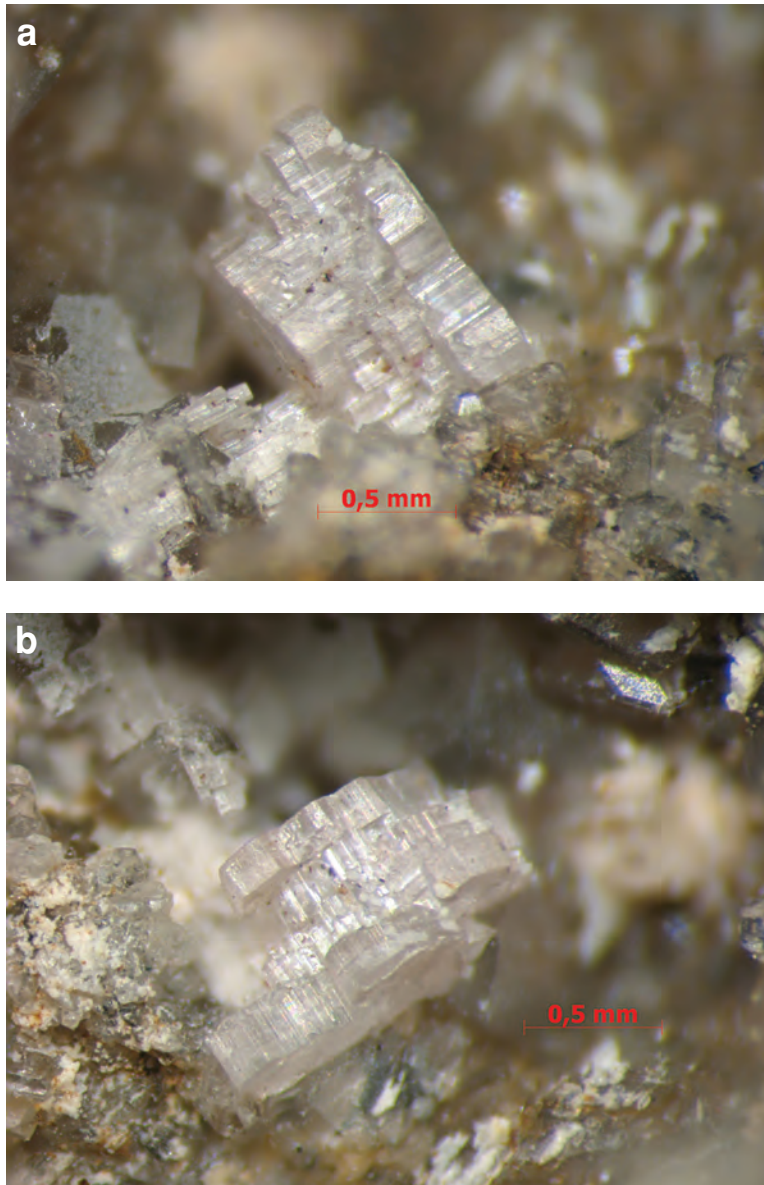


FIG. 2. Parallel intergrowth (1.25 mm; *a* and *b*: different sides) of tabular carlgieseckeite-(Nd) crystals epitaxially overgrowing a crystal of Sr-bearing fluorapatite. The matrix consists of albite crystals. Photo: I.V. Pekov and A.V. Kasatkin.

deloneite $(\text{Na}_{0.5}\text{REE}_{0.25}\text{Ca}_{0.25})(\text{Ca}_{0.75}\text{REE}_{0.25})\text{Sr}_{1.5}(\text{CaNa}_{0.25}\text{REE}_{0.25})(\text{PO}_4)_3\text{F}_{0.5}(\text{OH})_{0.5}$, belovite-(Ce) $\text{NaCeSr}_3(\text{PO}_4)_3\text{F}$, belovite-(La) $\text{NaLaSr}_3(\text{PO}_4)_3\text{F}$, kuannersuite-(Ce) $\text{NaCeBa}_3(\text{PO}_4)_3\text{F}_{0.5}\text{Cl}_{0.5}$ (see Pasero *et al.* 2010, and references therein) and the newly discovered carlgieseckeite-(Nd) $\text{NaNdCa}_3(\text{PO}_4)_3\text{F}$.

Different arrangements of the $M1$ and $M1'$ cations (Fig. 1) cause different symmetries in the minerals of the belovite group. The structure type of belovite *sensu stricto* is characterized by strong predominance of divalent cations at the $M2$ site [$M^{2+} = \text{Sr}$ in belovite, Ba in kuannersuite-(Ce), Ca in carlgieseckeite-(Nd)]

and replacement of $2M^{2+}$ by $Na^+ + REE^{3+}$ at the $M1$ and $M1'$ sites. The belovite-type pattern of order of Na and REE (Fig. 1b) at two independent sites $M1$ and $M1'$ lowers the symmetry from $P6_3/m$ to $P\bar{3}$ (Nadezhina *et al.* 1987, Pekov *et al.* 1995, Kabalov *et al.* 1997, Rakovan & Hughes 2000, Friis *et al.* 2004, this work). Unlike these, minerals of the fluoraphite–fluorstrophite series, containing divalent cations (Ca, Sr) prevalent at all M sites, show a different pattern of cation order at the $M1$ and $M1'$ sites (Figs. 1c, d); they crystallize in space group $P6_3$ (Klevtsova 1964, Rastsvetaeva & Khomyakov 1996a, Chakhmouradian *et al.* 2005). Deloneite, with both the $M1$ and $M2$ sites split, has the lowest symmetry, $P\bar{3}$ (Rastsvetaeva & Khomyakov 1996b).

