

## ALPINE MONAZITE: FURTHER DATA

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### ABSTRACT

Monazite specimens from various localities in the Alps have been examined by electron microprobe and by single-crystal X-ray diffraction. With the exception of Sm, which is higher in general in pegmatite specimens, the average distribution of the REE is similar for fissure and pegmatite samples. The general average is similar to the value reported in the literature for the mineral; appreciable variations, however, occur in several cases. The samples from pegmatites usually contain higher amounts of actinides (U, Th) than the samples from fissures; in some cases, the REE distribution of very highly thorian and uranoan monazite is markedly different from the average, but no unique correlation between such distribution and the actinide content is found. There is evidence that the Y-REE fractionation does not depend exclusively on differences in ionic radii. Particularly interesting is the presence of sulfate ion (up to about 1% SO<sub>3</sub>) in specimens of the Devero-Formazza-Veglia area.

**Keywords:** monazite, rare earths, yttrium, thorium, uranium, pegmatite, fissure, Alps, electron-microprobe analysis.

### SOMMAIRE

Nous avons étudié des échantillons de monazite de diverses localités dans les Alpes, par microsonde électronique et par diffraction X sur cristal unique. A l'exception du Sm, qui est enrichi dans les échantillons pegmatitiques, en général, les teneurs en terres rares de la monazite pegmatitique et celle des fentes alpines sont semblables. La composition moyenne ressemble d'ailleurs à la composition citée dans la littérature, mais il existe des variations importantes dans plusieurs cas. La monazite des pegmatites contient généralement plus d'uranium et de thorium que celle des

fentes alpines. Dans certains cas, la distribution des terres rares dans un monazite riche en Th et en U s'écarte beaucoup de la moyenne, mais sans corrélation évidente avec la teneur en Th et U. Le fractionnement entre Y et les terres rares ne dépendrait pas uniquement des différences en rayon ionique. Nous signalons la présence de sulfate (jusqu'à environ 1%) dans les échantillons de la région de Devero-Formazza-Veglia.

(Traduit par la Rédaction)

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

### INTRODUCTION

Monazite from the Alps has been known for more than a century and a half. On account of its rarity and the beauty of some samples, it has been considered as one of the most prized of Alpine fissure minerals. Many new localities of monazite have been discovered, even quite recently; this paper deals in considerable part with this new material. An account of some discovery sites was given by Gramaccioli (1977), but the situation has changed considerably since then. Yet, there are only a few complete chemical analyses available for Alpine monazite.

Some years ago, our group (Mannucci *et al.* 1986) made a preliminary comparative study of eleven monazite specimens from various Alpine localities, eight from pegmatitic occurrences and three from Alpine fissures. Our study showed that the composition of monazite varies considerably, and we found no correlation between the REE distribution and the

TABLE 1. CONDITIONS AND STANDARDS FOR ELECTRON-MICROPROBE ANALYSIS

Accelerating voltage: 20 kV	
Sample current on brass: 0.01 $\mu$ A	
Beam spot diameter: about 15 $\mu$ m	
Counting time: 10 s at peak position	
2 s at both backgrounds	
Analyzing crystals:	
PET	PKa, ThMa, UMB, CaKa, LaLa, CeLa, PrLa, NdLa, YLa, SKa
LIF	SmLa, GdLa
RAP	SiKa
Analytical standards:	
Si,P	apatite, USNM 104021*
S	synthetic standard celestine
Ca	enstatite, USNM 746
Y	synthetic glass, 4.41 wt.% Y <sub>2</sub> O <sub>3</sub>
La	synthetic glass, 14.45 wt.% La <sub>2</sub> O <sub>3</sub>
Ce	synthetic glass, 19.70 wt.% Ce <sub>2</sub> O <sub>3</sub>
Pr	synthetic glass, 8.50 wt.% Pr <sub>2</sub> O <sub>3</sub>
Nd	synthetic glass, 15.07 wt.% Nd <sub>2</sub> O <sub>3</sub>
Sm	synthetic glass, 4.73 wt.% Sm <sub>2</sub> O <sub>3</sub>
Gd	synthetic glass, 5.02 wt.% Gd <sub>2</sub> O <sub>3</sub>
Th	synthetic glass, 10.05 wt.% ThO <sub>2</sub>
U	synthetic uranium oxide 99.80 wt.% UO <sub>2</sub>
Method of correction: Magic IV (Colby 1969) <sup>2</sup>	

\* Jaroszewicz *et al.* (1980).

