

## FERRIALLANITE-(Ce) FROM THE BASTNÄS DEPOSIT, VÄSTMANLAND, SWEDEN

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### ABSTRACT

Ferriallanite-(Ce), previously reported as “cerine” or iron-rich “allanite”, is the most common lanthanide mineral next to cerite-(Ce) at the Bastnäs Fe–Cu–REE deposit, Skinnskatteberg, Västmanland, Sweden. It is closely associated with cerite-(Ce), bastnäsite-(Ce), bastnäsite-(La), törnebohmit-(Ce), quartz, fluocerite-(Ce) and sulfide minerals. The Fe<sub>2</sub>O<sub>3</sub> and FeO contents of ferriallanite-(Ce) are in the ranges 12.4–15.4 and 7.5–11.8 wt.%, respectively, and the dominant chemical variations are related to Fe<sup>2+</sup> ↔ Mg and Ce ↔ La substitutions. The concentrations of Th and U are extremely low, <3 ppm. A complete, averaged structural chemical formula for one sample, with unit-cell parameters *a* 8.941(4), *b* 5.799(2), *c* 10.151(6) Å, β 114.7(6)°, *V* 478.2(5) Å<sup>3</sup>, is <sup>A</sup>[(Ce<sub>0.51</sub>La<sub>0.41</sub>Nd<sub>0.10</sub>Pr<sub>0.03</sub>Y<sub>0.01</sub>Sm<sub>0.01</sub>)<sub>Σ1.07</sub>Ca<sub>0.95</sub>]<sup>M3</sup>[Fe<sup>2+</sup><sub>0.79</sub>Mg<sub>0.21</sub>]<sup>M2</sup>[Al<sub>0.83</sub>Fe<sup>3+</sup><sub>0.17</sub>]<sup>M1</sup>[Fe<sup>3+</sup><sub>0.92</sub>Mg<sub>0.08</sub>]<sup>T</sup>[Si<sub>2.96</sub>Al<sub>0.04</sub>]O<sub>12</sub>(OH<sub>0.90</sub>F<sub>0.10</sub>), based on electron-microprobe data and Mössbauer spectroscopy. The Bastnäs samples are distinct from the type ferriallanite-(Ce) from Ulyn Khuren, Mongolia, mainly in their higher REE and Mg contents.

*Keywords:* ferriallanite-(Ce), allanite subgroup, REE, lanthanides, Bastnäs, Sweden.

### SOMMAIRE

La ferriallanite-(Ce), précédemment connue sous le nom de “cérine” ou “allanite” riche en fer, est le minéral à terres rares (TR) le plus répandu, exception faite de la cérite-(Ce), au gisement de Fe–Cu–TR de Bastnäs, Skinnskatteberg, Västmanland, en Suède. Elle est étroitement associée à la cérite-(Ce), bastnäsite-(Ce), bastnäsite-(La), törnebohmit-(Ce), quartz, fluocérite-(Ce) et des minéraux sulfurés. Les teneurs en Fe<sub>2</sub>O<sub>3</sub> et FeO de la ferriallanite-(Ce) correspondent aux intervalles 12.4–15.4 et 7.5–11.85% (poids), respectivement, et les variations chimiques dominantes sont le résultat des substitutions Fe<sup>2+</sup> ↔ Mg et Ce ↔ La. Le niveau de concentration du thorium et de l’uranium est extrêmement faible, <3 ppm. Une formule chimique structurale moyenne d’un échantillon ayant les paramètres réticulaires *a* 8.941(4), *b* 5.799(2), *c* 10.151(6) Å, β 114.7(6)°, *V* 478.2(5) Å<sup>3</sup>, est <sup>A</sup>[(Ce<sub>0.51</sub>La<sub>0.41</sub>Nd<sub>0.10</sub>Pr<sub>0.03</sub>Y<sub>0.01</sub>Sm<sub>0.01</sub>)<sub>Σ1.07</sub>Ca<sub>0.95</sub>]<sup>M3</sup>[Fe<sup>2+</sup><sub>0.79</sub>Mg<sub>0.21</sub>]<sup>M2</sup>[Al<sub>0.83</sub>Fe<sup>3+</sup><sub>0.17</sub>]<sup>M1</sup>[Fe<sup>3+</sup><sub>0.92</sub>Mg<sub>0.08</sub>]<sup>T</sup>[Si<sub>2.96</sub>Al<sub>0.04</sub>]O<sub>12</sub>(OH<sub>0.90</sub>F<sub>0.10</sub>), selon les données obtenues avec une microsonde électronique et par spectroscopie de Mössbauer. Les échantillons de Bastnäs se distinguent de l’échantillon holotype de ferriallanite-(Ce) de Ulyn Khuren, en Mongolie, surtout par leur teneurs plus élevées en terres rares et en magnésium.