Carlgieseckeite-(Nd) is the isostructural Nd- and Ca-dominant analogue of belovite-(Ce) and belovite-(La). It is the first mineral of the apatite supergroup with Nd as a species-defining element. A synthetic chemical analogue of ideal carlgieseckeite-(Nd), $NaNdCa_3(PO_4)_3F$, was reported by Mayer *et al.* (1974).

OCCURRENCE AND GENERAL APPEARANCE

Carlgieseckeite-(Nd) was found on the Kuannersuit (formerly Kvanefjeld) Plateau in the northern part of the Ilmaussaq intrusion. This area mainly consists of sodalite nepheline syenites, aegirine–arfvedsonite nepheline syenites and augite syenites. The latter two are crosscut by series of albite veins known as a locality of tugtupite (Sørensen *et al.* 1971). Aegirine, analcime, pectolite, sphalerite and galena are subordinate minerals of these veins. Diverse products of rare-element mineralization also occur here, as well as minerals with species-defining beryllium (chkalovite, tugtupite, beryllite, lovdarite, nabesite), lithium (neptunite, polyolithionite), and niobium (pyrochlore). Some other late hydrothermal minerals were found in the cavities, namely opal, gonnardite, gmelinite-Na and apatite-supergroup members represented by fluorapatite and two endemic belovite-group minerals: kuannersuite-(Ce) (Friis *et al.* 2004) and carlgieseckeite-(Nd).

Carlgieseckeite-(Nd) was found by one of the authors (T.A.H.) in small cavities in veins of white sugar-like albite. The walls of these cavities are incrustated with colorless albite and analcime crystals. Carlgieseckeite-(Nd) forms hexagonal tabular (flattened on {001}) crystals up to $0.25 \times 1 \times 1.3$ mm in size, and their parallel intergrowths up to 0.7×1.3 mm epitaxially overgrowing prismatic crystals of Sr-bearing fluorapatite (Figs. 2, 3; column 3 in Table 1). Thin lamellae (up to $15 \mu\text{m}$ thick) of a phase with the idealized formula $Na_{1.5}Nd_{1.5}Ca_2(PO_4)_3F$ are found epitaxially overgrowing some crystals of carlgieseckeite-(Nd) (Fig. 4; column 2 in Table 1).

The main crystal form of carlgieseckeite-(Nd) is the pinacoid {001}. Faces of the prism zone, { $hk0$ }, are probably {100}, the most common for apatite-like

minerals; these faces are striated along [001] (Fig. 2). Microtwinning on {001} was observed under the microscope in polarized light and confirmed during structural studies. This twinning is not reflected in the morphology because carlgieseckeite-(Nd) crystals exhibit only pinacoidal and prism faces.

PHYSICAL PROPERTIES AND OPTICAL DATA

Carlgieseckeite-(Nd) is transparent and shows a distinct color-change effect depending on wavelength of light, which is very typical for Nd compounds: the mineral is almost colorless with a faint greenish hue in daylight and pink in yellow electric light. The streak is white. The luster is vitreous on crystal faces and between vitreous and greasy on broken surfaces. Carlgieseckeite-(Nd) is non-fluorescent in ultraviolet light and cathode rays. Its Mohs hardness is ca 5. The mineral is brittle, with no observed cleavage and an uneven fracture. Density could not be measured owing to the absence of heavy liquids of necessary density and an insufficient amount of pure material. The calculated density is 3.91 g/cm^3 .

Carlgieseckeite-(Nd) is optically uniaxial or biaxial negative. The indices of refraction of uniaxial crystals are: $\omega = 1.655(3)$, $\epsilon = 1.632(2)$. Some individuals show anomalous biaxiality that is typical for apatite-group minerals (Deer *et al.* 1992). Data for the sample with maximum birefringence are: $\alpha = 1.632(2)$, $\beta = 1.654(3)$, $\gamma = 1.656(3)$, $2V(\text{meas.}) = 15(5)^\circ$, $2V(\text{calc.}) = 33^\circ$. Carlgieseckeite-(Nd) is colorless and nonpleochroic in thin section.

CHEMICAL COMPOSITION

The chemical composition of carlgieseckeite-(Nd) was determined by electron microprobe, wavelength-dispersion mode, with a Camebax SX 100 instrument, operating at a voltage of 20 kV and a beam current of 20 nA. We employed an electron beam $3 \mu\text{m}$ in diameter. The following standards were used: albite (Na), fluorapatite (Ca), $SrSO_4$ (Sr), $BaSO_4$ (Ba), $LaPO_4$ (La, P), $CePO_4$ (Ce), $PrPO_4$ (Ce), $NdPO_4$ (Nd), $SmPO_4$ (Sm), $GdPO_4$ (Gd), diopside (Si), MgF_2 (F) and vanadinite (Cl). The contents of other elements with atomic numbers higher than O were below detection limits of the electron microprobe employed. The accuracy of the Na measurement was confirmed using energy-dispersion spectrometry operating at low beam-current: 1 nA. Neither H_2O nor CO_2 were determined because of the scarcity of material. The empirical formula (see below) shows the absence or very minor content of H_2O .

The chemical composition of carlgieseckeite-(Nd) is given in Table 1, column 1. The empirical formula calculated on the basis of 13 anions O + F + Cl is: $Na_{1.17}Ca_{2.11}Sr_{0.46}Ba_{0.01}La_{0.05}Ce_{0.41}Pr_{0.10}Nd_{0.57}Sm_{0.11}Gd_{0.02}Si_{0.06}P_{2.94}O_{12.05}F_{0.94}Cl_{0.01}$. The idealized, end-member

formula, taking into account the structural data (see below), is $\text{NaNdCa}_3(\text{PO}_4)_3\text{F}$.

