

Delhuyarite-(Ce) – $\text{Ce}_4\text{Mg}(\text{Fe}^{3+}_2\text{W})\square(\text{Si}_2\text{O}_7)_2\text{O}_6(\text{OH})_2$ – a new mineral of the chevkinite group, from the Nya Bastnäs Fe–Cu–REE deposit, Sweden

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Abstract: Delhuyarite-(Ce) is a new mineral (IMA no. 2016-091) with ideal formula $\text{Ce}_4\text{Mg}(\text{Fe}^{3+}_2\text{W})\square(\text{Si}_2\text{O}_7)_2\text{O}_6(\text{OH})_2$. It is named after Juan and Fausto de Elhuyar (Delhuyar), chemists and metallurgists, who in 1783 isolated tungsten metal for the first time. Associated minerals in the only known sample, from the Nya Bastnäs Fe–Cu–REE deposit (Västmanland, Sweden), include cerite-(Ce), tremolite–actinolite, percleveite-(Ce), bastnäsite-(Ce), ferriallanite-(Ce), törnebohmitite-(Ce), magnetite, chalcopyrite, quartz and scheelite. Delhuyarite-(Ce), which forms subhedral crystals up to 0.3 mm long, is brown–black with a dark brown streak and translucent with an adamantine lustre. It is pleochroic in black to rust red and optically biaxial (–). Calculated density and mean refractive index are $5.20 \text{ g}\cdot\text{cm}^{-3}$ and 1.94, respectively. Chemical analyses (electron microprobe) gave (in wt%) La_2O_3 14.58, Ce_2O_3 23.29, Pr_2O_3 1.89, Nd_2O_3 6.13, Sm_2O_3 0.74, Gd_2O_3 0.37, Dy_2O_3 0.03, Er_2O_3 0.04, Yb_2O_3 0.12, Y_2O_3 0.22, CaO 0.76, Fe_2O_3 12.86, MgO 2.43, Al_2O_3 0.73, SiO_2 18.16, TiO_2 0.09, WO_3 15.53, $\text{H}_2\text{O}_{\text{calc}}$ 1.33, F 0.05, Cl 0.03, O=(F, Cl) –0.03, sum 99.35, corresponding to an empirical formula: $(\text{Ce}_{1.89}\text{La}_{1.19}\text{Nd}_{0.48}\text{Pr}_{0.15}\text{Sm}_{0.06}\text{Gd}_{0.03}\text{Y}_{0.03}\text{Ca}_{0.18})_{\Sigma 4.01}(\text{Fe}^{3+}_{2.14}\text{W}_{0.89}\text{Mg}_{0.80}\text{Al}_{0.19}\text{Ti}_{0.02})_{\Sigma 4.04}\text{Si}_{4.01}\text{O}_{20}(\text{OH}_{1.96}\text{F}_{0.04})_{\Sigma 2}$, based on 22 O atoms per formula unit (apfu). The presence of H_2O is confirmed by IR-spectroscopy, from a strong absorption band at 3495 cm^{-1} . Delhuyarite-(Ce) is monoclinic, space group $C2/m$, with unit-cell parameters $a = 13.6020(6) \text{ \AA}$, $b = 5.7445(3) \text{ \AA}$, $c = 10.9996(5) \text{ \AA}$, $\beta = 100.721(4)^\circ$, $V = 844.47(6) \text{ \AA}^3$ and $Z = 2$ (data for natural crystal). The crystal structure was refined to an R_1 index of 3.9% (natural crystal) and 1.8% (annealed). Delhuyarite-(Ce) has the same structural topology as chevkinite-subgroup minerals, e.g. chevkinite-(Ce). It is the only mineral of the group with a significant content of $\text{W}^{6+} = 0.89$ apfu. In delhuyarite-(Ce), Mg is dominant at the $M1$ site as in polyakovite-(Ce); the composition of the $M2$, $M3$ and $M4$ sites is $[(\text{Fe}^{3+}_2\text{W}\square)]$, with $M2$ being 50% vacant.

Key-words: delhuyarite-(Ce); new mineral species; crystal structure; electron microprobe analysis; REE silicate; tungsten; chevkinite group; Bastnäs; Sweden.

1. Introduction

The Nya Bastnäs deposit is one among a group of small rare-earth element (REE) deposits, referred to as of ‘Bastnäs-type’ (Geijer, 1961), occurring along an 80-km-long zone in strongly altered Svecofennian (Orosirian) volcano-sedimentary and plutonic rocks in the Bergslagen ore province, south-central Sweden. The deposits comprise REE silicates and fluorocarbonates in association with major iron oxides (including historically economic magnetite concentrations), calcic amphibole skarns and minor Cu–Mo–Bi–Co–Au–Ag compounds and alloys (Geijer, 1921, 1927; Holtstam & Ensterö, 2002; Holtstam & Andersson, 2007). More than 20 REE minerals have been reported – with Nya Bastnäs as type-locality for cerite-(Ce), bastnäsite-(Ce), törnebohmitite-(Ce), percleveite-(Ce) and hāleniusite-(La) – and a few unknowns still await full characterization and recognition. Generally, the deposits are metasomatic skarn mineralizations (exoskarns).

Based on fluid-inclusion studies and stable and radiogenic isotope data, Holtstam *et al.* (2014) concluded that REE deposition occurred during an extended time interval 1.90–1.84 Ga ago, from hot (initially $\geq 400^\circ\text{C}$), originally juvenile magmatic fluids carrying Si, F, Cl, S, CO_2 and REE in addition to other metals, through reactions with pre-existing dolomitic carbonate layers.

2. Occurrence

The new mineral occurs in a single known sample from the Nya Bastnäs Fe–Cu–REE mines, Skinnskatteberg, Västmanland County, Sweden (lat. $59^\circ 50' 47''\text{N}$, long. $15^\circ 35' 15''\text{E}$, 220 m a.s.l.). At this deposit, which is part of the Riddarhyttan ore field, a quartz-banded hematite ore occurs in proximity with a magnetite-skarn ore, the latter replacing a dolomitic carbonate horizon. The dominant host rock is a quartz-rich, cordierite-bearing mica-schist,

interpreted as an extensively metasomatized (Mg–K alteration) and regionally metamorphosed (amphibolite facies) felsic volcanogenic unit originally deposited at *ca.* 1.9 Ga (Trägårdh, 1991; Holtstam *et al.*, 2014).

