

THE CRYSTAL CHEMISTRY OF NON-METAMICT PYROCHLORE-GROUP MINERALS FROM LATIUM, ITALY

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ABSTRACT

We here present results of a crystal-chemical study of a suite of pyrochlore-group minerals from the holocrystalline syenitic ejecta scattered within the Plio-Pleistocene pyroclastic deposits of Latium, in central Italy. Despite their high actinide content, the samples studied are non-metamict owing to their young age of formation, as suggested by the well-defined and sharp peaks in the X-ray powder-diffraction patterns. The measured *a* unit-cell dimension is correlated with the (Ti + Fe³⁺) content at the *B* site of the structure. Following the IMA classification scheme for pyrochlore-group minerals modified according to the "50% rule" adopted in 1992, the samples are classified as betafite, pyrochlore and uranpyrochlore. In comparison with known data for pyrochlore-group minerals, the samples have extremely high Ti contents (up to 81.3 atom % Ti relative to the Ti + Nb + Ta sum) and significant and variable contents of Zr (up to 8.44 wt.% ZrO₂) and W (up to 12.14 wt.% WO₃). Some crystals display strong compositional zoning, consistent with the substitution $3\text{Nb}^{5+} + \text{Na}^+ \rightleftharpoons 3\text{Ti}^{4+} + \text{U}^{4+}$. The accommodation of extremely high amounts of W⁶⁺ can be related to the coupled substitution $2(\text{Nb} + \text{Ta})^{5+} \rightleftharpoons \text{Ti}^{4+} + \text{W}^{6+}$ at the *B* site. Pyrochlore-group minerals from Latium have significantly high REE contents (up to 7.75 wt.% oxide). Chondrite-normalized patterns follow the general trend typical of unaltered pyrochlore, *i.e.*, with an extreme Ce-enrichment and a decrease toward the heavy REE.

Keywords: pyrochlore-group minerals, unit-cell parameters, electron-microprobe data, back-scattered-electron images, crystal chemistry, Latium, Italy.

SOMMAIRE

Nous présentons ici les résultats d'une étude cristalchimique d'une suite de minéraux du groupe du pyrochlore provenant de blocs syénitiques holocristallins éjectés lors d'éruptions pyroclastiques d'âge plio-pléistocène au Latium, en Italie centrale. Malgré leurs teneurs élevées en actinides, les échantillons étudiés ne sont pas devenus métamictes grâce à leur formation très récente, comme le montrent les raies bien définies et fines du spectre de diffraction X (méthode des poudres). La dimension *a* mesurée montre une corrélation avec la teneur en (Ti + Fe³⁺) au site *B* de la structure. Conforme à la classification des minéraux du groupe du pyrochlore de l'IMA, telle que modifiée selon la règle des 50% adoptée en 1992, les échantillons sont soit de la bétafite, du pyrochlore ou de l'uranpyrochlore. En comparaison avec les échantillons connus des minéraux du groupe du pyrochlore, ces échantillons ont une teneur très élevée en Ti, jusqu'à 81.3% de Ti relatif à la somme Ti + Nb + Ta, et des quantités importantes mais variables de Zr (jusqu'à 8.44% de ZrO₂, poids) et W (jusqu'à 12.14% de WO₃). Certains cristaux font preuve d'une forte zonation en composition selon la substitution $3\text{Nb}^{5+} + \text{Na}^+ \rightleftharpoons 3\text{Ti}^{4+} + \text{U}^{4+}$. L'accommodation de quantités très élevées de W⁶⁺ pourrait être liée à la substitution couplée $2(\text{Nb} + \text{Ta})^{5+} \rightleftharpoons \text{Ti}^{4+} + \text{W}^{6+}$ au site *B*. Les minéraux du groupe du pyrochlore au Latium

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contiennent des quantités importantes de terres rares (jusqu'à 7.75% des oxydes). Les tracés d'enrichissements normalisés à une chondrite suivent en général le tracé typique d'un pyrochlore non altéré, avec un enrichissement extrême en Ce et une diminution progressive vers les terres rares lourdes.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe du pyrochlore, paramètres réticulaires, données de microsonde électronique, image d'électrons rétrodiffusés, cristallographie, Latium, Italie.

INTRODUCTION

The pyrochlore group comprises a series of cubic oxides containing essential amounts of niobium, tantalum or titanium, and having as general formula $A_{2-m}B_2X_6Y_{1-n} \cdot pH_2O$ (Hogarth 1977). The *A* site is typically occupied by large cations such as Na, Ca, U, Pb, Sr, the rare-earth elements (REE), and Th, and the *B* site predominantly contains smaller, more highly charged cations, including Nb, Ta, W, Ti, Zr and Fe^{3+} . Of the anions, *X* is oxygen, and *Y* is O, OH and F. Values of *m* range from 0 to 2, *n*, from 0 to 1, and *p*, from 0 to 1. Vacancies are possible at the *A* and *Y* sites. The structure of pyrochlore is intimately related to that of fluorite and zirconolite (Pyatenko 1959, Chakoumakos 1984). In particular, it can be derived from that of fluorite (MX_2 , where *M* represents the cation) by removing 1/8 of the anions in an ordered manner, and as a consequence only half of the cations in pyrochlore are eight-fold coordinated, whereas the other half are six-fold coordinated (Smith & Lumpkin 1993). The structure of pyrochlore can alternatively be described as two interpenetrating three-dimensional networks (Subramanian *et al.* 1983, Smith & Lumpkin 1993): a B_2X_6 framework of octahedra and an A_2Y framework of tetrahedra, with both the *A* and the *Y* sites located within tunnels along [110] within the B_2X_6 framework. This latter description facilitates an understanding of the occurrence of defect pyrochlore structures, where *A* and *Y* adopt less than their ideal values. Pyrochlore-group minerals commonly are metamict owing to the alpha decay of constituent actinide elements (Lumpkin *et al.* 1986), which causes structural damage. Associated with metamictization, the mineral is susceptible to alteration, with a loss of ions from the *A* site and the incorporation of large ions such as K, Sr, Ba, Pb or H_2O into the structure (van der Veen 1963, Lumpkin & Ewing 1995, 1996).

In this paper, we describe the compositional variation observed in the pyrochlore-group minerals occurring in several holocrystalline ejecta scattered throughout the volcanic complexes of Latium in central Italy. We present a series of compositional substitutions that reflect the wide compositional ranges that are observed. This study constitutes a further contribution to the exotic mineralogy of the volcanic ejecta from Latium, building on several published descriptions of these ejecta (*e.g.*, Della Ventura *et al.* 1996, 1999a,

1999b, Bellatreccia *et al.* 2002; for pyrochlore-group minerals, in particular, see De Casa *et al.* 1986).

