

News from the hellandite group: the redefinition of mottanaite and ciprianiite and the new mineral description of ferri-mottanaite-(Ce), the first Fe³⁺-dominant hellandite

ROBERTA OBERTI^{1,*}, ANTONIO LANGONE¹, MASSIMO BOIOCCHI², EZIO BERNABÈ³ and FRANK C. HAWTHORNE⁴

¹CNR-Istituto di Geoscienze e Georisorse, sede di Pavia, via Ferrata 1, 27100 Pavia, Italy

*Corresponding author, e-mail: oberti@crystal.unipv.it

²Centro Grandi Strumenti, Università di Pavia, via Bassi 21, 27100 Pavia, Italy

³via Adriatica 110, 47838 Riccione, Italy

⁴Department of Geological Sciences, University of Manitoba, 125 Dysart Road, Winnipeg, MB R3T 2N2, Canada

Abstract: The ideal formulae of two root-names of the hellandite group, *i.e.* mottanaite and ciprianiite, were originally given as $^X\text{Ca}_4^Y(\text{CeCa})_2^Z\text{Al}^T\text{Be}_2[\text{B}_4\text{Si}_4\text{O}_{22}]^W\text{O}_2$ and $^X\text{Ca}_4^Y[(\text{Th,U})\text{REE}]_{\Sigma 2}\text{Al}^T\text{Be}_2[\text{B}_4\text{Si}_4\text{O}_{22}]^W(\text{OH})_2$. In order to conform to the later introduced dominant-valency nomenclature rule, they have been redefined as $^X\text{Ca}_4^Y\text{REE}_2^Z\text{Al}^T(\text{Be}_{1.5}\square_{0.5})[\text{B}_4\text{Si}_4\text{O}_{22}]^W\text{O}_2$ and $^X\text{Ca}_4^Y[(\text{Th,U})\text{Ca}]_{\Sigma 2}\text{Al}^T(\text{Be}_{0.5}\square_{0.5})_{\Sigma 2}[\text{B}_4\text{Si}_4\text{O}_{22}]^W(\text{OH})_2$, respectively (IMA-CNMNC vote 18D). Also, the mineral description is provided for the first Fe³⁺-dominant species of the hellandite group, ferri-mottanaite-(Ce), ideally $^X\text{Ca}_4^Y\text{Ce}_2^Z\text{Fe}^{3+T}(\text{Be}_{1.5}\square_{0.5})[\text{B}_4\text{Si}_4\text{O}_{22}]^W\text{O}_2$. The type specimen was found in an ejectum collected at Tre Croci (Vetralla, Vico volcanic province, Italy). The empirical formula derived from electron microprobe and LA-ICP-MS analyses, and validated by single-crystal structure refinement is: $^X(\text{Ca})_4^Y(\text{Ca}_{0.40}\text{REE}_{0.93}(\text{Th,U})_{0.54}\square_{0.13})_{\Sigma 2.00}^Z(\text{Fe}_{0.50}\text{Al}_{0.23}\text{Mn}_{0.17}\text{Ti}_{0.17})_{\Sigma 1.07}^T(\text{Be}_{1.04}\text{Li}_{0.04}\square_{0.92})_{\Sigma 2.00}[\text{Si}_{4.03}\text{B}_{3.89}\text{O}_{22}]^W(\text{OH})_{0.38}\text{F}_{0.53})_{\Sigma 2.00}$. Ferri-mottanaite-(Ce) is biaxial (–), with $\alpha = 1.748(5)$, $\beta = 1.762(5)$, $\gamma = 1.773(5)$ and $2V$ (meas.) = $85.9(5)^\circ$, $2V$ (calc.) = 82.5° . The unit-cell parameters are $a = 19.0548(9)$, $b = 4.7468(2)$, $c = 10.2560(5)$ Å, $\beta = 110.906(2)^\circ$, $V = 866.58(7)$ Å³, $Z = 2$, space group $P2_1/a$. The strongest reflections in the X-ray powder pattern obtained from single-crystal data [d values (in Å), I , (hkl)] are: 2.648, 100, (013, $\bar{4}$ 13); 2.857, 50, (411); 1.904, 48, (023, $\bar{4}$ 23, $\bar{6}$ 21); 2.919, 44, (212); 3.086, 44, ($\bar{4}$ 12); 3.246, 43, ($\bar{4}$ 10); 3.453, 36, ($\bar{2}$ 12); 4.745, 33, (010).

Key-words: nomenclature; new mineral; ferri-mottanaite-(Ce); crystal structure; hellandite group; mottanaite-(Ce); ciprianiite; borosilicate; rare-earth elements; Vico volcanic province.

1. Redefinition of the ideal formulae of mottanaite-(Ce) and ciprianiite

Mottanaite-(Ce) and ciprianiite are two hellandite-group minerals first described by Della Ventura *et al.* (2002). While involved in the characterization of ferri-mottanaite-(Ce), we realized that their ideal formulae were no longer consistent with the later IMA-CNMNC nomenclature rules introduced by Hatert & Burke (2008). It was therefore apparent that the ideal formulae of mottanaite-(Ce) and ciprianiite had to be modified to conform with current nomenclature rules. The new formulae were derived as follows.

The general chemical formula for hellandite-group minerals is written as $X_4Y_2ZT_2[\text{B}_4\text{Si}_4\text{O}_{22}]W_2$, where $X = \text{Na}, \text{Ca}, \text{REE}$; $Y = \text{Ca}, \text{REE}, \text{Th}^{4+}, \text{U}^{4+}$; $Z = \text{Al}, \text{Fe}^{3+}, \text{Mn}^{3+}, \text{Ti}^{4+}$; $T = \text{Li}, \text{Be}, \square$; $W = \text{OH}, \text{F}, \text{O}$ (Oberti *et al.*, 2002). Della Ventura *et al.* (2002) provided empirical formulae for mottanaite-(Ce) and ciprianiite, where B, Be, Li, OH and F were measured by SIMS:

$^X\text{Ca}_4^Y[\text{REE}_{1.45}\text{Ca}_{0.37}(\text{Th}, \text{U})_{0.17}^{\text{4+}}\text{Y}_{0.01}]_{\Sigma 2}^Z(\text{Al}_{0.50}\text{Fe}_{0.38}^{3+}\text{Mg}_{0.03}\text{Ti}_{0.07}^{4+})_{\Sigma 0.98}^T(\text{Be}_{1.18}\text{Li}_{0.02}\square_{0.37})_{\Sigma 1.57}[\text{B}_{3.99}\text{Si}_{3.98}\text{O}_{22}]^W(\text{O}_{1.04}\text{F}_{0.53}(\text{OH})_{0.43})_{\Sigma 2}$ for mottanaite-(Ce), $^X\text{Ca}_4^Y[\text{REE}_{0.72}^{3+}(\text{Th}, \text{U})_{0.66}^{\text{4+}}\text{Ca}_{0.60}\text{Y}_{0.02}]_{\Sigma 2}^Z(\text{Al}_{0.48}\text{Fe}_{0.38}^{3+}\text{Ti}_{0.10}^{4+}\text{Mg}_{0.05}\text{Mn}_{0.02}^{3+})_{\Sigma 1.03}^T(\text{Be}_{0.82}\square_{0.60}\text{Li}_{0.04})_{\Sigma 1.46}[\text{B}_{4.00}\text{Si}_{4.00}\text{O}_{22}]^W(\text{O}_{0.97}(\text{OH})_{0.54}\text{F}_{0.49})_{\Sigma 2}$ for ciprianiite. In these formulae, vacancies at the T sites ($T\square$) are assigned as (2 – Be – Li – OH) because H (but not F) occurs very close to the T cations and hence is locally incompatible with them.

