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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Mineralogia. — *Nonmetamict* U*-rich ekanite from Pitigliano* (*Tuscany, Italy*). Nota di GIANCARLO DELLA VENTURA (*), ADRIANA MARAS (*) e GIAN CARLO PARODI (**), presentata (***) dal Corrisp. A. MOTTANA.

RIASSUNTO. — Ekanite in cristalli rarissimi, trasparenti, di colore verde, è stata rinvenuta nelle piccole cavità all'interno di proietti a composizione sienitica (« sanidiniti ») dell'area di Pitigliano (Toscana, Italia). Il minerale è associato a quarzo, K-feldspato, pirosseno monoclino, ossidi metallici e titanite. Lo spettro di raggi X, ben definito in quanto il minerale non è metamittico, è stato indicizzato sulla base di una cella tetragonale con gruppo spaziale I422, di dimensioni: $a = 7.449$ (3) e $c = 15.000$ (7) A. La formula chimica ottenuta per analisi in microsonda elettronica per il campione Pit 1 (media di 7 analisi puntuali sul medesimo cristallo) è : $(Th_{0.65}\ U_{0.36})\ (Ca_{1.84}\ RE_{0.01}\ K_{0.01}\ \square_{0.14})\ Si_8\ O_{20}$, la formula ideale è $(Th, U)\ Ca_2Si_8O_{20}$. In confronto alle ekaniti precedentemente studiate, il campione Pit 1 mostra una notevole sostituzione di Th con U, facendo pensare alla possibile esistenza di un termine completamente uranifero. Viene pertanto discussa la differenza che esiste tra i diversi membri del gruppo dell'ekanite.

INTRODUCTION

Ekanite was discovered in gem quality dark-green cut stones by Mr. Ekanajake (to whom the name was dedicated) in a market of Colombo, Sri Lanka. The preliminary investigations on this mineral were reported by Mitchell (Gubelin, 1961). The sample proved to be completely metamict, consequently isotropic to X-ray. The chemical analyses showed the presence of Ca, Si, Pb and 28% Th.

Ekanite was reported as a new mineral species by Anderson *et al.* (1961), while details on its physical properties, radioactivity, chemical composition and inclusions were reported by Gubelin (1961, 1962).

Non-metamict ekanite from the Tombstone Mountains, Yukon Territory was reported by Szymanski *et al.* (1982). It occurred in a syenitic boulder associated with fluorite, garnet, thorogummite, zircon, titanite. The ekanite crystals were yellow to dark-red discrete grains, 2-3 mm in length, and clusters of grains.

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Microprobe analyses were given for different samples, but they were not considered to reflect the actual composition of the mineral because of degradation of the sample under electron bombardment, of the presence of fine inclusions and of intergrowth with thorogummite (Szymanski *et al.*, 1982).

K and Na bearing ekanites described from Central Asia (URSS) (Ginzburg *et al.*, 1965; Mokeyeva and Golovastikov, 1966) and from Mt. St. Hilaire (Perrault and Richard, 1973; Richard and Perrault, 1972) were later renamed as steacyite because they significantly differed both chemically and structurally from ekanite (Perrault and Szymanski, 1982). Another steacyite occurrence has been recently reported in nepheline-syenitic rocks from the Rouma Isle, Guinea (Parodi and Della Ventura, 1987). Iraqite, a mineral closely related to steacyite but notably different in chemistry, was described by Livingstone *et al.* (1976) from Iraq.

The first Italian occurrence of ekanite was reported by Demartin *et al.* (1983) from the Pitigliano area. The mineral was observed as rare, small green crystals in a volcanic ejectum of syenitic composition in association with quartz, feldspar and pyroxene. The symmetry of these crystals was established to be tetragonal, space group I422, by single crystal diffractometry. Only qualitative EMPA data were given, indicating the presence of major Si, Ca, Th and U plus K, Ce, Fe and Cu as trace elements.

During the same period, other samples of ekanite from the same locality were studied by the authors, and preliminary data were presented during the S.I.M.P. meeting held at Palermo (Della Ventura *et al.*, 1983). Chemical analysis on the same sample studied by Demartin *et al.* (1983) was later performed by Diella and Mannucci (1986).

A crystal-chemical characterization of the non-metamict U-rich ekanite from Pitigliano, Tuscany, Italy is the aim of this paper. This study is part of a more general project of a systematic research on the Th-U-REE minerals of Latium, Italy. Studies of the occurrences, distribution and crystal-chemistry of these minerals may result in a better understanding of the geochemical behaviour of Th, U and REE in this volcanic environment.