TABLE 2. A COMPARISON BETWEEN OUR RESULTS AND EXPECTED VALUES

	(1)		(2)		(3)	
La <sub>2</sub> O <sub>3</sub> wt.%	2.7	2.8	1.6	1.7	3.4	3.7
Ce <sub>2</sub> O <sub>3</sub>	5.9	6.2	7.0	6.8	8.0	8.2
Nd <sub>2</sub> O <sub>3</sub>	3.1	2.9	1.7	1.7	3.7	3.7
Pr <sub>2</sub> O <sub>3</sub>	1.7	1.6	0.5	0.5	-	-
Sm <sub>2</sub> O <sub>3</sub>	0.5	0.5	0.2	0.2	-	-
Gd <sub>2</sub> O <sub>3</sub>	0.5	0.5	0.1	0.2	-	-
Y <sub>2</sub> O <sub>3</sub>	1.1	1.1	0.4	0.3	-	-

Results presented for three synthetic glasses; average of 4 analyses (first column) and expected values of REE oxides (second column).

TABLE 3. ANALYTICAL RESULTS FOR THE DIFFERENT SAMPLES<sup>a</sup>

	(1)	(2)	(3)	(4)
La <sub>2</sub> O <sub>3</sub>	9.7 (9.2-10.1)	9.8 (9.0-10.2)	7.4 (6.9-7.6)	12.0 (11.4-12.6)
Ce <sub>2</sub> O <sub>3</sub>	23.3 (22.0-24.1)	23.1 (21.4-24.4)	22.2 (21.6-22.6)	26.0 (25.2-28.4)
Pr <sub>2</sub> O <sub>3</sub>	3.4 (2.7-4.3)	3.3 (2.8-3.9)	3.0 (2.9-3.3)	3.8 (3.1-5.5)
Nd <sub>2</sub> O <sub>3</sub>	10.6 (9.4-11.7)	10.9 (10.2-12.4)	11.2 (10.8-11.6)	11.0 (8.8-13.1)
Sm <sub>2</sub> O <sub>3</sub>	3.0 (2.5-3.4)	3.4 (3.1-3.7)	5.2 (5.9-5.5)	2.9 (2.4-3.5)
Gd <sub>2</sub> O <sub>3</sub>	2.3 (2.2-2.7)	2.5 (0.6-2.8)	2.6 (2.5-2.8)	2.8 (2.5-3.3)
Y <sub>2</sub> O <sub>3</sub>	3.6 (3.3-3.9)	3.0 (2.5-4.7)	0.3 (0.1-0.4)	2.7 (1.9-3.6)
ThO <sub>2</sub>	11.1 (10.2-12.2)	14.6 (14.2-16.0)	11.0 (10.6-11.6)	4.8 (3.8-5.4)
UO <sub>2</sub>	0.7 (0.6-0.9)	0.4 (0.2-0.6)	4.5 (4.1-4.9)	2.6 (0.7-3.4)
CaO	1.3 (1.1-2.1)	0.7 (0.6-0.7)	3.2 (3.0-3.4)	1.6 (1.3-1.9)
SO <sub>2</sub>	0.0	0.0	0.0	0.0
P <sub>2</sub> O <sub>5</sub>	28.5 (27.6-29.3)	27.0 (25.7-28.2)	29.4 (27.7-30.8)	31.5 (30.3-33.4)
SiO <sub>2</sub>	1.6 (0.7-1.8)	2.6 (2.1-3.3)	0.0	0.3 (0.0-0.7)
Total	99.1	101.3	100.0	102.0
EC/EA <sup>b</sup>	0.98/1.01	0.99/1.00	1.02/0.99	0.98/1.01
	(5)	(6)	(7)	(8)
La <sub>2</sub> O <sub>3</sub>	12.3 (11.8-12.7)	13.7 (13.0-14.1)	13.5 (12.7-14.7)	15.4 (14.8-15.9)
Ce <sub>2</sub> O <sub>3</sub>	28.1 (27.3-28.7)	21.7 (21.2-22.5)	28.4 (27.1-29.3)	31.0 (29.0-32.5)
Pr <sub>2</sub> O <sub>3</sub>	3.4 (2.7-3.7)	1.4 (0.9-1.2)	3.8 (3.6-4.7)	3.7 (3.1-4.6)
Nd <sub>2</sub> O <sub>3</sub>	10.9 (9.9-11.8)	3.6 (3.3-3.9)	12.9 (12.1-13.8)	11.2 (10.3-13.8)
Sm <sub>2</sub> O <sub>3</sub>	2.3 (2.0-2.6)	1.1 (1.0-1.3)	2.2 (1.9-2.5)	2.1 (1.8-2.8)
Gd <sub>2</sub> O <sub>3</sub>	1.7 (1.4-2.1)	1.1 (1.0-1.7)	1.8 (1.7-2.0)	2.0 (1.6-2.3)
Y <sub>2</sub> O <sub>3</sub>	0.3 (0.2-0.4)	0.6 (0.5-0.8)	0.7 (0.4-1.3)	0.9 (0.7-0.9)
ThO <sub>2</sub>	8.3 (7.9-8.8)	22.5 (21.7-23.6)	5.0 (3.8-6.0)	1.0 (0.6-1.8)
UO <sub>2</sub>	0.5 (0.4-0.6)	1.2 (0.9-1.3)	0.1 (0.0-0.2)	0.1 (0.0-0.2)
CaO	1.7 (1.6-1.9)	3.9 (3.8-4.2)	0.4 (0.3-0.5)	0.2 (0.1-0.3)
SO <sub>2</sub>	0.0	0.0	0.0	0.0
P <sub>2</sub> O <sub>5</sub>	30.6 (28.9-31.9)	28.4 (27.5-29.0)	30.1 (29.5-30.6)	31.0 (30.3-32.9)
SiO <sub>2</sub>	0.3 (0.0-0.4)	0.6 (0.3-0.9)	0.6 (0.0-1.2)	0.1 (0.0-0.2)
Total	100.4	100.1	99.5	98.7
EC/EA	0.98/1.01	1.02/0.98	0.96/1.03	1.00/0.93