We can further simplify these formulae by collecting ions of similar charge and representing their sum as that of the dominant ion. We obtain: $^X\text{Ca}_4^Y[\text{REE}_{1.46}\text{Ca}_{0.37}\text{Th}_{0.17}^{4+}]_{\Sigma 2}^Z\text{Al}_{0.98}^T(\text{Be}_{1.18}\text{Li}_{0.02}\square_{0.37})_{\Sigma 1.57}[\text{B}_4\text{Si}_4\text{O}_{22}]^W(\text{O}_{1.57}(\text{OH})_{0.43})_{\Sigma 2}$ for mottanaite-(Ce), and $^X\text{Ca}_4^Y[\text{REE}_{0.74}^{3+}\text{Th}_{0.66}^{4+}\text{Ca}_{0.60}]_{\Sigma 2}^Z\text{Al}_{1.03}^T(\text{Be}_{0.82}\square_{0.60}\text{Li}_{0.04})_{\Sigma 1.46}[\text{B}_4\text{Si}_4\text{O}_{22}]^W(\text{O}_{0.97}(\text{OH})_{1.03})_{\Sigma 2}$ for ciprianiite.

Hatert & Burke (2008) discussed the issue of heterovalent substitutions at a single site, *e.g.* $\text{A}_M^{n+} \rightarrow (\text{B}_{0.5}^{(n+1)+}\text{C}_{0.5}^{(n-1)+})_M$.

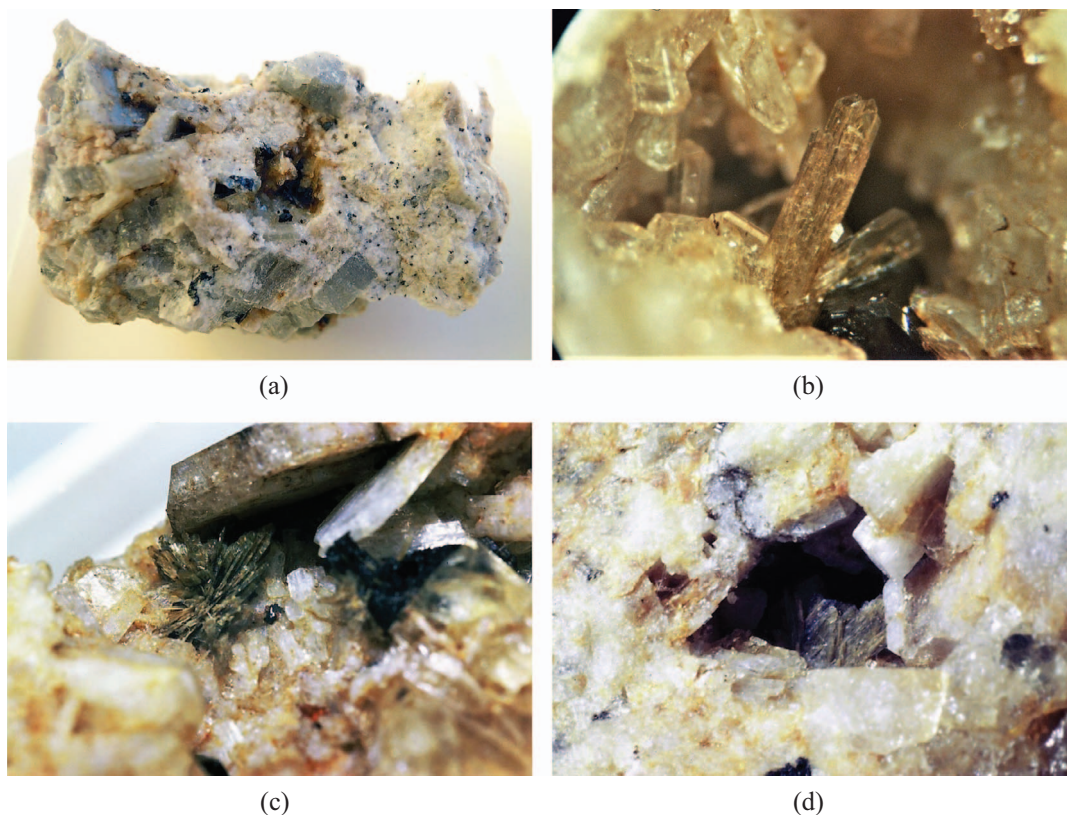


Fig. 1. Pictures from the collection of Ezio Bernabè, showing: (a) a fragment of the ejectum found at Vetralla (sample EB-1411, $4.3 \times 2.5 \times 2$ cm) with large crystals of K-feldspar; in the cavities, hellandite, titanite, hornblende and magnetite; (b) in the foreground, yellowish light-brown crystals of hellandite on ferro-hornblende; colourless sanidine crystals in background (sample EB-1528, field of view (FOV) 7 mm); (c) light-brown lamellar crystals of hellandite, with danburite, magnetite and sanidine crystals (EB-549, FOV 16 mm); (d) light-brown crystals of hellandite in a geode 5.5 mm in diameter (EB-1802, $5.5 \times 4.5 \times 3$ cm).

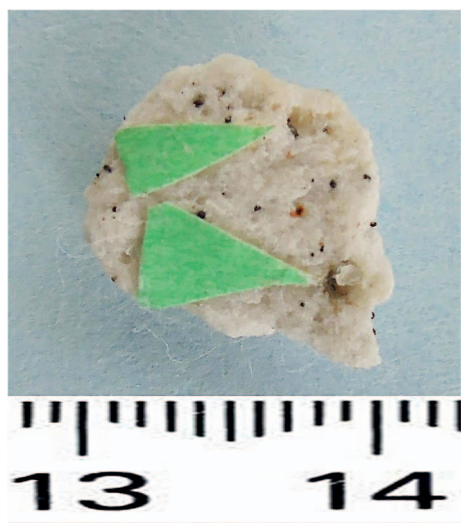


Fig. 2. The fragment used for the characterization of ferri-mottanaite-(Ce); a few crystals occur at the edges of the cavities indicated by the green arrows.

If we consider the chemical substitutions occurring in mottanaite-(Ce) and ciprianiite, $A^{3+} = \text{REE}^{3+}$, $B^{4+} = \text{Th}^{4+}$, $C^{2+} = \text{Ca}^{2+}$.

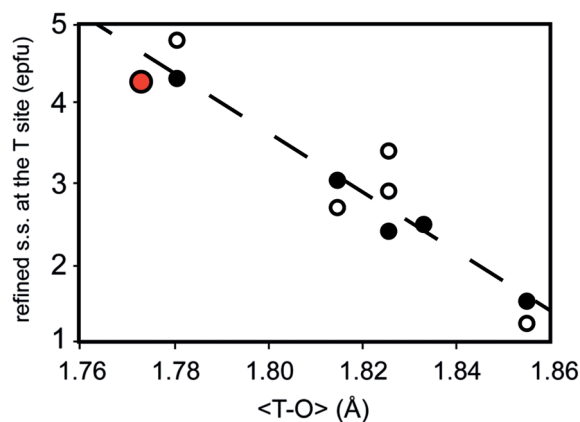


Fig. 3. Validation of the refined site-scattering value for $T(\text{Be} + \text{Li})$ based on the model of Oberti *et al.* (2002).

