



Article

Fluorbritholite-(Nd), Ca₂Nd₃(SiO₄)₃F, a new and key mineral for neodymium sequestration in REE skarns

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Abstract

Fluorbritholite-(Nd), ideally $Ca_2Nd_3(SiO_4)_3F$, has been approved by the International Mineralogical Association (IMA2023–001) and constitutes a new member of the britholite group of the apatite supergroup. It occurs in skarn from the Malmkärra iron mine, Norberg, Västmanland (one of the Bastnäs-type deposits in Sweden), associated with calcite, dolomite, magnetite, lizardite, talc, fluorite, baryte, scheelite, gadolinite-(Nd) and other REE minerals. Fluorbritholite-(Nd) forms anhedral and small grains, rarely up to 250 μ m across. They are brownish pink and transparent with a vitreous to greasy lustre. The mineral is brittle, with an uneven or subconchoidal fracture and lacks a cleavage. In thin section, the mineral is nonpleochroic, uniaxial (–). $D_{calc} = 4.92(1)$ g·cm⁻³ and $n_{calc} = 1.795$. The empirical chemical formula from electron microprobe (WDS) point analyses is $(Ca_{1.62}Nd_{0.97}Ce_{0.83}Y_{0.52}Sm_{0.30}Gd_{0.23}Pr_{0.17}La_{0.16}Dy_{0.11}Er_{0.03}Tb_{0.03}Ho_{0.01}Yb_{0.01})_{\Sigma 4.99}(Si_{2.92}P_{0.08}As_{0.01})_{\Sigma 3.01}O_{12.00}[O_{0.48}F_{0.26}(OH)_{0.14}Cl_{0.10}Br_{0.02}]_{\Sigma 1.00}$. The crystal structure of fluorbritholite-(Nd) was refined from single-crystal X-ray diffraction data to $R_1 = 0.043$ for 704 unique reflections. It belongs to the hexagonal system, space group $P6_3/m$, with unit cell parameters a = 9.5994(3), c = 6.9892(4) Å and V = 557.76(5) ų for Z = 2. Fluorbritholite-(Nd) and other britholite-group minerals are a major sink for neodymium in REE-bearing skarns of Bastnäs type.

Keywords: fluorbritholite-(Nd); britholite group; apatite supergroup; new mineral; crystal structure; neodymium; REE ore; skarn; Norberg; Sweden

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Introduction

The global quest for economic sources of rare earth elements (REE), prompted by the increased demand for neodymium (Nd) and related critical metals as components in e.g. permanent magnetic materials and lasers (Chakhmouradian and Wall, 2012; Goodenough et al., 2018), has revived interest in REE deposits of the Bergslagen ore region in Sweden (Sadeghi et al., 2019). In particular, the occurrences of skarn-hosted britholite-group minerals — referred to as Bastnäs-type deposits, subtype 2, by Holtstam and Andersson (2007) — in the Norberg District are of interest because of their unusual enrichment in heavier REE. Previous work (Holtstam and Andersson, 2007) included a few chemical analyses of britholite-group minerals suggesting the existence of a Nd-dominant species, corresponding to UM2007-044 in the list of valid unnamed mineral species (Smith and Nickel, 2007). It has now been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2023-001, Holtstam et al., 2023) with the name fluorbritholite-(Nd), ideally Ca2Nd3(SiO4)3F. The mineral was

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discovered at one of the Bastnäs-type deposits, Malmkärra, during a recent survey and sampling campaign. Type material is preserved in the mineral collection of the Department of Geosciences, Swedish Museum of Natural History, Box 50007, SE-10405 Stockholm, Sweden, under collection number GEO-NRM #20220221 (specimen and polished section). The accepted mineral symbol for fluorbritholite-(Nd) is Fbri-Nd.

