

# Graulichite-(Ce), a new arsenate mineral from the Stavelot Massif, Belgium

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**Abstract:** Graulichite-(Ce), ideally  $\text{CeFe}_3^{3+}(\text{AsO}_4)_2(\text{OH})_6$ , is a new mineral species from Hourt, Stavelot Massif, Belgium. It occurs in the most altered parts of a Devillian quartzite (Lower to Middle Cambrian), in close association with arsenopyrite, scorodite, mimetite, pharmacosiderite, and goethite. Graulichite-(Ce) forms 80 to 150  $\mu\text{m}$  spherical aggregates of rhombohedral crystals, 50 to 80  $\mu\text{m}$  length, which show the forms  $\{10\bar{1}2\}$  and  $\{10\bar{1}\bar{1}\}$ . The mineral is transparent and exhibits a light-green to brownish colour, with a resinous lustre. It is non-fluorescent and shows an irregular fracture, without any perceptible cleavage. The calculated density is 4.42  $\text{g}/\text{cm}^3$ . Graulichite-(Ce) is uniaxial negative, with a mean refractive index close to 1.97(1) ( $\lambda = 590 \text{ nm}$ ), pleochroic from light green to yellowish. Electron microprobe analyses gave  $\text{As}_2\text{O}_5$  31.20,  $\text{P}_2\text{O}_5$  0.03,  $\text{SO}_3$  0.06,  $\text{SiO}_2$  0.03,  $\text{Al}_2\text{O}_3$  3.09,  $\text{Fe}_2\text{O}_3$  30.65,  $\text{SrO}$  0.24,  $\text{PbO}$  0.07,  $\text{BaO}$  3.95,  $\text{CaO}$  0.03,  $\text{La}_2\text{O}_3$  2.26,  $\text{Ce}_2\text{O}_3$  15.73,  $\text{Nd}_2\text{O}_3$  2.08,  $\text{H}_2\text{O}$  (calc.) 8.37, total 97.79 wt. %. The resulting empirical formula, calculated on the basis of 6 cations, is  $(\text{Ce}_{0.67}\text{Ba}_{0.18}\text{La}_{0.10}\text{Nd}_{0.09}\text{Sr}_{0.02})_{\Sigma 1.06}(\text{Fe}_{2.68}^{3+}\text{Al}_{0.42})_{\Sigma 3.10}[(\text{As}_{1.89}\text{S}_{0.01}\text{O}_{10})_{\Sigma 2.00}\text{O}_8](\text{OH})_{5.57}(\text{H}_2\text{O})_{0.43}]_{\Sigma 6.00}$ . The single-crystal unit-cell parameters are  $a = 7.288(2)$  and  $c = 16.812(9)$  Å, space group  $R\bar{3}m$ . The seven strongest lines in the X-ray powder-diffraction pattern [ $d$ (in Å)( $I$ )( $hkl$ )] are: 3.052(100)(11 $\bar{2}$ 3), 3.636(40)(11 $\bar{2}$ 0), 2.239(35)(10 $\bar{1}$ 7), 1.817(35)(22 $\bar{4}$ 0), 2.792(30)(0006), 5.906(25)(10 $\bar{1}$ 1), 1.968(25)(30 $\bar{3}$ 3). Graulichite-(Ce) is the iron analogue of arsenoflorencite-(Ce), and belongs to the crandallite mineral group, with the alunite-type structure. The crystal structure of graulichite-(Ce) has been refined, based on single-crystal X-ray diffraction data, to  $R = 0.048$ .

**Key-words:** Graulichite-(Ce), new arsenate mineral, *REE*, crandallite group, Hourt, Stavelot Massif, Belgium, crystal structure.

## Introduction

In the southeastern border of the Stavelot Massif, Belgian Ardennes, the metapelites belonging to the recently defined stratigraphic Salm Group (Verniers *et al.*, 2001) of Cambro-Ordovician age are cross-cut by numerous quartz veins which host, among others, relatively rare Mn-rich aluminosilicates which crystallised during a low-grade metamorphism of Hercynian age (Schreyer, 1975). Besides the occurrence of these minerals, the presence of sulphides in the quartz veins is known for a long time (Hatert *et al.*, 2002). During the last decade, these sulphides have been carefully reinvestigated (Hatert, 1996; Hatert, submitted), as well as their oxidation and alteration products (Hatert *et al.*, 1998).

These mineralogical studies reveal the presence of arsenopyrite (Hatert, 1997), particularly as new occurrences in rocks of other stratigraphic position, like rocks of the Deville and Revin Groups (Verniers *et al.*, 2001). Recently, Hanson *et al.* (1999) discovered the association of gold and arsenopyrite in the quarry of Hourt, in rocks of the Deville Group. This description prompted us to investi-

gate the new occurrence of arsenopyrite and to study the mineralogical association of this quarry (Lefèvre, 2001; Lefèvre & Hatert, in press).

