

A CRYSTAL-CHEMICAL INVESTIGATION OF ALPINE GADOLINITE

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ABSTRACT

Gadolinite-(Y) specimens from various localities in the Alps have been examined by electron microprobe and single-crystal X-ray diffraction. In general, dysprosium is the most abundant rare-earth, although a few samples contain approximately equal amounts of Dy and Yb, and in one instance, Gd predominates. In contrast to many non-Alpine occurrences, most of these specimens show only limited amounts of the lighter REE. There is an almost constant presence of calcium (up to 4 wt% CaO, and possibly twice that amount for more questionable samples); iron is often markedly deficient with respect to the theoretical formula, and in at least one case (Glogstafelberg), the material should more properly be called hingganite-(Y) (4.0 wt% FeO). In some specimens, a significant substitution of B for Be (up to about 4.2 wt% B₂O₃) can be deduced from crystal-structure data, on the basis of linear interpolation of the measured Be-O bond lengths with respect to other gadolinite-group minerals. This substitution is more extensive for specimens high in Ca and low in Fe, and which therefore grade toward datolite. No evidence for replacement of Si by B has been found. Minor amounts of thorium (up to 0.4 wt% ThO₂) commonly are present, and uranium (0.3 wt% UO₂) was found in one specimen. As for xenotime and monazite, the behavior of Y is not uniquely determined by the ionic radius, some specimens being especially enriched in this element with respect to the middle-heavy rare earths (up to 41.5 wt% Y₂O₃).

Keywords: gadolinite, hingganite, rare earths, yttrium, beryllium, boron, pegmatite, fissure, Alps, crystal-structure analysis, electron-microprobe analysis.

SOMMAIRE

Nous avons caractérisé plusieurs échantillons de gadolinite-(Y) provenant de localités alpines par microsonde électronique et par diffraction X sur cristal unique. C'est en général le dysprosium qui est la plus abondante des terres rares, quoique certains échantillons contiennent une proportion équivalente de Dy et de Yb, et quoique le Gd prédomine dans un des échantillons. Contrairement à plusieurs exemples provenant d'ailleurs, la plupart des échantillons ne contiennent que de faibles quantités des terres rares légères. Le calcium est présent dans presque tous les cas, en quantités allant jusqu'à 4% de CaO, et pouvant atteindre le double de ceci dans certains échantillons moins bien caractérisés. Le fer est fortement déficitaire par rapport à la formule idéale; dans au moins un cas (Glogstafelberg), le matériau mériterait même d'être appelé hingganite-(Y) (4.0% FeO par poids). Dans certains échantillons, une proportion importante du Be est remplacée par le B (jusqu'à environ 4.2% de B₂O₃ par poids), d'après les données obtenues sur la structure cristalline de cette espèce, à la lumière d'une interpolation des longueurs Be-O mesurées pour certains de nos échantillons, par rapport à d'autres minéraux du groupe de la gadolinite. Cette substitution est plus répandue pour les échantillons riches en Ca et pauvres en Fe, et donc ceux qui montrent une tendance vers la composition de la datolite. Nous ne trouvons aucun indice d'un remplacement du Si par le B. De faibles quantités de Th (jusqu'à 0.4% de ThO₂ par poids) sont assez courantes, et 0.3% de UO₂ est présent dans un de nos échantillons. Comme dans le cas du xénotime et de la monazite, le comportement de l'yttrium ne semble pas dépendre uniquement du rayon ionique; certains échantillons sont fortement enrichis en Y par rapport aux terres rares moyennes et lourdes (jusqu'à 41.5% Y₂O₃).

(Traduit par la Rédaction)

Mots-clés: gadolinite, terres rares, yttrium, béryllium, bore, pegmatite granitique, fissure, Alpes, ébauche de la structure cristalline, analyse à la microsonde électronique.

INTRODUCTION

Whereas gadolinite has been known for nearly two centuries, its discovery as a fissure mineral in the Alpine region took place more recently (Parker *et al.* 1940). Because of its geologically "young" age, gadolinite from the Alps is very different from that of most other occurrences; it commonly is referred to as "noble" gadolinite, as the crystals are sharp and transparent, their color is generally pale green or blue-green, reminiscent of beryl or some bluish varieties of titanite, with which such crystals of gadolinite may easily be confused.

As is the case for monazite and xenotime, there are also occurrences in granitic pegmatites. Most of these have been discovered in Val Vigizzo (Ossola) (Mattioli 1977, 1978, Turconi 1982, Albertini 1988); in the eastern Alps, occurrences are known at the so-called "Plattenbrüche" in the Rauris Valley (Meixner 1976) and in the Markogel pegmatite near Villach (G. Niedermayr, pers. comm., 1990).

Most of the scientific work on Alpine gadolinite has been concerned with its mere identification. In a few cases, optical and morphological data and X-ray powder patterns are given; however, no structure refinement has been carried out so far, and accurate values for the unit-cell parameters are lacking in the literature. Similarly, recent results of quantitative chemical analyses, including the distribution of the rare-earth elements (*REE*), are not available.

The unusual perfection and "freshness" of the crystals, which are almost unique in nature, make them ideally suited for chemical analysis and a study by X-ray diffraction. Advanced metamictization and leaching accompanied by oxidation, commonly observed in non-Alpine gadolinite, might lead to grossly erroneous conclusions about the crystal chemistry of this mineral. For instance, a recent unpublished investigation carried out by our group on the glassy core of crystals from Baveno (which are much older than Alpine specimens, though found in the same vicinity) showed that there is an almost complete series of compositions between "true" gadolinite and an amorphous mass of hydrated iron oxide and silica.