contents of Th, U, Ca and Si. The reason for this lack of correlation is the ideal behavior of monazite as a solid solution. On the whole, pegmatite monazite is richer in Th (as well as Si and other non-REE metals) than fissure monazite, but there is no definite compositional distinction between the two fields. One group of pegmatitic monazite was found to be relatively high in U and Th: a specimen from Piona contains 10.5 wt.% ThO<sub>2</sub> and 12.0 wt.% UO<sub>2</sub>, and another from Rio Graia, Val Vigezzo, contains 19.5 wt.% ThO<sub>2</sub> and 1.6 wt.% UO<sub>2</sub>.

A previous study (Gramaccioli & Segalstad 1978) of another specimen of monazite from Piona showed the presence of 11.3 wt.% ThO<sub>2</sub> and 15.6 wt.% UO<sub>2</sub>; another study by Gulson & Krogh (1973) gave 9.5 wt.% UO<sub>2</sub> in the Bergell monazite, confirming the very unusual composition of some Alpine samples.

Recently, Graeser & Schwander (1987) showed the presence of other possible end-members in the monazite group, *i.e.*, gasparite (the As-equivalent of monazite) and monazite-(Nd), both found in Alpine fissures of the Devero (Cherbadung)-Formazza area.

#### EXPERIMENTAL PROCEDURE

We followed virtually the same experimental procedure as in our earlier study. Electron-microprobe analyses were performed on polished grain-mounts, using the ARL-SEM-Q instrument of

