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Re-definition, nomenclature and crystal-chemistry of the hellandite group

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ABSTRACT

Detailed X-ray single-crystal structure refinements and complete (SIMS + EMPA) microprobe chemical analyses of a series of non-metamict samples of hellandite recently found in Latium (Italy), together with a critical re-evaluation of the existing data on hellandite, allow a better understanding of the crystal-chemistry of the hellandite group. Relative to the crystal structure determined by Mellini and Merlino (1977) for a Y-rich sample from Predazzo (Italy), a new tetrahedrally coordinated site has been detected; this may be fully, or in part, occupied by Li and Be. These cations occur at the center of the tetrahedral cavity where the H atom, which is bonded to the O5 O atom, protrudes; thus the H content in hellandite is constrained to values ≤ 2 – (Li + Be + F).

A new general formula for hellandite-group minerals is proposed: $X_4Y_2ZT_2[B_4Si_4O_{22}]W_2$, where X = Na, Ca, Y, $LREE^{3+}$ at the eightfold-coordinated M3 and M4 sites; Y = Ca, Y, $HREE^{3+}$, Th^{4+}, U^{4+} at the eightfold-coordinated M2 site; Z = Al, Mn^{3+}, Fe^{3+}, Ti^{4+} at the octahedral M1 site; $T = \square$ (vacancy), Li, Be at the new tetrahedrally coordinated site; and W = OH, F, O^{2-} at the O5 site. Eight root end-member compositions were identified; four of these correspond to known compositions: hellandite-(REE), tadzhikite-(REE), and two new minerals, mottanaite-(Ce) and ciprianiite, which are described in a companion paper (Della Ventura et al. 2002). The root-name tadzhikite must be used for samples with $Ti^{4+} > 0.5$ apfu, with no reference to the OH content.

Hellandite is an REE mineral. Rare-earth elements occur at two distinct sites (M2 and M4), with a strong preference for M2 (particularly HREE). Thus, one or two Levinson modifiers can be added to the root name to correctly describe the species. A sequence of incorporation based on crystal-chemical arguments is provided and allows evaluation of the site populations for nomenclature purposes.

This redefinition of the hellandite group and the new nomenclature rules have been approved by the IMA Commission on New Minerals and Mineral names (code 00-F).

HELLANDITE AND TADZHIKITE: INTRODUCTION

Hellandite is a borosilicate mineral, typically associated with granitic rocks and granitic pegmatites. It was first found at Kragerö, Norway, and was studied by Brögger (1903, 1907, 1922), who established its monoclinic symmetry and gave incomplete chemical analyses. Oftedal (1964, 1965) proposed the formula $Ca_3(Y,REE)_4B_4Si_6O_{27}{\cdot}3H_2O$ for this sample and gave the first X-ray powder-diffraction pattern. The structure of hellandite was determined by Mellini and Merlino (1977) and was shown to consist of $[B_4Si_4O_{22}]$ chains oriented parallel to [001] and cross-linked into a framework by corner-sharing M1 octahedra (Figs. 1a and 1b). This arrangement produces tunnels extending along [001], which are filled by three distinct eightfold-coordinated sites (M2, M3, and M4) occupied by Ca, Y, REE, and actinides (± vacancies, $\square$). Mellini and Merlino (1977) also reported a strong REE ordering of the type M2 >> M4 > M3. The proposed structural formula, ${}^{M2,3,4}[Ca_{5.5}REE_{5.0}\square_{1.5}]$ ${}^{M1}(Al_{1.1}Fe^{3+}_{0.9})$ $(OH)_4[Si_8B_8O_{40}(OH)_4]$, includes significant vacancies at the (M2,3,4) sites and eight OH groups per formula unit (pfu), calculated from the requirement for electroneutrality.

Several new occurrences of hellandite were reported recently (see Oberti et al. 1999 for a compilation), and the chemical analyses of some of these samples show higher contents of OH relative to the sample refined by Mellini and Merlino (1977).

Yefimov et al. (1970) described a new mineral, tadzhikite, with an XRD pattern similar to that of hellandite, but with a different chemical composition: TiO_2 varying from 3.7 wt% in type-I tadzhikite to 6.5 wt% in type-II tadzhikite, and (apparently) no OH. Type-II tadzhikite was reported to be monoclinic (a = 17.93, b = 4.71, c = 10.39 Å, β = 100.27°) with the unit formula $Ca_6(Ce,Nd,La,\square)_6$ $(Ti,Fe,Al)_2$ $Si_8B_8O_{46}$; notably, 0.20 wt% BeO was found in sample II, but was not reported in subsequent studies. Mellini and Merlino (1977) noticed that the unit-cell parameters of tadzhikite could be transformed into

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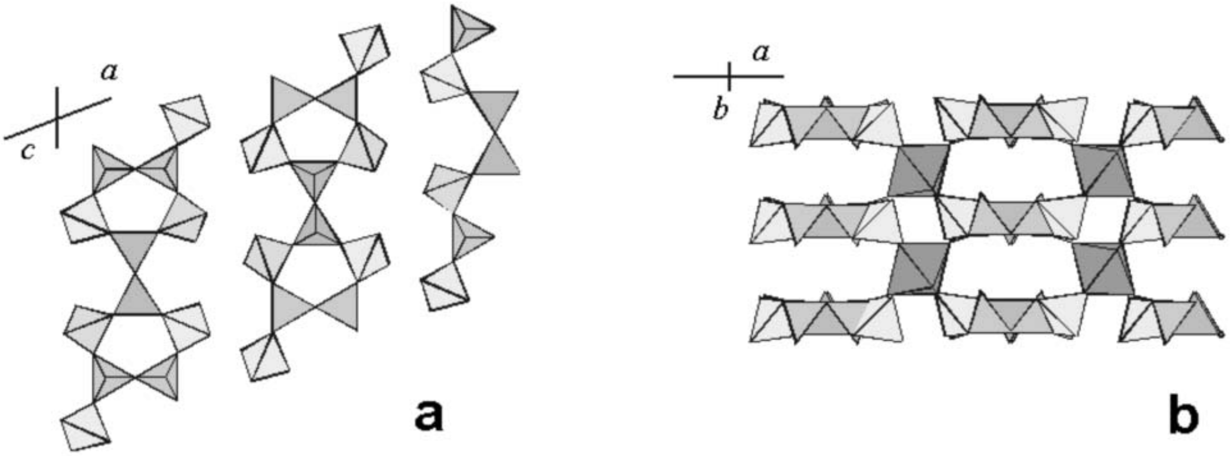

