THE CHEMICAL COMPOSITION OF XENOTIME FROM FISSURES AND PEGMATITES IN THE ALPS

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ABSTRACT

Eleven specimens of xenotime from the Alpine region (six from fissures, five from granitic pegmatites) have been analyzed by electron microprobe. Unit-cell parameters have been obtained from X-ray-diffraction data obtained on single crystals. The *REE* distribution is subject to important variation, some specimens being particularly rich in Gd, others in Dy or even in Yb. The Y_2O_3 content is nearly constant (average 46.5 wt.%), and there is little distinction between the pegmatite and the fissure samples. No substantial difference was found between the corresponding unit-cell parameters of all these crystals; the maximum variation does not exceed 0.02 Å. Substitution of the actinides and Ca for the *REE* and of Si for P is very limited. The uranium content (average 0.96 wt.% UO_2) is substantially higher than the thorium content (average 0.38 wt.% ThO_2).

Keywords: xenotime, rare earths, yttrium, uranium, pegmatite, fissure, Alps, electron-microprobe analysis.

SOMMAIRE

Nous avons analysé par microsonde électronique onze échantillons de xénotime des Alpes, dont six provenant de fentes alpines et cinq d'origine pegmatitique. Les paramètres réticulaires ont été calculés à partir des données de diffraction X obtenus sur cristal unique. La distribution des terres rares varie beaucoup, quelques cas étant particulièrement enrichis en Gd, et d'autres, en Dy, voire même en Yb. La teneur en Y_2O_3 est quasiment constante (46.5% par poids en moyenne), sans distinction selon le milieu de croissance. Aussi les paramètres réticulaires sont-ils relativement constants (±0.02 Å), indépendemment du milieu de croissance. La substitution de U + Th et du Ca pour les terres rares, et du Si pour le P, est très limitée. La teneur moyenne

en uranium, 0.96% UO_2, dépasse substantiellement la teneur moyenne en thorium, 0.38%.

(Traduit par la Rédaction)

Mots-clés: xénotime, terres rares, yttrium, uranium, pegmatite, fentes alpines, Alpes, analyse à la microsonde électronique.

INTRODUCTION

As for monazite, $CePO_4$, the presence of xenotime, YPO_4, in Alpine fissures has been known for more than a century (Kenngott 1864). Some specimens of this mineral, always considered as very rare by collectors, are indeed remarkable for the beauty of the crystals, and constitute "classic" examples in crystallography and mineralogy.

In spite of extensive studies of Alpine minerals, very few physical and chemical data are to be found for xenotime, even from the most renowned localities. In most cases, scientific documentation has rarely proceeded beyond the mere identification of the species. This is especially the case for the earliest discoveries of this mineral, when optical parameters, goniometric measurements, density and partial chemical analysis were the only quantitative data obtainable; precise analytical data about the distribution of the *REE* in each sample were practically impossible to obtain. Because of the scarcity of the material from Alpine localities, chemical analysis of these *REE* minerals by conventional procedures was then still more difficult than for most other occurrences. In fact, the crystals are generally very small, on the order of one millimeter or even less, although

in exceptional cases they may attain one centimeter or more in length.

In recent times, mainly owing to a systematic search by well organized and skilled amateurs, a considerable number of new occurrences of xenotime and other *REE* minerals have been found in the Alps (for a general description and references see, for instance, Gramaccioli 1977). Like monazite, xenotime is found in the Alpine region both in fissures and in granitic pegmatites; however, the latter occurrence is generally neglected, owing to the inconspicuous aspect of the samples, which only rarely are found in idiomorphic crystals.