Occurrence

The Malmkärra iron mine is situated close to the tarn Stora Malmtjärnen, Norberg, Västmanland County, Sweden (60° 3'34"N, 15°50'45"E, 200 m a.s.l.). The deposit is hosted in a synclinal marble layer (dolomite), intercalated with felsic metavolcanic beds, and is divided into separate ore bodies due to local faulting (Geijer, 1936). The underlying bedrock consists of plastically deformed mica-schist, with major quartz, muscovite and cordierite, along with accessory tourmaline, magnetite and allanite-(Ce). It grades into a Na-rich, less altered metavolcanic rock in certain sections. The magnetite-skarn ore has locally replaced the carbonate along its contact with the country rock (Geijer, 1936; Holtstam *et al.*, 2014).

The oldest record of the Malmkärra mine is from 1664. Magnetite ore was mined (~100,000 t of Fe) until production stopped in 1936 (Geijer and Magnusson, 1944). Geijer (1927)

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Figure 1. Colour image of cut slab of boulder from Malmkärra, GEO-NRM #20220221. Dark spots are mostly serpentine, greyish areas carbonate. Fluorbritholite-(Nd) was obtained from the magnetite-rich part encircled.

first noted the REE mineralisation, later referred to as Bastnäs-type (Geijer, 1961). The mineralisation occurs as bands of REE-bearing silicates deposited between magnetite-rich, tremolite-bearing skarns and dolomitic marble, with patches of Mg silicates (humite and serpentine) in recrystallised carbonate rock ('ophicalcite'). Malmkärra is the type locality for three rare mineral species so far: västmanlandite-(Ce) (Holtstam *et al.*, 2005), ulfanderssonite-(Ce) (Holtstam *et al.*, 2017) and gadolinite-(Nd) (Škoda *et al.*, 2018). According to a recent estimation (Rönnåsen, 2023), there is still 83,000 t of waste rock present in the mine area, with an average of 0.55% REE.

Fluorbritholite-(Nd) was discovered in a boulder from the old dumps (Fig. 1). All observed occurrences of the new mineral relate to a thin skarn zone situated at the contact between the 'ophicalcite' and magnetite ore. Associated minerals in this skarn band include calcite, dolomite, magnetite, lizardite, talc, fluorite, baryte, scheelite and gadolinite-(Nd), accompanied by an allanite-group mineral and a gatelite-group mineral.

The Palaeoproterozoic (Orosirian) Bastnäs-type REE–Fe (\pm Cu, Bi, Mo, Co and Au) skarn mineralisations in the area originated from reactions involving hot ($T > 400^{\circ}$ C) magmatic–hydrothermal fluids containing REE–Si–chloro–fluoro ion complexes and primary carbonate (Holtstam and Broman, 2002; Holtstam et al., 2014; Sahlström et al., 2019).

Appearance and physical properties

Fluorbritholite-(Nd) has an irregular morphology, forming anhedral grains of small size (rarely up 250 μ m across, Fig. 2). The colour is brownish pink, with a white streak. The crystals are transparent with a vitreous to greasy lustre. The hardness (Mohs) is estimated as 5, in analogy with fluorbritholite-(Ce). Fluorbritholite-(Nd) is brittle with an uneven or subconchoidal fracture. No parting or cleavage have been observed. Density was not measured because of the minute sample size; the calculated value is 4.92(1) g·cm⁻³. In a petrographic thin section, the mineral is nonpleochroic and uniaxial (–). The refractive indices were not measured due to limited amount of type material

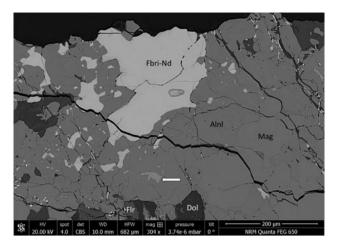


Figure 2. Back-scattered electron image of fluorbritholite-(Nd) (Fbri-Nd), an allanite-like mineral (Alnl), magnetite (Mag), fluorite (Flr) and dolomite (Dol). The white arrow points to a gatelite-like mineral. Sample GEO-NRM #20220221.

(only tiny fragments could be extracted from the one large grain in the type sample). Overall $n_{\rm calc} = 1.795$ from Gladstone–Dale coefficients (Mandarino, 1981), very close to the highest available index liquid (1.80).