Let us consider first mottanaite-(Ce). We may recast $Y[\text{REE}_{1.46}\text{Ca}_{0.37}\text{Th}_{0.17}]_{\Sigma 2}$ as $Y[\text{REE}_{1.46}(\text{Th}_{0.17}\text{Ca}_{0.17})_{\Sigma 0.34}\text{Ca}_{0.20}]_{\Sigma 2}$, so that $\text{REE}^{3+} > (\text{Th}^{4+}\text{Ca}^{2+}) > \text{Ca}$; REE^{3+} is the dominant Y-group species, and Y-group cations can be written as REE_2^{3+} . To have electroneutrality, we must write the T-group cations as $(\text{Be}_{1.5}\square_{0.5})$. Note that this is an example of the “valency-imposed double site-occupancy” (by Be

Table 1. Atom coordinates, refined site-scattering values (s.s., *epfu*), atom displacement parameters (B_{eq} , Å²; $\beta_{ij} \times 10^4$) for ferri-mottanaite-(Ce) sample UK-EB-1-08 n. 1.

Site	s.s.	x	y	z	B_{eq}	β^{11}	β^{22}	β^{33}	β^{12}	β^{13}	β^{23}
O1		0.04436(9)	0.2443(4)	0.5677(2)	0.88(4)	7(1)	95(7)	22(2)	−5(2)	4(1)	−10(3)
O2		0.17868(9)	0.3180(4)	0.7574(2)	0.75(4)	5(1)	74(6)	20(2)	2(1)	1(1)	0(3)
O3		0.07025(10)	−0.3101(4)	0.7399(2)	1.33(5)	8(1)	151(8)	42(2)	8(2)	4(1)	−40(3)
O4		0.13174(10)	−0.3296(4)	0.5419(2)	0.93(4)	9(1)	79(7)	29(2)	−1(2)	7(1)	10(3)
O5	16.22(4)	0.03666(10)	0.1978(4)	0.8693(2)	1.05(4)	9(1)	116(7)	27(2)	−2(2)	6(1)	0(3)
O6		0.24703(9)	−0.2430(4)	0.8578(2)	0.73(4)	7(1)	60(6)	20(2)	−1(2)	5(1)	−1(3)
O7		0.16795(9)	0.2320(4)	0.4461(2)	0.68(4)	6(1)	51(6)	22(2)	−1(1)	4(1)	−1(3)
O8		0.13307(10)	0.6782(4)	0.3075(2)	1.08(4)	10(1)	107(7)	24(2)	6(2)	2(1)	−8(3)
O9		0.18632(9)	0.3249(4)	0.1601(2)	0.91(4)	7(1)	94(7)	34(2)	2(2)	8(1)	11(3)
O10		0.08491(10)	0.7196(5)	0.0340(2)	1.60(5)	7(1)	243(9)	46(2)	2(2)	6(1)	66(4)
O11		0.05018(10)	0.2661(5)	0.1577(2)	1.56(5)	10(1)	255(9)	24(2)	−29(2)	1(1)	23(4)
O12		$\frac{1}{4}$	0.3386(5)	0	0.90(6)	12(1)	66(9)	17(2)	−	7(1)	−
O13		$\frac{1}{4}$	0.6513(5)	$\frac{1}{2}$	0.87(6)	5(1)	75(9)	35(2)	−	6(1)	−
Si1		0.10369(3)	0.48284(13)	0.65078(6)	0.52(1)	4(1)	54(2)	15(1)	0(1)	3(1)	−1(1)
Si2		0.11342(3)	0.49957(14)	0.16232(6)	0.64(1)	5(1)	81(2)	16(1)	−1(1)	3(1)	6(1)
B1	10.00(5)	0.17315(14)	0.5319(6)	0.4516(3)	0.72(6)	6(1)	81(9)	21(2)	−2(2)	4(1)	1(4)
B2	10.00(5)	0.25286(14)	0.4633(5)	0.1339(3)	0.59(5)	5(1)	62(9)	16(2)	0(2)	4(1)	−2(4)
T	4.28(4)	0.0382(3)	0.5411(14)	0.8661(7)	1.16(14)	6(2)	171(26)	34(6)	2(5)	8(2)	13(10)
M1	20.42(2)	0	0	0	0.69(1)	6(1)	76(2)	19(1)	−2(1)	4(1)	−3(1)
M2	104.32(5)	0.04283(2)	0.01508(3)	0.36128(2)	0.60(1)	5(1)	69(1)	16(1)	−2(1)	4(1)	−2(1)
M3	41.20(5)	0.24720(2)	0.00257(10)	0.66113(4)	0.78(1)	8(1)	73(2)	19(1)	1(1)	5(1)	−3(1)
M4	45.02(5)	0.15731(2)	−0.02886(9)	0.93122(4)	0.82(1)	6(1)	98(2)	25(1)	2(1)	6(1)	5(1)

Table 2. Selected bond lengths (Å) and polyhedral volume (V , Å³) for ferri-mottanaite-(Ce) sample UK-EB-1-08 n. 1.

B1–O4	1.560(3)	B2–O2	1.543(3)	Si1–O1	1.612(2)
B1–O7	1.427(3)	B2–O6	1.397(3)	Si1–O2	1.654(2)
B1–O8	1.564(3)	B2–O9	1.534(3)	Si1–O3	1.620(2)
B1–O13	1.481(3)	B2–O12	1.479(3)	Si1–O4	1.659(2)
<B1–O>	1.508	<B2–O>	1.488	<Si1–O>	1.636
V	1.739	V	1.670	V	2.244
Si2–O8	1.636(2)	T–O3	1.764(6)	M1–O5×2	1.958(2)
Si2–O9	1.625(2)	T–O5	1.631(7)	M1–O10×2	2.027(2)
Si2–O10	1.615(2)	T–O10	1.838(7)	M1–O11×2	2.006(2)
Si2–O11	1.625(2)	T–O11	1.855(7)	<M1–O>	1.997
<Si2–O>	1.625	<T–O>	1.772	V	10.466
V	2.199	V	2.750		
M2–O1	2.371(2)	M3–O2	2.417(2)	M4–O2	2.564(2)
M2–O1	2.382(2)	M3–O4	2.627(2)	M4–O3	2.462(2)
M2–O3	2.467(2)	M3–O6	2.331(2)	M4–O5	2.409(2)
M2–O4	2.596(2)	M3–O7	2.440(2)	M4–O6	2.333(2)
M2–O5	2.520(2)	M3–O7	2.506(2)	M4–O6	2.495(2)
M2–O7	2.454(2)	M3–O8	2.675(2)	M4–O9	2.777(2)
M2–O8	2.549(2)	M3–O9	2.377(2)	M4–O10	2.340(2)
M2–O11	2.451(2)	M3–O13	2.362(2)	M4–O12	2.402(2)
<M2–O>	2.474	<M3–O>	2.467	<M4–O>	2.473
V	25.775	V	25.308	V	25.550

and □) noted by [Hatert & Burke \(2008\)](#). Hence, the ideal formula for mottanaite is ${}^X\text{Ca}_4{}^Y\text{REE}_2{}^Z\text{Al}^T(\text{Be}_{1.5}\square_{0.5})[\text{B}_4\text{Si}_4\text{O}_{22}]^W\text{O}_2$, to be compared with the ideal formula originally assigned ([Oberti et al., 2002](#)), i.e. ${}^X\text{Ca}_4{}^Y(\text{REECa})_2{}^Z\text{Al}^T\text{Be}_2[\text{Si}_4\text{B}_4\text{O}_{22}]^W\text{O}_2$.

