

## Zirkelite from the Sebl'yavr carbonatite complex, Kola Peninsula, Russia: an X-ray and electron microprobe study of a partially metamict mineral

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### ABSTRACT

Zirkelite, a cubic mineral of general formula  $(\text{Ti,Ca,Zr})\text{O}_{2-x}$ , occurs as an accessory mineral in phoscorites, carbonatites and associated rocks in the Sebl'yavr complex. After pyrochlore, it is the main mineral concentrating niobium in these rocks. Zirkelite forms platy crystals comprising polysynthetic octahedral twins, often having a complex skeletal internal structure within a cuboctahedral external morphology. The mineral is largely metamict, but after heating to 800°C it produces a cubic crystalline structure with  $a_0 = 5.157 \pm 0.006 \text{ \AA}$ . It is black to brownish-black in colour, VHN = 760–780  $\text{kg}\cdot\text{mm}^{-2}$ , density =  $4.27 \text{ g}\cdot\text{cm}^{-3}$ , and reflectance = 12.5%.

Chemically, zirkelite is relatively enriched in  $\text{Nb}_2\text{O}_5$  (up to 14.5 wt.%) and  $\text{ThO}_2$  (up to 7.7 wt.%), and it displays four compositionally-distinct zones which probably formed during primary crystallisation processes. It is patchily altered where it is associated with an unidentified Ba, Ti, Nb, Zr silicate phase which partly replaces and pseudomorphs it. Under the current IMA-approved nomenclature scheme, non-crystalline (metamict) minerals of the composition described here would normally be given the general species name zirconolite, with the name zirkelite confined to the cubic mineral. However, at Sebl'yavr, the name zirkelite is used because the mineral displays a well-defined cubic crystal morphology and has a cubic structure after heating.

**KEYWORDS:** zirkelite, zirconolite, Sebl'yavr, Kola Peninsula, carbonatite.

### Introduction

ZIRKELITE is the cubic mineral with the general formula  $(\text{Ti,Ca,Zr})\text{O}_{2-x}$  which is very close compositionally to the more commonly occurring mineral with general name zirconolite,  $\text{CaZrTi}_2\text{O}_7$  for which new nomenclature rules have been approved (Bayliss *et al.*, 1989). This nomenclature reclassification of the  $\text{CaZrTi}_2\text{O}_7$  minerals (Bayliss *et al.*, 1989) has recommended that the name zirconolite is used for the non-crystalline (metamict) mineral, or mineral with undetermined polytypoid of  $\text{CaZrTi}_2\text{O}_7$ , and zirconolite-3O, -3T and -2M for different (crystalline) polytypoids, whereas the name zirkelite be confined to the cubic mineral.

Zirconolite (and more rarely, zirkelite) occurs as an accessory mineral in a wide range of rock types and parageneses (e.g. Williams and Gieré,

1996), but generally only as a trace or accessory mineral and rarely exceeding 100  $\mu\text{m}$  in size. Although essentially  $\text{CaZrTi}_2\text{O}_7$  in composition, the mineral can accommodate up to 30 elements at concentrations in excess of 0.1 wt.% with the major substitutions being Nb, Ta, rare earth elements (REE), Th and U (e.g. Gieré and Williams, 1992). Although zirconolite, originally reported as the now abandoned mineral name polymignite, was first described over 150 years ago (Berzelius, 1824), its small size and complex chemical composition has meant that detailed mineralogical and chemical descriptions have only recently become possible using modern microprobe techniques.

Zirconolite (and/or zirkelite) occurs as an accessory mineral in several carbonatite complexes within the Kola Peninsula, Russia. It has been reported from Sebl'yavr, Vuoriyarvi, Afrikanda,

Kovdor (Bulakh *et al.*, 1960; Williams and Gieré, 1996), and from the Turi peninsula (Anastassenko *et al.*, 1978; Bulakh and Ivanikov, 1984). Descriptions of the geological aspects of these carbonatites can be found in Kogarko *et al.* (1995). Previously-reported analyses of zirconolite from the Kola carbonatites are largely from bulk wet chemical analyses of separated mineral grains; however, a recent study of zirconolite from Kovdor (Williams, 1996) has shown significant compositional variations within single grains.

The mineral from Sebl'yavr was first described as zirkelite (Bulakh *et al.*, 1960; Bulakh, 1963), where it occurs as large millimetre-sized crystals which allows for a detailed physical, structural, morphological and chemical study to be made. The aims of this study were to re-examine this mineral from the Sebl'yavr carbonatite using a combination of modern microprobe techniques: (1) to ascertain whether compositional variations exist; and (2) with classical goniometric techniques coupled with X-ray diffraction measurements, to attempt to assign a definitive name to the mineral. This paper forms part of a continuing study of the accessory minerals associated with the carbonatites and related rocks in the Kola Peninsula, Russia.

#### Ca,Zr,Ti oxide mineral

At Sebl'yavr, this mineral occurs in phoscorites (magnetite-forsterite-apatite rocks), metasomatic

tetraferriphlogopite-bearing dolomite rocks, and in calcite-carbonatites. It is an accessory mineral associated with other zirconium and niobium minerals such as calzirtite (Bulakh and Shevaleevsky, 1962), baddeleyite and pyrochlore (Bulakh *et al.*, 1960). It usually forms as tabular (platy) crystals up to 2 mm in diameter, often with complex intergrowths (Fig. 1).

