

## A uranium- and thorium-rich monazite from a south-alpine pegmatite at Piona, Italy

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### Abstract

A green pegmatite mineral from Piona, northern Italy, originally described as a phosphate of lanthanum and cerium, has unit-cell parameters  $a = 6.78$ ,  $b = 6.96$ ,  $c = 6.48\text{\AA}$ ,  $\beta = 103^\circ 54'$ , in agreement with monazite. However, the unusual character of this mineral with respect to "ordinary" monazite is evident in some physical properties, such as the absorption spectrum in the visible region, which shows bands with their maxima at 640–680, 555, and 510 nm, with only weak absorption at 570–590 and 522 nm. The refractive indices ( $\alpha \approx \beta = 1.78$ ,  $\gamma = 1.82$ ) are slightly lower than for most monazite specimens.

Electron microprobe analysis indicates a content of uranium (16 percent  $\text{UO}_2$ ) which exceeds any previously-reported figure for members of the monazite group, and a moderately high content of thorium (11 percent  $\text{ThO}_2$ ). A relevant quantity of CaO (4.4 percent) is also present; silica is nearly absent (0.16 percent). From these data, relationships to cheralite are evident, and the mineral might be considered as a uranium-rich cheralite, or as its uranium-bearing equivalent; the name monazite is used on account of the ratio  $(\text{Ca} + \text{U} + \text{Th})/(\text{Ce} + \text{La} + \text{Pr} + \text{Nd})$ , which is below unity (0.91 against 1.47 for type cheralite). The rare-earth distribution shows considerable enrichment of  $\text{La}_2\text{O}_3$  (40 percent of the total rare-earth oxides), and depletion of  $\text{Nd}_2\text{O}_3$  (7.75 percent) and  $\text{Sm}_2\text{O}_3$  ( $\ll 1$  percent) with respect to the average observed for monazite. As for most well-documented cases of minerals with monazite structure, the substitution  $\text{Si} \rightarrow \text{P}$  is a relatively minor factor in reestablishing the charge balance when thorium or uranium are present.

### Introduction

The south-alpine pegmatites at Piona and Olgiasca, Lake Como, Italy, have long been known to mineralogists and collectors for their abundance of rare minerals. They contain chrysoberyl and graftonite, and recently many other species, such as columbite, tapiolite, uraninite, and cassiterite, have been found as good crystals (Gramaccioli, 1957, 1960).

Several years ago, interesting crystals of an unusual mineral were noticed by one of us (CMG), especially in the vein named "Filone della Malpensata", which at least up to the present time has proven to be the richest in rare minerals. These crystals are dark bottle-green, have a glassy luster, and resemble common epidote. Their maximum length barely reaches

1.5 mm in exceptional cases. The green mineral is commonly found together with small crystals of uraninite and zircon, and is generally enclosed in dark massive quartz. Sometimes films of deep-yellow secondary uranium minerals (including phosphuranylite, autunite, and uranophane) can be observed on fractures.

On the basis of optical properties and a preliminary spectrographic analysis that showed Ce and La to be major components, the mineral was classified as monazite (Cantadore and Gramaccioli, 1969; Gramaccioli, 1975). However, the remarkable weakness of emission lines due to Nd, at least with respect to the strong lines of La and Ce, and some characteristics of the absorption spectrum in the visible region pointed

to the possibility of an unusual distribution of rare-earth elements (REE), and to the presence of a high content of uranium.

Until very recently, the extreme rarity of the mineral virtually prevented further investigation. In the meantime, further interest in this mineral has arisen because similar crystals have been found over a wide area in the Valtellina and the Bergell Massif (Gramaccioli, 1975). A detailed examination was considered therefore to be appropriate.