Also, crystallographic data of good quality are rare on this species (Miyawaki *et al.* 1984). They can be important in view of the existence of extensive solid-solution with other minerals of the same group, *e.g.* hingganite $(Y, Yb)_2Be_2Si_2O_8(OH)_2$ (Semenov *et al.* 1963, Voloshin *et al.* 1983, Yakubovich *et al.* 1983) or even datolite $CaBSiO_4(OH)$, calcium-gadolinite, homilite $Ca_2FeB_3Si_2O_{10}$ (Miyawaki *et al.* 1985), *etc.* These solid solutions commonly involve compositional variation involving light elements such as Be or B, and presence of water. For this reason, electron-microprobe data must be supplemented by other data in order to establish the chemical composition exactly.

Besides these well-known schemes of substitution (Ito 1967, Ito & Hafner 1974, Miyawaki *et al.* 1984),

other types of substitution may not be excluded *a priori*. Among these, for instance, the presence of additional beryllium replacing silicon has been postulated by some authors, on the grounds of infrared absorption spectra (Aleksandrova *et al.* 1966); similarly, the presence of four OH groups substituting for SiO_4 , as in hydrogarnet, is another possibility; furthermore, significant amounts of P and F [in view of the isostructural relationship to herderite $CaBePO_4(F, OH)$ and its group] or of Bi [as in minasgeraisite $(Y, Bi)_2CaBe_2Si_2O_{10}$] also may be present.

CHEMICAL ANALYSIS

Electron-microprobe analyses were performed on polished grain-mounts, using the wavelength-dispersion ARL-SEMQ instrument of the Italian National Research Council (C.N.R.) at the Centro di Studi per la Stratigrafia e la Petrografia delle Alpi Centrali, Milan.

To determine the content of Si, Ca, Fe and U, a series of natural and synthetic standards was employed. For the rare earths, Y and Th, synthetic lithium metaborate glasses were prepared as specified in our contributions on Alpine monazite and xenotime (Mannucci *et al.* 1986, Demartin *et al.* 1991a, b). The accelerating potential was 20 kV, the sample current (on brass) 0.01 μA , and the MAGIC IV correction procedure was applied (Colby 1968, with modifications). In all the samples here examined, the concentrations of Tb, Ho, Mg, Sc, P, S, Sr, Ba, Na, F, and Al are below the limits of detection of our instrument (about 0.1 wt%); for Tm and Lu, owing to interference from Dy, the limit is higher (about 0.4 wt%).

Besides the interferences among the *REE*, the analytical line of dysprosium ($DyL\alpha$) is too close to a line of iron ($FeK\alpha$), so that on one side the background was too high, leading to unacceptably low values for the Dy_2O_3 content. This interference has been accounted for by measuring the background of $DyL\alpha$ on one side only.

Our data pertain to material from twelve localities (Table 1). The variation in oxide percentages reported includes both statistical uncertainty in counting and actual compositional variation in the sample, since for most specimens the reported values are the average of seven analyses, performed on different points. For the specimens from Hopffeldboden and Triolet, owing to lack of homogeneity of the samples and also to the impossibility of repeating the measurements in optimum conditions, the results are less accurate than for the other specimens. For example, the Y content is surely too high, and this also explains the unusually high value for the *Me/Si* ratio for the specimen from Hopffeldboden (see below).

Unfortunately, the amounts of some lighter elements could not be determined by our microprobe analysis; among these, boron and beryllium are particularly important for gadolinite. This lack of data can be

TABLE 1. ANALYTICAL DATA ON ALPINE GADOLINITE

Sample	(1)	(2)	(3)	(4)	(5)	(6)
La ₂ O ₃	-	-	0.2(1)	-	-	-
Ce ₂ O ₃	-	0.3(1)	0.9(7)	0.4(3)	-	-
Pr ₂ O ₃	-	-	0.2(2)	-	-	-
Nd ₂ O ₃	0.3(3)	0.7(2)	1.4(9)	0.9(5)	0.1(1)	0.2(4)
Sm ₂ O ₃	0.4(4)	0.7(2)	1.0(5)	1.2(6)	0.3(2)	0.2(3)
Gd ₂ O ₃	1.4(6)	1.8(6)	1.8(6)	3.5(12)	1.4(5)	1.1(14)
Dy ₂ O ₃	4.1(1)	4.0(1)	3.9(4)	6.6(6)	4.5(5)	4.0(9)
Er ₂ O ₃	3.4(3)	3.4(3)	3.0(2)	3.3(4)	3.2(5)	3.7(8)
Yb ₂ O ₃	3.8(8)	3.4(4)	3.4(8)	1.9(6)	2.5(10)	2.3(6)
Y ₂ O ₃	35.6(20)	33.3(35)	31.5(21)	35.2(35)	34.4(14)	33.7(28)
ThO ₂	-	-	0.2(2)	0.4(4)	0.3(4)	-
CaO	1.0(9)	1.8(2)	2.8(13)	1.1(5)	3.1(9)	4.0(9)
FeO	11.9(17)	10.2(3)	8.1(23)	11.5(14)	8.2(20)	8.8(12)
SiO ₂	24.8(8)	25.1(10)	25.4(4)	24.1(5)	25.8(6)	25.8(5)
B ₂ O ₃	-	2.3	4.2	-	-	4.0
(BeO)	-	8.6	7.5	-	-	7.9
(H ₂ O)	-	0.8	1.1	-	-	1.2
TOTAL	-	96.4	96.6	-	-	96.9
Me/Si*	0.98	0.95	0.97	1.06 [§]	0.98	0.99
REE/Y**	0.22	0.25	0.30	0.31	0.21	0.21
Ca/Y [‡]	0.05	0.09	0.16	0.06	0.16	0.21

