

Supplementary material

1. Chemistry

5 **Table S1.** Vielleaureite-(Ce) electron-microprobe analyses averaged in Table 1, formulae on the basis of 8 cations.

Constituent	An. 60	An. 61	An. 62	An. 63
P ₂ O ₅	0.00	0.02	0.05	0.05
SiO ₂	28.84	27.51	28.79	27.19
B ₂ O ₃	0.00	0.00	0,09	0,01
Al ₂ O ₃	8,59	8,00	8,20	8,97
V ₂ O ₃	1.33	0.39	0.78	4.00
Fe ₂ O ₃	0.60	0.18	0.30	1.73
MnO _{tot}	21.97	22.52	22.73	19.76
Y ₂ O ₃	0.05	0.04	0.06	0.03
La ₂ O ₃	9.03	8.10	8.09	8.22
Ce ₂ O ₃	17.47	17.18	17.16	17.11
Nd ₂ O ₃	0.15	0.71	0.60	0.81
Sm ₂ O ₃	0.03	0.00	0.03	0.07
Gd ₂ O ₃	0.00	0.00	0.02	0.19
Dy ₂ O ₃	0.00	0.06	0.00	0.00
Er ₂ O ₃	0.51	0.77	0.08	0.30
Yb ₂ O ₃	0.00	0.00	0.12	0.00
MgO	5.07	5.81	5.92	2.02
CaO	1.36	0.57	0.64	2.27
SrO	0.00	0.00	0.00	0.03
Na ₂ O	0.00	0.06	0.03	0.01
F	2.77	3.38	3.14	0.94
Cl	0.04	0.02	0.03	0.06
– O = F,Cl	1.18	1.43	1.33	0.41
Total	98.98	96.73	98.17	94.16
P	0.00	0.00	0.00	0.00
Si	2.95	2.91	2.96	2.93
B	0.00	0.00	0.02	0.00
Al	1.04	1.00	0.99	1.14
V	0.11	0.03	0.06	0.34
Fe	0.05	0.01	0.02	0.14
Mn	1.91	2.02	1.98	1.80
Y	0.00	0.00	0.00	0.00
La	0.34	0.32	0.31	0.33
Ce	0.66	0.66	0.65	0.67

Nd	0.01	0.03	0.02	0.03
Sm	0.00	0.00	0.00	0.00
Gd	0.00	0.00	0.00	0.01
Dy	0.00	0.00	0.00	0.00
Er	0.02	0.03	0.00	0.01
Yb	0.00	0.00	0.00	0.00
Mg	0.77	0.91	0.91	0.32
Ca	0.15	0.06	0.07	0.26
Sr	0.00	0.00	0.00	0.00
Na	0.00	0.01	0.01	0.00
F	0.90	1.13	1.02	0.32
Cl	0.01	0.00	0.00	0.01
Total cat.	8.000	8.000	8.000	8.000

2. Crystallography

15 **Table S2.** Observed and calculated X-ray powder diffraction data (d in Å) for vielleaureite-(Ce). The strongest observed reflections are given in bold.

hkl	1		2	
	d_{obs}	I_{est}	d_{calc}	I_{calc}
001	-	-	9.2202	30
100	-	-	8.1329	29
-101	-	-	7.7765	14
101	5.18	25	5.1829	19
011	-	-	4.8564	9
110	4.67	20	4.6749	20
002	-	-	4.6101	9
-112	-	-	3.7237	11
012	-	-	3.5877	10
-211	3.485	35	3.4883	42
210	-	-	3.3129	15
201	-	-	3.2804	11
-212	-	-	3.2144	6
-113	2.881	100	2.8797	100
-302	-	-	2.8743	20
020	2.858	40	2.8565	42
211	-	-	2.8448	14
300	-	-	2.7110	9
013	2.708	25	2.7066	30
120	2.693	30	2.6951	32
-311	2.600	55	2.6044	54
-303	-	-	2.5922	7
202	2.589	20	2.5914	26
-313	-	-	2.3606	10
-222	-	-	2.3021	11
-304	-	-	2.2354	6
122	-	-	2.2064	7
-401	2.169	15	2.1705	21
221	-	-	2.1543	16
014	-	-	2.1376	6
-223	2.098	15	2.0997	20
203	-	-	2.0924	10
023	-	-	2.0924	14
222	-	-	1.9193	17
114	-	-	1.9057	7
-224	-	-	1.8619	7
-231	-	-	1.7480	6
-415	-	-	1.6674	6
-206	-	-	1.6671	6
-133	-	-	1.6537	13
322	-	-	1.6490	8
-106	-	-	1.6297	9
-424	1.606	20	1.6072	21
115	-	-	1.5981	9
-331	-	-	1.5961	12
412	-	-	1.5765	8
-406	-	-	1.5484	6
-226	-	-	1.4399	7
215	-	-	1.4306	5
040	-	-	1.4283	14
422	-	-	1.4224	7

1 = observed diffraction pattern; 2 = calculated diffraction pattern obtained with the atom coordinates reported in Table 4 and with the site populations given in Table 5 (only reflections with $I_{\text{rel}} \geq 5$ are listed).