Mining for iron took place in the area already in late medieval times. The cerium ore at Nya Bastnäs was once worked in two small mines, mainly in the 19th century. It formed restricted bodies – of which the largest reached a width of 0.6 m and a length of *ca.* 7 m – consisting mainly of cerite-(Ce), actinolite, ferriallanite-(Ce), bastnäsite-(Ce)–bastnäsite-(La), törnebohmitte-(Ce) and an unnamed Fe³⁺–O analogue of västmanlandite-(Ce). Chalcopyrite, bismuthinite and molybdenite are closely associated with the REE minerals (Geijer, 1921; Holtstam & Andersson, 2007).

The exact original position of the present sample is unknown since it was found in an old museum specimen lacking any detailed locality information. It is also the type specimen for percleveite-(Ce) (Holtstam *et al.*, 2003a). Identified associated minerals are cerite-(Ce), tremolite–actinolite, bastnäsite-(Ce), magnetite, quartz, chalcopyrite, ferriallanite-(Ce), törnebohmitte-(Ce) and scheelite. The late-formed quartz appears in interstices and microcracks in the REE-mineral assemblage. Minute grains of scheelite (containing about 1 mol% CaMoO₄ in solid solution) occur sparingly, commonly contiguous to delhuyarite-(Ce).

3. Naming and type material

The name honours two prominent mineral chemists and metallurgists, Juan José (1754–1796) and Fausto Fermín (1755–1833) de Elhuyar y de Lubice, brothers who were of French-Basque ancestry and upheld important positions in the mining schools and mining industry of the Spanish Empire (Caswell & Stone Daley, 1999).

Juan de Elhuyar visited several North European seats of learning, including Uppsala University, and while in Sweden he worked with Torbern Bergman and Carl Wilhelm Scheele in 1781–1782. The two Swedish scientists had discovered tungstic acid and tungsten(VI) oxide and assumed they were a new metal on the tracks, before de Elhuyars' isolation of the element tungsten in 1783. Although Bergman and Scheele had investigated scheelite (then known as *Bispbergs tungsten* in Swedish), the Elhuyar brothers used wolframite from Zinnwald, Saxony, in their concluding experiments.

An interesting connection between the Elhuyars and the Nya Bastnäs mines (Trofast, 1996) is that Juan José was one of the first chemists who attempted to analyse cerite-(Ce), at the time called *Bastnäs tungsten*. The cerium-content escaped detection, as it did for Scheele in his contemporaneous efforts, and the new element was not described until 20 years later, by Hisinger & Berzelius (1804).

The surname is sometimes spelled D'Elhuyar or Delhuyar (the brothers were themselves not consistent in this respect). 'Elhuyarite' is an old synonym for allophane (Glocker, 1839). The Levinson suffix -(Ce) is motivated by the preponderance of cerium. We therefore

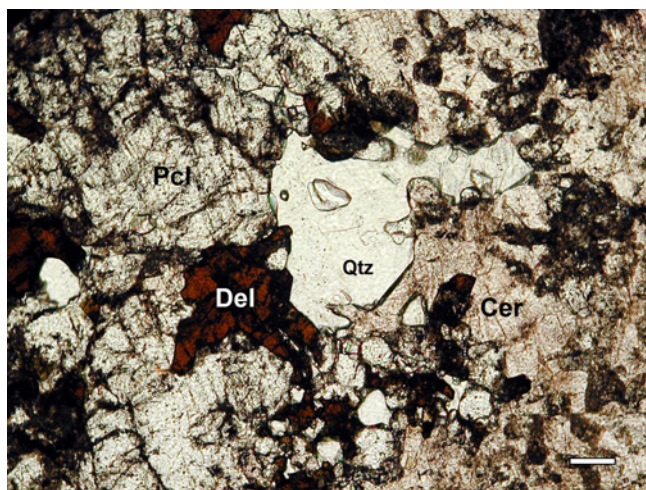


Fig. 1. Microphotograph of the type specimen of delhuyarite-(Ce), in polarized transmitted light. It shows the largest grain of delhuyarite-(Ce) [Del] found in the thin (30 μm) section. Associated minerals are cerite-(Ce) [Cer], percleveite-(Ce) [Pcl] and quartz [Qtz]. Length of white bar corresponds to 100 μm . Sample #NRM19060375. (Online version in colour.)

suggested the name delhuyarite-(Ce) for the new mineral, which has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA no. 2016-091). Delhuyarite-(Ce) is identical with unnamed 'mineral C' of Holtstam & Andersson (2007), which corresponds to UM2007-041 in the list of valid unnamed mineral species (Smith & Nickel, 2007).

The holotype material, including a polished thin section, is preserved in the mineral collections of the Department of Geosciences, Swedish Museum of Natural History, Sweden, under collection number NRM 19060375 [same as for percleveite-(Ce)].

4. Physical and optical properties

Delhuyarite-(Ce) is rare in the sample and forms subhedral, irregular to prismatic crystals up to 0.06×0.3 mm (Fig. 1), appearing essentially isolated in a mass of cerite-(Ce) and percleveite-(Ce). According to our interpretation of the textural relations, it is likely that delhuyarite-(Ce) formed after the main REE silicates. The colour of the new mineral is brown-black, with a dark brown streak. The crystals are translucent, with adamantine lustre. No cleavage has been observed; fracture is irregular to sub-conchoidal. Mohs hardness is estimated at $H = 5\text{--}6$, by analogy with chevkinite-group minerals. The density could not be measured because of the minute size of the crystals in combination with paucity of material; a calculated value from chemical analytical data and single-crystal X-ray diffraction data (see below) is $5.196 \text{ g}\cdot\text{cm}^{-3}$.

The strong absorption and high refraction of the crystals did not allow a complete determination of the optical properties. From the Gladstone–Dale relationship

Table 1. Chemical composition of the analysed grain of delhuyarite-(Ce).

Constituent	Mean	Range
SiO ₂	18.16	17.47–18.89
TiO ₂	0.09	0.07–0.12
Al ₂ O ₃	0.73	0.50–0.88
Fe ₂ O ₃ ^a	12.86	12.23–14.11
WO ₃	15.53	15.21–16.01
MgO	2.43	2.17–2.67
CaO	0.76	0.69–0.93
La ₂ O ₃	14.58	13.70–15.06
Ce ₂ O ₃	23.29	23.14–23.40
Pr ₂ O ₃	1.89	1.84–1.94
Nd ₂ O ₃	6.13	5.96–6.34
Sm ₂ O ₃	0.74	0.67–0.82
Gd ₂ O ₃	0.37	0.31–0.40
Dy ₂ O ₃	0.03	0.00–0.09
Er ₂ O ₃	0.04	0.00–0.06
Yb ₂ O ₃	0.12	0.10–0.17
Y ₂ O ₃	0.22	0.12–0.38
H ₂ O ^b	1.33	–
F	0.05	0.03–0.06
Cl	0.03	0.02–0.03
O=F	–0.02	
O=Cl	–0.01	
Total	99.35	

^a All Fe is considered to be trivalent, from bond-distances (see text) and charge-balance calculation; ^b Using 2 (OH,F).