### Unit-cell parameters

The unit-cell data have been obtained from X-ray diffraction of a single crystal, using MoK $\alpha$  radiation and a graphite monochromator. The peaks are quite clear and sharp, and no sign of metamictization has been observed. A least-squares fit to  $\sin^2\theta$  values resulted in the parameters reported in the first column of Table 1; standard deviations are 0.01Å for cell dimensions and 0.1° for the  $\beta$  angle. The Laue symmetry is  $2/m$ ; the observed extinctions ( $0k0$  for  $k = 2n + 1$ ;  $h0l$  for  $h + l = 2n + 1$ ) are in agreement with the space group  $P2_1/n$ . From these unit-cell data, a close similarity between our mineral and monazite is indeed evident. A comparison with other related species such as huttonite and cheralite is given in Table 1.

### Optical data

The optical properties are shown in Table 2. The  $\alpha$  and  $\beta$  indices have been measured by the immersion method, whereas  $\gamma$  has been estimated from birefringence (as determined from thickness and interference colors), and is considered to be less accurate.

The calculated axial angle  $2V = 16^\circ$  agrees satisfactorily with the observed angle ( $14.5^\circ$ ). Since the orientation of cleavage fragments in the microscope with respect to the crystal axes, as determined by X-rays, is tentative, and the two lower indices are virtu-

Table 1. Unit-cell data ( $a, b, c$  in Å;  $V$  in Å<sup>3</sup>) and densities (g/cm<sup>3</sup>) of minerals with a monazite structure

	Piona monazite	Monazites*	Cheralite**	Huttonite***
$a$	6.78	6.78	6.717	6.80
$b$	6.96	7.00	6.920	6.96
$c$	6.48	6.45	6.434	6.54
$\beta$	103°54'	103°39'	103°50'	104°58'
$V$	296.83	297.47	290.39	299.03
$\rho$ meas		4.6-5.4	5.3	7.1
$\rho$ calc	5.15	5.15-5.4	5.41	7.18

\* Average of four samples in Frondel (1958).

\*\* Finney and Rao (1967); Rao and Finney (1965).

\*\*\* Pabst (1951).

Table 2. Optical properties of minerals with a monazite structure

	Piona monazite	Monazites*	Cheralite**	Huttonite***
$\alpha$	1.777(2)	1.789	1.779	1.898
$\beta$	1.778(2)	1.790	1.780	1.900
$\gamma$	1.823(8)	1.842	1.816	1.922
$\gamma$ - $\alpha$	0.045	0.053	0.037	0.024
$2V$ meas	14.5°	17.5°	18.1°	25°
$ZAc$	$\sim 2^\circ$	2-6°	7°	$\sim 0^\circ$
Opt. sign	+	+	+	+
Pleochr.	very faint	very faint	distinct	absent
Color	green	yellow	green	colorless
Fluoresc.	no	no	?	yes

\* Average of four samples in Frondel (1958).

\*\* Bowie and Horne (1953).

\*\*\* Pabst (1951).

Parentthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left, thus 1.777(2) indicates an esd of 0.002.

ally equal, some doubts still remain as to the direction of vibration corresponding to the lowest index. Therefore it is not clear whether  $X = b$  or  $Y = b$ . The first possibility is presumed by analogy with monazite and cheralite. All refractive indices are significantly lower than the average values observed for monazite. Because of these data and the peculiar green color, the mineral is similar to cheralite.

### Absorption spectrum

Because of the unusual green color of this monazite, its absorption spectrum in the visible region has been carefully studied. This spectrum has been measured with the help of a small direct-vision spectroscopy replacing the microscope ocular. A calibrated scale ensures accuracy of wavelength measurements up to about 5 nm.

Strong absorption bands are observed in the red at 640-680 nm, in the green with maximum at 555 nm, and in the blue with maximum at 510 nm; all these bands are clearly defined at the higher wavelength side, and fade towards lower wavelengths. This phenomenon recalls the rotational fine structure of molecular spectra, and is probably due to vibration of the ions in the crystal. In addition, two weak bands are observed in the yellow region at about 570-590 nm and in the green at 522 nm; the latter one, which is absent in most specimens, is very sharp and particularly weak.

