

Mineral nomenclature: zirconolite

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Abstract

The nomenclature of $\text{CaZrTi}_2\text{O}_7$ minerals has become very confused, such that zirconolite, zirkelite and polymignite each have acquired multiple meanings and represent five different crystal structures. To resolve these inconsistencies, the IMA approved resolutions as follows. Zirconolite is the non-crystalline (metamict) mineral or mineral with undetermined polytypoid of $\text{CaZrTi}_2\text{O}_7$. Zirconolite-3O is the three-layered orthorhombic polytypoid of $\text{CaZrTi}_2\text{O}_7$. Zirconolite-3T is the three-layered trigonal polytypoid of $\text{CaZrTi}_2\text{O}_7$. Zirconolite-2M is the two-layered monoclinic polytypoid of $\text{CaZrTi}_2\text{O}_7$. Polymignite (metamict) is discarded as equivalent to zirconolite. Zirkelite is the cubic mineral with formula $(\text{Ti,Ca,Zr})\text{O}_{2-x}$.

KEYWORDS: zirconolite, polymignite, zirkelite, mineral nomenclature.

Introduction

FIVE minerals with stoichiometries close to $\text{CaZrTi}_2\text{O}_7$ have been reported, and on the basis of their external morphology, optical properties and X-ray powder diffraction patterns have been (variously and interchangeably) labelled polymignite, zirkelite and zirconolite. This confusion in the nomenclature has arisen partly because of the difficulty in distinguishing between the mineral species using traditional mineralogical techniques, and also because the incorporation of alpha-emitting isotopes of U and Th renders these minerals metamict, thereby limiting the usefulness of X-ray powder diffraction and optical methods for characterization. Since the crystal structures of these minerals have been recently determined (Rossell, 1980; Mazzi and Munno, 1983), it is timely to summarize their crystallographic and chemical

characteristics, record their historical documentation, and then to rationalize their nomenclature.

Crystallography

The cubic anion-deficient fluorite (CaF_{2-x}) structure-type ($a \approx 5\text{\AA}$) allows ordering (Rossell, 1980) of the compound $\text{CaZrTi}_2\text{O}_7$ to form three superstructures with symmetry as follows: monoclinic, orthorhombic and trigonal. The crystal structures of the monoclinic synthetic, $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$ with $x = 1.30$ and 0.85 , were described by Gatehouse *et al.* (1981). The crystal structure of the monoclinic mineral from Kaiserstuhl was solved by Sinclair and Eggleton (1982). The crystal structures of the orthorhombic and trigonal minerals from Campi Flegrei were solved by Mazzi and Munno (1983).

White *et al.* (1984) described these crystal struc-

Table 1. Polytype, space-group, layer-stacking sequence, unit-cell dimensions, and multiple unit-cell dimensions

Polytype	Unit-Cell Dimensions		
	<u>30</u>	<u>3T</u>	<u>2M</u>
Space-group	<u>Acam</u>	<u>P3₁²</u>	<u>C2/c</u>
Layer-stacking sequence	(m,m,m)	(t,t,t)	(-d,d)
a	10.1	7.3	12.6
b	14.1	7.3	7.3
c	7.3	16.9	11.4
β			100.5
Polytype	Multiple Unit-Cell Dimensions		
	<u>30</u>	<u>3T</u>	<u>2M</u>
a	2x12.4	12.6	12.6
b	7.3	7.3	7.3
c	17.4	16.9	4x16.9
β	91		90

tures as TiO_6 octahedral sheets alternating with planes of Ca and Zr atoms. The octahedral layers, which are similar to those found in hexagonal tungsten bronze, can be rotated and displaced with respect to each other to derive different symmetries. Therefore, the three minerals may be regarded as polytypes. As the monoclinic crystal structure has only two layers in its crystallographic repeat, White *et al.* (1984) suggested that this mineral be regarded as the aristotype (simplest structure from which the other polytypes can be derived) of the structural family, and introduced a layer stacking sequence composed of an interlayer stacking vector (Table 1) and a rotation.