(Traduit par la Rédaction)

*Mots-clés:* ferriallanite-(Ce), sous-groupe de l’allanite, terres rares, Bastnäs, Suède.

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## INTRODUCTION

The species ferriallanite-(Ce), ideally  $\text{CeCaFe}^{2+}\text{AlFe}^{3+}(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$ , was recently described as a new member of the epidote group, from Ulyn Khuren, Mongolia, by Kartashov *et al.* (2002, 2003). Specifically, it is closely related to allanite-(Ce) and has  $\text{Fe}^{3+}$  dominant at the M1 structural site instead of Al. If compilations of published analytical data on "allanite" (*e.g.*, Deer *et al.* 1997) are scrutinized, it appears that ferriallanite is probably a rare mineral. Here, we report an occurrence in Sweden, the Bastnäs deposit in the Skinnskatteberg district, Västmanland County. The Bastnäs mines belong to the Ridderhyttan ore field (Geijer 1923, Ambros 1983), where iron and copper mining activities started as early as five hundred years ago. Lanthanides were extracted mostly from cerite-(Ce), which was mined sporadically in the 19th century. This mineral was the source from which a new metal, named cerium, had been isolated by Hisinger & Berzelius (1804). Further discoveries of new elements (*e.g.*, La) and minerals (*e.g.*, bastnäsite, one of the industrially most important lanthanide minerals today) made the locality famous among scientists worldwide.

Ferriallanite-(Ce) from Bastnäs was observed long before its true nature was established. Cronstedt (1781, p. 38) called the mineral "schwarzen Wolfram"; Hisinger & Berzelius (1804) described it as "black hornblende". Later, Hisinger (1811) realized that it was a new Ce-bearing mineral and named it "cerine", and results of a more detailed study, including a partial chemical analysis of this material, were subsequently published (Hisinger 1815). "Cerine" was finally grouped with allanite by von Leonhard (1821). A more complete and reliable wet-chemical analysis was carried out by Cleve (1862).

In this note, we provide additional chemical data from new high-quality electron-microprobe analyses of ferriallanite-(Ce) from this classical locality and results of a reconnaissance analysis by laser-ablation ICP-MS.

## SAMPLE DESCRIPTIONS

Geijer (1921) described the mineral parageneses of the Bastnäs mineralization in some detail. Quartz-banded hematite ore occurs adjacent to a magnetite-skarn ore, the latter replacing a dolomite layer. The cerite ore was worked in two small mines, Ceritgruvan and Sankt Göransgruvan, where it formed a restricted layer (up to 0.6 m thick) in the skarn zone, composed mainly of cerite-(Ce), tremolitic amphibole, allanite-(Ce), bastnäsite-(Ce), törnebohmit-(Ce) and talc. Sulfide minerals, dominantly chalcopyrite, bismuthinite and molybdenite, are closely associated with the lanthanide minerals, and usually are interstitial to them.

Three samples from the mineral collection at the Swedish Museum of Natural History were analyzed, and

they can be considered representative of the different ferriallanite-(Ce) parageneses found at Bastnäs. Sample #882234 consists of coarse-grained ferriallanite-(Ce) forming euhedral crystals up to 8 mm long, together with bastnäsite-(Ce) – bastnäsite-(La) and quartz. They are commonly twinned on {100}. Bismuthinite, chalcopyrite and molybdenite occupy smaller voids between the ferriallanite-(Ce) crystals. Sample #A037 consists of rounded aggregates of fine-grained cerite-(Ce) with lesser amounts of bastnäsite-(Ce), surrounded by margins (up to 5 mm wide) of anhedral, irregular ferriallanite-(Ce) grains. Törnebohmit-(Ce) and a new sorosilicate mineral species, *ca.*  $(\text{Ce,L a})_3\text{CaAl}_2(\text{Fe,Mg})_2[\text{Si}_2\text{O}_7][\text{SiO}_4]_3(\text{O,F})(\text{OH})_2$  (the crystal structure of a more Mg-rich, isostructural mineral was recently solved by Kolitsch *et al.* 2002) are closely associated with the ferriallanite-(Ce). Patches of fluocerite-(Ce), partly altered to cerianite and bastnäsite-(La), occur sporadically in the cerite-bearing assemblage. Sample #390477 consists of euhedral to subhedral crystals of ferriallanite-(Ce) up to 1 mm long, together with cerite-(Ce) crystals, in massive bismuthinite with subordinate chalcopyrite and molybdenite.