The phase epitactically overgrowing carlgieseckeite-(Nd) (Fig. 4) has the simplified formula $\text{Na}_{1.34}(\text{Nd,Ce,Sm,Pr,Gd,La})_{1.72}(\text{Ca}_{1.5}\text{Sr}_{0.5})_{\Sigma 2}(\text{P}_{2.5}\text{Si}_{0.5}\text{O}_4)_3\text{F}$ (column 2 in Table 1) or, ideally, $\text{Na}_{1.5}\text{Nd}_{1.5}\text{Ca}_2(\text{PO}_4)_3\text{F}$. In comparison with carlgieseckeite-(Nd), it is characterized by Si enrichment and greater dominance of Nd over other REE. Cation-substitution schemes in these minerals are discussed below.

The chemical composition of fluorapatite, on which carlgieseckeite-(Nd) forms an epitactic overgrowth, corresponds to the empirical formula $(\text{Ca}_{4.74}\text{Sr}_{0.26}\text{Na}_{0.01})_{\Sigma 5.01}\text{P}_{3.00}\text{O}_{12.02}\text{F}_{0.98}$ (column 3 in Table 1).

TABLE 1. CHEMICAL COMPOSITION OF CARLIESECKEITE-(Nd) AND ASSOCIATED MINERALS

	1	2	3
Na_2O wt.%	5.68 (5.4–6.4)	6.13	0.04
CaO	18.53 (17.8–19.1)	12.14	50.96
SrO	7.55 (6.9–8.0)	7.59	5.20
BaO	0.14 (0.0–0.3)	b.d.l.	b.d.l.
La_2O_3	1.32 (0.6–1.9)	0.90	b.d.l.
Ce_2O_3	10.60 (8.1–12.4)	9.21	b.d.l.
Pr_2O_3	2.62 (2.4–2.9)	2.81	b.d.l.
Nd_2O_3	15.08 (13.6–17.7)	21.50	b.d.l.
Sm_2O_3	2.89 (2.1–3.7)	6.81	b.d.l.
Gd_2O_3	0.52 (0.3–0.7)	1.09	b.d.l.
SiO_2	0.56 (0.4–0.7)	4.51	0.05
P_2O_5	32.72 (31.8–33.2)	26.14	40.89
F	2.80 (2.6–2.9)	2.86	3.59
Cl	0.06 (0.0–0.1)	b.d.l.	b.d.l.
$-\text{O}=(\text{F,Cl})_2$	-1.19	-1.20	-1.51
Total	99.88	100.49	99.22
Na <i>apfu</i>	1.17	1.34	0.01
Ca	2.11	1.47	4.74
Sr	0.46	0.50	0.26
Ba	0.01	-	-
La	0.05	0.04	-
Ce	0.41	0.38	-
Pr	0.10	0.12	-
Nd	0.57	0.87	-
Sm	0.11	0.27	-
Gd	0.02	0.04	-
Si	0.06	0.51	-
P	2.94	2.50	3.00
F	0.94	1.02	0.98
Cl	0.01	-	-
O	12.05	11.98	12.02
$\Sigma(\text{Ca} + \text{Sr} + \text{Ba})$	2.58	1.97	5.00
ΣREE	1.26	1.72	-
$\Sigma(\text{P} + \text{Si})$	3.00	3.01	3.00

Column 1: carlgieseckeite-(Nd) (average result of 10 point analyses, with range given in parentheses); column 2: phase with the idealized formula $\text{Na}_{1.5}\text{Nd}_{1.5}\text{Ca}_2(\text{PO}_4)_3\text{F}$ (single point, representative composition); column 3: fluorapatite (single point, representative composition); b.d.l.: below detection limit.

X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

Powder X-ray diffraction data for carlgieseckeite-(Nd) (Table 2) were obtained with a STOE IPDS II diffractometer equipped with an image-plate detector, using the Gandolfi method (MoK α radiation). The pattern is generally typical of apatite-like compounds; however, the presence of a strong 001 reflection ($d = 7.02 \text{ \AA}$) clearly shows that the mineral cannot have space group $P6_3/m$ or $P6_3$. Parameters of the hexagonal (trigonal) unit-cell calculated from the powder data are: $a 9.451(5)$, $c 6.974(7) \text{ \AA}$, $V 539(1) \text{ \AA}^3$, $Z = 2$.

A single-crystal X-ray study of carlgieseckeite-(Nd) was carried out using an Xcalibur S diffractometer equipped with a CCD detector. The crystallographic characteristics of the mineral, details of the X-ray diffraction study and the structure-refinement parameters are given in Table 3. The crystal structure of carlgieseckeite-(Nd) was solved by direct methods using a twinned crystal and refined in the space group $P\bar{3}$ using the SHELX-97 program package (Sheldrick 2008) to $R = 0.0218$. The twin law $[\bar{1}00 \ 0\bar{1}0 \ 001]$ was applied, and the twin ratio refined to 53:47. The final positional and equivalent isotropic displacement parameters are given in Table 4, anisotropic displacement parameters, in Table 5, and selected interatomic distances, in Table 6. Tables of structure factors are available from the Depository of Unpublished Data on the MAC website [document Carlgieseckeite-(Nd) CM 50_571].

Carlgieseckeite-(Nd) is a representative of the structure type of belovite *sensu stricto* (Figs. 1b and 5). In this structure, large M cations occupy three sites with different coordination numbers: 9-fold polyhedra $M1$ (average distance $\langle M1-O \rangle 2.522 \text{ \AA}$), 6-fold polyhedra $M1'$ (reduced 9-fold polyhedra, $\langle M1'-O \rangle 2.445 \text{ \AA}$) and 7-fold polyhedra $M2$ ($\langle M2-O,F \rangle 2.486 [2.560$ in the case of F1] \AA). The numbers of electrons (e_{ref}) found for these sites are $M1 = 51.66$, $M1' = 11.19$ and $M2 = 26.58$. A calculation of mean atomic number of the M cations by two independent methods gave close values, 28.6 from structural data and 29.5 from electron-microprobe data. Taking into account the cation composition of the mineral, there is no doubt that $M1'$ is occupied only by Na, the REE strongly prevail at the $M1$ site, and the $M2$ site is Ca-dominant. This clearly confirms the formula $\text{NaREECa}_3(\text{PO}_4)_3\text{F}$. A small peak of electron density on the difference-Fourier map (2.03 e/\AA^3) was found at the site F1 typically occupied by a large anion in the structure of the apatite group. It could be formally assigned to Cl with low occupancy-factor ($\sim 6\%$) but, taking into account the very small quantity of Cl recorded in the chemical analysis (Table 1), it is probably (F + Cl) (Table 4, Fig. 5).