Graeser *et al.* (1973) made a remarkable discovery of chernovite and As-bearing xenotime in the Cervandone (Tscherbadung) area, across the Swiss–Italian border between the Binn Valley and Devero. This discovery indicates the possibility of compositional variation in the anionic sites. The possibility of local variation in the *REE* distribution of xenotime is well known; see for instance, the work by Åmli (1975) for a Norwegian pegmatite. Other useful data of this kind are given by Vainshtein *et al.* (1956) or by Lyakhovich & Barinskii (1961) for material from the Soviet Union, or by Jefford (1962) for Nigerian occurrences. For all these reasons, a systematic examination of Alpine xenotime specimens was deemed long overdue. In view of the difficulty in obtaining suitable specimens of xenotime, our task

was greatly facilitated by access to private collections.

Some of these xenotime specimens come from "classic" localities; others are from new localities, some of which have not been mentioned before in the literature. For these reasons, some information about the precise locality and occurrence is provided here.

The St. Gotthard specimen was found around 1970 in Alpine fissures on Monte Prosa near the Gotthard Pass, in a well-known classic occurrence for this mineral; associated minerals are black anatase and brookite, a member of the synchysite group, monazite, and apatite. In the case of Arvogno, Val Vigezzo, a granitic pegmatite occurrence, see Albertini (1988); the so-called Gorduno specimen comes from a granitic pegmatite outcrop near Monti di Gorduno, Canton Ticino. This outcrop is mentioned (as No.4) by Simonetti (1973), as a locality for euxenite, but no mention is made of xenotime or of zircon, which can be found here in close association with this mineral. For Ca' Mondei, another granitic pegmatite occurrence near Montescheno, Ossola, well known to collectors for fine specimens of uraninite, beryl and zircon, see Mattioli (1975); the mineral is present in greenish crystals in close association with zircon and monazite. The Val Nalps occurrence is the "classic" one, at Piz Blas, where synchysite and gadolinite were found for the first time in Alpine fissures (Parker *et al.* 1939, Parker & de Quervain 1940). The occurrence of xenotime in Val Codera has never been reported in the literature; here xenotime can be found very sparingly in the well-known beryl- and garnet-bearing granitic pegmatites, associated with zircon and green uraniferous monazite; the occurrence in the granitic pegmatite at Lavonchio, Val Vigezzo, is the same as for tanteuxenite, and xenotime is practically intergrown with zircon (Cantadore & Gramaccioli 1969). Monistier & Turconi (1983) described the Triolet occurrence, in fissures, near Mont Blanc; as for the Scimfüss (fissure) occurrence, see Gramaccioli (1974).

Experimental Procedure

Electron-microprobe analyses were performed on polished grain mounts by using the ARL–SEMQ instrument of the Italian National Research Council (C.N.R.) at Centro di Studi per la Stratigrafia e la Petrografia delle Alpi Centrali, Milan. To determine the concentrations of the various elements, the set of standards and the operating conditions reported in Table 1 were used. The glasses were synthesized as described in our article on monazite (Mannucci *et al.* 1986). To account for interferences in the X-ray spectrum of the *REE* (Åmli & Griffin 1975), a series of measurements of standards of known composition was carried out for all the ele-

TABLE 1. CONDITIONS AND STANDARDS FOR ELECTRON-
          MICROPROBE ANALYSIS

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Accelerating voltage:  20 kV
Sample current on brass:  0.01 μm
Beam-spot diameter:  about 15 μm
Counting time: 10 s at peak position,
                2 s at both background positions
Analyzing crystals:
PET    YLα, PKα, ThMα, UMβ, CaKα
LIF    EuLα, GdLα, TbLα, DyLα, ErLα, TmLα, YbLα,
       HoLα, LuLα
RAP    SiKα
Analytical standards:
Si,P   apatite, USNM 104021¹
Ca     enstatite, USNM 746¹
Y      synthetic glass, 30.22 wt.% Y₂O₃
Eu     synthetic glass, 3.02 wt.% Eu₂O₃
Gd     synthetic glass, 5.02 wt.% Gd₂O₃
Tb     synthetic glass, 1.00 wt.% Tb₂O₃
Dy     synthetic glass, 5.02 wt.% Dy₂O₃
Ho     synthetic glass, 2.05 wt.% Ho₂O₃
Er     synthetic glass, 4.18 wt.% Er₂O₃
Tm     synthetic glass, 1.00 wt.% Tm₂O₃
Yb     synthetic glass, 5.02 wt.% Yb₂O₃
Lu     synthetic glass, 0.97 wt.% Lu₂O₃
Th     synthetic glass, 10.05 wt.% ThO₂
U      synthetic uranium oxide 99.80 wt.% UO₂
Method of correction:  Magic IV (Colby 1968)²