Sample	(7)	(8)	(9)	(10)	(11)	(12)
La ₂ O ₃	0.5(2)	-	-	0.2(2)	-	-
Ce ₂ O ₃	1.8(2)	-	0.5(5)	1.3(4)	-	0.2(1)
Pr ₂ O ₃	0.3(1)	-	-	0.4(2)	-	-
Nd ₂ O ₃	1.6(3)	-	1.0(5)	3.6(9)	0.2(3)	0.6(2)
Sm ₂ O ₃	0.9(3)	-	1.1(5)	3.8(17)	0.3(4)	0.6(2)
Gd ₂ O ₃	2.4(4)	0.7(3)	2.9(12)	5.9(28)	1.5(14)	1.9(3)
Dy ₂ O ₃	3.1(1)	1.6(0)	4.6(3)	5.4(2)	3.2(9)	4.8(6)
Er ₂ O ₃	1.6(4)	1.4(4)	2.8(13)	2.6(9)	2.5(6)	3.4(5)
Yb ₂ O ₃	1.2(3)	1.6(4)	2.5(8)	2.0(9)	1.7(10)	2.4(3)
Y ₂ O ₃	34.6(16)	41.5(17)	31.1(19)	21.5(67)	28.0(49)	31.1(26)
ThO ₂	-	-	0.3(3)	-	-	-
UO ₂	-	-	0.3(2)	-	-	-
CaO	0.8(2)	1.7(4)	0.4(15)	3.2(24)	7.9(28)	3.7(8)
FeO	10.5(8)	11.0(10)	11.7(26)	4.0(14)	5.9(13)	9.3(13)
MnO	-	0.4(2)	-	-	-	-
SiO ₂	23.5(25)	25.8(10)	23.4(25)	23.4(15)	25.5(27)	25.0(27)
B ₂ O ₃	0.9	1.4	0.9	3.2	-	-
(BeO)	8.1	8.9	8.2	7.1	-	-
(H ₂ O)	0.3	0.6	0.1	2.0	-	-
TOTAL	92.1	96.6	91.7	89.6	-	-
Me/Si*	1.00	0.98	0.94	0.98	0.99	0.98
REE/Y**	0.24	0.08	0.30	0.73	0.21	0.27
Ca/Y [‡]	0.04	0.07	0.02	0.27	0.50	0.21

(wt%, range width $\times 10$ following each figure, within parentheses). Samples: (1) Böckstein, from fissure and (2) Moos, Rauris, from fissure: see Kontrus (1965), Melxner (1976), Fischer (1977), Strasser (1978, 1989), Schebesta (1984) and Winkler (1987); (3) Beura, Ossola, from fissure: see Calanchi (1979); (4) Hopfaldboden, Obersulzbachtal, from fissure: see Strasser (1981), Schebesta (1982) and Preite (1986); (5) Furka tunnel, Val Bedretto, from fissure: see Kipfer (1979); (6) Val Naips, Graubünden, from fissure: see Parker *et al.* (1940); (7) "Strada", Arvogno, Val Vigizzo, from pegmatite: see Mattioli (1977, 1978); (8) "Bosco", Arvogno, Val Vigizzo, from pegmatite: see Mattioli (1978) and Albertini (1988). This locality is mentioned as "Arvogno" in our work on Alpine xenotime (Demartin *et al.* 1991b); (9) Monte Bassetta, Val Vigizzo, from pegmatite: see Turconi (1982); (10) Glogstafelberg, Val Formazza, from fissure, in association with monazite-(Nd) (Graesser & Schwander 1987); (11) Triolet, Mont Blanc, from fissure (Palenzona 1990); (12) Alpe Veglia, Simplon, from fissure: see Albertini (1986). § This figure is not reliable, owing to overestimation of Y. * Ratio (atomic) of the metals in the Y position to Si. ** Ratio (atomic) of the REE to Y. ‡ Ratio (atomic) of Ca to Y.

obviated using results from crystal-structure refinement (see below), which indicate common partial substitution of B for Be. The presence of a realistic amount of boron in the Glogstafelberg sample was confirmed by a semiquantitative microprobe analysis performed with a XL SEM equipped with an EDAX energy-dispersion spectrometer.

Even for the most boron-rich specimens, the atomic ratio Me/Si evaluated from our data (see the last entries in Table 1), where Me indicates Y plus the other metals substituting for it, remains close to the theoretical value of 1.0, showing lack of extensive substitution of B or Be for silicon; a similar conclusion is reached by considering the values of the Si-O bond distances (see below) or the mean-square amplitudes obtained from crystal-structure refinement. Our results seem to contradict the assertions of some authors about gadolinite from other sources [see for instance: Oftedal (1964), Christ (1965)], but are in agreement with the findings of Miyawaki *et al.* (1984); moreover, in our case, because of the low temperature of origin, the possibility of such substitution in the Alpine environment (especially for the fissure specimens) is low. Full occupancy of the tetrahedral position by Si may be a general rule for all specimens of gadolinite.

The values for beryllium and water reported in Table 1 have been deduced from crystal-chemical considerations. For BeO (plus boron), a 1:1 atomic ratio with respect to Si has been assumed, because there is no evidence for appreciable substitution of Si by lighter elements.

Whereas the presence of Fe³⁺ was found in some natural and synthetic members of the gadolinite series (Nakai 1938, Ito 1967, Ito & Hafner 1974), here the average Fe-O distances in all the samples we have examined by X-ray diffraction range from 2.174 to 2.199 Å (see below). These values are in the usual range for Fe²⁺, and this is confirmed by the absence of evident oxidation in the samples. For these reasons, we have considered iron to be exclusively in the +2 state.