(Mandarino, 1981), an average index of refraction of 1.94 is predicted. Delhuyarite-(Ce) is optically biaxial (–), with strong pleochroism, in rust-red to nearly opaque.

5. Chemical and spectroscopic data

The chemical composition of the new mineral was determined using quantitative wavelength-dispersion analyses on a Cameca SX50 electron microprobe (EMP) run with an accelerating voltage of 20 kV, a beam current of 40 nA and a 3- μ m beam diameter. Standards used were pure synthetic REE phosphates (REEL α or REEL β), YPO₄ (YL α) Fe₂O₃ (FeK α), W metal (WL α), MnTiO₃ (TiK α), wollastonite (Ca, SiK α), Al₂O₃ (AlK α), MgO (MgK α), tugtupite (ClK α) and LiF (FK α). Each peak was measured for 30 or 50 s.

The Na, K, P, Sr, Ba, Mn, Th, U, Zr, Nb, Ho, Lu contents were found to be below the limits of detection (<0.01 wt %). Note that the concentration of Eu cannot be measured with the technique employed here, owing to interference with some of the other light REE. Further details on the experimental procedure and data treatment are given by Holtstam & Andersson (2007). Results from four point analyses of a grain in the type specimen are given in Table 1. As there was insufficient material for conventional C–H–N analyses, the H₂O concentration was calculated on the basis of 2 (OH[–],F[–]) per formula unit (*pfu*); see structure determination below. The empirical formula (based on 22 O atoms *pfu*) is (Ce_{1.89}La_{1.19}Nd_{0.48}Pr_{0.15}Sm_{0.06}Gd_{0.03}Y_{0.03}Ca_{0.18}) Σ 4.01(Fe³⁺_{2.14}W_{0.89}Mg_{0.80}Al_{0.19}Ti_{0.02}) Σ 4.04Si_{4.01}O₂₀(OH_{1.96}F_{0.04}) Σ 2.00.

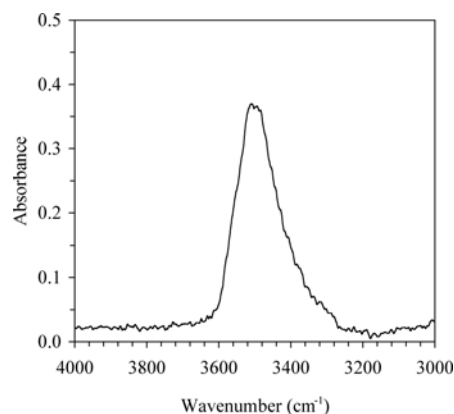


Fig. 2. Unpolarized, room-temperature FTIR spectrum of delhuyarite-(Ce) in the OH-stretching region.

A simplified, idealized formula is given as Ce₄Mg(Fe³⁺₂W) \square (Si₂O₇)₂O₆(OH)₂, which corresponds to (in wt%) 48.75 Ce₂O₃, 2.99 MgO, 11.86 Fe₂O₃, 17.22 WO₃, 17.84 SiO₂ and 1.34 H₂O, with a total of 100.00 wt%.

Fourier transform infrared (FTIR) spectroscopy was used to collect an unpolarized single-crystal spectrum (Fig. 2) in the range 2000–5000 cm^{–1} from a 30 \times 30 μ m area of a grain in a thin section (thickness = 30 μ m) with a Bruker Vertex 70 spectrometer attached to a Bruker Hyperion2000 IR-microscope at a spectral resolution of 2 cm^{–1}. The spectrum shows the presence of significant amounts of OH groups manifested by a strong OH stretching band at 3495 cm^{–1}. There is thus only one kind of OH $\cdot \cdot \cdot$ O bond and, accordingly, a unique OH-group is expected in the structure.

6. Crystal structure

6.1. Data collection and refinement

A single crystal fragment (0.035 \times 0.050 \times 0.055, in mm) of delhuyarite-(Ce) was studied using an Oxford Diffraction Xcalibur 3 diffractometer at room temperature, with MoK α radiation. The detector to crystal distance was 50 mm. A total of 803 frames were collected using ω scan mode, in 0.5° slices, with an exposure time of 50 s per frame. The data were corrected for Lorentz and polarization factors and absorption using the package of software *Crysalis* (Oxford Diffraction, 2006). The statistical tests on the distribution of $|E|$ values ($|E^2 - 1| = 0.868$) and the systematic absences suggested the space group *C2/m*. The refined cell parameters are $a = 13.6020(6)$, $b = 5.7445(3)$, $c = 10.9996(5)$ Å, $\beta = 100.721(4)^\circ$, $V = 844.47(6)$ Å³.

At this point, it was realized that delhuyarite-(Ce) could be a new member of the chevkinite group (e.g. Sokolova *et al.*, 2004). The crystal structure was refined using SHELX-97 (Sheldrick, 2008) starting from the atomic coordinates given by Sokolova *et al.* (2004). Scattering curves for neutral atoms were taken from the *International Tables for X-ray Crystallography* (Wilson, 1992). After several cycles of isotropic refinement, the R_1 converged to 0.097; by refining the anisotropic displacement parameters

Table 2. Crystallographic data and refinement parameters for the selected, heat-treated crystal of delhuyarite-(Ce).

<i>Crystal data</i>	
Ideal formula	Ce ₄ Mg(Fe ³⁺ ,W) ₃ □(Si ₂ O ₇) ₂ O ₆ (OH) ₂
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>m</i>
Unit-cell parameters (Å)	<i>a</i> = 13.5559(5), <i>b</i> = 5.7023(2) <i>c</i> = 10.9485(4), β = 100.481(4)
Unit-cell volume (Å ³)	832.20(5)
<i>Z</i>	2
Crystal size (mm)	0.035 × 0.050 × 0.055
<i>Data collection</i>	
Diffractometer	Oxford Diffraction Xcalibur 3
Temperature (K)	293(2)
Radiation, wavelength (Å)	MoKα, 0.71073
(sinθ/λ) _{max} (Å ⁻¹)	0.761
Crystal-detector dist. (mm)	60
<i>h</i> , <i>k</i> , <i>l</i> ranges	−19−19, −8−8, −16−16
Axis, frames, width (°), time per frame (s)	ω, 1021, 1.00, 50
Total reflections collected	5624
Unique reflections (<i>R</i> _{int})	1523 (0.026)
Unique reflections <i>I</i> > 2σ(<i>I</i>)	1213
Data completeness to θ _{max} (%)	99.9
Absorption correction method	Multi-scan
<i>Structure refinement</i>	
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1213/0/106
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.017
<i>R</i> ₁ all	0.020
Goodness-of-fit on <i>F</i> ²	1.087
Largest diff. peak and hole (e ⁻ /Å ³)	1.31, −2.46

for the metals only, the refinement yielded to a *R*₁ value of 0.072, thus confirming the correctness of the structural model. Successive cycles of refinement converged to *R*₁ = 0.039, with an anisotropic model for all the atoms.