	(9)	(10)	(11)	(12)
La <sub>2</sub> O <sub>3</sub>	16.1(15.4-16.9)	15.2(15.1-15.7)	15.5(14.3-16.7)	13.6(13.6-13.9)
Ce <sub>2</sub> O <sub>3</sub>	31.3(30.2-33.8)	29.8(28.5-30.6)	30.8(30.1-31.7)	29.9(29.4-30.6)
Pr <sub>2</sub> O <sub>3</sub>	3.1(2.1-3.8)	3.9(3.4-4.4)	3.5(3.2-4.0)	3.7(2.9-4.4)
Nd <sub>2</sub> O <sub>3</sub>	10.6(10.2-10.9)	11.8(10.9-13.2)	13.0(12.1-13.6)	12.9(11.4-13.8)
Sm <sub>2</sub> O <sub>3</sub>	2.0(1.9-2.1)	1.7(1.4-2.4)	1.7(1.2-2.0)	2.7(2.3-3.0)
Gd <sub>2</sub> O <sub>3</sub>	1.8(1.7-1.9)	1.9(1.6-2.5)	1.8(1.7-2.1)	2.0(1.8-2.2)
Y <sub>2</sub> O <sub>3</sub>	1.9(1.3-2.8)	0.6(0.4-0.9)	0.7(0.6-0.9)	0.7(0.5-0.9)
ThO <sub>2</sub>	0.9(0.1-1.8)	0.7(0.4-1.7)	1.4(0.9-1.9)	1.2(1.1-1.5)
UO <sub>2</sub>	0.1(0.0-0.3)	0.0	0.1(0.0-0.2)	0.0(0.0-0.1)
CaO	0.6(0.3-1.9)	1.6(1.2-1.8)	0.8(0.6-0.9)	0.2(0.1-0.2)
SO <sub>3</sub>	0.0	1.1(0.9-1.4)	0.0	0.0
P <sub>2</sub> O <sub>5</sub>	30.5(29.6-31.3)	31.0(30.5-31.9)	30.4(29.5-31.0)	31.6(30.2-32.2)
SiO <sub>2</sub>	0.0(0.0-0.2)	0.1(0.0-0.2)	0.2(0.1-0.3)	0.2(0.0-0.4)
Total	98.9	99.4	99.9	98.7
EC/EA	0.94/1.01	0.96/1.03	1.00/1.01	0.94/1.04
	(13)	(14)	(15)	(16)
La <sub>2</sub> O <sub>3</sub>	15.0(14.3-15.9)	12.5(11.7-13.2)	3.7(2.8-4.2)	12.7(12.4-12.9)
Ce <sub>2</sub> O <sub>3</sub>	30.9(29.2-33.3)	29.7(28.2-30.7)	16.9(15.6-19.5)	26.3(25.5-27.3)
Pr <sub>2</sub> O <sub>3</sub>	3.7(3.1-6.4)	3.9(2.8-4.3)	4.4(4.2-5.2)	3.5(2.8-3.9)
Nd <sub>2</sub> O <sub>3</sub>	12.0(10.9-13.1)	13.8(12.8-14.8)	29.7(29.1-30.5)	11.3(10.1-12.3)
Sm <sub>2</sub> O <sub>3</sub>	2.1(1.6-2.6)	3.4(2.8-4.0)	9.4(8.9-9.7)	1.7(1.4-2.0)
Gd <sub>2</sub> O <sub>3</sub>	2.0(1.7-2.5)	2.8(2.4-3.0)	4.1(4.0-4.3)	1.7(1.5-2.2)
Y <sub>2</sub> O <sub>3</sub>	0.6(0.2-1.0)	0.7(0.6-0.9)	0.7(0.5-0.8)	2.3(2.0-2.8)
ThO <sub>2</sub>	1.0(0.5-1.7)	1.1(0.3-2.3)	0.1(0.0-0.1)	7.9(7.3-8.5)
UO <sub>2</sub>	0.0(0.0-0.2)	0.1(0.0-0.2)	0.0	0.4(0.2-0.5)
CaO	1.1(1.0-1.2)	0.1(0.1-0.2)	0.1(0.0-0.1)	1.0(0.8-1.1)
SO <sub>3</sub>	0.9(0.8-0.9)	0.0	0.1(0.0-0.1)	0.0
P <sub>2</sub> O <sub>5</sub>	30.1(28.5-30.9)	30.6(29.5-32.1)	29.5(27.9-30.4)	29.7(28.1-31.8)
SiO <sub>2</sub>	0.2(0.0-0.9)	0.2(0.0-0.6)	1.8(0.5-2.4)	1.0(0.8-1.2)
Total	99.6	98.9	100.5	99.5
EC/EA	0.97/1.02	0.96/1.02	0.99/1.04	0.97/1.02