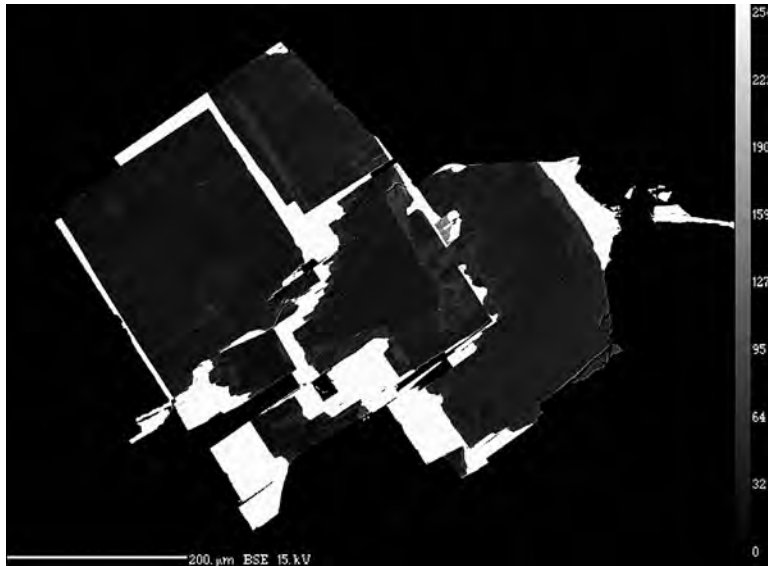


FIG. 3. Epitaxy of carlgieseckeite-(Nd) (white) on Sr-bearing fluorapatite (dark grey). Polished section, back-scattered electron (BSE) image.

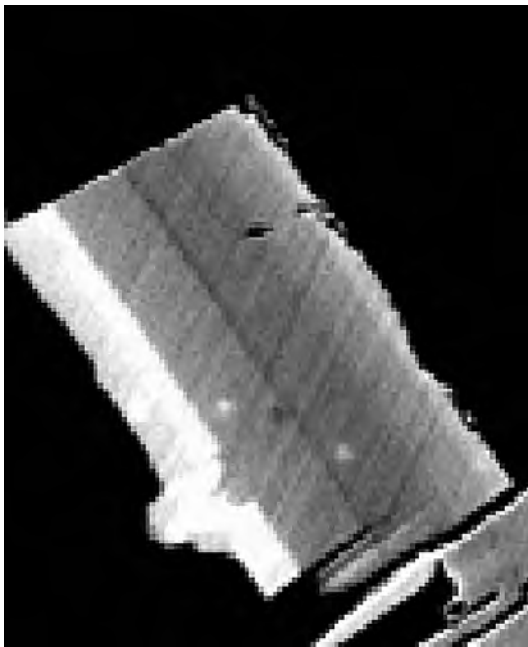


FIG. 4. Epitaxy of the phase with the idealized formula $\text{Na}_{1.5}\text{Nd}_{1.5}\text{Ca}_2(\text{PO}_4)_3\text{F}$ (white) on carlgieseckeite-(Nd) (grey). Field of view is 70 μm . Polished section, BSE image.

DISCUSSION

Carlgieseckeite-(Nd) is characterized by higher contents of both REE (1.26 *apfu*) and Na (1.17 *apfu*) (column 1 in Table 1) and, correspondingly, lower content of M^{2+} ($\text{Ca} + \text{Sr} + \text{Ba} = 2.58$ *apfu*) than typical belovite-like minerals, which show values closer to the stoichiometric proportions, $\text{REE}:\text{Na}:M^{2+} = 1:1:3$ (Pekov *et al.* 1995, 1996, Friis *et al.* 2004, Pekov 2005). The phase $\text{Na}_{1.34}(\text{Nd}, \text{Ce}, \text{Sm}, \text{Pr}, \text{Gd}, \text{La})_{1.72}(\text{Ca}_{1.5}\text{Sr}_{0.5})_{\Sigma 2}(\text{P}_{2.5}\text{Si}_{0.5}\text{O}_4)_3\text{F}$, containing even more REE and Na, and less M^{2+} (column 2 in Table 1) than carlgieseckeite-(Nd), is also considered as an apatite-like compound, on the basis of its stoichiometry and epitaxial relationship with carlgieseckeite-(Nd).

The deviations from ideal, stoichiometric cation proportions in both of these minerals are considered by us as a result of the combination of two substitution schemes: $\text{REE}^{3+} + \text{Si}^{4+} \rightarrow M^{2+} + \text{P}^{5+}$ (this could be named “the britholite scheme”) and, in addition, “the belovite scheme”, $\text{REE}^{3+} + \text{Na}^+ \rightarrow 2M^{2+}$. As the end-member for the latter scheme, the hypothetical compound $\text{Na}_{2.5}\text{REE}^{3+}_{2.5}(\text{PO}_4)_3\text{F}$ could be assumed. According to the empirical formula, proportions of the “end-members” in carlgieseckeite-(Nd) are as follows: (1) the belovite-type (carlgieseckeite proper) $\text{NaREE}^{3+}M^{2+}_3(\text{PO}_4)_3\text{F}$ component: 85 mol.%, (2) the $\text{Na}_{2.5}\text{REE}^{3+}_{2.5}(\text{PO}_4)_3\text{F}$ component: 13 mol.%, and (3) the britholite-type $\text{REE}^{3+}_3M^{2+}_2(\text{SiO}_4)_3\text{F}$ component: 2 mol.%.