FIGURE 1. The structure of hellandite projected along [010] (**a**) and [001] (**b**). The darker tetrahedra are occupied by B, the lighter by Si.

those of hellandite by means of the matrix [101/010/00-1], giving a = 18.99, b = 4.71, c = 10.39 Å, β = 111.4°, and concluded that hellandite and tadzhikite are isostructural. Chernitsova et al. (1982) refined the structure of a partly metamict tadzhikite (after heating the sample at 700 °C) from sample II of Yefimov et al. (1970), and confirmed that tadzhikite could be considered as an anhydrous (Ti, Ce)-rich end-member of the hellandite group. More recently, Hawthorne et al. (1998) refined the structure of unheated tadzhikite from the same locality, and found significant positional disorder of REE at the M2 site (four subsites), which was related to the partly metamict state of the sample. Bond-valence analysis suggested a significant amount of H_2O, and the authors proposed the following structural formula on the basis of the available EMP analyses: $^{M3}Ca_2{}^{M4}(Ca,Y)_2{}^{M2}(HREE^{3+},\square)_2{}^{M1}(Ti^{4+},Fe^{3+})[B_4Si_4O_{16}(O,OH)_6]^{O5}(OH)_2$.

RECENT WORK ON HELLANDITE SAMPLES FROM LATIUM (ITALY)

During the past few years, several non-metamict hellandite samples were found in tephra from the Latium volcanic province (Central Italy). (1) A (Th,U)-rich and Y-poor variety from an alkali-syenite ejectum found near Capranica, Viterbo province, Vico volcanic complex (Oberti et al. 1999), hereafter HELCe. (2) A (Th,U)-rich and Y-poor variety from Tre Croci, Viterbo province, Vico Volcanic complex (this work), hereafter D22. (3) Another sample with composition similar to D22, found in a sanidine ejectum near Vetralla, Viterbo province, Vico volcanic complex (this work), hereafter 9010. (4) An Y-deficient Be-rich variety from a syenitic ejectum collected at Monte Cavalluccio, Sacrofano, Rome (Della Ventura et al. 2002), hereafter MOTCe. (5) An Y-deficient variety (strongly enriched in Th) from a syenitic ejectum found in the area of Tre Croci, Viterbo province, Vico volcanic complex (Della Ventura et al. 2002), hereafter CIPRI.

All of these samples were characterized by microprobe techniques and single-crystal X-ray structure refinements. Secondary-ion mass-spectrometry (SIMS) was used to quantify H, Li, F, Be, B, REE, and actinides, and electron-microprobe analysis was used for all other elements. The strong spectral interferences in the REE region were treated as described by Oberti et al. (1999) and Ottolini and Oberti (2000). Unit-formulae were recalculated on the basis of 24 (O + F). The information from structure refinement (refined site-scattering values and mean bond lengths) is in excellent agreement with the results of chemical analysis, and provides a detailed picture of cation site populations and of the OH content and location. In particular, the variations in the unit-cell parameters (Table 1) and in the mean bond lengths (Table 2) are consistent with chemical variations in the sample set (Table 3).

This analytical work produced the following information:

(1) The Be and Li contents are significant, and they must be considered new constituents in hellandite. Structure refinement showed that they occur in a tetrahedrally coordinated site (hereafter, T) that connects the borosilicate chains to locally form a sheet of tetrahedra (Fig. 2).

(2) The H content is always low, and is lower in samples containing higher Be and Li contents. Structure refinement showed that H is bonded solely to the O5 O atom, and protrudes into the tetrahedrally coordinated cavity locally occupied by Be and Li.

(3) No vacancies occur at the M sites when all chemical constituents (from H to U) have been correctly analyzed.

(4) REE are ordered at the M2 and M4 sites, and HREE and actinides are strongly ordered at the M2 sites.

OPEN QUESTIONS IN NOMENCLATURE AND CRYSTAL-CHEMISTRY OF THE HELLANDITE GROUP

Nickel and Mandarino (1987) revised the names of the known REE-bearing minerals; in their Appendix Table 2, hellandite is renamed hellandite-(Y) and tadzhikite is renamed tadzhikite-(Ce). Conversely, Mandarino (1999) reports tadzhikite-(Y) but it should be considered a printing error (Mandarino, personal communication). However, no formal approval has been given to this new nomenclature for hellandite. In the IMA-CNMMN 1998 report, Nickel and Grice (1999) stated that "in a mineral with a particular structural site occupied by both Ca and REE, if the sum of REE (in mol props.) is

TABLE 1. A review of the available data showing unit-cell variations in the hellandite group (cf. also Fig. 3)

	Wakefield*	Kragerö*	Tadzhikite†	Predazzo‡	HAWTH§	CIPRI||	MOTCe||	HELCe#	D22**	9010**	MTCAV**
a (Å)	18.824(4)	18.845(5)	18.946(4)	18.99(1)	19.058(4)	19.059(5)	19.032(9)	19.068(8)	19.087(20)	19.114(22)	19.1369(8)
b (Å)	4.696(1)	4.687(1)	4.714(4)	4.715(5)	4.729(1)	4.729(1)	4.746(3)	4.745(2)	4.740(2)	4.736(5)	4.7439(2)
c (Å)	10.248(2)	10.269(3)	10.302(2)	10.30(1)	10.321(2)	10.291(4)	10.248(5)	10.289(3)	10.304(13)	10.363(17)	10.3265(6)
β (°)	111.43(1)	111.60(1)	111.58(2)	111.4(1)	111.39(1)	111.33(2)	110.97(5)	111.18(3)	111.27(12)	111.48(11)	111.28(1)
V (Å^3)	843.2	843.3	855.6	858.6	861.1	864.0	864.3	867.9	868.7	872.9	873.6

Notes: MTCAV is another crystal collected from the same rock sample as MOTCe.
* Hogarth et al. (1972) and this work.
† Chernitsova et al. (1982).
‡ Mellini and Merlino (1977).
§ Hawthorne et al. (1998) and this work.
|| Della Ventura et al. (2002).
Oberti et al. (1999).
** This work.