(1) Val Masino (average of 16 analyses), from pegmatite. (2) Arvogno, Val Vigezzo (average of 13 analyses), from pegmatite: Albertini (1988). (3) Val Codera (average of 8 analyses), from pegmatite: dark green crystal. (4) Val Dombastone, Valtellina (average of 15 analyses), from pegmatite: greenish crystal. (5) Cuzzago, Ossola (average of 11 analyses), from pegmatite: Mattioli (1983). (6) Lavonchio, Val Vigezzo (average of 8 analyses), from pegmatite: yellow-greenish crystal, Cantadore & Gramaccioli (1969). (7) Kamprisen, Obersulzbachtal (average of 8 analyses), from fissure. (8) Beura, Ossola (average of 10 analyses), from fissure: De Battisti & Scotti (1987). (9) Triolet, Mont Blanc (average of 7 analyses), from fissure. (10) Alpe Veglia (average of 6 analyses), from fissure. (11) Lohningbruch, Rauris (average of 7 analyses), from fissure: Kontrus & Niedermayr (1969) or Schebesta (1984). (12) Miage, Mont Blanc (average of 8 analyses), from fissure: Monistier & Turconi (1983). (13) Devero, Cervandone (average of 7 analyses), from fissure. (14) Hopffeldboden, Obersulzbachtal (average of 9 analyses), from fissure: Schebesta (1982) or Preite (1986). (15) Glogstafelberg, Val Formazza (average of 7 analyses), from fissure, monazite-(Nd) described in Graessler & Schwander (1987). (16) Torrente Elvo (average of 8 analyses), alluvial sample.

a) For each sample, the columns refer to weight per cent average (weight % range in parentheses). The reported range includes variation due to inhomogeneity of the samples, since every analysis was performed in a different point of the crystal. b) EC is the sum of the REE, Y, actinides and Ca atoms, EA is the sum of S, P and Si atoms on the basis of four oxygen atoms.

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Standards and the operating conditions are reported in Table 1. As recommended in Roeder (1985), a wavelength-dispersion spectral scan of average-composition samples or for each sample of unusual composition was conducted. To account for interferences in the X-ray spectrum of the REE (Åmli & Griffin 1975, Roeder 1985), a series of measurements of standards of known composition was carried out for all the elements considered. As in our

former work, such interferences were found to be noticeable for La (overlap of the  $L\alpha$  line with  $PrL\alpha$ ) and for Ce (overlap of the respective  $L\alpha$  line with Nd and Gd). The accuracy of our procedure is shown in Table 2. Here, three synthetic glasses of known composition were analyzed by us, and the results can be satisfactorily compared with the theoretical values. Another substantial proof of the validity of our procedure is given by the internal consistency of our results for monazite (Table 3): the total is always reasonably close to 100%, and the stoichiometric proportions are close to the theoretical values. There

is also substantial agreement with results published by other authors on material from the same occurrence (see, for instance, Graeser & Schwander 1987). A systematic search was made for a considerable number of other elements, such as Dy, Er, Yb, Eu, Tb, Ba, Sr, Na, Zr, As, V; in these operating conditions, their concentrations are lower than three times the standard deviation. This generally means that they are below 0.1% in all the samples examined.

Unit-cell data for some of these samples were obtained from X-ray diffraction of single-crystal fragments, using MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a CAD-4 diffractometer. For each crystal, the results (Table 4) were obtained from a least-squares fit of 25 reflections. The standard deviations were derived from full-matrix least-squares calculations.

## RESULTS

The chemical data (Table 3) pertain to 16 samples: of these, nine are from Alpine fissures, one consists of small grains of alluvial origin, and six are from granitic pegmatites. Three of these samples come from the same localities considered in our previous work (Val Masino, Val Dombastone, Miage); however, the analytical results given here correspond

to different crystals. Details about the origin of each specimen are given as a footnote in Table 3, with reference to the most recent literature dealing with their discovery.