On these grounds, and considering also the depletion of iron with respect to the theoretical end-member (see below), gadolinite from the Alps has been assumed to obey the general chemical formula: Y_{2-2z}Ca_{2y}Fe_{1-x}Be_{2-2z}B_{2z}Si₂O₁₀H_{2x+2y-2z} or (1-y)Y₂O₃·2yCaO·(1-x)FeO·2SiO₂·(2-2z)BeO·zB₂O₃·(x+y-z)H₂O. Here, the parameters x, y and z have been determined for each sample by measuring the contents in iron, calcium, and boron, respectively. Unfortunately, since our determination of the boron content is based on crystal-structure refinement, our general chemical formula can be used only where the necessary X-ray-diffraction data are available; for this reason, the entries relative to B₂O₃, BeO, H₂O, and the total, are left blank for five samples in Table 1.

Whereas in general the stoichiometric ratios Me/Si are satisfactory, the totals are low with respect to the theoretical values. In any case, the totals in Table 1 can

be raised if minor amounts of the less abundant *REE* (which are surely present, although below the detection limit) are considered. Another reason for the low values of the totals can be incipient metamictization (see below).

A general average of the *REE* distribution for all our Alpine samples is reported in the first column in Table 2, together with separate averages for fissure and pegmatite samples (columns 2 and 3), the corresponding values for selected other (non-Alpine) samples, and the overall crustal average.

The *REE* distribution clearly reflects the Oddo-Harkins rule (Oddo 1914, Harkins 1917), with the elements of odd atomic number less abundant than the corresponding elements of even atomic number. In the samples we have examined so far, with two exceptions only, dysprosium is the most abundant *REE*. In the sample from Bosco, the content of Yb_2O_3 (in weight) equals that of Dy_2O_3 , and in another case (Glogstafelberg), gadolinium prevails. With respect to other occurrences (Table 3), the greatest majority of the Alpine samples show a marked depletion of the lighter *REE* (La to Nd) in favor of the other members of the series. There is only a minor difference between the specimens from fissures and those from pegmatites: the heaviest *REE* are slightly more abundant in the former, and yttrium is more abundant in the latter. A more significant difference between the two kinds of occurrence is the content of boron, which is lower for the pegmatite specimens.

On the whole, the average distribution of *REE* (plus yttrium) is not far from the general average given by Aleksandrova *et al.* (1966) for one type of occurrence in granitic pegmatites (compare column 1 with column 7 in Table 2); with respect to the natural geochemical abundance, this corresponds to a marked enrichment in the middle-heavy *REE* (Dy, Er). The distribution of *REE*

TABLE 3. UNIT-CELL DATA ON ALPINE GADOLINITE, AND COMPARISON WITH OTHER SOURCES

	a (Å)	b (Å)	c (Å)	B(°)
Böckstein, Rauris(1)	4.737(3)	7.531(8)	9.920(7)	90.53(5)
Moos, Rauris(2)	4.747(1)	7.544(1)	9.931(1)	90.51(1)
Beura, Oseola(3)	4.743(2)	7.568(3)	9.900(3)	90.41(4)
Hopffeldboden(4)	4.754(4)	7.510(9)	9.955(9)	90.79(7)
Val Nalps(6)	4.746(1)	7.562(1)	9.903(2)	90.48(1)
"Strada", V. Vigizzo(7)	4.759(1)	7.564(1)	9.968(2)	90.43(1)
"Bosco", V. Vigizzo(8)	4.743(1)	7.518(1)	9.933(2)	90.52(1)
Monte Bassetta(9)	4.757(1)	7.553(2)	9.970(1)	90.50(1)
Glogstafelberg(10)	4.752(1)	7.629(2)	9.894(2)	90.24(2)
Alpe Veglia(12)	4.739(4)	7.598(11)	9.926(10)	90.68(7)
Gadolinite-(Y)				
Japan(13)	4.768(1)	7.565(2)	10.000(2)	90.31(2)
Gadolinite-(Y)				
Norway(14)	4.80	7.60	10.07	90.8
Gadolinite-(Ce)				
Skien, Norway(15)	4.82(2)	7.58(2)	10.01(3)	90.5(3)
Hingganite-(Yb)				
Kola(16)	4.740(2)	7.607(3)	9.888(5)	90.45(4)
Hingganite-(Y)				
Tuva(17)	4.90	7.80	10.20	92
Hingganite-(Ce)				
Japan(18)	4.792(4)	7.705(7)	9.996(10)	90.06(4)
Hemilite				
Norway(19)	4.776(1)	7.621(2)	9.786(2)	90.61(2)
Mineral A(20)				
YCaBeSi ₂ O ₈ (OH) ₂	4.66	7.48	9.86	88.5
Datolite				
Massachusetts(21)	4.832(4)	7.608(4)	9.636(8)	90.40(7)
Herderite-(OH)				
Brazil(22)	4.804(1)	7.661(1)	9.879(2)	90.02(1)
Minasgeraisite				
Brazil(23)	4.702(1)	7.562(1)	9.833(2)	90.46(1)

Samples from 1 to 12 are labeled as in Table 1. (13) Miyawaki *et al.* (1984), 12.08 wt% FeO, no B_2O_3 . (14) Nilssen (1973). (15) Segalstad & Larsen (1978), about 10 wt% FeO, 0.55 wt% B_2O_3 . (16) Voloshin *et al.* (1983), 1.31 wt% FeO, no B_2O_3 . (17) Semenov *et al.* (1983), mineral not named at that time; 3.44 wt% B_2O_3 , 1.26 wt% FeO. (18) Miyawaki *et al.* (1987), 5.65 wt% FeO, traces of B_2O_3 . (19) Miyawaki *et al.* (1985), 17.03 wt% FeO. (20) Semenov *et al.* (1983), 3.80 wt% FeO. (21) Foit *et al.* (1973). (22) Lager & Gibbs (1974). (23) Foord *et al.* (1986).