TABLE 2. Single-crystal structure-refinement data available for hellandites

	Predazzo	HAWTH	CIPRI	MOTCe	HELCe	D22	9010	MTCAV
<B1-O>	1.512	1.498	1.496	1.503	1.495	1.496	1.493	1.495
<B2-O>	1.507	1.486	1.485	1.495	1.487	1.484	1.488	1.489
<Si1-O>	1.641	1.623	1.633	1.637	1.636	1.634	1.638	1.637
<Si2-O>	1.626	1.614	1.624	1.622	1.626	1.625	1.624	1.628
<M1-O>	1.971	1.994	1.966	1.977	1.975	1.966	1.966	1.962
<M2-O>	2.439	4 sub-sites	2.473	2.468	2.479	2.482	2.486	2.492
<M3-O>	2.466	2.475	2.469	2.473	2.473	2.475	2.479	2.474
<M4-O>	2.457	2.470	2.467	2.469	2.471	2.474	2.477	2.488
<T-O>	n.d.	n.d.	1.827	1.781	1.815	1.826	1.855	1.833
ss at M1	n.a.	20.4	18.2	18.4	19.6	18.6	18.2	19.5
ss at M2	n.a.	92.5	115.2	110.0	119.6	121.0	112.8	111.5
ss at M3	n.a.	41.7	41.7	41.6	42.1	41.4	40.0	42.1
ss at M4	n.a.	56.7	53.7	43.3	52.0	50.9	50.0	53.4
ss at T	n.d.	n.d.	2.4	4.3	3.1	2.9	1.5	2.5
ss at O5	n.a.	n.d.	16.3	16.4	16.7	16.4	16.3	16.3
$R_{\rm all}$ %	n.a.	n.a.	4.8	8.8	2.3	4.4	6.8	3.4
$R_{\rm obs}$ %	5.0	4.9	2.8	6.2	1.5	1.8	3.5	2.2

Notes: Mean bond lengths (Å) and site-scattering (ss, electrons per formula unit) at the relevant structural sites. References as in Table 1.
n.d. = not determined.
n.a. = not available.

greater than that of Ca, but individual REE are subordinate to that of Ca, the mineral must be regarded as a rare-earth mineral, with a Levinson modifier (Levinson 1966) specifying the predominant REE." Bayliss and Levinson (1988) stated that, when different REE occupy two different crystallographic sites, their chemical symbols should both appear in the mineral name.

From this discussion and from the new data given above, it is apparent that the following aspects of the crystal-chemistry and systematics of the hellandite group should be redefined: (1) the correct structural formula; (2) the number and location of the OH anions in the structure; (3) the correct formula of tadzhikite, and its status as a distinct species; (4) the use of Levinson modifiers, considering that REEs are ordered at the M2 site.

To investigate whether the results obtained for the samples from Latium are of general validity, the authors of previous studies were asked to provide material which could be re-analyzed according to the same procedure. We obtained the tadzhikite crystal refined by Hawthorne et al. (1998) (hereafter, HAWTH), and a slab of the rock sample from Wakefield Lake (Canada) described by Hogarth et al. (1972) (hereafter, HOGAR); the latter contains large veins of hellandite. The sample from Pedrazzo refined by Mellini and Merlino (1977) is no longer available; however, the refinement results allowed us to draw some conclusions.

VARIATIONS IN UNIT-CELL PARAMETERS

Examination of all available data for hellandite and tadzhikite shows that the unit-cell parameters increase as a function of the CaO content (Fig. 3, updated after Oberti et al. 1999), the most sensitive parameter being the a edge. Plots against Ca (apfu) do not show any rational correlation, perhaps a result of incomplete chemical analyses and incorrect formula recalculation. Significant deviations from the trends (i.e., longer a, b, and c values than expected) occur for the Na-bearing sample HAWTH, and are generally indicative of the presence of Na. Short c values (departing from the trend) are diagnostic of significant (Li + Be) at the T site.

INCORPORATION OF HIGH-Z ELEMENTS

Comparison of all available chondrite-normalized (cn) patterns for REE and actinides (Fig. 4; updated after Oberti et al. 1999) shows that enrichments in the LREE region (HELCe), in the MREE (Mattagami Lake), and in the HREE region (Kragerö) are all possible in hellandite. Hellandites from pegmatites (Quyang and Tahara) have nearly flat REE$_{\rm cn}$ patterns, slightly depleted in LREE. Thus hellandite does not show any selectivity toward incorporation of REE, their proportions being a function of fluid composition. This is confirmed by strong differences in chemical composition of different crystals from the same ejectum, and by the strong zoning observed on the 10 micrometer scale in thin sections of the sample of

TABLE 3. Chemical analyses, unit-formulae calculated on the basis of 24 (O + F) atoms, and comparison with refinement results for the hellandite samples