On the whole, the average *REE* distribution in monazite from fissures and pegmatites is substantially the same (Tables 3, 5); however, the monazite from pegmatites has a significantly higher content of the actinides (U, Th) and Ca. No definite boundary between these groups can be traced on grounds of the Th content alone, but if the sum of ThO<sub>2</sub> and UO<sub>2</sub> contents is considered, then a 5.5 wt. % limit appears to be a possible discriminant between the two groups, at least on the basis of the data obtained so far. The actinide content of the alluvial sample (8.3 wt. %) is significantly higher than the maximum content for fissure material.

Within each group, there is significant compositional variation: for instance, monazite-(Nd), from a fissure, is quite different from all the other samples, and among the samples from pegmatite, a further division between "normal" and highly uranoan-thorian members could be made (Mannucci *et al.* 1986); however, in this new data-set, this distinction is not so sharp.

A maximum content in the sum of ThO<sub>2</sub> and UO<sub>2</sub> (23.7 wt. %) can be observed for the specimen from Lavonchio: this monazite may be considered to be the thorian equivalent of the monazite from Piona, and its composition approaches that of cheralite. But if the distinction between the two species is based on 50 mole % of the *REE* phosphates, we are not dealing with a true cheralite, because *REE* prevail over actinides and Ca. The silicon content is low, and charge balance has been achieved (as in most cases) by substituting Ca and actinides for the *REE* instead of Si for P. As for the monazite from Piona, the *REE* distribution in the Lavonchio monazite differs considerably from the average, and it corresponds to a marked enrichment of La (and Ce) with respect to Nd. The pegmatites from Piona and Lavonchio are among the most renowned Alpine occurrences for a number of unusual minerals and have been known as such for many years (see, for instance, Boscardin *et al.* 1970, Gramaccioli 1977, and references therein).

From Table 5, the average distribution of the *REE* in the monazite samples appears to be substantially the same for pegmatite and fissure material; the agreement between the two groups is very close for La, Ce and Pr, whereas some discrepancies occur, especially for Nd, and also for Sm and Gd. However, if a very unusual sample such as monazite-(Nd) (Glogstafelberg, Val Formazza) is omitted from our "fissure" average, the average content of Nd<sub>2</sub>O<sub>3</sub> of the two groups becomes closer, and it becomes still closer if the Lavonchio monazite also is omitted from our "pegmatite" average (19.2 *versus* 18.7 wt. %).

TABLE 4. UNIT-CELL DATA ON SOME MONAZITE-GROUP SAMPLES

	a (Å)	b (Å)	c (Å)	$\beta$ (°)	V (Å <sup>3</sup> )
Hopffeldboden	6.790(3)	7.002(2)	6.469(2)	103.65(3)	298.96
Cervandone	6.769(4)	7.013(3)	6.453(2)	103.11(4)	298.34
Val Codera	6.776(3)	6.985(1)	6.452(8)	103.86(6)	296.98
Lavonchio 1	6.788(4)	7.008(3)	6.477(2)	103.70(4)	299.35
Lavonchio 2	6.795(4)	7.011(3)	6.480(2)	103.69(4)	299.72

TABLE 5. AVERAGE OF OUR RESULTS AND COMPARISON WITH CORRESPONDING DATA ( $\sum REE_2O_3 + Y_2O_3 = 100$ )

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
La <sub>2</sub> O <sub>3</sub>	20.2	20.2	19.8	22.2	18.0	22.2	20.3	23.9
Ce <sub>2</sub> O <sub>3</sub>	43.7	43.4	44.1	45.9	43.2	45.9	43.8	45.8
Pr <sub>2</sub> O <sub>3</sub>	5.7	5.7	5.6	5.6	5.9	5.5	5.6	4.9
Nd <sub>2</sub> O <sub>3</sub>	20.1	21.5	17.8	18.7	19.2	19.0	19.1	13.5
Sm <sub>2</sub> O <sub>3</sub>	4.8	4.6	5.5	3.4	5.9	3.0	5.2	6.3
Gd <sub>2</sub> O <sub>3</sub>	3.5	3.4	4.0	3.0	4.4	1.4	2.7	2.5
Y <sub>2</sub> O <sub>3</sub>	2.0	1.2	3.2	1.3	3.5	2.2	2.6	3.0
ThO <sub>2</sub>	5.8	1.4	12.1	1.5	10.0	-	-	7.7
UO <sub>2</sub>	0.7	0.1	1.7	0.1	1.8	-	-	3.0
CaO	1.1	0.6	2.1	0.6	1.7	-	-	1.4
SiO <sub>2</sub>	0.6	0.4	0.9	0.2	0.9	-	-	0.6
Y <sub>2</sub> O <sub>3</sub> /Gd <sub>2</sub> O <sub>3</sub>	0.6	0.4	0.8	0.4	0.8	1.6	1.0	1.2

