

Calciobetafite (new mineral of the pyrochlore group) and related minerals from Campi Flegrei, Italy; crystal structures of polymignyte and zirkelite: comparison with pyrochlore and zirconolite

FIorenzo MAZZI

C.N.R. Centro di Studio per la Cristallografia Strutturale
Istituto di Mineralogia dell'Università
Via A. Bassi 4, Pavia, Italy

AND ROSALBA MUNNO

Istituto di Mineralogia dell'Università
Via Mezzocannone 8, Naples, Italy

Abstract

Polymignyte, zirkelite and zirconolite have often been considered the same mineral. Their occurrence, with calciobetafite (a new member of the pyrochlore group), in a "sanidinite" from Campi Flegrei has allowed their crystal-chemical study and identification as three distinct phases. The three minerals are polymorphs of the compound: $(\text{Ca,Na,REE,Th} \dots)_2^{\text{VIII}}\text{Zr}_2^{\text{VI}}(\text{Ti,Nb} \dots)_3^{\text{VI}}(\text{Fe,Ti})^{\text{V,IV}}\text{O}_{14}$. The crystal structure of zirconolite (space group $C2/c$) has been previously determined (Gatehouse *et al.*, 1981) on synthetic crystals; those of polymignyte (*e.g.*, $Acam$) and zirkelite (*e.g.*, $P3_12$) are described in the present paper. The crystal structures of polymignyte, zirkelite and zirconolite may be derived from that of pyrochlore. Chains, formed by distorted $(\text{Ca,REE} \dots)$ cubes alternating with $(\text{Ti,Nb} \dots)$ octahedra in pyrochlore, are replaced in the remaining minerals by either chains of Zr polyhedra with seven vertices or chains in which $(\text{Ti,Nb} \dots)$ octahedra alternate with distorted $(\text{Fe,Ti} \dots)$ tetrahedra or trigonal bipyramids. The different arrangement of these chains gives rise to the different symmetries of the three phases. The crystal structures of zirkelite and zirconolite are very similar, as they differ only in the stacking of identical pairs of layers of polyhedra. The difficulties in distinguishing the three polymorphs by X-ray powder diagrams are discussed.

Introduction

Calciobetafite, a new species of the pyrochlore group, and related minerals have been found at Monte di Procida (Campi Flegrei, Campania, Italy) in a rock known as "sanidinite". This subvolcanic rock is present in a phreatomagmatic explosion breccia. The age of this pyroclastic formation, determined on an alkali-trachitic obsidian by the K/Ar method (Gillot, pers. comm.) is 0.035 m.y., whereas the absolute age of sanidinite, determined with the same method on the enriched feldspathic fraction, is 0.084 (± 0.008) m.y. (Civetta, pers. comm.). The sanidinite is composed of 75% sanidine (Or_{65}), 16% plagioclase (An_{35}), Mg-hastingsitic amphibole (occasionally with a core of clinopyroxene), biotite, magnetite, apatite and sphene. Minor interstitial glass is also present. Occasional small colored crystals were found scattered throughout the rock: three possible species were tentatively recog-

nized on the basis of their morphology and some optical features: (1) small (0.1–0.2 mm) octahedral crystals, reddish brown in color and isotropic; (2) elongated prisms (maximum 0.4 mm) enclosed in sanidine and sometimes in the interstitial glass bordering the K-feldspar, dark red in color, showing parallel extinction and very weak pleochroism; (3) platy crystals with roughly hexagonal outline; luster resinous, brittle with splintery fracture; black in color and reddish brown in very thin splinters, showing birefringence with extinction parallel to an edge.

By X-ray analyses the three species were identified as a member of the pyrochlore group, polymignyte and zirkelite respectively; the last mineral is always the dominant phase in intergrowths of zirkelite, zirconolite and pyrochlore. Conflicting data have been reported in the literature concerning polymignyte, zirkelite and zirconolite, which have

often been considered the same mineral. As it will be seen later, distinguishing among these three minerals is very difficult: fortunately their occurrence in the sanidinite, as well-developed crystals (not in their usual metamict form), allowed their crystal-chemical study and consequently their identification as three distinct phases.

Previous work and identification of the specimens

Polymignyte, found in a pegmatite from Fredricksvärn (Norway) was first described by Berzelius (1824); more detailed studies of its morphological, physical and chemical properties were reported by Brögger (1890). This material is metamict; Lima-de-Faria (1958, 1964), on the basis of X-ray powder diagrams from the Fredricksvärn mineral heated at 700, 1000 and 1300°C (Table 17), concluded that polymignyte and zirconolite are synonymous. Pudovkina *et al.* (1969) calculated approximate lattice parameters ($a = 10.31$, $b = 14.48$, $c = 7.41 \text{ \AA}$) from the axial ratios given by Brögger (1890) and the unit cell volume, indirectly obtained from molecular weight and density.

The identification of the mineral from Campi Flegrei with polymignyte was made through a comparison of its properties with those given by Brögger: color, luster and particularly the [100] elongation of the crystals, the orthorhombic symmetry and the axial ratios ($a:b:c = 0.712 : 1 : 0.512$ for the Norwegian polymignyte) are the same; also the stoichiometric unit calculated from the chemical analysis by Brögger agrees well with that obtained from our crystals (Table 1). Finally, the measured lattice constants are similar to those calculated by Pudovkina *et al.* (1969).

The definitions of zirkelite and of zirconolite have been a topic of debate and several studies have reached contradictory conclusions. According to Hussak and Prior (1895), who first described the mineral from Jacupiranga (São Paulo, Brazil), zirkelite occurs as cubic crystals flattened parallel to an octahedral face, black in color, transparent in very tiny splinters, with a dark brown color. A complete chemical analysis of this material was subsequently given by Prior (1897) (Table 1). Blake and Smith (1913), after having reexamined the morphology of the Brazilian type material, considered some crystals from Walaweduwa (Ceylon) to be zirkelite. The latter were hexagonal (0001) plates or [0001] prisms, brownish-black in color, opaque or sometimes reddish-brown in thin section. Blake and Smith suggested either hexagonal or trigonal symmetry for

zirkelite and also gave the axial ratio $a : c = 1 : 1.1647$. Actually the zirkelites from the two localities appear different with respect to their contents of Zr and Ti (Table 1), even if the sum of the two oxides and amounts of REE, Ca, Fe and Th are similar. Borodin *et al.* (1956) described the new mineral zirconolite, pseudo-cubic and metamict, similar to zirkelite in several properties, but considered it to be a different species because of the higher REE and lower U and Th contents of the former. These authors suggested the ideal formula unit: $\text{CaZrTi}_2\text{O}_7$ for zirconolite. Further data were given by Borodin *et al.* (1961), who also described a Nb-rich zirconolite. In studying the system $\text{CaO-ZrO}_2\text{-TiO}_2$, Pyatenko and Pudovkina (1964) synthesized the compound $\text{CaZrTi}_2\text{O}_7$, which they identified with the natural zirconolite (or zirkelite, which they considered synonymous). This material is monoclinic: $a = 12.43$, $b = 7.26$, $c = 11.35 \text{ \AA}$, $\beta = 100.34^\circ$. They noted the structural similarities of zirconolite and pyrochlore. In his survey of the minerals of the pyrochlore group, Hogarth (1977) considered zirkelite and zirconolite as synonyms. Recently, Gatehouse *et al.* (1981), working on synthetic crystals, determined the crystal structures of two zirconolites: $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$. The lattice parameters are as follows: $a = 12.445$; $b = 7.288$; $c = 11.487 \text{ \AA}$, $\beta = 100.39^\circ$ for $x = 1.304$, and $a = 12.444$; $b = 7.266$; $c = 11.341 \text{ \AA}$, $\beta = 100.59^\circ$ for $x = 0.850$. Finally the refinement of this monoclinic structure was carried out by Sinclair and Eggleton (1982) on natural crystals of "zirkelite" from Kaiserstuhl.

The examination of the platy crystals from Campi Flegrei led to a clarification of some of the above contradictions. This material always appears as an oriented intergrowth of three crystalline phases: subordinate amounts of pyrochlore and of a monoclinic zirconolite phase (Pyatenko and Pudovkina, 1964 and Gatehouse *et al.*, 1981) and, dominantly, a trigonal phase with an axial ratio $a : c = 1 : 2.317 = 1 : 2 \times 1.159$, fairly similar to that given by Blake and Smith (1913) for zirkelite from Ceylon. *We suggest, therefore, the retention of the name zirkelite for this trigonal phase.*

Chemical composition

Chemical compositions were determined by electron microprobe analysis. However, the scarcity of crystals, the large number of chemical components, and the common lack of suitable standards for unusual chemical elements made it difficult to obtain completely satisfactory results: the sum of the

Table 1. Calciobetafite, polymignyte, zirkelite and zirconolite: chemical analyses and formula units

	Ca-betafite		Polymignyte			Zirkelite and Zirconolite								
	a	b	a	b	Fr	a*	Bzk	Czk	Czk*	Czk**	zi	zi*		
CaO	16.0	16.0	7.6	8.6	6.98	8.6	10.79	6.87	8.55	8.18	11.05	11.00		
Na ₂ O	1.7	1.7		0.4	0.59						0.37	1.40		
La ₂ O ₃	0.7	0.7	n.a	0.8	5.13	0.7								
CeO ₂	4.0	4.0	n.a	3.7	6.20	2.6	2.64	} 2.68	} 0.32		6.52	4.19		
Pr ₂ O ₃	n.a	0.6	n.a	0.6		n.a.								
Nd ₂ O ₃	1.2	1.4	n.a	2.3		2.1								
Y ₂ O ₃	0.6	0.6	n.a	2.5	2.26	2.4	0.21	1.08						
ThO ₂	n.a	4.5	n.a	3.5	3.92	n.a	7.31	20.44	8.33	0.23	0.58	2.90		
UO ₂	n.a	4.8	n.a	0.7		n.a	1.40	1.02	4.48	13.77	1.47	0.38		
ZrO ₂	1.1	1.0	25.4	25.8	29.71	23.7	52.89	30.73	34.19	35.27	32.84	25.00		
MnO		n.a	0.9	n.a	1.32				0.03		0.06	0.38		
MgO		n.a	0.2	n.a	0.16		0.22	2.34	1.33	1.96	0.45			
FeO	1.9	2.0	8.7	8.0	2.08	8.1	7.72	4.07	4.72	3.73		6.00		
Fe ₂ O ₃					7.66						5.49	1.11		
Al ₂ O ₃		n.a	0.4	n.a	0.19						1.03			
TiO ₂	14.3	15.0	18.0	19.5	18.90	18.1	14.95	29.50	36.26	34.87	31.69	18.19		
Nb ₂ O ₅	27.5	32.9	n.a	12.7	11.99	10.5					3.26	24.84		
Ta ₂ O ₅	n.a	2.4	n.a	0.6	1.35	n.a						2.00		
F	1.3	n.a	n.a	n.a		n.a						0.60		
Rem.					2.04		1.02	0.84	1.70	2.12	5.40	2.48		
Total	69.8§	87.6	61.2	89.7	100.48	76.8	99.15	99.60	99.88	100.13	100.21	100.22§		