OCCURRENCE AND DESCRIPTION OF THE SAMPLES

The pyrochlore crystals described here occur within the holocrystalline ejecta (Della Ventura *et al.* 1992, Renzulli *et al.* 1995, 1998) that are commonly present in some pyroclastic deposits of the Roman Comagmatic Region (Washington 1906). This Plio-Pleistocene volcanic area extends from southern Tuscany to Campania in central Italy and is divided into four main complexes (Fig. 1), as well as several minor ones. In Table 1, we summarize the samples studied, their localities and characteristic assemblages of minerals.

Pyrochlore-group minerals from the Latera volcanic center (Vulsini complex)

Sample SFP1 was collected from the Case Collina pumice quarry, within the so-called "vulcanite complessa di Pitigliano", a pyroclastic formation (Nicoletti *et al.* 1979). Syenitic ejecta from this locality are well known for the diversity of rare or new minerals that they contain (*e.g.*, Orlandi *et al.* 1977, Merlino *et al.* 1996); see also Renzulli *et al.* (1995, 1998) for petrological and geochemical descriptions. The host rock-type for the pyrochlore described here is a saturated syenite (Renzulli *et al.* 1998), with the main constituents being K-feldspar, plagioclase, biotite and minor quartz. Accessory minerals, observed under the binocular microscope within miarolitic cavities and with an analytical SEM in thin section, include zircon, thorite, pyrochlore, stillwellite and a (Ca,REE) silicophosphate close in composition to cheralite. One crystal of pyrochlore was extracted from the rock, its cell parameters were determined by X-ray diffraction (XRD) using a Gandolfi camera, and its composition was established by electron-probe micro-analysis (EPMA).

Pyrochlore-group minerals from the Vico volcanic center

Samples D22, 1FE4 and EPV1 were collected at three different localities (Table 1) of the Vico area, all within the pyroclastic flow deposit known as "ignimbrite C" (Locardi 1965); samples 8EC8 and 2EC5 were

collected from “ignimbrite A” of Locardi (1965). The host rocks can be classified as syenitic to feldspathoid-bearing syenitic ejecta, and their minerals have been described in several recent papers (*e.g.*, Della Ventura *et al.* 1999a, b, Oberti *et al.* 1999, Bellatreccia *et al.* 2002). The samples are predominantly composed of K-feldspar, plagioclase, biotite, clinopyroxene \pm feldspathoid (predominantly sodalite). Accessory minerals include magnetite, titanite, zircon, thorite, hellandite, stillwellite, zirconolite, britholite, REE-bearing phosphates and silicophosphates, pyrochlore, helvite and gadolinite. Analytical SEM studies reveal an exotic assemblage of accessory minerals, particularly in sample EPV1, which contains (Pb,Mn)-oxides (possibly coronadite?), Th-rich uraninite, the rare end-member pollucite ($\text{CsAlSi}_2\text{O}_6$), together with dispersed sulfides (pyrite) and (Ba,Sr) sulfates. Fluorite is commonly present as a late-stage mineral coating the cavities, and (Th,U)-bearing zirconolite also was observed. Two crystals of pyrochlore (Table 1) were extracted from sample 1FE4, three from 2EC5, three from 8EC8, and one each from EPV1 and D22. For three of these crystals (samples 1FE4, D22 and EPV1), we were able to obtain both XRD patterns (using a Gandolfi camera) and EPMA data from the same crystals.

Pyrochlore-group minerals from the Sacrofano caldera (Sabatini volcanic center)

Two samples (EMC3 and PR-up, Table 1) were collected from the “upper pyroclastic flow” of the Sacrofano caldera in the Sabatini volcanic group (De Rita *et al.* 1983). These samples, classified as “type-A holocrystalline ejecta”, were originally described by Della Ventura *et al.* (1992). They are composed of K-feldspar, plagioclase, biotite, clinopyroxene, magnetite, a feldspathoid (nepheline–sodalite) and andradite. Accessory minerals include titanite, zircon, allanite-(Ce), baddeleyite, pyrochlore, vanadinite, REE-bearing silicophosphates (cheralite), dispersed barite and pyrite. Several phases, including a (Bi,Pb) vanadate and a Pb oxide (or carbonate), were identified only using an analytical SEM, and have not yet been fully characterized. Two crystals of pyrochlore were extracted from sample PR-up, and one from EMC3 (for which both XRD and EPMA data were obtained).

Pyrochlore-group minerals from the Alban Hills area

One sample (SFA1, Table 1) was collected from inside the Albano Crater Lake, within the hydro-magmatic unit number IV that forms part of the final hydromagmatic phase of the Albano eruptive center

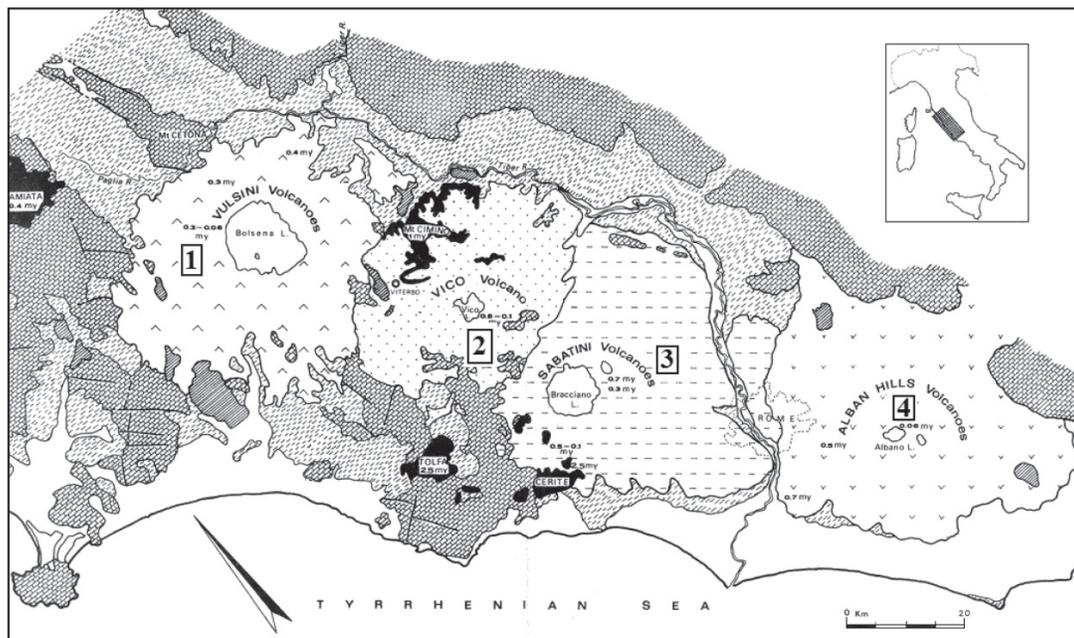


FIG. 1. Schematic geological map of Latium. The areas sampled are numbered. From Locardi *et al.* (1976), modified.

