

## CHARACTERIZATION OF GADOLINITE-GROUP MINERALS USING CRYSTALLOGRAPHIC DATA ONLY: THE CASE OF HINGGANITE-(Y) FROM CUASSO AL MONTE, ITALY

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### ABSTRACT

Important data concerning chemical composition of a mineral of the gadolinite group can be obtained from a refinement of its crystal structure. In spite of the complexities, an entirely crystallographic procedure performed on a single grain can afford a practical way to identify and characterize these species; such a procedure is often successful, provided the quality of the crystal allows it. We consider the crystal-chemical mechanisms corresponding to the most important substitutions, and apply such a method to identify the Fe-poor and Ca-rich gadolinite-group minerals from Cuasso al Monte, Varese, Italy. These crystals can be ascribed to hingganite-(Y), with minor amounts of gadolinite (0.26–0.31 molar fraction) and datolite components (0.15–0.25 molar fraction) in solid solution. The component minasgeraisite-(Y) is not present, even as a minor one, in the samples studied.

*Keywords:* gadolinite-group minerals, datolite, hingganite-(Y), minasgeraisite-(Y), crystal-structure refinement, rare-earth elements, Cuasso al Monte, Italy.

### SOMMAIRE

On peut obtenir des données importantes à propos de la composition chimique d'un minéral du groupe de la gadolinite à partir des détails affinés de sa structure. En dépit des complexités, une procédure entièrement cristallographique effectuée sur un seul grain peut fournir une façon pratique d'identifier et de caractériser ces espèces. Une telle procédure réussit dans plusieurs cas, pourvu que la qualité du cristal est adéquate. Nous considérons les mécanismes cristalochimiques correspondant aux substitutions les plus importantes, et nous faisons l'essai d'une telle méthode afin d'identifier les échantillons du groupe de la gadolinite riches en Ca et à faible teneur en Fe provenant de Cuasso al Monte, Varese, Italie. Ces échantillons seraient des exemples de hingganite-(Y), avec une proportion mineure des composantes gadolinite (fraction molaire 0.26–0.31) et datolite (fraction molaire 0.15–0.25) en solution solide. La composante minasgeraisite-(Y) n'est pas présente dans nos échantillons, même en proportion mineure.

(Traduit par la Rédaction)

*Mots-clés:* minéraux du groupe de la gadolinite, datolite, hingganite-(Y), minasgeraisite-(Y), affinement de la structure cristalline, terres rares, Cuasso al Monte, Italie.

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## INTRODUCTION

Over the last few years, highly crystalline specimens of a Ca-rich, Fe-poor member of the gadolinite group have been found in miarolitic cavities in granophyre from Cuasso al Monte, Varese, Italy. This occurrence, in spite of its proximity to the Alps, is of Permian age, and is related to the well-known granite of Baveno (Bakos *et al.* 1990, Boriani *et al.* 1992). These specimens were tentatively classified as minasgeraisite-(Y) or "herderite" by collectors on the basis of very limited evidence. Recently, such material was studied by Pezzotta *et al.* (1999), who attributed it to Nd-rich gadolinite-(Y), or hingganite-(Y) on the basis of electron-microprobe data. However, neither crystallographic data nor information about its contents of the light elements were provided.

Therefore, we considered the crystal-structure refinement of "gadolinite" from Cuasso al Monte to be a worthwhile objective. In more general terms, owing to grain-size limitations, we seek to establish whether, and within which limits, appropriate crystal-chemical considerations could permit the identification of a mineral of the gadolinite group using crystallographic data only.

## BACKGROUND INFORMATION

The general chemical formula of minerals of the gadolinite group, which includes datolite, can be written as  $A_2Z_2XS_i_2O_8(O,OH)_2$ . In gadolinite-(Y), for in-

stance, A is yttrium (with some lanthanides), and Z is beryllium; in datolite, A is calcium and Z is boron. If there is a cation at the X site, it is usually  $Fe^{2+}$ , the only exception being minasgeraisite-(Y), where it is reported to be  $Ca^{2+}$  instead. There are other mineral species in the group, such as hingganite-(Yb), hingganite-(Y), hingganite-(Ce), gadolinite-(Ce), homilite, *etc.*, as well as synthetic compounds such as "calciogadolinite" (Table 1). In connection with the existence of iron-free end members, iron is commonly deficient in gadolinite-(Y) with respect to the "ideal" formula (see, for instance, Demartin *et al.* 1993).

The correct assignment of a sample to a certain species, at least in principle, must involve a quantitative determination of the concentration of the light elements, such as beryllium, boron, and hydrogen, which are difficult to monitor routinely with the equipment usually available. Lacking results of a chemical analysis that include data for these elements, an accurate crystal-structure refinement would seem to be imperative; in practice, crystals of good quality are difficult to obtain, most natural samples of the lanthanide-rich members of the group being metamict owing to the presence of small amounts of Th and U. As a direct consequence of all these difficulties, a non-negligible number of samples of so-called "gadolinite" found in several typical occurrences still remain to be classified.

There is an advantage to using, wherever possible, accurate, self-consistent crystallographic data to derive the chemical composition: the samples are commonly inhomogeneous, so that the results of an electron-microprobe analysis may not exactly correspond to those obtained from the X-ray data. In particular, the gadolinite-group minerals from Cuasso al Monte provide significant examples of inhomogeneity (see Table 2 in Pezzotta *et al.* 1999).