Formula unit based on 14 oxygens:

Ca,Na	3.05	1.49	1.17	1.55	1.65	1.02	1.18	1.14	1.60	1.91
REE	0.40	0.59	0.71	0.54	0.14	0.21	0.01	0.29	0.29	0.19
Th	0.15	0.12	0.12		0.24	0.64	0.24	0.01	0.02	0.09
U	0.16	0.02			0.04	0.03	0.13	0.40	0.04	0.01
Total (Ca,Na,REE,Th,U)	3.76	2.22	2.00	2.09	2.07	1.90	1.56	1.55	1.95	2.20
Zr	0.07	1.87	1.97	1.94	3.67	2.08	2.14	2.23	2.04	1.61
Fe,Mn,Mg,Al	0.25	1.00	1.24	1.14	0.97	0.95	0.76	0.78	0.77	0.81
Ti	1.68	2.18	1.94	2.28	1.60	3.07	3.50	3.40	3.04	1.80
Nb,Ta	2.32	0.88	0.79	0.80					0.19	1.55
Total (Fe,..Ti,Nb,..)	4.25	4.06	3.97	4.22	2.57	4.02	4.26	4.18	4.00	4.16
Total cations	8.08	8.15	7.94	8.25	8.31	8.00	7.96	7.96	7.99	7.97

Fr: polymignyte from Fredricksvärn. Rem. is SiO₂ 0.45, PbO 0.39, SnO₂ 0.15, K₂O 0.77, H₂O 0.28 (Brögger, 1890).

a*: intergrowth of zirkelite, zirconolite and pyrochlore. a, a* : incomplete analyses.

Bzk: zirkelite from Brazil. Rem. is H₂O (Prior, 1897).Czk: three zirkelites from Ceylon with different amounts of Th and U. Rem. is: Czk PbO 0.38, H₂O 0.46; Czk* H₂O 1.70; Czk** PbO 0.44, H₂O 1.68 (Blake and Smith, 1913).zi: zirconolite. Rem. is SiO₂ 2.05, H₂O 3.35; zi*: Nb-rich zirconolite. Rem. is H₂O (Borodin et al., 1961)

§ after subtraction of O = F. n.a : not analyzed.

oxides is much less than 100% even though it could be increased (roughly 1%) to account for those rare earths, which were not analyzed. Nevertheless, the formula units derived from the chemical analyses appear fairly reliable and in good agreement with the results of the crystal structure determinations.

Sets of analyses were carried out by us in the

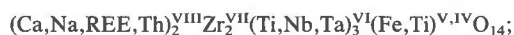
Institute of Mineralogy of Modena University (marked with *a* in Table 1) and by W. L. Griffin at the Mineralogisk-Geologisk Museum of Oslo, Norway (marked with *b* in the same table). Apparatus and techniques used for the chemical analyses were as follows: (a) ARL-SEM-Q electron microprobe operated in the wavelength dispersive mode; (b) ARL-

EMX microprobe: the major elements were measured by energy-dispersive techniques and the rare earths by WDS (Åmli and Griffin, 1975).

Table 1 summarizes the results obtained on the samples from Campi Flegrei together with some other analyses of polymignyte, zirkelites and zirconolites taken from the literature. The formula units were calculated for 14 oxygens (including fluorine) and only those obtained from the analyses with the highest oxide sum are given in Table 1.

According to the chemical classification of pyrochlores: $A_2B_2O_6$ (O,F) (Hogarth, 1977), "pyrochlore" from Campi Flegrei may be considered as a new species, since it fills a void (Ca dominant in A) in the list of the minerals of the betafite subgroup ($2Ti > Nb+Ta$ in B). After the resolution of the IMA Subcommittee on Nomenclature of the Pyrochlore Group, its name is *calciobetafite*.

Nearly all the calculations and the results of the crystal structure determinations, which will be seen in a following section, suggest the same crystal-chemical formula unit for all three minerals, polymignyte, zirkelite and zirconolite:



only the analysis of the original zirkelite by Prior (1897) shows a Zr amount nearly double those obtained from the remaining analyses.

The following points are emphasized: (1) Zirconium, almost absent in calciobetafite from Campi Flegrei, is an essential component of the remaining minerals; it apparently replaces (Ca,REE, .) (Table 1), but, as will be seen in a following section, (Ti,Nb, . .) are also involved in the replacement. (2) Very likely, iron is also an essential component of natural polymignyte, zirkelite and zirconolite, although the synthetic zirconolites studied by Pyatenko and Pudovkina (1964) and by Gatehouse *et al.* (1981) contain no iron. (3) The above formula unit is to some extent a theoretical one: Zr-contents somewhat different from two, and consequent variations in the amounts of the remaining cations, result both from the data of Table 1 and from those of synthetic zirconolites. (4) There is strong evidence that polymignyte, zirkelite and zirconolite are polymorphs of the same chemical compound.

Experimental

General remarks

All X-ray determinations were carried out with an automatic single crystal Philips PW 1100 diffrac-

tometer and with $MoK\alpha$ radiation. The lattice parameters were obtained using a least squares technique applied to the diffraction angles of 25 strong reflections, measured at the center of gravity of the profile of each reflection. Diffraction intensities were measured in the ω -scan mode, and the backgrounds were examined on both sides of each reflection, for a total time equal to that of the scan of the reflection. The intensities of three standard reflections, taken at three-hourly intervals, did not show changes during the data collection larger than 2–3%. A preliminary absorption correction was applied to all intensities to account for the shape of the crystal (North *et al.*, 1968). A further absorption correction was employed assuming that the sample is a sphere with a volume nearly equal to that of the crystal: the intensities were practically unaffected by the latter correction, as the crystals were small. Two or more equivalent reflections were always measured, and their intensities were averaged to obtain a set of independent reflections. Intensities with $F^2/\sigma(F^2)$ greater or equal to a chosen value L were assumed as "observed" and used in the refinements of the crystal structures.

A particular strategy was followed during the refinements to obtain a partial independence of the structural results from those of the chemical analyses: thus, it was possible to verify the consistency of both results. Two sets of scattering factor curves (f_1 and f_2) were used for some cationic sites in the structures: for instance, the f_1 curve for (Ca,Na) and f_2 curve for (REE,Th,U), all these atoms being replaceable cations in the same site. In each curve, the ratios among the atoms were derived from the actual chemical analyses. Scattering factors for neutral atoms were used (*International Tables for X-ray Crystallography*, v. 4, 71–101). The occupancy of each atomic site was then varied during the refinements, made with a locally modified ORFLS program (Busing *et al.*, 1962): for instance the occupancy o_1 of (Ca,Na) was varied against that o_2 of (REE,Th,U), with the constraint $o_1+o_2 = 1$. In the same way the occupancy of Ti was varied against that of (Nb,Ta). Only one scattering curve was employed for the sites occupied by Zr and by Fe, and their occupancies were refined against vacancy if there was evidence of an incomplete filling of the atomic positions. During the refinements of the crystal structures of calciobetafite, polymignyte and zirkelite, the variables which showed high correlation coefficients were alternately treated in separate cycles; the refinement was

terminated when the changes in the variables were lower than the corresponding standard deviations. The coherency between the chemical and site occupancy results was finally verified by comparing the total number of electrons in the cationic positions, derived from the site occupancy refinement, with that obtained from the stoichiometric units of Table 1 (Tables 4, 7 and 11). Table 2 gives a summary of the most relevant conditions used in the data collections and in the refinements. Lattice parameters and space groups are reported in Table 3. The dimensions of C-centered "orthorhombic" multiple cells, obtained from the lattice parameters of the four minerals (calciobetafite, polymignyte, zirkelite and zirconolite) are given in the same table, together with the corresponding transformation matrices of the axes. As zirkelite and zirconolite are present in the same intergrowth, their lattice parameters were obtained from the measurements of the corresponding diffraction angles for non-superposed reflections.

Calciobetafite

The crystal structure of pyrochlore, $(\text{Ca,REE,Th,U,} \dots)_2\text{VIII}(\text{Nb,Ti,} \dots)_2\text{VI}^1\text{O}_6(\text{O,F})$, is well known (Gaertner, 1930): however, as good intensities of the reflections were obtainable, we decided to collect them from a single crystal of calciobetafite from Campi Flegrei and to refine its crystal structure mainly for two reasons: (1) as far as we know, the structural studies on natural crystals were made starting from powder diffraction intensities (*e.g.* Perrault, 1968), and no detailed information has been given until now about the anisotropic tempera-

Table 3. Calciobetafite, polymignyte, zirkelite and zirconolite: lattice parameters

Space group	Ca-betafite	Polymignyte	Zirkelite	Zirconolite								
	Fd3m	Acam	P3 ₁ 2	C2/c								
Unit cells:												
a (Å)	10.2978(5)	10.148(4)	7.287(2)	12.611(5)								
b	10.2978(5)	14.147(5)	7.287(2)	7.311(2)								
c	10.2978(5)	7.278(3)	16.886(9)	11.444(8)								
α (°)	90	90	90	90								
β	90	90	90	100.52(5)								
γ	90	90	120	90								
a:b:c	1:1:1	0.717:1:0.515	1:1:2.317	1.725:1:1.565								
V (Å ³)	1092	1045	776.5	1037								
Z	8 *	4	3	4								
V(14) (Å ³)	273	261	259	259								
Multiple cells:												
a (Å)	12.61	2 x 12.37	12.62	12.61								
b	7.28	7.28	7.29	7.31								
c	17.84	17.41	16.89	4 x 16.88								
α (°)	90	90	90	90								
β	90	90.77	90	89.94								
γ	90	90	90	90								
V _m	1.5 V	3 V	2 V	6 V								
Transformation matrices:												
	-1	0.5	0.5	2	1	0	2	1	0	1	0	0
	0	-0.5	0.5	0	0	1	0	1	0	0	-1	0
	1	1	1	-1	1	0	0	0	1	1	0	6

V = volume of the unit cell; V(14) = volume based on the formula unit with 14 oxygens; V_m = volume of the multiple cell.
 Estimated standard deviations (in parentheses) refer to the last digit.
 * calculated from the usual formula unit with 7 (O,F).