Note that in the empirical formula provided by [Della Ventura et al. \(2002\)](#), (i) the aggregate charge of the Y-group

cations is 5.80, closer to the value of 6.00 in the revised ideal formula than the value of 5.00 in the original ideal formula; (ii) the Be content of the T-group cations is 1.18 *apfu*, closer to the value of 1.5 Be *apfu* in the revised ideal formula than the value of 2.0 Be *apfu* in the original ideal formula.

Similarly, in ciprianiite, we may recast $[\text{REE}_{0.74}\text{Th}_{0.66}\text{Ca}_{0.60}]_{\Sigma 2}$ as $[\text{REE}_{0.74}(\text{Th}_{0.60}\text{Ca}_{0.60})_{\Sigma 1.2}\text{Th}_{0.06}]_{\Sigma 2}$, so that $(\text{Th}^{4+}\text{Ca}^{2+}) > \text{REE}^{3+} > \text{Th}^{4+}$, and $(\text{Th}^{4+}\text{Ca}^{2+})$ is the dominant Y-group species. Hence, we must write Y-group cations as $(\text{Th}^{4+}\text{Ca}^{2+})_2$.

There are two possible ideal formulae compatible with this Y-group cation content:

1. ${}^X\text{Ca}_4{}^Y(\text{ThCa})_2{}^Z\text{Al}^T(\text{Be}_{0.5}\square_{1.5})[\text{B}_4\text{Si}_4\text{O}_{22}]^W(\text{OH})_2$;
2. ${}^X\text{Ca}_4{}^Y(\text{ThCa})_2{}^Z\text{Al}^T(\text{Be}_{1.5}\square_{0.5})[\text{B}_4\text{Si}_4\text{O}_{22}]^W\text{O}_2$.

For formula 1, the apparent violation of the constraint that $T_{\square} = 2 - \text{Be} - \text{Li} - \text{OH}$ disappears if we consider that in the empirical formula of ciprianiite, $\text{Be} = 0.82$, $\text{Li} = 0.04$ and $\text{F} = 0.49$ *apfu*. Indeed, [Oberti et al. \(2002\)](#) showed that in hellandite, $\text{OH} \leq (2 - \text{Li} - \text{Be} - \text{F})$ *apfu*, so that in ciprianiite, OH is ≤ 0.65 *apfu* and $(\text{OH} + \text{F}) \leq 1.14$ *apfu*. The value of $\text{Be} = 0.82$ is closer to ideal formula (1) (with $\text{Be} = 0.50$ *apfu*) than to ideal formula (2) (with $\text{Be} = 1.50$ *apfu*), whereas that estimated for the monovalent-anion content of O5 ($\text{OH} + \text{F}$) is compatible with both formulae (1) and (2). Hence the empirical formula of ciprianiite is closer to that of ideal formula (1).

In agreement with our conclusions, in July 2018 IMA-CNMNC approved (with vote 18 D) the redefinition of the ideal formulae of mottanaite-(Ce) as ${}^X\text{Ca}_4{}^Y\text{Ce}_2{}^Z\text{Al}^T(\text{Be}_{1.5}\square_{0.5})_{\Sigma 2}[\text{B}_4\text{Si}_4\text{O}_{22}]^W\text{O}_2$, and ciprianiite as ${}^X\text{Ca}_4{}^Y(\text{ThCa})_{\Sigma 2}{}^Z\text{Al}^T(\text{Be}_{0.5}\square_{1.5})_{\Sigma 2}[\text{B}_4\text{Si}_4\text{O}_{22}]^W(\text{OH})_2$.

Table 3. Powder X-ray diffraction data (d in Å) for ferri-mottanaite-(Ce) sample UK-EB-1-08. The strongest reflections are in bold.

I_{rel}	$d_{\text{(calc)}}$	hkl	I_{rel}	$d_{\text{(calc)}}$	hkl	I_{rel}	$d_{\text{(calc)}}$	hkl	I_{rel}	$d_{\text{(calc)}}$	hkl
8	9.580	0 0 1	8	2.712	2 0 3	4	2.077	$\bar{6}$ 1 4	8	1.743	$\bar{10}$ 1 1
22	8.900	2 0 0	100	2.648	0 1 3	6	2.049	4 2 2	9	1.738	2 2 4
15	5.600	2 0 1			4 1 3	11	1.993	6 1 2	10	1.725	4 1 4
33	4.745	0 1 0	8	2.553	$\bar{2}$ 0 4	16	1.978	4 2 1	11	1.709	$\bar{4}$ 0 6
24	4.188	2 1 0	12	2.395	0 0 4	48	1.904	0 2 3	14	1.686	$\bar{8}$ 1 5
10	3.620	2 1 1	20	2.366	$\bar{8}$ 0 2			4 2 3			0 2 4
11	3.578	4 0 1	11	2.309	$\bar{6}$ 0 4			6 2 1	19	1.675	$\bar{8}$ 2 2
36	3.453	2 1 2	5	2.295	$\bar{2}$ 2 0	10	1.874	$\bar{10}$ 0 1	15	1.667	$\bar{10}$ 1 0
14	3.421	2 0 3	14	2.253	3 1 4	9	1.867	6 0 3	18	1.651	$\bar{10}$ 1 4
6	3.372	0 $\bar{1}$ 2	14	2.242	$\bar{7}$ 1 0			$\bar{10}$ 0 3	9	1.642	2 1 5
43	3.246	4 1 0	25	2.189	3 1 3	6	1.852	4 0 4	24	1.609	6 2 2
28	3.191	0 0 3			$\bar{7}$ 1 3	9	1.805	$\bar{8}$ 0 5			$\bar{4}$ 1 6
		$\bar{4}$ 0 3	9	2.139	0 1 4	13	1.788	8 0 2	8	1.596	0 0 6
44	3.086	4 1 2	10	2.116	$\bar{8}$ 1 2	10	1.781	$\bar{10}$ 0 0			$\bar{8}$ 0 6
44	2.919	2 1 2			$\bar{8}$ 1 1	9	1.761	$\bar{10}$ 0 4	11	1.583	$\bar{2}$ 1 6
50	2.857	4 1 1	2	2.095	4 2 0	10	1.749	2 0 5			0 3 0