Among the secondary minerals associated with arsenopyrite from Hourt, collected by S. Puccio, M. Blondieau, J. Daille and J. Dehove, brown to greenish coatings, constituted by well-developed rhombohedral crystals, were identified as a mineral of the crandallite group. The preliminary chemical analyses performed by one of us (F.H.) indicated that this mineral probably corresponds to the  $\text{Fe}^{3+}$ -rich equivalent of arsenoflorencite,  $(\text{Ce},\text{La})\text{Al}_3(\text{AsO}_4)_2(\text{OH})_6$ , not yet described. The detailed study of this species by Lefèvre (2001) confirmed the existence of a new mineral species, which was approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (no. 2002-001) under the name graulichite-(Ce). The mineral is named in honour of Jean-Marie Graulich (1920-2001), mining engineer and honorary Director of the Geological Survey of Belgium, particularly for his contribution to the geology of the Stavelot Massif. The holotype is stored in the collection of the Laboratory of Mineralogy, University of Liège,

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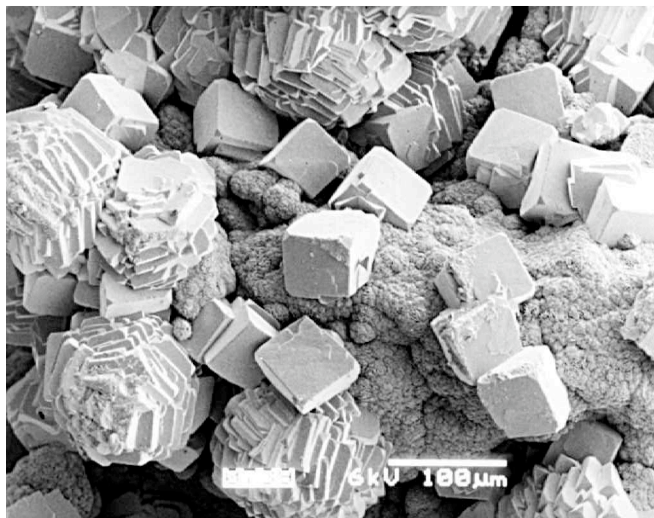


Fig. 1. Scanning electron microscope photograph of graulichite-(Ce) from Hourt. The mineral forms spherical crystal aggregates or isolated  $\{10\bar{1}2\}$  rhombohedra, lying on a goethite coating.

Belgium (no. 20325) and in the collection of the Royal Belgian Institute of Natural Sciences, Brussels (no. RN 6419).

## Geological setting

Graulichite-(Ce) has been discovered in the quartzites mined in the quarry of Hourt, 2 km north of Vielsalm, in the southeastern border region of the Stavelot Massif. Geologically, the Stavelot Massif constitutes an exposed part of the Caledonian basement situated near the north-western border of the Hercynian Rhenish Massif. The whitish quartzites from Hourt are of Cambrian age and stratigraphically belong to the Deville Group (Verniers *et al.*, 2001). The area of Hourt is extremely tectonised, with a lot of faults and folds, and was affected by two orogenic phases, a Caledonian and an Hercynian one (Bless *et al.*, 1990). The study of fluid inclusions, observed in quartz pebbles by Ferket *et al.* (1998) and Schroyen & Muechez (2000), indicates that pressure and temperature conditions close to 3 kbar and 380°C have probably been reached during the first Caledonian orogenic phase. In the region of Salmchâteau-Otré-Lierneux, Kramm (1982) and Kramm *et al.* (1985) estimated the metamorphic conditions prevailing during the Hercynian phase to about 360–420°C and  $\sim 2$  kbar, as indicated by both the presence of andalusite and the paragonite content of muscovite.

## Physical properties

Graulichite-(Ce) has been found in the most altered parts of the quartzite of Hourt, where it is associated with arsenopyrite, scorodite, mimetite, pharmacosiderite, barium-pharmacosiderite and goethite (Lefèvre, 2001; Lefèvre & Hatert, in press). The mineral occurs as spher-

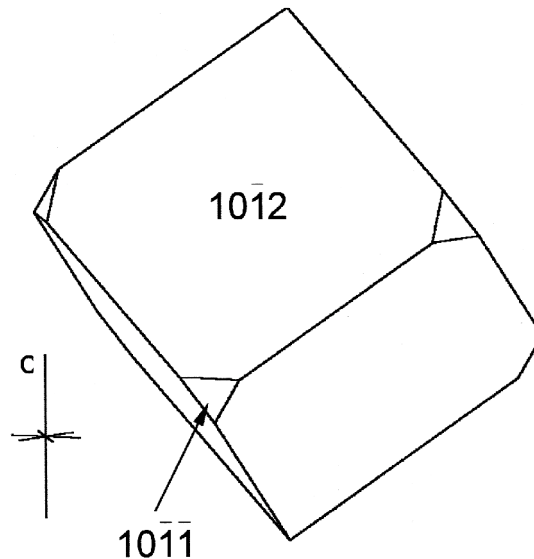


Fig. 2. Morphology of graulichite-(Ce) from Hourt, showing the combination  $\{10\bar{1}2\}\{10\bar{1}1\}$ .

ical aggregates, 80 to 150  $\mu\text{m}$  in diameter, constituted by rhombohedral crystals, 50 to 80  $\mu\text{m}$  length (Fig. 1). Goniometric measurements, performed on isolated crystals reaching 50  $\mu\text{m}$  length, indicate the presence of the  $\{10\bar{1}2\}$  rhombohedron, associated with smaller  $\{10\bar{1}1\}$  faces (Fig. 2).

