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A COMPARATIVE STUDY OF SOME PEGMATITIC AND FISSURE MONAZITE FROM THE ALPS

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ABSTRACT

Eleven specimens of monazite from different occurrences in fissures and pegmatites in the Alps have been analyzed by electron microprobe. For some samples from pegmatites, unit-cell data have been obtained. Fissure monazite is poorer in nonessential elements (Si, Ca, Y, Th, U) than monazite coming from pegmatites; the latter can in places be extraordinarily enriched in uranium and thorium. In all the samples, the rare-earth distribution shows a low Nd and high Sm content, relative to the averages given in literature. Appreciable variations of such distribution do occur, especially where large quantities of nonessential elements are present. Such deviations, however, are irregular. In view of the constancy of the unit-cell volume, even for large substitution of the *REE* by U and Th, the monazite crystals behave as ideal solutions, and the *REE* distribution is practically independent of temperature or pressure, or of the presence of other components in the solid state. Therefore, if some correlations are found, these only depend on processes of fractionation that occurred during the evolution of the melt or solution before monazite crystals were formed. The Y content seems larger than usual, especially for pegmatite samples. The Y-*REE* fractionation does not depend exclusively on differences in ionic radii.

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

SOMMAIRE

On a analysé, à la microsonde électronique, onze spécimens de monazite provenant de divers gîtes dans des fissures et des pegmatites des Alpes. Pour certains échantillons de pegmatites, on a déterminé les données de la maille. La monazite des fissures est plus pauvre en éléments nonessentiels (Si, Ca, Y, Th, U) que celle qui provient des pegmatites; cette dernière peut, par endroits, être extrêmement enrichie en uranium et thorium. Dans tous les échantillons, la distribution des terres rares indique une teneur basse en Nd et haute en Sm, relativement aux moyennes données dans la littérature. Des variations appréciables de pareilles distributions sont observées, surtout là où les éléments nonessentiels sont présents en grande quantité. De telles variations sont cependant irrégulières. Vu la constance du volume de la maille, même dans le cas de substitution importante des terres rares (TR) par U et Th, les cristaux de monazite se comportent en solutions idéales, et la distribution des terres rares est pratiquement indépendante de la température ou de la pression, ou encore de la teneur des autres composants à l'état solide. Par conséquent, si quelques corrélations étaient découvertes, elles ne pourraient dépendre que de processus de fractionnement qui se présentèrent au cours de l'évolution du bain fondu ou de la solution avant que ne se forment les cristaux de monazite. La teneur en Y paraît plus grande qu'à l'ordinaire, particulièrement pour les échantillons de pegmatites. Le fractionnement Y–TR ne dépend pas uniquement de différences entre rayons ioniques.

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

INTRODUCTION

Monazite was discovered long ago in the Alps (Lévy 1823) but it is considered to be rare, at least in macroscopic specimens. The crystals that have been analyzed in recent times are still comparatively few, and many of the older analyses are not very reliable.

However, some modern results are particularly interesting; for instance, in the Alpine region some occurrences correspond to the present "world record" in uranium content: 15.64 wt.% UO_2 in the Piona monazite (Gramaccioli & Segalstad 1978); 9.5 wt.% UO_2 in the Bergell monazite (Gulson & Krogh 1973). Moreover, at least two different groups of monazite occurrences, *i.e.*, the "classic" fissure mineral and pegmatitic samples, are found in the Alps. Therefore, a systematic difference in composition between at least these two groups might be expected (Murata *et al.* 1953, Semënov 1963, Fleischer & Altschuler 1969). In view of our relatively extensive collection of various Alpine specimens of monazite, a systematic investigation was considered worthwhile.

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 content of P, Si, Ca and U, a series of natural and synthetic standards was employed (Table 1). For the rare earths, Y and Th, synthetic lithium metaborate glasses were used. We started with pure lithium tetraborate (>99%) and added a weighted quantity of freshly ignited rare-earth oxides (99.9+% purity level). Homogeneity of such glasses was checked by microprobe analysis; no deviation exceeding 2 wt.% relative was detected between different points. For the rare earths and yttrium, *Lα* lines were used, and for thorium and uranium, the corresponding *Mα* lines; for the lighter elements, the *Kα* lines were measured. The data were corrected using a modified version of the MAGIC IV computer program (Colby 1968).