Table 2. Calciobetafite, polymignyte and zirkelite: experimental conditions in data collection and crystal structure refinement

	Ca-betafite	Polymignyte	Zirkelite
Dimensions of the crystal (mm)	0.13x0.13	0.04x0.04	0.05x
Maximum 2θ (°) MoKα	x0.13	x0.40	0.09x0.20
Scan width (°)	60	60	60
Scan speed (°/sec)	1.5	1.8	2.5
Scan speed (°/sec)	0.05	0.09	0.05
Measured reflections	1571	1671	3605
Independent reflections	99	826	907
"Observed" reflections:			
F ₂ /σ(F ₂) ≥ L	75	743	659
L	4	1	2
Variables in refinement	13	71	75
Extinction coefficient (x 10 ⁶)	45(5)	48(2)	0
R ("observed" reflections)	0.019	0.025	0.063
R (independent reflections)	0.027	0.031	0.130

Estimated standard deviations (in parentheses) refer to the last digit.

ture factors of the atoms; (2) the population refinements of the cationic sites in this particular crystal would have been a good test for the reliability of the corresponding results obtained from the remaining minerals from Campi Flegrei, which have comparable chemical composition. In this respect the concordance between the total number of electrons in cations calculated from the site population and that obtained from the chemical analysis of calciobetafite is surprisingly very good (Table 4). The results of the refinement are given in Table 4 (atomic coordinate and temperature parameters, and interatomic distances and angles), and Table 5¹ (thermal vibration ellipsoid parameters and electrostatic charge balance). The list of observed and calculated structure factors is given in Table 6¹

Polymignyte

The results of the crystal structure determination are given in Table 7 (atomic coordinate and tem-

¹ To obtain a copy of Tables 5, 6, 8, 9, 10, 12, and 13, order Document AM-83-215 from the Mineralogical Society of America, Business Office, 2000 Florida Avenue, N.W., Washington D.C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 4. Calciobetafite: atomic coordinate and temperature parameters; bond distances (Å) and angles (°)

Atom	Multip.	Point symm.	x	y	z	B _{eq.}	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃	N° of electrons §
Me8	16	$\bar{3}m$	0	0	0	0.77(1)	181(7)	181	181	-13(4)	-13	-13	123.5(4)
Me6	16	$\bar{3}m$	0.5	0.5	0.5	0.94(1)	222(7)	222	222	-58(4)	-58	-58	125.8(5)
0	48	mm	-0.1771(4)	0.125	0.125	0.87(5)	256(30)	179(19)	179	0	0	93(25)	
(0,F)	8	$\bar{4}3m$	0.125	0.125	0.125	1.77(6)	416(40)	416	416	0	0	0	
site population: Me8 0.761(2) (Ca,Na, 19.1 electrons), 0.239 (REE,Th,U, 68.4 electrons);													249.3 *
Me6 0.535(6) (Ti, 22 electrons), 0.465 (Nb,Ta, 42.3 electrons)													250 **
Me8 polyhedron						Me6 polyhedron							
Me8 - 0	2.577(3) x6						Me6 - 0					1.969(3) x6	
Me8 - (0,F)	2.2295 x2												
0 ^ 0	62.8(1)	x6	117.2(1)	x6	180	x3	0 ^ 0	85.9(1)	x6	94.1(1)	x6	180	x3
0 ^ (0,F)	80.3(1)	x6	99.7(1)	x6									
§ based on 8 cations: * from site population, ** from chemical analysis.													
B _{eq.} is the equivalent isotropic temperature factor.													
The anisotropic thermal parameters are defined by: $\exp -(h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk \beta_{12} + 2hl \beta_{13} + 2kl \beta_{23}) \times 10^{-5}$.													
Estimated standard deviations (in parentheses) refer to the last digit.													

perature parameters), Table 8¹ (parameters for the ellipsoids of vibration), Table 9¹ (electrostatic charge balance) and Table 10¹ (comparison between observed and calculated structure factors).

Zirkelite and zirconolite

Since we did not find true single crystals of zirkelite, we decided to collect X-ray intensities from a zirkelite-zirconolite-pyrochlore intergrowth and to use them for the determination of the crystal

structure of zirkelite. A simple explanation of the epitaxy of pyrochlore, zirconolite and zirkelite follows from the observation of the parameters of the multiple cells (Table 3) derived from the lattices of the three minerals: *a*- and *b*-edges are practically the same and the corresponding axes are parallel in the crystalline intergrowth. Furthermore, the *c*-axis of zirconolite is just four times that of zirkelite, whereas the *c*-axis of pyrochlore is somewhat larger than that of zirkelite. Because of the similarities of

Table 7. Polymignyte: atomic coordinate and temperature parameters

Atom	M	PS	x	y	z	B _{eq.}	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃	N° of electrons §
Me8	8	2	0.75	0.11594(4)	0.25	0.63(1)	14(1)	9(0)	29(1)	0	2(1)	0	72.7(5)
Me7	8	m	0.01505(6)	0.23319(4)	0.5	0.55(1)	13(1)	5(0)	33(1)	-1(0)	0	0	80.0
Me6(1)	4	2/m	0	0	0	0.79(2)	15(1)	9(0)	49(2)	-1(1)	0	0	31.6(3)
Me6(2)	8	2	0.25	0.13323(7)	0.25	0.56(2)	13(1)	8(0)	26(2)	0	2(1)	0	48.9(5)
Me4	8	2	0	0	0.4306(6)	1.97(10)	51(4)	16(1)	120(10)	21(2)	0	0	24.0(3)
Me5	8	m	0.039(5)	0.015(2)	0.5	0.3(9)							1.5(2)
0(1)	16	1	0.1259(3)	0.0333(3)	0.1903(5)	0.96(7)	16(3)	11(2)	63(6)	2(2)	-11(4)	-1(3)	
0(2)	16	1	0.1197(3)	0.2331(2)	0.2104(5)	0.92(7)	17(3)	9(2)	64(7)	5(2)	-4(4)	3(3)	
0(3)	8	m	-0.1007(5)	0.1089(4)	0.5	0.97(11)	21(4)	8(2)	66(10)	-2(3)	0	0	
0(4)	8	m	-0.0904(5)	0.1295(4)	0	0.84(10)	25(4)	9(2)	39(9)	-2(3)	0	0	
0(5)	8	m	0.1799(5)	0.1396(4)	0.5	0.94(10)	24(4)	16(2)	27(8)	6(3)	0	0	
site population: Me8 0.574(7) (Ca,Na, 19.3 electrons), 0.426 (REE,Th, 59.3 electrons); Me7 (Zr, 40 electrons);													258.7 *
Me6(1) 0.517(8) (Ti, 22 electrons), 0.483 (Nb,Ta, 41.9 electrons);													253.1 **
Me6(2) 0.878(11) (Ti, 22 electrons), 0.122 (Nb, Ta, 41.9 electrons);													
Me4 0.462(6) (Fe, 26 electrons); Me5 0.029(4) (Fe).													

M = multiplicity; PS = point symmetry. B_{eq.} is the equivalent isotropic temperature factor.

§ based on 8 cations: * from site population, ** from chemical analysis.

Estimated standard deviations (in parentheses) refer to the last digit.

The anisotropic thermal parameters are defined by: $\exp -(h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk \beta_{12} + 2hl \beta_{13} + 2kl \beta_{23}) \times 10^{-4}$

the lattice parameters, several superpositions of the X-ray reflections of the three phases occurred. It was necessary to take this into account to obtain "clean" intensities of the zirkelite reflections. The subtraction of the contributions of pyrochlore from the observed reflections was fairly easy: total or partial superpositions were limited to the following reflections (zirkelite: hkl , pyrochlore: HKL): $-H + K + L = 3n$ (the only ones possible for pyrochlore in the trigonal indexing) and $h = H, k = K, 0 < l = L < 5$ or $13 < l = L + 1 < 22$. Because of the high multiplicities of the pyrochlore reflections, it was possible to measure the intensities of a complete set of independent reflections of this mineral at points of the reciprocal lattice free of superpositions, then to subtract them from the intensities of the superposed reflections. The correction for the superposed reflections from zirconolite was more difficult because of the greater similarity of the two lattices. Zirkelite reflections with $2h + k + 4l = 6n$ were perfectly superposed and those with $2h + k + 4l = 6n \pm 1$ partly superimposed with those of zirconolite. However, having collected the intensities of six (sometimes three) equivalents for each reflection, it was possible to find one, two, or four of them without any superposition for all diffraction effects, except those with $-h + k + l = 3n$ and $h, k = 2n$, which are unfortunately the strongest observed reflections. An approximate correction was possible after the calculation of the theoretical

intensities of zirconolite by using the parameters given by Gatehouse *et al.* (1981). Even though the final intensities obtained this way were adequate for the determination of the crystal structure of zirkelite, they were too imprecise for a satisfactory refinement: for instance the temperature factors of the oxygens were treated as isotropic because any attempt to consider them anisotropic produced thermal vibration ellipsoids with negative axes. In addition the anisotropic temperature factors of cations are not completely satisfactory. The results of the crystal structure determination of zirkelite are given in Table 11 (atomic coordinate and temperature parameters), Table 12¹ (electrostatic charge balance) and Table 13¹ (comparison between observed and calculated structure factors).