Sample	HOGAR	HAWTH	CIPRI	MOTCe	HELCe	D22	9010
SiO_2	22.25	22.04	22.94	23.85	22.78	22.50	21.50
B_2O_3	12.88	12.80	13.28	13.85	12.99	13.05	12.46
BeO	0.041	0.167	1.95	2.94	1.14	1.35	0.473
Li_2O	0.003	0.376	0.053	0.037	0.340	0.270	0.161
TiO_2	0.117	4.13	0.730	0.560	1.52	1.95	1.86
Al_2O_3	3.42	0.330	2.33	2.53	1.97	2.14	2.14
Fe_2O_3	1.70	2.17	2.87	3.06	2.44	1.98	1.90
Mn_2O_3	0.478	0.280	0.371	0.00	0.202	0.00	0.00
MgO	0.00	0.00	0.180	0.140	0.247	0.090	0.101
Na_2O	0.00	0.960	0.00	0.00	0.00	0.00	0.00
CaO	12.74	14.68	24.60	24.46	21.52	20.89	19.30
BaO (SrO in HOGAR)	0.059	0.002	0.002	0.002	0.020	0.002	0.002
La_2O_3	0.113	2.86	1.39	7.42	4.51	4.95	5.89
Ce_2O_3	0.133	10.59	5.48	12.63	10.01	11.38	12.57
Y_2O_3	28.11	9.86	0.185	0.073	1.34	1.44	0.891
Pr_2O_3	0.162	1.59	0.863	1.103	1.12	1.26	1.32
Nd_2O_3	1.90	6.15	3.03	2.36	3.65	3.51	3.61
Sm_2O_3	1.89	1.23	0.332	0.137	0.510	0.461	0.418
Eu_2O_3	0.092	0.164	0.051	0.020	0.049	0.032	0.028
Gd_2O_3	3.23	1.30	0.139	0.094	0.319	0.303	0.257
Dy_2O_3	3.56	1.82	0.049	0.024	0.240	0.207	0.161
Er_2O_3	2.42	0.879	0.012	0.005	0.129	0.120	0.065
Yb_2O_3	1.96	0.333	0.006	0.002	0.133	0.094	0.047
ThO_2	0.885	0.078	15.80	4.01	9.52	10.05	10.37
UO_2	0.130	0.594	0.872	0.430	1.40	1.48	1.086
H_2O	1.40	0.887	0.465	0.390	0.430	0.511	0.650
F	0.216	0.147	0.89	1.00	0.87	0.530	0.410
O=F	0.091	0.062	0.370	0.421	0.366	0.223	0.173
Total	99.74	96.36	98.50	100.71	99.04	100.33	97.49
Si	3.933	4.058	4.007	3.978	4.053	3.996	4.022
B	3.930	4.068	4.003	3.987	3.988	4.001	4.023
Be	0.017	0.074	0.818	1.180	0.488	0.576	0.213
Li	0.002	0.278	0.037	0.025	0.243	0.193	0.121
Σ tetrahedral sites	7.883	8.479	8.865	9.169	8.772	8.766	8.378
Ti	0.016	0.572	0.096	0.070	0.203	0.260	0.262
Al	0.712	0.072	0.479	0.497	0.413	0.448	0.472
Fe^{3+}	0.226	0.301	0.377	0.384	0.327	0.265	0.267
Mn^{3+}	0.021	0.013	0.016	0.000	0.009	0.000	0.000
Mg	0.000	0.000	0.047	0.035	0.066	0.024	0.028
Σ M1	0.974	0.957	1.017	0.986	1.019	0.997	1.029
Na	0.000	0.343	0.000	0.000	0.000	0.000	0.000
Ca	2.412	2.896	4.603	4.371	4.102	3.975	3.868
Ba (Sr in HOGAR)	0.002	0.000	0.000	0.000	0.001	0.000	0.000
La	0.007	0.194	0.090	0.456	0.296	0.324	0.406
Ce	0.009	0.714	0.351	0.771	0.652	0.740	0.861
Y	2.640	0.967	0.017	0.006	0.127	0.136	0.089
Pr	0.010	0.106	0.055	0.067	0.073	0.081	0.090
Nd	0.120	0.404	0.189	0.141	0.232	0.223	0.241
Sm	0.115	0.078	0.020	0.008	0.031	0.028	0.027
Eu	0.006	0.010	0.003	0.001	0.003	0.002	0.002
Gd	0.189	0.080	0.008	0.005	0.019	0.018	0.016
Dy	0.203	0.108	0.003	0.001	0.014	0.012	0.010
Er	0.135	0.051	0.001	0.000	0.007	0.007	0.004
Yb	0.105	0.019	0.000	0.000	0.007	0.005	0.003
Th	0.036	0.003	0.628	0.152	0.385	0.406	0.441
U	0.005	0.024	0.034	0.016	0.055	0.058	0.045
ΣM2, M3, M4	5.993	5.997	6.000	5.997	6.006	6.016	6.102
F	0.121	0.086	0.490	0.527	0.490	0.298	0.243
OH	1.647	1.090	0.543	0.434	0.511	0.606	0.812
Σ O5	1.767	1.176	1.033	0.962	1.001	0.904	1.054
Σ (O5, T)	1.787	1.528	1.888	2.166	1.731	1.672	1.388
ss at T cal	0.1	1.1	3.4	4.8	2.7	2.9	1.2
ss at M1 cal	16.0	21.7	19.16	18.4	19.4	18.7	19.2
ss at (M2, M3, M4) cal	212.6	201.1	191.3	183.0	200.7	206.1	216.1
ss at O5 cal	16.1	16.1	16.5	16.5	16.5	16.3	16.2
ss at T sref			2.4	1.5	4.3	3.0	2.9
ss at M1 sref		20.4	18.1	18.2	18.4	19.6	18.6
ss at (M2, M3, M4) sref		190.9	185.1	202.8	194.9	213.6	213.3
ss at O5 sref			16.3	16.4	16.4	16.7	16.4
End-member (cf. Table 5)	(1)	(2)	(3)	(7)	(1)	(1)	(1)

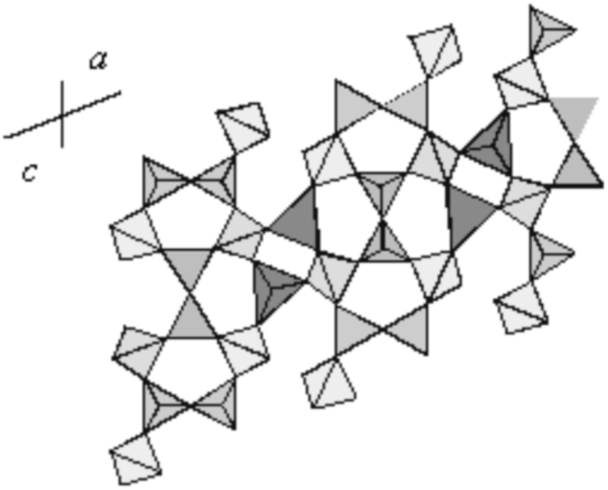

FIGURE 2. The tetrahedral sheet of hellandite occurring when the T sites (darkest gray) are fully occupied by Li and Be (2 apfu).