No data on natural or synthetic apatite-like phases with composition $\text{Na}_{2.5}\text{REE}^{3+}_{2.5}(\text{PO}_4)_3\text{X}$ were found in the literature or in databases. However, the apatite-type compounds $\text{Na}_2\text{REE}^{3+}_2\text{M}^{2+}(\text{PO}_4)_3\text{F}$ and $\text{Na}_{1.5}\text{REE}^{3+}_{1.5}\text{M}^{2+}_2(\text{PO}_4)_3\text{F}$ with different REE cations and $\text{M}^{2+} = \text{Ca}, \text{Sr}, \text{Ba}$ have been synthesized (Mayer *et al.* 1974, Mathew *et al.* 1979, Mayer & Cohen 1983, Toumi *et al.* 2000). The phase $\text{Na}_{1.34}(\text{Nd}, \text{Ce}, \text{Sm}, \text{Pr}, \text{Gd}, \text{La})_{1.72}(\text{Ca}_{1.5}\text{Sr}_{0.5})_{\Sigma 2}(\text{P}_{2.5}\text{Si}_{0.5}\text{O}_4)_3\text{F}$ (column 2 in Table 1) overgrowing carlgieseckeite-(Nd) could be a natural analogue (with impurities of Si and Sr) of the compound $\text{Na}_{1.5}\text{Nd}_{1.5}\text{Ca}_2(\text{PO}_4)_3\text{F}$ synthesized by Mayer *et al.* (1974). However, it is possible that this mineral, studied only using the electron microprobe, is, in spite of sharp boundaries with carlgieseckeite-(Nd) (Fig. 4), a REE-, Na- and Si-enriched variety of the latter.

It is interesting to note the presence of two closely related minerals with belovite-type structures, kuannersuite-(Ce) $\text{Na}(\text{Ce}, \text{Nd}, \text{La})(\text{Ba}, \text{Sr})_3(\text{PO}_4)_3\text{F}_{0.5}\text{Cl}_{0.5}$ (Friis *et al.* 2004) and carlgieseckeite-(Nd) $\text{Na}(\text{Nd}, \text{Ce}, \text{Sm})(\text{Ca}, \text{Sr})_3(\text{PO}_4)_3\text{F}$, in cavities of the same albite vein. This point is the only known locality, worldwide, for minerals with the belovite structure-type *sensu stricto* containing Ca or Ba as prevailing $\text{M}2$ cations. Strontium-dominant minerals of this structure type, *i.e.*, belovite proper, are not found there, unlike the Lovozero and Khibiny alkaline intrusions at Kola Peninsula, Russia, where they are widespread in many peralkaline assemblages (Khomyakov 1995, Pekov *et al.* 1995, Pekov 2005). This indicates a strong affinity of the belovite structure-type for Sr as the $\text{M}2$ cation. The formation of Ca- or Ba-dominant belovite-type minerals may only be possible in Sr-poor environments. Indeed, the Ilímaussaq complex is depleted in Sr (mean content: 0.01 wt.%; Bailey *et al.* 2001) in comparison

with Lovozero (0.061%: Gerasimovsky *et al.* 1966) and, especially, Khibiny (0.145%: Kukhareno & Il'insky 1984). Strontium minerals are very rare at Ilímaussaq (Sørensen 2001).

Kuannersuite-(Ce) and carlgieseckeite-(Nd) (with the empirical formulae $\text{Na}_{1.09}\text{K}_{0.02}\text{Sr}_{0.08}\text{Ba}_{2.79}\text{La}_{0.12}\text{Ce}_{0.50}\text{Pr}_{0.01}\text{Nd}_{0.22}\text{Sm}_{0.03}\text{Th}_{0.01}\text{Si}_{0.08}\text{P}_{2.99}\text{O}_{11.84}\text{F}_{0.86}\text{Cl}_{0.30}$ and $\text{Na}_{1.17}\text{Ca}_{2.11}\text{Sr}_{0.46}\text{Ba}_{0.01}\text{La}_{0.05}\text{Ce}_{0.41}\text{Pr}_{0.10}\text{Nd}_{0.57}\text{Sm}_{0.11}\text{Gd}_{0.02}\text{Si}_{0.06}\text{P}_{2.94}\text{O}_{12.05}\text{F}_{0.94}\text{Cl}_{0.01}$, respectively) strongly differ from one another in proportions of the individual REE: the former is relatively enriched in Ce^{3+} and La^{3+} , the lanthanides with the largest ionic radii. This seems to be related to the relative ionic radii of the major M cation: Ba^{2+} is significantly larger than Ca^{2+} and increases the unit-cell volume, which favors entry of REE^{3+} with larger atomic radii in kuannersuite in comparison with carlgieseckeite. The same situation has been observed in carbonates of the ancylite – calcioancylite series $[\text{Sr}_{2-x}\text{REE}_x(\text{CO}_3)_2(\text{OH})_x \cdot n\text{H}_2\text{O} - \text{Ca}_{2-x}\text{REE}_x(\text{CO}_3)_2(\text{OH})_x \cdot n\text{H}_2\text{O}]$, including their complex crystals containing zones of ancylite-(Ce) and calcioancylite-(Ce): the strontium members are enriched in La and are Nd-depleted, whereas the opposite is true for the calcium members (Pekov *et al.* 1997).

A positive correlation between radii of the M cations and the X anions is observed in apatite-supergruop members: the minerals with the largest M cations, namely Pb^{2+} and Ba^{2+} , typically contain the largest X anion, Cl^- : pyromorphite, mimetite, vanadinite, matthedleyite, alforsite, hedyphane, phosphohedyphane, morelandite and caracolite. Among them, only pyromorphite, matthedleyite, hedyphane and phosphohedyphane have OH^- or F^- -dominant analogues, as this is extremely rare in nature, whereas Cl^- -dominant Pb minerals of the apatite supergroup are common.