Graulichite-(Ce) is transparent and exhibits a light green to brownish colour, with a resinous lustre. The mineral is non-fluorescent and shows an irregular fracture, without any perceptible cleavage. The density exceeds 3.9  $\text{g}/\text{cm}^3$ , because the crystals sink in diluted Clerici solution. The calculated density, based on the empirical formula, is 4.42  $\text{g}/\text{cm}^3$ . Under the polarising microscope, crystals are uniaxial negative, with a mean refractive index close to 1.97(1) ( $\lambda = 590$  nm). Pleochroism is from light green to yellowish. Birefringence is difficult to estimate, because the interference colours are masked by the green colour of the mineral.

## Chemical composition

Quantitative chemical analyses were performed on isolated crystals with a Cameca SX-50 electron microprobe (CAMST, Louvain-la-Neuve, Belgium) operating in the wavelength-dispersion mode, with an accelerating voltage of 20 kV and a beam current of 20 nA. The following standards were used: corundum (Al), fayalite (Si, Fe), barite (S, Ba), strontianite (Sr), apatite (P), synthetic wulfenite (Pb), wollastonite (Ca), pure metal (As), and synthetic glasses (Ce, La, and Nd).

As graulichite-(Ce) belongs to the crandallite group, according to its X-ray powder diffraction pattern, the chemical formula of this mineral was calculated on the basis of 6 cations (Table 1). As already observed for other minerals of the crandallite group (Hanson, 1983; Nickel & Temperly, 1987), a deficit of As occurs on the tetrahedral

Table 1. Electron-microprobe analyses of graulichite-(Ce) from Hourt.

	1	2
As <sub>2</sub> O <sub>5</sub>	31.20 (0.58)	1.893
P <sub>2</sub> O <sub>5</sub>	0.03 (0.04)	0.003
SO <sub>3</sub>	0.06 (0.05)	0.005
SiO <sub>2</sub>	0.03 (0.02)	0.004
Al <sub>2</sub> O <sub>3</sub>	3.09 (1.41)	0.423
Fe <sub>2</sub> O <sub>3</sub>	30.65 (2.16)	2.676
SrO	0.24 (0.10)	0.016
PbO	0.07 (0.07)	0.002
BaO	3.95 (0.82)	0.180
CaO	0.03 (0.03)	0.004
La <sub>2</sub> O <sub>3</sub>	2.26 (0.67)	0.097
Ce <sub>2</sub> O <sub>3</sub>	15.73 (0.87)	0.668
Nd <sub>2</sub> O <sub>3</sub>	2.08 (0.47)	0.086
H <sub>2</sub> O (*)	8.37	6.425
<b>Total</b>	<b>97.79</b>	

Analyst : J. Wautier. 1: Average of 33 analyses (in wt. %, with  $\sigma$  given in parentheses). 2: Number of cations based on 6 cations per formula unit. \*: calculated value based on 6(OH,H<sub>2</sub>O) per formula unit.

site of the structure. Because V was not detected qualitatively by SEM-EDS, and because P and Si are only present in very small amounts (Table 1), we suspect the occurrence of vacancies in this crystallographic site. The large cationic site of the structure contains Ce, La, Nd and Ba as major cations, whereas Fe<sup>3+</sup> and subordinate Al occupy the octahedral site.

The substitution of REE<sup>3+</sup> by Ba<sup>2+</sup> on the large cationic site implies an excess of negative charges, which is compensated by the replacement of (OH)<sup>-</sup> groups by H<sub>2</sub>O. This substitution mechanism has already been observed by Kolitsch *et al.* (1999) in dussertite, BaFe<sup>3+</sup>(AsO<sub>4</sub>)<sub>2</sub>(OH,H<sub>2</sub>O)<sub>6</sub>. The empirical formula of graulichite-(Ce), deduced from the microprobe analyses (Table 1), corresponds to (Ce<sub>0.66</sub>Ba<sub>0.18</sub>La<sub>0.10</sub>Nd<sub>0.09</sub>Sr<sub>0.02</sub>)<sub>Σ1.06</sub>(Fe<sup>3+</sup><sub>2.68</sub>Al<sub>0.42</sub>)<sub>Σ3.10</sub>[(As<sub>1.89</sub>S<sub>0.01</sub>□<sub>0.10</sub>)<sub>Σ2.00</sub>O<sub>8</sub>][(OH)<sub>5.57</sub>(H<sub>2</sub>O)<sub>0.43</sub>]<sub>Σ6.00</sub>.