Single platy crystals have a triangular or hexagonal appearance with faces similar to basal pinacoid and prominent rhombohedral faces. The 'basal pinacoid' faces typically have a surface lustre, whereas the 'rhombohedral' faces are invariably tarnished. Three platy crystals were measured with a goniometer and gave a trigonal symmetry; a stereographic projection of the measured faces (Fig. 2) corresponds to a cubic  $Fm\bar{3}m$  point symmetry. From these measurements, calculation gives values close to an ideal octahedron, i.e.  $\varphi = 44^\circ 57'$  (close to  $45^\circ 00'$ ),  $\rho = 54^\circ 58'$  (close to  $54^\circ 44'$ ). Of note is the observation that the 'rhombohedral' faces are covered with thin striations and that the platy crystals very often consist of stacked sheets. These single platy crystals are considered to be polysynthetic octahedral twins similar to the octahedrons of zirkelite described by Hussak and Prior (1895) from the type locality in Brazil.

At Sebl'yavr, intergrowths of several platy crystals, illustrated in the secondary electron image (Fig. 3a), are typically seen. Where four plates have intergrown, a cubo-octahedron is the

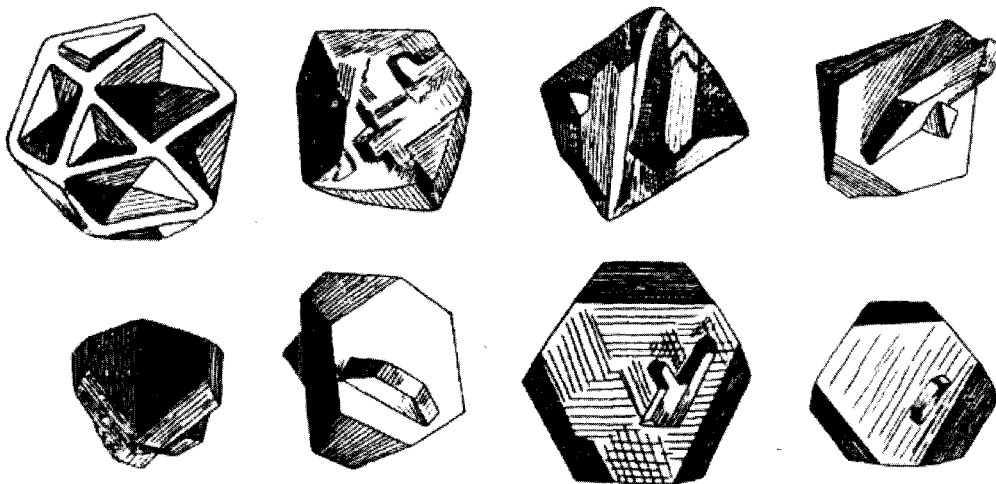


Fig. 1. Crystal drawings of separated grains of zirkelite, size of crystals approximately 0.5 mm.

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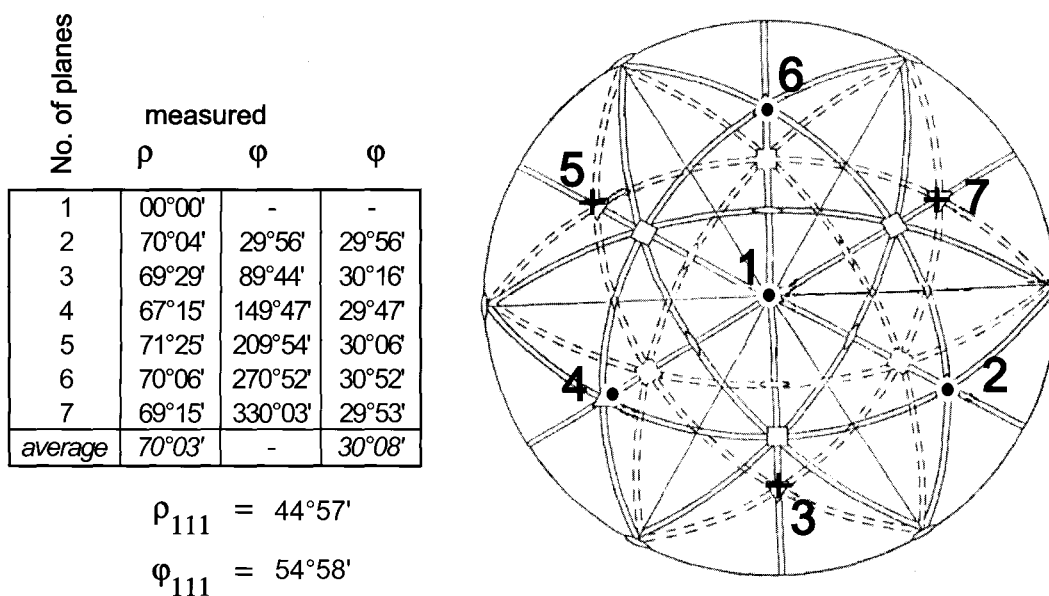


FIG. 2. Stereographic projection of faces measured from three platy zirkelite crystals. Recalculation from the stereogram gives values close to an ideal octahedron, i.e.  $\phi = 44^\circ 57'$  (close to  $45^\circ 00'$ ),  $\rho = 54^\circ 58'$  (close to  $54^\circ 44'$ ).