Chemical data

The chemical composition (Table 1) was determined using a JEOL JXA-8230 electron-microprobe operated in wavelengthdispersive mode (20 kV acceleration voltage, 10 nA sample current and 5 µm beam size). The number of spot analyses was 12. Natural and synthetic reference materials were used (Table 1). Measurements involved the following X-ray spectral lines and analysing crystals: Si and Al ($K\alpha$, TAP); Y and As ($L\alpha$, TAP); P, Ca and Cl ($K\alpha$, PETH); La, Ce and Lu ($L\alpha$, LIF); Gd and Tb (Lβ, LIF); Pr, Nd, Sm, Dy, Ho and Er (Lβ, LIFL); Yb (Lα, LIFL); F (Kα, LD1); Br (Kα, LIFL). Peak overlaps between various REE and F-Ce were corrected empirically. Thulium was not measured but calculated from chondrite normalisation. Iron, Ti, Al, Mg, U, Pb and Th were sought but found to be below the detection limit. The H₂O content was not measured directly because of the small sample volume; it was inferred from structural, chemical and spectroscopic data.

The empirical formula calculated on the basis of 8 cations can be written as: $(Ca_{1.62}Nd_{0.97}Ce_{0.83}Y_{0.52}Sm_{0.30}Gd_{0.23}Pr_{0.17}La_{0.16}Dy_{0.11}Er_{0.03}Tb_{0.03}Ho_{0.01}Yb_{0.01})_{\Sigma 4.99}(Si_{2.92}P_{0.08}As_{0.01})_{\Sigma 3.01}O_{12}[O_{0.48}F_{0.26}(OH)_{0.14}Cl_{0.10}Br_{0.02}]_{\Sigma 1.00}$ The ideal mineral formula is $Ca_2Nd_3(SiO_4)_3F$, which requires (in wt.%) CaO 13.88, Nd_2O_3 62.45, SiO_2 22.31, F2.35, $F\equiv O$ 0.99, sum 100.00.

Raman spectroscopy

Micro-Raman measurements were conducted using a Horiba (Jobin Yvon) LabRam HR Evolution instrument on a randomly oriented crystal. The sample was excited with frequency-doubled 532 nm and 785 nm Nd–YAG lasers utilising an Olympus $100\times$ objective (numerical aperture = 0.9). The lateral resolution of the unpolarised confocal laser beam was in the order of 1 μm . Raman spectra of the sample were collected through two acquisition cycles with single counting times of 45 s. Spectra were generated in the range of 100 to 4000 cm $^{-1}$ utilising a 600 grooves/cm

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Table 1. Chemical data (in wt.%) for fluorbritholite-(Nd).

| Constituent | Mean | Range | 2σ | Reference materia |
|--------------------------------|-------|-------------|------|-------------------|
| P ₂ O ₅ | 0.68 | 0.60-0.78 | 0.14 | CePO ₄ |
| As_2O_5 | 0.08 | 0.00-0.14 | 0.08 | cobaltite |
| SiO ₂ | 21.03 | 20.60-21.26 | 0.45 | wollastonite |
| Y_2O_3 | 7.01 | 6.78-7.39 | 0.40 | YPO ₄ |
| La ₂ O ₃ | 3.23 | 2.90-3.45 | 0.36 | LaPO ₄ |
| Ce_2O_3 | 16.35 | 15.43-17.20 | 1.10 | CePO ₄ |
| Pr_2O_3 | 3.31 | 3.12-3.46 | 0.22 | PrPO ₄ |
| Nd_2O_3 | 19.51 | 19.19-19.84 | 0.42 | NdPO ₄ |
| Sm_2O_3 | 6.34 | 5.93-6.66 | 0.39 | SmPO ₄ |
| Gd_2O_3 | 4.95 | 4.65-5.46 | 0.49 | GdPO ₄ |
| Tb_2O_3 | 0.56 | 0.46-0.66 | 0.13 | TbPO₄ |
| Dy_2O_3 | 2.52 | 2.33-2.76 | 0.28 | DyPO ₄ |
| Ho_2O_3 | 0.32 | 0.27-0.43 | 0.08 | HoPO ₄ |
| Er ₂ O ₃ | 0.67 | 0.56-0.75 | 0.10 | ErPO ₄ |
| Tm2O3* | 0.07 | 0.06-0.09 | 0.02 | |
| Yb_2O_3 | 0.31 | 0.27-0.39 | 0.06 | YbPO ₄ |
| Lu_2O_3 | 0.03 | 0.01-0.04 | 0.02 | LuPO ₄ |
| CaO | 10.86 | 10.65-11.07 | 0.29 | apatite |
| H ₂ O** | 0.15 | | | |
| F | 0.60 | 0.49-0.70 | 0.14 | fluorite |
| Cl | 0.42 | 0.39-0.45 | 0.04 | tugtupite |
| Br | 0.17 | 0.00-0.47 | 0.33 | bromargyrite |
| F = 0 | -0.25 | | | |
| Cl = O | -0.09 | | | |
| Br = O | -0.02 | | | |
| Total | 98.81 | | | |
| | | | | |