## X-ray powder diffraction

The X-ray powder-diffraction pattern of graulichite-(Ce), given in Table 2, was recorded on a PHILIPS PW-3710 diffractometer using FeK $\alpha$  radiation ( $\lambda = 1.9373 \text{ \AA}$ ). This powder pattern is similar to those of arsenate members of the crandallite group. On the basis of the *d*-spacings shown in Table 2, which were calibrated with an internal standard of quartz, the least-squares refinement program LCLSQ 8.4 (Burnham, 1991) has served to calculate the unit-cell parameters in an hexagonal orientation. The cell dimensions obtained are  $a = 7.260(5)$  and  $c = 16.77(2) \text{ \AA}$ .

## Structure refinement

Several crystals of graulichite-(Ce) were preliminarily tested by rotation and Weissenberg methods. The unit cell

Table 2. Indexed X-ray powder-diffraction pattern of graulichite-(Ce).

<i>I</i> <sub>obs.</sub>	<i>d</i> <sub>obs.</sub> ( $\text{\AA}$ )	<i>d</i> <sub>calc.</sub> ( $\text{\AA}$ )	<i>h k l</i>
25	5.906	5.887	1 0 $\bar{1}$ 1
40	3.636	3.630	1 1 $\bar{2}$ 0
10	3.088	3.090	2 0 $\bar{2}$ 1
100	3.052	3.044	1 1 $\bar{2}$ 3
30	2.792	2.794	0 0 0 6
10	2.519	2.515	2 0 $\bar{2}$ 4
35	2.239	2.238	1 0 $\bar{1}$ 7
25	1.968	1.962	3 0 $\bar{3}$ 3
35	1.817	1.815	2 2 $\bar{4}$ 0
15	1.681	1.687	2 1 $\bar{3}$ 7
10	1.543	1.545	4 0 $\bar{4}$ 2
10	1.481	1.479	2 0 $\bar{2}$ 10
5	1.371	1.372	4 1 $\bar{5}$ 0

metrics, the Laue symmetry and the systematic absences, as well as the crystal morphology, were consistent with the space groups  $R\bar{3}m$ ,  $R32$  and  $R\bar{3}$ . By analogy with other minerals of the crandallite group (Jambor, 1999), the space group  $R\bar{3}m$  was inferred.

Single crystals of graulichite-(Ce) always consist of several subparallel individuals, and show a powder-like pattern, with diffuse streaks on which only weak and bad-shaped reflection spots are superimposed. We crushed some of them aiming to obtain a crystal fragment suitable for intensity data measurements, and a very small fragment was eventually brought to the Elettra synchrotron laboratory. The high energy of the synchrotron radiation raised the brightness of the diffraction spots, however, it caused the enhancement of the powder-like effect as well. As a consequence, the procedure of indexing of the reflection spots frames recorded with a CCD detector failed.

Therefore, the structural study was carried out on a conventional four-circle diffractometer, using a small crystal fragment which apparently showed a good degree of crystallinity and an only small tendency for subparallel intergrowth. The overall low intensity of the reflections prevented us to obtain a reliable set of  $\psi$ -scan data for an empirical absorption correction. For that reason, despite the higher point group symmetry, a whole sphere of reflections was measured. In such a way, as a partial compensation for the lack of absorption correction, we got a set of independent squared amplitudes, each resulting from averaging several equivalent measurements. We also tried a semi-empirical treatment of absorption effects with the program MULTISCAN included in the WinGX package (Farrugia, 1999), which performs an absorption correction based upon the Blessing algorithm (Blessing, 1995). However, this did not result in any significant improvement of the model, and was eventually left out.

The refinement was started using the atomic coordinates of florencite (Kato, 1990) and setting cation occupancies in keeping with the chemical composition of graulichite-(Ce). For the sake of simplicity, Ce only was allocated to the large interlayer site, since its atomic number (58) was quite close to the average atomic number (57.4) resulting from the chemical analysis. Then, the occu-

Table 3. Experimental details for the single-crystal X-ray diffraction study of graulichite-(Ce).

Dimensions of the crystal (mm)	ca. 0.05 x 0.04 x 0.03
Unit-cell parameters (Å)	<i>a</i> 7.288(2), <i>c</i> 16.812(9)
Space group	$R\bar{3}m$
Diffractometer	Siemens
Operating conditions	50 kV, 40 mA
Radiation	MoK $\alpha$ ( $\lambda = 0.71069$ Å)
Scan mode	$\theta$ -2 $\theta$
Scan width (in $\theta$ )	$\pm 0.6^\circ$
Scan speed	1°/min
2 $\theta_{\max}$	50°
Range of indices	$-8 \leq h \leq 8, -8 \leq k \leq 8, -19 \leq l \leq 19$
Measured intensities	1720
Independent non-zero [ $F_o > 4\sigma(F_o)$ ] reflections	151
Absorption correction	None
l.s. refinement program	SHELXL-93 (Sheldrick, 1993)
Refined parameters	27
<i>R</i> (on <i>F</i> 's)	0.0475
<i>R</i> <sub>w</sub> (on squared <i>F</i> 's)	0.1246
<i>S</i> (goodness of fit)	1.124
Max $\Delta/\sigma$ in the last l.s. cycle	0.000
Max peak and hole in the final $\Delta F$ map ( $e/\text{Å}^3$ )	+1.97 and -1.23