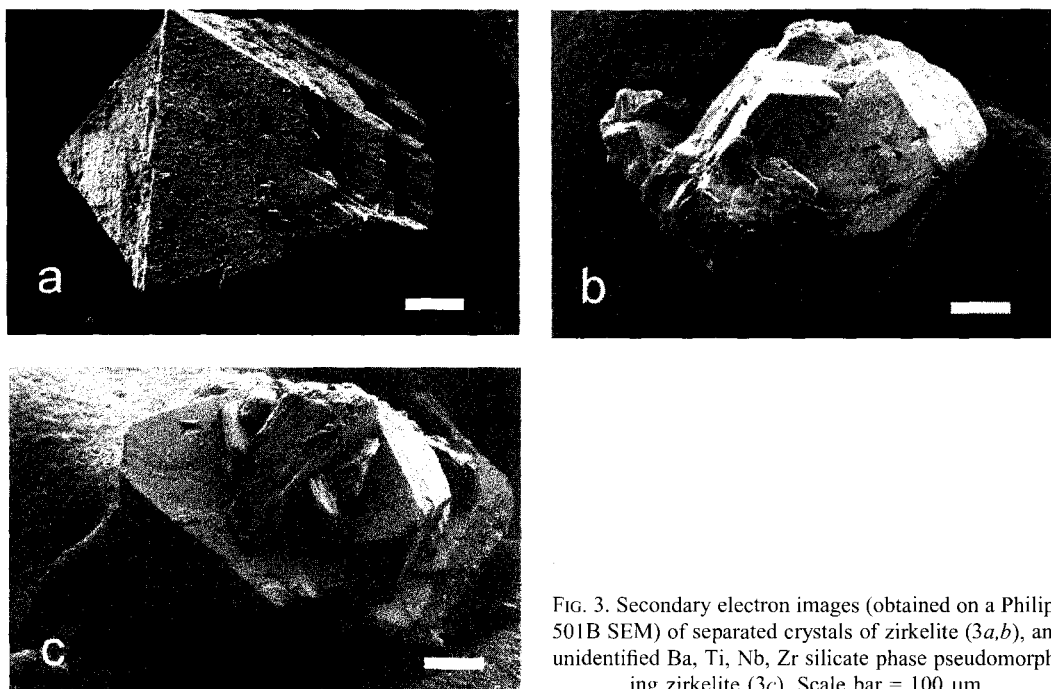


FIG. 3. Secondary electron images (obtained on a Philips 501B SEM) of separated crystals of zirkelite (3a,b), and unidentified Ba, Ti, Nb, Zr silicate phase pseudomorphing zirkelite (3c). Scale bar = 100  $\mu\text{m}$ .

resulting overall external morphology, but often a gap is present between the different plates (Fig. 1).

These crystals are mainly black in colour, more rarely brownish-black, with a conchoidal fracture and a semi-metallic or waxy lustre. It has a hardness of 6–6.5 on Mohs' Hardness scale, and 760–780 kg.mm<sup>-2</sup> on the Vickers Hardness scale. The density measured on a 500 mg mass of sample was 4.27 g.cm<sup>-3</sup>. In thin section, grains are brown in colour, semi-transparent and optically isotropic with a refractive index measured at 2.25–2.28: reflectance in air was 12.5%. Occasionally seen are small areas which are anomalously anisotropic and with a very low birefringence.

Differential thermal analysis was undertaken on several (predominantly black-coloured) grains weighing approximately 500 mg. The results show the presence of a large endothermic peak at about 750°C, which we interpret as being the result of recrystallisation of the metamict material to a crystalline phase, confirmed by X-ray diffraction studies. Exothermic peaks, at 100–300, 450 and 850°C, correspond with weight losses most probably due to loss of H<sub>2</sub>O.

The mineral is largely, but not completely, metamict. The first attempts at X-ray powder photography were made by Dr A.I. Komkov (Bulakh *et al.*, 1960), who showed that a few crystals retained some degree of crystallinity and gave a faint pattern which showed several very weak lines. In this original study (Bulakh *et al.*, 1960), a few grains of zirkelite, chemical composition given in Table 2 (analysis 6), were heated at 600, 800 and 1000°C for 30 minutes each and at each temperature subjected to X-ray powder analysis. Distinct lines were observed from the samples heated at 800 and 1000°C (Table 1, samples 1 and 2), the most intense lines corresponding to those obtained on the unheated material. The resultant patterns were typical for the structure type of CaF<sub>2</sub> with  $a = 5.04\text{--}5.06$  Å, i.e. similar to that of cubic ZrO<sub>2</sub>. Thus, the samples subject to heating are considered to have reconstructed the crystalline structure of zirkelite *sensu stricto*. Komkov (in Bulakh *et al.*, 1960), noted that the same pattern could correspond to a pyrochlore structure type with  $a_0 = 10.08\text{--}10.12$  Å if weak lines with odd indices were absent. After heating the sample above 1000°C (to 1100 and 1200°C), some new lines did in fact appear on the X-ray powder patterns. This effect has been reported also for metamict priorite

(Komkov, 1959), where a crystalline structure is observed at 450–600°C coupled with a compositional phase change between 800–1200°C.

We repeated the X-ray study on two of the black coloured grains selected from the samples separated for microprobe analysis (Table 2), using a diffraction technique rather than a film technique. Samples were heated at 800°C for two hours and, after this period, their colour changed from black to brown, and their X-ray powder diffractograms showed the same lines that were present on Komkov's powder film (Bulakh *et al.*, 1960), but included also some new weak lines (Table 1, sample 3). The crystal system is probably cubic with  $a_0 = 5.157 \pm 0.006$  Å, and similar to cubic ZrO<sub>2</sub>. The sample was then kept at room temperature for 14 days in order to attain a stable state, and a new diffractogram obtained which showed that the weaker lines had disappeared (Table 1, sample 3a), thus confirming the cubic crystal system. The X-ray crystallographic studies are thus in agreement with the external crystal morphology and goniometry, and the criteria for reporting a crystallographic system for metamict minerals (Nickel, 1995) have been met. Therefore, on structural grounds, the mineral can be definitively named as zirkelite.