A COMPARISON BETWEEN OUR RESULTS AND EXPECTED
VALUES³

    Gd₂O₃ wt.%        0.4       0.3
    Dy₂O₃             1.1       1.1
    Er₂O₃             1.0       1.0
    Yb₂O₃             1.2       1.2
    Y₂O₃             12.2      12.4
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¹ Jarosewich et al. (1980)
² Synthetic glass, average of 6 analyses (first
column) and expected values of REE oxides
(second column).

ments considered. Besides the interferences already observed for the lighter lanthanides (Mannucci *et al.* 1986, Demartin *et al.* 1991), but here not important, owing to the negligible content of La and Ce, the values for Lu and Tm are subject to significant inter-ference from Dy. A linear correction formula $Q_{corr} = Q_{app} - KQ_{int}$ [where Q_{corr} and Q_{app} are the corrected and apparent content, respectively, Q_{int} is the content of the interfering element and $K = 0.089$], was applied to obtain a correct value for the

TABLE 2. CHEMICAL COMPOSITION OF XENOTIME FROM THE ALPS

	(1)			(2)			(3)		
Eu_2O_3	0.0	0.00		0.0	0.00		0.0	0.00	
Gd_2O_3	2.3 (2.1-2.4)	0.03		0.7 (0.6-0.9)	0.01		0.8 (0.6-1.1)	0.01	
Tb_2O_3	0.7 (0.5-0.9)	0.01		0.3 (0.2-0.3)	0.00		0.3 (0.2-0.5)	0.00	
Dy_2O_3	6.0 (5.6-6.3)	0.07		2.1 (1.8-2.3)	0.02		2.9 (2.8-3.0)	0.03	
Ho_2O_3	1.1 (0.7-1.5)	0.01		0.5 (0.2-0.8)	0.00		0.6 (0.3-1.2)	0.01	
Er_2O_3	4.4 (4.1-4.6)	0.05	1.04	1.9 (1.8-2.0)	0.02	0.99	3.8 (3.7-4.1)	0.04	1.01
Yb_2O_3	4.3 (3.9-4.8)	0.05		2.8 (2.6-2.9)	0.03		8.4 (8.2-8.5)	0.08	
Lu_2O_3	0.5 (0.7-0.4)	0.01		0.4 (0.5-0.3)	0.00		1.4 (1.7-1.1)	0.01	
Y_2O_3	45.2(43.6-45.8)	0.81		53.5(51.7-55.1)	0.90		48.3(47.6-49.0)	0.82	
ThO_2	0.3 (0.0-0.5)	0.00		0.1 (0.0-0.3)	0.00		0.3 (0.1-0.4)	0.00	
UO_2	1.2 (0.9-1.9)	0.01		0.2 (0.1-0.3)	0.00		0.7 (0.7-0.8)	0.01	
CaO	0.1 (0.1-0.2)	0.00		0.0	0.00		0.0	0.00	
P_2O_5	34.0(31.7-35.5)	0.98	0.98	37.4(37.1-38.2)	1.00	1.01	36.9(35.7-38.7)	0.99	0.99
SiO_2	0.0	0.00		0.0	0.00		0.0	0.00	
Total	100.1			100.0			104.4		