In the monoclinic crystal structure, the two layers are related to each other by a 180° rotation, and interlayer stacking vectors $[\bar{1}30]$ and $[\bar{1}\bar{3}0]$ with a 2.1\AA displacement. In the trigonal crystal structure, three layers are related by a cyclic 120° rotation, and interlayer stacking vectors $[\bar{1}30]$, $[\bar{1}\bar{3}0]$, and $[100]$ with a 2.1\AA displacement. In the orthorhombic crystal structure, the stacking layer is distinct from that found in the monoclinic and trigonal crystal structures in that it is sheared on (100) to produce strings of edge-capped octahedral sites. Each layer is offset in the $[130]$ direction with a 5.5\AA displacement (White, 1984; White *et al.*, 1985).

Chemistry

The crystallochemical formula of these minerals can be formally presented as $M(1)_2^{\text{VIII}}$

$M(2)_2^{\text{VII}}M(3)_3^{\text{VI}}M(4)^{\text{IV,V}}\text{O}_{14}\square_2$; the end-member formula is $\text{Ca}_2^{\text{VIII}}\text{Zr}_2^{\text{VII}}\text{Ti}_3^{\text{VI}}\text{Ti}^{\text{V}}\text{O}_{14}$. The crystal structure formulae of minerals and synthetics in Table 2 have been slightly condensed from the tables of atomic coordinates and occupancy factors to enable easy comparison. The crystal structure refinement with multiple occupancies of many atomic sites by atoms with similar scattering factors is inconclusive as shown by the R index, because the correlation is high between atomic occupancies, temperatures factors and scale factor. Therefore the simple end-member formula of $\text{CaZrTi}_2\text{O}_7$ has been chosen.

In the mineral specimens, the major replacements are trivalent rare-earth elements (*REE*) and tetravalent actinides (*ACT*) for $[\text{Ca}]^{\text{VIII}}$, Nb and Ta for $[\text{Ti}]^{\text{VI}}$ and Fe for $[\text{Ti}]^{\text{IV,V}}$. Trivalent titanium can enter the $[\text{Zr}]^{\text{VII}}$ site to a small extent. Chemical data alone are insufficient for identification. Because the layer structures differ from one another by more than 0.25 atoms per formula unit of some constituent elements, they are called polytypoids rather than polytypes (Bailey *et al.*, 1977).

Historical documentation

Type polymignite described by Berzelius (1824) from Fredricksv rn, Norway is metamict. The mineral has an orthorhombic axial ratio (0.71:1:0.51), $n = 2.22(1)$ since isotropic (metamict), and $D_m = 4.8$. Type polymignite was heated by Lima-de-Faria (1964) at 700°C to give a cubic phase with $a = 5.06\text{\AA}$ and a fluorite structure-type; further heating at 1300°C produced in addition to the cubic phase another unidentified crystalline phase. An orthorhombic mineral with an axial ratio of 0.717:1.0:0.515 from Campi Flegrei was described by Mazzi and Munno (1983) as polymignite. Therefore polymignite has been described as a non-crystalline mineral (orthorhombic?), a cubic mineral and an orthorhombic mineral.

Type zirkelite described by Hussak and Prior (1895) from Jacupiranga, Brazil, is metamict with cubic morphology, $n = 2.19(1)$, and $D_m = 4.74$. Zirkelite (?) described by Blake and Smith (1913) from Ceylon is metamict with the morphology revised as hexagonal, and $D_m = 4.72$. Type zirkelite was heated by Pudovkina *et al.* (1974) at 1200°C and then indexed on a monoclinic unit-cell with $a = 12.55$, $b = 7.23$, $c = 11.39\text{\AA}$ and $\beta = 100.5^\circ$. A trigonal mineral from Campi Flegrei was described by Mazzi and Munno (1983) as zirkelite. Therefore zirkelite has been described as a non-crystalline mineral (cubic?), a hexagonal

Table 2. Crystal structure formulae of CaZrTi₂O₇ phases.