TABLE 1. MEMBERS OF THE GADOLINITE GROUP

General chemical formula: $A_2Z_2XS_i_2O_8(O,OH)_2$		A	Z	X
$Y_2Be_2FeSi_2O_8O_2$	gadolinite-(Y)	Y	Be	$Fe^{2+}$
$Ce_2Be_2FeSi_2O_8O_2$	gadolinite-(Ce)	Ce	Be	$Fe^{2+}$
$Ca_2B_2Si_2O_8(OH)_2$	datolite	Ca	B	"vacant" <sup>§§</sup>
$Ca_2B_2FeSi_2O_8O_2$	homilite	Ca	B	$Fe^{2+}$
$Yb_2Be_2Si_2O_8(OH)_2$	hingganite-(Yb)	Yb	Be	"vacant" <sup>§§</sup>
$Y_2Be_2Si_2O_8(OH)_2$	hingganite-(Y)	Y	Be	"vacant" <sup>§§</sup>
$Ce_2Be_2Si_2O_8(OH)_2$	hingganite-(Ce)	Ce	Be	"vacant" <sup>§§</sup>
$Y_2Be_2CaSi_2O_8O_2$	minasgeraisite-(Y)*	Y	Be	Ca
$Ca_2B_2(BO_3)(SiO_3)(OH)_2 \cdot H_2O ?$	bakerite*	Ca	B	"vacant" <sup>§§</sup>
<i>Possible additional end-members (not yet approved by the CNMNM, IMA)</i>				
$(Y,Ca)_2(B,Be)_2Si_2O_8(O,OH)_2$	"calcybeborosilite-(Y)"	Y,Ca	B,Be	"nearly vacant" <sup>§§§</sup>
$CaYBe_2FeSi_2O_8O_2$	"calciogadolinite" <sup>*†</sup>	Ca+Y	Be	$Fe^{2+}$

<sup>§</sup> The formula of datolite is in some cases written as  $Ca_2B_2\Box Si_2O_8(OH)_2$  (Burt 1989), and similar formulae can be written for the other Fe-poor species, but true vacancies are unlikely to exist in these structures. Wherever accurate crystal-structure data are available, the assumed "vacancies" do not show up as voids, but correspond to the presence of two hydrogen atoms close to the X site (see text).

\* In our opinion, a detailed study of the crystal structure of these minerals would be particularly useful.

<sup>†</sup> According to our interpretation, this phase, described by Rastsvetaeva *et al.* (1996), is an intermediate between hingganite-(Y) and datolite.

<sup>‡</sup> Ito & Hafner (1974).

## COLLECTION OF X-RAY DATA AND STRUCTURE REFINEMENT

Three selected fragments (about 0.1 mm in diameter) of the more external portions of different crystals of "gadolinite" from Cuasso al Monte were mounted on a Enraf-Nonius CAD4 single-crystal diffractometer (graphite-monochromatized  $MoK\alpha$  radiation). The unexpected high quality of the diffraction data turned out to be adequate to obtain significant results from a refinement of the crystal structure. The crystallinity of the material leads us to suggest that the material may be younger than the parent rock (or the original crystal). Although it was not possible to polish these same fragments to analyze them with an electron microprobe, an examination of the energy-dispersion spectra showed no substantial differences with the specimens examined by Pezzotta *et al.* (1999).

Details of the data collection and refinement are reported in Table 2. Reflections were collected up to a  $2\theta$  of  $60^\circ$ , Lorentz and polarization corrections were ap-

TABLE 2. CRYSTALLOGRAPHIC DATA FOR HINGGANITE-(Y) FROM CUASSO AL MONTE, ITALY

Monoclinic Sample	Space group: $P2_1/c$		Z = 2
	1	2	
a (Å)	4.744(7)	4.739(3)	4.743(3)
b (Å)	7.571(8)	7.607(4)	7.617(6)
c (Å)	9.811(11)	9.898(2)	9.905(7)
$\beta$ (°)	90.26(2)	90.45(3)	90.47(5)
V	352.4(8)	356.8(3)	357.8(5)
Measured unique reflections	1106	1046	1051
Transmission factors	0.706-1.363	0.676-1.320	0.866-0.997
Observed reflections { $I > 3\sigma(I)$ }	689	611	610
Number of parameters refined	86	85 <sup>(3)</sup>	86
R <sup>(1)</sup>	0.042	0.039	0.033
R <sub>w</sub> <sup>(2)</sup>	0.054	0.043	0.038
Min/Max $\Delta\rho(e^{-7}\text{Å}^3)$	-0.88/0.91	-1.02/1.30	-1.19/1.64

<sup>(1)</sup>  $R = \{[\sum(|F_o| - |F_c|)] / [\sum|F_o|]\}$ ; <sup>(2)</sup>  $R_w = \{\sum[w(|F_o| - |F_c|)^2] / \sum[w(|F_o|)^2]\}$ <sup>12</sup>  
<sup>(3)</sup> Extinction not refined.

plied, as well as an absorption correction as described in Demartin *et al.* (1992a). The structures were refined using the full-matrix least-squares approach starting from the atom coordinates of gadolinite in our previous work (Demartin *et al.* 1993) and allowing the occupancy of the A, Z and X sites to vary. The function minimized was  $\sum_w(F_o - F_c)^2$ . Scattering factors of neutral atoms for Y (A site), Fe (X site), Si, O, and Be (Z site) were taken from Cromer & Waber (1974), and anomalous dispersion effects were considered, using the values for  $\delta f'$  and  $\delta f''$  reported by Cromer (1974). All the calculations were performed using the Personal SDP software [Frenz 1988, 1991].