pancy of Fe<sup>3+</sup> against Al was refined in the octahedral site, and the occupancy of As against vacancy was refined in the tetrahedral site. The refinement was completed using anisotropic displacement parameters for all atoms. The final conventional *R* factor was 0.0475. Further details of the intensity data collection and refinement are given in Table 3.

Table 4a. Final fractional coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for graulichite-(Ce).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Ce	0	0	0	0.0269(10)
Fe*	0.5	0.5	0.5	0.0158(11)
As**	0	0	0.3168(2)	0.0174(12)
O1	0	0	0.416(1)	0.024(5)
O2	0.2076(10)	-0.2076(10)	-0.0512(7)	0.027(3)
OH	0.1244(9)	-0.1244(9)	0.1328(7)	0.026(3)

\* Refined site occupancy: Fe 83.0(7)% + Al 17.0(7)%

\*\* Refined site occupancy: As 92.4(3)% + □ 7.6(3)%

## Discussion

### Compatibility

The compatibility of graulichite-(Ce) is calculated with the relationship proposed by Mandarino (1981). Because no accurate density measurements are available, the calculations were performed with the calculated density of 4.42 g/cm<sup>3</sup>. The compatibility index,  $1 - (K_p/K_C)$ , is equal to 0.005, thus indicating a superior compatibility.

### Structural features

Final positional and displacement parameters for graulichite-(Ce) are given in Table 4, whereas selected bond distances are given in Table 5. The greatest  $r_{\max}/r_{\min}$  ratio between axes of the displacement ellipsoids is 2.76 for the Ce site.

The basic features of the structure of graulichite-(Ce) are identical to those of the other members of the alunite-crandallite structure-type, therefore they will not be considered in detail here. It is just worth noting that the

Table 4b. Anisotropic displacement parameters for graulichite-(Ce).

Atom	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
Ce	0.034(1)	0.034(1)	0.012(1)	0	0	0.0171(6)
Fe	0.020(2)	0.020(2)	0.010(2)	-0.0012(7)	0.0012(7)	0.011(2)
As	0.021(1)	0.021(1)	0.011(2)	0	0	0.0104(7)
O1	0.027(7)	0.027(7)	0.017(10)	0	0	0.014(3)
O2	0.032(5)	0.032(5)	0.021(6)	0.001(3)	-0.001(3)	0.019(6)
OH	0.020(5)	0.020(5)	0.037(7)	-0.003(3)	0.003(3)	0.010(5)

Table 5. Selected bond distances (Å) for graulichite-(Ce).

Ce-OH (x6)	2.731(12)	Fe-OH (x4)	1.978(5)	As-O1	1.660(19)
Ce-O2 (x6)	2.758(12)	Fe-O2 (x2)	2.010(11)	As-O2 (x3)	1.690(12)
<Ce-O>	2.74	<Fe-O>	1.99	<As-O>	1.68

Table 6. Site occupancies and mean cation-oxygen distances (Å) in some minerals of the crandallite group.

Mineral	XII-coordinated site		VI-coordinated site		IV-coordinated site	
Crandallite <sup>1</sup>	Ca	2.711	Al	1.902	P	1.537
Gorceixite <sup>2</sup>	Ba	2.847	Al	1.901	P	1.533
Goyazite <sup>3</sup>	Sr	2.748	Al	1.896	P	1.535
Florenceite <sup>4</sup>	Ce	2.681	Al	1.893	P	1.546
Kintoreite <sup>5</sup>	Pb	2.859	Fe	2.011	P <sub>0.73</sub> As <sub>0.16</sub> S <sub>0.11</sub>	1.563
Dussertite <sup>6</sup>	Ba	2.874	Fe <sub>0.84</sub> Sb <sub>0.16</sub>	2.009	As	1.684
Graulichite-(Ce) <sup>7</sup>	Ce	2.74	Fe <sub>0.83</sub> Al <sub>0.17</sub>	1.99	As <sub>0.92</sub> □ <sub>0.08</sub>	1.68

1. Blount (1974); 2. Radoslovich (1982); 3. Kato (1987); 4. Kato (1990); 5. Kharisun *et al.* (1997); 6. Kolitsch *et al.* (1999); 7. This study.

Table 7. Comparison of graulichite-(Ce) with other arsenate minerals of the crandallite group.