These data are very characteristic and markedly different from the usual ("yellow") monazite absorption spectrum (Adams, 1965), where the predominant maxima, which are particularly marked, are observed in coincidence with the two weaker bands reported

above for the Piona monazite at 570–590 (very strong) and 522 nm. No other coincidence is found, since the stronger absorption bands observed for the Piona mineral are absent in the spectrum of yellow monazite; conversely, all the weaker bands observed for yellow monazite are altogether absent in the Piona mineral. A comparison with cheralite would be quite interesting, but it cannot be made at present because absorption spectra for cheralite are not available in the literature.

The explanation of this difference in absorption spectra becomes quite evident if one considers neodymium to be the main element responsible for the absorption spectrum of most monazite specimens, in view of its relative abundance and richness in absorption bands of  $\text{Nd}^{3+}$  (Prandtl and Scheiner, 1934; Adams, 1965). Therefore the weakness of the bands at 570–590 and 522 nm, and the absence of the other bands characteristic for yellow monazite, substantially indicate an unusually low content of Nd, which is confirmed by the microprobe analysis. The other bands in the spectrum of the monazite from Piona are virtually coincident with the absorption spectrum of  $\text{U}^{4+}$  (Stewart, 1952), and their presence is also in agreement with the results of the microprobe analysis, which indicates a high uranium content; this spectrum can also be considered as direct evidence of tetravalent uranium in our mineral. On account of its noble-gas electron configuration, the  $\text{Th}^{4+}$  ion does not give any absorption band in these spectra.

### Chemical composition

Electron microprobe analyses on polished grain mounts were made by one of us (TVS) on an ARL-EMX microprobe at the Central Institute of Industrial Research, Oslo, using a series of natural and synthetic standards. Matrix corrections were made according to the method of Bence and Albee (1968), using correction factors from Albee and Ray (1970) and Åmli and Griffin (1975). The rare-earth elements were analysed by the procedure described by Åmli and Griffin (1975), using the same standards and thus achieving similar accuracy. The mineral showed a faint zoning, with generally higher amounts of Th and U and less REE in the core relative to the rim. The average chemical composition of four analysed points in the rim is given in Table 3.

### Discussion

The relative distribution of rare-earth elements in the rim and in the core is shown in Table 4. The rare-

Table 3. Chemical composition (rim) of uranium- and thorium-rich monazite from Piona, Italy. Structural formula (right column) based on 16 oxygens

	Weight percent	Atomic proportion		
FeO	tr			
CaO	4.45	0.742	}	
$\text{K}_2\text{O}$	0.71	0.140		
$\text{ThO}_2$	11.34	0.401		
$\text{UO}_2$	15.64	0.541		
$\text{Y}_2\text{O}_3$	1.01	0.083		
$\text{La}_2\text{O}_3$	13.89	0.796		3.856
$\text{Ce}_2\text{O}_3$	16.31	0.928		
$\text{Pr}_2\text{O}_3$	1.64	0.093		
$\text{Nd}_2\text{O}_3$	2.34	0.130		
$\text{Dy}_2\text{O}_3$	0.05	0.002		
$\text{P}_2\text{O}_5$	31.02	4.082	}	
$\text{SiO}_2$	0.16	0.025		4.107
Sum	98.56			

tr = traces.  
Not detected: Sc, Cr, Nb, Ta, Zr, Hf, Al, Ti, Mn, Na, Sm, Eu, Gd, Tb, Ho, Er, Tm, Yb, Lu.

earth oxide values are recalculated to a total of 100 percent and compared with an average monazite, derived from the data of Mertie (1960). A definite enrichment of La over Nd compared with the average monazite is quite evident for our mineral; the drastic depletion of rare-earth elements with increasing atomic number is confirmed by the virtual absence of samarium. The deviation from the average monazite becomes even more apparent if one considers the maximum values of enrichment of La over Nd in monazite, as reported in extensive works on this subject; e.g., Murata *et al.* (1957) examined the rare-

Table 4. Relative rare-earth distribution in uranium- and thorium-rich monazite from Piona, Italy;  $\text{La}_2\text{O}_3$  to  $\text{Gd}_2\text{O}_3$  = 100 percent