Structural relationships among pyrochlore, polymignyte, zirkelite and zirconolite

The crystal structures of polymignyte, zirkelite and zirconolite are based on the same kinds of polyhedra: distorted cubes (P8), octahedra (P6), as well as polyhedra with seven (P7), five (P5) or four (P4) vertices. The cubes are always centered by Me8 cations (Ca, REE, Th. .), and octahedra by Me6 cations (Ti, Nb, Ta). Me7 cations (Zr) are at the centers of P7 polyhedra and Me5 or Me4 cations (Fe in natural samples and Ti in synthetic zirconolites) at those of P5 or P4 polyhedra. Only P8 and P6 polyhedra (symmetry $\bar{3}m$) are present in pyroch-

Table 11. Zirkelite: atomic coordinate and temperature parameters

Atom	M	PS	x	y	z	B (B _{eq})	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	N° of electrons§
Me8(1)	3	2	0.8324(7)	0	0.3333	1.0(1)	38(7)	30(11)	17(1)	15	-3(2)	-6	33(1)
Me8(2)	3	2	0.3295(7)	0	0.3333	0.9(1)	16(5)	64(10)	16(1)	32	2(2)	4	39(1)
Me7	6	1	0.1653(6)	0.6676(8)	0.0166(1)	0.7(1)	35(7)	42(7)	10(1)	20(5)	-6(2)	-4(2)	80
Me6(1)	3	2	0.333(2)	0	0.8333	1.1(2)	76(11)	86(21)	6(1)	43	-11(2)	22	26(1)
Me6(2)	6	1	0.497(1)	0.334(2)	0.1640(1)	0.7(1)	48(8)	45(8)	5(1)	21(9)	9(2)	3(2)	56(1)
Me5	6	1	0.044(3)	0.894(2)	0.169(1)	3.0(6)	267(64)	334(34)	1(1)	179(40)	-16(12)	-17(11)	26
O(1)	6	1	0.595(2)	0.634(3)	0.1428(7)	1.0(2)							
O(2)	6	1	0.010(2)	0.820(2)	0.0579(5)	0.7(2)							
O(3)	6	1	0.527(2)	0.314(2)	0.0488(7)	1.5(3)							
O(4)	6	1	0.202(3)	0.227(2)	0.1442(7)	1.4(2)							
O(5)	6	1	0.532(2)	0.890(2)	0.0536(6)	1.2(2)							
O(6)	6	1	0.947(2)	0.312(2)	0.0540(6)	0.7(2)							
O(7)	6	1	0.207(2)	0.616(2)	0.1425(7)	1.2(2)							
site population: Me8(1) 0.64(1) (Ca, Na, 19.3 electrons), 0.36 (REE, Th, 59.3 electrons);													260 *
Me8(2) 0.50(1) (Ca, Na), 0.50 (REE, Th); Me7 (Zr, 40 electrons);													241 **
Me6(1) 0.78(1) (Ti, 22 electrons), 0.22 (Nb, Ta, 41.9 electrons);													
Me6(2) 0.69(1) (Ti), 0.31 (Nb, Ta); Me5 0.5 (Fe, 26 electrons).													

M = multiplicity; PS = point symmetry. B_{eq} is the equivalent isotropic temperature factor.

§ based on 8 cations: * from site population, ** from chemical analysis.

Estimated standard deviations (in parentheses) refer to the last digit.

The anisotropic thermal parameters are defined by: $\exp [-(h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk \beta_{12} + 2hl \beta_{13} + 2kl \beta_{23})] \times 10^{-4}$

lore, where each cube shares an edge with six other cubes and with six octahedra, and each octahedron is connected by an edge to six cubes and by a vertex to six other octahedra.

The bond distances and angles in polymignyte, zirkelite and zirconolite (Tables 14, 15 and 16),

show that the shape of each kind of polyhedra is practically the same in all these minerals.

As in pyrochlore, the P8 polyhedron is still a distorted cube, but, whereas in the former structure two Me8-(O,F) distances are 0.35Å shorter than the remaining six Me8-O distances, the bond lengths

Table 14. Polymignyte, zirkelite and zirconolite: bond distances (Å) and angles (°) in P8 cubes and P7 polyhedra

	P8 -polyhedra						P7 -polyhedra									
	Polymignyte		Zirkelite		Zirconolite§		Polymignyte		Zirkelite		Zirconolite§					
	Me8-	Me8(1)-	Me8(2)-	Ca-	(a)	(b)	Me7-	Me7-	Zr-	(a)	(b)					
0(i)	-0(4)	2.443(4)	-0(3)	2.42(3)	-0(3)	2.41(3)	-0(3)	2.404	2.420	-0(2)	2.360(4)	-0(6)	2.35(3)	-0(6)	2.360	2.390
0(ii)	-0(3)	2.370(4)	-0(3)	2.42(3)	-0(3)	2.41(3)	-0(3)	2.396	2.393	-0(2)	2.360(4)	-0(5)	2.42(3)	-0(5)	2.310	2.321
0(iii)	-0(3)	2.370(4)	-0(2)	2.41(2)	-0(2)	2.36(2)	-0(2)	2.457	2.467	-0(2)	2.108(4)	-0(5)	2.10(1)	-0(6)	2.105	2.082
0(iv)	-0(4)	2.443(4)	-0(2)	2.41(2)	-0(2)	2.36(2)	-0(2)	2.401	2.400	-0(2)	2.108(4)	-0(6)	2.13(1)	-0(5)	2.117	2.091
0(v)	-0(2)	2.529(4)	-0(4)	2.46(1)	-0(1)	2.46(1)	-0(1)	2.452	2.420	-0(4)	2.088(5)	-0(3)	2.14(1)	-0(3)	2.039	2.011
0(vi)	-0(1)	2.498(4)	-0(4)	2.46(1)	-0(1)	2.46(1)	-0(4)	2.533	2.508	-0(3)	2.115(5)	-0(2)	2.06(1)	-0(2)	2.181	2.196
0(vii)	-0(2)	2.529(4)	-0(6)	2.50(2)	-0(5)	2.45(3)	-0(5)	2.517	2.502	-0(5)	2.133(5)	-0(7)	2.21(1)	-0(7)	2.142	2.109
0(viii)	-0(1)	2.498(4)	-0(6)	2.50(2)	-0(5)	2.45(3)	-0(6)	2.546	2.507							
mean		2.460		2.45		2.42		2.463	2.452		2.182		2.20		2.179	2.171
0(i)~0(ii)	81.7(1)*		81 (1)*		82 (1)*		83.9	84.5*		126.5(2)		125.7(4)		128.5	128.2	
0(iii)	98.7(1)		99.6(7)		98.4(6)		95.9	95.7		69.1(1)**		70.9(7)**		69.5	69.6**	
0(iv)	171.0(3)		175.1(5)		175.0(4)		172.8	171.0		160.2(1)		160.8(5)		159.1	158.9	
0(v)	101.3(2)		101.2(5)		98.9(5)		102.6	101.0		80.6(1)*		80.6(7)*		81.7	80.7*	
0(vi)	66.6(2)***		66.1(8)***		66.0(7)***		66.8	67.3***		104.4(1)		104.5(6)		102.1	102.3	
0(vii)	70.9(2)**		72.4(9)**		72.8(8)**		72.0	71.2**		69.3(1)***		68.1(8)***		68.5	68.6***	
0(viii)	122.0(2)		118.1(4)		118.6(5)		118.4	119.9								
0(ii)~0(iii)	175.2(3)		175.1(5)		175.0(4)		169.3	167.9		160.2(1)		159.5(5)		159.6	159.5	
0(iv)	98.7(1)		99.6(7)		98.4(6)		98.6	98.7		69.1(1)**		69.1(6)**		70.1	70.1**	
0(v)	67.3(2)**		66.1(8)***		66.0(7)***		68.5	68.3***		80.6(1)*		78.4(7)*		83.2	82.5*	
0(vi)	98.8(2)		101.2(5)		98.9(5)		101.6	101.2		104.4(1)		105.8(6)		101.2	101.8	
0(vii)	117.2(2)		118.1(4)		118.6(5)		121.7	122.7		69.3(1)***		70.4(8)***		69.6	70.0***	
0(viii)	77.0(2)****		72.4(9)**		72.8(8)**		71.4	71.5**								
0(iii)~0(iv)	81.7(1)*		80.0(8)*		82.0(7)*		82.8	83.0*		93.2(2)		92.2(5)		90.7	90.6	
0(v)	117.2(2)		118.4(7)		118.8(7)		121.7	123.3		92.1(1)		94.5(6)		91.3	92.0	
0(vi)	77.0(2)****		74.8(4)****		76.7(4)****		68.8	67.9****		80.1(1)*		78.0(8)*		81.5	81.2*	
0(vii)	67.3(2)**		66.6(5)**		66.0(5)**		68.0	68.4**		130.5(1)		130.1(9)		130.6	130.3	
0(viii)	98.8(2)		103.9(6)		102.9(6)		99.5	98.3								
0(iv)~0(v)	70.9(2)**		74.8(4)****		76.7(4)****		72.3	72.6****		91.5(1)		92.0(6)		92.4	93.0	
0(vi)	122.0(2)		118.4(7)		118.8(7)		118.9	119.9		80.1(1)*		79.9(7)*		80.7	81.2*	
0(vii)	101.3(2)		103.9(6)		102.9(7)		101.0	100.1		130.5(1)		131.1(9)		132.3	132.4	
0(viii)	66.6(2)***		66.6(5)**		66.0(5)**		68.8	69.1**								
0(v)~0(vi)	163.4(1)		164.0(9)		160.9(9)		166.8	165.6		167.8(2)		168.6(5)		169.9	171.0	
0(vii)	64.7(2)***		66.0(7)***		64.3(7)***		66.5	66.9***		106.9(2)		105.6(5)		107.0	106.4	
0(viii)	118.1(1)		116.0(7)		118.3(7)		117.7	118.0								
0(vi)~0(vii)	118.1(1)		116.0(7)		118.3(7)		115.0	114.5		85.4(2)****		85.8(5)		83.1	82.6	
0(viii)	64.5(2)***		66.0(7)***		64.3(7)***		64.6	64.9***								
0(vii)~0(viii)	163.4(1)		168 (1)		166 (1)		165.4	164.3								