*Calculated value from chondrite normalisation ** H_2O calculated on the basis of (OH + F + Cl + Br + O) = 13 apfu.

grating and a thermoelectric-cooled charge-coupled device (CCD). The wavenumber calibration was performed using the 520.7 cm⁻¹ Raman band on a polished silicon wafer with a wavenumber accuracy usually better than 0.5 cm⁻¹.

The spectra are largely overwhelmed by fluorescence. There is a distinct peak at $852~\rm cm^{-1}$ in the $532~\rm nm$ spectrum (Fig. 3), resulting from symmetric stretching of SiO_4 groups, and a weak one at $950~\rm cm^{-1}$ corresponding to a contribution from the minor PO_4 group (v_1 symmetric stretching; cf. Boughzala *et al.*, 2008). A sample of P-rich fluorbritholite-(Ce) from Norra Kärr, Sweden, has bands close to these positions (RRUFF no. R070412). A weak signal at $3300-3400~\rm cm^{-1}$ in the $785~\rm nm$ spectrum (Fig. 4) can be related to O–H stretching vibration modes.

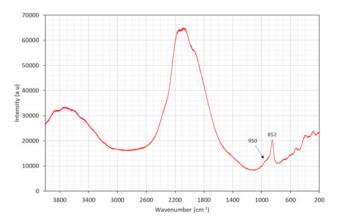


Figure 3. Raman spectrum of fluorbritholite-(Nd), obtained with a 532 nm laser.

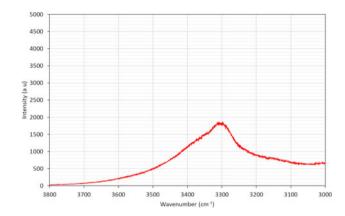


Figure 4. Raman spectrum of fluorbritholite-(Nd), obtained with a 785 nm laser.

X-ray crystallography

Single-crystal X-ray diffraction

Single-crystal X-ray diffraction data were collected with a Bruker D8 Advance from a $0.060 \times 0.055 \times 0.045$ mm fragment, extracted from the largest available grain previously analysed with the electron microprobe (Fig. 1). The crystal structure of fluorbritholite-(Nd) was refined using SHELXL-2013 (Sheldrick, 2008) starting from the atom coordinates of fluorbritholite-(Y) (Pekov *et al.*, 2011) to R_1 = 0.043 for 704 unique reflections. Crystal parameters and refinement conditions are given in Table 2. Refined atom coordinates, site occupancies and equivalent isotropic displacement parameters are reported in Table 3. Selected interatomic distances are provided in Table 4. The bond valence sums (site populations given in the notes to the

Table 2. Single-crystal data and experimental details.