	Core, Piona monazite	Rim, Piona monazite	Average monazite*	Monazite** Arkansas
$\text{La}_2\text{O}_3$	39.66	40.64	23.84	39
$\text{Ce}_2\text{O}_3$	47.00	47.72	46.56	43
$\text{Pr}_2\text{O}_3$	5.59	4.80	5.30	4
$\text{Nd}_2\text{O}_3$	7.75	6.85	18.64	10
$\text{Sm}_2\text{O}_3$	nd	nd	3.68	1
$\text{Eu}_2\text{O}_3$	tr	nd	-	-
$\text{Gd}_2\text{O}_3$	tr	nd	1.98	0

tr = traces. nd = not detected.

\* Mertie (1960).

\*\* Previous maximum enrichment in La over Nd (Murata *et al.*, 1957).

earth distribution in 24 monazite specimens. Of these specimens 23 had  $\text{La}_2\text{O}_3$  contents between 13.1 and 26.9 weight percent and  $\text{Nd}_2\text{O}_3$  contents of 15.3 to 31.8 weight percent. Only one specimen, from Magnet Cove, Arkansas (Table 4), shows a distribution comparable with the Piona mineral. The microprobe analysis explains the preliminary results obtained from arc spectroscopy, and also the relative weakness of the  $\text{Nd}^{3+}$  absorption bands in the visible region. It would be interesting to compare the rare-earth distribution in the monazite from Piona with that of the type cheralite, in order to see whether this enrichment in La might be characteristic of this species, but unfortunately no such data on the type cheralite are available in the literature.

As for other rare-earth minerals, there are some differences in composition between the rim and the core (Åmli, 1975). This is hardly surprising in view of the selective enrichment or depletion of certain elements occurring during formation of mixed crystals. These differences between the rim and the core might be enhanced by partial oxidation (of  $\text{U}^{4+}$ ) at the surface of the mineral grains, with consequent greater tendency for some components to be leached out or absorbed.

The most remarkable feature is the particularly high content of uranium, which exceeds any previously reported figure for minerals of the monazite group. The content of  $\text{U}_3\text{O}_8$  in natural monazite seems to be generally less than 1 weight percent (Fron del, 1958). Overstreet *et al.* (1970) applied the term "uranium-rich" to monazites with  $\text{U}_3\text{O}_8$  in excess of 0.95 weight percent, and these constitute the upper 5 percent of the range in percentage of  $\text{U}_3\text{O}_8$  found in monazites from the United States. A uranium-rich variety from North Carolina has a maximum content of 2.34 weight percent  $\text{U}_3\text{O}_8$  (Overstreet *et al.*, 1970). Fresh monazite from Moon Plains, Ceylon, contains 2.66 weight percent  $\text{U}_3\text{O}_8$ , whereas the weathered monazite from the same pegmatite has similar composition but only traces of uranium (Overstreet, 1967). Monazite rich in uranium has also been reported from granodiorite in the Bergell area, 20–40 km NE of Piona; it contains 10.65 weight percent U (Gulson and Krogh, 1973) and is probably similar to the monazite at Piona.

The thorium content is high although not exceptional, since a value of 12 weight percent  $\text{ThO}_2$  still can be considered as "usual" (Heinrich, 1958). Analyses of specimens with substantially higher contents of  $\text{ThO}_2$  are reported in the literature, although the accuracy of some of these might be questionable

(Fron del, 1958). Overstreet (1960) and Overstreet *et al.* (1970) have shown that the abundance of thorium in monazite appears to be partly determined by pressure and temperature of crystallization, but the chemical composition of the enclosing rock is also involved. High metamorphic grade has been correlated with high Th concentration in monazites.

As in cheralite, the excess of charge on the rare-earth position in the crystal lattice due to the presence of  $\text{Th}^{4+}$  and  $\text{U}^{4+}$  is essentially balanced by the presence of ions of lower charge distributed in the same lattice positions. An additional charge of  $-0.942$  electrons per formula unit due to U ( $-0.541$ ) and Th ( $-0.401$ ) is balanced by an opposite charge of 1.022 electrons due to Ca ( $+0.742$ ) and K ( $+0.140 \times 2$ ).