Fractional coordinates of atoms and selected bond-distances are reported in Tables 3 and 4, respectively; anisotropic atomic-displacement parameters (ADP) and tables of structure factors have been sent to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

CRYSTAL-CHEMICAL MECHANISMS OF SUBSTITUTION

For gadolinite-(Y), there are several possibilities of substitution occurring at different sites. For instance, in the A site, Y<sup>3+</sup> is commonly partially replaced by Ca<sup>2+</sup>, or by a number of other lanthanide ions and (very rarely) by Bi<sup>3+</sup>; other possibilities widely occurring in nature are the substitution of B<sup>3+</sup> for Be<sup>2+</sup> at the Z site, and that of OH groups for O(5). Another important and nearly ubiquitous feature is the partial occupancy of the X site by Fe<sup>2+</sup>.

These substitutions lead to the end-members datolite, gadolinite-(Ce), and hingganite-(Y) as extreme limits; charge balancing is achieved by various schemes of coupled substitution, such as those expressed by the

TABLE 3. FRACTIONAL ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC-DISPLACEMENT PARAMETERS FOR HINGGANITE-(Y) FROM CUASSO AL MONTE, ITALY

	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
A	0.0014(1)	0.1086(1)	0.33164(7)	1.71(1)
	0.0002(1)	0.10851(8)	0.33239(7)	1.115(9)
	0.0002(1)	0.10852(8)	0.33238(6)	1.150(9)
X	0	0	0	2.0(1)
	0	0	0	1.73(9)
	0	0	0	1.9(1)
Si	0.5197(5)	0.2743(3)	0.0802(2)	1.65(4)
	0.5182(4)	0.2757(2)	0.0796(2)	1.19(3)
	0.5197(4)	0.2756(2)	0.0795(2)	1.09(1)
O(1)	0.761(1)	0.4103(8)	0.0326(6)	1.9(1)
	0.760(1)	0.4111(7)	0.0337(5)	1.47(9)
	0.7595(9)	0.4112(6)	0.0325(5)	1.38(8)
O(2)	0.325(1)	0.2866(8)	0.4511(2)	1.9(1)
	0.325(1)	0.2875(7)	0.4526(5)	1.48(9)
	0.3284(9)	0.2879(6)	0.4505(5)	1.35(8)
O(3)	0.308(1)	0.3434(9)	0.1974(6)	2.1(1)
	0.303(1)	0.3460(7)	0.1952(5)	1.48(9)
	0.3032(9)	0.3452(6)	0.1959(5)	1.25(8)
O(4)	0.685(1)	0.1060(8)	0.1458(5)	2.0(1)
	0.684(1)	0.1075(7)	0.1457(6)	1.77(9)
	0.687(1)	0.1085(6)	0.1467(5)	1.42(8)
O(5)	0.780(1)	0.4094(9)	0.3313(6)	2.2(1)
	0.788(1)	0.4118(7)	0.3317(6)	1.52(9)
	0.786(1)	0.4127(6)	0.3316(5)	1.35(8)
Z	0.452(2)	0.413(1)	0.335(1)	1.8(2)
	0.449(2)	0.413(1)	0.3362(9)	0.9(1)
	0.448(1)	0.4145(9)	0.3357(7)	1.0(1)

In each case, first row: sample 1, second row: sample 2, third row: sample 3.  
 $B_{eq} = 4/3[\alpha^2\beta(1,1) + \beta^2\beta(2,2) + \gamma^2\beta(3,3) + ac(\cos\beta)b(1,3)]$

TABLE 4. INTERATOMIC DISTANCES (Å) FOR HINGGANITE-(Y) FROM CUASSO AL MONTE, ITALY

	Sample 1	Sample 2	Sample 3
A-O(1)	2.299(5)	2.308(6)	2.308(5)
A-O(1)	2.287(5)	2.298(6)	2.300(5)
A-O(2)	2.352(5)	2.369(6)	2.372(5)
A-O(3)	2.652(5)	2.684(6)	2.678(5)
A-O(3)	2.503(5)	2.475(6)	2.483(5)
A-O(4)	2.357(4)	2.369(6)	2.356(5)
A-O(5)	2.508(5)	2.516(6)	2.529(5)
A-O(5)	2.432(5)	2.430(6)	2.432(5)
X-O(2)	2.287(5) (× 2)	2.284(5) (× 2)	2.300(5) (× 2)
X-O(4)	2.224(5) (× 2)	2.240(6) (× 2)	2.245(5) (× 2)
X-O(5)	2.069(5) (× 2)	2.051(6) (× 2)	2.055(5) (× 2)
Si-O(1)	1.610(5)	1.609(5)	1.608(5)
Si-O(2)	1.631(5)	1.622(6)	1.634(5)
Si-O(3)	1.617(5)	1.628(6)	1.639(5)
Si-O(4)	1.627(5)	1.636(6)	1.637(5)
Z-O(2)	1.605(9)	1.612(10)	1.599(9)
Z-O(3)	1.598(9)	1.634(11)	1.628(9)
Z-O(4)	1.613(10)	1.617(10)	1.620(9)
Z-O(5)	1.558(9)	1.610(9)	1.606(8)

exchange operators  $\text{CaB}(\text{YBe})_{-1}$ , or  $\square(\text{OH})_2(\text{FeO}_2)_{-1}$ , following the convention of Burt (1989).

Because of the usually low occupancy of  $\text{Fe}^{2+}$  in the X site, the situation is often described in terms of “vacancies”. However, it is unlikely that such “vacancies” exist as simple “voids” or “broken bonds” in the structure. The situation actually corresponds to the presence of two symmetry-related O(5)-bonded hydrogen atoms instead of the central Fe atom. This mechanism of substitution is proved by the structure of datolite, where iron is completely absent, but the energetically favored  $sp^3$  four-bond formation around O(5) is maintained.