1.	$[(Ca,Na)_{0.57}(REE,Th)_{0.43}]_2^{VIII}[Zr]_2^{VII}[Ti_{0.76}(Nb,Ta)_{0.24}]_3^{VI}[Fe]^{IV}V_{0.14}$			
2.	$[(Ca,Na)_{0.57}(REE,Th)_{0.43}]_2^{VIII}[Zr]_2^{VII}[Ti_{0.75}(Nb,Ta)_{0.25}]_3^{VI}[Fe]^{IV}V_{0.14}$			
3.	$[Ca_{0.87}(REE,U,Th)_{0.13}]_2^{VIII}[Zr_{0.85}Ti_{0.15}]_2^{VII}[Ti_{0.49}Nb_{0.33}Zr_{0.10}Fe_{0.08}]_3^{VI}[Fe_{0.66}Ti_{0.34}]^{IV}V_{0.14}$			
4.	$[Ca_{0.99}Zr_{0.01}]_2^{VIII}[Zr_{0.98}(Ca,Ti)_{0.02}]_2^{VII}[Ti_{0.87}Zr_{0.13}]_3^{VI}[Ti_{0.84}Zr_{0.16}]^{IV}V_{0.14}$			
5.	$[Ca]_2^{VIII}[Zr_{0.93}Ti_{0.07}]_2^{VII}[Ti]_3^{VI}[Ti_{0.86}Zr_{0.14}]^{IV}V_{0.14}$			
6.	$[Ca_{0.98}Zr_{0.02}]_2^{VIII}[Zr_{0.84}Ti_{0.16}]_2^{VII}[Ti]_3^{VI}[Ti]^{IV}V_{0.14}$			
1.	Orthorhombic	Mazzi and Munno (1983)	Campi Flegrei	R=0.031
2.	Trigonal	Mazzi and Munno (1983)	Campi Flegrei	R=0.130
3.	Monoclinic	Sinclair and Eggleton (1982)	Kaiserstuhl	R=0.052
4.	Monoclinic	Gatehouse <i>et al.</i> (1981)	synthetic	R=0.045
5.	Monoclinic	Rossell (1980)	synthetic	R=0.054
6.	Monoclinic	Gatehouse <i>et al.</i> (1981)	synthetic	R=0.045

$$R \text{ (residual index)} = \sum |F_o(hkl) - |F_c(hkl)|| / \sum |F_o(hkl)|$$

mineral, a monoclinic mineral and a trigonal mineral.

Type zirconolite described by Borodin *et al.* (1956) from Afrikanda massif, Kola peninsula, USSR, is metamict with pseudo-cubic morphology, $n = 2.12$, and $D_m = 4.13$. Zirconolite from Alden, Arbarasthkh massif, USSR, described by Borodin *et al.* (1960) is not completely metamict, but has weak and diffuse reflections that correspond to a cubic symmetry with $a = 5.02 \text{ \AA}$ and a fluorite structure-type. Type zirconolite was heated to 650–800°C and gave a similar X-ray powder diffraction pattern. Further heating to 1100°C gives a phase (PDF 15–12), which is distinctly optically anisotropic, but the symmetry cannot be determined. Zirconolite, which was heated by Pudovkina and Pyatenko (1964) at 1200°C, gave an X-ray powder diffraction pattern similar to synthetic CaZrTi₂O₇ (PDF 17–495), which was indexed on a monoclinic cell by Pyatenko and Pudovkina (1964). Therefore zirconolite has been described as a non-crystalline mineral (cubic?), a cubic mineral, and a monoclinic mineral.

Zirconolite (which one not given) was shown by Hogarth (1977), who reported on behalf of the International Mineralogical Association Commission on New Minerals and Mineral Names (IMA-CNMMN) Pyrochlore Subcommittee, to be a synonym for zirkelite (which one not given), even though the minerals do not belong to the pyrochlore group. This resolution has not been

followed except by Fleischer (1987). Zirconolite has been used frequently of late (e.g. Wark *et al.*, 1973; Frondel, 1975; Gatehouse *et al.*, 1981; Sinclair and Ringwood, 1981; White *et al.*, 1984; Purtscheller and Tessardi, 1985; Fowler and Williams, 1986; Giéré, 1986; Agrell *et al.*, 1986; Platt *et al.*, 1987; Lorand and Cottin, 1987; Lorand *et al.*, 1987) and especially in the radioactive waste management literature (e.g. Ringwood, 1985).