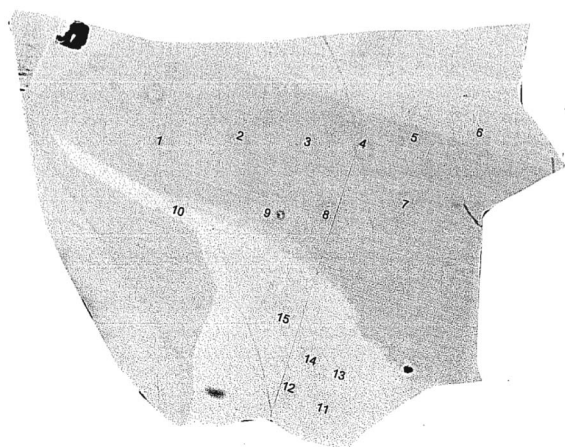
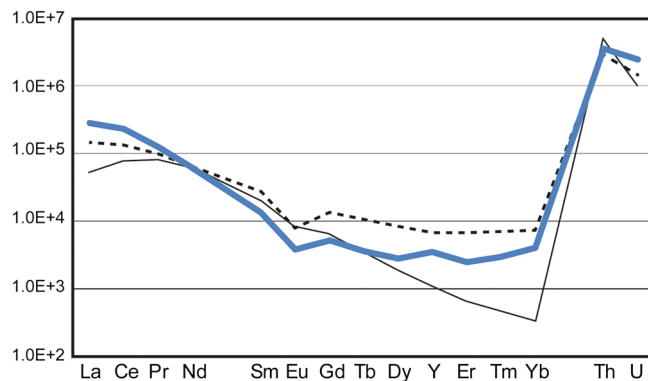


Fig. 4. BSE image of crystal UK-EB-1-08 n. 1 showing the position of the different point analyses.

Fig. 5. Chondrite-normalized patterns of ferri-mottanaite-(Ce) from Tre Croci (solid blue line), mottanaite-(Ce) from Monte Cavalluccio (dashed line) and ciprianiite from Tre Croci (solid black line); the two latter patterns are taken from Della Ventura *et al.* (2002). Experimental data for Th, U, and Y [plotted in the position of Ho (not measured) due to the similarity in their ionic radii] are compared to those of REE.

2. Ferri-mottanaite-(Ce) from Tre Croci (Vetralla, Viterbo, Italy)

2.1. Occurrence

On 27 March 1986, at Tre Croci, close to Vetralla (Viterbo), Ezio Bernabè found a large rounded sanidine-syenite ejectum, approximately $50 \times 40 \times 40$ cm in size, part of the Vico volcanic complex. It showed some brownish oxidized areas, and other parts with light-grey crystals of K-feldspar; two geodes with danburite crystals and pale-brown platy or lamellar crystals of an unknown species were also observed. These geodes were carefully separated before cutting the ejectum. Below an external crust about 2 cm thick, there were many fresh zones with colourless to whitish sanidine crystals which alternated with fine-grained compact beige to pale-grey peperino (volcanic tuff). Coexisting minerals were titanite, magnetite, hornblende, thorite/ekanite,

danburite, vonsenite, fluorite, “apatite”, cancrinite, zircon and zirconolite. Details of the mineralogy are reported in Fig. 1.

The small fragment studied in this work is shown in Fig. 2. Isolated magnetite crystals and brownish-yellow titanite crystals occur in a crystalline K-feldspar matrix. Two cavities (indicated by arrows) contain large colourless fluorite crystals; the light-brown rims of these cavities are ferri-mottanaite-(Ce). Fluorite and feldspar were identified by X-ray diffraction.

Type material is deposited in the collection of the Museo di Mineralogia, Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia, under the catalogue number 2018-02.

2.2. Appearance and physical properties

Ferri-mottanaite-(Ce) occurs as light yellow-brown subhedral tabular crystals smaller than 1 mm; it is non-fluorescent,

Table 4. Chemical data (wt%) for the refined crystal of ferri-mottanaite-(Ce) UK-EB-1-08 n. 1. Zone 1 = EMP points 1–9; Zone 2 = EMP points 10–15. The last column reports the integrated EMP + LA-ICP-MS analysis used for the calculation of the unit formula.

	Zone 1			Zone 2			Crystal weighted mean	EMP + LAM
	Mean	Range	esd	Mean	Range	esd		
SiO ₂	23.75	23.42–23.92	0.16	23.46	23.16–23.72	0.20	23.63	23.63
B ₂ O ₃ ^{calc} *	12.77	11.76–13.67	0.58	13.92	13.46–14.41	0.35	13.23	13.23
Mn ₂ O ₃	1.55	1.42–1.70	0.08	1.02	0.95–1.08	0.04	1.34	1.34
Al ₂ O ₃	0.86	0.77–1.00	0.09	1.54	1.49–1.60	0.04	1.13	1.13
TiO ₂	1.29	1.22–1.43	0.06	1.35	1.12–1.49	0.14	1.32	1.32
Fe ₂ O ₃	4.28	4.19–4.41	0.08	3.39	3.27–3.56	0.11	3.93	3.93
CaO	24.73	24.50–24.83	0.12	23.11	22.77–23.31	0.26	24.08	24.08
La ₂ O ₃	3.29	3.17–3.45	0.11	4.53	4.38–4.72	1.15	3.79	3.79
Ce ₂ O ₃	6.43	6.20–6.71	0.16	8.90	8.78–9.02	0.10	7.42	7.42
ThO ₂	11.88	11.20–12.95	0.56	11.28	10.98–11.53	0.22	11.64	11.64
UO ₂	2.10	1.57–2.62	0.32	2.72	2.15–3.75	0.65	2.35	2.35
Y ₂ O ₃								0.43
Pr ₂ O ₃	0.61	0.56–0.66	0.04	0.76	0.70–0.87	0.07	0.67	0.83
Nd ₂ O ₃	1.58	1.48–1.69	0.07	1.98	1.74–2.17	0.19	1.74	2.02
Sm ₂ O ₃	0.18	0.09–0.28	0.06	0.22	0.13–0.28	0.06	0.20	0.14
Eu ₂ O ₃	0.13	0.06–0.21	0.05	0.19	0.14–0.27	0.06	0.15	0.02
Gd ₂ O ₃	0.09	0.0–0.21	0.11	0.12	0.02–0.20	0.08	0.10	0.08
Dy ₂ O ₃	0.02	0.0–0.24	0.13	0.01	0.00–0.13	0.09	0.02	0.05
Er ₂ O ₃	0.06	0.0–0.15	0.08	0.01	0.00–0.10	0.07	0.04	0.03
Yb ₂ O ₃	0.05	0.02–0.09	0.03	0.10	0.06–0.16	0.05	0.07	0.05
F	1.25	1.13–1.47	0.13	0.59	0.40–0.75	0.14	0.99	0.99
BeO ^{calc} **	2.59			2.63				2.53
Li ₂ O								0.06
H ₂ O ^{calc} ***	0.21			0.54				0.34
–O=F	0.53			0.25				0.42
Total	99.18			102.11			100.35	101.00

*The B₂O₃ content was calculated for all the points analysed.

**The BeO content was calculated based on the refined site-scattering value for T cations (4.28 electrons). This value is validated from the linear correlation found by [Oberti et al. \(2002\)](#) between the refined <T–O> distance and the site-scattering at the T site both refined or calculated from SIMS analysis ([Fig. 4](#)).