At this stage, a careful analysis of the mean electron numbers (m.e.n.s.) obtained at the structural sites indicated a major discrepancy between the number of electrons at the *M* sites determined directly from site-scattering refinement and those derived from the chemical composition determined by electron-microprobe analysis (EMPA): there is about 5% difference between these two values (140.7 *versus* 133.0 *epfu*, respectively). This difference is much larger than expected for these two methods. As observed by Sokolova *et al.* (2004) for chevkinite-(Ce), we began to suspect that delhuyarite-(Ce) may not be completely crystalline, as partial metamictization can affect the X-ray scattering characteristics of crystals (*e.g.* Hawthorne *et al.*, 1991). Thus, the crystal was annealed under inert atmosphere (N₂) for 20 h at 800 °C using a gas-mixing vertical furnace, and a new data collection was carried out. Following data reduction, a new refinement was performed, starting from the previous model. Crystallographic data and refinement parameters for the heat-treated crystal are reported in Table 2. A comparison between the atomic coordinates, m.e.n.s. and anisotropic

Table 3. Site, mean electron number, atom coordinates and isotropic temperature factors (Å²) for delhuyarite-(Ce) before and after thermal treatment.

Atom	Electr. number	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^{iso}
<i>A</i> 1	55.56(2)	0.35274(3)	0	0.73349(4)	0.0180(2)
<i>A</i> 2	55.45(2)	0.07035(3)	0	0.74109(4)	0.0214(2)
<i>M</i> 1	21.98(2)	½	0	½	0.0193(6)
<i>M</i> 2	21.92(2)	¼	¼	0	0.0259(4)
<i>M</i> 3	33.76(2)	0	0	0	0.0158(3)
<i>M</i> 4	41.12(2)	½	0	0	0.0217(3)
Si1	0.2011(2)	½	0.7306(2)	0.0097(4)	0.0100(4)
Si2	0.3586(2)	½	0.5482(2)	0.0100(4)	0.0212(9)
O1	0.4779(3)	0.2492(7)	0.8716(3)	0.0212(9)	0.020(1)
O2	0.1436(4)	0	0.9772(5)	0.020(1)	0.016(1)
O3	0.1851(4)	0	0.5967(5)	0.016(1)	0.017(1)
O4	0.3520(4)	0	0.9868(4)	0.017(1)	0.024(1)
O5	0.4259(3)	0.2716(8)	0.5954(4)	0.024(1)	0.0175(8)
O6	0.2278(3)	0.2647(6)	0.8131(3)	0.0175(8)	0.032(4)
O7	0.0866(4)	½	0.6679(5)	0.032(4)	0.042(2)
O8	0.2705(5)	½	0.6278(6)	0.042(2)	
<i>After annealing</i>					
<i>A</i> 1	55.33(2)	0.35278(4)	0	0.73348(4)	0.0164(2)
<i>A</i> 2	55.62(2)	0.07041(3)	0	0.74104(4)	0.0198(2)
<i>M</i> 1	20.59(2)	½	0	½	0.0181(6)
<i>M</i> 2	20.76(2)	¼	¼	0	0.0224(5)
<i>M</i> 3	31.15(2)	0	0	0	0.0142(4)
<i>M</i> 4	39.50(2)	½	0	0	0.0200(3)
Si1	0.2010(2)	½	0.7306(2)	0.0090(4)	0.0097(5)
Si2	0.3588(2)	½	0.5481(2)	0.0097(5)	0.0184(9)
O1	0.4772(3)	0.2498(7)	0.8702(3)	0.0184(9)	0.022(1)
O2	0.1431(4)	0	0.9767(5)	0.022(1)	0.013(1)
O3	0.1854(4)	0	0.5970(4)	0.013(1)	0.017(1)
O4	0.3508(4)	0	0.9866(5)	0.017(1)	0.024(1)
O5	0.4273(3)	0.2689(8)	0.5882(3)	0.024(1)	0.0149(8)
O6	0.2269(3)	0.2641(6)	0.8126(3)	0.0149(8)	0.0314(8)
O7	0.0866(4)	½	0.6632(5)	0.0314(8)	0.040(2)
O8	0.2693(5)	½	0.6272(6)	0.040(2)	

displacement parameters for the untreated and heat-treated crystal are given in Tables 3 and 4. The refined unit-cell values for the heated crystal are *a* = 13.5559(5), *b* = 5.7023(2), *c* = 10.9485(4) Å, β = 100.481(4)°, *V* = 832.20(5) Å³ and imply a small contraction (about 1%) typical of slightly metamict material. The new refinement was converged to *R*₁ = 0.017, with an anisotropic model for all the atoms. Unfortunately, no H atoms could be located in the difference Fourier maps.

A comparison of the m.e.n. at the *A* and *M* sites obtained in the new refinement with those calculated from the chemical data (with the cation distribution reported above) gives an excellent match: m.e.n. at the *A* sites (from EMPA) = 108.1 e⁻ *versus* m.e.n. at the *A* sites (from X-ray) = 110.9 e⁻; m.e.n. at the *M* sites (from EMPA) = 133.0 e⁻ *versus* m.e.n. at the *M* sites (from X-ray) = 132.8 e⁻. At this stage, we also tried to distribute the different cations in the five octahedral sites (*M*1, *2M*2, *M*3 and *M*4) taking into account the observed m.e.n. at the sites and the mean polyhedral bond distances (Table 5), and comparing them with the calculated values from the sum

Table 4. Atom anisotropic displacement parameters (\AA^2) for delhuyarite-(Ce) before and after thermal treatment.