A bulk 'wet' chemical analysis of approximately 500 mg of separated zirkelite has previously been made and is reported here alongside microprobe analyses from this study (Table 2). Here, forty-two individual microprobe analyses were obtained on five separated black-coloured grains of zirkelite. Microprobe analyses were performed using a Cameca SX50 wavelength-dispersive electron microprobe. Operating conditions were: 20 kV accelerating potential, 25 nA specimen current, 1 μm spot size and a PAP  $\phi\rho z$  matrix correction procedure. Standards used were a combination of well-characterised minerals, pure metals and synthetic compounds (including for the major elements — perovskite, sodium niobate and zirconium oxide). Backscattered electron images were obtained on a Hitachi S.2500 scanning electron microscope with KE Developments solid state backscattered detector.

There is a relatively good agreement between the original wet chemical data and the modern microprobe data (Table 2). Differences in SiO<sub>2</sub> and ZrO<sub>2</sub> can be best explained by the bulk sample containing impurities of titanite, baddeleyite and silicate phases, whereas differences in

TABLE 1. X-ray powder diffraction pattern for zirkelite from Sebl'yavr (cubic system)

$I/I_0$	Sample 1		$I/I_0$	Sample 2		$I/I_0$	Sample 3			$I/I_0$	Sample 3a		
	$d$ (Å)	$hkl$		$d$ (Å)	$hkl$		$d$ (Å)	$hkl$	$d$ (Å)		$d$ (Å)	$hkl$	$d$ (Å)
	measured		measured			measured	calculated		measured		measured	calculated	
—	—	—	—	—	—	11	3.39	1 1 0	3.64	10	3.37	1 1 0	3.560
4	3.23	—	1	(3.20)	—	22	3.15	—	—	—	—	—	
10	2.92	1 1 1	5	2.91	1 1 1	100	2.96	1 1 1	2.970	100	2.91	1 1 1	2.910
—	—	—	—	—	—	22	2.57	2 0 0	2.578	—	—	—	—
—	—	—	—	—	—	19	2.55	—	—	—	—	—	—
3	2.52	2 0 0	2	2.52	2 2 2	15	2.52	—	—	20	2.52	2 0 0	2.520
—	—	—	—	—	—	1	2.19	—	—	—	—	—	—
—	—	—	—	—	—	4	2.09	—	—	—	—	—	—
—	—	—	0.5	(1.97)	2 2 0	—	—	—	—	—	—	—	—
8	1.8	2 2 0	5	1.79	2 2 0	50	1.82	2 2 0	1.823	40	1.78	2 2 0	1.781
1	1.76	—	—	—	—	—	—	—	—	—	—	—	—
1	(1.54)	3 1 1	3	1.578	3 1 1	41	1.560	3 1 1	1.555	30	1.530	3 1 1	—
8	1.522	3 1 1	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	11	1.484	2 2 2	1.472	—	—	—	—
4	1.460	2 2 2	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	10	1.289	—	—	—	—	—	—
2	1.260	—	—	—	—	10	1.260	3 2 2	1.251	—	—	—	—
—	—	—	—	—	—	17	1.184	3 3 1	1.180	—	—	—	—
—	—	—	—	—	—	9	1.052	4 2 2	1.050	—	—	—	—

Heated at 1000°C for 30 minutes $a_0 = 5.04 \pm 0.01 \text{ \AA}$ $V_0 = 128 \pm 0.9$ A.I. Komkov (Bulakh <i>et al.</i> , 1960)	Heated at 1000°C for 30 minutes $a_0 = 5.04 \pm 0.01 \text{ \AA}$ $V_0 = 128 \pm 0.9$	Heated at 800°C for 120 minutes $a_0 = 5.157 \pm 0.006 \text{ \AA}$ $V_0 = 136.6 \pm 0.9$ I.S. Anisimov (this paper)	Kept at 20°C for 14 days after heating $a_0 = 5.04 \pm 0.01 \text{ \AA}$ $V_0 = 128 \pm 2$
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TABLE 2. Zirkelite and baddeleyite from Sebl'yavr, Kola Peninsula