DESCRIPTION OF THE SPECIMEN

The studied crystals of ekanite from Pitigliano were found by G. Guglielmini, and S. Fiori, amateur mineralogists, inside little cavities of two ejecta collected from a pyroclastic formation known as " vulcanite complessa di Pitigliano " at the locality Case Collina. Various types of ejecta from this locality have long been known to contain several rare and interesting minerals (Santacroce 1970, Stoppani and Curti, 1982). Th and U bearing minerals, such as the pyrochlore group minerals, had already been observed in these ejecta by the writers (Della Ventura *et al.*, 1983).

The euhedral, transparent-green crystals of ekanite (max. length 0.5 mm) are very rare inside the studied ejectum and occur together with predominant quartz, K-feldspar and clinopyroxene, with Fe-oxides, apatite and titanite as accessory phases. Ekanite shows a complex morphology with the {110}, {100}, {101} and {001} forms. In ekanite from Pitigliano the basal {001} pinachoid is the best-developed form giving an overall tabular habit to the mineral.

CRYSTALLOGRAPHY

The structure of steacyite was solved by Mokeyeva and Golovastikov (1966) on a sample from Central Asia and by Richard and Perrault (1972) on the UK-4 Th-silicate from St. Hilaire in the space group P 4/mcc. The main feature of the structure is the Si_8O_{20} group arranged in a double tetrahedral ring to form a pseudo-cubic cage linked by Th (A site) in square antiprism coordination, Ca plus Na (B site) and K (C site) in distorted tetrahedral coordination. All of the cation sites were found to be incompletely occupied.

TABLE I.

Unit-cell data for Ekanite (A)

	1	2	3	4
a . .	7.449 (3)	7.447 (1)	7.46	7.483 (3)
c . .	15.000 (7)	14.987 (15)	14.96	14.893 (6)
c:*a* .	2.014 (1)	2.012 (2)	2.01	1.990 (2)

1) Ekanite from Pitigliano (this work, sample Pit 1); 2) Ekanite from Pitigliano (Demartin *et al.*, 1983); 3) Ekanite from Sri Lanka (Anderson *et al.*, 1961; determined after heating at 1000 °C); 4) Ekanite from Tombstone (Szymanski *et al.*, 1982).

The structure of ekanite is solved in the space group I 422 but shows close similarities to that of steacyite, assuming the potential K site to be vacant and the only non-stoichiometric site to be the Th site (Szymanski *et al.*, 1982). The silicate units are grouped to form Si_8O_{20} sheets.

The X-ray pattern of the sample Pit 1 was obtained by a 114.60 mm Gandolfi camera, CuKα radiation, Ni filter. The x-ray pattern is very similar to the pattern of crystalline ekanite both from the Tombstone Mountains, Yukon Territory (Szymanski *et al.*, 1982) and from Pitigliano (Demartin *et al.*, 1983), but the measured intensities differ slightly and some peaks are resolved (i.e.

their single (206, 321) reflection is resolved into two strong peaks at 2.073 and 2.044 Å respectively).

The cell parameters were refined by a least-squares program (Hubbard *et al.*, 1982) on the basis of the space group I 422. Table I gives the cell parameters for sample Pit 1 compared to those of previous works. The cell dimensions are very close to those given by Demartin *et al.* (1983) for the ekanite from the same locality, but are significantly different from those of other ekanites: *a* is constantly shorter, and *c* is larger.

CHEMICAL PROPERTIES

Few chemical data exist on ekanite, while many are found in the mineralogical literature concerning steacyite. The latter is characterized by a substitution of half of the Ca ions by Na plus additional K ions. As pointed out by Perrault and Szymanski (1982), the phases from central Asia (Ginzburg *et al.*, 1965, Mokeyeva and Golovastikov, 1966) and Mt. St. Hilaire (Richard and Perrault 1972) define a complete substitutional series between Th—Na—K and Th—Ca—K silicate end-members, with the A and C sites occupied respectively by Th and K whereas the B site is predominantly occupied by Na in steacyite and by Ca in an unnamed phase.