Site	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
A1	0.0170(2)	0.0174(3)	0.0214(3)	0	0.0084(2)	0
A2	0.0116(2)	0.0356(3)	0.0159(2)	0	-0.0004(2)	0
M1	0.0236(9)	0.018(1)	0.0155(9)	0	0.0020(6)	0
M2	0.0412(9)	0.0194(7)	0.0158(6)	0.0018(6)	0.0022(5)	-0.0015(5)
M3	0.0123(5)	0.0274(7)	0.0081(5)	0	0.0032(3)	0
M4	0.0109(4)	0.0453(7)	0.0089(4)	0	0.0016(3)	0
Si1	0.0115(9)	0.0074(9)	0.0104(9)	0	0.0027(7)	0
Si2	0.0112(9)	0.010(1)	0.0086(8)	0	0.0013(7)	0
O1	0.021(2)	0.028(2)	0.016(2)	-0.009(2)	0.005(2)	-0.001(2)
O2	0.022(3)	0.024(3)	0.016(3)	0	0.005(2)	0
O3	0.020(3)	0.014(3)	0.011(2)	0	-0.002(2)	0
O4	0.018(3)	0.018(3)	0.014(2)	0	0.004(2)	0
O5	0.030(2)	0.023(2)	0.016(2)	0.009(2)	-0.001(2)	0.002(2)
O6	0.029(2)	0.011(2)	0.012(2)	0.005(2)	0.003(1)	0.001(2)
O7	0.010(3)	0.067(5)	0.017(3)	0	0.000(2)	0
O8	0.029(4)	0.078(6)	0.025(3)	0	0.019(3)	0
<i>After annealing</i>						
A1	0.0169(2)	0.0171(3)	0.0171(3)	0	0.0085(2)	0
A2	0.0115(2)	0.0349(3)	0.0120(2)	0	-0.0003(2)	0
M1	0.025(1)	0.017(1)	0.0116(9)	0	0.0026(7)	0
M2	0.0394(9)	0.0160(7)	0.0110(6)	0.0022(6)	0.0025(5)	-0.0012(5)
M3	0.0129(6)	0.0261(7)	0.0042(5)	0	0.0033(4)	0
M4	0.0111(4)	0.0438(7)	0.0051(4)	0	0.0017(3)	0
Si1	0.014(1)	0.0072(9)	0.0068(9)	0	0.0038(7)	0
Si2	0.0136(9)	0.012(1)	0.0033(8)	0	0.0015(7)	0
O1	0.019(2)	0.024(2)	0.013(2)	-0.013(2)	0.006(2)	-0.005(2)
O2	0.023(3)	0.033(4)	0.010(3)	0	0.006(2)	0
O3	0.016(3)	0.014(3)	0.007(2)	0	-0.002(2)	0
O4	0.024(3)	0.019(3)	0.009(2)	0	0.005(2)	0
O5	0.035(2)	0.024(2)	0.010(2)	0.009(2)	-0.001(2)	0.004(2)
O6	0.031(2)	0.008(2)	0.006(2)	0.003(2)	0.004(1)	0.001(1)
O7	0.011(3)	0.069(5)	0.013(3)	0	-0.002(2)	0
O8	0.032(4)	0.075(6)	0.020(3)	0	0.020(3)	0

Table 5. Selected bond distances (\AA) for delhuyarite-(Ce) after thermal treatment.

A1–O3	2.479(5)	M3–O1 ($\times 4$)	1.998(4)
A1–O1 ($\times 2$)	2.489(4)	M3–O2 ($\times 2$)	2.002(6)
A1–O6 ($\times 2$)	2.543(4)	$\langle M3-O \rangle$	1.999
A1–O5 ($\times 2$)	2.547(4)		
A1–O4	2.776(5)	M4–O1 ($\times 4$)	1.996(4)
$\langle A1-O \rangle$	2.552	M4–O4 ($\times 2$)	2.001(6)
		$\langle M4-O \rangle$	1.998
A2–O3	2.411(5)		
A2–O1 ($\times 2$)	2.507(4)	Si1–O8	1.587(6)
A2–O2	2.589(5)	Si1–O7	1.591(6)
A2–O6 ($\times 2$)	2.603(4)	Si1–O6 ($\times 2$)	1.620(4)
A2–O5 ($\times 2$)	2.668(4)	$\langle Si1-O \rangle$	1.605
$\langle A2-O \rangle$	2.570		
		Si2–O3	1.592(5)
M1–O7 ($\times 2$)	1.951(5)	Si2–O8	1.614(6)
M1–O5 ($\times 4$)	2.145(4)	Si2–O5 ($\times 2$)	1.627(4)
$\langle M1-O \rangle$	2.080	$\langle Si2-O \rangle$	1.615
M2–O4 ($\times 2$)	1.999(4)		
M2–O2 ($\times 2$)	2.016(4)		
M2–O6 ($\times 2$)	2.020(3)		
$\langle M2-O \rangle$	2.012		

Table 6. Mean observed and calculated electron numbers and bond distances in the structure of delhuyarite (heat-treated crystal) according to the proposed site-assignment of the cations.

Site	Composition	e^-_{EMPA}	$e^-_{\text{X-ray}}$	$\langle M-O \rangle_{\text{calc}}$	$\langle M-O \rangle_{\text{obs}}$
M1	$[\text{Mg}_{0.80}\text{W}_{0.12}\text{Fe}^{3+}_{0.08}]$	20.56	20.59	2.080	2.080
M2	$[\text{Fe}^{3+}_{0.67}\text{W}_{0.33}\square_{1.00}]$	41.84	41.52	*	2.012
M3	$[\text{Fe}^{3+}_{0.64}\text{Al}_{0.19}\text{W}_{0.16}\text{Ti}_{0.01}]$	31.17	31.15	1.997	1.999
M4	$[\text{Fe}^{3+}_{0.72}\text{W}_{0.28}]$	39.44	39.50	2.012	1.998

*Calculated value cannot be obtained because of the presence of a structural vacancy.

of ionic radii taken from Shannon (1976). The proposed cation distribution presented in Table 6 shows an excellent match between both observed and calculated bond distances and observed and calculated m.e.n.s.