For this reason, the substitution described by Burt (1989) as  $\square(\text{OH})_2(\text{FeO}_2)_{-1}$ , which should actually be written  $(\text{OH})_2(\text{FeO}_2)_{-1}$ , *i.e.*, not involving real vacancies, is the one greatly favored on crystal-chemical grounds for balancing the charge variation due to the low  $\text{Fe}^{2+}$  occupancy.

To date, no convincing evidence has been obtained for 1) non-negligible substitution of Be for Si, 2) the presence of substantial amounts of the  $\text{Fe}^{3+}$  ion in natural samples of gadolinite not subject to alteration, or 3) the presence of OH groups at sites of the gadolinite structure other than O(5). Therefore, a reasonable assumption is that *on replacing  $\text{Be}^{2+}$  by  $\text{B}^{3+}$ , the resulting charge-balance is attained in practice by replacing  $\text{Y}^{3+}$  by  $\text{Ca}^{2+}$ , *i.e.*, according to the operator  $\text{CaB}(\text{YBe})_{-1}$  in Burt's (1989) notation.*

A problem concerning the possibility that Ca occupies different sites in Fe-poor minerals of the gadolinite group has been raised by the description of minasgeraisite-(Y),  $\text{Y}_2\text{Be}_2\text{CaSi}_2\text{O}_8\text{O}_2$  (Foord *et al.* 1986), in which Ca is assumed to replace iron at the X site, according to the operator  $\text{CaFe}^{2+}_{-1}$  in Burt's notation. On the sole grounds of refined occupancy-parameters, it is impossible to establish whether the X site contains iron with the only alternative of “vacancies” (or H atoms), or Fe is instead partially replaced by a lighter cation, such as Ca. However, if important amounts of Ca were indeed present at this site, the X–O distances would in some way be affected, since the Ca–O bonds are much longer (about 2.40 Å for a coordination number of 6) than either the Fe–O bonds (about 2.18 Å), or the distance between the center of the site and O in datolite (2.161 Å; Foit *et al.* 1973, Ito & Hafner 1974).

The notable difference between these bond lengths (or, in other words, the much larger size of the  $\text{Ca}^{2+}$  ion with respect to  $\text{Fe}^{2+}$ ), in our opinion, casts doubts about the *very existence* of minasgeraisite-(Y), a mineral needing a detailed crystallographic investigation, because the replacement of Fe by Ca would require a considerable structural re-arrangement, which is hard to imagine. Unfortunately, no crystal-structure determination of the mineral or of its synthetic equivalent has yet been done.

In addition to such crystallographic arguments, the atomic  $(\text{Ca} + \text{REE})/\text{Si}$  ratio, where REE stands for yttrium and the lanthanides, which should be equal to one

for gadolinite, would become higher, attaining a maximum of 1.5 for a mineral having the theoretical composition of minasgeraisite-(Y). In all the reference specimens we have considered so far, including the one from Clogstafelberg (CLOG), which bears some similarities to the samples from Cuasso al Monte, and is free of alteration, the  $(\text{Ca} + \text{REE})/\text{Si}$  value determined by electron-microprobe analysis is always close to unity, confirming that significant amounts of calcium cannot be present at the X site. Our conclusions are in line with the results of a series of electron-microprobe analyses carried out by Pezzotta *et al.* (1999) on their gadolinite-group samples from Cuasso al Monte, for which no significant deviation of  $(\text{Ca} + \text{REE})/\text{Si}$  from unity has been reported.

A similar situation can also be observed for the calcium-bearing gadolinite-like mineral [probably an intermediate between hingganite-(Y) and datolite] observed at Strange Lake, Quebec (Jambor *et al.* 1998). The ratio  $(\text{Ca} + \text{Na} + \text{Mn} + \text{REE})/\text{Si}$  does not exceed unity; furthermore, no positive evidence for  $\text{Ca}^{2+}$  replacing  $\text{Fe}^{2+}$  in the X site of the structure has been obtained yet for UK-48, the calcium-bearing gadolinite-group mineral containing B from Mont Saint-Hilaire, Quebec (Chao *et al.* 1990). It is also most probably an intermediate between hingganite-(Y) and datolite. Therefore, if a certain end-member such as minasgeraisite-(Y) has not been proven to be present in a solid solution, where it is stabilized by the entropy of mixing, even in minor amounts, its existence as a pure or nearly pure mineral should be regarded as *very* doubtful.

In conclusion, apart from the replacement of Y by the lanthanides, the operators  $\text{CaB}(\text{YBe})_{-1}$ , and  $(\text{OH})_2(\text{FeO}_2)_{-1}$  should be the only ones important in practice in gadolinite. Therefore, *the amounts of B and Ca present (atomic proportions) should be equal*. On such grounds, starting from gadolinite, the above operators will lead to the end members homilite or hingganite, respectively, and if they operate together, the final end-member will be datolite.

In some samples of minerals of the gadolinite group, there can be significant amounts of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , or  $\text{Mn}^{2+}$  (see for instance Jambor *et al.* 1998). On account of its relatively large ionic radius,  $\text{Na}^+$  should enter the A site together with  $\text{Ca}^{2+}$ , and for the opposite reason,  $\text{Mg}^{2+}$  should replace instead  $\text{Fe}^{2+}$  in the X site, so that the mechanisms of substitution described above can be easily adjusted. A more difficult situation concerns  $\text{Mn}^{2+}$ . Its ionic radius is intermediate between that of  $\text{Ca}^{2+}$  and that of  $\text{Fe}^{2+}$ , thereby suggesting the possibility of some distribution between the A and the X sites. However, the content of manganese is usually so small as not to interfere in practice with our general statements.