	(4)			(5)			(6)		
Eu_2O_3	0.1 (0.0-0.1)	0.00		0.0	0.00		0.1 (0.0-0.1)	0.00	
Gd_2O_3	2.2 (2.0-2.4)	0.03		2.2 (2.0-2.4)	0.03		2.4 (2.0-2.9)	0.03	
Tb_2O_3	0.6 (0.4-0.8)	0.01		0.6 (0.5-0.7)	0.01		0.9 (0.6-1.0)	0.01	
Dy_2O_3	5.5 (5.3-5.7)	0.06		4.4 (4.2-4.4)	0.05		7.2 (6.9-7.3)	0.08	
Ho_2O_3	1.2 (0.6-1.6)	0.01		0.6 (0.3-1.3)	0.01		1.2 (0.9-1.6)	0.01	
Er_2O_3	4.0 (3.9-4.2)	0.04	1.00	2.7 (2.5-3.0)	0.03	0.96	4.0 (3.8-4.2)	0.04	1.04
Yb_2O_3	4.7 (4.5-4.9)	0.05		3.3 (3.1-3.4)	0.03		2.2 (2.1-2.2)	0.02	
Lu_2O_3	0.6 (0.7-0.4)	0.01		0.4 (0.5-0.2)	0.00		0.2 (0.0-0.3)	0.00	
Y_2O_3	40.9(38.8-41.6)	0.75		46.9(46.0-48.5)	0.80		47.5(46.4-48.4)	0.84	
ThO_2	0.4 (0.3-0.4)	0.00		1.2 (0.8-1.7)	0.01		0.3 (0.2-0.4)	0.00	
UO_2	3.7 (3.5-4.0)	0.03		0.6 (0.2-1.3)	0.01		1.0 (0.7-1.3)	0.01	
CaO	0.4 (0.3-0.4)	0.01		0.1 (0.0-0.1)	0.00		0.0	0.00	
P_2O_5	34.4(34.1-34.9)	1.00	1.00	37.4(36.6-38.1)	1.02	1.02	34.9(33.6-36.6)	0.98	0.98
SiO_2	0.0	0.00		0.0	0.00		0.0	0.00	
Total	98.8			100.5			101.7		

	(7)			(8)			(9)		
Eu_2O_3	0.0	0.00		0.0	0.00		0.1 (0.0-0.2)	0.00	
Gd_2O_3	1.6 (0.9-2.9)	0.02		0.5 (0.5-0.6)	0.01		3.0 (1.4-4.7)	0.03	
Tb_2O_3	0.6 (0.4-1.0)	0.01		0.3 (0.1-0.3)	0.00		0.8 (0.5-1.2)	0.01	
Dy_2O_3	5.8 (4.6-7.0)	0.06		4.0 (3.5-4.4)	0.04		6.5 (5.3-7.6)	0.07	
Ho_2O_3	1.5 (1.0-2.0)	0.02		1.2 (0.3-1.7)	0.01		1.3 (0.6-2.0)	0.01	
Er_2O_3	4.0 (3.8-4.3)	0.04	1.01	5.1 (4.8-5.4)	0.05	1.04	4.1 (3.7-4.5)	0.04	1.03
Yb_2O_3	2.6 (2.2-3.1)	0.03		5.4 (4.9-6.1)	0.06		3.5 (2.2-5.5)	0.04	
Lu_2O_3	0.4 (0.3-0.5)	0.00		0.5 (0.3-0.8)	0.01		0.5 (0.1-0.9)	0.01	
Y_2O_3	46.3(43.9-48.5)	0.82		48.7(47.1-49.6)	0.86		45.3(44.5-47.2)	0.81	
ThO_2	0.6 (0.2-1.0)	0.00		0.3 (0.1-0.5)	0.00		0.8 (0.4-1.5)	0.01	
UO_2	1.8 (1.3-2.0)	0.01		0.8 (0.3-1.1)	0.01		0.2 (0.1-0.4)	0.00	
CaO	0.0	0.00		0.0	0.00		0.0	0.00	
P_2O_5	35.1(34.3-35.6)	0.99	0.99	34.8(33.7-35.4)	0.97	0.97	34.3(32.8-35.1)	0.98	0.98
SiO_2	0.0	0.00		0.0	0.00		0.0	0.00	
Total	100.4			101.6			100.6		