TABLE 1. CONDITIONS AND STANDARDS FOR MICROPROBE ANALYSIS

Accelerating voltage	: 20 kV
Sample current on brass	: 0.01 μA
Beam spot diameter	: about 15 μm
Counting times	: 10 s at peak position 2 s at both backgrounds
Analyzing crystals	: PET P*Kα*, Ca*Kα*, Y*Lα*, La*Lα*, Ce*Lα*, Pr*Lα*, Nd*Lα*, Th*Mα*, U*Mα* LIF Sm*Lα*, Gd*Lα* ADP Si*Kα*
Analytical standards	: Si, P apatite, USNM 104021 (Jarosewich *et al.* 1980)
	: Ca hypersthene, USNM 746 (Jarosewich *et al.* 1980)
	: Y synthetic glass, 5.00 wt. Y_2O_3
	: La synthetic glass, 16.67 wt. % La_2O_3
	: Ce synthetic glass, 25.00 wt. % Ce_2O_3
	: Pr synthetic glass, 10.00 wt. % Pr_2O_3
	: Nd synthetic glass, 16.67 wt. % Nd_2O_3
	: Sm synthetic glass, 5.00 wt. % Sm_2O_3
	: Gd synthetic glass, 5.00 wt. % Gd_2O_3
	: Th synthetic glass; 10.00 wt. ThO_2
	: U synthetic uranium oxide, 99.80 wt. % UO_2
Correction method	: Magic IV (Colby 1968)

TABLE 2. A COMPARISON BETWEEN OUR RESULTS AND EXPECTED VALUES

	(1)		(2)		(3)	
La_2O_3 wt. %	8.2	8.3	1.9	1.7	0.8	0.73
Ce_2O_3	18.6	18.4	2.6	2.5	2.5	2.62
Pr_2O_3	5.5	5.3	1.2	1.1	0.5	0.56
Nd_2O_3	8.8	9.1	1.8	1.7	2.0	1.84
Sm_2O_3	1.4	1.3	0.1	0.1	1.2	1.07
Gd_2O_3	1.5	1.7	0.1	0.1	1.6	1.61
Y_2O_3	3.4	3.2	0.5	0.5	17.5	17.77

(1) Synthetic glass, average of 8 analyses (first column) and expected values of RE oxides (second column);
(2) Synthetic glass, average of 5 analyses (first column) and expected values of RE oxides (second column);
(3) Spencite, average of 7 analyses (first column), and reported composition by Joensuu & Ingamells (1966) (second column).

To account for interferences in the X-ray spectra of the *REE* (Åmli & Griffin 1975), a series of measurements of standards of known composition was carried out for the elements which are present in monazite. Such interferences were found to be non-negligible only for La (overlap with Pr) and for Ce (overlap with Nd and Gd). This effect is linear, at least in the range used here (up to about 27 wt.% of La_2O_3 or Ce_2O_3 content). Accordingly, a correction formula can be adopted, such as $E_o = E_a - KI_o$, where E_o is the true content (in %) of the element undergoing interference, E_a is the apparent content of the same element that would result if no interference were taken into account, and I_o is the content of the interfering element in the sample analyzed. From a least-squares fit, K was found to be equal to 0.34 (±0.02) for the interference of La with Pr (from 23 measurements on 6 samples), 0.12 (±0.01) for the interference of Ce with Nd (from 19 measurements on 6 samples) and 0.06 (±0.00) for the interference of Ce with Gd (from 19 measurements on 6 samples).

The accuracy of our procedure is shown in Table 2. Here, two synthetic glasses and one mineral (spencite, Joensuu & Ingamells 1966) of known composition were analyzed by us, and the results can be compared with the theoretical values. The agreement is satisfactory. Another indirect proof of the validity of our analytical results is given by the internal consistency of our results for monazite (Table 3). The total is always reasonably close to 100 wt.%, and also the stoichiometric proportions are essentially the same as the theoretical values. Na, K, Cl, Fe, S, Eu and Dy are below the limit of detection with our instrument.

Unit-cell data for some of these samples have been obtained from X-ray diffraction of single-crystal fragments, using Mo*Kα* radiation (λ = 0.71069 Å), and a CAD-4 diffractometer. For each crystal, the results (Table 4) were obtained by a least-squares fit of about 25 reflections. The standard deviations were derived from the residuals and the inverse of the matrix of normal equations.