Hogarth et al. (1972), where hellandite veins show marked local variations in REE content. Thus different fluid compositions may produce several species with different REE patterns.

CHEMICAL COMPOSITION AND CATION ORDERING IN HELLANDITE

Tetrahedrally coordinated sites (B1, B2, Si1, Si2)

Structural and chemical analyses are always consistent with 4 Si and 4 B apfu at these sites.

The additional tetrahedrally coordinated site (T)

SIMS analysis shows the presence of significant Be (up to 1.18 apfu, and thus dominant at this site) and Li (up to 0.56 apfu) in all samples but HOGAR. The refined scattering at this site is also in reasonable accord with the values calculated from SIMS analyses of Be and Li (cf. Table 3). Notably, 0.20 wt% BeO was reported by Yefimov et al. (1970) in type-II tadzhikite, and 0.59 Be pfu was reported in hellandite from Quyang (Ma et al. 1986). Be and Li should thus be considered as typical constituents of hellandite, and should be carefully checked during analysis. There is a good linear relation between the (Li + Be) content at the T site and the <T-O> distance (Fig. 5); thus the (Li + Be) content may be estimated solely from structure refinements.

Octahedrally coordinated site (M1)

The dimensions of the tetrahedral sheet in hellandite-group minerals are fairly constant because of the fixed composition of the sheet. Thus the possibility of incorporating larger elements at the eightfold-coordinated sites is controlled mainly

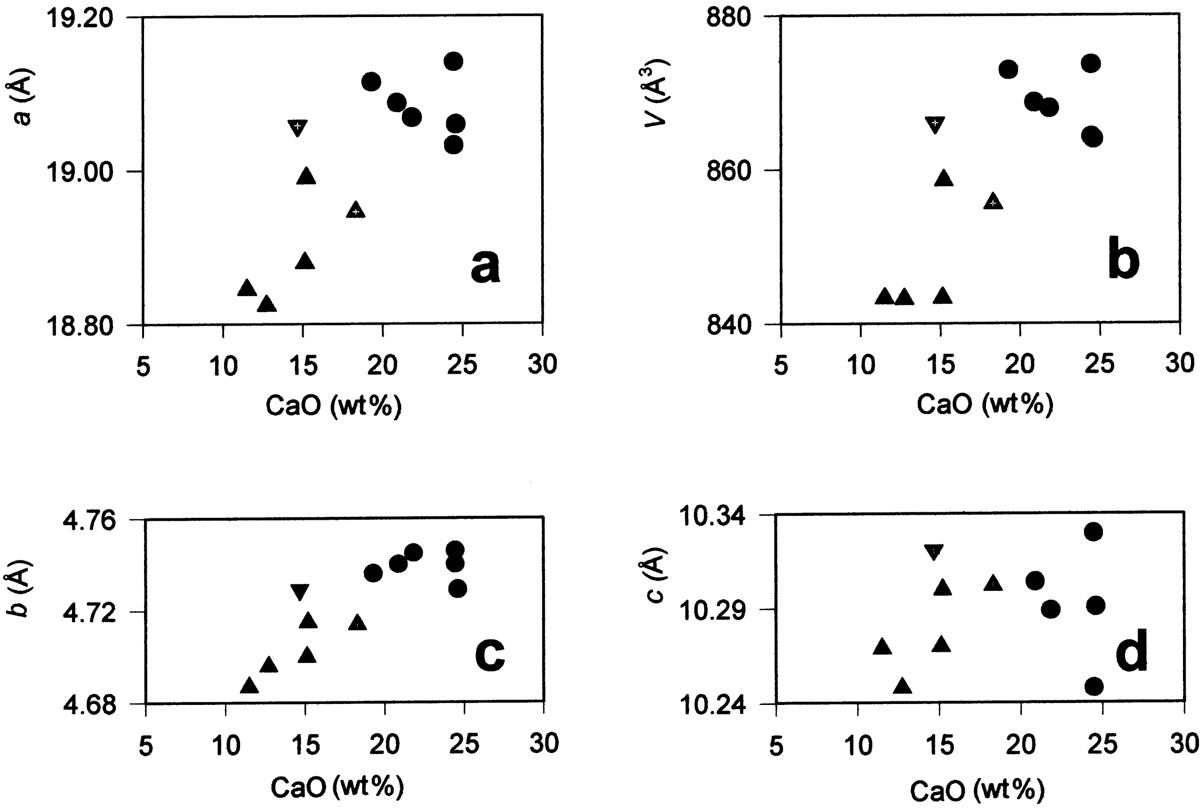

FIGURE 3. Variations in unit-cell dimensions as a function of composition. Circles = hellandite from Latium; triangles = data from the literature; crossed triangles = tadzhikite.