| Crystal data | | |
|---|--|--|
| Ideal formula | $Ca_2Nd_3(SiO_4)_3F$ | |
| Crystal system | Hexagonal | |
| Space group | P6 ₃ /m | |
| a (Å) | 9.5994(3) | |
| c (Å) | 6.9892(4) | |
| $V (Å^3)$ | 557.76(5) | |
| Z | 2 | |
| Data collection | | |
| Diffractometer | Bruker D8 Advance | |
| Distance to detector (cm) | 5 | |
| Scan modes | ω | |
| Exposure time per frame (s) | 25 | |
| Radiation type | Mo K α (λ = 0.71073 Å) | |
| Temperature (K) | 293 | |
| Collected reflections | 14017 | |
| Unique reflections | 704 | |
| Reflections with $F_o > 4\sigma(F_o)$ | 578 | |
| 2θ range (°) | 2.45-32.04 | |
| R _{int} | 0.071 | |
| Refinement | | |
| Refinement | Full-matrix least square on F ² | |
| No. of least-square parameters | 42 | |
| Final R_1 $[F_0 > 4\sigma(F_0)]$ | 0.043 | |
| Final R_1 | 0.055 | |
| Final wR^2 $[F_0 > 4\sigma(F_0)]$ | 0.100 | |
| Final wR^2 | 0.108 | |
| GooF | 1.102 | |
| $\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e^- \times \mathring{A}^{-3})$ | 3.03, -3.29 | |

Note: $wR^2 = [\Sigma \ w \ (|F_o|^2 - |F_c|^2)^2 \ / \ \Sigma \ w \ (|F_o|^4)]^{\frac{1}{2}}$.

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Table 3. Refined fractional atom coordinates, equivalent displacement parameters (\mathring{A}^2) and site occupancies in fluorbritholite-(Nd).

| Site | Site occupancy | X | У | Z | $U_{\rm eq}$ |
|------|---|------------|------------|-------------|--------------|
| M1 | La _{0.658(13)} Ca _{0.342(13)} | 0.3333 | 0.6667 | 0.00045(13) | 0.0237(3) |
| M2 | La _{0,705(13)} Ca _{0,295(13)} | 0.24039(9) | 0.99206(9) | 1/4 | 0.0265(3) |
| Si | Si _{1.00} | 0.4017(3) | 0.3730(3) | 1/4 | 0.0206(7) |
| 02 | O _{1.00} | 0.3268(11) | 0.4899(10) | 1/4 | 0.0339(18) |
| 03 | O _{1.00} | 0.5962(9) | 0.4683(9) | 1/4 | 0.037(2) |
| 04 | O _{1.00} | 0.3461(11) | 0.2556(8) | 0.0643(10) | 0.052(2) |
| 01 | O _{0.81} | 0.0000 | 0.0000 | 1/4 | 0.081(12) |
| Cl1 | Cl _{0.095} | 0.0000 | 0.0000 | 0.093(13) | 0.081(12) |

table), computed with the parameters given by Brese and O'Keeffe (1991), are listed in Table 5. Considering the correspondence in atomic number ('mean' atomic number of [REE+Y]=56.8 in fluorbritholite-(Nd)), we used La (atomic number = 57) as the average REE in the refinement. The crystallographic information file has been deposited with the Principal Editor of Mineralogical Magazine and is available as Supplementary material (see below).

Powder X-ray diffraction

Powder X-ray diffraction data (Table 6) were collected with an Oxford Diffraction Excalibur PX Ultra diffractometer fitted with a 165 mm diagonal Onyx CCD detector and using copper radiation (CuK α , λ = 1.54138 Å) from the same crystal used for the single-crystal experiment. The hexagonal $P6_3/m$ unit-cell parameters refined from powder data are a = 9.5966(7) Å, c = 6.9816(8) Å and V = 556.83(7) Å³.