Generally, the crystals of ferriallanite-(Ce) in these samples are fresh, *i.e.*, non-metamict and unaltered. As seen on back-scattered electron images, the crystals are relatively homogeneous, in contrast to the pronounced patterns of zonation that commonly are found in hydrothermally precipitated or modified allanite (*e.g.*, Sorensen 1991, Poitrasson 2002). The optical character is biaxial negative, with the pleochroic colors *X* olive green, *Y* brown and *Z* dark reddish brown to nearly opaque.

## ANALYTICAL METHODS AND RESULTS

*Chemical analyses*

Chemical analyses were carried out using a Cameca SX50 electron microprobe in wavelength-dispersion mode at GeoForschungsZentrum, Potsdam, run with an accelerating voltage of 20 kV, a beam current of 40 nA and a beam 3  $\mu\text{m}$  in diameter. We used the following standards: pure synthetic rare-earth-element (REE) phosphates (REEL $\beta$ ),  $\text{YPO}_4$  (YL $\alpha$ )  $\text{Fe}_2\text{O}_3$  (FeK $\alpha$ ),  $\text{MnTiO}_3$  (TiK $\alpha$ ), wollastonite (CaK $\alpha$ , SiK $\alpha$ ),  $\text{Al}_2\text{O}_3$  (AlK $\alpha$ ), MgO (MgK $\alpha$ ), and LiF (FK $\alpha$ ). Each peak was measured for 30 or 50 s (10 and 25 s for the background, respectively). Data reduction was carried out using a Cameca version of the PAP (Pouchou & Pichoir 1991) routine. Na, Cl, Mn, P, Sr, Ba, Th, and U were below the limit of detection ( $\leq 0.05$  wt%) in all cases. Results from seven point analyses of #882234 and values for the two other samples are given in Table 1. The atom proportions given in the table were calculated according to the procedure recently advocated for allanite by Ercit (2002): the sum of the octahedrally and tetrahe-

drally coordinated cations,  $\Sigma(\text{Mg} + \text{Fe} + \text{Ti} + \text{Al} + \text{Si})$ , was normalized to 6 atoms, and  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were partitioned to balance 25 negative charges.

To obtain concentration values for the lanthanides in ferriallanite-(Ce), including those below the level of detection of the electron microprobe, a reconnaissance