TABLE 1. SUMMARY OF PYROCHLORE SAMPLES STUDIED, ARRANGED ACCORDING TO THE VOLCANIC CENTER, WITH LABEL, LOCALITY AND ASSOCIATED MINERALS INDICATED

Sample label	Pyrochlore-group species	Locality	Associated accessory minerals	Host unit
Vulsini				
SFP1	Betafite	Case Collina, Pitigliano (GR)	Thorite, zircon, stillwellite, REE phosphate	Saturated syenite, within the "vulcanite complessa di Pitigliano" (Renzulli <i>et al.</i> 1998)
Vico				
EPV1	Betafite	Tre Croci, Vetralla (VT)	Fluorite, titanite, thorite, (Pb,Mn) oxide, uraninite, barite, monazite, hellandite, pollucite, Fe sulfide	Feldspathoid-bearing syenite, within ignimbrite "C" (Locardi 1965)
1FE4	Betafite	Mt. Fogliano, Vetralla (VT)	Titanite, zircon, britholite, zirconolite, hellandite, stillwellite	Saturated syenite, within ignimbrite "C" (Locardi 1965)
2EC5	Betafite	Fosso Paliano, Capranica (VT)	Titanite, zircon, hellandite, thorite, vonsenite	Saturated syenite, within ignimbrite "C" (Locardi 1965)
8EC8	Betafite	Fosso Caiolo, Capranica (VT)	Titanite, britholite, monazite, REE silicophosphate	Feldspathoid-bearing syenite, within ignimbrite "A" (Locardi 1965)
D22	Betafite	Fosso Paliano, Capranica (VT)	Titanite, zircon, apatite, hellandite, stillwellite, thorite, vonsenite, helvite, gadolinite	Saturated syenite, within ignimbrite "C" (Locardi 1965)
Sabatini				
EMC3	Pyrochlore s.s.	Mt. Cavalluccio, Sacrofano (Rome)	Baddeleyite, allanite, REE silicophosphate, vanadinite, barite, Fe sulfide, (Bi,Pb) vanadate, Pb oxide	Feldspathoid-bearing syenite, within the "upper pyroclastic flow" (De Rita <i>et al.</i> 1983)
PR-up	Pyrochlore s.s.	Mt. Tozzo, Sacrofano (Rome)	Zircon, baddeleyite, allanite	Feldspathoid-bearing syenite, within the "upper pyroclastic flow" (De Rita <i>et al.</i> 1983)
Alban Hills				
SFA1	Uranpyrochlore	Albano Laziale (Rome)	Apatite, fluorite, baddeleyite, pyrochlore, zirconolite and REE silicophosphate	IV th hydromagmatic unit (De Rita <i>et al.</i> 1995)

(*e.g.*, De Rita *et al.* 1995). The host rock is a feldspathoid-bearing syenite predominantly containing K-feldspar, biotite, nepheline and magnetite. Accessory minerals include apatite, fluorite, baddeleyite, pyrochlore, zirconolite and REE-bearing silicophosphates close to cheralite in composition. One pyrochlore crystal was extracted from this rock and analyzed by both XRD and EPMA.

EXPERIMENTAL METHODS

Electron-microprobe analyses were undertaken at the Natural History Museum, London, and Museum National d'Histoire Naturelle, Paris, using a Cameca

SX50 wavelength-dispersion instrument operated at 20 kV accelerating voltage and 20 nA beam current. Standards used were a combination of well-characterized minerals, synthetic compounds and pure metals. Background positions, particularly for the rare-earth elements, were carefully selected to avoid contributions from potentially interfering lines, and corrections were made for interfering elements following the procedure given in Williams (1996). The structural formulae were calculated according to Lumpkin *et al.* (1986), with the assumption that the sum of (Nb + Ta + Ti + W + Sn + Fe³⁺) at the B site is equal to 2. Back-scattered-electron (BSE) images and energy-dispersion analyses were obtained at LIME (Laboratorio Interdipartimentale di

Microscopia Elettronica, Università Roma Tre) using a Philips XL30 analytical scanning electron microscope (SEM) equipped with a super UTW nitrogen-cooled EDAX detector, and at the Natural History Museum, London, using a JEOL LV5900 analytical SEM.

X-ray powder-diffraction patterns were obtained on single crystals manually extracted from the rock specimens. Individual crystals were mounted in a Gandolfi camera (114 mm diameter), and irradiated with $\text{CuK}\alpha$, Ni-filtered radiation (at 40 kV, 20 mA) for an exposure time of 50 to 80 hrs, depending on the dimensions of the crystal.

Unpolarized-light FTIR spectra were collected at the University of Roma Tre from a single doubly polished crystal from sample D22 using a Nicolet NicPlan microscope equipped with a KBr beam splitter and an MCT nitrogen-cooled detector. This technique was used to indicate whether any secondary alteration had occurred, as revealed by the presence of H_2O present in the crystal structure. However, no absorptions due to OH or H_2O were found in the OH-stretching region. Although this is not conclusive evidence for the absence of alteration in all samples (only two small crystals were analyzed), we saw no evidence for processes of secondary alteration in any of the pyrochlore samples from Latium.

X-RAY DIFFRACTION

The XRD powder patterns for all pyrochlore-group minerals from Latium display sharp lines, indicative of a high degree of crystallinity despite the high contents of actinide elements. They are very similar to the X-ray pattern of calciobetafite from the Phlegrean Fields (Mazzi & Munno 1983). The non-metamict nature of pyrochlore-group minerals from Latium reflects the young age of formation of these minerals, and is analogous to the crystalline nature of coexisting actinide-rich zirconolite from the same area (Bellatreccia *et al.* 2002). Lumpkin *et al.* (1994) observed a good correlation between the concentration of actinides, the degree of metamictization and age of crystallization for both these minerals. On the basis of these correlations, one would predict highly crystalline structures for the Latium actinide-rich minerals.

All X-ray lines were fully indexed on the basis of the $Fd3m$ space group of pyrochlore, and the cell dimen-

sions were refined using the conventional Appleman & Evans (1973) least-square program (Table 2). As already shown by Ginzburg *et al.* (1958) and Hogarth (1961), there is a well-defined relationship between the a cell-dimension parameter and the $(\text{Ti} + \text{Fe}^{3+})$ content at the B site of the structure (Fig. 2). The data of Hogarth (1961) for heated (metamict) samples of pyrochlore are also included in Figure 2.

CHEMICAL COMPOSITION AND NOMENCLATURE

A total of 278 microprobe analyses on 15 pyrochlore grains from 9 samples were obtained. The majority of these analyses were made in rim-to-core traverses across compositionally zoned grains, and the data combined in the crystal chemical diagrams. Average compositions are presented in Table 3.