Results and discussion

Crystal structure

Fluorbritholite-(Nd) has the hexagonal P63/m apatite-type structure, with the general formula $M1_2M2_3(TO_4)_3X$, in this case based on T = Si plus minor P at the tetrahedrally coordinated sites and polyhedra of $M1O_9$ and $M2O_6X$ (M = Ca and REE; X =O, F, OH and Cl). Calcium and the REE are essentially disordered over the M sites. The slight preponderance of REE at M2 agrees with the pattern seen in previously studied LREE-rich fluorbritholite-(Ce) (Oberti et al., 2001; Zubkova et al., 2015), where this preference is even more pronounced. The X anions are in channels parallel to the 6-fold axis. The X site is split; whereas the smaller anions lie on the mirror plane at $z = \frac{1}{4}$ and Cl is found at distance of 1.1 Å below or above. The site occupancy of the two split sites was fixed during the refinement according to the compositional data obtained from microprobe analyses. The bond valence sums are in good agreement with the site populations and conformable with all lanthanides being

Table 4. Selected interatomic distances (Å) in fluorbritholite-(Nd).*

| M1-O2 | 2.412(5) ×3 | M2-O1 | 2.3466(8) |
|-------|-------------|--------|-------------|
| M1-O3 | 2.465(6) ×3 | M2-O4 | 2.365(6) ×2 |
| M1-O4 | 2.816(9) ×3 | M2-03 | 2.424(8) |
| | | M2-O4' | 2.558(7) ×2 |
| Si-02 | 1.608(8) | M2-Cl1 | 2.59(4) ×2 |
| Si-03 | 1.617(8) | M2-O2 | 2.765(10) |
| Si-04 | 1.624(6) ×2 | | |
| | | | |

^{*}The O1/Cl1 positions, giving rise to the 7-fold coordinated M2 polyhedron, are mutually present.

Table 5. Bond valence sums (BVS) for fluorbritholite-(Nd) calculated with the parameters of Brese and O'Keeffe (1991).*

| | <i>M</i> 1 | M2 | Si | ΣΟ |
|-----------|-------------------------|---|----------------------|------|
| O1 (81%) | | 0.442 ^{×3→} | | 1.33 |
| 02 | 0.390 ^{×3↓×2→} | 0.153 | 1.047 | 1.98 |
| 03 | 0.337 ^{×3↓×2→} | 0.383 | 1.023 | 2.08 |
| 04 | 0.130 ^{×3↓×2→} | 0.450 ^{×2↓} 0.267 ^{×2↓} | 1.003 ^{×2↓} | 1.98 |
| Cl1 (19%) | | 0.131 ^{×2↓×3→} | | 0.39 |
| BVS | 2.57 | 2.67 | 4.08 | |

* $M1 = REE_{0.66}Ca_{0.34}$; $M2 = REE_{0.70}Ca_{0.30}$, with REE = $Nd_{0.31}Ce_{0.26}Y_{0.16}Sm_{0.10}Gd_{0.07}Pr_{0.05}La_{0.05}$

trivalent (the presence of tetravalent Ce is highly unlikely as the mineral was deposited in a magnetite-bearing skarn). No symmetry lowering was observed for this sample (cf. Oberti *et al.*, 2001).

Remarks on nomenclature

The type specimen of fluorbritholite-(Nd) has a surplus of Σ REE atoms (> 3 atoms per formula unit) relative the ideal formula, which must be charge-compensated by introducing a significant REE oxysilicate apatite (Ca Ln_4 [SiO₄]₃O) component (e.g.

Table 6. Observed and calculated X-ray powder diffraction data (d in Å) for fluorbritholite-(Nd).*