TABLE 1. CHEMICAL COMPOSITION OF FERRIALLANITE-(Ce) SAMPLES FROM BASTNÄS

	882234							A037			390477		
	mean <i>n</i> = 7												
La <sub>2</sub> O <sub>3</sub>	8.74	10.72	9.08	11.44	12.41	11.20	11.27	10.69	9.10	10.07	10.17	10.15	10.32
Ce <sub>2</sub> O <sub>3</sub>	13.35	13.82	13.17	13.56	12.89	13.59	13.39	13.40	14.92	14.68	14.91	13.61	13.76
Pr <sub>2</sub> O <sub>3</sub>	1.11	0.88	1.05	0.81	0.83	0.87	0.84	0.91	1.19	0.95	0.98	1.07	0.96
Nd <sub>2</sub> O <sub>3</sub>	3.72	2.20	3.63	2.27	1.86	2.17	2.28	2.59	2.97	2.42	2.47	2.97	2.64
Sm <sub>2</sub> O <sub>3</sub>	0.45	0.08	0.34	0.26	0.09	0.14	0.14	0.21	0.20	0.13	0.17	0.22	0.16
Gd <sub>2</sub> O <sub>3</sub>	0.23	0.10	0.17	0.11	0.12	0.09	0.13	0.14	0.09	0.06	0.03	0.14	0.08
Dy <sub>2</sub> O <sub>3</sub>	0.05	0.00	0.14	0.00	0.00	0.01	0.02	0.03	0.00	0.00	0.02	0.08	0.05
Ho <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.05	0.00	0.07	0.00	0.06	0.03	0.00	0.00	0.00	0.04	0.02
Er <sub>2</sub> O <sub>3</sub>	0.00	0.08	0.08	0.02	0.06	0.07	0.00	0.04	0.00	0.01	0.11	0.13	0.06
Yb <sub>2</sub> O <sub>3</sub>	0.08	0.03	0.02	0.00	0.00	0.00	0.01	0.02	0.05	0.01	0.02	0.06	0.00
Lu <sub>2</sub> O <sub>3</sub>	0.05	0.06	0.01	0.03	0.00	0.03	0.01	0.03	0.02	0.00	0.00	0.07	0.01
MgO	1.45	1.59	0.76	2.57	2.21	2.45	2.01	1.86	1.96	1.97	2.01	2.48	2.57
Al <sub>2</sub> O <sub>3</sub>	7.42	7.05	7.21	7.16	6.71	6.84	7.19	7.08	5.77	5.59	5.80	7.33	7.34
SiO <sub>2</sub>	29.09	28.82	28.41	28.54	28.08	28.18	29.14	28.61	28.55	28.44	28.29	27.98	28.94
Y <sub>2</sub> O <sub>3</sub>	0.24	0.11	0.34	0.15	0.14	0.17	0.14	0.19	0.31	0.13	0.16	0.27	0.23
CaO	8.92	8.69	8.74	8.30	8.25	8.40	8.39	8.53	8.07	8.12	8.08	8.14	8.34
TiO <sub>2</sub>	0.03	0.07	0.03	0.05	0.05	0.05	0.04	0.04	0.01	0.00	0.01	0.08	0.10
FeO	10.65	9.75	11.80	7.74	7.99	7.52	8.62	9.15	9.72	9.23	9.93	8.12	8.14
Fe <sub>2</sub> O <sub>3</sub>	12.38	13.86	12.69	14.11	15.38	15.45	13.97	13.98	14.24	15.03	13.79	13.26	12.59
F	0.23	0.28	0.11	0.49	0.41	0.44	0.29	0.32	0.27	0.28	0.27	0.33	0.42
Sum	98.19	98.19	97.89	97.61	97.56	97.69	97.97	97.87	97.43	97.13	97.21	96.52	96.72
O=F	0.09	0.12	0.05	0.21	0.17	0.19	0.12	0.14	0.11	0.12	0.11	0.14	0.18
Total	98.10	98.07	97.84	97.40	97.39	97.50	97.85	97.74	97.32	97.01	97.09	96.38	96.54
<b>cations</b>													
La	0.332	0.408	0.350	0.437	0.477	0.428	0.427	0.408	0.352	0.391	0.396	0.393	0.395
Ce	0.504	0.522	0.503	0.514	0.492	0.516	0.504	0.508	0.574	0.566	0.576	0.523	0.523
Pr	0.042	0.033	0.040	0.030	0.032	0.033	0.032	0.034	0.046	0.036	0.038	0.041	0.036
Nd	0.137	0.081	0.135	0.084	0.069	0.080	0.084	0.096	0.111	0.091	0.093	0.112	0.098
Sm	0.016	0.003	0.012	0.009	0.003	0.005	0.005	0.008	0.007	0.005	0.006	0.008	0.006
Gd	0.008	0.004	0.006	0.004	0.004	0.003	0.005	0.005	0.003	0.002	0.001	0.005	0.003
Dy	0.002	0.000	0.005	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.001	0.003	0.002
Ho	0.000	0.000	0.002	0.000	0.002	0.000	0.002	0.001	0.000	0.000	0.000	0.001	0.001
Er	0.000	0.003	0.003	0.001	0.002	0.002	0.000	0.001	0.000	0.000	0.004	0.004	0.002
Yb	0.003	0.001	0.001	0.000	0.000	0.000	0.000	0.001	0.002	0.000	0.001	0.002	0.000
Lu	0.002	0.002	0.000	0.001	0.000	0.001	0.000	0.001	0.001	0.000	0.000	0.002	0.000
Mg	0.222	0.245	0.118	0.397	0.343	0.379	0.307	0.287	0.307	0.309	0.316	0.389	0.397
Al	0.901	0.858	0.887	0.873	0.825	0.836	0.872	0.864	0.714	0.694	0.722	0.907	0.898
Si	2.997	2.974	2.964	2.956	2.926	2.922	2.995	2.962	2.998	2.994	2.988	2.937	3.005
Y	0.013	0.006	0.019	0.008	0.008	0.009	0.008	0.010	0.017	0.007	0.009	0.015	0.012
Ca	0.985	0.960	0.977	0.921	0.921	0.933	0.924	0.946	0.908	0.916	0.914	0.915	0.929
Ti	0.002	0.005	0.002	0.004	0.004	0.004	0.003	0.003	0.001	0.000	0.001	0.006	0.007
Fe <sup>2+</sup>	0.917	0.841	1.030	0.670	0.696	0.652	0.741	0.793	0.854	0.813	0.877	0.712	0.707
Fe <sup>3+</sup>	0.960	1.076	0.997	1.100	1.206	1.206	1.080	1.089	1.125	1.191	1.096	1.048	0.984
F	0.074	0.092	0.037	0.160	0.134	0.145	0.093	0.105	0.088	0.093	0.089	0.110	0.139
Σcations	8.041	8.022	8.052	8.009	8.010	8.012	7.991	8.020	8.020	8.015	8.039	8.023	8.006
ΣREE	1.057	1.062	1.075	1.088	1.089	1.078	1.067	1.074	1.113	1.099	1.125	1.109	1.078

*n* = number of point analyses. Compositions are reported in wt.%, and then transformed to atoms per formula unit.