	(10)			(11)		
Eu_2O_3	0.1 (0.0-0.2)	0.00		0.1 (0.0-0.2)	0.00	
Gd_2O_3	1.4 (1.2-1.5)	0.02		3.5 (3.3-3.9)	0.04	
Tb_2O_3	0.6 (0.4-0.7)	0.01		0.9 (0.7-1.0)	0.01	
Dy_2O_3	5.4 (5.2-5.6)	0.06		6.9 (6.4-7.0)	0.08	
Ho_2O_3	1.1 (0.5-1.9)	0.01		1.2 (0.6-1.6)	0.01	
Er_2O_3	4.8 (4.6-4.9)	0.05	1.03	3.8 (3.2-4.3)	0.04	1.02
Yb_2O_3	4.9 (4.6-5.5)	0.05		3.0 (2.8-3.3)	0.03	
Lu_2O_3	0.6 (0.4-0.6)	0.01		0.3 (0.0-0.5)	0.00	
Y_2O_3	46.1(44.9-47.2)	0.83		42.9(40.9-43.6)	0.80	
ThO_2	0.0	0.00		0.1 (0.0-0.1)	0.00	
UO_2	0.1 (0.0-0.1)	0.00		0.2 (0.1-0.3)	0.00	
CaO	0.0	0.00		0.1 (0.0-0.1)	0.00	
P_2O_5	34.4(32.0-36.0)	0.98	0.98	32.6(31.7-34.2)	0.96	1.00
SiO_2	0.0	0.00		1.0 (1.0-1.3)	0.04	
Total	99.4			96.3		

(1) Ca' Mondei, Montescheno (average of 8 analyses), from granitic pegmatite (Mattioli 1975). (2) Arvogno, val Vigezzo (average of 7 analyses), from granitic pegmatite (Albertini 1988). (3) Monti di Gorduno, Canton Ticino (average of 7 analyses), from granitic pegmatite (Simonetti 1973). (4) Val Codera (average of 7 analyses), from granitic pegmatite (Simonetti 1973). (5) Lavonchio, Val Vigezzo (average of 7 analyses), from pegmatite (Cantadore & Gramaccioli 1969). (6) Piz Blas, Val Nalps (average of 7 analyses), from fissure (Parker et al. 1939, Parker & de Quervain 1940). (7) Northern P.ta d'Arbola, Val Formazza (average of 7 analyses), from fissure. (8) Monte Prosa, San Gottardo (average of 7 analyses), from fissure. (9) Monte Cervandone (average of 8 analyses), from fissure. (10) Scimfüss, Airolo (average of 9 analyses), from fissure (Gramaccioli 1974). (11) Triolet, Mont Blanc (average of 8 analyses), from fissure (Monistier & Turconi 1983). Contains 0.5% Nd_2O_3 and 1.2% Sm_2O_3.

For each sample, the columns provide information on composition (wt.%) and number of corres-ponding ions on the basis of 4 oxygen atoms. The range of variation for each value reflects statistical fluctuations in the counting and also inhomogeneity of the sample, since each analysis was carried out on a different point.

Lu_2O_3 content. No satisfactory result could be obtained for Tm_2O_3: for this reason, and also because thulium is very scarce in our samples, no concentrations of Tm are reported in this study.

Information on the accuracy of our procedure is shown in Table 1. We analyzed one synthetic glass of known composition: the results compare satisfactorily with the theoretical values. Another proof of the validity of our analyzed results is given by the internal consistency of our results for xenotime (Table 2). The total is always reasonably near to 100%, and the stoichiometric proportions are very close to the theoretical values. Further validation of our procedure comes in practice from the regular trend in *REE* abundance as a function of atomic number (see below). A systematic search was made for a considerable number of other elements, such as La, Ce, Pr, Na, Mg, As, V, Zr, Hf, Al, Sc, Fe and Mn; all of them are below the limit of detection of our instrument (generally, 0.1 wt.%), in all the samples examined. This means that the apparent content is less than three times the standard deviation. Nd and Sm could be detected only in the sample from Triolet (11 in Table 2). Unit-cell data for some of these samples have been obtained by X-ray diffraction of single-crystal fragments, using MoKα radiation ($\gamma = 0.71073$ Å) and a CAD–4 diffractometer. For each crystal, the results (Table 3) were obtained by least-squares refinement using 25 reflections. The standard deviations were derived from the residuals and the inverse of the matrix of the normal equations.