***The H₂O content listed is the *maximum* value allowed by the stoichiometry ($\text{OH} \leq 2 - \text{Li} - \text{Be} - \text{Cl} - \text{F}$; [Oberti et al., 2002](#)).

and has a very pale-yellow streak and a vitreous lustre. Ferri-mottanaite-(Ce) is brittle and no cleavage or parting were observed.

Optical properties were measured on a different crystal (UK-EB-1-08 n. 2). In order to check for its composition, a structure refinement was done, which produced crystal-chemical parameters very similar to those of crystal UK-EB-1-08 n. 1 ([Table 6](#)). A Bloss spindle stage was used to orient a crystal to measure refractive indices and 2V by extinction curves in Na light. The resulting measurements were processed using Excalibr II ([Bartelmehs et al., 1992](#)). The optical orientation was determined by transferring the crystal from the spindle stage to a single-crystal diffractometer and measuring the relative axial relations by X-ray diffraction ([Gunter & Twamley, 2001](#)). In transmitted plane-polarized light, ferri-mottanaite-(Ce) is pleochroic ($\alpha = \beta = \tan$, $\gamma = \text{yellow-brown}$; $X \sim Y < Z$). It is biaxial (–), $\alpha = 1.748(5)$, $\beta = 1.762(5)$, $\gamma = 1.773(3)$, 2V (meas.) = 85.9(5)°, 2V (calc.) = 82.5°. The dispersion is strong ($r > v$), and the orientation is: $X \parallel b$, $Y \wedge a = 10.1^\circ$ (β acute), $Z \wedge c = 21.0^\circ$ (β obtuse). The compatibility index ($1 - (K_p/K_c)$; [Mandarino, 1981](#)) is 0.031 (excellent) based on the proposed chemical formula.

2.3. Single-crystal and powder-diffraction analysis

Diffraction data for a tabular [on (010)] single crystal $180 \times 140 \times 100 \mu\text{m}$ in size were collected in the θ range $2\text{--}30^\circ$ with a Bruker-AXS CCD diffractometer, working with graphite-monochromated MoK α X-radiation ($\lambda = 0.7107 \text{ \AA}$). Omega-rotation frames (scan width 0.3° , scan time 20 s, sample-to-detector distance 50 mm) were processed with the SAINT software ([Bruker, 2003](#)) and intensities were corrected for Lorentz and polarization effects; absorption effects were empirically evaluated by the SADABS software ([Krause et al., 2015](#)) and an absorption correction was applied to the data. Ferri-mottanaite-(Ce) is monoclinic, space group: $P2_1/a$; $a = 19.0548(9) \text{ \AA}$, $b = 4.7468(2) \text{ \AA}$, $c = 10.2560(5) \text{ \AA}$, $\beta = 110.906(2)^\circ$, $V = 866.58(7) \text{ \AA}^3$, $Z = 2$. The $a:b:c$ ratio calculated from the unit-cell parameters is 4.014:1:2.161. No twinning was observed.

A total of 10,052 collected reflections was reduced to 2538 unique reflections (mean redundancy = 4, $R_{\text{int}} = 1.5\%$). Of these, 2400 reflections with $I_o > 3\sigma_I$ were considered as observed during unweighted full-matrix least-squares refinement on F using a program written in Pavia ([Cannillo et al., 1983](#)), which allows the use of neutral *versus* ionized

scattering curves at all sites where solid solution does not occur [in this case, the B, Si and anion sites, except O(5)], and of combinations of ionized scattering curves at all the other sites (Hawthorne *et al.*, 1995; Oberti *et al.*, 2017). At convergence, $R_{\text{obs}} = 1.8\%$ (2400 reflections) and $R_{\text{all}} = 2.0\%$ (2538 reflections).

The values of the site scattering (s.s., in electrons per formula unit, *epfu*) and mean bond length refined at the *T* site are in good agreement with the trend defined in Fig. 5 in Oberti *et al.* (2002), thus validating our estimate of the (Be + Li) content at this site (Fig. 3).

Crystal UK-EB-1-08 n. 1, which was used for structure refinement and chemical analysis, has the code *jen* in the crystallographic database of the CNR-IGG in Pavia, Italy; its refined atom coordinates and displacement parameters, and selected bond lengths and angles are given in Tables 1 and 2, respectively. Crystal UK-EB-1-08 n. 2, which was used to measure optical properties and for trace-element analysis, has the code *kcq* in the crystallographic database; the results of its structure refinement are provided only as supplementary information as a CIF file. The deposited CIF file contains structural data and observed structure factors for both crystals and is freely available online as Supplementary Material linked to this article on the GSW website of the journal, <https://pubs.geoscienceworld.org/eurjmin/>.

X-ray powder-diffraction data ($\text{CuK}\alpha$, $\lambda = 1.54178 \text{ \AA}$) were obtained using the XPREP utility of SAINT (Bruker, 2003), which generates a 2D powder diffractogram (Debye-Scherrer technique) starting from the F_{obs}^2 collected on the single crystal and taking into account solely the information concerning the unit-cell dimensions and the Laue symmetry. No Lorentz and polarization corrections were applied. Data are given in Table 3.

2.4. Chemical analyses and unit formula

During electron-microprobe (EMP) analysis, the refined crystal (UK-EB-1-08 n. 1) was found to be inhomogeneous. A backscattered-electron image shows that the crystal can be described in terms of two slightly different compositions (Fig. 4). Chemical analyses were done with a Cameca SX100 electron microprobe (WDS mode, 15 kV, 10 nA, 5 μm beam diameter) at the University of Manitoba in Winnipeg. The standards used are: diopside (Si, Ca; TAP); titanite (Ti, LPET); andalusite (Al, TAP); REEPO₄ (REE, LLiF); fayalite (Fe, LLiF); spessartine (Mn, LLiF); forsterite (Mg, LTAP); UO₂ (U); ThO₂ (Th); fluoro-riebeckite (F, TAP). B₂O₃ values were calculated for each point analysis based on eight – Si *apfu* and then the calculated values were averaged. The data were reduced and corrected by the PAP method of Pouchou & Pichoir (1985). Mg, Y, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu were not detected in many point analyses.

Trace-element composition was analysed also by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), combining an Eximer laser (Geolas) working at 193 nm with a quadrupole ICP mass spectrometer of type DRCE from Perkin Elmer. For trace-element determinations, the laser was operated at a repetition rate of 10 Hz, with a

Table 5. Unit formulae calculated based on 24 anions for the refined crystal of ferri-mottanaite-(Ce) UK-EB-1-08 n. 1. Zone 1 = points 1–9; Zone 2 = points 10–15. Refined (SREF) and calculated (calc) site-scattering values (ss, in electrons per formula unit, *epfu*) are compared to show the reliability of the chemical analysis.