Equivalent positions (referred to the tables of the atomic coordinate parameters):

Me	x y z	(y-x+1)	(1-x)	(2/3+z)	x y z	x y z	x y z	x y z
0(i)	(1+x) y z	x y z	x y z		x y z	x y z	(x-1) y z	x -y z-1/2
0(ii)	(1/2-x)y(1/2-z)	y x -z	y x -z		(1/2-x)(1/2-y)(1-z)	x y (1-z)	x y z	(1-x) y (1/2-z)
0(iii)	(1+x) y z	x (x-1) z	(x+1) y z		x -y (1/2+z)	-x (1/2-y)(1/2-z)	(y-1)x -z	-x y (1/2-z)
0(iv)	(1/2-x)y(1/2-z)	(y-1)x -z	y (x+1) -z		(1-x) y (1/2-z)	-x (1/2-y)(1/2+z)	y x -z	(x-1/2)(1/2-y)
								(z-1/2)
0(v)	(1/2+x)(1/2-y)z	y x -z	y x -z		x y z	-x (1/2-y)(1/2-z)	y x -z	x -y (z-1/2)
0(vi)	(1-x) -y z	x y z	x y z		x y z	x y z	x y z	(1/2-x)(1/2-y)-z
0(vii)	(1-x)(1/2-y)(1/2-z)	y (x-1) -z	y x -z		(1-x) -y (1-z)	x y z	x y z	x y (z-1)
0(viii)	(1/2+x)-y(1/2-z)	(x-1) y z	x y z		(1/2-x)(1/2-y)(1-z)			

§ after Gatehouse et al. (1981): (a) Ca_{0.993}Zr_{1.304}Ti_{1.700}O₇; (b) Ca_{0.961}Zr_{0.850}Ti_{2.169}O₇.

Shared edges: * with P8, ** with P7, *** with P6, **** with P4/5. Estimated standard errors (in parentheses) refer to the last digit.

Table 15. Polymignyte, zirkelite and zirconolite: bond distances (Å) and angles (°) in P6(1) and P6(2) octahedra

P6- polyhedra														
	Polymignyte		Zirkelite		Zirconolite§		Polymignyte		Zirkelite		Zirconolite§			
Me-	Me6(1)-	Me6(1)-	Ti(3)-	(a)	(b)	Me6(2)-	Me6(2)-	Ti(1)-	(a)	(b)				
O(i)	-0(1)	1.942(4)	-0(4)	2.01(3)	-0(4)	1.977	1.964	-0(1)	1.942(4)	-0(7)	2.00(3)	-0(7)	1.942	1.933
O(ii)	-0(1)	1.942(4)	-0(4)	2.01(3)	-0(4)	1.977	1.964	-0(5)	1.956(2)	-0(1)	1.96(3)	-0(1)	1.940	1.933
O(iii)	-0(1)	1.942(4)	-0(7)	1.89(3)	-0(7)	1.913	1.910	-0(2)	1.956(3)	-0(4)	1.92(3)	-0(4)	1.959	1.975
O(iv)	-0(1)	1.942(4)	-0(7)	1.89(3)	-0(7)	1.913	1.910	-0(5)	1.956(2)	-0(1)	1.96(3)	-0(1)	2.000	1.969
O(v)	-0(4)	2.049(5)	-0(6)	1.93(1)	-0(6)	1.933	1.916	-0(2)	1.956(3)	-0(3)	1.97(1)	-0(3)	1.997	1.986
O(vi)	-0(4)	2.049(5)	-0(6)	1.93(1)	-0(6)	1.933	1.916	-0(1)	1.942(4)	-0(5)	1.98(1)	-0(5)	1.971	1.948
mean		1.978		1.94		1.941	1.930		1.951		1.96		1.968	1.957
O(i)~O(ii)	89.0(2)****		83 (1)****			78.4	78.4****		90.4(2)****		89.7(8)		89.3	89.5
O(iii)	180		175.1(9)			171.6	171.8		175.3(2)		172.6(9)		169.1	170.8
O(iv)	91.0(2)		92.2(6)			93.5	93.9		93.5(2)		88.7(5)		89.5	90.1
O(v)	94.4(2)		95.4(9)			94.7	93.5		93.1(1)		95.8(8)		98.5	98.4
O(vi)	85.6(2)*		86.7(8)*			87.9	87.8*		86.7(2)*		84.3(8)**		81.1	82.1**
O(ii)~O(iii)	91.0(2)		92.2(6)			93.5	93.9		94.3(2)		97.6(6)		100.4	98.0
O(iii)	180		175.1(9)			171.6	171.8		174.7(3)		177.1(3)		177.4	177.9
O(v)	85.6(2)*		86.7(8)*			87.9	87.8*		81.8(2)**		84.8(9)*		87.8	87.1*
O(vi)	94.4(2)		95.4(9)			94.7	93.5		93.5(2)		94.5(9)		90.9	90.3
O(iii)~O(iv)	89.0(2)****		92 (1)			94.7	94.0		81.8(2)**		84.0(8)****		80.5	82.2****
O(v)	85.6(2)*		83.8(9)**			82.6	83.3**		87.6(2)*		86.6(9)*		86.8	87.3*
O(vi)	94.4(2)		94.4(8)			95.1	95.5		93.1(1)		93.4(9)		93.7	92.6
O(iv)~O(v)	94.4(2)		94.4(8)			95.1	95.5		94.3(2)		97.7(9)		94.6	94.9
O(vi)	85.6(2)*		83.8(9)**			82.6	83.3**		90.4(2)****		83.0(9)*		86.6	87.7*
O(v)~O(vi)	180		177 (2)			176.6	178.3		175.3(2)		179 (2)		178.7	177.4

Equivalent positions (referred to the tables of the atomic coordinate parameters):

Me	x y z	-y(x-y)(1/3+z)	x y z	x y z	x y z	x y z	x y z	x y z
O(i)	x y z	x y z	(x-1/2)(1/2-y)(z-1/2)	x y z	x y z	(1-x)(y-x)(1/3-z)	x y z	x y z
O(ii)	-x -y -z	-x(y-x)(1/3-z)	(1/2-x)(1/2-y)(1-z)	x y z	x y z	(1/2-x)y(1/2-z)	x y z	(1/2-x)(1/2-y)(1-z)
O(iii)	-x -y -z	-x(y-x)(1/3-z)	x -y (z-1/2)	(1/2-x)y(1/2-z)	x y z	(1-x)(y-x)(1/3-z)	x y z	x -y (1/2+z)
O(iv)	x y -z	x y z	-x -y (1-z)	(1/2-x)y(1/2-z)	(1-x)(y-x)(1/3-z)	(1-x)(y-x)(1/3-z)	x -y (1/2+z)	x -y (1/2+z)
O(v)	x y z	(1-x)(y-x+1)(1/3-z)	x y z	x y z	x y z	x y z	x y z	x y z
O(vi)	-x -y z	(x-1) y z	-x y (1/2-z)	(1/2-x)y(1/2-z)	(1-x)(y-x)(1/3-z)	(1-x)(y-x)(1/3-z)	(1-x) y (3/2-z)	(1-x) y (3/2-z)

§ after Gatehouse et al. (1981): (a) Ca_{0.993}Zr_{1.304}Ti_{1.700}O₇; (b) Ca_{0.961}Zr_{0.850}Ti_{2.169}O₇.

Shared edges: * with P8, ** with P7, **** with P4/5. Estimated standard errors (in parentheses) refer to the last digit.

are somewhat more uniform in the other minerals, the largest difference being about 0.16Å. All cubes have the same type of distortion, as may be seen from the bond angles (Table 14), and nearly 222 symmetry: one of these twofold axes is real in polymignyte and zirkelite, but none of them are retained in the crystal structure of zirconolite. Two independent P8 polyhedra are present in zirkelite, and only one in the remaining minerals. The mean value of the eight Me8-O distances in each polyhedron ranges from 2.42 and 2.46Å.

The P7 polyhedra have almost *m* symmetry: the mirror plane is real only in the crystal structure of polymignyte. Three oxygens lie in the plane, and one of them (O(v) or O(vi) in Table 14) shows the shortest distance from the Me7 cation. On the other hand, two oxygens (O(i) and O(ii)), lying at opposite sides of the plane, have bond lengths 0.30Å larger than the mean of the other distances. This polyhe-

dron can be described alternatively as a distorted cube without one vertex, or a distorted octahedron with a centered face: actually the P7 polyhedron replaces both P8 and P6 polyhedra present in the crystal structure of pyrochlore. The mean value of the seven Me7-O distances in each polyhedron ranges from 2.17 and 2.20Å.

All the crystal structures show two independent octahedra (P6(1) and P6(2)) having different symmetry, respectively *2/m* and *2* in polymignyte, *2* and *1* in zirkelite or zirconolite. In general the Ti content is different in the two independent octahedra, but there is no evidence for a correlation between the site population and the symmetry of the polyhedra. The mean value of the six Me6-O distances in each octahedron ranges from 1.93 and 1.98Å.

Finally P4 and P5 polyhedra are formed around a cation, which does not center a cavity among eight oxygens, but is shifted toward four or five of them.