Nomenclature problems

After a mineral has formed, the radioactive elements (U, Th) will disrupt the regular internal crystal structure so that the mineral becomes non-crystalline (i.e. metamict); however, the external morphology remains intact so that the axial ratio may be measured. If the same axial ratio is determined by X-ray diffraction after the mineral is recrystallized by heating, even though the change may involve the loss or addition of oxygen, nitrogen, fluorine or water, depending on the heating conditions, then the unit-cell dimensions are assumed correct. Since the cubic mineral and the three non-cubic polytypoids have similar multiple unit-cell dimensions (Table 1), external morphology cannot be used safely to separate these minerals.

The X-ray powder diffraction patterns of the three polytypoids are similar as shown by Table 17 of Mazzi and Munno (1983). For instance, the symmetry cannot be determined from the data

(PDF 15–12) of Borodin *et al.* (1960). Therefore X-ray single-crystal diffraction studies are necessary to make a clear distinction between these polytypoids.

Since all the type specimens are metamict, their refractive indexes are isotropic. Because of chemical variation, neither refractive indices nor measured density can differentiate these type specimens.

Because three of these minerals are polytypoids, they could be given the same root name, but with suffixed polytype symbols to indicate the number of octahedral layers in a crystallographic repeat and the supercell symmetry. This notation introduced by Ramsdell (1947) has recently been recommended by the IMA-CNMMN (Nickel and Mandarino, 1988).

In mineralogical practice, the appropriate suffix should be added when the polytypoid is determined (orthorhombic, trigonal, or monoclinic). Although at present only the letters for the crystal system are needed to differentiate the polytypoids, a notation of numbers and letters is needed, so that additional polytypoids may be added when found without disruption to the existing nomenclature. The root name only should be used when the polytypoid has not been determined, or the mineral is poorly crystalline or non-crystalline (e.g. metamict). Non-crystalline compounds are included here from a pragmatic point-of-view, because they are neither polytypoids nor polymorphs; and now as a general rule, they are not given separate species names.

Although the root name should be polymignite, based upon the rule of priority for mineral names, the name zirconolite has been used extensively by mineralogists (e.g. in publications appearing in *American Mineralogist*, *Canadian Mineralogist*, *Mineralogical Magazine*, among others) and waste management scientists, since its rejection by IMA-CNMMN in 1977. From a pragmatic point of view, it appears better to follow current usage than attempt to change current usage. The rare-earth nomenclature (4 minerals) of Levinson (1966) and the pyrochlore nomenclature (8 minerals) of Hogarth (1977) have not followed the rule of priority for mineral names in the interest of simplicity and clarity.

The orthorhombic mineral could be given a distinct species name based upon chemical composition and layer type; however, Tables 1 and 2 show that a chemical analysis and X-ray powder diffraction data are insufficient to distinguish the orthorhombic structure, so that this suggestion is unsatisfactory.

A species name needs to be given to the cubic phase, because it does not have a layered structure

and can readily be identified by X-ray powder diffraction. Cubic morphology was mentioned for zirkelite initially, so that based upon the rule of priority for mineral names, zirkelite is appropriate for the cubic phase.

At present, there are two valid names and one invalid name each with multiple meanings for the five different crystal structures. The nomenclature of these minerals has become so confused that the record should be set straight, and a simple scheme is given as follows:

1. The non-crystalline (metamict) mineral or mineral with undetermined polytypoid of $\text{CaZrTi}_2\text{O}_7$ shall be called zirconolite.
2. The orthorhombic mineral of $\text{CaZrTi}_2\text{O}_7$ shall be called zirconolite-3O.
3. The trigonal mineral of $\text{CaZrTi}_2\text{O}_7$ shall be called zirconolite-3T.
4. The monoclinic mineral of $\text{CaZrTi}_2\text{O}_7$ shall be called zirconolite-2M.
5. Polymignite (metamict) is zirconolite.
6. The cubic mineral of $(\text{Ti,Ca,Zr})\text{O}_{2-x}$ shall be called zirkelite.

Conclusion

In 1988, the IMA-CNMMN voted to approve this nomenclature scheme. A few negative votes were recorded, mainly because the rule of priority for mineral names was not followed.

Acknowledgements

Members of IMA-CNMMN including Dr E. H. Nickel, vice-chairman and Dr A. Kato, past-chairman, provided valuable advice.

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[Manuscript received 16 December 1988;
revised 20 March 1989]