in nonmetamict gadolinite from Hundholmen, Norway, reported by Nilssen (1973), looks even more similar to the average of our data (column 5); there is, on the other hand, a remarkable difference with respect to the other non-metamict gadolinite from Japan studied by Miyawaki *et al.* (see column 4), which is considerably richer in the lighter *REE* and poorer in yttrium. In our Alpine samples, the greatest amount of lighter rare-earths has been observed in the fissure sample from Glogstafelberg (5.5 wt%), and the next highest amount (4.2 wt%), in the pegmatite sample from "Strada", Arvigno. These figures correspond to 11.8 wt% and 8.9 wt%, respectively, of the total of the *REE* oxides (plus Y). The Glogstafelberg sample also shows remarkably high amounts of Sm and Gd (8.1 and 12.6 wt% of the total of the *REE* oxides), pointing out the unusual character of this occurrence; note that the *REE* distribution of hingganite-(Y) from Tuva (Semenov *et al.* 1963) is similar (compare columns 8 and 9 in Table 2).

The range of the observed values for the Y_2O_3 content (21.5 to 41.5 wt%) and the atomic *REE*/Y ratio vary widely (Table 1). The Y_2O_3/Dy_2O_3 ratio (in terms of weight), reported in the last line of Table 2, in general is

TABLE 2. A COMPARISON OF THE REE DISTRIBUTION IN ALPINE GADOLINITE, COMPARED TO THAT IN GADOLINITE FROM OTHER LOCALITIES

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
La ₂ O ₃	0.1	-	-	0.4	0.1	-	-	0.4	1.8	14.7
Ce ₂ O ₃	1.0	0.4	1.7	5.2	0.5	1.6	3.1	2.8	7.2	30.4
Pr ₂ O ₃	0.1	-	-	2.5	0.1	-	-	0.9	2.6	3.6
Nd ₂ O ₃	1.9	1.3	1.9	9.3	0.8	7.8	4.5	7.7	7.4	14.7
Sm ₂ O ₃	1.9	1.3	1.5	5.8	1.1	6.0	3.6	8.1	7.3	3.2
Gd ₂ O ₃	4.7	3.9	4.3	6.0	4.1	6.2	4.8	12.6	8.0	3.0
Dy ₂ O ₃	8.2	9.5	6.6	8.3	7.7	8.9	7.9	11.6	6.0	3.4
Er ₂ O ₃	6.2	6.9	4.1	3.1	7.8	5.4	5.3	5.6	3.0	2.0
Yb ₂ O ₃	5.1	5.8	3.8	1.2	6.8	4.6	2.8	4.3	3.3	2.0
Y ₂ O ₃	70.2	70.9	76.1	58.3	65.1	59.6	68.1	46.0	-50.0	20.0
Y/Dy [§]	8.6	7.5	11.5	7.0	8.5	6.7	8.6	4.0	8.3	5.9

The values, in wt%, are calculated on the total of the *REE* oxides + Y_2O_3 . (1) Total average of our data; (2) average of our data for fissure samples, with exception of the specimen from Glogstafelberg; (3) average of our data for pegmatite samples; (4) fresh sample from Miyazuma-kyo, Japan (Miyawaki *et al.* 1984); (5) fresh sample from Hundholmen, Norway (Nilssen 1973); (6-7) averages for gadolinite from granite pegmatites (Aleksandrova *et al.* 1986); (8) Glogstafelberg, our data; (9) hingganite-(Y), Tuva (Semenov *et al.* 1983); (10) crustal average (Taylor & McLennan 1985). § ratio (by weight) Y_2O_3/Dy_2O_3 .

higher than for the crustal average. This parameter is important because the ionic radii of Y^{3+} and Dy^{3+} are virtually the same; accordingly, there is evidence for processes of fractionation depending not only upon differences in ionic radius (see also Mannucci *et al.* 1986, Demartin *et al.* 1991a). This is in line with our observations for xenotime, in particular concerning the sample from Bosco (Demartin *et al.* 1991b): it is worth noting that for the same locality, the Y_2O_3/Dy_2O_3 ratio in gadolinite is 25.9. Another peculiarity of the gadolinite from Bosco is the virtual absence of all the *REE* lighter than Gd.

Among the elements substituting for Y and the *REE*, the most important is Ca, generally present in quantities of the order of 1–2 wt% CaO. There are also specimens containing up to 4 wt% CaO (Val Nalps, Glogstafelberg); a still higher figure (nearly 8 wt%) has been obtained for gadolinite from Triolet, but the analytical data are not as reliable, owing to the extremely small size of our crystal and to the possible presence of impurities. Unfortunately, the poor quality of the specimen precluded an investigation by X-ray diffraction.

Small quantities of the actinides also are present. Thorium could be detected in four cases (about 0.3 wt% ThO_2); in one case only (Monte Bassetta), a similar amount of UO_2 also has been detected. From these data, no substantial difference between the specimens from fissures and pegmatites can be observed.

In nearly all our specimens, the Fe content shows substantial departure with respect to the ideal formula of gadolinite (see below, Table 5). In one case, at least (Glogstafelberg), the occupancy of the Fe position is decidedly less than 50%; therefore, the material should be more properly ascribed to hingganite-(Y), whose presence in the Alps has not been documented so far. It is interesting to note that this mineral is associated with monazite-(Nd), another very rare *REE* mineral. For this reason, the very peculiar occurrence of Alpine *REE* minerals, first mentioned by Graeser & Schwander (1987), appears to be even more unusual. The depletion of Fe is in agreement with the results of refinement of the site occupancy (see below, Table 5); this rules out the possibility for calcium to be present in the Fe site, as in minasgeraisite (Foord *et al.* 1986), since otherwise the inferred occupancy would be greater than the corresponding value determined by microprobe analysis.