Other components of some importance may be the lanthanide-rich equivalents of hingganite-(Y) and gadolinite-(Y), or homilite; however, if such rarer components were present in notable quantity, the crystallographic data would be affected to permit their recogni-

tion (see below). Even in such cases, our inferences about the presence of equal amounts of B and Ca would still hold.

On considering the above mechanisms, homilite can be imagined to be a constituent of a given sample of gadolinite only if the first operator prevails over the second, *i.e.*, the proportion of iron exceeds that of beryllium. Such a case appears to be quite rare, however (homilite itself is very rare, and occurs only at Langesundsfjord, Norway), and it never occurs for all the specimens listed in Table 5. Therefore, to a good approximation, *most gadolinite-(Y) specimens can be considered to be mixtures of gadolinite, hingganite, and datolite end-members*. For the lanthanide-bearing end members, a further distinction according to Levinson's (1996) nomenclature is of course necessary.

## RESULTS AND DISCUSSION

### Reference samples

Selected samples of minerals in the gadolinite group for which reliable crystal-structure and chemical data are available have been taken as standards for compar-

ison with our results. Besides datolite (DATO: Foit *et al.* 1973), these are, respectively: the sample of gadolinite-(Y) from Japan (MIYA) studied by Miyawaki *et al.* (1984), the unapproved phase "calcybeborosilite" (CALCYB) found at Dara-Pioz, Tajikistan by Rastsvetaeva *et al.* (1996), and a number of specimens from Alpine fissures and pegmatites (Demartin *et al.* 1993).

The notable proportion of Alpine samples in these reference samples is due to their relatively young age and low temperature of formation, which factors account for the very good quality of the crystals. However, there may be important compositional differences between Alpine and non-Alpine samples, as is encountered for instance with other rare minerals such as bazzite (Gramaccioli *et al.* 2000, Demartin *et al.* 2000, and references therein). This point in fact provided part of the motivation for the present investigation on non-Alpine material.

A non-metamict sample of "gadolinite" of relatively recent origin also occurs in volcanic xenoliths of the Vico complex in Latium, Italy. This material would be particularly interesting for a detailed crystallographic investigation, because it shows unusually high contents

TABLE 5. RELEVANT DATA FOR SELECTED CRYSTALS OF GADOLINITE-GROUP MINERALS

	Cuasso 1	Cuasso 2	Cuasso 3	MOOS (7)	BEUR (7)	NALPSARVO (7)	STRA (7)	BASS (7)	CLOG (8)	MIYA (9)
Fe occupancy (crystallographic)	0.27	0.31	0.26	0.66	0.50	0.54	0.82	0.76	0.78	0.22
Fe occupancy (microprobe)	0.70	0.54	0.59	0.80	0.86	0.92	0.30	0.86	0.92	0.30
A occupancy (crystallographic) <sup>(1)</sup>	1.07	1.05	1.07	1.17	1.07	1.09	1.09	1.19	1.17	1.36
A occupancy (microprobe) <sup>(2)</sup>	1.11	1.10	1.04	1.02	1.11	1.17	1.18	1.22		
Be (Z) occupancy (refined)	1.07	1.02	1.03							
B molar fraction (from <Z-O>) <sup>(3)</sup>	0.16	0.29	0.26	0.10	0.08	0.08	0.24			
B molar fraction (from <Z-O>) <sup>(4)</sup>	0.25	0.16	0.18	0.09	0.22	0.19	0.04	0.03	0.02	0.20
B molar fraction (from the Be occupancy at Z)	0.26	0.07	0.12							0.00
Ca occupancy (microprobe)				0.08	0.12	0.17	0.07	0.04	0.02	0.15
<A-O>	2.424	2.431	2.432	2.424	2.428	2.428	2.420	2.432	2.429	2.438
<Fe-O>	2.193	2.192	2.200	2.180	2.180	2.183	2.174	2.184	2.182	2.199
<Si-O>	1.621	1.624	1.629	1.629	1.631	1.631	1.627	1.631	1.633	1.627
<Z-O> <sup>(5)</sup>	1.605	1.621	1.616	1.627	1.607	1.612	1.636	1.638	1.638	1.610
Z-O(5)	1.558	1.610	1.606	1.604	1.598	1.595	1.589	1.605	1.602	1.622
ΣB.V. at O(5) <sup>(10)</sup>	1.32	1.23	1.20	1.48	1.38	1.39	1.58	1.51	1.58	1.21

All the bond lengths are given in Å; the *e.s.d.* for the A-O, Fe-O and Si-O averages is 0.001 Å, and that for the Z-O averages and Z-O(5) are 0.002 and 0.004 Å, respectively. For the site occupancies, the *e.s.d.* is about 0.01.

<sup>(1)</sup> Obtained from crystal-structure refinement, on using the scattering factor of yttrium.

<sup>(2)</sup> From the electron-microprobe analysis, on considering the respective amounts of the elements and their atomic numbers, and dividing the results by 39 (atomic number of yttrium).

<sup>(3)</sup> The reported values derive from interpolation of bond lengths as in Demartin *et al.* (1993).

<sup>(4)</sup> The reported values derive from interpolation of bond lengths, using the relationship shown in Figure 1 (see text).

<sup>(5)</sup> This average does not include the Be-O(5) bond.

<sup>(6)</sup> The corresponding value reported by Miyawaki *et al.* (1984) using the criterion of Donnay & Allmann (1970) is 1.78.

<sup>(7)</sup> From Demartin *et al.* (1993).

<sup>(8)</sup> More properly, hingganite-(Y), from Demartin *et al.* (1993).

<sup>(9)</sup> From Miyawaki *et al.* (1984), sample without boron.