(1) Average of all results in this work (148 analyses on 16 samples). (2) Average of fissure samples in this work (69 analyses on 9 samples). (3) Average of pegmatite samples in this work (71 analyses on 6 samples). (4) Average of fissure samples in this work excluding monazite-(Nd) (62 analyses on 8 samples). (5) Average of pegmatite samples in this work excluding Lavonchio monazite (63 analyses on 5 samples). (6) Average of data reported by Fleischer & Rosenblum (1990) on a total of 583 samples. (7) Average of 117 samples from granitic pegmatites, taken from the compilation of Fleischer & Rosenblum (1990). (8) General average in Mannucci *et al.* (1986). \* The first seven entries (La<sub>2</sub>O<sub>3</sub> to Y<sub>2</sub>O<sub>3</sub>) are referred to a total of 100 wt. % for these oxides only; the others are referred to the general total.

Considering the average excluding monazite-(Nd), Sm and Gd appear to be somewhat more abundant in monazite from pegmatite; this difference is probably linked to the different average concentration of Y, which is also more abundant in these samples. A possible explanation is that associated xenotime tends to absorb the "middle" and heavy REE preferentially. This species is relatively widespread in Alpine fissures, whereas it seems to be quite rare in pegmatites. On the other hand, in many Alpine pegmatites, rare-earth niobotantalates rich in Y are found, but a close association of monazite with these oxides has never been noticed. As for the other Alpine samples studied by Mannucci *et al.* (1986), here again no unique correlation between the content in  $\text{La}_2\text{O}_3$  and the actinide content (as sum of  $\text{UO}_2 + \text{ThO}_2$ ) is found (Fig. 1). This confirms our earlier conclusions that the concentration of the REE in a crystal is not influenced by its actinide content, because solid solutions of end members like  $\text{CaTh}(\text{PO}_4)_2$  and the REE phosphates approach ideality. In line with this behavior, the unit-cell parameters (and volume) show little variation, even if some extreme cases are taken into account (see Table 4, and Table 4 in Mannucci *et al.* 1986).

In the sixth and seventh columns of Table 5, general averages for all kinds of occurrences and for granitic pegmatites are reported for a world-wide sampling, as given by Fleischer & Rosenblum (1990); the adjacent eighth column shows the general average on Alpine monazite quoted by Mannucci *et al.* (1986). On the whole, there is a good agreement among all these data, with the exception of the Nd content, which is systematically too low in Mannucci *et al.* (1986), both with respect to our new analyses and to the world-wide general average. This seems to indicate a systematic error on the low side in our group's earlier data on Nd. Although the samples examined are not the same (though they came from the same fissure), our data and those of Graeser & Schwander (1987) do not differ substantially for monazite-(Nd), especially in the  $\text{Nd}_2\text{O}_3$  content (30.3 wt.% against 29.7 wt.%); this is additional evidence in favor of our new procedure. Whereas a re-examination of all our former samples and standards was not possible, owing to their loss, discrepancies in results can be explained by variation of the correction coefficients depending on the particular session of analysis. In particular, a correction coefficient for the interference of Ce with Nd was found to be 0.12 and was assumed to be constant, whereas in many instances we now know it can drop to zero, depending on the adjustment of the slit width in the spectrometer. By considering an average  $\text{Ce}_2\text{O}_3$  content of 26 wt.%, and assuming that in most cases the correction coefficient should have been zero instead of 0.12, in our older analyses the  $\text{Nd}_2\text{O}_3$  contents (with respect to the total REE oxides) should