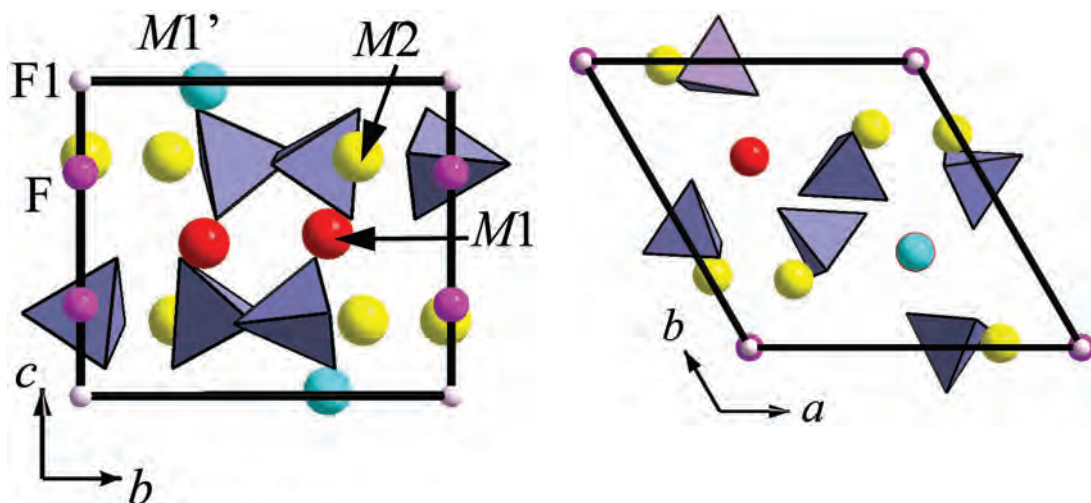


FIG. 5. The crystal structure of carlgieseckeite-(Nd) in **b-c** (a) and **a-c** (b) projections. The PO_4 groups are shown as tetrahedra, and the M cations and F anions, as circles. The unit cell is outlined.

Furthermore, the Cl-dominant apatite-group minerals with other prevailing *M* cations are relatively rare (Ca: chlorapatite, turneurite; NaBi: aiolosite) or unknown. In the belovite group, only the Ba member, kuanneruite-(Ce), contains Cl as a significant constituent.

The existence of Ca-dominant (at the *M2* site) analogues of belovite was supposed earlier ("calcio-belovite": Pekov *et al.* 1995) in the Ilímaussaq complex, a Sr-depleted intrusion in comparison with Lovozero and

Khibiny. A Na- and REE-enriched variety of hydroxyl-apatite from Ilímaussaq (aegirine-feldspar pegmatite) was reported by Rønsbo (1989), and additional studies have been carried out by us on the same sample kindly provided by J. Rønsbo. Its empirical formula based on $O + OH + F = 13 \text{ apfu}$ is $(\text{Ca}_{4.23}\text{Na}_{0.36}\text{Ce}_{0.18}\text{La}_{0.11}\text{Nd}_{0.04}\text{Sr}_{0.04}\text{Pr}_{0.01})_{\Sigma 4.97}\text{P}_{2.99}\text{Si}_{0.03}\text{O}_{12.01}(\text{OH})_{0.57}\text{F}_{0.42}$. The X-ray powder data (absence of reflections with odd *l* in the 00*l* series) and IR spectrum show that this sample belongs to the apatite and not the belovite structure-type (Pekov 2005). This mineral contains *ca.* 35 mol.% of the carlgieseckeite (belovite-type) component. The belovite-type pattern of order in apatite-like compounds