laser-ablation ICP–MS analysis was performed with a Finnigan MAT Element high-resolution ICP–MS (inductively coupled plasma – mass spectrometer) equipped with a MAT UV Laser Probe operated at 266 nm in *ca.* 200 × 100 μm rasters. Instrument settings, laser operation, and data retrieval essentially followed the method of Flem *et al.* (2002). Note that the analysis was done on a chip of ferriallanite-(Ce) that was removed from sample #882234 before the thin section used for electron-microprobe work was prepared. The results thus pertain to different spots and are not directly comparable. The concentrations of the REE, Y, Pb, Th, and U were measured at low mass-resolution (*ca.* 300 m/Δm), whereas major elements, La, Ce, and Pr were measured with a nominal mass-resolution of 3000 m/Δm, thus avoiding both saturation of the detector and most of the mass interferences for the transition elements. Multiple calibration-curves were established using the NIST glass standards 610, 612, 614, the NIST SRM 1830, Soda-Lime Float Glass, and two fused-rock standards (RGM–1 and BCR–2). Calibration and normalization of measured elements were performed with a “total normalization” method developed for major- and trace-element data pertaining to unknown silicate phases. In this method, all measured major elements and REE are evaluated as ratios of Si. The basis of the method is that the sum of the major elements + REE is normalized to 100%, followed by calculation of the Si concentration from the calculated Si/(major element + REE) ratio. The concentrations of all elements are then determined conventionally using Si as internal standard. The advantage of the method is that there is no need for a previously known internal standard. Furthermore, the data can be recalculated using any arbitrary element as internal standard. Calculations using Pr as internal standard yielded similar results for the ferriallanite, whereas the results of the standards deviated significantly owing

to the very low concentrations of Pr. Fused rock standards and NIST standards determined with the method and with Si as an internal standard normally yield major- and trace-element concentrations within 5% and 10% of certified values, respectively.

The results are given in Table 2, together with estimated 1σ uncertainties, calculated using error propagation from the uncertainties in countings of the element and the internal standard, and the uncertainty in the linear calibration curves obtained. As there is no homogeneous and certified standard having high concentrations of the REE suitable for laser-ablation analyses, the absolute concentrations of REE in the ferriallanite-(Ce) can deviate from the true values, as the linearity of the calibration curves may not hold at such high concentrations. This could explain why the LA–ICP–MS analyses generally yield higher concentrations than the electron-microprobe analyses. The normalization and method of calculation will, however, give true relative values (*e.g.*, as shown in the shape of a chondrite-normalized curve).

#### Mössbauer spectroscopy

Mössbauer spectra were obtained from a 20-mg powder sample of #882234, run at magic-angle-geometry (54.7°) at room and liquid N<sub>2</sub> temperatures using a constant-acceleration Mössbauer spectrometer and stored in a 1024-channel analyzer. Velocity calibration in the spectral range of ±4 mm/s was done using a 25-μm foil of α-Fe. Spectral analyses, assuming a thin absorber and a Lorentzian line-shape, were carried out using the software developed by Jernberg & Sundqvist (1983). The absorption peak-area, centroid shift (*CS*), quadrupole splitting (*QS*) and line width (*Γ*) are parameters used to characterize the three absorption doublets present (Table 3); starting parameters were taken from published Mössbauer data for allanite (Dollase 1973). The fitted room-temperature spectrum is given in Figure 1. The low-temperature experiment produced no significant change in spectrum shape, except in that higher values of *CS* (owing to the second-order Doppler effect) were obtained (Table 3). Under the assumption

TABLE 2. CONCENTRATIONS OF SELECTED ELEMENTS IN FERRIALLANITE-(Ce)\* OBTAINED BY LA-ICP-MS

element	(ppm)	oxide	(wt.%)
Y	1337 ±40	Y <sub>2</sub> O <sub>3</sub>	0.17
La	86600 ±2500	La <sub>2</sub> O <sub>3</sub>	10.16
Ce	122200 ±3300	Ce <sub>2</sub> O <sub>3</sub>	14.32
Pr	8100 ±300	Pr <sub>2</sub> O <sub>3</sub>	0.95
Nd	21300 ±610	Nd <sub>2</sub> O <sub>3</sub>	2.48
Sm	2900 ±260	Sm <sub>2</sub> O <sub>3</sub>	0.34
Eu	49 ±4		
Gd	1550 ±130	Gd <sub>2</sub> O <sub>3</sub>	0.18
Tb	104 ±9		
Dy	440 ±40		
Ho	55 ±5		
Er	95 ±9		
Tm	8 ±1		
Yb	38 ±4		
Lu	3.9 ±0.4		
Pb	5.1 ±0.6		
Th	0.25 ±0.03		
U	2.6 ±0.2		

\*Sample #882234, single analysis. Uncertainties are equal to one standard deviation.