Analysis No.	Highest z (hz)		Medium z (mz1)		Medium z (mz2)		Lowest z (lz)		Altered region	'Wet' chemical	Baddeleyite
	Mean (8)	s.d.	Mean (9)	s.d.	Mean (11)	s.d.	Mean (11)	s.d.			
	1		2		3		4		5	6	7
MgO	0.64	0.09	0.55	0.07	0.46	0.06	0.31	0.11	0.54	trace	<.05
Al <sub>2</sub> O <sub>3</sub>	<.05	—	<.05	—	<.05	—	<.05	—	0.05	—	<.05
SiO <sub>2</sub>	<.05	—	0.07	0.06	<.05	—	0.05	0.03	0.06	1.23	<.05
CaO	10.32	0.31	10.86	0.23	11.14	0.18	11.57	0.24	9.76	10.22	0.13
TiO <sub>2</sub>	19.51	0.55	19.45	0.87	20.97	0.92	23.69	1.93	19.29	20.00	0.48
MnO	0.38	0.07	0.33	0.05	0.31	0.03	0.27	0.03	0.34	—	<.05
FeO	7.26	0.16	7.39	0.13	7.34	0.13	7.12	0.19	6.01	3.19	0.31
Fe <sub>2</sub> O <sub>3</sub>	—	—	—	—	—	—	—	—	—	4.81	—
Y <sub>2</sub> O <sub>3</sub>	0.29	0.06	0.30	0.07	0.32	0.05	0.40	0.05	0.29	—	<.05
ZrO <sub>2</sub>	29.31	0.32	29.80	0.27	30.06	0.48	30.56	0.58	28.39	33.42	96.35
Nb <sub>2</sub> O <sub>5</sub>	14.48	0.58	14.48	0.98	14.23	0.78	13.02	1.54	12.53	11.25	0.58
La <sub>2</sub> O <sub>3</sub>	0.13	0.06	0.10	0.04	0.14	0.02	0.12	0.02	0.11	—	<.05
Ce <sub>2</sub> O <sub>3</sub>	1.28	0.23	1.04	0.25	1.22	0.12	1.21	0.09	1.14	—	<.05
Pr <sub>2</sub> O <sub>3</sub>	<.15	—	<.15	—	<.15	—	<.15	—	<.15	—	<.15
Nd <sub>2</sub> O <sub>3</sub>	1.20	0.17	1.05	0.23	1.17	0.12	1.24	0.11	1.03	—	<.15
Sm <sub>2</sub> O <sub>3</sub>	0.30	0.07	0.25	0.08	0.28	0.04	0.33	0.05	0.25	—	<.15
Eu <sub>2</sub> O <sub>3</sub>	<.15	—	<.15	—	<.15	—	<.15	—	<.15	—	<.15
Gd <sub>2</sub> O <sub>3</sub>	0.20	0.04	<.15	—	0.16	0.11	0.24	0.04	0.25	—	<.15
Dy <sub>2</sub> O <sub>3</sub>	<.15	—	<.15	—	<.15	—	0.19	0.04	<.15	—	<.15
HfO <sub>2</sub>	0.55	0.06	0.56	0.11	0.59	0.09	0.53	0.13	0.57	0.64	2.23
Ta <sub>2</sub> O <sub>5</sub>	2.21	0.66	2.78	0.82	2.02	0.71	1.14	0.54	2.42	1.50	0.36
PbO	0.20	0.08	0.20	0.08	0.13	0.07	0.10	0.11	0.18	—	0.12
ThO <sub>2</sub>	7.71	0.35	6.34	0.30	5.53	0.20	4.26	0.55	6.74	2.73	<.1
UO <sub>2</sub>	1.59	0.26	1.55	0.45	1.21	0.43	0.66	0.34	1.73	0.96	<.1
Total	97.57	0.46	97.09	0.87	97.28	0.79	97.02	0.89	91.63	98.85*	100.55
Y+REE <sub>2</sub> O <sub>3</sub>	3.40	0.54	2.73	0.71	3.28	0.40	3.74	0.25	3.05	6.1***	—
Cations to 7 oxygens											
Ca <sup>2+</sup>	0.768	0.023	0.804	0.015	0.813	0.011	0.829	0.009	0.767	—	**
Y <sup>3+</sup>	0.011	0.002	0.011	0.002	0.012	0.002	0.014	0.002	0.011	—	0.006
La <sup>3+</sup>	0.003	0.002	0.003	0.001	0.003	0.001	0.003	0.000	0.003	—	0.000
Ce <sup>3+</sup>	0.032	0.006	0.026	0.006	0.031	0.003	0.030	0.003	0.031	—	0.000
Pr <sup>3+</sup>	0.000	0.000	0.000	—	0.000	—	0.000	—	0.000	—	0.000
Nd <sup>3+</sup>	0.030	0.004	0.026	0.006	0.028	0.003	0.030	0.002	0.027	—	0.000
Sm <sup>3+</sup>	0.007	0.002	0.006	0.002	0.007	0.001	0.008	0.001	0.006	—	0.000
Eu <sup>3+</sup>	0.000	0.001	0.000	—	0.000	—	0.000	—	0.000	—	0.000
Gd <sup>3+</sup>	0.005	0.001	0.000	—	0.004	0.002	0.005	0.001	0.006	—	0.000
Dy <sup>3+</sup>	0.000	—	0.000	—	0.000	—	0.004	0.001	0.000	—	0.000
Pb <sup>2+</sup>	0.004	0.001	0.004	0.001	0.002	0.001	0.002	0.002	0.003	—	0.000
Th <sup>4+</sup>	0.122	0.006	0.100	0.005	0.086	0.003	0.065	0.009	0.113	—	0.000
U <sup>4+</sup>	0.025	0.004	0.024	0.007	0.018	0.006	0.010	0.005	0.028	—	0.000
Sum Ca	1.006	0.008	1.003	0.006	1.003	0.008	0.999	0.010	0.995	—	0.006
Zr <sup>4+</sup>	0.992	0.010	1.004	0.010	0.998	0.012	0.996	0.011	1.016	—	1.930
Hf <sup>4+</sup>	0.011	0.001	0.011	0.002	0.011	0.002	0.010	0.003	0.012	—	0.026
Sum Zr	1.003	0.011	1.015	0.011	1.010	0.012	1.006	0.011	1.028	—	1.956
Ti <sup>2+</sup>	1.018	0.029	1.011	0.040	1.074	0.046	1.190	0.088	1.065	—	0.015
Si <sup>4+</sup>	0.000	—	0.005	0.004	0.000	—	0.003	0.002	0.004	—	0.000
Mg <sup>2+</sup>	0.066	0.009	0.056	0.007	0.046	0.006	0.031	0.011	0.059	—	0.000
Mn <sup>2+</sup>	0.023	0.004	0.019	0.003	0.018	0.002	0.015	0.002	0.021	—	0.000
Fe <sup>2+</sup>	0.421	0.009	0.427	0.007	0.418	0.008	0.398	0.014	0.369	—	0.010
Al <sup>3+</sup>	0.000	—	0.002	0.003	0.000	—	0.001	—	0.004	—	0.000
Nb <sup>5+</sup>	0.455	0.018	0.453	0.032	0.438	0.025	0.394	0.048	0.416	—	0.011
Ta <sup>5+</sup>	0.042	0.012	0.052	0.015	0.037	0.013	0.021	0.010	0.048	—	0.004
Sum Ti	2.025	0.010	2.025	0.014	2.033	0.014	2.053	0.015	1.985	—	0.040
Total	4.035	0.006	4.044	0.007	4.046	0.005	4.057	0.007	4.009	—	2.002