TABLE 2. CARLGEISECKEITE-(Nd):
X-RAY POWDER-DIFFRACTION DATA

<i>l</i> _{obs}	<i>d</i> _{obs}	<i>l</i> _{calc} *	<i>d</i> _{calc}	<i>h k l</i>
13	8.22	15	8.189	100
22	7.02	37	6.983	001
18	5.33	36, 9	5.313, 5.313	101, 011
3	4.73	3	4.728	110
10	4.094	27	4.094	200
27	3.923	43, 32	3.915, 3.915	111, 11 $\bar{1}$
23	3.463	37	3.491	002
14	3.202	15, 29	3.212, 3.212	012, 102
19	3.095	40, 10	3.095, 3.095	210, 120
100	2.815	37, 23, 75, 36, 51, 67	2.829, 2.829, 2.829, 2.829, 2.809, 2.809	211, 121, 21 $\bar{1}$, 12 $\bar{1}$, 112, 11 $\bar{2}$
42	2.727	100	2.729	300
15	2.647	8, 18	2.657, 2.657	202, 022
8	2.541	5, 17	2.542, 2.542	301, 031
2	2.367	3	2.364	220
5	2.320	6, 2, 4	2.328, 2.316, 2.316	003, 122, 212
17	2.255	17, 9, 2, 19, 6	2.271, 2.271, 2.239, 2.239, 2.239	130, 310, 22 $\bar{1}$, 221, 103
8	2.154	7, 10, 5,	2.160, 2.160, 2.150,	31 $\bar{1}$, 131, 302,
4	2.084	2	2.150	032
1	2.021	17	2.088	11 $\bar{3}$
16	1.953	7	2.023	203
8	1.896	5, 2, 35, 26	1.964, 1.964, 1.957, 1.957	401, 041, 22 $\bar{2}$, 222
17	1.852	2, 18, 10, 7	1.904, 1.904, 1.904, 1.904	312, 132, 13 $\bar{2}$, 31 $\bar{2}$
13	1.777	15, 49, 12, 2	1.860, 1.860, 1.860, 1.860	123, 213, 21 $\bar{3}$, 123
11	1.752	27, 15, 2, 5	1.787, 1.787, 1.771, 1.771	140, 410, 303, 042
11	1.732	14, 27, 27, 1, 2, 4, 10	1.766, 1.766, 1.746 1.731, 1.731, 1.731, 1.731	042, 402, 004 141, 411, 14 $\bar{1}$, 41 $\bar{1}$
5	1.645	2, 5, 2, 2	1.654, 1.654, 1.654, 1.638	32 $\bar{2}$, 322, 23 $\bar{2}$, 114
3	1.612	5, 3	1.625, 1.606	313, 024
3	1.592	2, 3, 2	1.594, 1.591, 1.591	501, 41 $\bar{2}$, 412
6	1.537	14	1.537	33 $\bar{1}$
5	1.528	3, 1, 4, 7	1.521, 1.521, 1.521, 1.521	214, 124, 214, 124
3	1.507	3	1.511	24 $\bar{1}$
10	1.470	5, 9, 9	1.471, 1.471, 1.471	510, 304, 034
9	1.464	6, 1, 12	1.462, 1.462, 1.462	233, 323, 32 $\bar{3}$
5	1.434	7, 3, 3, 7, 4	1.439, 1.439, 1.439, 1.436, 1.436	51 $\bar{1}$, 15 $\bar{1}$, 511, 332, 33 $\bar{2}$
1	1.407	1	1.404	224
2	1.342	4, 3, 1	1.339, 1.339, 1.339	601, 115, 115
3	1.313	1, 5	1.311, 1.311	250, 520
3	1.291	9, 4, 1, 1, 7	1.289, 1.289, 1.289, 1.289, 1.289	251, 521, 24 $\bar{3}$, 42 $\bar{3}$, 243
4	1.279	1, 1, 3	1.279, 1.279, 1.279	234, 234, 324
5	1.250	3, 4, 6, 4, 3, 8	1.249, 1.249, 1.249, 1.249, 1.249, 1.249	160, 610, 144, 414, 414, 144
5	1.243	8, 2, 1, 1	1.243, 1.243, 1.243, 1.243	513, 51 $\bar{3}$, 305 035

* For the calculated X-ray powder pattern, only reflections with intensities ≥ 1 are given.

TABLE 3. CARLGEISECKEITE-(Nd): CRYSTAL DATA,
DATA-COLLECTION INFORMATION
AND DETAILS ABOUT THE STRUCTURE REFINEMENT

Space group	$P\bar{3}$
Unit-cell parameters <i>a</i> , <i>c</i> (Å)	9.4553(1), 6.9825(1)
<i>V</i> (Å ³)	540.620(11)
<i>Z</i>	2
λ (MoK α) (Å), <i>T</i> (K)	0.71073, 293(2)
Crystal-detector distance (mm)	45
Collection mode	(Full) sphere
$2\theta_{\text{max}}$ (°)	69.74
Crystal size (mm)	0.10 × 0.13 × 0.25
<i>h</i> , <i>k</i> , <i>l</i> ranges	-15/15, -15/15, -11/11
Reflections collected	25812
Unique reflections	1557 ($R_{\text{int}} = 0.0643$)
Refinement on	F^2
<i>R</i> 1 (<i>F</i>)	0.0218
$wR2_{\text{all}}$ (F^2)*	0.0506
"Observed" reflections	1520 [$F_o > 4\sigma(F_o)$]
No. of refined parameters	70
GoF	1.117
$(\Delta\rho)_{\text{max}}$	0.001
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ (e/Å ³)	-1.022, 1.031

* $w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 0.1304P]$; $P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_o^2)/3$.

TABLE 4. COORDINATES AND EQUIVALENT
THERMAL DISPLACEMENT PARAMETERS (U_{eq} , Å²)
OF ATOMS IN CARLGEISECKEITE-(Nd)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
M1	0.3333	0.6667	0.51466(4)	0.00955(7)
M1'	0.3333	0.6667	0.0163(3)	0.0179(6)
M2	0.23744(5)	-0.01473(5)	0.24062(6)	0.01273(12)
P	0.39810(8)	0.36995(8)	0.25166(10)	0.01063(18)
F*	0.0	0.0	0.2900(7)	0.0319(11)**
F1*	0.0	0.0	0.0	0.0319(11)**
O1	0.4849(3)	0.1570(3)	0.7360(3)	0.0169(4)
O2	0.3143(3)	0.2483(3)	0.0882(3)	0.0227(5)
O3	0.3664(3)	0.2688(3)	0.4384(3)	0.0182(5)
O4	0.5331(3)	0.1184(3)	0.2289(3)	0.0175(4)

* Site-occupancy factors for F and F1 = (F + Cl) are 0.883(11) and 0.118(11), respectively (formally calculated for pure fluorine).

** Anisotropic displacement parameters for F and F1 were fixed to be equal during the refinement. The M1 site is REE-dominant, the M1' site is occupied by Na, and the M2 site is Ca-dominant.

TABLE 5. ANISOTROPIC DISPLACEMENT PARAMETERS (Å²) FOR CARLIESECKEITE-(Nd)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M1	0.01023(8)	0.01023(8)	0.00819(11)	0.000	0.000	0.00511(4)
M1'	0.0207(7)	0.0207(7)	0.0123(8)	0.000	0.000	0.0104(4)
M2	0.0156(2)	0.01279(19)	0.01046(19)	0.00062(13)	0.00032(13)	0.00760(15)
P	0.0113(3)	0.0110(3)	0.0103(3)	-0.0001(2)	-0.0004(2)	0.0061(2)
F	0.0227(12)	0.0227(12)	0.050(3)	0.000	0.000	0.0114(6)
F1	0.0227(12)	0.0227(12)	0.050(3)	0.000	0.000	0.0114(6)
O1	0.0202(10)	0.0110(8)	0.0125(9)	0.0003(7)	-0.0011(8)	0.0026(8)
O2	0.0352(14)	0.0179(11)	0.0168(10)	-0.0067(8)	-0.0128(9)	0.0145(10)
O3	0.0240(11)	0.0204(10)	0.0135(9)	0.0056(7)	0.0032(8)	0.0136(9)
O4	0.0157(9)	0.0165(9)	0.0238(11)	0.0006(8)	-0.0007(8)	0.0107(8)

with Ca, Na and REE probably occurs with higher contents of the latter two cations.