Table 16. Polymignyte, zirkelite and zirconolite: bond distances (Å) and angles (°) in P4 tetrahedra and P5 trigonal bipyramids

P4/5 - polyhedra							
Polymignyte			Zirkelite		Zirconolite §		
Me-	Me4-	Me5-	Me5-	Ti(2)-	(a)	(b)	
O(i)	- 0(3)	1.916(5)	- 0(3)	1.95(3)	- 0(2)	1.845	1.815
O(ii)	- 0(3)	1.916(5)	- 0(3)	1.86(3)	- 0(2)	1.832	1.792
O(iii)	- 0(1)	2.217(5)	- 0(5)	2.26(4)	- 0(4)	1.890	1.792
O(iv)	- 0(1)	2.217(5)	- 0(1)	2.43(2)	- 0(4)	2.234	2.253
O(v)			- 0(1)	2.43(2)	- 0(1)	2.228	2.194
mean		2.067		2.19		2.006	1.969
O(i)^O(ii)	149.5(3)		153 (3)		149 (1)	138.4	132.1
O(iii)	94.1(2)*		86 (1)**		93 (1)	98.1	100.8
O(iv)	101.1(2)		101 (1)		103 (1)	106.6	103.4
O(v)			101 (1)		104 (1)	101.1	103.3
O(ii)^O(iii)	110.1(2)		122 (2)		117 (1)	123.5	126.7
O(iv)	94.1(2)*		89 (1)*		85 (1)*	87.2	86.0*
O(v)			89 (1)*		90 (1)*	89.2	90.0*
O(iii)^O(iv)	75.8(2)***		72 (1)***		70 (2)***	74.1	74.8***
O(v)			72 (1)***		71 (1)***	76.4	80.5***
O(iv)^O(v)			136 (2)		133 (1)	141.7	146.3
Equivalent positions (referred to the tables of the atomic coordinate parameters):							
Me	x y z		x y z		x y z		x y z
O(i)	x y z		x y z		x y z		x y z
O(ii)	-x -y z		-x -y z		-x (y-x) (1/3-z)		(1-x) y (1/2-z)
O(iii)	-x -y z		x y z		x (y+1) z		x -y (z-1/2)
O(iv)	x y z		x y z		-x (y-x+1) (1/3-z)		(1-x) -y (1-z)
O(v)			x y (1-z)		(1-x) (y-x+1) (1/3-z)		x y z
§ after Gatehouse et al. (1981): (a) Ca _{0.993} Zr _{1.304} Ti _{1.700} O ₇ ; (b) Ca _{0.961} Zr _{0.850} Ti _{2.169} O ₇ *							
Shared edges: * with P8, ** with P7, *** with P6 . Estimated standard errors (in parentheses) refer to the last digit.							

Me4 and Me5 sites, whose multiplicity is double that of the point at the center of the cavity, are incompletely and statistically occupied. Both Me4 and, to much lesser extent, Me5 positions are occupied in polymignyte. Apparently only Me5 sites are occupied in zirconolite and zirkelite, even if in the latter mineral Me5-O(iv) distance is larger than in the former (Table 16). In fact, only a slight shift of the position of the cation is able to change one coordination into the other, and very likely the local charge balance is responsible for the choice of either cationic position Me4 or Me5. The P4 polyhedron is a very distorted tetrahedron and P5 a distorted trigonal bipyramid. The mean of the four or five distances in these polyhedra ranges between 1.97 and 2.19 Å: the lower values are in synthetic zirconolites, where the central cation is titanium rather than iron as in the crystals from Campi Flegrei.

A comparison of the crystal structures of pyrochlore, polymignyte, zirkelite and zirconolite can

be easily made by an examination of the arrangement of the atoms in the multiple cells reported in Table 3. All these crystal structures are obtained by repeating along the *c*-axis pairs of adjacent layers of polyhedra (say M- and N-layers). Figures 1, 2 and 3 show the positions of the atoms in these two layers respectively for pyrochlore, for zirkelite-zirconolite and for polymignyte: the crystal structures of zirkelite and zirconolite are practically based on the same pair of layers. All figures have been drawn in such a way that one Me6(1) cation is always at the point 000 of the M-layer on a twofold axis parallel to the *b*-edges of the multiple cells. The thickness of each layer is slightly less than 3 Å: twelve pairs of M- N-layers are contained in the multiple cell of zirconolite and only three in those of the remaining minerals. The most regular atomic arrangement is obviously in the cubic pyrochlore: the M-layer shows P6 octahedra and distorted P8 cubes in a frequency ratio 3:1; the same thing occurs in the N-layer, but with an inversion of the frequency ratio.

Table 17. Calciobetafite, polymignyte, zirkelite and zirconolite: X-ray powder diffraction data.

Ca-betafite			Polymignyte			Zirkelite			Zirconolites								
(a)§			(a)§			(a)§			(a)*			(b)**		(b)***		(c)	
h k l	d	I	h k l	d	I	h k l	d	I	h k l	d	I	d	I	d	I	d	I
			1 3 1	3.687	12				1 1 1			5.241	8				
									1 1 2			3.976	11				
									1 1 3			3.333	11				
									3 1 1			} 3.240	10				
									3 1 2								
2 2 2	2.973	100	2 0 2	2.957	93	2 0 2	2.956	100	2 2 1			2.935	100	2.929	100	2.94	10
			2 4 0	2.901	100				4 0 2			2.916	54	2.903	78		
						0 0 6	2.814	27	0 0 4	2.813	29	2.787	38	2.789	56	2.81	3
4 0 0	2.574	27	0 4 2	} 2.536	50	0 2 4	2.527	26	2 2 3	2.530	19	2.509	19	2.503	54	2.52	4
			4 0 0							4 0 2	2.525	8	2.494	11	2.490	19	
3 3 1	2.363	5	3 2 2	2.338	10	2 0 5	2.306	5	2 2 3	2.308	3	2.287	8				
			1 6 0	2.296	5				4 0 4	2.302	2	2.278	4				
3 3 3	} 1.982	3							3 3 1			} 2.012	5				
5 1 1										3 3 2							
									0 2 5			} 1.900	4				
									2 2 5								
4 4 0	1.820	53	0 0 4	1.819	15	2 2 0	1.822	32	0 4 0	1.828	11	1.815	15	1.815	27	1.82	8
			4 4 2	1.794	68				6 2 1	1.821	18	1.800	32	1.798	67		
			0 8 0	1.768	14	2 0 8	1.754	24	2 2 5	1.755	16	1.739	26	1.740	66	1.75	5
									4 0 6	1.752	7	1.736	17	1.737	58		
6 2 2	1.552	45	2 4 4	1.541	24	0 4 2	1.551	12	4 4 2	1.554	8	1.541	10	1.541	32	1.55	5
			6 0 2	1.534	13				8 0 0	1.549	3	1.529	5	1.528	12		
			6 4 0	1.526	15	2 2 6	1.529	18	0 4 4	1.533	6	1.521	7	1.522	20	1.53	5
			2 8 2	1.518	22				6 2 3			} 1.512	13	} 1.512	42		
						0 2 10	1.489	8	6 2 5								
									2 2 7			1.476	6	1.479	17	1.48	2b
4 4 4	1.486	10	4 0 4	1.479	10	4 0 4	1.478	7	4 0 6			1.472	4	1.475	24		
			4 8 0	1.451	7				4 4 2	1.481	4	1.467	5	1.469	14		
									8 0 4	1.475	2	1.458	4	1.457	15		
									0 0 8					1.398	2		
8 0 0	1.287	7	0 8 4	} 1.268	9	0 4 8	1.264	5	4 4 6			1.254	4			1.26	1
			8 0 0							8 0 4	1.264	5	1.247	2			
6 6 2	1.181	16	2 0 6	1.180	5	4 2 2	1.181	8	2 6 1	1.185	3	1.176	3			1.179	5
			6 4 4	1.169	9				8 4 0			} 1.168	8				
									10 2 3								
8 4 0	1.151	13	0 4 6	} 1.148	5	2 4 4	1.148	5	2 6 3	1.151	2	1.143	2			1.149	2b
			2 12 0							8 4 4			1.137	2			
									10 2 1	1.147	3	1.132	2				
			8 4 2	} 1.135	10	2 2 12	1.114	3	0 4 8			} 1.103	3			1.115	1
			4 8 4							6 2 7							
									6 2 9								
8 4 4	1.051	12	4 4 6	1.045	7	6 0 0	1.052	3	6 6 1	1.054	2	1.045	3			1.050	2
									12 0 2	1.050	2	1.037	2				
			4 12 2	1.026	4	4 2 8	1.038	4	2 6 5							1.038	3
									8 4 4			} 1.039	4				
									10 2 7								

(a) calculated with the experimental lattice parameters of the minerals from Campi Flegrei;

(b) synthetic crystals;

(c) heated polymignyte from Fredricksvärn (Lima-de-Faria, 1958);

§ calculated from the experimental single crystal intensities;

* calculated from the theoretical intensities obtained for a crystal structure and a chemical composition analogous to those of zirkelite from Campi Flegrei;

** calculated from the theoretical intensities obtained from the data by Gatehouse et al. (1981);

*** after Pyatenko and Pudovkina (1964).

Both layers are formed by chains of polyhedra, which develop in three directions at 120° to each other. Chains of octahedra sharing vertices (P6 chains) alternate with mixed chains of octahedra and cubes sharing edges (P68 chains) in each of the three directions at 120° in the M-layer. Conversely

chains of cubes sharing edges (P8 chains) alternate with P68 chains in the N-layer.

The crystal structure of pyrochlore is modified in the remaining minerals by the introduction of zirconium, which centers P7 polyhedra. Half of the P68 chains, pointing in one of the three directions