Analyses 1–5 and 7 are by wavelength-dispersive electron microprobe

F, Cl <0.1%; Na<sub>2</sub>O <0.05%; SrO <0.1%; BaO <0.1%; WO<sub>3</sub> <0.2%

Analysis 6 by 'wet' chemical analysis of separated grains

\* Total of 'wet' chemical analysis (1959) includes SrO = 0.21%; H<sub>2</sub>O<sup>-</sup> = 0.33%; H<sub>2</sub>O<sup>+</sup> = 3.26%

\*\* Baddeleyite: cations to 4 oxygens

\*\*\* Individual REE not analysed

## ZIRKELITE FROM THE KOLA PENINSULA

Nb, REE, and Th probably result from errors associated with the wet chemical analytical methods used. Nevertheless, mineral formulae obtained by both methods are similar:  $(\text{Ca}_{0.75}\text{REE}_{0.16}\text{Th}_{0.04}\text{U}_{0.02}\text{Sr}_{0.01})_{\Sigma 0.98}(\text{Zr}_{1.09}\text{Hf}_{0.01})_{\Sigma 1.10}(\text{Ti}_{1.02}\text{Nb}_{0.35}\text{Fe}_{0.24}^{3+}\text{Fe}_{0.18}^{2+}\text{Si}_{0.08}\text{Ta}_{0.03})_{\Sigma 1.91}\text{O}_{7.00}$  by wet chemistry, and  $(\text{Ca}_{0.77}\text{REE}_{0.08}\text{Th}_{0.12}\text{U}_{0.03})_{\Sigma 1.00}(\text{Zr}_{0.99}\text{Hf}_{0.01})_{\Sigma 1.00}(\text{Ti}_{1.02}\text{Nb}_{0.46}\text{Fe}_{0.42}\text{Mg}_{0.07}\text{Ta}_{0.04}\text{Mn}_{0.02})_{\Sigma 2.03}\text{O}_{7.00}$  by electron microprobe (mean *hz*, Table 2, analysis 1): here the cations have been calculated to 7 oxygens, based on the structural formula of  $\text{CaZrTi}_2\text{O}_7$ , in order to compare them with the compilation data in Williams and Gieré (1996). It should be noted, however, that cubic mineral zirkelite has the formula  $(\text{Ti,Ca,Zr})\text{O}_{2-x}$  (Bayliss *et al.*, 1989), and a further compositionally-similar mineral tazheranite has the formula  $(\text{Zr,Ca,Ti})\text{O}_2$  (Konev *et al.*, 1969).

All of the five grains analysed in this study are complexly zoned, have been altered to varying degrees, and have inclusions of calcite, apatite and occasionally small (<5  $\mu\text{m}$ ) grains of galena. The galena is associated with alteration areas and is probably secondary. Also included in zirkelite was a 10  $\mu\text{m}$  diameter grain of baddeleyite (Table 2, analysis 7), and unidentified Ba, Nb, Ti, Zr silicate phases (see below).

Four distinct zones of zirkelite were identified on the basis of backscattered electron images (BEI) (Figs 4a,b) and chemical compositions (Table 2, analyses 1–4). The zones do not appear to be randomly distributed throughout the grains, and probably correspond to some crystallographic orientation(s), but are believed to be primary in origin and not some exsolution phenomenon. They are labelled in Table 2 as ‘*hz*’ (with the highest backscattered component); ‘*mz1*’, ‘*mz2*’, and ‘*lz*’ (with decreasing backscattered component). The main differences between zones are in the Th (and U) concentrations, and correspondingly in Ca. Minor correlations involving Th also occur with Mg and Mn, but there is no pattern of Nb or Ta correlating with Th. The highest  $\Sigma\text{REE}$  correspond to the lowest Th zone and has a slightly more enriched heavy-REE chondrite-normalised pattern than the other zones. The chondrite-normalised REE patterns for all the zones have a maximum enrichment at Nd and are similar to those seen for zirconolites from other carbonatites, including Kovdor (Williams, 1996). Although binary plots involving cations such as  $\text{Ca}^{2+}$  and  $\text{Th}^{4+}$  do not uniquely distinguish the zones, distinct boundaries between adjacent zones

are observed in individual grains on the BEI (e.g. area labelled A in Fig. 4a). The low analytical totals of 97.0–97.6% are probably due to some degree of hydration, often seen in metamict zirconolite minerals, and the water content on a bulk sample and gave concentrations of 3.26% for  $\text{H}_2\text{O}^+$ , and 0.33% for  $\text{H}_2\text{O}^-$ .

Where zirkelite is replaced by the unidentified Ba, Ti, Nb, Zr silicate phase(s), there is always a small (<5  $\mu\text{m}$ ) region of relatively lower back-scattering component which corresponds to zirkelite depleted mainly in Fe, but also in Ca, and with a much lower analytical total (analysis 5, Table 2).