B-site populations and nomenclature

According to the recommended IMA classification scheme (Hogarth 1977), the nomenclature of pyrochlore is essentially based on the relative amounts of Ti, Nb and Ta at the B site. In the pyrochlore-group minerals from Latium, Ti and Nb are the major constituents in the B site (Table 3), with Ta virtually absent (maximum 1.97 wt.% Ta_2O_5 in sample PR-up2). The majority of the microprobe data, when plotted in the ternary Ti–Nb–Ta diagram modified according to Nickel (1992), as suggested by the reviewers, plot within the betafite subgroup field (samples from Vulcini and Vico);

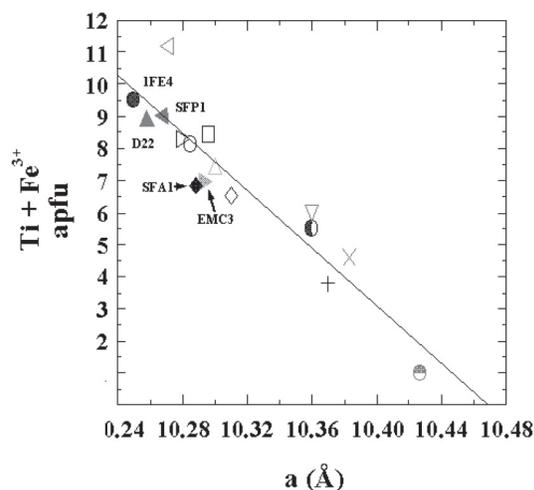


FIG. 2. Relation between the $(\text{Ti} + \text{Fe}^{3+})$ content of pyrochlore-group minerals from Latium (in atoms per formula unit, apfu) versus the a cell-edge. Filled symbols: this work (see Table 1 for sample labels). Other symbols: heated samples of pyrochlore from Hogarth (1961).

TABLE 2. REFINED UNIT-CELL PARAMETERS FOR PYROCHLORE-GROUP MINERALS FROM LATIUM

Sample	a (Å)	V (Å ³)	Sample	a (Å)	V (Å ³)
D22	10.257(8)	1079.3	EMC3	10.294(2)	1090.9
IFE4	10.249(8)	1076.8	SFA1	10.288(1)	1088.9
SFP1	10.267(4)	1083.2	CF	10.298(1)	1092.0

CF: calciobetafite from Campi Flegrei (Mazzi & Munno 1983).

some samples from Sabatini and Alban Hills plot in the pyrochlore subgroup field (Fig. 3). In comparison with the data for pyrochlore-group minerals reported in the literature, the samples studied here have extremely high Ti contents (up to 81.3% *apfu* Ti relative to the Ti + Nb + Ta = 100%). To our knowledge, this is the highest Ti value so far recorded. Relatively high amounts of Ti were previously reported only from metamict betafite (maximum relative Ti content ~66%) from Finland, described by Lumpkin & Ewing (1996). However, these authors assigned the high Ti content of their samples to the leaching of some elements due to a late episode of alteration, with a consequent relative enrichment in Ti. All samples from Latium are crystalline (see below) and do not show signs of secondary alteration; thus, we contend that the high Ti content is primary.

Pyrochlore-group minerals from Latium also have variable contents of Zr and W (Table 3), in some cases to relatively high concentrations. The level of tungsten, in particular, varies widely. It is relatively low for samples from the Alban Hills and Sacrofano, but exceptionally high in samples from Vico (up to 12.14 wt.% WO_3 , sample 2EC5) and Latera (up to 10.41 wt.% WO_3 , sample SFP1). To our knowledge, these are amongst the highest WO_3 contents recorded in pyrochlore-group minerals: the highest value so far (~12 wt.% WO_3) is reported for betafite from Adamello, Italy (e.g., Lumpkin *et al.* 1999). A tungsten-rich pyrochlore-

group mineral has also been described by Ohnenstetter & Piantone (1992) from the Massif Central, France (4.42 wt.% WO_3). In Latium, it is noteworthy that minerals of tungsten, scheelite (CaWO_4) and ferberite (FeWO_4), occur as late-crystallizing phases associated with Th-, U- and REE-bearing accessory phases within the syenitic ejecta collected at Capranica (VT) in the Vico complex (Bellatreccia *et al.* 1999).

Zirconium also has a wide range of concentration, with the highest value recorded in pyrochlore *sensu stricto* from Sacrofano (8.44 wt.% ZrO_2). The Zr contents of betafite from Vico seems to be associated with the pyroclastic deposit: those samples of betafite from the "C" ignimbrite (three samples) have relatively low Zr contents (up to 0.55 wt.% ZrO_2), whereas betafite from sample 8EC8, collected within the "A" ignimbrite, has a high Zr content (up to 5.04 wt.%). Betafite from Latera also has very low Zr contents (up to 0.03 wt.% ZrO_2). In the mineralogical literature, comparable levels of Zr are reported for pyrochlore *sensu stricto* from the Alnö carbonatite, Sweden (3.24 wt.%, Lumpkin & Ewing 1995), from the Amba Dongar carbonatite, India (2.54 wt.%, Ghose *et al.* 1997), and from the Kovdor carbonatite, Kola Peninsula (3.09 wt.%, Williams 1996). The highest reported content of Zr in pyrochlore is from the San Vicente carbonatite, Cape Verde (10.25 wt.% ZrO_2 , Hodgson & Le Bas 1992).

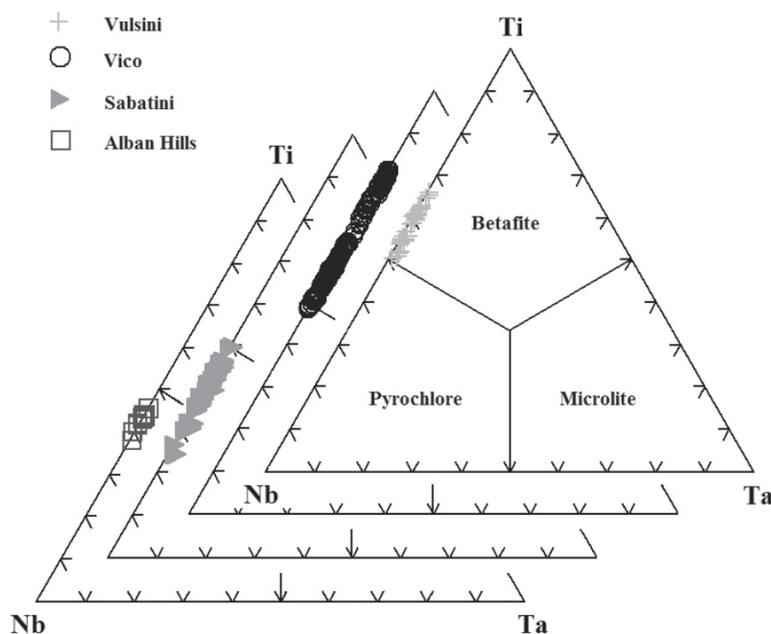


FIG. 3. EPMA data for pyrochlore-group minerals from Latium projected onto the Nb-Ta-Ti triangular diagram (Hogarth 1977), modified according to the 50% rule as recommended by Nickel (1992).