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TABLE 6. SELECTED INTERATOMIC DISTANCES (Å) IN CARLIESECKEITE-(Nd)

M1 – O1	2.435(2) × 3	M2 – F / F1	2.3433(8) / 2.8627(4)
– O4	2.523(2) × 3	– O2	2.360(2)
– O3	2.609(2) × 3	– O4	2.427(2)
<M1 – O>	2.522	– O3	2.441(2)
		– O2	2.457(3)
M1' – O1	2.421(3) × 3	– O1	2.668(2)
– O4	2.468(3) × 3	– O3	2.704(2)
<M1' – O>	2.445	<M2 – F, O>	2.486 / 2.560
		P – O2	1.530(2)
		– O1	1.533(2)
		– O4	1.541(2)
		– O3	1.555(2)
		<P – O>	1.540

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data_apati

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_chemical_name_systematic
;
?
;
_chemical_name_common           ?
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'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Ca' 'Ca' 0.2262 0.3064
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Sr' 'Sr' -1.5307 3.2498
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Nd' 'Nd' -0.1943 3.0179
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Na' 'Na' 0.0362 0.0249
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'P' 'P' 0.1023 0.0942
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'F' 'F' 0.0171 0.0103
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
'Cl' 'Cl' 0.1484 0.1585
'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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'-y, x-y, z'
'-x+y, -x, z'
'-x, -y, -z'
'y, -x+y, -z'
'x-y, x, -z'
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_cell_length_b                  9.45530(10)
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_cell_angle_alpha               90.00
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_cell_angle_gamma	120.00
_cell_volume	540.620(11)
_cell_formula_units_Z	2
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_cell_measurement_theta_min	?
_cell_measurement_theta_max	?
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_exptl_crystal_colour	?
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_exptl_crystal_size_mid	?
_exptl_crystal_size_min	?
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_exptl_crystal_F_000	597
_exptl_absorpt_coefficient_mu	9.842
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_exptl_absorpt_process_details	?
_exptl_special_details	
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?	
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_diffn_reflns_limit_l_min	-11
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_computing_cell_refinement     ?
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_computing_publication_material ?

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Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

```
;
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'calc w=1/[\s^2^(Fo^2^)+(0.0291P)^2^+0.1304P] where P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
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_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns         1557
_refine_ls_number_parameters      70
_refine_ls_number_restraints     1
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_refine_ls_wR_factor_ref          0.0506
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loop_
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_atom_site_fract_z
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_atom_site_adp_type
_atom_site_occupancy
_atom_site_symmetry_multiplicity
_atom_site_calc_flag
_atom_site_refinement_flags
_atom_site_disorder_assembly

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_atom_site_disorder_group

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M1' Na 0.3333 0.6667 0.0163(3) 0.0179(6) Uani 1.017(11) 3 d SP . .
M2 Ca 0.23744(5) -0.01473(5) 0.24062(6) 0.01273(12) Uani 1.329(6) 1 d P . .
P P 0.39810(8) 0.36995(8) 0.25166(10) 0.01063(18) Uani 1 1 d . . .
F F 0.0000 0.0000 0.2900(7) 0.0319(11) Uani 0.883(11) 3 d SP . .
F1 F 0.0000 0.0000 0.0000 0.0319(11) Uani 0.118(11) 6 d SP . .
O1 O 0.4849(3) 0.1570(3) 0.7360(3) 0.0169(4) Uani 1 1 d . . .
O2 O 0.3143(3) 0.2483(3) 0.0882(3) 0.0227(5) Uani 1 1 d . . .
O3 O 0.3664(3) 0.2688(3) 0.4384(3) 0.0182(5) Uani 1 1 d . . .
O4 O 0.5331(3) 0.1184(3) 0.2289(3) 0.0175(4) Uani 1 1 d . . .

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_atom_site_aniso_U_22
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_atom_site_aniso_U_13
_atom_site_aniso_U_12
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M1' 0.0207(7) 0.0207(7) 0.0123(8) 0.000 0.000 0.0104(4)
M2 0.0156(2) 0.01279(19) 0.01046(19) 0.00062(13) 0.00032(13) 0.000760(15)
P 0.0113(3) 0.0110(3) 0.0103(3) -0.0001(2) -0.0004(2) 0.0061(2)
F 0.0227(12) 0.0227(12) 0.050(3) 0.000 0.000 0.0114(6)
F1 0.0227(12) 0.0227(12) 0.050(3) 0.000 0.000 0.0114(6)
O1 0.0202(10) 0.0110(8) 0.0125(9) 0.0003(7) -0.0011(8) 0.0026(8)
O2 0.0352(14) 0.0179(11) 0.0168(10) -0.0067(8) -0.0128(9) 0.0145(10)
O3 0.0240(11) 0.0204(10) 0.0135(9) 0.0056(7) 0.0032(8) 0.0136(9)
O4 0.0157(9) 0.0165(9) 0.0238(11) 0.0006(8) -0.0007(8) 0.0107(8)

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;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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M1 O4 2.523(2) 4_666 ?
M1 O4 2.523(2) 5_566 ?
M1 O4 2.523(2) 6_556 ?
M1 O3 2.609(2) 5_566 ?
M1 O3 2.609(2) 6_556 ?