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A uranium-rich ekanite, $(Th_{0.78}, U_{0.21})(Ca_{2.01}, Fe_{0.04}, Mn_{0.01})Si_{7.99}O_{20}$, from Pitigliano, Italy

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ABSTRACT. — Apparently non-metamict ekanite with a relatively high U/Th ratio of 0.27 has been observed in volcanic alkaline xenoliths at Pitigliano, Tuscany, Italy.

The previously published data, unit cell parameters ($a = 7.447$ Å; $c = 14.987$ Å) and space group ($I\bar{4}2d$), are supplemented by measurement of the refractive index $\omega = 1.570$ and microprobe analysis; the chemical formula is: $(Th_{0.78}, U_{0.21})(Ca_{2.01}, Fe_{0.04}, Mn_{0.01})Si_{7.99}O_{20}$.

The calculated density (3.41 g cm^{-3}) is sensibly higher than the observed density (3.22 g cm^{-3}): a similar problem is encountered also for the other occurrences.

Key words: ekanite, volcanic xenoliths, Pitigliano, Italy, electron microprobe analyses.

RIASSUNTO. — È stata osservata in alcuni xenoliti alcalini di Pitigliano (Toscana, Italia) dell'ekanite apparentemente non metamittica con alto rapporto U/Th (0.27).

La misura dell'indice di rifrazione $\omega = 1.570$, della densità (3.22 g cm^{-3}) e l'analisi chimica alla microsonda elettronica $(Th_{0.78}, U_{0.21})(Ca_{2.01}, Fe_{0.04}, Mn_{0.01})Si_{7.99}O_{20}$, completano i dati strutturali precedentemente determinati (parametri di cella $a = 7.447$ Å; $c = 14.987$ Å e gruppo spaziale $I\bar{4}2d$).

La densità calcolata (3.41 g cm^{-3}) è sensibilmente più elevata di quella misurata: una situazione analoga si riscontra nei campioni di minerali del gruppo dell'ekanite riportati in letteratura.

Parole chiave: ekanite, xenoliti vulcanici, Pitigliano, Italia, microsonda elettronica.

Introduction

The name ekanite is referred to a mineralogical species with vitreous aspect and bottle-green colour, which was found in metamict state, for the first time, in Sri Lanka (ANDERSON et al., 1961; GUBELIN, 1961); because of its rarity and its optical properties ekanite is a valuable gemstone.

The identification of ekanite needs some attention: many of the reference data, which appeared in the literature until a few years ago, were obtained from steacyite, another mineral which is very similar to, but not identical, with ekanite (PERRAULT & RICHARD, 1973). This mineral differs from true ekanite because of its structure and space group ($P4/mcc$ instead of $I\bar{4}2d$); this corresponds to presence of potassium and of complete fourfold double rings in the structure.

A few years ago, non-metamict ekanite was found for the first time in the Tombstone Mountains, Yukon Territory, Canada (SZYMANSKI et al., 1982). A further occurrence of apparently non-metamict ekanite was discovered in some volcanic alkaline xenoliths at Pitigliano, Tuscany, Italy (DEMARTIN et al., 1982).

Although exhaustive crystallographic evidence for the identification of ekanite from Pitigliano has been given, some important

experimental data, such as — for instance — chemical analysis, are still lacking. Such information was expected to be particularly interesting, in view of a presumably high uranium content as suggested by semiquantitative measurements. For this reason, and because of the unusual occurrence of this species, a completion of previous study was considered necessary.

The additional data here reported were obtained from another single crystal fragment from the original sample found by Mr. C. TUMAINI.

Optical and physical properties

Perfect transparent ekanite from Pitigliano occurs as prismatic crystals or very brittle small grains with uniform bottle-green colour. This colour is easily recognizable even in very small fragments.

The absorption spectrum in the visible is characterized by some sharp bands which are due, in all probability, to the U^{4+} ion (DEMARTIN et al., 1982).

The observed density, measured by flotation in a mixture of diiodmethane and bromoform, is 3.21 g cm^{-3} ($\pm$ 0.01); a slightly higher value (3.23 g cm^{-3}, $\pm$ 0.01) has been obtained using dilute Thoulet liquid. The corresponding calculated value as obtained from crystallographic data (a = 7.447 Å, c = 14.987 Å of DEMARTIN et al., 1982) and our chemical analysis (see below) is much higher: 3.41 g cm^{-3}. This remarkable discrepancy amounts to about 6 %; a similar result was found by all the other authors who studied the ekanite group minerals (table 1). According to SZYMANSKI et al. (1982), this effect is due to inclusions of extraneous material as haematite, thorogummite, air and water in the microfractures. In our case, however, optical examination seems to exclude the presence of any solid or liquid inclusions.

The value of the refractive index ω (1.570) was obtained by the immersion method; owing to the shortage of material, we could not measure the ε index with sufficient accuracy. The birefringence is however low.