TABLE 3. SELECTED RESULTS OF ELECTRON-MICROPROBE ANALYSES OF PYROCHLORE-GROUP MINERALS

Sample # points	Vico suite						Sabatini, Vulsini and Alban Hills suites				
	IFE4-1 24	IFE4-2 27	8EC8 25	D22 20	2EC5 14	EPV1 25	EMC3 10	PR-up1 23	PR-up2 10	SFP1 33	SFA1 11
WO ₃	0.74(1.77)	0.48(1.14)	1.20(0.31)	5.81(0.83)	6.64(2.07)	0.75(0.25)	0.00(0.00)	0.00(0.00)	0.01(0.04)	2.47(2.58)	0.00(0.01)
Nb ₂ O ₅	22.07(1.83)	24.96(2.38)	26.66(0.87)	23.86(0.74)	16.29(2.08)	27.77(0.95)	33.03(2.03)	35.57(3.70)	42.53(2.23)	23.17(1.44)	32.06(2.07)
Ta ₂ O ₅	0.36(0.15)	0.43(0.14)	0.40(0.18)	0.55(0.20)	0.47(0.25)	0.44(0.13)	0.82(0.13)	0.69(0.29)	1.56(0.51)	0.70(0.37)	0.44(0.14)
SiO ₂	0.00(0.00)	0.00(0.00)	0.01(0.03)	0.00(0.00)	0.01(0.01)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.07(0.30)	0.00(0.00)
TiO ₂	21.12(0.77)	20.13(0.98)	16.61(0.49)	20.38(0.87)	23.29(1.88)	19.88(0.44)	15.35(0.92)	15.21(1.40)	10.35(1.11)	19.73(2.60)	14.53(0.41)
ZrO ₂	0.06(0.16)	0.04(0.08)	4.38(0.55)	0.18(0.14)	0.06(0.06)	0.11(0.05)	1.07(0.05)	0.59(1.11)	3.06(3.81)	0.00(0.01)	1.56(1.18)
SnO ₂	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.10(0.36)	0.00(0.00)	0.03(0.03)	0.00(0.00)	0.00(0.00)	0.58(0.97)	0.09(0.07)
UO ₂	33.68(1.20)	32.32(1.85)	29.38(0.91)	29.36(0.87)	30.13(1.89)	30.28(0.62)	22.11(1.99)	22.86(4.68)	14.74(7.43)	30.43(2.11)	27.33(0.65)
ThO ₂	0.89(0.79)	1.13(0.85)	0.56(0.11)	0.44(0.18)	0.69(0.34)	0.48(0.17)	2.84(0.36)	2.20(1.56)	1.81(1.71)	0.51(0.25)	0.44(0.07)
Y ₂ O ₃	0.03(0.07)	0.03(0.06)	0.05(0.05)	0.01(0.03)	0.16(0.07)	0.02(0.03)	0.01(0.02)	0.00(0.02)	0.00(0.00)	0.22(0.11)	0.01(0.02)
La ₂ O ₃	0.04(0.05)	0.16(0.17)	0.23(0.04)	0.09(0.03)	0.12(0.05)	0.06(0.04)	0.10(0.04)	0.17(0.07)	0.64(0.33)	0.17(0.06)	0.13(0.09)
Ce ₂ O ₃	0.44(0.26)	0.93(0.74)	0.57(0.16)	0.37(0.14)	1.01(0.19)	0.36(0.10)	0.77(0.14)	1.20(0.26)	2.26(1.56)	0.82(0.23)	0.45(0.12)
Pr ₂ O ₃	0.06(0.07)	0.07(0.08)	n. a.	0.07(0.08)	0.14(0.16)	n. a.	n. a.				
Nd ₂ O ₃	0.10(0.09)	0.20(0.20)	n. a.	0.27(0.08)	0.24(0.19)	n. a.	n. a.				
Sm ₂ O ₃	0.03(0.04)	0.04(0.05)	n. a.	0.04(0.04)	0.02(0.02)	n. a.	n. a.				
Fe ₂ O ₃	0.53(0.19)	0.68(0.22)	1.04(0.11)	0.77(0.17)	0.32(0.06)	1.13(0.12)	0.75(0.05)	0.75(0.11)	0.52(0.19)	0.34(0.11)	0.98(0.21)
Sb ₂ O ₃	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.06(0.24)	0.00(0.00)	0.05(0.06)	0.00(0.00)	0.00(0.00)	0.15(0.22)	0.19(0.22)
CaO	14.20(0.21)	14.22(0.24)	14.42(0.34)	13.74(0.15)	12.20(0.40)	14.08(0.18)	15.77(0.16)	16.27(0.47)	13.25(0.92)	10.78(1.05)	14.52(0.44)
BaO	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.01(0.03)	0.04(0.07)	0.00(0.00)	0.00(0.00)
SrO	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.02(0.06)	0.17(0.16)	0.00(0.00)	0.00(0.00)
PbO	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.01(0.02)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)
MnO	0.33(0.21)	0.42(0.27)	0.31(0.03)	0.46(0.05)	0.60(0.13)	0.31(0.02)	0.17(0.04)	0.14(0.10)	0.15(0.14)	0.60(0.24)	0.16(0.05)
Na ₂ O	2.34(0.23)	2.37(0.31)	1.70(0.18)	2.50(0.18)	2.49(0.31)	2.53(0.07)	2.13(0.16)	2.74(0.30)	4.66(0.19)	3.19(0.53)	2.42(0.44)
K ₂ O	0.00(0.00)	0.00(0.00)	0.06(0.01)	0.06(0.01)	0.05(0.01)	0.06(0.01)	0.06(0.01)	0.00(0.00)	0.00(0.00)	0.17(0.59)	0.06(0.01)
F	0.24(0.18)	0.29(0.17)	0.00(0.00)	0.00(0.00)	0.02(0.07)	0.00(0.00)	0.49(0.12)	1.11(0.40)	2.16(0.37)	0.12(0.14)	0.29(0.10)
Total	97.26	98.90	97.58	98.58	94.71	98.26	95.56	99.91	98.31	94.22	95.66
O = F	0.10	0.12	0.00	0.00	0.01	0.00	0.21	0.47	0.91	0.05	0.12
Total	97.16	98.78	97.58	98.58	94.70	98.26	95.35	99.44	97.40	94.17	95.54
Ca	1.146	1.121	1.108	1.035	0.967	1.050	1.216	1.234	1.020	0.867	1.149
U	0.565	0.529	0.469	0.460	0.496	0.469	0.354	0.360	0.236	0.508	0.449
Th	0.015	0.019	0.009	0.007	0.012	0.008	0.047	0.035	0.030	0.009	0.007
Y	0.001	0.001	0.002	0.000	0.006	0.001	0.000	0.000	0.000	0.009	0.000
La	0.001	0.004	0.006	0.002	0.003	0.002	0.003	0.004	0.017	0.005	0.004
Ce	0.012	0.025	0.015	0.010	0.027	0.009	0.020	0.031	0.059	0.023	0.012
Pr	0.002	0.002	-	-	-	-	-	0.002	0.004	-	-
Nd	0.003	0.005	-	-	-	-	-	0.007	0.006	-	-
Sm	0.001	0.001	-	-	-	-	-	0.001	0.000	-	-
Sr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.007	0.000	0.000
Ba	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Mn	0.021	0.026	0.019	0.027	0.038	0.018	0.010	0.008	0.009	0.038	0.010
Pb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sb	0.000	0.000	0.000	0.000	0.002	0.000	0.001	0.000	0.000	0.005	0.006
Na	0.342	0.338	0.236	0.341	0.357	0.432	0.297	0.376	0.649	0.464	0.347
K	0.000	0.000	0.005	0.005	0.005	0.005	0.006	0.000	0.000	0.016	0.006
A site	2.109	2.071	1.869	1.887	1.911	1.904	1.953	2.059	2.038	1.939	1.984
Ti	1.197	1.114	0.896	1.078	1.295	1.041	0.831	0.810	0.560	1.114	0.807
Nb	0.752	0.830	0.864	0.759	0.545	0.874	1.074	1.138	1.382	0.786	1.017
Ta	0.007	0.009	0.008	0.011	0.009	0.008	0.016	0.013	0.030	0.014	0.009
W	0.014	0.009	0.022	0.106	0.127	0.014	0.000	0.000	0.000	0.048	0.000
Zr	0.002	0.001	0.153	0.006	0.002	0.004	0.038	0.020	0.107	0.000	0.056
Fe	0.030	0.038	0.056	0.041	0.018	0.059	0.041	0.040	0.028	0.019	0.054
Sn	0.000	0.000	0.000	0.000	0.003	0.000	0.001	0.000	0.000	0.017	0.003
B site	2.002	2.001	1.999	2.001	2.001	2.000	2.002	2.021	2.107	2.003	2.006
F	0.057	0.067	0.056	0.000	0.005	0.000	0.111	0.248	0.491	0.028	0.068
Si	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000	0.005	0.000