RESULTS

The data here obtained refer to 11 samples from various localities. From inspection of Table 3, the samples of Alpine monazite can be divided into three groups: the first group includes the fissure specimens (Nos. 1 to 3); the second group includes the pegmatite samples with normal Th and U contents (Nos. 4 to 8), and a third group includes highly thorian and uranoan specimens from pegmatites (Nos. 9 to 11). A detailed description of the various samples is given in the footnotes of Table 3. The averages for each of these groups are reported in Table 5 (columns 3-5), together with the average for all our samples (column 2), and the average of 88 samples of monazite reported by Semënov (1963) and Murata *et al.* (1953, 1957, 1958) (column 1). The analytical data reported by Fleischer & Altschuler (1969) relative to monazite specimens from granitic rocks are incomplete and substantially very similar to those reported by Semënov (1963) and Murata *et al.* (1953, 1957, 1958).

On the whole, the fissure specimens contain the lowest amounts of the actinides (uranium and thorium), as well as of calcium and silicon, whereas the converse is generally true for pegmatite specimens. In some cases (specimens 9–11), the substitution of

TABLE 3. ANALYTICAL RESULTS ON THE DIFFERENT SAMPLES*

	(1)				(2)				(3)				(4)			
La_2O_3	15.5	(14.9-17.4)	0.22	0.95	16.9	(16.0-17.8)	0.24	0.97	15.7	(14.3-16.3)	0.22	0.96	13.4	(13.2-13.6)	0.19	0.96
Ce_2O_3	29.6	(28.8-29.7)	0.42		32.0	(30.7-32.6)	0.45		31.5	(30.5-32.2)	0.44		27.1	(26.5-27.6)	0.38	
Pr_2O_3	3.1	(2.9-4.0)	0.04		3.0	(2.7-3.7)	0.04		3.0	(2.7-4.0)	0.04		2.8	(2.6-2.9)	0.04	
Nd_2O_3	9.9	(8.9-10.7)	0.14		9.7	(8.7-10.0)	0.13		9.5	(8.5-10.3)	0.13		7.8	(7.5-8.4)	0.10	
Sm_2O_3	3.3	(2.9-4.1)	0.04		3.5	(3.2-3.9)	0.05		3.5	(2.7-3.9)	0.05		4.2	(3.6-4.6)	0.05	
Gd_2O_3	1.4	(0.9-2.0)	0.02		1.2	(0.9-1.4)	0.02		1.5	(1.0-1.8)	0.02		2.2	(2.0-2.4)	0.03	
Y_2O_3	0.6	(0.4-0.7)	0.01		0.9	(0.7-1.0)	0.02		0.7	(0.4-1.0)	0.02		2.7	(2.3-2.9)	0.05	
ThO_2	4.1	(3.0-5.5)	0.04		0.8	(0.4-1.0)	0.01		1.3	(0.9-1.5)	0.01		4.5	(4.2-4.9)	0.04	
UO_2	0.1	(0.0-0.2)	0.00		0.1	(0.0-0.1)	0.00		0.0	-	0.00		2.5	(2.4-2.7)	0.02	
CaO	0.4	(0.2-0.5)	0.02		0.1	(0.1-0.3)	0.01		0.8	(0.5-0.9)	0.03		1.4	(1.3-1.5)	0.06	
P_2O_5	31.0	(29.0-32.0)	1.02	1.03	31.8	(30.6-32.7)	1.02	1.03	31.6	(29.8-32.2)	1.02	1.03	31.8	(30.8-32.1)	1.02	1.03
SiO_2	0.4	(0.3-0.6)	0.01		0.1	(0.1-0.3)	0.01		0.2	(0.1-0.2)	0.01		0.2	(0.1-0.2)	0.01	
Total	99.4				100.1				99.3				100.6			