RESULTS AND DISCUSSION

The data refer to eleven samples from various localities. The average composition for fissure samples (6 specimens) and granitic pegmatite samples (5 specimens) is reported in Table 4, together with the general average and the corresponding data in the literature. Analytical results for the different samples are reported in Table 2, together with the minimum and maximum values observed in our series of different analyses on the same crystal.

The Y_2O_3 content is almost constant in the fissure specimens (42.9 to 48.7 wt.%), whereas it is subject to a more consistent variation in the pegmatite samples (40.9 to 53.5 wt.%); the averages for these two groups are, however, nearly exactly the same (46.2 and 46.9 wt.%, respectively). The atomic ratio $100Y/(REE + Y)$ is around 82%. This is higher than for many corresponding data reported in the literature, with the exception of the data of Åmli (1975), who found an average value of 87% for this ratio in samples from a Norwegian pegmatite; our values are also slightly overestimated, owing to the presence of small amounts of other rare-earth elements, such as Tm and the lighter lanthanides, which have not been detected. The total *REE* content ranges from 8.7 wt.% (Arvogno specimen, the highest in Y) to 21.2 wt.% (Triolet). The distribution of the *REE* in xenotime varies considerably: some samples are particularly rich in Gd, and others, in Dy or Yb. In contrast, the Er content seems more constant (17.9 to 25.3 wt.% Er_2O_3 with respect to the total *REE* oxides, with most values between 20 and 23%); the *REE* of odd atomic number are, as usual, less abundant than the corresponding ones with even atomic number, and their abundance regularly follows the observed trend: for instance, where Yb is high, Lu also is higher, and where Gd or Dy are high, Tb also is relatively high. The average distribution is close to the values in the literature, with the exception of Dy_2O_3, which is high in our samples.

It is difficult to associate a particular kind of *REE* distribution with fissure or pegmatite samples, although most of the samples richest in Gd and Dy are from fissures; on the other hand, not all the xenotime specimens from fissures are necessarily rich in either Gd or Dy. Similarly, the samples from granitic pegmatites are, on average, richer in Yb and Lu than the samples from fissures; however, the distinction is not sharp, since there are also fissure specimens that are rich in Yb (see, for instance, the one from St. Gotthard).

The value of 45.9 wt.% Yb_2O_3 (of the total of *REE* oxides) for the Gorduno specimen may seem

TABLE 3. UNIT-CELL DATA ON XENOTIME CRYSTALS FROM THE ALPS[*]

	a(Å)	c(Å)	V(Å³)
Triolet	6.900(1)	6.038(1)	287.45
M. di Gorduno	6.884(4)	6.021(4)	285.27
St. Gotthard	6.893(2)	6.030(2)	286.53
Lavonchio	6.902(1)	6.034(3)	287.30
Val Nalps	6.895(2)	6.032(1)	286.97

[*] The cell parameters were obtained from the same crystal fragments for which analytical data are reported in Table 2. Standard deviations follow the corresponding figures in parentheses, and refer to the last digit each case.