<sup>(10)</sup> Bond-valence sum for O(5).

Chemical formulae of the three samples from Cuasso al Monte:

Cuasso 1: [(Y,REE)<sub>1.5</sub>Ca<sub>0.5</sub>]<sub>2</sub>; [Be<sub>1.3</sub>B<sub>0.3</sub>]<sub>2</sub>; Fe<sub>0.3</sub> Si<sub>2</sub> O<sub>4</sub>[O<sub>0.5</sub>(OH)<sub>1.5</sub>]<sub>2</sub>

Cuasso 2: [(Y,REE)<sub>1.7</sub>Ca<sub>0.3</sub>]<sub>2</sub>; [Be<sub>1.7</sub>B<sub>0.3</sub>]<sub>2</sub>; Fe<sub>0.3</sub> Si<sub>2</sub> O<sub>4</sub>[O<sub>0.6</sub>(OH)<sub>1.4</sub>]<sub>2</sub>

Cuasso 3: [(Y,REE)<sub>1.6</sub>Ca<sub>0.4</sub>]<sub>2</sub>; [Be<sub>1.6</sub>B<sub>0.4</sub>]<sub>2</sub>; Fe<sub>0.3</sub> Si<sub>2</sub> O<sub>4</sub>[O<sub>0.5</sub>(OH)<sub>1.5</sub>]<sub>2</sub>

of the light lanthanides, Th and B (Della Ventura *et al.* 1990), presumably as a result of the different conditions of formation (higher temperature?). No suitable crystals for X-ray diffraction studies have been found so far, however.

The Alpine specimens considered here come from Moos, Rauris (MOOS), from Beura, Ossola (BEUR), from Val Nalps, Grisons (NALPS), from the Strada and Bosco pegmatites at Arvogno, Val Vigezzo [(STRA) and (ARVO)], from Monte Bassetta, Val Vigezzo (BASS), and from Clogstafelberg (Monte Giove), Val Formazza (CLOG). Three of those samples (MIYA, ARVO and BASS) are reasonably close to end-member gadolinite-(Y), ARVO and BASS being the closest of all the Alpine specimens studied.

CLOG is a most unusual sample, and from a unique occurrence (Graeser & Schwander 1987). This material shows a low content of iron, which suggests that hingganite-(Y) is the most acceptable classification (Demartin *et al.* 1993). It is particularly interesting here because in some respects it shows close similarities to our samples from Cuasso al Monte (see Table 5 and below).

For the Alpine reference samples, in view of the lack of analytical data concerning the lightest elements, the content of B was derived by Demartin *et al.* (1993) by carrying out a linear interpolation of the Z–O average bond lengths [omitting Z–O(5)]; the reference material for such an interpolation had been DATO, MIYA, and a sample of homilite studied by Miyawaki *et al.* (1985).

#### *Selection of crystallographic information*

On varying the composition of a specific sample of "gadolinite", a number of crystallographic parameters are subject to variation. However, for some of these parameters, the variation can be barely significant or even misleading. For instance, the content of boron does affect the values of the unit-cell parameters, but more specific information can be obtained instead by examining the occupancy of the Z site and the average of the Z–O bond lengths (see below).

Similarly, with respect to the X–O average bond distance for the Fe-rich samples [*e.g.*, 2.182(1) Å for MIYA: see below and Table 5], the corresponding distances for the Fe-poor samples from Cuasso al Monte, as well as for the Alpine sample in Fe (CLOG), are significantly longer [2.192 to 2.200(1) Å]; therefore, the X–O average distance would seem to provide useful information concerning the Fe<sup>2+</sup> occupancy of the X site.

However, the situation is not so simple. For instance, MOOS and BEUR show the same X–O distance (2.180 Å), but their X-site occupancy by Fe is 0.70 and 0.54(1), respectively; similarly, the corresponding distance for STRA [2.184(1) Å] does not differ substantially from the above value, whereas the occupancy by Fe is much higher [0.86(1)]. Moreover, such a distance is only 2.161(1) Å for the iron-free datolite (Foit *et al.* 1973, Miyawaki *et al.* 1984), instead of attaining a maximum

value. The situation becomes even more confusing on considering the bond angles in the XO<sub>6</sub> octahedron; for instance, for samples 2 and 3 from Cuasso al Monte, the X-site occupancy is 0.31 and 0.26(1), respectively, the average X–O distance is 2.192(1) and 2.200(1) Å, respectively (Table 5), but the respective O(2)–X–O(4) angles do not differ significantly: 70.8°(2) *versus* 70.6°(2).

Such a lack of correlation occurs because the geometry of the XO<sub>6</sub> polyhedron does not only depend on the composition of the X site; all the oxygen atoms also are linked to the atoms in the Z site, where substitution of B for Be can occur. For this reason, and considering that the site occupancy is strongly affected by the absence of a 24-electron ion, we contend that the value obtained from crystal-structure refinement is the most reliable indicator, at least for the gadolinite group. The slight but significant disagreement that can in some cases be observed between the crystallographic values and the corresponding values obtained by electron-microprobe analysis (especially for STRA: Table 5) can be most likely explained because the analyzed fragment and the fragment submitted to X-ray investigation were not the same, although they were part of the same crystal.

Other examples of crystallographic data of minor importance for our purposes concern the average A–O and the Z–O(5) bond lengths (see below).