The chemical analyses for the ekanite from Pitigliano were performed by a CAMEBAX microprobe at the University of Paris VI. Standards were na-

TABLE II.
Analyses of Ekanite (*wt* %)

	1	2	3	4	5
SiO_2 . . .	53.36	53.74	56.02	55.6	56.10
Al_2O_3 . . .	—	—	< 0.05	—	—
Fe_2O_3 . . .	—	—	0.42	0.5	—
ThO_2 . . .	18.96	22.93	24.01	27.6	30.81
UO_2	10.75	4.62	6.41	2.1	—
RE_2O_3 . . .	0.14	0.11	—	—	—
PbO	0.11	0.04	—	0.8	—
CaO	11.44	11.06	13.29	13.7	13.09
Na_2O . . .	—	—	< 0.05	—	—
K_2O	0.03	0.02	—	—	—
Total . .	94.79	92.52	100.26	100.3	100.00

1) Ekanite from Pitigliano (this work, sample Pit 1, EMPA average of 7 analyses); 2) Ekanite from Pitigliano (this work, sample Pit 2, EMPA average of 7 analyses); 3) Ekanite from Pitigliano (Diella and Mannucci, 1986, EMPA average of 17 spots total includes 0.11 MnO); 4) Ekanite from Sri Lanka (Anderson *et al.*, 1961; wet chemical analysis, containing traces of Al_2O_3, MnO and MgO); 5) Ekanite from Tombstone (theoretical composition derived from structural determination; Szymanski *et al.*, 1982).

TABLE III.

Empirical formulae for Ekanite calculated on the basis of 8 Si.

	1	2	3	4	5	5 bis
A site						
Th^{+4} . .	0.647	0.777	0.78	0.90	1.00	0.894
U^{+4} . .	0.359	0.153	0.20	0.06		0.047
Fe^{+3} . .				0.05		
Pb^{+4} . .	0.004	0.002		0.03		
Σ (A) . .	1.010	0.932	0.98	1.04	1.00	0.941
B site						
Ca^{+2}. . .	1.838	1.764	2.03	2.11	2.00	1.912
Mn^{+2} . .			0.01			0.029
Na^{+} . .						
Fe^{+3}. . .			0.04			0.059
RE^{+3} . .	0.007	0.005				
K^{+} . . .	0.006	0.004				
Σ (B) . .	1.851	1.773	2.08	2.11	2.00	2.000
T site						
Si^{+4} . . .	8.000	8.000	8.00	8.00	8.00	8.00

Numbers as in Table II. 5 bis is the formula used by Szymansky *et al.*, 1982 for the calculation of density.

tural monazite (Ce, Th, Pr), diopside (Si, Ca), orthoclase (K), galena (Pb), uraninite (U) and synthetic La—Re—O (La), Nd—Re—O (Nd). Two specimens (Pit 1 and Pit 2) from two different ejecta were selected for the microprobe analyses. Sample Pit 2 had only one very small crystal; its U/Th ratio is close to that found by Diella and Mannucci (1986) (0.20 vs. 0.26) so that no crystallographic determinations were made. Table II and III give the chemical data and crystal-chemical formulas for both ekanites from Pitigliano and for the previously analysed ekanites. The chemical composition of the analysed samples is in good agreement with the previous data but a significant difference is found in the U/Th ratio, especially for Pit 1 (0.55) which is the highest ever detected in such a mineral. The holotype from Sri Lanka has a U/Th ratio = = 0.07; the Tombstone Mts. sample has no significant U content. The theoretical formula of ekanite is $ThCa_2Si_8O_{20}$; but the samples from Pitigliano show considerable replacements of Th by U so that their crystal-chemical formula may be written in the form of solid solution, as $(Th, U)Ca_2Si_8O_{20}$.

In fact, sample Pit 1 has 35% of the A site occupied by U. The compositional trends for the minerals of the ekanite group are shown in figure 1. The two substitutional series between ekanite and steacyite end-members are differentiated by plotting U/(Th + U + Pb) against the monovalent/(monovalent + divalent) cation ratio.

The role of water is rather uncertain in the ekanite (as well as the steacyite) structure; weight losses on heating up to 9% for ekanite (Szymanski *et al.*, 1982) and 13.7% for steacyite (Perrault and Richard 1973) have been detected. From detailed IR and structural investigations, this water was interpreted to be zeolitic water trapped in structural channels. Only minor amounts of hydroxyl ions are expected to substitute for non-bridging oxygens at the corners of the silicate tetrahedra (Richard and Perrault, 1972). The analysis of Diella and Mannucci (1986) indicates a fully anhydrous material.

The water content estimated by difference from 100% for samples Pit 1 and Pit 2 are in agreement with the water contents previously determined for other ekanites and steacyites. The formulas, calculated as anhydrous, conform to expectations and show a charge balance suggesting that our ekanites do not contain appreciable hydroxyl.