	(5)				(6)				(7)				(8)			
La_2O_3	12.9	(12.8-13.1)	0.19	0.97	13.3	(13.0-13.8)	0.19	0.97	14.0	(13.5-14.3)	0.21	0.96	13.4	(12.9-13.6)	0.19	0.97
Ce_2O_3	26.2	(25.8-27.0)	0.37		29.0	(28.8-29.2)	0.41		28.3	(27.8-28.8)	0.42		28.5	(27.2-28.9)	0.40	
Pr_2O_3	3.4	(2.8-4.1)	0.05		3.5	(3.1-3.7)	0.05		3.0	(2.8-3.2)	0.04		3.4	(2.9-4.0)	0.05	
Nd_2O_3	9.4	(9.3-9.6)	0.13		8.8	(8.7-9.1)	0.12		8.6	(8.6-8.7)	0.13		9.6	(9.1-10.5)	0.13	
Sm_2O_3	3.8	(2.9-4.6)	0.05		3.3	(2.9-3.7)	0.04		3.4	(2.8-4.5)	0.05		3.3	(2.8-3.7)	0.04	
Gd_2O_3	1.6	(1.0-2.0)	0.02		1.1	(0.4-1.4)	0.01		1.7	(1.0-2.3)	0.02		1.0	(0.9-1.3)	0.01	
Y_2O_3	3.0	(2.5-3.2)	0.06		2.3	(2.2-2.4)	0.05		0.7	(0.4-0.8)	0.01		0.3	(0.2-0.3)	0.01	
ThO_2	5.6	(5.1-5.7)	0.05		6.5	(6.2-6.6)	0.06		5.6	(4.2-6.6)	0.06		7.7	(7.2-8.5)	0.07	
UO_2	0.4	(0.2-0.5)	0.01		0.2	(0.2-0.3)	0.01		0.2	(0.1-0.2)	0.01		0.4	(0.3-0.6)	0.01	
CaO	1.0	(0.9-1.0)	0.04		0.8	-	0.03		0.3	(0.3-0.4)	0.01		1.4	(1.4-1.6)	0.06	
P_2O_5	30.6	(28.9-32.1)	1.01	1.03	30.3	(29.1-32.1)	0.99	1.02	30.0	(28.5-31.5)	1.01	1.04	31.0	(29.8-31.9)	1.01	1.02
SiO_2	0.5	(0.4-0.6)	0.02		0.9	(0.8-0.9)	0.03		0.8	(0.4-1.0)	0.03		0.2	(0.1-0.2)	0.01	
Total	98.5				100.0				96.6				100.2			

	(9)				(10)				(11)			
La_2O_3	9.6	(9.6-9.8)	0.14	1.00	9.4	(9.1-9.6)	0.14	1.02	16.2	(15.6-16.8)	0.23	0.96
Ce_2O_3	19.6	(19.1-20.2)	0.28		21.6	(20.9-22.0)	0.32		19.3	(19.0-20.0)	0.27	
Pr_2O_3	2.5	(2.1-3.2)	0.04		3.2	(3.0-3.4)	0.05		1.0	(0.7-1.1)	0.01	
Nd_2O_3	4.5	(4.2-4.8)	0.06		9.2	(8.9-9.5)	0.13		1.5	(1.2-2.1)	0.02	
Sm_2O_3	5.4	(5.2-5.7)	0.07		5.0	(4.7-5.1)	0.07		1.1	(0.7-1.2)	0.01	
Gd_2O_3	2.0	(1.7-2.5)	0.03		2.0	(1.7-2.3)	0.03		0.5	(0.3-0.8)	0.01	
Y_2O_3	2.7	(2.6-3.0)	0.06		3.1	(2.8-3.3)	0.07		1.5	(1.3-1.6)	0.03	
ThO_2	19.5	(19.3-19.9)	0.17		18.6	(18.2-19.2)	0.17		10.5	(9.9-10.8)	0.09	
UO_2	1.6	(1.3-1.8)	0.01		0.6	(0.5-0.6)	0.01		12.0	(11.9-12.1)	0.10	
CaO	3.3	(3.3-3.5)	0.14		0.6	(0.6-0.7)	0.03		4.7	(4.4-4.9)	0.19	
P_2O_5	30.0	(29.3-30.9)	0.98	1.01	25.4	(24.9-26.4)	0.87	0.99	31.9	(31.5-32.3)	1.02	1.02
SiO_2	0.8	(0.8-1.0)	0.03		2.8	(2.6-3.1)	0.12		0.1	-	0.00	
Total	101.5				101.5				100.3			