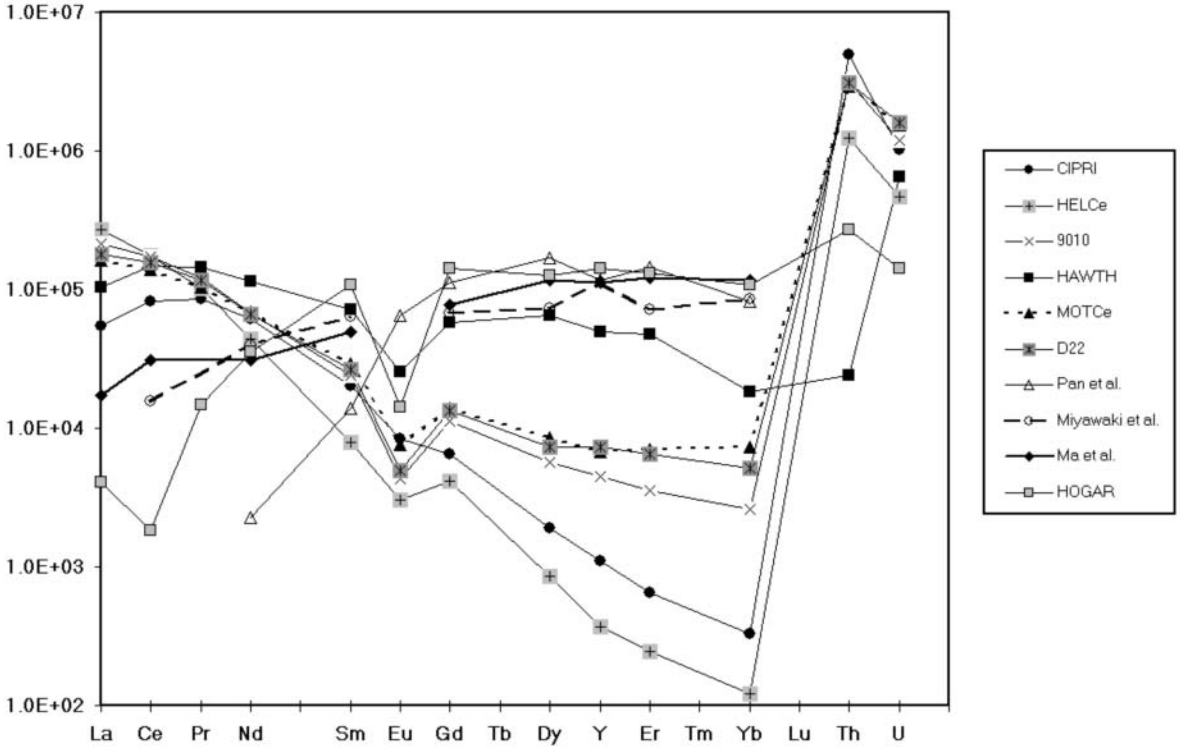

FIGURE 4. The chondrite-normalized patterns available for hellandites. Experimental data for Th, U, and Y [plotted in the position of Ho (not measured) due to the similarity in their ionic radii] are compared to those of REE.

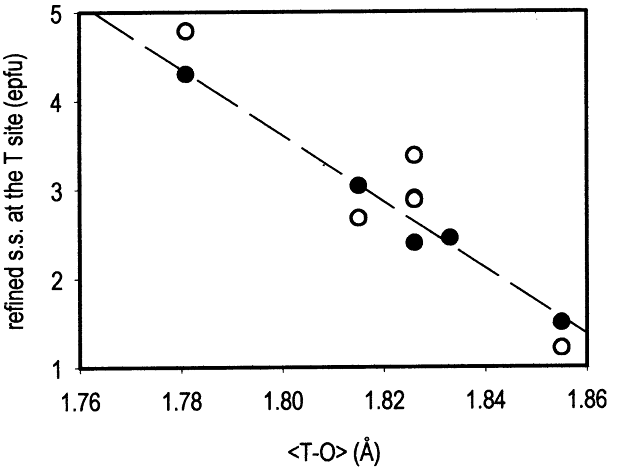

FIGURE 5. Evaluation of the (Li + Be) content at the T site from structure refinement. Black circles = SREF data, open circles = SIMS data.

by the composition of the M1 site, e.g., increasing Fe^{3+} at M1 should promote incorporation of LREE into the structure. The M1 octahedron is occupied mainly by Al and Fe^{3+} (and Mn^{3+}), but crystals with Ti^{4+} dominant at M1 have been also described (Hawthorne et al. 1998). The M1 cations bond to the O5 anion; therefore, high Ti^{4+} content at M1 may also constrain the (OH,F) content at O5 to be less than 2 apfu.

Eightfold-coordinated sites (M2, M3, M4)

These sites contain Na, Ca, REE, and actinides. The mean atomic numbers observed at the single eightfold-coordinated sites in the hellandite samples of this work are 46–60 for M2, 20–21 for M3, and 21–28 for M4 (Table 3). This shows that: (1) Ca always dominates at the M3 site; (2) Y may occur at the M4 site, together with residual Ca; (3) elements with higher atomic number (REE and actinides) order at the M2 site. The calculated site occupancies for the sample from Predazzo are also consistent with REE incorporated in the sequence M2 >> M4 >> M3, and dominant only at the M2 site. Ca may even exceed 8 apfu, as in the recently studied samples from Latium; if this is the case, excess Ca occupies the M2 site. Therefore, Y cannot be regarded as essential to the hellandite structure. Hellandite is thus a REE mineral, for which Levinson modifiers are needed for the M2 site, and possibly for the M4 site. In contrast to sample HAWTH, the non-metamict samples from Latium (and that refined by Mellini and Merlino 1977) do not show significant disorder of REE at M2; actually, the displacement parameter at the M2 site is the smallest of those of the eightfold-coordinated sites.

Vacancies

There are no cation vacancies at the M2-4 sites in any of the hellandite samples examined in this work, in which nearly all REE and actinides elements were analyzed by SIMS. This conclusion is most probably of general validity, as is also shown below.