### Unidentified Ba, Ti, Nb, Zr silicate phase(s)

This phase (or phases) is clearly seen in the BEI where it replaces the black-coloured grains of zirkelite along cracks (Fig. 4c,d). Also, it forms separate brown semi-transparent platy crystals which are pseudomorphs after zirkelite, but here the tabular crystals comprise a number of plates as seen on the secondary electron image (Fig. 3b,c).

The unidentified phase(s) is a silicate containing varying proportions of Ba, Ti, Zr and Nb (also with Ta, Th and U) with low analytical totals (Table 3). The low totals strongly suggest the mineral is hydrated with up to 7–9%  $\text{H}_2\text{O}$  present. Although the presence of Li, Be, or B (or a carbonate) cannot be ruled out, other elements at major concentrations would have been detected on the microprobe.

On the BEI, zones corresponding to analyses 1 and 2 (Table 3) are clearly distinct and have consistent compositions from more than one grain. Another area which has a consistent composition is represented by analysis 3 (Table 3). Analyses 4–7 are single spot analyses on areas which are quite distinct on the BEI, and illustrate the large compositional variation present, and suggest that more than one phase may be present. Of note is the relatively high concentrations of  $\text{Ta}_2\text{O}_5$  present in some areas (analyses 5–7, Table 3). A fuller investigation of this mineral is currently in progress by one of us (ISA), and preliminary results show it to be metamict.

### Discussion

Over the last two decades, zirconolite (and, to a much lesser extent, zirkelite) has been reported from a variety of rock types and localities

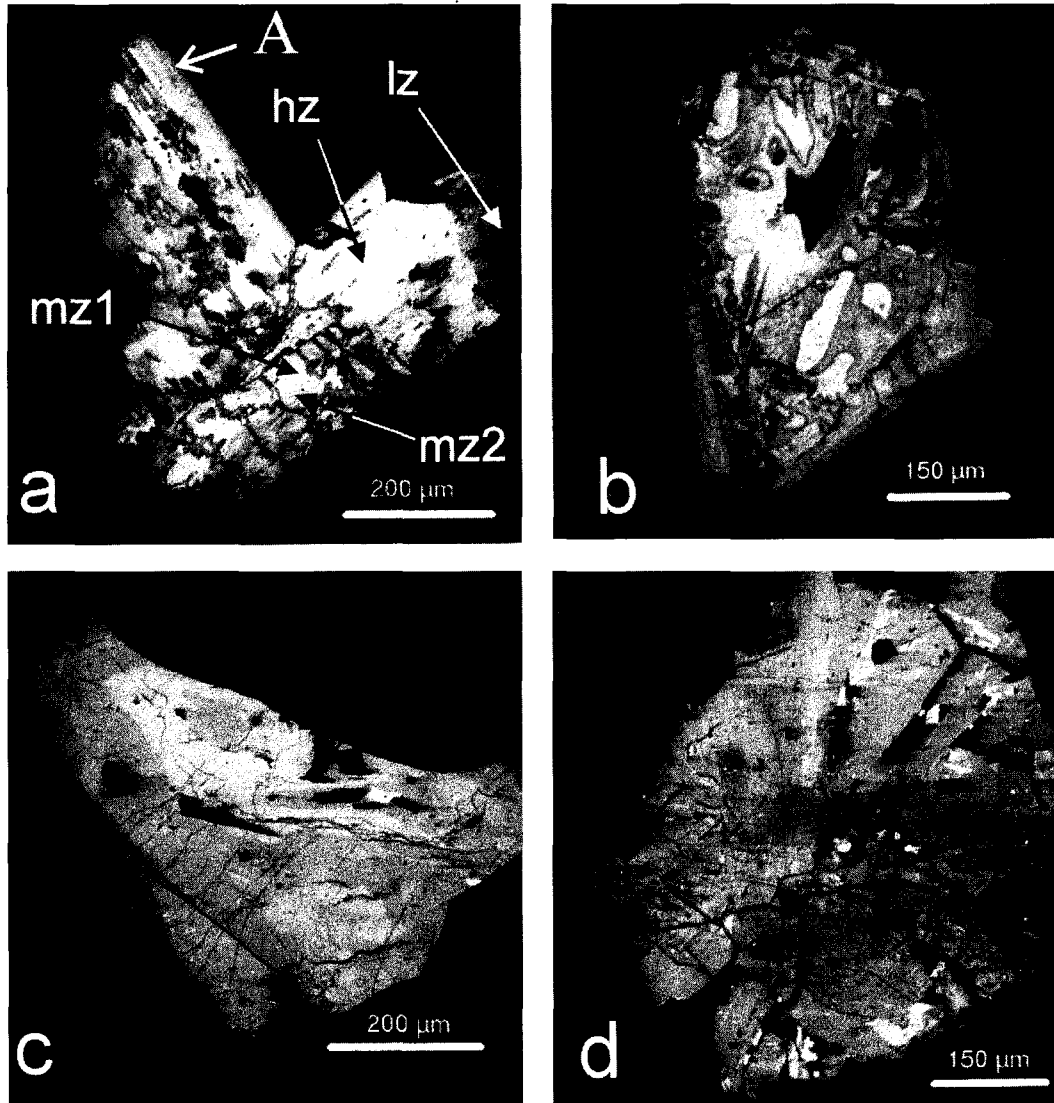


FIG. 4. Backscattered electron images (obtained on a Hitachi S2500 SEM) of zirkelite grains (4a,b) and unidentified Ba, Ti, Nb, Zr silicate phase (4c,d).