6.2. Atomic arrangement

In the crystal structure of delhuyarite-(Ce) (Fig. 3), there are two crystallographically distinct rutile-like chains of octahedra ($[M3 + M4]$ and $[M2 + M2]$) that extend in the b

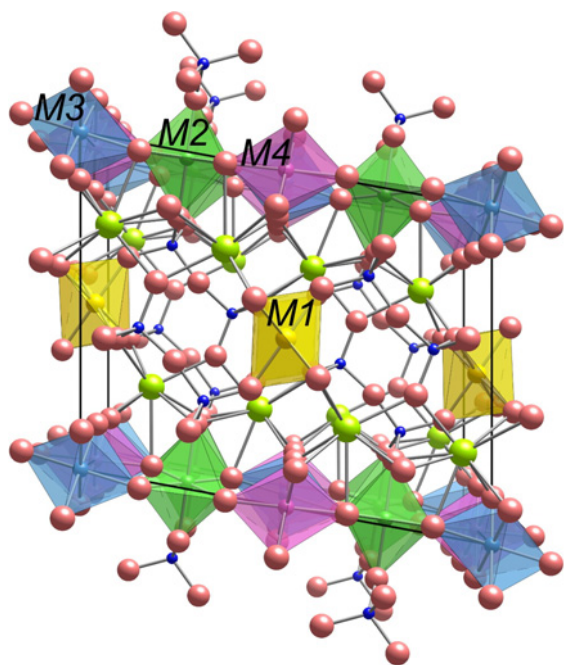


Fig. 3. The delhuyarite-(Ce) crystal structure seen along $[0\ 1\ 0]$. The octahedral $M1$ – $M4$ sites are shown as coloured polyhedra. $M2$ is 50% vacant. Si atoms = dark blue; REE = green; oxygen = red. The hydrogen atoms cannot be placed exactly. Unit-cell outline is in black. (Online version in colour.)

direction and link to form a layer of octahedra parallel to $(0\ 0\ 1)$. Between the layers, there are insular $M1$ octahedra. The layers of octahedra link through $[\text{Si}_2\text{O}_7]$ groups to form a framework with two interstitial A sites, in which Ce is dominant over other REE and Ca. In the Strunz classification (Strunz & Nickel, 2001), delhuyarite is a sorosilicate with Si_2O_7 groups, with additional anions; cations in octahedral $[6]$ and greater coordination (9.BE.70).

6.3. Powder diffraction data

The sample did not provide sufficient material to allow collection of conventional powder-diffraction data. Thus, a diffraction pattern was calculated from the crystal-structure information (natural sample). The pattern is summarized in Table 7 (only reflections with $I/I_0 \geq 3\%$ are included).

7. Discussion

Delhuyarite-(Ce) belongs to the same structure type as the chevkinite-group minerals (chevkinite subgroup with $\beta \sim 100^\circ$), but with some major differences (see Table 8 for a comparison with approved chevkinite-group minerals). It has a high nominal H_2O content corresponding to one hydroxyl group, absence of a site filled with Ti, and an octahedral cation vacancy, \square . Like for the member polyakovite-(Ce), ideally $(\text{REE}, \text{Ca})_4\text{MgCr}_2\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_8$, Mg^{2+} is prevalent at the $M1$ octahedral site. Half of the octahedral $M2$ -site constitutes the vacancy in delhuyarite-(Ce).

Table 7. X-ray powder diffraction pattern ($\text{CuK}\alpha = 1.54178\ \text{\AA}$) for delhuyarite-(Ce), calculated from crystal-structure data (untreated sample). Most intense reflections in bold.

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc}	<i>I</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc}	<i>I</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc}	<i>I</i> _{calc}
0	0	1	10.808	99	0	2	4	1.968	42	8	2	-3	1.422	7
2	0	-1	6.225	5	2	2	-4	1.961	26	8	0	3	1.418	6
0	0	2	5.404	15	2	0	5	1.953	4	3	3	-5	1.416	8
1	1	0	5.278	9	1	1	5	1.951	16	5	1	-7	1.415	0
2	0	1	5.263	9	1	3	-1	1.875	4	7	1	-6	1.408	6
1	1	-1	4.886	43	1	3	1	1.859	9	1	3	5	1.407	4
2	0	-2	4.646	7	2	2	4	1.822	22	2	4	0	1.404	0
1	1	1	4.611	71	7	1	-2	1.817	24	8	1	1	1.402	8
0	0	3	3.603	48	7	1	0	1.812	16	7	1	4	1.395	6
3	1	0	3.520	34	4	2	-4	1.806	9	6	2	4	1.385	7
3	1	-1	3.502	31	4	2	3	1.771	12	6	2	-6	1.363	13
3	1	1	3.211	100	6	2	0	1.760	13	7	3	-2	1.354	10
3	1	-2	3.170	66	3	3	0	1.759	5	7	3	0	1.352	6
4	0	-2	3.113	55	3	3	-1	1.757	5	0	0	8	1.351	10
1	1	-3	3.083	31	6	0	3	1.754	8	8	2	2	1.342	5
4	0	1	3.037	71	6	2	-2	1.751	22	0	4	3	1.334	5
2	0	3	2.950	7	2	2	-5	1.736	8	4	4	-2	1.304	9
1	1	3	2.879	21	3	1	5	1.732	4	8	2	-5	1.301	4
0	2	0	2.872	54	0	2	5	1.727	8	4	4	1	1.298	11
0	2	1	2.776	15	4	0	-6	1.725	20	5	3	4	1.290	4
3	1	2	2.769	53	6	0	-5	1.719	12	7	3	-4	1.278	6
3	1	-3	2.726	91	3	3	1	1.716	16	6	2	5	1.276	13
4	0	-3	2.714	33	3	3	-2	1.710	8	7	3	2	1.273	5
0	0	4	2.702	83	8	0	-1	1.699	21	4	4	-3	1.269	6
2	2	0	2.639	22	6	2	1	1.698	22	0	4	4	1.268	17
4	0	2	2.631	20	1	3	-3	1.696	5	4	4	2	1.261	4
2	2	-1	2.608	19	8	0	-2	1.687	10	6	2	-7	1.256	11
0	2	2	2.536	49	6	2	-3	1.682	17	10	2	-1	1.227	13
2	2	1	2.521	25	4	0	5	1.678	16	0	2	8	1.222	4
5	1	-1	2.455	4	5	1	4	1.670	9	3	3	6	1.215	3
2	2	-2	2.443	11	1	1	6	1.668	3	6	4	-1	1.213	4
5	1	0	2.423	5	1	3	3	1.660	4	11	1	-1	1.206	7
3	1	3	2.351	7	7	1	-4	1.645	11	3	3	-7	1.205	9
1	1	4	2.336	6	3	3	2	1.638	13	3	1	8	1.203	5
4	0	-4	2.323	3	4	2	-5	1.637	5	4	2	7	1.193	8
3	1	-4	2.314	7	7	1	2	1.633	10	3	1	-9	1.191	6
2	2	2	2.305	6	3	3	-3	1.629	17	7	1	-8	1.188	5
6	0	-1	2.267	12	6	2	2	1.606	7	7	1	6	1.178	4
4	0	3	2.250	8	4	2	4	1.603	4	2	4	5	1.157	4
0	2	3	2.246	7	6	2	-4	1.585	5	7	3	4	1.150	4
2	2	-3	2.208	4	0	0	7	1.544	11	10	2	-5	1.142	8
4	2	-1	2.187	56	0	2	6	1.526	11	10	2	2	1.142	9
4	2	0	2.178	30	8	0	2	1.518	6	11	1	-5	1.132	4
4	2	-2	2.111	8	3	1	6	1.516	6	8	0	6	1.125	7
6	0	1	2.106	7	1	1	-7	1.512	5	3	3	7	1.120	4
4	2	1	2.087	10	3	1	-7	1.497	17	10	0	-7	1.119	3
5	1	2	2.084	5	4	0	6	1.475	4	6	4	3	1.111	4
6	0	-3	2.075	4	8	0	-5	1.460	7	4	4	-6	1.104	9
2	2	3	2.058	9	4	2	5	1.449	3	6	4	-5	1.102	5
3	1	4	2.006	23	2	2	6	1.439	8	3	5	1	1.101	4
3	1	-5	1.976	22	0	4	0	1.436	29	8	4	-1	1.097	9
4	2	-3	1.973	3	3	3	4	1.427	8	10	2	-6	1.095	5