TABLE 4. AVERAGE OF OUR RESULTS AND COMPARISON WITH THE LITERATURE

		(1)	(2)	(3)	(4)	(5)	(6)	(7)
Eu_2O_3	wt.%	0.05	0.03	0.04	0.23	0.0	0.0	0.5
Gd_2O_3		2.06	1.68	1.89	10.88	3.4	14.9	11.6
Tb_2O_3		0.68	0.51	0.60	3.45	1.8	3.8	2.8
Dy_2O_3		5.97	4.17	5.15	29.64	18.9	29.0	21.8
Ho_2O_3		1.26	0.82	1.06	6.10	2.4	7.7	4.7
Er_2O_3		4.28	3.36	3.86	22.22	18.4	20.7	19.5
Yb_2O_3		3.62	4.68	4.10	23.60	44.2	17.8	22.3
Lu_2O_3		0.40	0.66	0.52	3.00	3.6	3.3	4.4
Y_2O_3		46.12	46.94	46.49				
$Y/(Y+ΣREE)$%		80.6	83.2	81.8		68.5		67.7
ThO_2		0.33	0.44	0.38				
UO_2		0.68	1.29	0.96				
CaO		0.02	0.13	0.07				
SiO_2		0.17	0.00	0.1				

(1) Average of our fissure specimens (46 analyses on 6 samples). (2) Average of our pegmatite specimens (36 analyses on 5 samples). (3) Average of all our results (82 analyses on 11 samples). (4) Data of column (3) recalculated to 100% of REE oxides. (5) Data of Jefford (1962) recalculated to 100% of REE oxides. (6) Data of Vainshtein et al. (1956) on xenotime from St. Gotthard recalculated to 100% of REE oxides by Jefford (1962). (7) Data of Fleischer (1989), average of 54 published analyses.

high; however, this value is close to Jefford's (1962) value for xenotime from Rayfield, Nigeria (44.2 wt.%). The Val Nalps value for Dy_2O_3 (39.9 wt.%) seems high with respect to most data reported in the literature, but such a degree of enrichment in Dy does not seem to be exceptional in the Alps (Table 2). Furthermore, a xenotime crystal from Gloserheia, Norway, has a corresponding value of 31.2 wt.% Dy_2O_3 (Åmli 1975). The range of Gd_2O_3 content (3.2 to 16.4 wt.% of the total of the *REE* oxides) is quite similar to the general range already reported in the literature [see, for instance, Table 2 in Jefford (1962), or Table 2 in Åmli (1975)]. On the whole, the average distribution of *REE* in our samples does not differ much from the *REE* distribution in a sample from St. Gotthard studied by Vainshtein *et al.* (1956) (columns 4 and 6 in Table 4). However, this agreement with the data corresponding to one specimen only might be fortuitous, especially in view of the variations we have observed; for instance, our sample from St. Gotthard shows a markedly different distribution, richer in Yb (Table 2).

Similarly to what we have already observed for monazite, the chemical behavior of Y with respect to the lanthanides does not depend on the ionic radius only, because Y does not behave exactly as a lanthanide to be inserted at a certain point in the series. For instance, the Arvogno sample shows the maximum content in Y_2O_3 (and the minimum in the lanthanides), but its *REE* distribution is similar to that of the St. Gotthard sample, in which an enrichment of the lanthanides with respect to yttrium is observed.

As for monazite, the contents in actinide elements (Th and U) and calcium seem to be systematically higher in pegmatite samples than in fissure specimens; however, concentrations of these elements invariably are low, and cannot be compared with the very extensive substitution that may occur in monazite. For silicon, the extent of substitution is also smaller than for monazite, but there are exceptions: for instance, here two specimens only show a non-negligible SiO_2 content, and the highest of all (1.0 wt.%) pertains to the remarkable sample from Triolet, which is a fissure specimen.

In other studies, for instance in that of Jefford (1962), considerable quantities of SiO_2 (about 3 wt.%) are reported, and similar quantities are reported for other occurrences (see, for instance, Palache *et al.* 1951). All these high contents should be considered suspect, because they derive from bulk analysis, and not from microprobe data; also, many of these results are quite old. Most of these old analyses show a rather high content of Al_2O_3 (about 2 wt.%), ZrO_2 (2–3 wt.%), and minor Fe_2O_3 (0.4–0.7 wt.%), MnO, *etc.* In our opinion, such high contents of extraneous elements are due to contamination from other minerals. For instance, zircon is well

known to accompany xenotime, and they may even be intergrown in an epitactic relationship, as in most of the pegmatite samples. At least in Alpine specimens, the extent of solid solution between zircon and xenotime is very limited; it may exist at high temperature, and this could explain the strict association with zircon.