Although X-ray data of good quality can be obtained from single crystals of many of our Alpine samples, even without heating, signs of incipient metamictization seem to be indicated by the width of the X-ray-diffraction peaks of some samples, even if these are perfectly transparent and show sharp crystal faces. This spread has been accounted for by selecting an appropriate scan-width in our collection of X-ray data (see the second line in Table 4).

Since the lowest totals for the compositions reported in Table 1 correspond to the highest degrees of peak broadening, these effects may, at least in part, both be

TABLE 4. DETAILS OF X-RAY DATA-COLLECTION AND REFINEMENT OF STRUCTURE OF ALPINE GADOLINITE

Sample	(2)	(3)	(6)	(7)	(8)	(9)	(10)
T parameter in the scan [‡]	1.0	1.0	1.0	1.1	1.1	1.1	1.5
Measured refl.n.s	3304	3102	3102	3079	3110	3140	3145
R _{int}	0.016	0.013	0.013	0.013	0.013	0.022	0.019
Independent refl.n.s with I>3σ(I)	1314	1179	1237	1185	1204	1049	1225
Final R §	0.018	0.019	0.019	0.016	0.017	0.016	0.021
Final R _w *	0.032	0.032	0.034	0.022	0.024	0.020	0.030
P value in the weighting scheme [¶]	0.050	0.040	0.040	0.030	0.040	0.025	0.040
GoF &	1.118	1.254	1.387	1.087	0.982	0.990	1.157

[‡]The scan width for each reflection (degrees) is equal to $T+0.35\tan\theta$.

[§] $R = \sum(|F_o| - k|F_c|) / \sum|F_o|$; * $R_w = [\sum(|F_o| - k|F_c|)^2 / \sum|F_o|^2]^{1/2}$.

[&] $GoF = [\sum(|F_o| - k|F_c|)^2 / (N_{\text{Observations}} - N_{\text{Variables}})]^{1/2}$.

[¶]Weighting scheme: $w = 1/(\sigma(F_o))^2$, $\sigma(F_o) = \{s^2(I) + (pI)^2\}^{1/2} / 2F_oLp$.

due to incipient metamictization. The reduction of analytical totals may be due to density variations: in fact, these phenomena already appear at the beginning of the metamictization process. In this respect, a classical example is provided by zircon (Holland & Gottfried 1955); another good example is shown by the minerals of the ekanite group (Diella & Mannucci 1986, and references therein); for gadolinite, the unit-cell volume decreases by about 3% after heating (Ueda 1957). Some samples (no. 7) showing incipient metamictization do not seem to contain appreciable amounts of U and Th. However, such an occurrence seems to be well known in this mineral (Ewing 1975).

CRYSTAL-STRUCTURE ANALYSIS

Wherever possible, transparent fragments of single crystals of gadolinite were mounted on a NONIUS CAD-4 diffractometer, using $MoK\alpha$ radiation (λ 0.71073 Å). Intensity data for the structure refinements were obtained from seven specimens; in addition to these, for three samples, only unit-cell data could be obtained, from a least-squares fit of 25 reflections with 2θ ranging from 30° to 38°; these are compared in Table 3 with those of related minerals. The minor variations are undoubtedly due to compositional differences.

For the boron-rich samples, the value of c tends to be small; this is consistent with the differences in unit-cell parameters between gadolinite and either datolite or homilite. The value of c seems to be particularly sensitive also with respect to the *REE* distribution. For instance, for the specimen from Japan (which is richer in lighter *REE* elements than our Alpine samples), the value of c is large; following this trend, it is still larger for gadolinite-(Ce) from Norway (Segalstad & Larsen 1978). In any case, the volume of the unit cell of