Mineral name	Chemical formula	Space group	<i>a</i> (Å)	<i>c</i> (Å)	Refractive index	Optical <i>D</i> <sub>meas</sub> sign	<i>D</i> <sub>meas</sub> (g/cm <sup>3</sup> )	<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )
Graulichite-(Ce) <sup>1</sup>	CeFe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	<i>R</i> $\bar{3}m$	7.260(5)	16.77(2)	1.97(1)	U-	> 3.9	4.42
Dussertite <sup>2,3,4</sup>	BaFe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>	<i>R</i> $\bar{3}m$	7.410(3)	17.484(4)	$\omega=1.87$ $\epsilon=1.85$	U-	3.75	4.293
Segnitite <sup>5</sup>	PbFe <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>	<i>R</i> $\bar{3}m$	7.359(3)	17.11(8)	$\omega=1.975$ $\epsilon=1.955$	U-	> 4.2	4.77(1)
Arsenogorceixite <sup>6</sup>	BaAl <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>	<i>R</i> $\bar{3}m$	7.10(2)	17.39(4)	n.g.	n.g.	n.g.	n.g.
Arsenocrandallite <sup>6</sup>	CaAl <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>	<i>R</i> $\bar{3}m$ or <i>R3m</i>	7.08	17.27	1.625(10)	n.g.	3.25(1)	3.30
Arsenogoyazite <sup>7</sup>	SrAl <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>	<i>R</i> $\bar{3}m$ or <i>R3m</i>	7.10	17.16	1.64(3)	n.g.	3.35(5)	3.65
Philipsbornite <sup>8</sup>	PbAl <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH,H <sub>2</sub> O) <sub>6</sub>	<i>R</i> $\bar{3}m$ or <i>R3m</i>	7.11	17.05	1.790(3)	n.g.	> 4.10	4.33
Arsenoflorenceite-(Ce) <sup>9</sup>	CeAl <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	<i>R</i> $\bar{3}m$	7.03	16.517	$\omega=1.739$ $\epsilon=1.745$	U+	4.10	4.09

1. This study; 2. Barthoux (1925); 3. Walenta (1966); 4. Kolitsch *et al.* (1999); 5. Birch *et al.* (1992); 6. Walenta (1981); 7. Walenta & Dunn (1984); 8. Walenta *et al.* (1982); 9. Nickel & Temperly (1987). n.g. : not given.

average bond distances (Table 5) are in fairly good agreement with the cation site occupancies, and the latter match well the chemical composition of graulichite-(Ce).

A number of structure refinements are available for minerals of the alunite- and the crandallite-type. In Table 6 the mean cation-oxygen distances in some crandallite subgroup minerals are compared.

### Graulichite-(Ce) in the crandallite mineral group

Electron microprobe analyses (Table 1) indicate that graulichite-(Ce) is the Fe<sup>3+</sup>-rich analogue of arsenoflorenceite-(Ce). The nomenclature of the crandallite group has recently been revisited by Jambor (1999). Comparisons of the physical properties of graulichite-(Ce) and those of other arsenate minerals of this group are given in Table 7.

As shown in Fig. 3, the chemical data of the graulichite-(Ce) crystals from the Hourt quarry are clearly localised in the Ce-rich part of the Ce-La-Nd diagram. For this reason, and according to the nomenclature proposed by Jambor (1999) for minerals of the crandallite group, the mineral is named graulichite-(Ce). "Graulichite-(La)" and "graulichite-(Nd)" are hypothetical end-members.

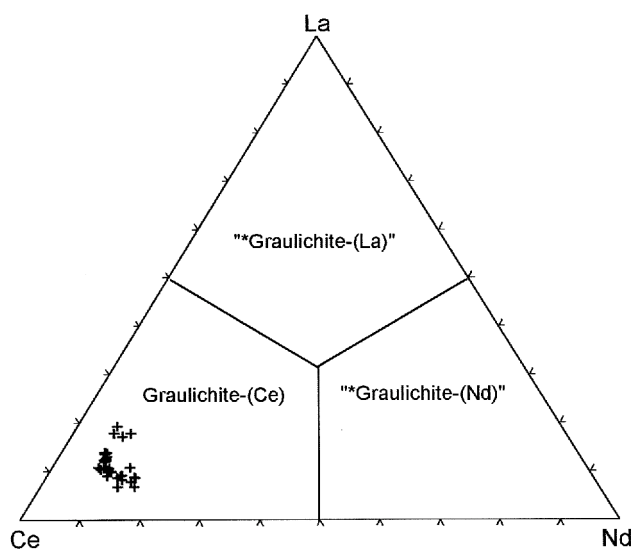


Fig. 3. Results of electron microprobe analyses of graulichite-(Ce), plotted in the Ce-La-Nd diagram. \*: "Graulichite-(La)" and "graulichite-(Nd)" are the hypothetical La- and Nd- analogues of graulichite-(Ce).