The O5 site and the OH content of hellandite

The O5 site is occupied by F or O (either OH or O^{2-}). The presence of OH groups at O5 is indicated by an electron-density peak ~1 Å from O5 in the direction of the center of the T cavity; the presence of F at O5 is indicated by refinement of the site scattering. The OH content at O5 is therefore constrained to values ≤(2 -Li - Be - F). When (Li + Be + H + F) < 2.0 apfu, some T cavities pfu are vacant; the associated O5 site is occupied by O^{2-}, and local charge-balance is provided by tetravalent cations at adjacent M1 and M2 sites. Given the complete occupancy of the M2-4 sites indicated by our chemical analyses, the other O sites in hellandite do not require further bond-strength contributions; in accord with this, no residual suitable for H was found in difference-Fourier maps (apart from the peak near O5). Micro-infrared spectra in the OH-stretching region (Della Ventura et al. 2002) were collected on doubly polished single-crystals of all hellandite samples from Latium. All spectra show a single broad absorption centered at 3450 cm^{-1}. This feature suggests a single type of OH molecule in the structure, involved in a strong hydrogen bond with the next-neighbor O atoms.

Hellandite: a chain or a sheet mineral?

When the T site is occupied, hellandite should be described as a sheet structure. The sheet of tetrahedra is composed of four-, five- and eight-membered rings: T_2Si2_2, $TB2_2Si1Si2$, $B1_2B2Si1Si2$, and $T_2B1_2Si1_2Si2_2$, respectively (Fig. 2). These sheets alternate with sheets composed of M1 octahedra and M2, M3, and M4 square antiprisms.

Hellandite and tadzhikite

Hellandite and tadzhikite are isostructural and should be considered as members of the same mineral group. Tadzhikite was first reported as anhydrous, but bond-valence considerations later suggested significant OH content (Chernitsova et al. 1982; Hawthorne et al. 1998). We report here, for the first time, accurate analyses of the OH content in hellandite and tadzhikite, and show that they are strictly analogous in this respect. Thus, the root-name tadzhikite must be used with reference to the Ti^{4+} content (>0.5 apfu).

STRUCTURAL AND CHEMICAL FORMULA

Hellandite-group minerals have the following structural formula:

$$^{M3,4}(Ca,Na,REE)_4{}^{M2}(Ca,Th,U,REE)_2{}^{M1}(Al,Mn^{3+},Fe^{3+},Ti^{4+}){}^{T}(Be,Li,\square)_{2-x}Si_4B_4O_{22}{}^{O5}(O,F,OH_x)_2.$$

In this formula, the amount of OH is constrained to 2 – (Be + Li + F) apfu, and overall electroneutrality is maintained by appropriate combinations of heterovalent substituents at the M sites.

The general chemical formula (as distinct from a structural formula) for the hellandite-group is: $X_4Y_2ZT_2[B_4Si_4O_{22}]W_2$ where X = Na, Ca, REE, Y = Ca, REE, Th^{4+}, U^{4+}, Z = Al^{3+}, Fe^{3+}, Mn^{3+}, Ti^{4+}, T = Li, Be, □, W = OH, F, O.

NOMENCLATURE OF THE HELLANDITE GROUP

End-member compositions distinguished by heterovalent substitutions are assigned a *root name*. End-member compositions distinguished by homovalent substitutions are assigned the appropriate root name plus a *prefix* that identifies the dominant component of the homovalent substitution that distinguishes it from the root composition itself. In hellandite, the only possible prefixes refer to M1 composition, but are not required yet on the basis of the available analyses.

Assignment of cations to groups. (1) Na is assigned to the X-group; (2) Ca is assigned to the X-group up to a maximum of 4 apfu; any excess Ca is assigned to the Y group; (3) REE^{3+} are assigned to the X-group (as 4 – Na – Ca), and the balance is assigned to the Y group; (4) actinides and HREE are assigned to the Y group. The remaining cations are assigned as indicated in Table 4.

Root names are given in Table 5 for the possible charge arrangements. The compositions of Table 3 are associated with their closest end-member compositions at the bottom of Table 3.

Hellandite is composition 1 in Table 5, and is the dominant species in Table 3. *Tadzhikite* is composition 2 in Table 5, and is represented by the sample HAWTH in Table 3; according to this definition, there is no reason to maintain the terms tadzhikite I and tadzhikite II (Yefimov et al. 1970). This root name refers to the dominance of an R^{4+} cation at M1, and does not have any relation to the H content. *Ciprianiite* is composition 3 in Table 5, with Th^{4+} dominant at Y. *Mottanaite* is composition 7 in Table 5 with Be dominant at T.

A summary of the known hellandite end-members is reported in Table 6. It is important to note that other substitutions also occur, besides those implicit in Table 5. For example, in HAWTH, the substitution $^{X}Na + {}^{X}Y \rightarrow {}^{X}Ca_2$ is operative, reducing ^{X}Ca below the end-member value of 4 apfu. In HOGAR, the substitution $^{X}Y + {}^{O5}O^{2-} \rightarrow {}^{X}Ca + {}^{O5}(OH)$ reduces ^{X}Ca below the end-member value of 3 apfu. However, apart from REE, these are not dominant substitutions in our well-characterized samples.

Levinson modifiers. According to the discussion of cation ordering and to the nomenclature scheme given above, a Levinson modifier must be used to identify the dominant REE at the Y site (i.e., at M2); a second Levinson modifier might

TABLE 4. Site nomenclature and chemical substitutions so far observed in hellandites

Label	Sites and site nomenclature	Species
B	4 tetrahedral sites pfu (2 B1 + 2 B2)	B^{3+}
Si	4 tetrahedral sites pfu (2 Si1 + 2 Si2)	Si^{4+}
T	2 tetrahedral sites pfu (T)	Li^{+}, Be^{2+}, □, (H)
Z	1 octahedral site pfu (M1)	Mg, Al^{3+}, Fe^{3+}, Mn^{3+}, Ti^{4+}
Y	2 eightfold-coordinated sites pfu (M2)	Y^{3+}, (H) REE^{3+}, Th^{4+}, U^{4+}, Ca^{2+}
X	4 eightfold-coordinated sites pfu	M3: Ca^{2+}, Y^{3+}
	(2 M3 + 2 M4)	M4: Na^{+}, Ca^{2+}, Y^{3+}, (L) REE^{3+}
W	2 sites pfu (O5)	OH^{-}, F^{-}, O^{2-}.