#### *Unit-cell parameters*

For each sample from Cuasso al Monte, the unit-cell parameters were obtained using 25 reflections with  $9.6 < \theta < 20.4^\circ$ , and are reported in Table 2. All the values of *c* are small in comparison with those of most gadolinite samples (see Table 2 in Demartin *et al.* 1993), and on these grounds, we expected notable amounts of boron to be present. Furthermore, a significant variation in *c* values is evident, and on these grounds a non-negligible compositional difference also can be expected. Such results are fully confirmed by crystal-structure refinement (see below).

#### *The X site*

In Table 5, the refined values of the site occupancy and the corresponding values derived from electron-microprobe analysis are shown for the specimens studied by Demartin *et al.* (1993); the agreement is satisfactory. The refined values of the occupancy for the X site (see also Table 5) for the three samples from Cuasso al Monte indicate only a partial occupancy by iron; in all cases, it is below 31%, and lower than for all the specimens analyzed by Pezzotta *et al.* (1999). Furthermore, the iron deficiency in the X site is never accompanied by an extensive rearrangement of the adjacent oxygen atoms (see also Demartin *et al.* 1993): this detail is important as it confirms the absence of voids and the role of Ca<sup>2+</sup> in the above-described mechanisms of substitution.

### The Z site

The possible substitution of boron for beryllium is fundamental, because of the existence of Be- and B-rich species in the gadolinite group, and non-negligible amounts of boron have in some cases been observed in samples of gadolinite (see, for instance, Demartin *et al.* 1993, Rastsvetaeva *et al.* 1996). However, the boron content of gadolinite has not been routinely determined in most instances; therefore, in our search of appropriate references, only the works where the content of B was measured have been considered.

There are two different kinds of important (and independent) crystallographic information in this respect: 1) the scattering at the Z site, and 2) the average of the Z–O distances, which become appreciably shorter if Be is replaced by B. For instance, the average in B-free gadolinite (1.648 Å in MIYA) is much greater than the corresponding average B–O distance in datolite (1.475 Å according to Foit *et al.* 1973). As with datolite or hingganite, the simultaneous replacement of O(5) by an OH group might affect the average of such distances, and for this reason the Z–O(5) bond should be omitted from consideration.

The relationship between the average Z–O bond distance and the corresponding molar fraction of Be, as derived from site scattering, is shown in Figure 1. Here, all the points representing the Alpine samples lie clearly above the interpolated line, thereby suggesting that a systematic overestimation of B content was made by Demartin *et al.* (1993); this error is probably due to improper consideration of homilite among the end members in interpolating the Z–O bond distances (see above). The corrected values of the B content, derived using this new interpolation, are reported in Table 5, as are the estimates of Demartin *et al.* (1993).

Since Figure 1 shows a reasonable plot, the two different kinds of information shown are consistent. This agreement justifies the use of crystallographic procedures to evaluate the boron content in minerals of the gadolinite group; even the point representing the intermediate member CALCYB is reasonably close to the interpolated line. Following this criterion, we infer the existence of a notable replacement of Be by B in our specimens from Cuasso al Monte, attaining a maximum of 25% atomic for sample 1 (Table 5).

### The OH-for-O substitution

The replacement of the oxygen atom by an OH group should be reflected in the length of the Be–O(5) bond. For instance, in CLOG, which contains a significant amount of OH, this distance [1.622(5) Å] is significantly longer than the corresponding values observed in all the other Alpine samples of gadolinite or MIYA (Table 5). Such a difference in bond lengths seems to suggest the possibility of obtaining an independent crystallographic estimate of the OH content.

Bond-valence sums (Brown 1981) for O(5) in all the samples considered here are reported in the last line of Table 5. For the three samples from Cuasso al Monte and for CLOG, these sums are appreciably lower than in all the other cases; such lower values could be construed to indicate the presence of a high content of hydrogen, in agreement with the low iron content of these samples.

However, the situation seems to be more complex. For instance, for MIYA, ARVO, and BASS, where the iron contents are high, the bond-valence sum at O(5) is too low to be used in a quantitative interpretation, ranging from 1.56 to 1.58 valence units, and corresponding to an OH content (atomic) of 0.42–0.44, which is unreasonably high, although it is lower than the corresponding values for all samples of hingganite.

A similar situation can be observed for euclase,  $\text{BeAlSiO}_4(\text{OH})$ , a mineral showing close structural similarities to gadolinite. Instead of being longer, the Be–OH distance in euclase is actually significantly shorter than the average for the Be–O distances [1.608(1) versus 1.654(1) Å: see Demartin *et al.* (1992b)]. Such a phenomenon has also been observed by other authors for the same mineral (Hazen *et al.* 1986), and for bertrandite  $\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$  (Hazen & Au 1986); therefore, straightforward use of bond-valence sums requires caution, at least in the present state and where beryllium is implied.

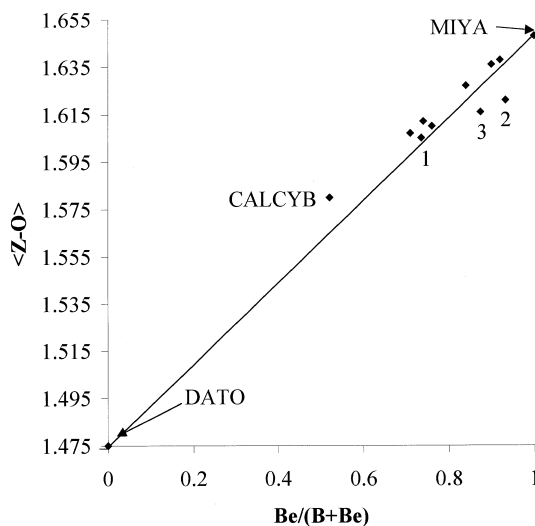


FIG. 1. A plot of the average Z–O distance versus the molar fraction  $\text{Be}/(\text{B} + \text{Be})$  at the Z site. The unlabeled points correspond to Alpine samples of gadolinite studied by Demartin *et al.* (1993). The straight line joins the points representing datolite and the gadolinite-(Y) sample studied by Miyawaki *et al.* (1984); it almost coincides with a least-squares fit.