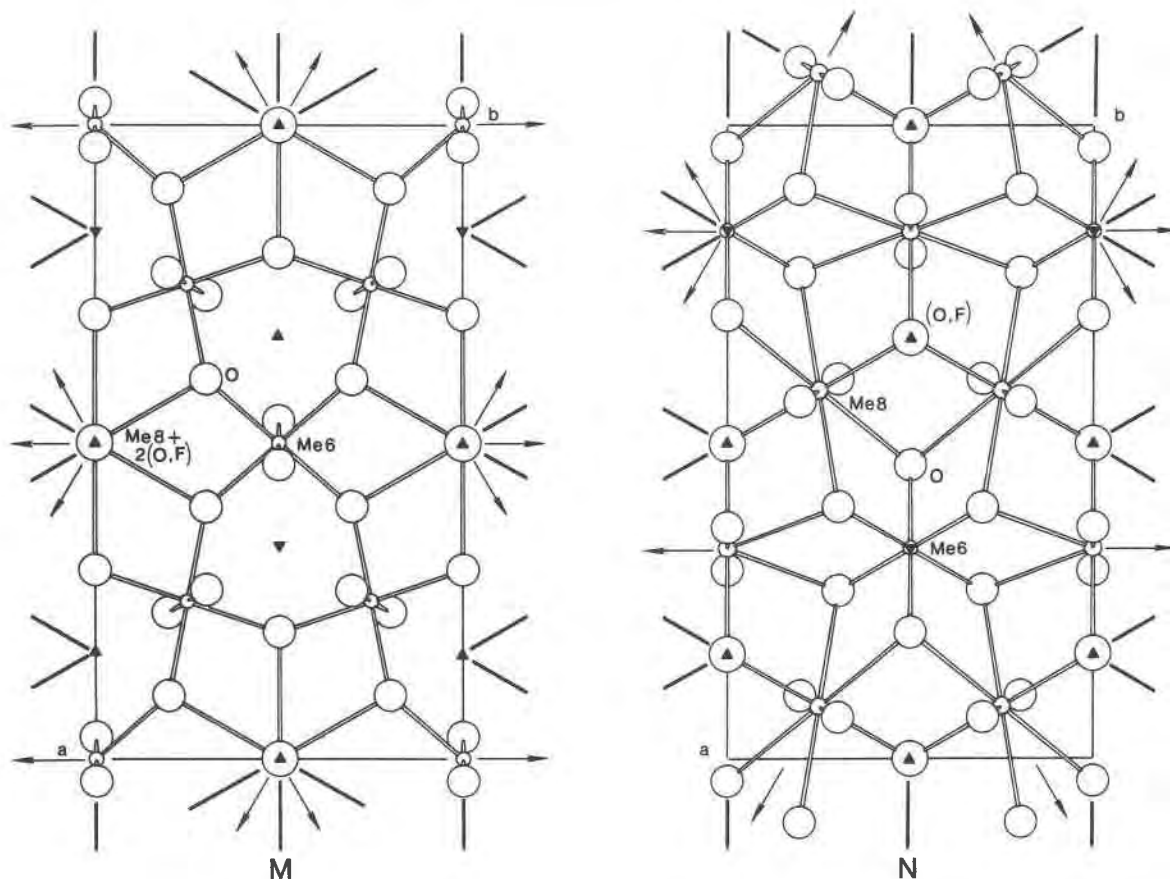


Fig. 1. Pyrochlore: adjacent M- and N-layers (see text) of the crystal structure projected along [111]; *a*-edge corresponds to $[-1\ 0.5\ 0.5]$ and *b*-edge to $[0\ -0.5\ 0.5]$. Threefold and twofold axes, and mirror planes determined by the arrangement of the atoms in each layer have been traced.

described above for pyrochlore, are replaced by P7 chains: pairs of P7 polyhedra replace couples of P6–P8 polyhedra. In order to achieve this, one oxygen is moved away from each P8 polyhedron and at the same time another oxygen approaches each P6. The remaining oxygens show minor shifts. The P7 chains are present only in the N-layers of the zirkelite–zirconolite structures, where they have replaced all P68 chains pointing in one direction. When such chains are formed, the consequent shifts of the oxygens give rise to a reduction of the volume of the P8 cavities of the P8 chains in the adjacent M-layer. In particular, two oxygens approach each other, leaving no space for a (Ca, REE . . .) atom at the center of the cavity: then a smaller cation (Fe in our minerals, Ti in synthetic zirconolites) locates itself statistically on one or two nearby sites, which have multiplicities double that of the central position and are surrounded by four or five oxygens. The passage from the pyrochlore structure to those of zirkelite or zirconolite accordingly involves

changes in one of the three sets of parallel P68 chains: all of these are changed into P7 chains in the N-layer and into P64/5 chains in the M-layer. The same transformations also take place in polymignyte, but here P7 chains, and consequently also P64/5 chains, are formed in both M- and N-layers, where they alternately replace P68 chains of pyrochlore. Consequently, the positions of P6 and P4/5 polyhedra are interchanged in alternate P64/5 chains, with respect to the original structure of pyrochlore, and the *a*-edge of the multiple cell of polymignyte is double those of the remaining minerals.

The arrangement of the atoms gives rise to symmetry elements parallel (twofold axes) or perpendicular (threefold axes and symmetry planes) to the M- and N-layers.

The highest symmetry ($C\bar{3}m$) is obviously presented by both layers of pyrochlore. The symmetry is nearly the same also for the M-layer of zirkelite–zirconolite, if one ignores the positions statistically

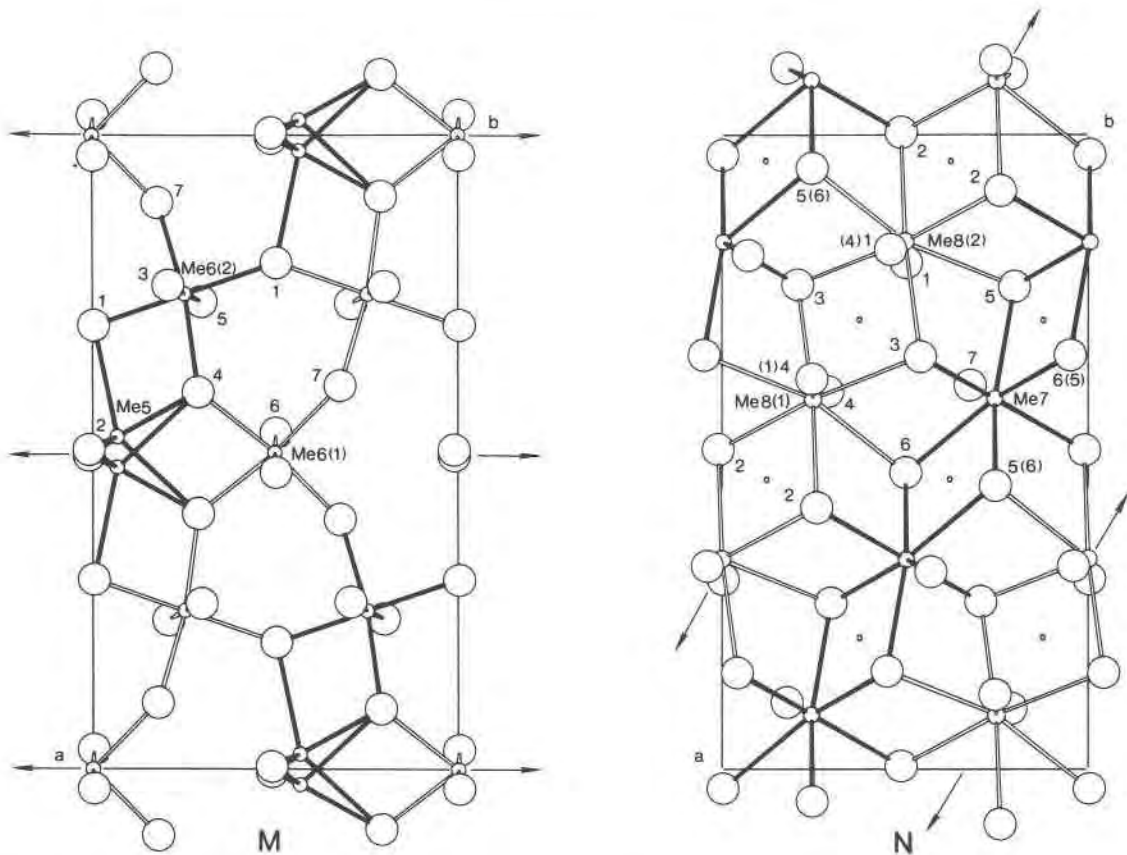


Fig. 2. Zirkelite-zirconolite: M- and N-layers of the crystal structure projected along [001] (zirkelite) or [106] (zirconolite); *a*-edge is [201] of zirkelite or [100] of zirconolite, *b*-edge is [010] of zirkelite or [0-10] of zirconolite. Twofold axes (real in the M-layer of both minerals and in the N-layer of zirkelite) and symmetry centers (real only in zirconolite) determined by the arrangement of the atoms in each layer have been traced. Numbering of oxygen atoms corresponds to that reported in Table 11 (zirkelite) or by Gatehouse *et al.* (1981) (zirconolite); the same figures generally hold for both minerals: when different, those in parentheses refer to zirconolite. Me8(1) and Me8(2) are equivalent in zirconolite. Bonds in P7 and P64/5 chains are identified by solid lines.

occupied by Me4 and Me5 atoms. The epitaxy and the consequent intergrowths among pyrochlore, zirkelite and zirconolite most likely originate from the similarities of the M-layers of the three minerals. The $C3m$ symmetry is reduced to that of its subgroup $C2/m$ in the layers where the P7 chains replace P68 chains, that is in the N-layer of zirkelite-zirconolite and in both layers of polymignyte. All the symmetry elements present in both layers of pyrochlore and polymignyte are retained in the whole crystal structure, obtained by the repeat MN MN MN of the layers along the *c*-axis. However, only part of the symmetry of the layers is retained in the crystal structures of zirkelite and zirconolite: the mirror planes disappear, and either one twofold axis or the symmetry centers present in each layer become real elements of symmetry for the whole crystal. The twofold axis is maintained in the M-

layer for both minerals, whereas the N-layer of zirkelite still shows a twofold axis (rotated 120° with respect to that of the M-layer) and that of zirconolite shows only symmetry centers. In this way one obtains the centrosymmetric space group $C2/c$ in zirconolite and the acentric one $P3_12$ for zirkelite, even though slabs of the crystal structures are practically the same.