| | Observed | | Calculated | |
|-----|--------------------|------------------|------------|-------------------|
| hkl | d_{obs} | I _{est} | d_{calc} | I _{calc} |
| 110 | | | 4.7997 | 4 |
| 200 | 4.16 | 20 | 4.1567 | 27 |
| 111 | | | 3.9566 | 19 |
| 002 | | | 3.4946 | 14 |
| 102 | 3.223 | 30 | 3.2215 | 31 |
| 120 | 3.144 | 30 | 3.1421 | 32 |
| 121 | 2.866 | 100 | 2.8658 | 100 |
| 112 | 2.823 | 55 | 2.8251 | 62 |
| 300 | 2.769 | 35 | 2.7711 | 44 |
| 202 | | | 2.6749 | 5 |
| 130 | | | 2.3057 | 6 |
| 302 | | | 2.1713 | 4 |
| 113 | | | 2.0959 | 10 |
| 400 | | | 2.0783 | 4 |
| 222 | 1.977 | 40 | 1.9783 | 31 |
| 132 | | | 1.9245 | 16 |
| 230 | | | 1.9072 | 4 |
| 123 | 1.869 | 25 | 1.8714 | 29 |
| 231 | | | 1.8399 | 18 |
| 140 | | | 1.8141 | 19 |
| 402 | 1.785 | 25 | 1.7863 | 24 |
| 004 | | | 1.7473 | 12 |
| 240 | | | 1.5711 | 3 |
| 331 | | | 1.5596 | 6 |
| 124 | | | 1.5271 | 8 |
| 502 | | | 1.5014 | 9 |
| 304 | | | 1.4780 | 8 |
| 323 | | | 1.4758 | 5 |
| 511 | | | 1.4602 | 4 |
| 332 | | | 1.4547 | 6 |
| 215 | | | 1.2772 | 3 |
| 414 | | | 1.2585 | 10 |
| 252 | | | 1.2440 | 6 |
| 440 | | | 1.1999 | 4 |
| 116 | | | 1.1320 | 3 |

^{*}The calculated diffraction pattern is obtained with the atom coordinates reported and the site occupancies given in Table 3 (only reflections with $I_{\rm rel} \ge 3$ are listed); the strongest observed Bragg reflections are given in bold.

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Kobayashi and Sakka, 2014). A similar component was in part inferred for fluorbritholite-(Y) (Pekov *et al.*, 2011). However, as the sum of monovalent X atoms exceeds the amount of O^{2-} , the name prefix is decided by the dominating F (see Pasero *et al.*, 2010), in accord with the dominant-valency rule (Hatert and Burke, 2008). The small Br concentration varies to some extent within the grain and is essentially antipathetic to Cl (linear correlation coefficient $R^2 = -0.33$), but is not correlated with any other element. It is thus ascertained that the sum of monovalent ions is > 0.5 apfu in this crystal. Fluorbritholite-(Nd) is a member of the britholite group of the apatite supergroup (Pasero *et al.*, 2010). It represents the Nd-analogue of fluorbritholite-(Ce) and fluorbritholite-(Y) (Table 7), and belongs to the Strunz group 9.AH.25 (Strunz and Nickel, 2001).

Geochemical considerations

In the present mineral assemblage, the allanite-like mineral, with large Ce, La, Mg and Fe³⁺ contents but no measurable F, represents the dominant REE mineral. REE-fluorocarbonates (e.g. bastnäsite) are notably absent, but quite common elsewhere in the REE skarn. As it appears from the chondrite-normalised patterns of the two major REE minerals and a bulk sample from Malmkärra, fluorbritholite-(Nd) is a major sink for Nd in the skarn system (Fig. 5). Similar, nearly flat REE profiles also prevail for gadolinite-subgroup minerals (Škoda et al., 2018), arrheniusite-(Ce) (Holtstam et al., 2021) and magnesiorowlandite-(Y) (Holtstam and Andersson, 2007), but these minerals occur in much less quantities in the deposits of the Norberg District. In fact, all fluorbritholite samples here (Fig. 6) contain significant Nd (11.5-19.8 wt.% Nd₂O₃; Holtstam and Andersson, 2007, and this work), with a generally antipathetic relation between Ce and Y (12.8-31.7% Ce₂O₃ vs. 13.9-0.9% Y₂O₃). In the Nya Bastnäs deposit (belonging to sub-type 1 in the terminology of Holtstam and Andersson, 2007), the cerite-group minerals are similarly enriched in Nd, however no Nd-dominant member has been found to date.