(1) Kollergraben, Binn (average of 7 analyses), fissure material.
(2) Monte Bianco unstated locality, presumably Miage Glacier (average of 7 analyses), fissure material.
(3) PlattenbrÜche, Rauris (average of 7 analyses), fissure material.
(4) Val Dombastone, Sondalo (average of 7 analyses), greenish crystal from pegmatite.
(5) Val Masino (average of 10 analyses), large yellow crystal from pegmatite.
(6) Val Codera (average of 7 analyses), yellow crystal from pegmatite.
(7) Mondei, Valle Antrona (average of 7 analyses), yellowish-pink crystal, with zircon and xenotime from pegmatite.
(8) Nibbio, Val d' Ossola (average of 7 analyses), yellow crystal with zircon from pegmatite.
(9) Rio Graia, Val Vigezzo (average of 7 analyses), greenish crystal from pegmatite.
(10) Arvogno, Val Vigezzo (average of 8 analyses), large yellow crystal with euxenite, gadolinite, etc. from pegmatite.
(11) Piona (average of 9 analyses), small dark-green crystal from pegmatite; the sample is different from the one studied by Gramaccioli & Segalstad (1978).

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* For each sample, the columns refer to: composition (wt. %); maximum and minimum values (between parentheses); number of corresponding ions on the basis of 4 oxygen atoms.

TABLE 4. UNIT-CELL DATA ON SOME MONAZITE-GROUP SAMPLES AND ON SOME SYNTHETIC END-MEMBERS.

	a (Å)	b (Å)	c (Å)	β (°)	V (Å³)
Rio Graia	6.771(1)	6.982(1)	6.471(1)	103.81(1)	297.07
V. Masino	6.776(1)	6.992(2)	6.475(1)	103.79(1)	297.73
Nibbio	6.788(3)	7.009(2)	6.464(1)	103.57(1)	298.95
Arvogno	6.782(1)	6.997(1)	6.485(1)	103.85(1)	298.79
Piona *	6.68	6.96	6.48	103.90	296.83
Huttonite **	6.80	6.96	6.54	104.97	299.02
$LaPO_4$**	6.89	7.05	6.48	104.57	304.64
$CePO_4$**	6.76	7.00	6.44	103.63	296.16
$PrPO_4$**	6.75	6.94	6.40	103.35	291.71
$NdPO_4$**	6.71	6.92	6.36	103.47	287.19
Cheralite ***	6.74	7.00	6.43	104.36	293.89
$CaTh(PO_4)_2$***	6.69	6.93	6.38	104.4	286.49

* From Gramaccioli & Segalstad (1978).
** From Semënov (1963).
*** From Bowie & Horne (1953).

rare-earth elements by uranium and thorium becomes quite extensive, although the *REE* always predominate, thereby excluding the presence of cheralite instead of monazite.

The substitution of *REE* by Th or U implies a problem of charge balance, which can be resolved in two ways, *i.e.*, by concomitant substitution of the *REE* by Ca, or by substitution of P by Si. Both these processes seem to occur in our samples, with a maximum in the Piona (11) and the Arvogno (10) specimens, respectively. The specimen from Arvogno is actually higher in SiO_2 than type cheralite (2.8 wt.% *versus* 2.1 wt.%, according to Bowles *et al.* 1980). However, in all our analyses the stoichiometric ratio between the lanthanides, the actinides and calcium on one side and phosphorus plus silicon on the other is always substantially respected.

TABLE 5. AVERAGE OF OUR RESULTS AND COMPARISON WITH CORRESPONDING DATA°.

	(1)	(2)	(3)	(4)	(5)
La_2O_3	23.7	23.9	24.5	22.3	25.9
Ce_2O_3	44.6	45.8	47.6	46.2	43.2
Pr_2O_3	5.2	4.9	4.6	5.3	4.6
Nd_2O_3	19.2	13.5	14.9	14.7	10.2
Sm_2O_3	4.1	6.3	5.3	6.0	7.9
Gd_2O_3	2.1	2.5	2.0	2.5	3.1
Y_2O_3	1.0	3.0	1.1	2.9	5.2
ThO_2	8.5*	7.7	2.1	6.0	16.2
UO_2	0.3**	3.0	0.03	3.6	4.8
CaO	-	1.4	0.4	1.0	2.9
SiO_2	-	0.6	0.2	0.5	1.3
Y_2O_3/Gd_2O_3	0.5	1.2	0.5	1.2	1.7