TABLE 3. MÖSSBAUER PARAMETERS FOR FERRIALLANITE-(Ce) FROM BASTNÄS

	<i>CS</i> * (mm/s)	<i>QS</i> ** (mm/s)	<i>Γ</i> *** (mm/s)	<i>Abs. area</i> (%)
<b>298 K</b>				
<sup>57</sup> Fe <sup>2+</sup>	0.35	1.81	0.31	50(4)
<sup>57</sup> Fe <sup>3+</sup>	0.33	0.79	0.31	6(2)
<sup>57</sup> Fe <sup>2+</sup>	1.07	1.60	0.31	44(3)
<b>77 K</b>				
<sup>57</sup> Fe <sup>2+</sup>	0.44	1.82	0.32	49(4)
<sup>57</sup> Fe <sup>3+</sup>	0.44	0.81	0.32	5(2)
<sup>57</sup> Fe <sup>2+</sup>	1.17	1.64	0.32	46(3)

\*centroid shift, \*\*quadrupole split, \*\*\* line width.

of identical recoil-free fraction for the crystallographic sites involved, the ratio  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ratio is established as 0.56(4), in excellent agreement with the average value 0.58 obtained by recalculation of the chemical analytical data for the same sample (Table 1).

#### X-ray diffraction data

Powder X-ray-diffraction data were recorded with step ( $0.01^\circ$ ) scans in the  $2\theta$  range 5 to  $75^\circ$  on an automated Philips PW1710 diffractometer using graphite-monochromatized  $\text{CuK}\alpha$  radiation. Peak positions were determined with the X'Pert Graphics & Identify program and corrected against an external silicon powder standard (NBS 640b). The unit-cell parameters of monoclinic ferriallanite-(Ce) from sample #882234, refined from twenty-seven unambiguously indexed reflections using a least-squares program (Novak & Colville 1989), are  $a$  8.941(4) Å,  $b$  5.799(2) Å,  $c$  10.151(6) Å,  $\beta$  114.7(6)°,  $V$  478.2(5) Å<sup>3</sup>.

#### DISCUSSION AND CONCLUSIONS

Assuming an ordered distribution of cations, an averaged structural chemical formula for ferriallanite-(Ce) in sample #882234 (based on the electron-microprobe data in Table 1) can be written as  $A[(\text{Ce}_{0.51}\text{La}_{0.41}\text{Nd}_{0.10}\text{Pr}_{0.03}\text{Y}_{0.01}\text{Sm}_{0.01})_{\Sigma 1.07}\text{Ca}_{0.95}]^{M3}[\text{Fe}^{2+}_{0.79}\text{Mg}_{0.21}]^{M2}[\text{Al}_{0.83}\text{Fe}^{3+}_{0.17}]^{M1}[\text{Fe}^{3+}_{0.92}\text{Mg}_{0.08}]^T[\text{Si}_{2.96}\text{Al}_{0.04}]\text{O}_{12}(\text{OH}_{0.90}\text{F}_{0.10})$ , following the standard site-nomenclature (e.g., Deer *et al.* 1997) and recommended site-assignment procedures for the epidote group (Ercit 2002). An independent measure of the correctness of this expression is given by the  $^{M2}[\text{Fe}^{3+}]/^{M1}[\text{Fe}^{3+}]$  ratio obtained from Mössbauer data; the value is 0.12(4), to be compared to the one calculated directly from the structural formula, 0.19. The assumption that Al is ordered at  $M2$  and  $\text{Fe}^{3+}$  at  $M1$  thus appears acceptable.

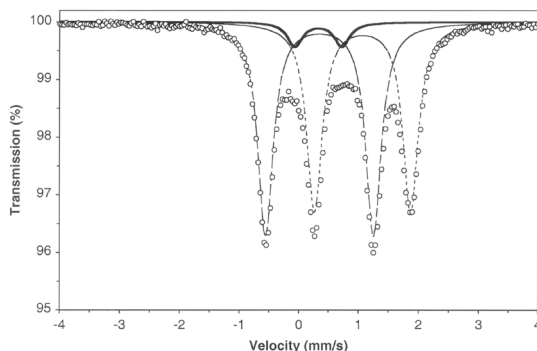


FIG. 1. Fitted Mössbauer spectrum of ferriallanite-(Ce). Dashed and solid curves are the  $^{M1}\text{Fe}^{3+}$  and  $^{M2}\text{Fe}^{3+}$  subspectra, respectively. The finely dashed curve represents  $^{M3}\text{Fe}^{2+}$ .