7.1. Hydrogen-bonding system

Delhuyarite-(Ce) is the second mineral related to the chevkinite group known to exhibit cation vacancies and the presence of OH groups, the first being a Fe-rich

Table 8. Dominant components at the cation sites of delhuyarite-(Ce) and chevkinite subgroup minerals.

Mineral	Formula	A1/A3	A2/A4	M1	M2/M2'	M3	M4	S.G.	β (°)	Ref.
Delhuyarite-(Ce)	(REE,Ca) ₄ Mg(Fe ³⁺ ,W,Al) ₃ □ ₁ Si ₄ O ₂₀ (OH) ₂	Ce	Ce	Mg	(□, Fe ³⁺ , W)	Fe ³⁺	(Fe ³⁺)	C2/m	100.72	[1]
Christofschäferite-(Ce)	(REE,Ca) ₄ Mn ²⁺ (Ti,Fe ³⁺) ₃ (Fe ³⁺ ,Fe ²⁺ ,Ti)Si ₄ O ₂₂	Ce/Ce	Ce/Ce	Mn	Ti/Ti	Ti	(Fe ³⁺ ,Ti)	P2 ₁ /m	100.58	[2]
Chevkinite-(Ce)	(REE,Ca) ₄ Fe ²⁺ (Ti,Fe ³⁺ ,Nb) ₄ Si ₄ O ₂₂	Ce	Ce	Fe ²⁺	Ti	Ti	Ti	C2/m	100.54	[3]
Maonipiungite-(Ce)	(REE,Ca) ₄ (Fe ³⁺ ,Ti,Fe ²⁺ ,□)(Ti,Fe ³⁺ ,Fe ²⁺ ,Nb) ₄ Si ₄ O ₂₂	Ce	Ce	Fe ³⁺	Ti	Ti	Ti	C2/m	100.60	[4]
Dingdaohengite-(Ce)	(REE,Ca) ₄ Fe ²⁺ (Ti,Fe ²⁺ ,Mg,Fe ³⁺) ₂ Ti ₂ Si ₄ O ₂₂	Ce	Ce	Fe ²⁺	Ti	Ti	Ti	P2 ₁ /a	100.64	[5]
Polyakovite-(Ce)	(REE,Ca) ₄ (Mg,Fe ²⁺)(Cr ³⁺ ,Fe ³⁺) ₂ (Ti,Nb) ₂ Si ₄ O ₂₂	Ce	Ce	Mg	Ti	Cr	Cr	C2/m	100.54	[6]

[1] This work, [2] Chukanov *et al.* (2012), [3] Sokolova *et al.* (2004), [4] Shen *et al.* (2005), [5] Xu *et al.* (2008), [6] Popov *et al.* (2001).

Table 9. Bond-valence (v.u.) arrangement for delhuyarite-(Ce) using the cation populations reported in Table 6.

	A1	A2	M1	M2	M3	M4	Si1	Si2	Σ O
O1	0.40 ^{×2} ↓	0.38 ^{×2} ↓			0.54 ^{×4} ↓	0.61 ^{×4} ↓			1.93
O2		0.31		0.29 ^{×2}	0.53 ^{×2}				1.95
O3	0.41	0.50						1.14	2.05
O4	0.19			0.31 ^{×2}		0.60 ^{×2}			2.01
O5	0.34 ^{×2} ↓	0.25 ^{×2} ↓	0.33 ^{×4} ↓					1.04 ^{×2} ↓	1.96
O6	0.35 ^{×2} ↓	0.30 ^{×2} ↓		0.29 ^{×2} ↓			1.06 ^{×2} ↓		2.00
O7		0.10 ^{×2} ↓	0.55 ^{×2} ↓				1.14		1.79
O8	0.06 ^{×2} ↓						1.15	1.07	2.34
	2.90	2.87	2.42	1.78	3.22	3.64	4.41	4.29	

Note: Calculated from the bond-valence curves of Brese & O'Keeffe (1991).

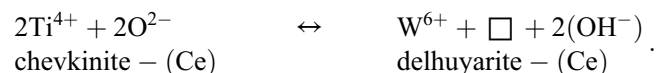
chevkinite-(Ce) reported by Yang *et al.* (2002), although vacancies were inferred for both *A* and *M* sites in that case. In addition, for Fe-rich chevkinite-(Ce), no hydrogen atoms could with certainty be located in the difference Fourier maps. In a later study of this material, using FTIR spectroscopy, Yang *et al.* (2008) presented evidence for OH⁻ groups in multiple sites in the form of two strong absorption bands at 3035 and 3394 cm⁻¹, respectively.

Bond-valence calculations (Table 9) of the structure of delhuyarite-(Ce) calculated according to the proposed site-distribution for the *M* sites given in Table 6 do not give a clear indication about which oxygen atoms could be involved in the hydrogen bonding system. The only oxygen atom that shows signs of under-saturation is O7, but its valence unit of 1.79 approaches well that observed for anhydrous chevkinite (O7 = 1.87 v.u.; Sokolova *et al.*, 2004). Nevertheless, distances suitable for hydrogen bonds were examined by analysing O...O contacts that are not polyhedral edges, but no clear indications could be found. Based on the correlation relation of Libowitzky (1999), the observed O–H stretching frequency (3495 cm⁻¹) suggests an O...O distance of ~2.89 Å. In the delhuyarite-(Ce) structure, all O...O distances that are not polyhedral edges are longer. We note that the occurrence of *M2* vacancies in the structure opens up for O–H...O bonds of non-edge character that are very close, 2.88 Å, to the expected length. However, the empirical Libowitzky correlation shows substantial scattering, up to 150 cm⁻¹, because it, *e.g.* does not take variations in O...H...O angles into account. Consequently, it is not possible from FTIR data to exclude several of the O atoms from hydrogen bonding.