The substitution of Si for P, which has been claimed to be responsible, at least in part, for allowing the presence of Th in monazite (see Fron del, 1958, for a discussion on this subject) seems here to be of minor importance, since the analysis shows only 0.16 percent  $\text{SiO}_2$ . In type cheralite the presence of  $\text{Th}^{4+}$  is apparently largely accomplished by the concomitant substitution of  $\text{Ca}^{2+}$  for the REE, and the substitution of Si for P is comparatively small. The apparent contradictions in many monazite analyses may be due to deficient determinations of Ca, which is coprecipitated with REE oxalates in gravimetric determination. Such contamination is very difficult to avoid (Vickery, 1953).

If the Th and U contents are summed for the Piona mineral, it plots in the region assigned to cheralite by Bowie and Horne (1953). Although incomplete data are available in the literature concerning cheralite from localities other than Travancore, the Piona mineral has no less claim to be considered as cheralite than nontype material from other occurrences (Apolonov and Petrova, 1965; Haapala, 1966). In the type cheralite, however, a major part of the REE has been replaced by Th, U, and Ca, the ratio  $(\text{Th} + \text{U} + \text{Ca})/(\text{Ce} + \text{La} + \text{Pr} + \text{Nd})$  being equal to 1.47, whereas it is 0.91 in the Piona mineral. For this reason we still prefer to consider the latter as a variety of monazite.

Other distinctions from the type cheralite are the silica content, and the definite prevalence of U over Th. Although cheralite contains more uranium (4–6.5 weight percent  $\text{U}_3\text{O}_8$ ) than ordinary monazite, these figures are well below that for the Piona mineral, which might also be considered as the uranium-bearing equivalent of cheralite. The Piona mineral and cheralite thus bear a close resemblance to monazite in all physical properties, but are significantly different from normal monazite in composition.

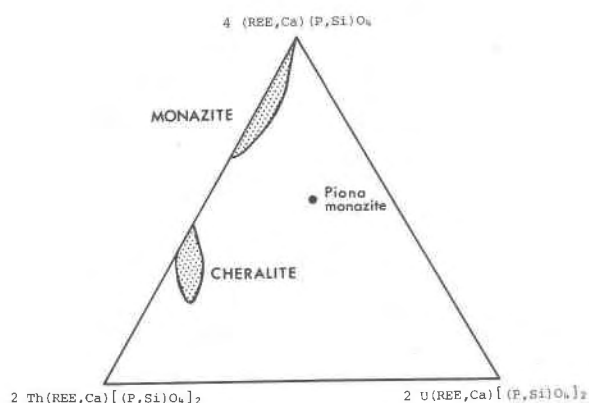


Fig. 1. Monazite, cheralite, and the Piona mineral plotted as atomic proportions in the upper half of the  $(\text{REE,Ca})(\text{P,Si})\text{O}_4$ - $\text{Th}(\text{P,Si})\text{O}_4$ - $\text{U}(\text{P,Si})\text{O}_4$  diagram.

Representative monazite and cheralite analyses taken from the literature plot in two separate fields in Figure 1, and the Piona mineral plots outside these fields. Most monazites contain up to 18 weight percent  $\text{ThO}_2$  and up to 2.7 weight percent  $\text{U}_3\text{O}_8$ ; cheralites contain approximately 28–36.3 weight percent  $\text{ThO}_2$  and up to 6.5 weight percent  $\text{U}_3\text{O}_8$ ; but the Piona mineral and the Bergell monazite (Gulson and Krogh, 1973) contain approximately 11 weight percent  $\text{ThO}_2$  (Piona mineral) and 11–16 weight percent  $\text{UO}_2$ . From these analyses there seems to be a gap in Th and U contents between minerals with the monazite structure. Further work is necessary in order to ascertain whether this gap is due to partial miscibility, or rather to a limited variation in the conditions of formation.

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