TABLE 1

Density of ekanite group minerals (g cm^{-3})

	(1)	(2)	(3)	(4)
Calc. density	3.41	3.36	3.32	3.27
Obs. density	3.22	3.08	2.95	2.96

(1) Ekanite from Pitigliano. (2) Ekanite from Tombstone Mountains (SZYMANSKI et al., 1982). (3) Steacyite from Saint-Hilaire (PERRAULT & RICHARD, 1973). (4) Iraqite from North-Iraq (LIVINGSTONE et al., 1976).

The apparent non-metamict character of ekanite from Pitigliano is very probably due to its recent age of formation.

Chemical analyses

Electron microprobe analysis has been carried on polished grain mounts using an ARL-SEMQ instrument of C.N.R. (Centro per la Stratigrafia e Petrografia delle Alpi Centrali in Milan). The used standards and analytical conditions are reported in table 2; in these conditions no decomposition on the crystal surface is observed. The mineral does not show any significant zoning and it is pratically homogeneous from the core to the rim.

The average chemical composition of 17 analysed spots is given in table 3 together with the corresponding results from the other occurrences. From analytical and crystallographic data, the chemical formula for ekanite is: $(Th_{0.78},U_{0.21})(Ca_{2.01},Fe_{0.04},Mn_{0.01})Si_{7.99}O_{20}$. The agreement with the theoretical formula is good.

Because of the scarcity of the substance (only a minute grain of about 0.5 mm diameter was available), the possible presence of water was investigated using single crystal Raman microprobe, but not evidence for it was noticed. This seems to exclude the presence of important amount of water in the

TABLE 2
Conditions and standards for microprobe analysis

Accelerating voltage	: 15 kV
Sample current on brass	: 0.015 μA
Beam spot diameter	: about 10 μm
Counting times	: 20 s at peak position 2 s at both backgrounds
Analyzing crystals	: LIF - MnKα, FeKα PET - ThMα, UMα, CaKα ADP - SiKα
Analytical standards	: Mn - fayalite, USNM 85276, (Jarosewich et al., 1980) Fe - wollastonite, BM 68773 - augite, USNM 122142, (Jarosewich et al., 1980) Th - synthetic glass, 25.00 wt. % ThO_2 U - synthetic uranium oxide, 99.80 wt. % UO_2 Ca - wollastonite, BM 68773 - augite, USNM 122142, (Jarosewich et al., 1980) Si - wollastonite, BM 68773
Correction method	: MAGIC IV (Colby, 1968).

TABLE 3
Analytical data for ekanite group minerals (wt. %)

	(1)		(2)	(3)	(4)	(5)
SiO_2	56.02	(55.71-56.40)	56.10	43.4	47.6	55.6
Al_2O_3	<0.05		-	0.9	0.8	tr.
ThO_2	24.01	(23.76-24.81)	30.81	36.6	37.8	27.6
UO_2	6.41	(5.99-6.69)	-	1.2	1.1	2.1
Fe_2O_3	0.42	(0.39-0.46)	-	0.3	0.4	0.5
PbO	x		-	-	-	0.8
CaO	13.29	(13.01-13.55)	13.09	8.6	9.6	13.7
MnO	0.11	(0.09-0.25)	-	0.3	0.2	tr.
Na_2O	<0.05		-	-	-	-
H_2O^+	x°		-	7.8*	7.8*	-
F	x		-	3.4*	3.4*	-
Tot.	100.26		100.00	91.3	97.5	100.3

(1) Ekanite from Pitigliano, average of 17 spots: maximum and minimum observed values are between parentheses; Cl, P, K, Cu, As, Rb, Sr, Y, Zr, Ba, REE are below the limit of detection (0.01 wt.%) or absent. (2) Theoretical ekanite, $ThCa_2Si_8O_{20}$. (3) Ekanite, Tombstone Mountains, unheated specimens, average of 2 samples (SZYMANSKI et al., 1982). (4) Ekanite, Tombstone Mountains, heated specimen (SZYMANSKI et al., 1982). (5) Ekanite, Sri Lanka (ANDERSON et al., 1961).
x = Below the limit of detection (0.01 wt.%) or absent at electron microprobe. **x°** = Absent at Raman microprobe. * = Bulk chemical analyses, not included in the total.

mineral, in agreement with the results of electron microprobe analysis, where the sum matches 100 wt.% nearly exactly.

Discussion

The U/Th ratio (0.27) of ekanite from Pitigliano is considerably higher than for most ekanite specimens whose identification is certain (the maximum which has been observed until now is 0.10). Moreover, ekanite from Pitigliano seems to be substantially anhydrous, whereas the material from the Yukon occurrence is considerably rich in water.

The only difficult point to explain is the marked difference between the theoretical and the calculated density, a phenomenon which seems to be general for ekanite and its group. Such a phenomenon cannot be due to the presence of water in the crystal, since in this case the mineral should be still heavier and not lighter than the corresponding calculated value.

A possibility might be connected with the beginning of a process of metamictization, which causes a little decrease of density without sharp modifications in the diffractometric data (PABST, 1952; EWING, 1975).

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