## Genesis of graulichite-(Ce)

All the arsenate minerals occurring in the quarry of Hourt, including graulichite-(Ce), derive from the oxidation of arsenopyrite. Indeed, these secondary minerals crystallise in small cavities produced by the leaching of arsenopyrite. Graulichite-(Ce) contains significant amounts of Ba in the A site of the alunite-type structure. It is noteworthy that Lefèvre (2001) described barium-pharmacosiderite,  $\text{BaFe}_3^{3+}(\text{AsO}_4)_6(\text{OH})_8 \cdot 14\text{H}_2\text{O}$ , in very close association with the new mineral species. Although no geochemical data are available up to now for the enclosing rocks of the Deville Group, the presence of Ba is known as major element in hollandite (Schreyer *et al.*, 2001) or in Ba-rich mica (Kramm, 1980; Schreyer *et al.*, 2001) in rocks of the Salm Group from Vielsalm and Salmchâteau, whereas florencite-(Ce) was detected in the same area (Theunissen & Martin, 1969; Hanson, 1983). It can be assumed that these particular elements (REE, Ba) were leached during the intense alteration undergone by the whole Stavelot Massif during the tropical climate of the Tertiary period (Alexandre & Thorez, 1995). As the minerals of the crandallite group with prevailing Al and Fe are able to easily stabilise elements such as Ba and REE (Kolitsch & Pring, 2001), the formation of graulichite-(Ce) and of the associated arsenates from Hourt can be attributed to Tertiary processes of weathering.

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## References

- Alexandre, J. & Thorez, J. (1995): Au Secondaire et au Tertiaire, l'Ardenne tropicale. in A. Demoulin ed.: "L'Ardenne, essai de géographie physique". Groupe Graphique Chauveheid Liège, 238 p.
- Barthoux, J. (1925): Description d'un minéral nouveau: la dusserite. *C. R. Acad. Sci., Paris*, **180**, 299-301.
- Birch, W.D., Pring, A., Gatehouse, B.M. (1992): Segnitite,  $\text{PbFe}_3\text{H}(\text{AsO}_4)_2(\text{OH})_6$ , a new mineral in the lusungite group from Broken Hill, New South Wales, Australia. *Am. Mineral.*, **77**, 656-659.
- Bless, M., Bouckaert, J., Camelbeek, T., Dejonghe, L., Demoulin, A., Dupuis, C., Felder, P., Geukens, F., Gullentops, F., Hance, L., Jagt, J., Juvigné, E., Kramm, U., Ozer, A., Pissart, A., Robaszynski, F., Schumacker, R., Smolderen, A., Spaeth, G., Steemans, P., Streel, M., Vandeven, G., Vanguetstaine, M., Walter, R., Wolf, M. (1990): The Stavelot massif from Cambrian to recent. A survey of the present state of knowledge. *Annales de la Société géologique de Belgique*, **113**, 53-73.
- Blessing, R.H. (1995): An empirical correction for absorption anisotropy. *Acta Cryst.*, **A51**, 33-38.
- Blount, A.M. (1974): The crystal structure of crandallite. *Am. Mineral.*, **59**, 41-47.
- Burnham, C.W. (1991): LCLSQ version 8.4, last-squares refinement of crystallographic lattice parameters. Dept. of Earth & Planetary Sciences, Harvard University, 24 p.
- Farrugia, L.J. (1999): WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Cryst.*, **32**, 837-838.
- Ferket, H., Muchez, P., Schroyen, K., Sintubin, M. (1998): Metamorphism in the Stavelot-Venn Massif: a study of quartz veins in the basal devonian conglomerates (Lochkovian). *Aardkundige Mededelingen*, **9**, 7-16.
- Hanson, A. (1983): Etude minéralogique de filons de la bordure méridionale du Massif de Stavelot. Unpublished Diploma Thesis, University of Liège, 84 p.
- Hanson, A., Dehove, J., Debbaut, V., Brunel, J. (1999): La découverte d'or natif dans le quartzite devillien de Hourt autorise un autre regard sur le site de "Rompt-le-Cou". *Glain et Salm, Haute Ardenne*, **51**, 4-10.
- Hatert, F. (1996): Etude minéralogique préliminaire de quelques sulfures du massif de Stavelot. Unpublished Diploma Thesis, University of Liège, 48 p.
- (1997): L'arsénopyrite du Massif de Stavelot, Belgique. *Bull. Société royale des Sciences de Liège*, **66(6)**, 381-390.
- Hatert, F., Blondieau, M., Dehove, J., Fransolet, A.M. (1998): Les minéraux secondaires en relation avec les sulfures de la région de Vielsalm, Belgique. *Bull. Société royale des Sciences de Liège*, **67(6)**, 281-289.
- Hatert, F., Deliens, M., Fransolet, A.-M., Van Der Meersche, E. (2002): Les minéraux de Belgique. Deuxième édition. Editions de l'Institut royal des Sciences naturelles de Belgique, 304 p.
- Jambor, J.L. (1999): Nomenclature of the alunite supergroup. *Can. Mineral.*, **37**, 1323-1341.
- Kato, T. (1987): Further refinement of the goyazite structure. *Mineral. J.*, **13**, 390-396.
- (1990): The crystal structure of florencite. *N. Jb. Mineral. Mh.*, **1990**, 227-231.
- Kharisun, Taylor, M.R., Bevan, D.J.M., Pring, A. (1997): The crystal structure of kintoreite,  $\text{PbFe}_3(\text{PO}_4)_2(\text{OH}, \text{H}_2\text{O})_6$ . *Min. Mag.*, **61**, 123-129.
- Kolitsch, U. & Pring, A. (2001): Crystal chemistry of the crandallite, beudantite and alunite groups: a review and evaluation of the suitability as storage materials for toxic metals. *J. Mineral. Petrol. Sci.*, **96**, 67-78.
- Kolitsch, U., Slade, P.G., Tiekink, E.R.T., Pring, A. (1999): The structure of antimonian dusserite and the role of antimony in oxysalt minerals. *Min. Mag.*, **63**, 17-26.
- Kramm, U. (1980): Muskovit-Paragonit Phasenbeziehungen in niedriggradig metamorphen Schieferen des Venn-Stavelot Massivs, Ardennen. *Tschermaks Mineralogische und Petrographische Mitteilungen*, **27**, 153-167.
- (1982): Die Metamorphose des Venn-Stavelot-Massivs nordwestliches Rheinisches Schiefergebirge: Grad, Alter und Ursache. *Decheniana*, **135**, 121-178.
- Kramm, U., Spaeth, G., Wolf, M. (1985): Variscan metamorphism in the NE Stavelot-Venn Massif, Ardennes: a new approach to the question of regional dynamothermal or contact metamorphism. *N. Jb. Geol. Paläont. Abh.*, **171**, 311-327.
- Lefèvre, P. (2001): La présence d'arsenic dans les filons à sulfures du Devillien de Hourt, Massif de Stavelot. Unpublished Diploma Thesis, University of Liège, 45 p.
- Lefèvre, P. & Hatert, F. (in press): Or natif, arsénopyrite et minéraux secondaires dans les quartzites devilliens de Hourt, Massif de Stavelot, Belgique. *Geologica Belgica*.
- Mandarino, J.A. (1981): The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Can. Mineral.*, **19**, 441-450.
- Nickel, E.H. & Temperly, J.E. (1987): Arsenoflorencite-(Ce): a new arsenate mineral from Australia. *Min. Mag.*, **51**, 605-609.