(1) Average of data reported by Semënov (1963) and Murata et al. (1957); a total of 88 samples.
(2) Average of all our results (84 analyses on 11 samples).
(3) Average for fissure specimens (21 analyses on 3 samples).
(4) Average for moderately thorium-rich pegmatite specimens (39 analyses on 5 samples).
(5) Average for highly uranium and thorium-rich pegmatite specimens (24 analyses on 3 samples).

° The first 7 entries (La_2O_3 to Y_2O_3) are referred to a total of 100 wt. % for these oxides only; the others are referred to the general total.
* Average of results published by Murata et al. (1957, 1958).
** Average value, derived from reliable analyses of representative monazite samples reported by Semënov (1963).

The rare-earth distribution in the different samples shows some significant variation. In order to show such variation with particular emphasis, the relative percentages of the *REE* oxides (plus yttrium) are shown in Table 5.

On examining Tables 3 and 5, we notice that the contents of lanthanum and cerium do not deviate considerably from the general average value. In our samples, only two (high in U/Th) show remarkable deviations: the Piona monazite is higher in La than the average, whereas the Arvogno monazite is lower.

The Y_2O_3/Gd_2O_3 ratio is important from the theoretical point of view. In fact, of the rare earths contained in monazite in substantial amounts, Gd^{3+} is the ion whose radius (0.94 Å) is the closest to Y^{3+} (0.90 Å: Shannon 1976). Therefore, if the fractionation of the rare earths and yttrium during the various geochemical processes were solely a reflection of the difference in ionic radius, then the Y_2O_3/Gd_2O_3 ratio should remain essentially constant, or at least it should not show considerable variations. Instead, in our samples we observe a variation of about one order of magnitude, with a maximum (3.3) and a minimum (0.3), both in pegmatitic samples. It is difficult to compare such results with other data in the literature, in particular because some previous analytical results are not suitable for this purpose (Murata *et al.* 1958, Fleischer & Altschuler 1969).

DISCUSSION

As we have already mentioned, the stoichiometric balance between the metals and Si or P shows that the ideal formula XPO_4 is substantially obeyed. This implies a correlation between the contents of Si and Ca and the actinides and excludes any mechanism implying a considerable number of vacancies or other lattice defects for such substitution. Therefore, all former claims about this possibility (Wylie 1948) were due to analytical errors: in the older gravimetric determinations, calcium in fact was underestimated or completely overlooked owing to its tendency to accompany the rare earths in the oxalate precipitate (Vickery 1953).

This is expected from the theoretical point of view, since the structure of monazite is substantially ionic, with strong charges in the lattice. In these compounds, the energy of formation E_v of such defects is particularly high. According to the classic formula,

$$n/N = e^{\Delta S/k}\ e^{-E_v/kT}$$

where n is the number of defects, N is the number of atoms, ΔS is the entropy change for vacancy and k is the Boltzmann constant (Dekker 1957), the fraction n/N at the equilibrium must be very small at finite values of temperature, and escapes analytical detection.

From the stoichiometric balance, which is respected even in the highly uranoan samples, the presence of uranium in the 4+ valence state is confirmed. Such a possibility was already indicated by the absorption spectrum in the visible (Gramaccioli & Segalstad 1978). Also from crystal-chemistry considerations it is difficult to imagine how any U^{6+} could enter the monazite structure, at least at the moment of formation, owing to the strong difference in the ionic radii, and to the tendency to form UO_2^{2+} ions, which would result in a considerable deformation of the oxygen framework.