Cations/anions	Zone 1	Zone 2	Crystal	EMP + LAM
	Ave	Ave	Ave	
Si	4.10	3.96	4.04	4.03
B	3.80	4.06	3.91	3.89
Be	1.07	1.07	1.07	1.04
Li				0.04
$\Sigma T + \text{Si} + B$	8.97	9.09	9.02	9.00
Ti	0.17	0.17	0.17	0.17
Al	0.18	0.31	0.23	0.23
Fe ³⁺	0.56	0.43	0.51	0.50
Mn ³⁺	0.20	0.13	0.17	0.17
ΣZ	1.11	1.04	1.08	1.07
Ca	4.57	4.18	4.41	4.40
La	0.21	0.28	0.24	0.24
Ce	0.41	0.55	0.46	0.46
Th	0.47	0.43	0.45	0.45
U	0.08	0.10	0.09	0.09
Y				0.04
Pr	0.04	0.05	0.04	0.05
Nd	0.10	0.12	0.11	0.12
Sm	0.01	0.01	0.01	0.01
Eu	0.01	0.01	0.01	0.00
Other REE				0.01
$\Sigma X + Y$	5.90	5.73	5.82	5.87
F	0.68	0.31	0.53	0.53
(OH) [−]	0.24	0.61	0.39	0.38
O ^{2−}	1.08	1.08	1.08	1.09
ΣO5	2.00	2.00	2.00	2.00
ss <i>T</i> calc	4.28	4.28	4.28	4.28
ss <i>Z</i> calc	25.64	22.20	24.24	23.98
ss <i>X + Y</i> calc	186.42	190.76	187.55	190.05
ss <i>T</i> SREF	4.28	4.28	4.28	4.28
ss <i>Z</i> SREF	20.42	20.42	20.42	20.42
ss <i>X + Y</i> SREF	190.54	190.54	190.54	190.54

fluence of *ca.* 8.8 J cm^{−2} and an ablation spot of *ca.* 50 μm in size. NBS NIST-610 and ⁴³Ca were used as external and internal standards, respectively. Precision and accuracy for trace elements were assessed on the BCR-2 USGS and NBS NIST-612 reference glasses and are better than 6% relative. Data reduction was done using the GLITTER software package (van Achterbergh *et al.*, 2001). Because crystal n. 1 was lost in the mail, LA-ICP-MS analysis for light elements and REE were done on crystal n. 2 at the LA-ICP-MS CNR-IGG laboratory, the procedures/standards of which are however settled for trace-element analysis (so that the signals for B, Be, La, Ce, Th and U were saturated or close to saturation and could not be used). Due to the size of the crystal, only three point analyses could be made. LA-ICP-MS analysis confirmed that (i) the Li content is very low (550 ppm with esd ~50 ppm, corresponding to 0.06 Li₂O wt% and 0.04 Li *apfu* in crystal n. 2); in holotype mottanaite-(Ce), Li was 0.02 *apfu* (Della Ventura *et al.*, 2002); (ii) Ce dominates among REE (a REE pattern obtained for crystal n. 2 is

Table 6. Comparison of the optical and crystallographic properties reported for the two minerals related to the rootname mottanaite and for ciprianiite.

	Mottanaite-(Ce)	Ciprianiite	Ferri-mottanaite-(Ce) UK-EB-1-08 n.1	Ferri-mottanaite-(Ce) UK-EB-1-08 n. 2
Colour	Brownish	Brownish	Light yellow-brown	Light yellow-brown
Optical class	Biaxial (–)	*		Biaxial (–)
Pleochroism	Non pleochroic			$\alpha = \beta = \tan$, $\gamma =$ yellow-brown
Orientation	Not reported			$X \parallel b$, $Y \wedge a = 10.1$ (β acute) $Z \wedge c = 21.0^\circ$ (β obtuse)
α	1.680(5)			1.664(2)
β	1.694(2)			1.692(2)
γ	1.708(5)			1.722(5)
$2V_{\text{meas}} (^\circ)$	90			85.9 (5)
a (Å)	19.032(9)	19.059(5)	19.0548(9)	19.0579(10)
b (Å)	4.746(3)	4.729(1)	4.7468(2)	4.7451(3)
c (Å)	10.248(5)	10.291(4)	10.2560(5)	10.2684(6)
β (°)	110.97(5)	111.33(2)	110.906(2)	111.035(2)
V (Å ³)	864.3(9)	864.0(5)	866.58(7)	866.71(9)
<B1–O> (Å)	1.503	1.496	1.508	1.500
<B2–O> (Å)	1.495	1.485	1.488	1.489
<Si1–O> (Å)	1.637	1.633	1.636	1.634
<Si2–O> (Å)	1.622	1.624	1.625	1.625
<M1–O> (Å)	1.977	1.966	1.997	1.985
<M2–O> (Å)	2.468	2.473	2.474	2.479
<M3–O> (Å)	2.473	2.469	2.467	2.469
<M4–O> (Å)	2.469	2.467	2.473	2.471
<T–O> (Å)	1.781	1.827	1.772	1.793
s.s. B1	10.00	10.00	10.00	10.00
s.s. B2	10.00	10.00	10.00	10.00
s.s. M1	18.4	18.2	20.42	19.47
s.s. M2	110.0	115.7	104.32	104.58
s.s. M3	41.7	41.9	41.20	40.46
s.s. M4	43.3	53.7	45.02	45.24
s.s. T	4.4	2.5	4.28	3.48
Reference	Della Ventura <i>et al.</i> (2002)	Della Ventura <i>et al.</i> (2002)	This work	This work

*Crystals are typically twinned.

reported in Fig. 5); (iii) Na is ~ 0.01 apfu and Sr is ~ 0.001 apfu. These results and the LA-ICP-MS values for the less abundant REE (Y, Pr, Nd, Sm, Eu, Gd, Dy, Er, and Yb) were used together with EMP results to obtain the complete formula of the studied sample. Because the Li, Be and F contents were analysed and validated with SREF, the H₂O content was calculated based on the observation that ^WOH in hellandite is constrained by the relation $\text{OH} \leq (2 - \text{Li} - \text{Be} - \text{F})$ (Oberti *et al.*, 2002). For ferri-mottanaite-(Ce), the calculated $\text{OH}_{\text{max}} = 0.39$ apfu. A qualitative reflectance FTIR analysis was done at the Istituto Nazionale di Fisica Nucleare, Frascati, Rome (courtesy of Giancarlo Della Ventura) but did not show evidence of O–H stretching bands.

Analytical data are given in Table 4 for the two zones reported in Fig. 4 and for the averaged crystal (for comparison with the SREF results) both based only on EMP and on EMP + LA-ICP-MS results.

The unit formulae were calculated based on 24 anions: $[\text{O}_{22}(\text{O}, \text{OH}, \text{F}, \text{Cl})_2]$. Oberti *et al.* (2002) provided the following rules for group-site assignment in hellandite [with the

general formula: $X_4 Y_2 ZT_2[\text{Si}_4\text{B}_4\text{O}_{22}]\text{W}_2$: $T = \text{Li}^+$, Be^{2+} , $\square$ $Z = \text{Mg}$, Al^{3+} , Fe^{3+} , Mn^{3+} , Ti^{4+} , $Y = \text{Y}^{3+}$, $(\text{H})\text{REE}^{3+}$, Th^{4+} , U^{4+} , Ca^{2+} , $X = \text{Ca}^{2+}$, Y^{3+} (in M3) and Na^+ , Ca^{2+} , Y^{3+} , $(\text{L})\text{REE}^{3+}$ (in M4), $W = (\text{OH})^-$, F^- , O^{2-} , with $\text{OH} \leq (2 - \text{Be} - \text{Li} - \text{F})$. The results for the crystals of this work are reported in Table 5. Notwithstanding the small but significant compositional variations, all the compositions (both in the two zones and in the averaged crystal) have T cations $(\text{Li} + \text{Be}) > 1$ apfu (which implies the use of the root-name mottanaite according to Oberti *et al.*, 2002), Fe^{3+} is dominant over Al among the Z cations and Ce is dominant over REEs among the Y cations. Therefore, these compositions must be named ferri-mottanaite-(Ce).