Means and standard deviations are expressed in wt.%. Atom proportions are expressed in atoms per formula unit (apfu). n.a.: not analyzed.

A-site populations and individual species

As recommended by the IMA commission (Hogarth 1977), the individual species within each subgroup are defined on the basis of their relative populations at the A site. In the pyrochlore samples from Latium, the principal cations at the A site are Ca, Na and U, with only minor amounts of Sr, Ba and Pb. For most samples, the sum Ca + Na is greater than 20%, of the A atoms, as is the proportion (Table 3). Therefore, these samples are classified as *betafite* (all samples from Vico and Latera), and *uranpyrochlore* (sample SFA1 from the Alban Hills). Samples from Sacrofano have U less than 20% of the A atoms, thus they are classified as *pyrochlore sensu stricto*. Note that, according to the "50% rule" as required by Nickel (1992) and used here, none of the samples studied by us can be classified as calciobetafite; in addition, the holotype calciobetafite from Phlegrean Fields (Mazzi & Munno 1983) should also be reclassified as a pyrochlore *sensu stricto*, since its Ti/(Ti + Nb + Ta) content amounts to 42%, and thus under the median point of the Nb–Ti join.

CHEMICAL ZONING

Compositional zoning, both primary magmatic and secondary, is a common feature in pyrochlore-group minerals (*e.g.*, Lottermoser & England 1988, Ohnenstetter & Piantone 1992, Wall *et al.* 1996, Hogarth *et al.* 2000), related to the evolution of the physicochemical conditions during the formation of these minerals. High-resolution, detailed BSE images show that some of the crystals studied (*e.g.*, pyrochlore *sensu stricto* from Sacrofano and betafite 1FE4 from Vico) have a pronounced range of zonation patterns. In particular, both crystals extracted from rock sample 1FE4 (Figs. 4a, b) show an irregular, almost sector-like, zonation. Detailed electron-microprobe traverses (Fig. 5) across the crystal show that the core of crystal 1 (Fig. 4a) is enriched in Ti and U, and depleted in Nb, whereas crystal 2 (Fig. 4b), extracted from the same ejectum, shows the inverse relationship, with a core depleted in Ti, Ca and U, and enriched in Nb (and to a lesser extent, in Th). From a crystal-chemical point of view, these patterns are consistent with the substitution $3\text{Nb}^{5+} + \text{Na}^+ \rightleftharpoons 3\text{Ti}^{4+} + \text{U}^{4+}$ (see below).

BSE images show that both crystals from sample PR-up from Sacrofano (Figs. 4c, d) exhibit yet more complex zonation features. A normal systematic core-to-rim zonation can be seen in Figure 4c, but there is a distinctive resorption and overgrowth of complex, irregular nature at the lower margin of this crystal. In the second crystal from this sample (Fig. 4c), remnants of a finely developed, oscillatory, lamellar zoning is present on one side of the grain, with a more patchy zonation (resorption and recrystallization?) developed on the opposite side. We interpret the lamellar zoning to be structurally controlled, with the lamellae parallel

to crystallographic planes of low Miller indices (Shore & Fowler 1996). The zoning in both crystals from specimen PR-up can be described by means of the $\text{Nb}_3\text{NaTi}_3\text{U}_{-1}$ substitutional vector, similar to that for sample 1FE4. Owing to the very fine width of most lamellae at the rim of the second PR-up crystal (Fig. 4d), the precise chemical variations were not resolvable by EMPA. However, there is a general increase in levels of Nb, Na and Th, and a significant decrease in the levels of Ti, Ca and U toward the rim.