In view of these difficulties, the only reasonable way to determine the OH content in "gadolinite" samples on crystallographic grounds appears to be to assume 2 OH groups to correspond to each "vacancy" instead of Fe at the X site.

#### The A site

In the gadolinite group, the refined value of the occupancy of yttrium at the A site can be affected in an opposite way from that expected where it is replaced either by calcium or by the lanthanides, owing to variation in the average number of electrons. In general, for gadolinite-(Y), the yttrium content ranges from 1.1 to 1.2 atoms per formula unit, *apfu* (Table 5), although it can increase significantly for some samples containing an amount of lanthanides higher than usual. For instance, a notably high value (1.36 *apfu*) was observed for CLOG, which is comparatively rich in Ce and Nd; the corresponding value derived from the average number of electrons based on the results of the electron-microprobe analysis is, however, appreciably lower (1.18).

A value systematically lower than that expected is also exhibited by most samples we have examined; such a phenomenon might be ascribed, at least in part, to the different shape of the atomic scattering factors for elements widely differing in atomic number; however, in spite of such disagreement, the highest values of the occupancy correspond indeed to comparatively lanthanide-rich samples, thereby providing the possibility of some distinction on such grounds (Table 5). In any case, we do not claim that even roughly significant estimates of the REE distribution can be achieved in this way.

Furthermore, the possibility of dealing with gadolinite-(Ce) or strongly calcian gadolinite-(Y) could be confirmed by examining the average value of the A–O bonds, because the ionic radius of  $\text{Ce}^{3+}$  or  $\text{Ca}^{2+}$  is notably greater than that of  $\text{Y}^{3+}$ . Unfortunately, for gadolinite-(Ce), no crystal-structure data accurate enough for a significant comparison are available yet; the only experimental evidence for a higher value of this bond-length average is provided by the comparatively lanthanide-rich CLOG (Table 5), although the substitution of Y for Ca is only partial.

In our reference samples, the average A–O bond length [2.420 to 2.438(1) Å] does not show a reasonable trend with respect to the Ca (or Ce) content (Table 5). The highest values correspond to CLOG and MIYA, which lie near the opposite extremes in this respect. As a result, no satisfactory conclusions can be achieved on applying bond-valence sums, in line with the general situation concerning highly ionic bonds.

For this reason, our criterion of correspondence between the molar proportions of Ca and B turns out to be particularly useful, and in this way the presence of notable amounts of calcium is indicated in our samples from Cuasso al Monte, as in the case for CLOG (see below and Table 5).

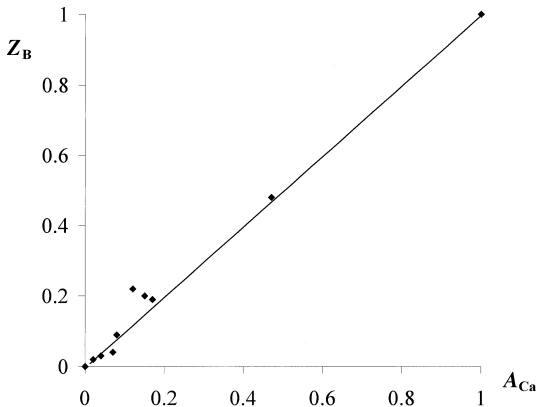


FIG. 2. A plot of the molar fraction of calcium in the A site versus the molar fraction of boron at the Z site. The interpolated line follows the same criterion as in Figure 1.

A plot of the molar fraction of calcium (in A) versus the molar fraction of boron (in Z) is shown in Figure 2 for all the reference samples mentioned here. The substantial agreement attained shows that our crystal-chemical inferences hold in practice, the deviations from the plot being acceptable in view of 1) the rather drastic simplifications implied, 2) the various experimental errors, and 3) the inhomogeneity of the crystals. Therefore, in all these samples, the amount of calcium (atomic) indeed equals that of boron, to a reasonable approximation, and the presence of other significant mechanisms of substitution in addition to those considered above can reasonably be excluded.

#### CONCLUSIONS

In the light of all the evidence, our samples from Cuasso al Monte can be correctly classified as borian hingganite-(Y). Although they are similar to CLOG in many respects, the occupancy of the A site (1.05–1.07 *apfu*) is in the range usually found for gadolinite-group phases; therefore, as the Ca content is comparable, the yttrium content should be notably higher than for CLOG.

The corresponding minerals from Cuasso al Monte that were analyzed by Pezzotta *et al.* (1999) are invariably richer in Fe (between 0.36 and 0.98 in the X site), in agreement with their classification as gadolinite-(Y) and hingganite-(Y). Even without analytical data concerning boron, notable amounts of this element should be present, in the range 0.06–0.15 *apfu*, on the basis of the assumption that the atomic ratio Ca/B is equal to 1, although the amount inferred is inferior to the content of our samples. Moreover, the high lanthanide content shown in the chemical analyses (between 0.24 and 0.53 *apfu*), which is in the same range as in CLOG (0.38



*apfu*), should be notably higher than in our samples of hingganite-(Y).

In conclusion, the great compositional variability shown by our samples from Cuasso al Monte, as well as those analyzed by Pezzotta *et al.* (1999), reflects the fact that they represent different stages of crystallization in the miarolitic cavities. The high crystallinity of the fragments studied here suggests that the last stages of formation occurred in comparatively recent times.

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