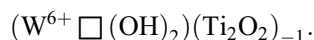
A final discussion on the hydrogen-bonding system in delhuyarite-(Ce) must await the availability of either more suitable crystals, allowing polarized single-crystal FTIR-spectroscopy, or the application of different, non-conventional techniques.

7.2. The significance of tungsten

An unusual feature for a silicate mineral is the high concentration of WO₃ in delhuyarite-(Ce). As described here (Table 6), W is mainly distributed over the *M2*, *M3* and *M4* sites, together with Fe³⁺. The presence of hexavalent tungsten or some other highly charged ionic species of suitable size should be necessary to stabilize the structure in the absence of Ti, as explained by a charge-balanced exchange mechanism of the type:



Alternatively, delhuyarite-(Ce) is described as related to a hypothetical Fe³⁺-analogue of polyakovite-(Ce), with end-member composition Ce₄MgFe³⁺₂Ti₂(Si₂O₇)₂O₈, via the exchange vector



Delhuyarite-(Ce) is one of few known nominally W-bearing silicates, the other ones being johnsenite-(Ce), khomyakovite, manganokhomyakovite (all of the eudialyte group), and welinite, Mn₆[W,Mg]₂Si₂(O,OH)₁₄. Johnsenite-(Ce) is the only REE and W-bearing silicate

mineral recognized so far (Grice & Gault, 2006). Tungsten substitutes for Nb or Ti in the octahedral *M3* site of eudialyte-group minerals (Johnsen *et al.*, 2003). In the welinite crystal structure, W partly occupies an octahedral position along with a vacancy and some Mg (Dunn *et al.*, 1986). The mean *M*–O interatomic distances for the W-dominant sites in these crystal structures are 1.943 (johnsenite-(Ce)) and 1.96 Å (welinite), respectively. Our average (Fe,W)–O distances group tightly around 2.00 Å, and the slightly longer bond lengths are in agreement with the substantial fraction of Fe³⁺ sharing the same site as W in delhuyarite-(Ce). It might also be noted that a similar mechanism as given above has been invoked to explain compositional variations in welinite (Holtstam, 2001).

The REE ores in Bastnäs-type deposits are high in W relative to the host rock, and this is generally attributed to the presence of minor scheelite (Holtstam *et al.*, 2014). However, one important REE mineral, cerite-(Ce), may also host significant amounts of W. In a reconnaissance study of trace elements in REE silicates from Bastnäs-type deposits using the laser-ablation (LA) ICP-MS technique, it was noted that cerite-(Ce) typically has high W concentrations, 190–620 ppm, whereas levels in closely associated ferriallanite-(Ce) and törnebohmitte-(Ce) reaches only 30 ppm as a maximum (Holtstam & Mansfeld, unpublished data). Cerite-(Ce), as major host for W, as well as for Fe, Mg, Ca and REE, could have supplied all the metal components needed for delhuyarite-(Ce) formation. This is in accord with our observation of the textural relations, and it is thus likely that delhuyarite-(Ce) formed after the dominating REE-silicates in the sample. The low F content of delhuyarite-(Ce), close to the detection limit, is notable when compared to cerite-(Ce) (with 1.1 wt% F; Holtstam *et al.*, 2003a). This indicates a very limited F–OH exchange in the delhuyarite-(Ce) structure, or that a low F activity prevailed during delhuyarite-(Ce) formation.

7.3. The A site composition and REE distribution

It is notable that delhuyarite-(Ce) has a lower total REE contents than associated cerite-(Ce) and percleveite-(Ce) but also displays different proportions between the individual REE. In terms of chondrite-normalized concentration values (Fig. 4), delhuyarite-(Ce) is significantly depleted in the heavier REE and Y relative the other REE main silicates in the sample. The REE pattern is, in fact, more similar to that of ferriallanite-(Ce) from the deposit (Holtstam *et al.*, 2003b), with a steep slope of the curve towards the middle REE. We believe that this is mainly a crystal-chemical effect, rather than being related to hydrothermal fluid fractionation.

A final comment on the inferred poor crystallinity of the delhuyarite-(Ce) crystal subjected to the X-ray diffraction experiment is warranted. The REE mineral assemblages at Nya Bastnäs are typically low in their actinide contents (*cf.* Holtstam & Andersson, 2007). In the present sample, U and Th were below the limit of detection for the EMP (0.1 wt %). Ferriallanite-(Ce) from the deposit was previously shown to contain <1 ppm Th and 3 ppm U, from LA ICP-

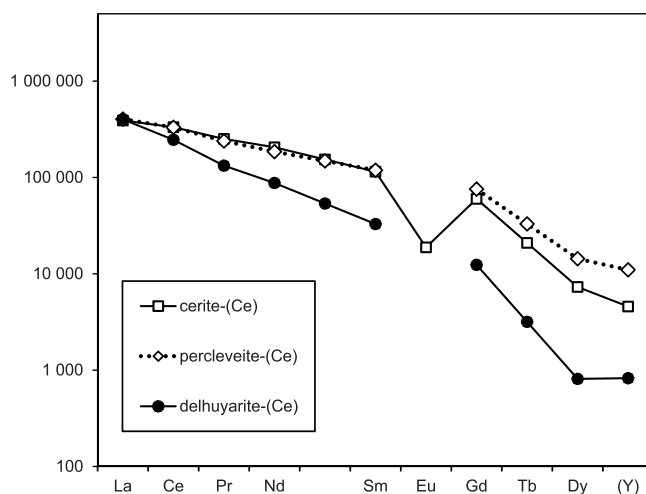


Fig. 4. Normalized REE + Y patterns for coexisting minerals in the type specimen, using the chondrite abundance-values of Boynton (1984). Elemental analyses are from Holtstam *et al.* (2003a) and Table 1 in this paper.

MS analyses (Holtstam *et al.*, 2003b). The question is then whether the initial concentration of radionuclides in delhuyarite-(Ce) was large enough to create radiation damage over time. An alternative explanation to the apparent improved crystalline long-range order obtained by thermal treatment (*i.e.* healing of defects) is that recrystallization occurred at significantly higher temperature (*i.e.* 800 °C) than the moderate temperatures prevailing during initial mineral formation or peak metamorphic conditions in this part of the Bergslagen ore province (≤ 600 °C; Stephens *et al.*, 2009). It is also possible that late-stage, post-metamorphic fluids in some way have affected the crystalline character of the mineral.

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