CHEMICAL SUBSTITUTIONS

The chemical complexity of pyrochlore arises from the several substitutions possible in its structure. At the B site, Nb and Ta are replaced mostly by lower-valency cations (except W^{6+} , see below), but a large number of atoms with different charges can occupy the A site. Therefore, the chemical substitutions in pyrochlore are mostly heterovalent (with the exception of monovalent $\text{Ti}^{4+} \rightleftharpoons \text{Zr}^{4+}$ substitution in Zr-bearing pyrochlore) and coupled, involving more than one site (*e.g.*, A + B + anionic site). In pyrochlore from Latium, the most obvious substitution at the B site is the $\text{Ti}^{4+} \rightleftharpoons \text{Nb}^{5+}$ exchange (Fig. 6). This heterovalent exchange requires a simultaneous substitution at the A site. Following Hogarth & Horne (1989), the coupled substitution of $^A\text{Na}^+$ with $^A\text{U}^{4+}$ provides the necessary charge balance for the $\text{Ti}^{4+} \rightleftharpoons \text{Nb}^{5+}$ exchange at the B site, and gives rise to the coupled substitution $3\text{Nb}^{5+} + \text{Na}^+ \rightleftharpoons 3\text{Ti}^{4+} + \text{U}^{4+}$ (Fig. 7). The accommodation of extremely high amounts of W^{6+} in pyrochlore from Latium can be related to the coupled substitution $2(\text{Nb} + \text{Ta})^{5+} \rightleftharpoons \text{Ti}^{4+} + \text{W}^{6+}$ at the B site (Fig. 8), as suggested by Ohnenstetter & Piantone (1992) for W-bearing pyrochlore-group minerals from the Massif Central. Other substitutions involving Na, Ca, REE, actinides and the anions F, OH, O are much more complex to decipher.

DISTRIBUTION OF THE REE

The REE, particularly the light REE, substitute for Ca at the A site, and the distribution of the REE can be correlated with the host rock and its pattern of alteration. Average values of the atomic ratio Y/Ce for unaltered pyrochlore-group minerals associated with nepheline syenites, carbonatites and granitic pegmatites, respectively, are 0.16, 0.27 and 1.4 (Lumpkin & Ewing 1995). However, the Y/Ce value may increase with an increase in the degree of alteration of the rock (Burt 1989, Lumpkin & Ewing 1995). Pyrochlore-group minerals from nepheline syenites and carbonatites are typically enriched in Ce and the light REE (*i.e.*, from La to Sm), whereas the heavier REE are strongly depleted, with Y contents also very low, typically up to 0.4 wt.% (Lumpkin & Ewing 1995). Pyrochlore-group minerals from Latium have significantly high REE contents, up to 5.68 wt.% oxide in pyrochlore *sensu stricto* PR-up2

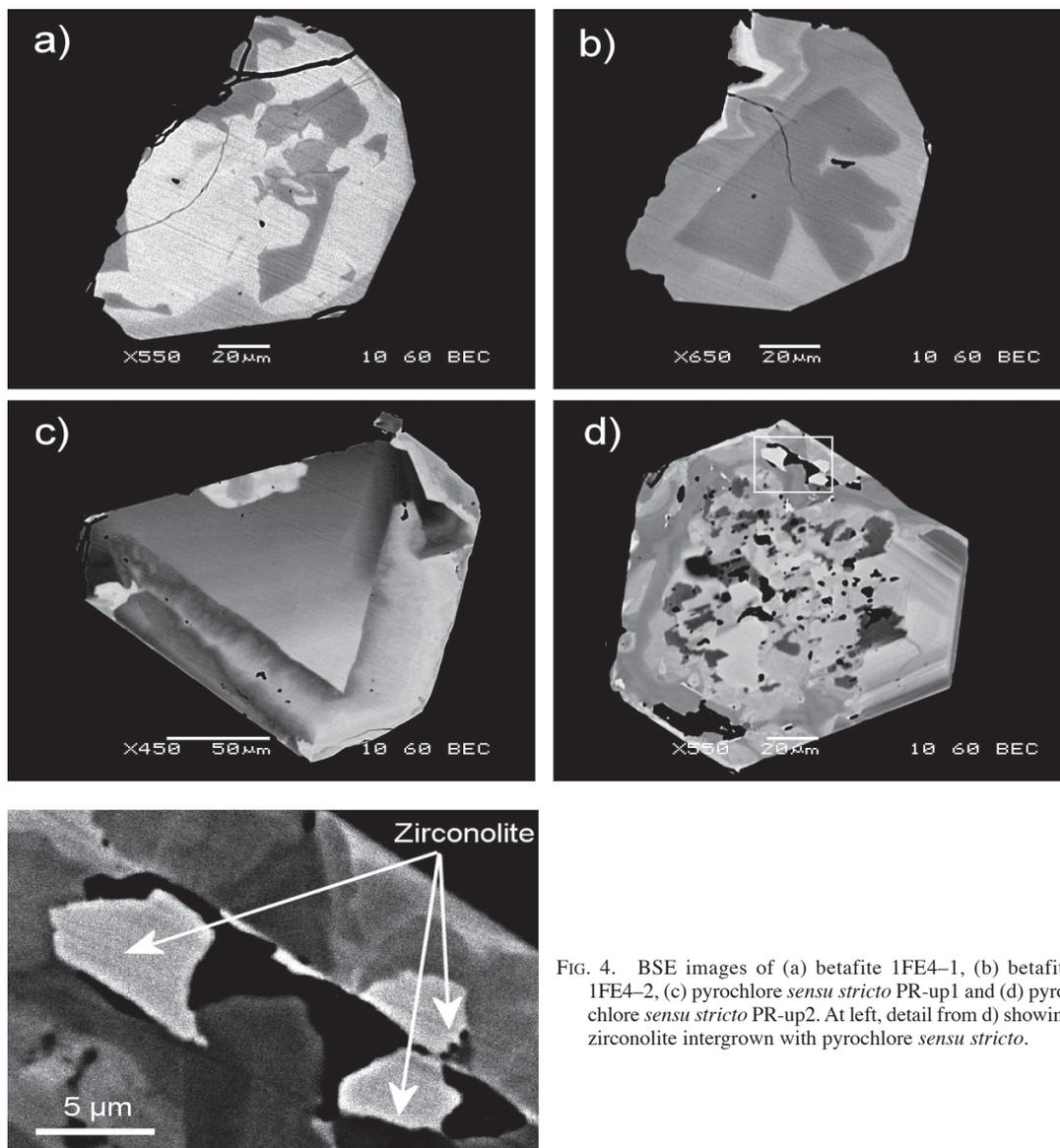


FIG. 4. BSE images of (a) betafite 1FE4-1, (b) betafite 1FE4-2, (c) pyrochlore *sensu stricto* PR-up1 and (d) pyrochlore *sensu stricto* PR-up2. At left, detail from d) showing zirconolite intergrown with pyrochlore *sensu stricto*.

from Sacrofano. Chondrite-normalized patterns (Fig. 9) follow the general trend typically associated with unaltered pyrochlore-group minerals, *i.e.*, with an extreme Ce-enrichment and a decrease toward the heavy REE. This pattern is similar to those observed for several REE-bearing minerals associated with pyrochlore in the ejecta studied (*e.g.*, Della Ventura *et al.* 1999a, b).

CONCLUSIONS

1) Pyrochlore-group minerals are relatively common accessories in the vugs and miarolitic cavities of holo-

crystalline ejecta scattered throughout the volcanic complexes of Latium (Italy).