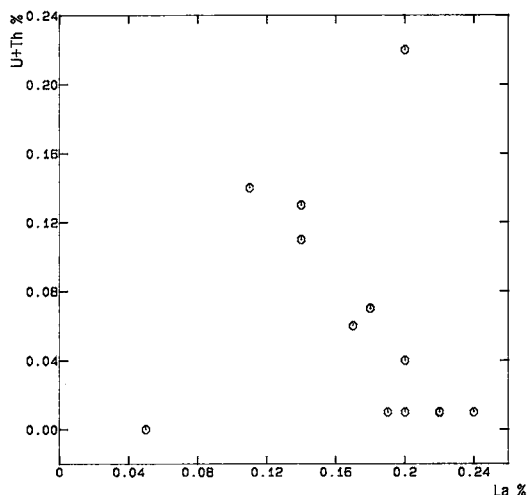


FIG. 1. Relation between La and U + Th (atomic % over the cation sum) in samples of monazite.

be raised by about 4.8 wt.%, the right amount to account for these discrepancies. Following these considerations, the general composition of the Alpine monazite sample studied by us (column 1 in Table 5) does not show substantial differences from the average of the world-wide sampling (column 6).

As in our former work, we can observe that the ratio  $\text{Y}_2\text{O}_3/\text{Gd}_2\text{O}_3$  is not constant, and this indicates a mechanism of fractionation of the REE and Y that is not purely ionic. On average, this ratio is lower for fissure monazite and higher for pegmatite samples (Table 5); however, within each one of these groups there is considerable variation.

As pointed out by its discoverers (Graeser & Schwander 1987), monazite-(Nd) from Glogstafelberg is particularly interesting, and not only for its unusual Nd content. Of the range in composition of the fissure monazite samples here studied, monazite-(Nd) corresponds to the extremes in contents of Sm, Gd, La, Ce, Pr, Nd, Ca, Th and Si. Sm and Gd attain very high levels, whereas the contents in Th and Ca are particularly low. The reason for this unusual composition is not obvious. In many cases, in fact, REE minerals rich in Nd or La are formed in a strongly oxidizing environment, with pH high enough to ensure hydrolysis of  $\text{Ce}^{4+}$ , so that the greatest part of cerium is carried away (as  $\text{CeO}_2$ ) from solution, together with other oxides (e.g., Fe, Al, Mn, Ti, etc.); from the solution rich in lighter REE ions, but poor in cerium, a mineral with Nd or La predominant may subsequently crystallize. This process is, for instance, very likely to have been the origin of the lanthanite-(Nd) from Brazil (Cesbron *et al.* 1979). In such case, where tropical conditions favor oxidation and hydrolysis, the oxygen

potential is so high that Eu is not reduced to the 2+ state and remains together with the other lanthanides. In monazite-(Nd) from Glogstafel, which was not formed in tropical conditions, a considerable depletion in La and the enrichment of lanthanides such as Sm, which is close to Nd, seem to point out to a highly specific process of fractionation. A possibility is that such monazite is formed from alteration of gadolinite.

According to our analysis, the monazite-(Nd) from Glogstafelberg contains a small amount of SO<sub>3</sub> (0.13 wt. %). The sulfate ion also is present, in more consistent amounts (around 1%), in a specimen of monazite-(Ce) from Cervandone-Tscherbadung and in another sample from Alpe Veglia; in all the other samples we have analyzed so far, no trace of sulfate has been found.

Since Alpe Veglia and Glogstafelberg are not far from Pizzo Cervandone (8 and 13 km, respectively) the presence of sulfate ions in monazite samples of this limited area might be connected with Graeser's observation (1975) about the origin of the Binn Valley sulfosalts and of the As-bearing Alpine fissure minerals at Cervandone. According to this author, As-rich solutions have transformed Pb and Ag sulfides (essentially galena) into sulfosalts and have deposited As sulfides (such as realgar and orpiment) in the famous Lengenbach quarry: a part of these solutions migrated into the adjacent gneiss and underwent oxidation, thereby forming arsenites (cafarsite, etc.) and also arsenates like chernovite. Therefore, since As-rich solutions also are rich in sulfur, and in view of the greater mobility of the sulfate ion, the presence of a small amount of sulfate in Alpine fissure minerals from a wider area nearby Pizzo Cervandone is not surprising.

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