TABLE 5. COMPARISON BETWEEN INTERATOMIC DISTANCES (Å) IN ALPINE GADOLINITE

Sample	(2)	(3)	(6)	(7)	(8)	(9)	(10)
Y-O(1)	2.306(2)	2.299(2)	2.305(2)	2.322(2)	2.310(2)	2.316(2)	2.313(2)
Y-O(1)'	2.313(2)	2.299(2)	2.306(2)	2.324(2)	2.310(2)	2.317(2)	2.316(2)
Y-O(2)	2.372(2)	2.376(2)	2.371(2)	2.380(2)	2.369(2)	2.380(2)	2.372(2)
Y-O(3)	2.681(2)	2.677(2)	2.677(2)	2.691(2)	2.677(2)	2.695(2)	2.667(2)
Y-O(3)'	2.459(2)	2.474(2)	2.474(2)	2.467(2)	2.452(2)	2.457(2)	2.502(2)
Y-O(4)	2.364(2)	2.365(2)	2.369(2)	2.378(2)	2.364(2)	2.374(2)	2.368(2)
Y-O(5)	2.490(2)	2.514(2)	2.505(2)	2.497(2)	2.487(2)	2.501(2)	2.520(2)
Y-O(5)'	2.406(2)	2.423(2)	2.416(2)	2.398(2)	2.388(2)	2.394(2)	2.446(2)
Y-O(average)	2.424	2.428	2.428	2.432	2.420	2.429	2.438
Y occupancy	1.17	1.07	1.09	1.19	1.09	1.17	1.36
B.V. sum ^a	2.80	2.78	2.77	2.73	2.83	2.76	2.69
Si-O(1)	1.604(2)	1.607(2)	1.603(2)	1.612(2)	1.607(2)	1.613(2)	1.611(2)
Si-O(2)	1.636(2)	1.635(2)	1.638(2)	1.635(2)	1.634(2)	1.638(2)	1.628(2)
Si-O(3)	1.633(2)	1.636(2)	1.634(2)	1.631(2)	1.627(2)	1.632(2)	1.633(2)
Si-O(4)	1.642(2)	1.645(2)	1.640(2)	1.645(2)	1.641(2)	1.650(2)	1.634(2)
Si-O(average)	1.629	1.631	1.631	1.631	1.627	1.633	1.627
Be-O(2)	1.629(3)	1.606(4)	1.612(3)	1.640(3)	1.633(3)	1.638(3)	1.601(5)
Be-O(3)	1.641(3)	1.619(4)	1.625(3)	1.647(3)	1.647(3)	1.646(4)	1.631(5)
Be-O(4)	1.614(4)	1.597(4)	1.598(3)	1.628(3)	1.628(3)	1.630(4)	1.598(5)
Be-O(5)	1.604(3)	1.598(4)	1.595(2)	1.605(3)	1.589(3)	1.602(3)	1.622(5)
Be-O(average)	1.627	1.607	1.612	1.638	1.636	1.638	1.610
B occupancy	0.16	0.29	0.26	0.08	0.10	0.08	0.24
B.V. sum	2.06	2.15	2.14	2.02	2.05	2.03	2.11
Formal charge ^a	2.16	2.29	2.26	2.08	2.10	2.08	2.24
Fe-O(2)x2	2.281(2)	2.275(2)	2.279(2)	2.291(2)	2.273(2)	2.286(2)	2.298(2)
Fe-O(4)x2	2.223(2)	2.221(2)	2.225(2)	2.227(2)	2.220(2)	2.222(2)	2.248(2)
Fe-O(5)x2	2.035(2)	2.045(2)	2.044(2)	2.035(2)	2.028(2)	2.037(2)	2.052(2)
Fe-O(aver.)	2.180	2.180	2.183	2.184	2.174	2.182	2.199
Fe occupancy ^a	0.66	0.50	0.54	0.76	0.82	0.78	0.22
Fe occupancy ^b	0.70	0.54	0.59	0.86	0.80	0.92	0.30
B.V. sum	1.96	1.94	1.94	1.94	1.99	1.95	1.87
B.V. sum [O(5)]	1.48	1.38	1.39	1.51	1.58	1.58	1.21

The atoms are labeled according to Miyawaki *et al.* (1984); the numbering of the samples is the same as in Table 1. ^a From crystal-structure analysis; ^b from results of electron-microprobe analyses. ^c Bond-valence sum in v.u. (Brown 1981). ^d See text.

gadolinite decreases with increasing content of the heavier *REE* elements, as expected from the lanthanide contraction. As for hingganite, if the position of the Fe atom is not fully occupied, the unit-cell parameter *b* tends to be larger, in line with the increase of the Fe-O distances (see below, and Table 5).

For the crystals of best quality (irregular fragments whose diameters range from 0.1 to 0.2 mm, untreated by heating or other manipulations), reflections with a maximum value of the Bragg angle θ of 35° with MoK α radiation have been collected. Detailed data about such collections are reported in Table 4. For all crystals, empirical absorption corrections were derived according to the "psi-scan" technique of North *et al.* (1968), followed by the DIFABS routine (Walker & Stuart 1983), as described by Demartin *et al.* (1992). After correcting for absorption, the disagreement factors between the F_o values corresponding to symmetrically equivalent reflections in the same crystal are quite satisfactory (Table 4).

Scattering factors for neutral atoms, along with corrections for anomalous dispersion, have been taken from Cromer & Waber (1974) and Cromer (1974), respectively, including the real and the imaginary part. For the *REE*, we have assumed the scattering factor of Y. Because of this assumption, and the partial

replacement of Y by the heavier *REE*, the occupancy for yttrium is always greater than unity, even where appreciable quantities of calcium also are present (Table 5).

The refinement was carried out separately for each crystal by full-matrix least squares, minimizing the quantity $\sum w(F_o - F_c)^2$, and considering a total of 82 variables. These include symmetry-unconstrained positional and anisotropic thermal parameters for all the atoms, plus the scale factor, an overall extinction parameter and the occupancy for Y and Fe. The atomic coordinates of the starting model were those of Miyawaki *et al.* (1984). The weighting in the last cycles, the final values of the *R* index and the corresponding weighted index R_w are reported in Table 4. Fractional atomic coordinates, anisotropic thermal parameters and tables of structure factors are deposited at CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. All the calculations were performed on a PDP11/73 computer using the SDP-Plus Structure Determination Package (Frenz *et al.* 1980). In the final Fourier difference syntheses, no peaks exceeding 1.1 - 0.6 e/Å³ have been found. These peaks are always close to the *REE* position and do not imply presence of additional atoms.

Interatomic distances are reported in Table 5, together

with values of the e.s.d. The main features of the structure are in close agreement with the conclusions of the earlier works on the same subject, especially with those of Miyawaki *et al.* (1984), which is taken here as the main reference. The minor differences we have observed are significant but can easily be explained. For instance, the average (Y+REE)-O distance in our samples is 2.428 Å, a smaller value than the corresponding average (2.437 Å) found by Miyawaki *et al.* This is clearly related to the difference in the proportion of the REE, our samples being poorer in the lighter REE, whose ionic radius is comparatively large. This result of the lanthanide contraction is evident even within our set of samples, the smallest (Y+REE)-O distance (2.420 Å) and the largest one (2.438 Å) being observed for the samples from Bosco and from Glogstafelberg, respectively (Table 5). Among the specimens for which data are reported in this table, the former is the poorest in the lighter lanthanides, and the latter is the richest. In some cases, these average distances and especially the occupancy of Y also are affected by the presence of significant amounts of Ca; the smallest figures for the Y occupancy correspond in fact to the specimens that are relatively rich in Ca and Y and poor in the lanthanides.