2) Despite the high concentrations of actinide elements, these minerals are still crystalline, owing to their young age of formation.

3) Pyrochlore-group minerals from Latium can be classified as betafite, pyrochlore *sensu stricto* and uranpyrochlore; some samples are unusually rich in W and, to a lesser extent, Zr.

4) Most samples show pronounced chemical zoning, consistent with the substitution scheme $3\text{Nb}^{5+} + \text{Na}^+ \rightleftharpoons 3\text{Ti}^{4+} + \text{U}^{4+}$ in the structure.

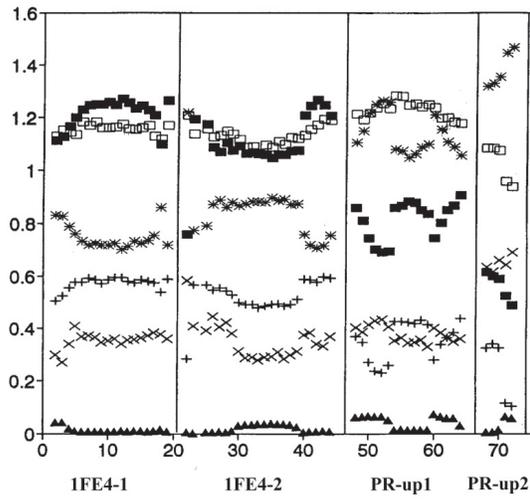


FIG. 5. Compositional variations across the same crystals as in Figure 4. Symbols: Ti^{4+} : black square, U^{4+} : +, Nb^{5+} : *, Ca^{2+} : open square, Na^+ : x, Th^{4+} : black triangle.

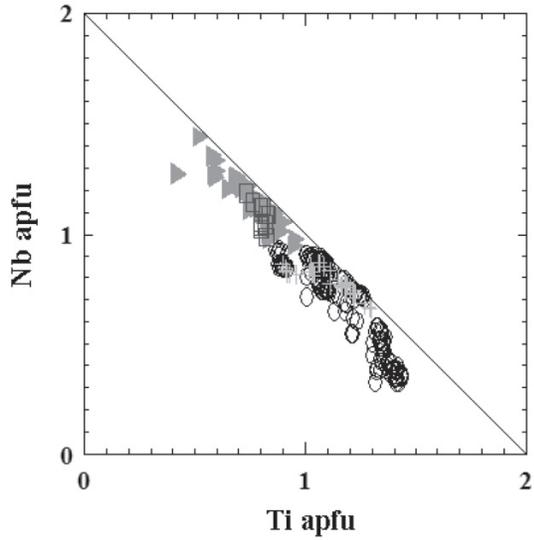


FIG. 6. Relation between the Nb versus Ti content for pyrochlore-group minerals from Latium. Same symbols as in Figure 3.

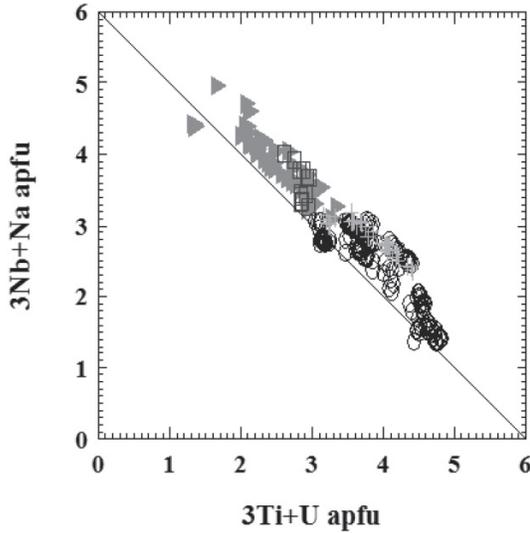


FIG. 7. Relation between the $3Nb + Na$ versus $3Ti + U$ content for pyrochlore-group minerals from Latium. Same symbols as in Figure 3.

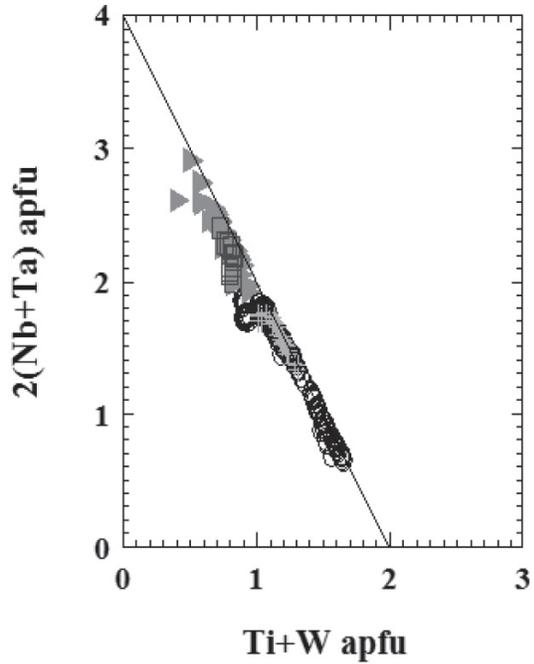


FIG. 8. Relation between the $2(Nb + Ta)$ versus $Ti + W$ content for pyrochlore-group minerals from Latium. Same symbols as in Figure 3.

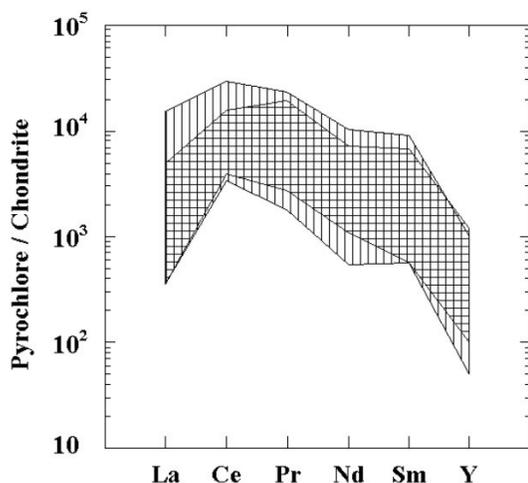


FIG. 9. Chondrite-normalized REE patterns of two betafite crystals extracted from sample 1FE4 (24 and 27 point analyses, respectively).

ACKNOWLEDGEMENTS

Financial support to GDV was supplied by INRM (Istituto Nazionale per la Ricerca Scientifica e Tecnologica sulla Montagna). Thanks are due to A. Mottana, D. Ohnenstetter and R.F. Martin for constructive criticism. Part of the work was done during the stay of GDV at the Museum d'Histoire Naturelle, Paris, thanks to a grant from MNHN, Minéralogie, Paris.

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Received July 7, 2004, revised manuscript accepted October 31, 2005.