CONCLUDING REMARKS

Ekanite, essentially a Th—Ca—silicate, is significantly different from steacyite and iraqite both from structural and chemical standpoints. The latter

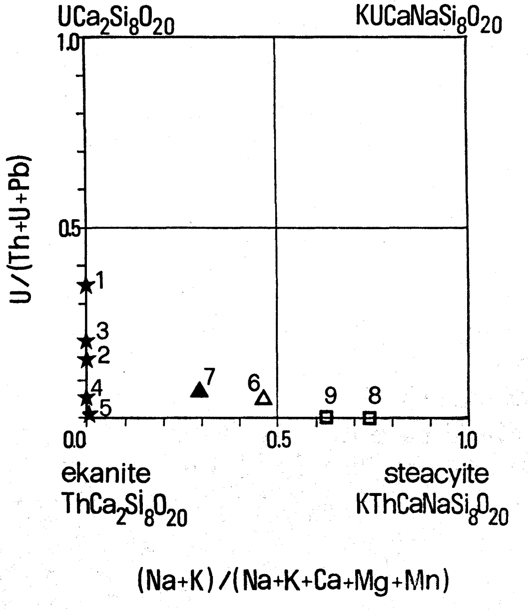

Fig. 1. - Compositional trends in minerals of the ekanite group: the enrichment in U of Latium ekanites differentiates them from steacyites. Iraqite is also plotted for comparison. $UCa_2Si_8O_{20}$ and $KUCaNaSi_8O_{20}$ refer respectively to the hypothetical uranium analogues of ekanite and of steacyite. ✱ 1-5. Ekanite see Table II - △ 6. Unnamed Th-Ca-K silicate spec. 65185 (Ginzburg *et al.* 1965) - ▲ 7. Iraqite (Livingstone *et al.* 1976) - □ Steacyite - 8. Rouma Isle (Parodi and Della Ventura, 1987) - 9. Mt. St. Hilaire (Perrault and Richard, 1973).

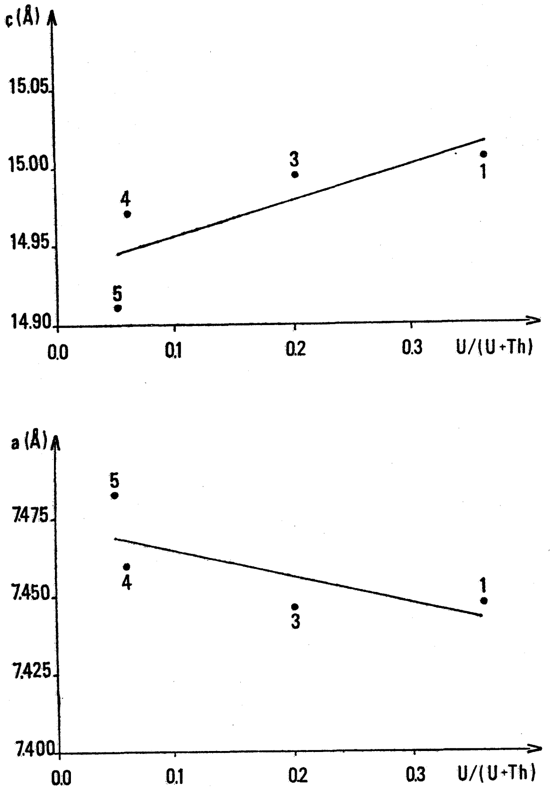

Fig. 2. – Plots of *c* and *a* versus U/(U + Th) in ekanites.

two minerals are isostructural and show extensive substitutions at the cation sites. Steacyite forms a complete series between Th—Ca—K and Th—Na—K—silicate whereas iraqite is characterized by an almost complete coupled substitution of Th+Ca by REE, such as already described for the hellandite-structure type (Della Ventura *et al.*, 1986).

Alternatively, data for ekanite from Pitigliano indicate that considerable U—Th substitution is possible at for the ekanite structure. As shown in Table I, differences occur in the cell parameters of the ekanites, due to the different occupancy of the metal sites. The dimensions of both *a* and *c* appear to be predominantly affected by the Th content (or Th/U ratio) of the unit cell, since the Ca content (Table II) is very similar in all the analyses.

The interpretation of these data in terms of the topology of the structure is not easy. The presence of high quantities of U probably elongates *c* and shrinks *a*. The linear correlation is not good ($r^2 = 0.62$) (fig. 2), but, from a qualitative point of view, the increase in the U/(U+Th) ratio corresponds to an increase in *c* and a decrease in *a*.

The estensive substitution of Th by U, found in sample Pit 1, may indicate the possibility of a U end-member to ekanite.

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