Conclusions

The same types of polyhedral chains are present in all three minerals. P6 and P8 chains are always in alternate layers (M and N respectively); the same holds for P64/5 and P7 chains in zirkelite and zirconolite, whereas the latter chains are in all layers of polymignyte. As the P7 and P8 chains are parallel to the twofold axis, they point only in one direction [001] in the structure of polymignyte;

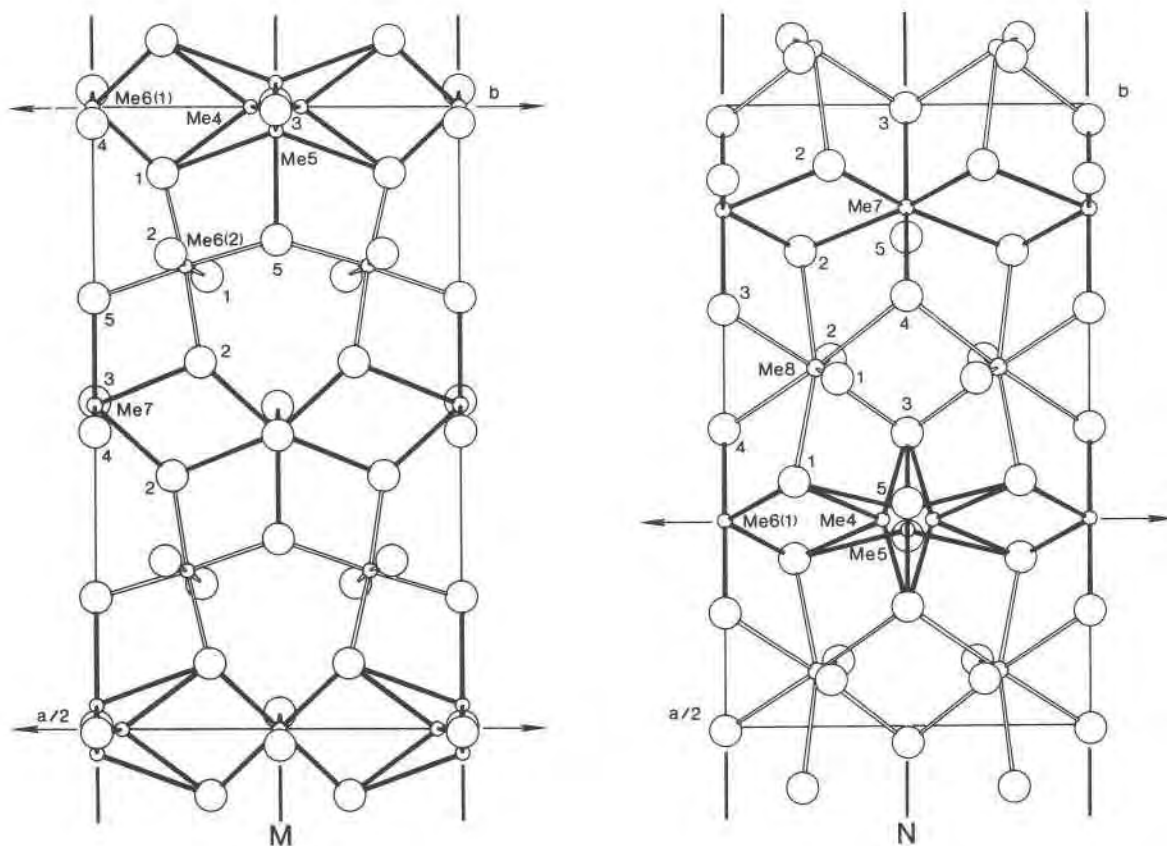


Fig. 3. Polymignyte: M- and N-layers of the crystal structure projected along $[-110]$; a -edge corresponds to $[210]$ and b -edge to $[001]$. Twofold axes and mirror planes determined by the arrangement of the atoms in each layer have been traced. Numbering of oxygen atoms refers to Table 7. Bonds in P7 and P64/5 chains are identified by solid lines.

however, as the same chains make an angle of 60° with the twofold axis in the M-layer, they are alternately in two directions at 120° ($[110]$ and $[\bar{1}10]$) in successive N-layers of zirconolite; finally, because of the presence of the additional twofold axis rotated 120° in the N-layer, the P7 and P8 chains develop in three directions at 120° ($[100]$, $[010]$ and $[\bar{1}\bar{1}0]$) in successive N-layers of zirkelite. The results of the crystal structure determinations therefore confirm that polymignyte, zirkelite and zirconolite are polymorphs of the same compound.

Acknowledgments

We are greatly indebted to Dr. W. L. Griffin for the microprobe analyses made at the Mineralogisk-Geologisk Museum of Oslo. The Consiglio Nazionale delle Ricerche is acknowledged for financing the electron microprobe laboratory at the Istituto di Mineralogia e Petrologia of the University of Modena. Many sincere thanks also to Dr. A. Kato, Chairman of the Commission on New Minerals and Mineral Names of IMA, who, in reading the manuscript, first noticed that the Campi Flegrei pyrochlore is a new member of the betafite subgroup. Thanks are extended to Mr. G. Germani for his valuable technical assistance in the computational aspect of this research.

References

- Åmli, Reidar and Griffin, W. L. (1975) Microprobe analysis of REE minerals using empirical correction factors. *American Mineralogist*, 60, 599–606.
- Berzelius (1824). *Svenska Vetenskapsakademien, Handlingar*, 338 (not seen; extracted from Palache, C., Berman, H., and Frondel, C. (1944) *Dana's System of Mineralogy*, 7th ed., vol. 1, Wiley, New York).
- Blake, G. S. and Herbert Smith, G. F. (1913) On varieties of zirkelite from Ceylon. *Mineralogical Magazine*, 16, 309–316.
- Borodin, L. S., Bykova, A. V., Kapitonova, T. A., and Pyatenko, Yu. A. (1961) New data on zirconolite and its niobium variety. *Doklady Akademiyi Nauk SSSR*, 134, 1022–1024 (not seen; extracted from *Mineralogical Abstracts*, 15, 538).
- Borodin, L. S., Nazarenko, I. I., and Rikhter, T. L. (1956) On a new mineral zirconolite—a complex oxide of AB_3O_7 type. *Doklady Akademiyi Nauk SSSR*, 110, 845–848 (not seen; extracted from *Mineralogical Abstracts*, 13, 383).
- Brögger, W. C. (1890) Die Mineralien der Syenitpegmatitgänge der sudnorwegischen Augit- und Nephelinsyenite. *Zeitschrift für Kristallographie*, 16, 387–396.
- Busing, W. R., Martin, K. O., and Levy, H. A. (1962) ORFLS, a Fortran crystallographic least-squares refinement program. U.S. National Technical Information Service ORNL-TM-305.
- Donnay, Gabrielle and Allmann, Rudolf (1970) How to recognize

- O²⁻, OH⁻ and H₂O in crystal structures determined by X-rays. *American Mineralogist*, 55, 1003–1015.
- Gaertner, H. R. (1930) Die Kristallstrukturen von Loparit und Pyrochlor. *Neues Jahrbuch für Mineralogie*, 61, 1–30.
- Gatehouse, B. M., Grey, I. E., Hill, R. J., and Rossell, H. J. (1981) Zirconolite, CaZr_xTi_{3-x}O₇; structure refinements for near-end-member compositions with x=0.85 and 1.30. *Acta Crystallographica*, B37, 306–312.
- Hogarth, D. D. (1977) Classification and nomenclature of the pyrochlore group. *American Mineralogist*, 62, 403–410.
- Hussak, Eugen and Prior, G. T. (1895) Lewisite and zirkelite, two new Brazilian minerals. *Mineralogical Magazine*, 11, 80–88.
- Lima-de-Faria, J. (1958) Heat treatment of metamict euxenites, polymignites, yttrantalites, samarskites, pyrochlores, and allanites. *Mineralogical Magazine*, 31, 937–942.
- Lima-de Faria, J. (1964) Identification of metamict minerals by X-ray powder photographs. *Junta de Invest. do Ultramar, Portugal; Estud., Ensaios & Documentos*, 112 (not seen; extracted from *Mineralogical Abstracts*, 17, 243).
- North, A. C., Phillips, D. C., and Mathews, F. S. (1968) A semi-empirical method of absorption correction. *Acta Crystallographica*, A24, 351–359.
- Perrault, Guy (1968) La composition chimique et la structure cristalline du pyrochlore d'Oka, PQ. *Canadian Mineralogist*, 9, 383–402.
- Prior, G. T. (1897) On the chemical composition of zirkelite. *Mineralogical Magazine*, 11, 180–183.
- Pudovkina, Z. V., Chernitzova, N. M. and Pyatenko, Yu. A. (1969). Crystallographic study of polymignyte (in Russian). *Zapiski Vsesoiuznogo Mineralogicheskogo Obshchestva*, 98, 193–199.
- Pyatenko, Yu. A. and Pudovkina, Z. V. (1964) The lattice metric of CaZrTi₂O₇ crystals. *Kristallografiya*, 9, 98–100 (transl. *Soviet Physics-Crystallography*, 9, 76–78).
- Sinclair, William and Eggleton, R. A. (1982) Structure refinement of zirkelite from Kaiserstuhl, West Germany. *American Mineralogist*, 67, 615–620.

Appendix: The identification of polymignyte, zirkelite and zirconolite

It is very likely that at other localities where only one of the polymorphs (polymignyte, zirkelite and zirconolite) has been recorded, all three minerals may actually occur together, as described here for the Campi Flegrei rock. We suspect that the properties of each of these minerals reported in the literature are often an "average" of the properties of all three minerals; for instance both polymignyte and zirkelite were described as prismatic or platy crystals: as for the Campi Flegrei material, it is likely that the former crystals are polymignyte and the latter zirkelite-zirconolite. Also, discovery of pure zirkelite or zirconolite should be very rare: as they differ only in the stacking of some layers, the epitaxy of the two species should be nearly always present.

Apart from the above possible distinction based on the morphological features, the identification of the three minerals by X-ray powder patterns is clearly not straightforward. Table 17 gives the spacings and the intensities for the strongest reflections of calciobetafite, polymignyte, zirkelite and zirconolite, calculated from the lattice parameters and the intensities collected in the single crystal studies of the Campi Flegrei material. Analogous data are reported for the synthetic zirconolite studied by Gatehouse *et al.* (1981). Table 17 also lists the experimental X-ray powder data of synthetic zirconolite (Pyatenko and Pudovkina, 1964) as well as those reported by Lima-de-Faria (1958) for the metamict polymignyte from Fredricksvärn heated to 1000° C. The differences in the spacings of the three minerals are very small: the calculated and observed diffraction patterns of synthetic zirconolite are comparable, but both are more similar to the calculated pattern of polymignyte, than that of zirconolite from Campi Flegrei. On the other hand, the powder diffraction data for heated polymignyte are more similar to those of zirkelite and zirconolite from Campi Flegrei, the latter ones being practically indistinguishable from each other. Surely the differences, which derive from the variations of the lattice parameters caused by the isomorphous replacements, overwhelm those due to the different crystal structures. Only single crystal X-ray studies, made on non-metamict materials, allow a clear distinction between these minerals.

Manuscript received, May 11, 1982;
accepted for publication, August 23, 1982.