Chemical substitutions in allanite are commonly reported to mainly follow the cation exchange  $\text{Ca} + (\text{Al} + \text{Fe})^{3+} \leftrightarrow \text{REE}^{3+} + (\text{Fe} + \text{Mg})^{2+}$  (e.g., Sorensen 1991, Peterson & MacFarlane 1993, Petrik *et al.* 1995, Ercit 2002), which shows very limited variation in the Bastnäs samples. Instead, the fluctuation in  $\text{Fe}^{2+}$  observed (Table 1) is best explained by a simple homovalent exchange with  $\text{Mg}^{2+}$ . In combination with a less strong variation in the  $\text{Fe}^{3+}/\text{Al}$  ratio, most of the compositional variation can be described in terms of solid solutions between four principal end-members,  $\text{CeCaFe}^{2+}\text{AlFe}^{3+}\text{Si}_3\text{O}_{12}(\text{OH})$  [ferriallanite-(Ce)],  $\text{CeCaMgAlFe}^{3+}\text{Si}_3\text{O}_{12}(\text{OH})$ ,  $\text{CeCaFe}^{2+}\text{Fe}^{3+}_2\text{Si}_3\text{O}_{12}(\text{OH})$  and  $\text{CeCaMgFe}^{3+}_2\text{Si}_3\text{O}_{12}(\text{OH})$ . The composition of the present samples has been plotted in terms of  $\text{Fe}^{3+}/(\text{Fe}^{3+} + {}^{\text{VI}}\text{Al})$  versus  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ , together with the data of Kartashov *et al.* (2002) for comparison (Fig. 2). The amount of octahedrally coordinated Al is estimated as  ${}^{\text{VI}}\text{Al} = \text{Al} - (3 - \text{Si})$ .

Note that the contents of the A1 and A2 sites are grouped together in the structural formula above; although we can expect that Ca is essentially confined to A1 (Dollase 1971), it is not possible to predict how the individual lanthanide cations will be distributed. The chemical data clearly show that the A sites are fully occupied in ferriallanite-(Ce) from Bastnäs, and that the present specimens are exceptional among allanite-subgroup minerals in their high lanthanide content; a search of the literature in fact suggests that compositions with

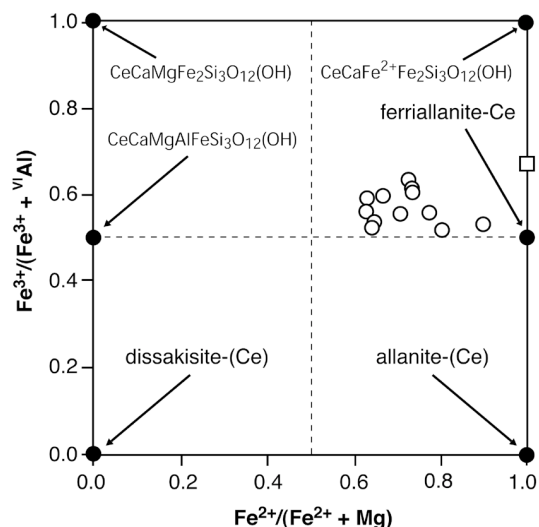


FIG. 2. Compositional variations in ferriallanite-(Ce) from Bastnäs, expressed as  $\text{Fe}^{3+}/(\text{Fe}^{3+} + {}^{\text{VI}}\text{Al})$  plotted against  $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ . Open circles are the measured samples; filled circles correspond to ideal end-members. The open square corresponds to type ferriallanite-(Ce), described by Kartashov *et al.* (2002).

$\Sigma\text{REE} > 1$  atom per formula unit (*apfu*) are rare (*e.g.*, Deer *et al.* 1997). The samples are also unusual in their extremely low Th contents (below 1 ppm according to the LA-ICP-MS analysis), a feature that is typical for all REE-minerals in Bastnäs and a result of the petroge- netic history of the deposit.

The likely charge-compensating exchange mechanisms that allow an excess of  $\text{REE}^{3+}$  in the structure are  $\text{Al} \leftrightarrow \text{Si}$  at the *T* site (Ercit 2002) and  $\text{Mg} \leftrightarrow \text{Fe}^{3+}$  at *M1*. Although  $\Sigma\text{REE}$  is relatively constant in the present population of samples (1.06–1.12 *apfu*), there is a wide variation, even within samples, in the overall lanthanide proportions and amounts. The Ce/La values (atomic) range from 1.03 to 1.63, and some points approach a theoretical, La-dominant type of ferriallanite (Fig. 3). The chondrite-normalized REE pattern of ferriallanite-(Ce) is shown in Figure 4; the pattern is similar to what is normally found for unaltered allanite-(Ce), with a negative Eu anomaly and a smooth decrease in abundance with decreasing ionic radius (*e.g.*, Gieré 1996, Deer *et al.* 1997). The analyzed specimens contain a significant amount of fluorine, but the role of the  $\text{F}^-$  anion in ferriallanite-(Ce) is not clear. A positive relationship, with the linear correlation coefficient  $r = 0.90$ , exists for Mg *versus* F (Fig. 5), and at first sight seems to suggest a dollaseite-type substitution (Peacor & Dunn 1988), but the value obtained for the slope (2.1) is not compatible with a exchange mechanism of the type  $\text{Mg}^{2+} + \text{F}^- \leftrightarrow \text{M}^{3+} + \text{O}^{2-}$ , and there is no corresponding