TABLE 5. Possible end-member compositions in the hellandite group

Number	X	Y	Z	T		W
(1)	$Ca_3\ R^{3+}$	R^{3+}_2	Al	$\square_2$	$[B_4\ Si_4\ O_{22}]$	$(OH)_2$
(2)	Ca_4	R^{3+}_2	Ti	$\square_2$	$[B_4\ Si_4\ O_{22}]$	$(OH)_2$
(3)	Ca_4	$R^{4+}\ R^{3+}$	Al	$\square_2$	$[B_4\ Si_4\ O_{22}]$	$(OH)_2$
(4)	Ca_4	R^{3+}_2	Ti	Li_2	$[B_4\ Si_4\ O_{22}]$	O^{2-}_2
(5)	$Ca_3\ R^{3+}$	R^{3+}_2	Al	Li_2	$[B_4\ Si_4\ O_{22}]$	O^{2-}_2
(6)	Ca_4	$R^{4+}\ R^{3+}$	Al	Li_2	$[B_4\ Si_4\ O_{22}]$	O^{2-}_2
(7)	Ca_4	$Ca\ R^{3+}$	Al	Be_2	$[B_4\ Si_4\ O_{22}]$	O^{2-}_2
(8)	Ca_4	Ca_2	Ti	Be_2	$[B_4\ Si_4\ O_{22}]$	O^{2-}_2

Note: $R^{3+} = (Y^{3+} + REE^{3+})$; R^{4+} = (Th + U); Al = $(Al^{3+} + Mn^{3+} + Fe^{3+})$; OH = $(OH^{-} + F^{-})$

TABLE 6. The hellandite end-members known so far

End-member name	Sample code (this work)	Ideal formula
hellandite-(Y)*	HOGAR, Quyang, Tahara, Mattagami Lake	$(Ca_3REE)_4\ Y_2\ Al\ \square_2[Si_4\ B_4O_{22}]\ (OH)_2$
hellandite-(Ce)†	D22, HELCe, 9010	$(Ca_3REE)_4\ Ce_2\ Al\ \square_2\ [Si_4\ B_4O_{22}]\ (OH)_2$
tadzhikite-(Ce)*	HAWTH	$Ca_4\ Ce_2\ Ti\ \square_2\ [Si_4\ B_4O_{22}]\ (OH)_2$
mottanaite-(Ce)‡	MOTCe	$Ca_4\ (CeCa)_2\ Al\ Be_2\ [Si_4\ B_4O_{22}]\ O_2$
ciprianiite‡	CIPRI	$Ca_4\ [(Th,U)REE)]_2\ Al\ \square_2\ [Si_4\ B_4\ O_{22}]\ (OH)_2$

* Already existing species, Levinson modifier added.
† new end-member (Oberti et al. 1999).
‡ new end-member (Della Ventura et al. 2002).

also be used to identify the dominant REE at the M4 site. Therefore, of the compositions reported in Table 3:

- composition HOGAR is named *hellandite-(Y)*;
- compositions D22, HELCe and 9010 are named *hellandite-(Ce)*;
- composition HAWTH is named *tadzhikite-(Ce)*;
- composition MOTCe is named *mottanaite-(Ce)*;
- composition CIPRI is named simply *ciprianiite*, as REE are not dominant at the Y site.

Available formulae for the samples from Tahara (Japan; Miyawaki et al. 1987), Quyang (China, Ma et al. 1986) and Mattagami Lake (Canada; Pan et al. 1994) are not close to the stoichiometric values (probably due to strong interferences among REE peaks during electron-microprobe analysis); to better evaluate their composition, the atomic proportions were reconverted to oxides, and formulae were recalculated according to the new constraints (i.e., 24 O atoms, Be + Li + OH = 2) after converting FeO into Fe_2O_3 and MnO into Mn_2O_3. The results are generally much more consistent with the expected stoichiometry (in particular, there are far fewer cation vacancies):

Quyang: $^{M3}(Ca)_2\ ^{M4}(Ca_{0.25}Na_{0.03}K_{0.08}Y_{1.64})_{\Sigma=2}\ ^{M2}(Y_{0.47}\ REE_{0.99}\square_{0.54})_{\Sigma=2}\ ^{M1}(Al_{0.88}Fe^{3+}_{0.10}\ Mn^{3+}_{0.02})_{\Sigma=1.00}\ ^{T}(Be_{0.61}\square_{0.03})\ B_{3.99}Si_{4.58}O_{22}(OH)_{1.36}$ (Li not determined; H calculated);

Tahra: $^{M3}(Ca)_2\ ^{M4}(Ca_{1.18}Y_{0.82})_{\Sigma=2}\ ^{M2}(Y_{1.23}\ REE_{0.66}\square_{0.23})_{\Sigma=2}\ ^{M1}(Al_{0.80}\ Mn^{3+}{}_{0.04}\ Ti_{0.11}\ Fe^{3+}{}_{0.06})_{\Sigma=2.01}\ Si_{4.02}B_{4.02}\ O_{22}\ (OH)_2]$ (Li and Be not determined; H calculated);

Mattagami Lake: $^{M3}(Ca)_2\ ^{M4}(Ca_{0.83}Y_{1.17})_{\Sigma=2}\ ^{M2}(Y_{0.97}\ REE_{0.69}Mg_{0.15}Zn_{0.04}\square_{0.15})_{\Sigma=2}\ ^{M1}(Al_{0.99}Fe^{3+}_{0.11})_{\Sigma=2.10}\ B_{4.01}Si_{4.04}\ O_{22}(OH)_2]$ (Li and Be not determined; H calculated).

All these compositions should be named *hellandite-(Y)*. The composition from Quyang might even suggest a further possible end-member with Ca_2Y_2 at the X sites, however, more complete analyses are needed to correctly classify this sample. Modern and more complete analyses are also needed to correctly name the samples from Predazzo (Italy; Mellini and Merlino 1977), and Kragerö (Norway; Oftedal 1965; Hogarth et al. 1972); from the available data, the former should be named *hellandite-(Gd)* and the latter *hellandite-(Y)*.

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