Based on the empirical formula $^{X}_{0.54}\text{Ca}_{0.13}\text{Y}_{0.23}\text{Z}_{0.17}\text{Fe}_{0.50}\text{Al}_{0.23}\text{Mn}_{0.17}\text{Ti}_{0.17}\text{Be}_{1.04}\text{Li}_{0.04}\text{REE}_{0.93}\text{O}_{22}[\text{Si}_{4.03}\text{B}_{3.89}\text{O}_{22}](\text{O}_{1.09}\text{OH}_{0.38}\text{F}_{0.53})_2$, the calculated density of the ferri-mottanaite-(Ce) sample of this work is 3.952 g/cm³. The ideal formula of ferri-mottanaite-(Ce) is: $\text{Ca}_4\text{Ce}_2\text{Fe}^{3+}(\text{Be}_{1.5}\square_{0.5})_2[\text{Si}_4\text{B}_4\text{O}_{22}]\text{O}_2$, which corresponds to: SiO_2 22.90, B_2O_3 13.27, BeO 3.57, Fe_2O_3 7.61, Ce_2O_3 31.28, CaO 21.37, total 100 wt%.

2.5. Comparison with other species

The sample described in this work is the only one where Fe^{3+} has been shown to be the dominant Z cation. A specimen of mottanaite-(Ce) with Al close to Fe^{3+} (UKGPI003-Vetra) was found some years ago at Tre Croci as lamellar crystals (Ciriotti & Biagioni, 2011).

Table 6 compares the results of this work and the data available in the literature for mottanaite-(Ce) (from Sacrofano, Latium, Italy) and ciprianiite (from Tre Croci). Because holotype mottanaite-(Ce) also has a significant Fe^{3+} content in its empirical formula, *i.e.* $^{\text{X}}\text{Ca}_4^{\text{Y}}[\text{REE}]_{1.45}\text{Ca}_{0.37}(\text{Th}, \text{U})_{0.17}^{4+}\text{Y}_{0.01}]_{\Sigma=2}^{\text{Z}}(\text{Al}_{0.50}\text{Fe}_{0.38}^{3+}\text{Mg}_{0.03}\text{Ti}_{0.07}^{4+})_{\Sigma=0.98}^{\text{T}}(\text{Be}_{1.18}\text{Li}_{0.02}\square_{0.37})_{\Sigma=1.57}[\text{B}_{3.99}\text{Si}_{3.98}\text{O}_{22}]^{\text{W}}(\text{O}_{1.04}\text{F}_{0.53}(\text{OH})_{0.43})_{\Sigma=2}$, all the data reported are quite similar. However, in ferri-mottanaite-(Ce) we observe a higher site-scattering refined at the M1 site, which corresponds to a longer <M1–O> distance. The difference in composition also corresponds to higher values of the *a* and *c* edges and of the unit-cell volume, whereas the *b* edge seems to be insensitive to these compositional variations.

Figure 5 compares the chondrite-normalized REE patterns obtained for the same three samples. Those of mottanaite-(Ce) from Monte Cavalluccio and of ferri-mottanaite-(Ce) from Tre Croci are quite similar, and the higher compatibility for LREE in ferri-mottanaite-(Ce) is in accord with the presence of a larger M2 (and M1) cation as already noted by Oberti *et al.* (2002). Ciprianiite from Tre Croci is depleted in HREE with respect to ferri-mottanaite-(Ce) from the same locality, which may suggest further crystal-chemical constraints on REE incorporation.

Acknowledgements: We are really pleased to dedicate this manuscript to Christian Chopin to recognize not only his seminal scientific work but especially his long-lasting and invaluable contribution to the success of the *European Journal of Mineralogy*. Part of Christian's researches has been devoted to unravel the crystal chemistry and the classification of complex REE bearing minerals. Therefore we think that this subject is particularly suitable for this issue. Giancarlo Della Ventura is warmly acknowledged for providing a qualitative FTIR analysis of the sample under investigation.

References

- Bartelmehs, K.L., Bloss, F.D., Downs, R.T., Birch, J.B. (1992): Excalibr II. *Zeit. Kristallogr.*, **199**, 186–196.
- Bruker (2003): SAINT Software Reference Manual. Version 6. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cannillo, E., Germani, G., Mazzi, F. (1983): New crystallographic software for Philips PW11000 single crystal diffractometer. CNR Centro di Studio per la Cristallografia, Internal Report 2.
- Ciriotti, M.E. & Biagioni, C. (2011): Pot-pourri 2011: identificazione di minerali di interesse. *Micro*, **3**, 125–133.
- Della Ventura, G., Bonazzi, P., Oberti, R., Ottolini, L. (2002): Ciprianiite and mottanaite-(Ce), two new minerals of the hellandite group from Latium (Italy). *Am. Mineral.*, **87**, 739–744.
- Gunter, M.E. & Twamley, B. (2001): A new method to determine the optical orientation of biaxial minerals: a mathematical approach. *Can. Mineral.*, **39**, 1701–1711.
- Hatert, F. & Burke, E.A.J. (2008): The IMA–CNMNC dominant-constituent rule revisited and extended. *Can. Mineral.*, **46**, 717–728.
- Hawthorne, F.C., Ungaretti, L., Oberti, R. (1995): Site populations in minerals: terminology and presentation of results. *Can. Mineral.*, **33**, 907–911.
- Krause, L., Herbst-Irmer, R., Sheldrick, G.M., Stalke, D. (2015): Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Cryst.*, **48**, 3–10.
- Mandarino, J.A. (1981): The Gladstone–Dale relationship: part IV. The compatibility concept and its applications. *Can. Mineral.*, **19**, 441–450.
- Oberti, R., Della Ventura, G., Ottolini, L., Hawthorne, F.C., Bonazzi, P. (2002): Re-definition, nomenclature and crystal-chemistry of the hellandite group. *Am. Mineral.*, **87**, 745–752.
- Oberti, R., Della Ventura, G., Boiocchi, M., Zanetti, A., Hawthorne, F.C. (2017): New data on the crystal-chemistry of oxo-mangani-leakeite and mangano-mangani-ungarettiite from the Hoskins mine and their impossible solid-solution – An XRD and FTIR study. *Mineral. Mag.*, **81**, 707–722.
- Pouchou, J.L. & Pichoir, F. (1985): 'PAP' $\phi(\rho Z)$ procedure for improved quantitative microanalysis. in "Microbeam analysis – 1985", San Francisco Press, San Francisco, 104–160.
- van Acherterbergh, E., Ryan, C., Jackson, S., Griffin, W. (2001): Data reduction software for LAICPMS. in "Laser Ablation ICPMS in the Earth Science Principles and Application", Sylvester, P., ed. Mineralogical Association of Canada, 239–243, Short Course no. 29.

Received 9 January 2019

Modified version received 3 April 2019

Accepted 7 April 2019