- Radoslovich, E.W. (1982): Refinement of gorceixite in Cm. *N. Jb. Mineral. Mh*, **1982**, 446-464.
- Schreyer, W. (1975): New petrologic evidence for Hercynian metamorphism in the Venn-Stavelot Massif, Belgium. *Geologische Rundschau*, **64**, 819-830.
- Schreyer, W., Fransolet, A.-M., Bernhardt, H.-J. (2001): Hollandite-strontiomelane solid solutions coexisting with kanonaite and braunite in late quartz veins of the Stavelot Massif, Ardennes, Belgium. *Contrib. Mineral. Petrol.*, **141**, 560-571.
- Schroyen, K. & Muechez, Ph. (2000): Evolution of metamorphic fluids at the Variscan fold-and-thrust belt in Eastern Belgium. *Sedimentary Geology*, **131**, 163-180.
- Sheldrick, G.M. (1993): SHELXL93. Program for the Refinement of Crystal Structures. University of Göttingen, Germany.
- Theunissen, K. & Martin, H. (1969): Découverte d'un phosphate alumineux de terres rares dans un coticule de Vielsalm. *Annales de la Société géologique de Belgique*, **92**, 173-176.
- Verniers, J., Herbosch, A., Vanguetaine, M., Geukens, F., Delcambre, B., Pingot, J.L., Belanger, I., Hennebert, M., Debacker, T., Sintubin, M., De Vos, W. (2001): Cambrian-Ordovician-Silurian lithostratigraphic units (Belgium). *Geologica Belgica*, **4**, 5-38.
- Walenta, K. (1966): Beiträge zur Kenntnis seltener Arsenatminerale unter besonderer Berücksichtigung von Vorkommen des Schwarzwaldes. *Tschermaks Mineralogische und Petrographische Mitteilungen*, **11**, 121-164.
- Walenta, K. (1981): Mineralien der Beudantit-Crandallitgruppe aus dem Schwarzwald : Arsenocrandallit und sulfatfreier Weilerit. *Schweiz. Mineral. Petrogr. Mitt.*, **61**, 23-35.
- Walenta, K. & Dunn, P.J. (1984): Arsenogoyazit, ein neues Mineral der Crandallitgruppe aus dem Schwarzwald. *Schweiz. Mineral. Petrogr. Mitt.*, **64**, 11-19.
- Walenta, K., Zwiener, M., Dunn, P.J. (1982): Philipsbornit, ein neues Mineral der Crandallitreihe von Dundas auf Tasmanien. *N. Jb. Mineral. Mh*, **1982**, 1-5.

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