Compared to the chemical fingerprint of britholite-group minerals, which are predominantly of magmatic-volcanic origin (Della Ventura *et al.*, 1999; Zozulya *et al.*, 2015; Zubkova *et al.*, 2015; Zozulya *et al.*, 2017; Lorentz *et al.*, 2019), the Norberg samples are poor in Ca, despite crystallisation in a carbonate-rich

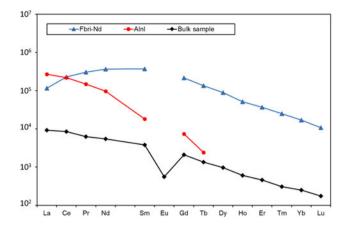


Figure 5. Chondrite-normalised REE patterns for fluorbritholite-(Nd) (Fbri-Nd), the coexisting allanite-like mineral (Alnl) and the bulk system (obtained with lithium borate fusion and ICP-MS) at Malmkärra. Chondrite values were taken from Boynton (1984).

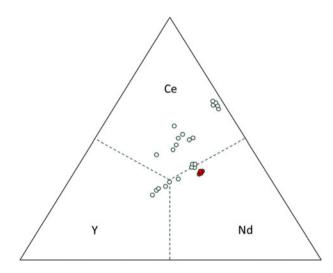


Figure 6. Triangular plot of Ce:Nd:Y atomic ratios in fluorbritholite samples from the Norberg area, Västmanland, Sweden. Filled circles correspond to the analyses of fluorbritholite-(Nd) from this study. Open symbols refer to data reported by Holtstam and Andersson (2007).

Table 7. Comparison of fluorbritholite species.

| | Fluorbritholite-(Nd) | Fluorbritholite-(Ce) | Fluorbritholite-(Y) |
|---|--|---|--|
| Ideal IMA formula | Ca ₂ Nd ₃ (SiO ₄) ₃ F | (Ce,Ca) ₅ (SiO ₄) ₃ F | (Y,Ca) ₅ (SiO ₄) ₃ F |
| Ideal advised formula | $Ca_2Nd_3(SiO_4)_3F$ | $Ca_2Ce_3(SiO_4)_3F$ | $Ca_2Y_3(SiO_4)_3F$ |
| Space group | P6 ₃ /m | P6 ₃ /m | P6 ₃ /m |
| Unit-cell parameters | a = 9.5994(3) Å | a = 9.517 Å | a = 9.4437(2) Å |
| · | c = 6.9892(4) Å | b = 6.983 Å | c = 6.8169 (2) Å |
| | $V = 557.76(5) \text{ Å}^3$ | $V = 547.7 \text{ Å}^3$ | $V = 526.50(2)^{\circ} \text{Å}^3$ |
| | Z = 2 | Z=2 | Z=2 |
| Strongest Bragg | 4.16 (20) | | 4.10 (27) |
| peaks, Å (%) | 3.22 (30) | | 3.16 (27) |
| • | 3.144 (30) | | 3.102 (29) |
| | 2.866 (100) | 2.845 (100) | 2.826 (100) |
| | 2.823 (55) | 2.822 (40) | 2.775 (58) |
| | 2.769 (35) | 2.747 (30) | 2.737 (46) |
| | 1.977 (40) | 1.970 (30) | 1.948 (25) |
| Colour | pink to brownish | pale yellow – reddish brown | light pinkish-brown to dark brown |
| $D_{\rm calc}$ (g/cm ³) | 4.91 | 4.66 | 4.61 |
| Reference | This paper | Gu <i>et al.</i> (1994) | Pekov et al. (2011) |

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environment (dolomite). The apatite-type substitution, $Ca^{2+} + P^{5+} \leftrightarrow REE^{3+} + Si^{4+}$, is accordingly modest. Interestingly, the Ca-poor britholite samples of the skarn-related Anadol REE ores of the eastern Azov region, Ukraine (Khomenko *et al.*, 2013), are Nd-rich as well (up to 14 wt.% Nd₂O₃). The Norberg britholite-group minerals are also practically devoid of the actinides (<0.05 wt.%), which is exceptional. Exploitation of skarn-hosted REE deposits of this type is thus more environmentally friendly (owing to the toxicity and radiation protection aspects related to U and Th) and economically attractive, provided that larger tonnages can be secured.

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Competing interest. The authors declare none.

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