Contrary to the findings of Graeser *et al.* (1973), who found significant amounts of As in one sample of xenotime from Cervandone, and extensive PO_4-AsO_4 substitution in chernovite of the same area, no As was found in our specimens, although one comes from the same region. However, this discrepancy is very likely due to mere chance, probably because our specimens did not come from the zones rich in chernovite or from the immediately adjacent areas.

The lower concentrations of the actinides in xenotime than in monazite can be easily explained by considering that the size of the Th^{4+} ion is much closer to that of Ce^{3+} than of Y^{3+}; another reason is that Ca and Si can enter the monazite structure quite easily, and therefore permit a charge balance to be reached in cases of extensive substitution of Th and U for the *REE*. The xenotime structure, however, does not allow the presence of high amounts of Ca^{2+} (on account of its large size).

On similar crystal-chemical grounds, the (general) absence of Si can be explained. There is in fact too little room for adjustment of the adjacent PO_4 groups if a larger SiO_4 group replaces a PO_4 group in the structure. The curious behavior of the Triolet specimen, which is the richest in Si, may be at least partly explained on account of its unusual richness in lighter *REE,* which render its unit-cell volume slightly larger than usual (Table 3).

In spite of the low level of substitution of the actinides for the *REE,* the uranium content is rarely negligible in xenotime, and it usually exceeds the thorium content considerably, contrary to what happens in monazite. This finding implies a marked difference between U and Th in crystal-chemical behavior, which is difficult to explain on the basis of the contraction in ionic radius occurring in the actinide series; the difference in the two atomic numbers would in fact be very small.

A much better explanation involves the possibility of at least partial oxidation of U^{4+} to higher states (very likely U^{5+}, on account of the particular steric requirements of U^{6+}, which are incompatible with the structure of this mineral). This oxidation would provide further contraction in the ionic radius, so that uranium might enter the xenotime structure without problem. This would not happen for thorium, which cannot attain higher oxidation states than $4+$.

Although our claim for the presence of U^{5+} may seem unfounded, because in aqueous solution it is

eminently unstable (giving place to uranyl UO_2^{2+} and U^{4+} ions), this unusual oxidation state could be stabilized by the crystal structure and by considerations involving the entropy of mixing with the *REE* ions. Considerable support to this hypothesis is found in the spectroscopic studies of Vance & Mackey (1974, 1978) on zircon, hafnon, and thorite; in these minerals, whose structure is the same as for xenotime, U^{5+} (possibly together with U^{4+}) can be present, especially if other ions such as Y^{3+} also are present.

Notwithstanding the small amount of U and Th in xenotime, a charge-balance mechanism should exist, and the contents of Ca and Si are always too low for this purpose. However, no element that can provide for this balance could be detected with the microprobe. A possible explanation of this situation is linked to the relatively poor sensitivity of our instrument for elements of low atomic number, such as Mg or Na, which might be present in quantities around 0.05 wt.% replacing yttrium. Such amounts would be sufficient for a balance of charges, but would escape detection; a still smaller content of boron (replacing phosphorus) would be sufficient to counterbalance the presence of actinides in the structure, but unfortunately small quantities of boron cannot be detected using the electron-microprobe approach.

The crystal data reported in Table 3 show the unit-cell parameters to be remarkably constant, the maximum variations being within 0.02 Å; such variations are even smaller than for monazite. Owing to the high accuracy of our data, some slight variations can be clearly correlated with composition. For instance, the Gorduno sample, which is particularly high in Yb, has the smallest unit-cell volume; similarly, the largest unit-cell parameters correspond to specimens high in Gd. The Lavonchio sample is comparatively rich also in Th. This is in good agreement with what is expected on grounds of ionic size, which for the *REE* is essentially determined by the lanthanide contraction.

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