negative correlation for the trivalent cations. Instead, the observed pattern is possibly an expression of the “iron–fluorine avoidance” encountered in some  $\text{Fe}^{2+}$ -bearing silicates where there is an opportunity for  $\text{F} \leftrightarrow \text{OH}$  substitution (Rosenberg & Foit 1977), and for that reason  $\text{F}^-$  is provisionally grouped with  $\text{OH}^-$  in the structural formula given above.

In summary, ferriallanite-(Ce) from the Bastnäs deposit mainly differs from the type material (Kartashov *et al.* 2002) in its higher contents of REE, Mg and F, and lower level of Ca. The specimens from Ulyn Khuren are exceptional (for an epidote-group mineral) in their apparent total lack of Mg. The slightly smaller unit-cell volume of sample #882234 ( $478.2 \text{ \AA}^3$ ) compared to the type specimen ( $482.6 \text{ \AA}^3$ ) is consistent with its lower

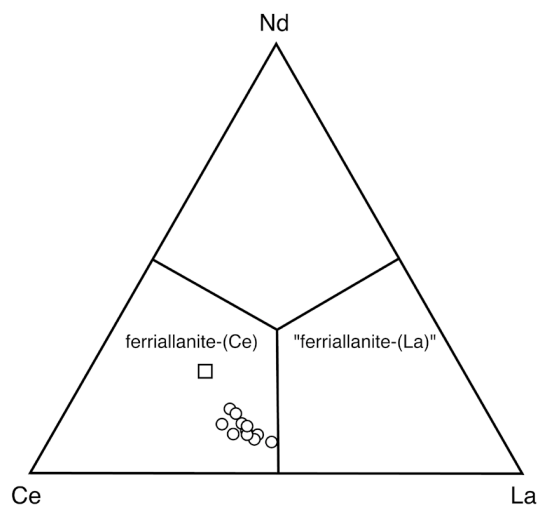


FIG. 3. Triangular plot showing the composition of ferriallanite-(Ce) from Bastnäs, in terms of the three dominant lanthanide cations Ce, La and Nd. The open square corresponds to type ferriallanite-(Ce), described by Kartashov *et al.* (2002).

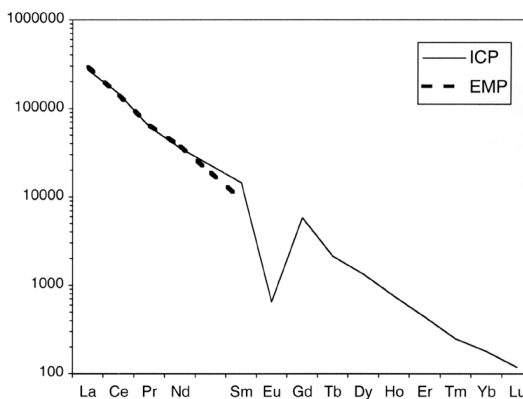


FIG. 4. Chondrite-normalized REE patterns for ferriallanite-(Ce), based on electron-microprobe (EMP) and laser-ablation ICP-MS measurements. Abundances in chondrite were taken from Boynton (1984).

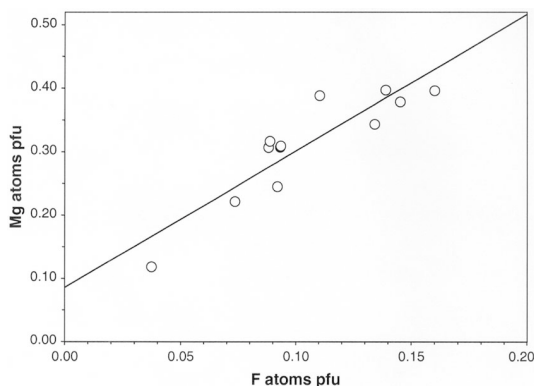


FIG. 5. Plot of Mg *versus* F in ferriallanite-(Ce). The regression line is given by  $y = 0.086 + 2.15x$ , and  $r$  is equal to 0.90.

Fe<sup>2+</sup>/Mg and Fe<sup>3+</sup>/Al values, given the relative sizes of those cations.

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