(Williams and Gieré, 1996). It has a large compositional range, and in carbonatites and associated rocks it can be a major host for elements such as Nb and Ta. In a phlogopite-bearing calcite carbonatite from the Turij Peninsula, Murmansk, up to 63% of the Ta is calculated to be present in zirkelite (Anastesenko *et al.*, 1978).

The often metamict nature of these minerals are a result of the ubiquitous presence of actinide

elements (Th and U), and the existence of five different structural polytypoids has led to nomenclature problems now resolved by Bayliss *et al.* (1989). Among their IMA-approved recommendations are that the non-crystalline (metamict) mineral or mineral with undetermined polytypoid of  $\text{CaZrTi}_2\text{O}_7$  shall be called zirconolite, and that the cubic mineral shall be called zirkelite with a formula of  $(\text{Ti,Ca,Zr})\text{O}_{2-x}$ . Comparison of our X-ray powder data (Table 1)



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TABLE 3. Microprobe analyses of the Ba, Ti, Nb, Zr silicate phases from Sebl'yavr, Kola, Russia

Analysis	1	2	3	std. dev.	4	5	6	7
Al <sub>2</sub> O <sub>3</sub>	<0.05	0.11	0.20	0.02	0.10	0.22	0.30	0.19
SiO <sub>2</sub>	13.93	12.19	9.04	0.84	4.03	8.40	7.95	3.96
CaO	1.51	1.48	1.22	0.11	2.85	1.59	1.02	2.04
TiO <sub>2</sub>	9.96	10.36	14.72	1.05	19.92	11.71	7.59	10.31
MnO	0.25	0.23	0.32	0.06	0.64	0.19	0.21	0.37
FeO	2.03	1.94	1.76	0.29	3.46	1.19	1.18	1.89
SrO	0.50	0.22	0.22	0.07	0.22	0.38	0.27	0.35
Y <sub>2</sub> O <sub>3</sub>	0.40	0.27	0.09	0.05	0.30	<0.05	<0.05	<0.05
ZrO <sub>2</sub>	35.05	31.31	19.61	2.09	27.71	7.72	3.67	2.69
Nb <sub>2</sub> O <sub>5</sub>	12.54	13.47	17.82	0.87	15.06	27.14	34.79	31.72
BaO	4.61	8.55	15.08	1.15	6.55	19.57	21.21	14.92
La <sub>2</sub> O <sub>3</sub>	<.1	<.1	0.11	0.03	0.12	0.18	0.22	0.10
Ce <sub>2</sub> O <sub>3</sub>	0.63	0.45	0.26	0.15	0.80	0.71	0.42	<.2
Nd <sub>2</sub> O <sub>3</sub>	0.60	0.40	<.15	—	0.61	<.15	<.15	<.15
Gd <sub>2</sub> O <sub>3</sub>	<.15	<.15	<.15	—	<.15	<.15	<.15	<.15
Dy <sub>2</sub> O <sub>3</sub>	<.15	<.15	<.15	—	<.15	<.15	<.15	<.15
HfO <sub>2</sub>	0.91	0.72	0.33	0.03	0.52	0.19	0.24	0.19
Ta <sub>2</sub> O <sub>5</sub>	1.75	2.39	3.40	0.81	0.94	6.49	7.72	6.17
PbO	<.1	0.12	0.12	0.10	<.1	0.23	0.26	0.67
ThO <sub>2</sub>	5.60	5.79	5.30	0.74	4.26	4.01	0.85	2.54
UO <sub>2</sub>	1.26	1.23	1.75	0.58	0.40	3.84	4.76	15.59
Total	91.53	91.22	91.35	1.28	88.49	93.77	92.65	93.67
Y+REE <sub>2</sub> O <sub>3</sub>	1.63	1.12	0.46	0.17	1.84	0.89	0.64	0.10

MgO <0.05%; F, Cl <0.1%; Na<sub>2</sub>O, K<sub>2</sub>O <0.1%; Pr<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub> <0.15%; WO<sub>3</sub> <0.2%

1 = mean of 3

2 = mean of 3

3 = mean of 10

4, 5, 6, 7 are individual analyses representing the compositional range of the Ba, Ti, Nb, Zr silicate phases

of samples from Sebl'yavr, with those of monoclinic zirconolite from Aldan (Pudovkina and Pjatenko, 1964) and with the PDF card 15-0012, shows many similarities. However, the cubic system is preferred for the Sebl'yavr samples, because of the goniometric measurements on large single crystals. Zirconolite (zirkelite) from other carbonatites in the Kola Peninsula show subtle differences in both X-ray diffraction patterns and external crystal morphologies. Goniometric measurements on crystals from Sayan mountains give a trigonal symmetry (Yakovlevskaya, 1967), whereas heated samples from Vuoryarvi (Bulakh *et al.*, 1960) produce a more complicated X-ray pattern than that from Sebl'yavr. It appears likely then that more than one polytype of the CaZrTi<sub>2</sub>O<sub>7</sub> mineral occurs in the various carbonatite intrusions within the Kola Peninsula.

### Conclusions

X-ray diffraction data obtained after heating the metamict CaZrTi<sub>2</sub>O<sub>7</sub> mineral, coupled with morphological observations and goniometric measurements on single crystals indicated the crystal system to be cubic. This information allows the mineral to be identified as zirkelite.

Compositional variations, thought to be of a primary nature, are present in separated grains of zirkelite. A secondary alteration process has occurred, resulting in the breakdown of zirkelite and replacement by an unidentified Ba, Ti, Nb, Zr silicate phase(s).

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