3. NanoSIMS analysis of hellandite

25 The B, Be, Li and H concentrations in hellandite were determined with the Cameca
NanoSIMS 50 operated at Muséum national d'Histoire naturelle in Paris. We used the oxygen
RF plasma source to produce a 16 keV O⁻ primary beam. Samples were gold coated (20 nm
thick before analysis). During a first session, secondary ions of ⁷Li⁺, ⁹Be⁺, ¹¹B⁺, ²⁷Al⁺ and
28Si⁺ were collected in multicollection mode using electron multipliers with a dead time of 44
30 ns. Mass resolution exceeded 5500 to resolve mass interferences. Data acquisition was
performed with the primary beam set at 20 pA and rastered over a 3×3 μm² surface area. Ions
were exclusively collected from the inner 1.5×1.5 μm² using the beam blanking mode, in
order to minimize surface contamination. Each analysis consisted of 100 cycles with a
duration of 1.024 s. Each analysis was preceded by pre-sputtering on a 5×5 μm² surface area
35 for 1 min using a 500 pA primary beam to remove gold coating, surface contamination and
achieve a steady-state sputtering regime (Stephant et al., 2014). To determine OH content,
secondary ions of ²⁸SiH⁺ and ³⁰Si⁺ were monitored in multicollection mode. Settings were
identical with the exception of the primary-beam intensity set at 800 pA (for both analysis and
presputtering). Ion ratios were converted into elemental ratios using a set of gem-quality
40 crystals as standards (Table S3). The vacuum in the analysis chamber has never exceeded
2.10⁻⁹ torr.

Table S3. NanoSIMS calibrations.

45	Calibration standards used for Li, Be and B analysis		
	Quartz, elbaite, spodumene, avdeevite, gadolinite, bertrandite, hingganite		
	Calibration equations		
	Li/Si	$y = -0.037 x^2 + 0.269 x + 0.0097$	$R^2 = 0.978$
50	Be/Si	$y = 0.1856 x^2 + 0.496 x + 0.0064$	$R^2 = 0.982$
	B/Si	$y = 2.5483 x$	$R^2 = 0.999$
	Calibration standards used for H analysis		
	Quartz, elbaite, hingganite		
55	Calibration equation		
	OH/Si	$y = 26,18263 x$	$R^2 = 0.971$

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For each, the observed pattern is shown in the left panel. The right panel shows the pattern

indexed with the structure of Mn-rich hellandite-(Y) (Miyawaki et al., 2015); the mean angular deviation is 0.63° and 0.66° , respectively. Sample VAIN86.

5. On the nomenclature of Mn-rich hellandites

Considering the hellandite structural formula $M3_2M4_2M2_2M1 \text{ }^T\Box_2\text{Si}_4\text{B}_4\text{O}_{22}(\text{OH},\text{F},\text{O})_2$ (Oberti et al., 2002, where $^T\Box$ stands for tetrahedral vacancy) and that Mn is partitioned in $M3$ in Mn-rich hellandite (Miyawaki et al., 2015), it may not be fortuitous that the Mn/(Mn+Ca) ratio of hellandite coexisting with vielleaureite-(Ce) does not exceed 0.67, suggesting that the endmember formula of the tentative new species could be $\text{Mn}_2(\text{CaY})\text{Y}_2\text{AlB}_4\text{Si}_4\text{O}_{22}(\text{OH})_2$ as anticipated by Miyawaki et al. (2015), with a valency-imposed double occupancy in $M4$. In such case the divide between Ca-dominant and Mn-dominant hellandite would be $\text{Mn}/(\text{Mn} + \text{Ca}) = 1/3$. However, the nomenclature of the hellandite group (Oberti et al., 2002, 2019) is not based on individual crystallographic sites but on groups of similar sites, with the formula $X_4Y_2ZT_2[\text{B}_4\text{Si}_4\text{O}_{22}]\text{W}_2$ in which $X = M3 + M4$, hence with the $^X(\text{R}^{2+}_3\text{R}^{3+})$ charge arrangement in hellandite proper. In this case the divide between Ca-dominant and Mn-dominant hellandite is $\text{Mn}^{2+}/(\text{Mn}^{2+} + \text{Ca}) = 0.5$. The hellandite analysed in the vielleaureite-(Ce) samples satisfies the Mn^{2+} -dominance criterion in any event, it is a potential new species.

Supplement references

Miyawaki, R., Moma, K., Yokoyama, K., Shigeoka, M., Matsubara, S., Ito, M., Nakai, I. and Kristiansen, R.: Mn-bearing hellandite-(Y) from the Heftetjern pegmatite, Tørdal, Norway, Can. Mineral., 53, 345-356, 2015.

Oberti, R., Della Ventura, G., Ottolini, L., Hawthorne, F.C., and Bonazzi, P.: Re-definition, nomenclature and crystal-chemistry of the hellandite group, Am. Mineral., 87, 745-752, 2002.

Oberti, R., Langone, A., Boiocchi, M., Bernabè, E., and Hawthorne, F.C.: News from the hellandite group: the redefinition of mottanaite and ciprianiite and the new mineral description of ferri-mottanaite-(Ce), the first Fe^{3+} -dominant hellandite, Eur. J. Mineral., 31, 799-806, <https://doi-org/10.1127/ejm/2019/0031-2858>, 2019.

Stephant, A., Remusat, L., Thomen, A., and Robert, F.: Reduction of OH contamination in quantification of water contents using NanoSIMS imaging, Chem. Geol., 380, 20-26, 2014.