In general, the Fe-O distances of our samples are very close to the values obtained by Miyawaki *et al.* (1984); the averages for our specimens can be compared with the average (2.182 Å) obtained by these authors. For the Glogstafelberg sample, these distances are slightly but significantly larger than for all the others. This difference is probably due to the absence of a large part of the iron atoms, whose presence would counteract the electrostatic repulsion between the neighboring atoms of oxygen.

The average Si-O distances for each one of our crystals (see Table 5) do not show remarkable differences from the general average of all our data (1.629 Å); the corresponding values in Miyawaki *et al.* (1984, 1985) for gadolinite and homilite (1.633 and 1.634 Å, respectively) are only slightly larger, and the difference may not be significant. With respect to the range of average length of the Si-O bond in well-documented orthosilicates (1.628–1.655 Å), as for instance in the olivine-monticellite group (Brown 1970) or the garnet group (Novak & Gibbs 1971), our values are situated at the shorter extreme, but there is substantial agreement, taking the possible overall influence of the crystal structure into account.

Our data thus confirm the virtual absence of replacement of Si by other elements, especially boron. Furthermore, since in the case of the presence of any substituent in two different structural sites a partition coefficient between these sites is implied, the highest amounts of boron substituting for Be should correspond to the highest concentrations in the Si site; if these concentrations are significant, a considerable shrinking of the Si-O bond-length should result. However, no correla-

tion between the Be-O and the Si-O average bond-lengths has been observed.

In the Japanese material studied by Miyawaki *et al.* (1984), the average length of the Be-O bond is 1.634(2) Å. This value is significantly larger than the corresponding results for all our Alpine specimens; similarly, there are significant differences even within our set of samples, in contrast with the uniform values for the Si-O bond lengths (see Table 5). The most plausible explanation for all this involves partial replacement of Be by other elements. Of these substituents, Si can be ruled out, since the Be-O and the Si-O bonds are very similar in length. Instead, boron is the most likely candidate, in view of the structural relationships between gadolinite and datolite. For the latter mineral, the average of B-O distances is 1.480(1) Å (Pant & Cruickshank 1967, Foit *et al.* 1973), a value much shorter than the average value (1.65 Å) reported by Ondik & Smith (1962) for the Be-O bond length; for homilite, the corresponding average distance is 1.504 Å (Miyawaki *et al.* 1985).

Since in datolite and in many members of the gadolinite series one atom [corresponding to O(5)] is totally or partially replaced by an OH group, the shrinking effect due to the substitution of Be by B could become less clear, because the bonds with OH would differ in length from the corresponding bonds with oxygen. For this reason, a better result can be achieved if the Be-O(5) bond is not considered, and the average of the remaining three Be-O bond lengths is used for comparison. This average amounts to 1.475 Å for datolite, to 1.530 Å for homilite, and to 1.648 Å for the Japanese gadolinite, respectively (Foit *et al.* 1973, Miyawaki *et al.* 1984, 1985), the last value being practically identical to the general average of Ondik & Smith (1962). In line with these results, the Be-O(5) distance for the Glogstafelberg sample [1.622(5) Å] is remarkably different from the corresponding distances for all the other samples, including Nos. 2, 3 and 6, which also are B-rich (1.595 to 1.604 Å, respectively). This confirms the possibility of the presence of a significant amount of OH replacing O, thereby supporting our assumption of a relatively high water content: a similar conclusion can be drawn on the basis of a bond-valence summation (see below).

By carrying out a linear interpolation with respect to these end members of known composition, the occupancy factor for B (in the Be position) reported in Table 5 has been calculated for all our specimens for which adequate crystal-structure data are available. This index corresponds to a B₂O₃ content of the order of 1–3 wt%, with a maximum of 4.2 wt% for the sample from Beura. These figures are not surprising; according to Oftedal (1964), the B₂O₃ content of 81 samples of gadolinite from 22 different localities ranges from 0.05 to 2.5 wt%, with an average of 0.2 wt%. In most cases, B₂O₃ ranges between 0.05 and 0.5 wt%; another study by Aleksandrova *et al.* (1966) showed appreciable amounts of B₂O₃ (up to nearly 5.0 wt%) in gadolinite samples from the

USSR. Therefore, our results for the Alpine specimens are in the range of values already reported in the literature for gadolinite.

On applying bond-valence sums (Brown 1980), there is a general, although only qualitative, agreement with the observed substitutions, as can be expected for partly disordered structures. For instance, for the Be site, this sum ranges from 2.02 to 2.15, and the highest values correspond to the highest contents of boron (see Table 5); however, if the bond-valence s is assumed to be a weighted average for Be and B ($s = 2$ and 3 , respectively), the values are slightly different (see the next line in Table 5). A similar situation occurs for Fe, where the lowest valence-sum (1.87) is obtained for the sample from Glogstafelberg, which is the poorest in Fe. For O(5), whose bond-valence sums are reported in the last line of Table 5, the lowest value (1.21) is also relative to the sample from Glogstafelberg, which, according to our chemical considerations, should be the richest in water (OH). However, the corresponding values for O(5) in the other samples never exceed 1.58, even for the OH-poor specimens. For the Y site, the bond-valence sums range from 2.69 to 2.83; here, the correlation with the chemical composition is less clear.

The partial replacement of Be or Si by other elements could also be reflected in the refined values of the occupancy factor; however, attempts in this respect have failed to give reliable results. Similarly, if the occupancy is not refined, the average (apparent) mean-square displacement should show appreciable variation with respect to the δ_{normal} value. However, the thermal parameters are difficult to compare and interpret, since they vary considerably from one sample to another, showing the combined effects of difference in number of electrons, of variation in bond lengths, and of residual absorption.

The bond angles around Si range from about 106° to 117° , and those around Be, from 101° to 116° , in agreement with the tendency of oxygen-bonded beryllium to form less regular tetrahedra than either silicon or boron.

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