The ratio between the contents of two rare-earth phosphates (*e.g.*, $LaPO_4$ and $NdPO_4$) in the crystal can be expressed as:

$$x_{La}/x_{Nd} = W\ y_{La}/y_{Nd}$$

where x_{La} and x_{Nd} are the mole fractions of $LaPO_4$ and $NdPO_4$ in the crystal (monazite), and y_{La} and y_{Nd} are the corresponding mole fractions in the solution (melt) in equilibrium with the crystal. Here the enrichment factor W can be expressed as $W = W_1/W_2$, where:

$$W_i = \gamma_{La}^{(i)}/\gamma_{Nd}^{(i)} \bullet \exp\ (\mu_{La}^{o(i)}-\mu_{Nd}^{o(i)})/RT$$

where $\gamma_{La}^{(i)}$ and $\gamma_{Nd}^{(i)}$ are the activity coefficients of La and Nd phosphate, respectively, $\mu^{o(i)}$ is the standard chemical potential (corresponding to pure $LaPO_4$ or $NdPO_4$), and the indices i = 1 and i = 2 refer to the melt and to the crystal, respectively. The above expression can be easily derived from the classical expressions for chemical potential in solutions.

Therefore, the presence of U or Th in the crystal may affect the enrichment factor only by changing W_2, since W_1 does not depend on the nature of the crystal. However, the unit-cell volume of the various end-members with the monazite structure is almost the same, as well as the cell volume of the samples here described (Table 4), even for extensive substitution of nonessential elements for *REE* phosphates. This supports an ideal-solution behavior of monazite.

For an ideal solution, we have: $\gamma_{La}^{(2)} = \gamma_{Nd}^{(2)} = 1$. Therefore, W_2 is independent of the presence of U or Th in the structure, and the ratio between two different *REE* phosphates should be independent of the content of nonessential elements. If such variations are observed, these depend on the particular composition of the melt, and not on a particular enrichment due to the different monazite crystal.

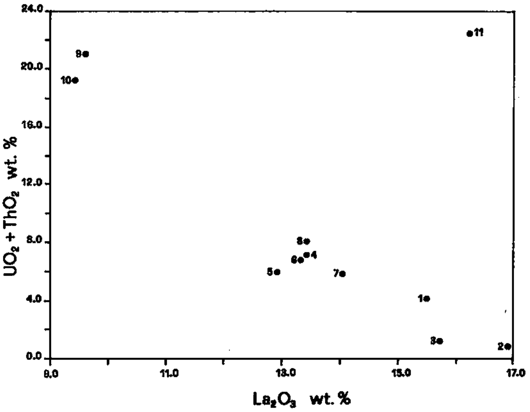

FIG. 1. Relation between La_2O_3 and the sum $UO_2 + ThO_2$ (wt.%) in monazite samples.

On a thermodynamic basis, the greater purity of fissure monazite (with respect to nonessential components) might be ascribed to a low-temperature effect, since the entropy-controlled term in the free energy of mixing expression $\Delta G = \Delta H - T\Delta S$ is less effective at low T. However, for an ideal solution $\Delta H = 0$, and for this reason the solubility of Th, Ca and U containing end-members should be instead substantially independent of temperature. Therefore, as for the different *REE*, here the controlling factor is again the composition of the solution (or melt) from which the crystal grew.

On such basis, the peculiar composition of some monazite crystals derives from a series of previous enrichment processes, very probably due to fractional crystallization of other minerals (possibly rock-forming components). There is no direct relationship between composition and physical conditions at the moment of formation (temperature, pressure) to be expected. Similarly, according to this model, the different contents in the *REE* or other elements should not be directly connected with each other through the modified properties of the monazite crystal.

Our results seem to agree quite well with this situation. For instance (Fig. 1), a good negative correlation between the La_2O_3 content and the $UO_2 + ThO_2$ content seems to show up for most samples. However, the Piona monazite (sample 11) shows exactly the contrary, *i.e.*, it is quite rich in La, and does not fit at all in the scheme. Therefore, a monazite rich in U or Th can be equally La-deficient or La-rich, according to the circumstances. If we assume that all the other samples (except Piona) derive from a similar process of solution enrichment, then the correlation is linked to the nature of such a process. The process of solution enrichment might be quite different for the Piona sample, where the unusually high concentration of uranium points to a different origin.

Similarly, although the fissure monazite, as a bulk, is distinctly less uranoan and thorian than the samples coming from pegmatites, the composition limit between the two groups is not sharp: for instance, the composition of the specimens 1 (Kollergraben) and 7 (Mondei) is nearly identical, although presumably the physical conditions of formation are different. This is in line with the ideal-solution behavior of monazite which, even at low temperature, is liable to absorb any quantity of the nonessential end-members shown in Table 4, if they are available.

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