The occurrence of niobian zirconolite, pyrochlore and baddeleyite in the Kovdor carbonatite complex, Kola Peninsula, Russia

C. TERRY WILLIAMS

Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, UK

Abstract

The compositions and textural relationships of the oxide minerals zirconolite, pyrochlore and baddeleyite are described. These occur as accessory minerals, often intergrown with each other, from a phoscorite rock associated with the Kovdor carbonatite complex. Both the zirconolite and baddeleyite have relatively high concentrations of Nb and Ta; the pyrochlore is rich in U and Ta. Backscattered electron images, coupled with detailed microprobe analyses, reveal complex compositional zoning in zirconolite and pyrochlore which reflect changes in the fluid composition during growth of these minerals. A comparison is made of incompatible element ratios Zr/Hf, Nb/Ta and Th/U between the three accessory minerals.

KEYWORDS: zirconolite, baddeleyite, pyrochlore, carbonatites, Kola Peninsula, Russia.

Introduction

DURING a compilation of localities and compositions of natural zirconolite, essentially $CaZrTi_2O_7$, (Williams and Gieré, 1996) a reference to zirconolite from the Kovdor carbonatite complex reported the presence of exceptionally high levels of Nb and Ta from a wet chemical analysis on separated grains (Kapustin, 1980). In order to confirm this compositional variant of zirconolite, a zirconolite-bearing sample of the Kovdor carbonatite was re-examined and this note reports on the detailed mineralogy and chemistry of zirconolite and associated Nb-bearing minerals.

The general geology and mineralogy of the carbonatites and associated rocks from Kovdor, Kola Peninsula, Russia are described by Kukharenko *et al.* (1965), Kapustin (1980) and outlined in Kogarko *et al.* (1995). Associated with, and cross-cutting the carbonatite are magnetite-forsterite-apatite rocks (phoscorites) which form sheet-like intrusions with brecciated contacts, up to 600m thick, in which zirconolite occurs as an accessory mineral (Kapustin, 1980). The zirconolite, described as niobozirconolite, is reported to have replaced baddeleyite and pyrochlore during dolomitization and amphibolitization of the carbonatite. The

specimen described here, BM No. 1994,P1 donated by the Kovdor Mining Museum, was collected from the magnetite mine at Kovdor, and is a typical example of this phoscorite. The rock consists of coarse-grained, unzoned, euhedral fluorapatite (with up to 0.5 wt.% ΣREE_2O_3 , in which Ce is dominant, and 0.6 wt.% SrO), magnetite (containing typically 3.5 wt.% TiO2, 2.4 wt.% MgO, 1 wt.% MnO and <0.1 wt.% Nb₂O₅), olivine (Fo₉₂ with up to 0.9 wt.% MnO) and minor tetraferri-phlogopite, rhombohedral calcite and accessory interstitial dolomite.

Petrology and mineral chemistry

The Ti, Zr, Nb, *REE* and actinide minerals zirconolite, pyrochlore and baddeleyite occur as accessory minerals, up to $150-200 \mu m$ in diameter, often intergrown with each other and usually associated with magnetite and apatite. The zirconolite is generally euhedral and appears to have crystallized later than, and in some cases, replaces pyrochlore and baddeleyite (Fig. 1*a*,*b*), both of which occur as subhedral to anhedral grains. Other potential Nb-bearing minerals such as ilmenite and rutile were not observed.

Microprobe analyses were performed on a Cameca SX50 wavelength-dispersive microprobe operated at

Mineralogical Magazine, August 1996, Vol. 60, pp. 639–646 © Copyright the Mineralogical Society

C. T. WILLIAMS

		-	-	•		
	1	2	3	4	5	6
MgO	0.27	0.27	0.30	0.58	0.60	0.65
Al_2O_3	<0.05	< 0.05	<0.05	<0.05	<0.05	<0.05
SiO ₂	<0.05	<0.05	<0.05	<0.05	<0.05	< 0.05
CaO	12.66	12.74	11.85	12.30	11.67	11.12
TiO ₂	23.67	23.54	22.77	18.68	16.75	17.00
MnO	0.10	0.05	0.34	0.20	0.28	0.26
FeO	6.79	7.10	6.79	7.66	7.39	7.65
Y_2O_3	0.15	0.13	0.18	0.25	0.17	0.30
ZrO ₂	30.71	31.18	30.72	30.29	29.07	29.44
Nb ₂ O ₅	13.97	14.54	14.47	18.25	21.21	20.12
La_2O_3	0.37	0.26	0.18	0.21	0.33	0.37
Ce_2O_3	1.46	1.42	1.46	1.61	1.27	1.76
Pr ₂ O ₃	0.30	0.14	0.41	0.41	0.26	0.23
Nd ₂ O ₃	1.12	1.31	1.16	1.56	1.14	1.75
Sm ₂ O ₃	0.29	0.33	0.18	0.20	0.21	0.23
Gd_2O_3	0.23	0.24	0.35	0.34	0.30	0.33
Dy ₂ O ₃	<0.15	<0.15	<0.15	0.18	<0.15	0.20
Er ₂ O ₃	<0.15	<0.15	<0.15	<0.15	<0.15	< 0.15
Yb ₂ O ₃	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18
HfO ₂	0.66	0.62	0.67	0.72	0.56	0.54
Ta ₂ O ₅	1.70	1.66	2.78	3.27	1.61	2.20
WO ₃	<0.25	< 0.25	<0.25	<0.25	<0.25	< 0.25
РЬО	<0.1	<0.1	<0.1	0.20	<0.1	<0.1
ThO ₂	2.21	1.36	2.46	1.09	4.09	4.01
UO ₂	0.63	0.56	1.07	0.40	0.51	0.35
Total	97.29	97.45	98.14	98.40	97.42	98.51
$Y + REE_2O_3$	3.92	3.83	3.92	4.76	3.68	5.17
Cations calcu	lated to 7 oxyg	ens				
Ca ²⁺	0.895	0.895	0.840	0.880	0.850	0.808
Y ³⁺	0.005	0.005	0.006	0.009	0.006	0.011
La ³⁺	0.009	0.006	0.004	0.005	0.008	0.009
Ce ³⁺	0.035	0.034	0.035	0.039	0.032	0.044
Ce ³⁺ Pr ³⁺	0.007	0.003	0.010	0.010	0.006	0.006
Nd ³⁺	0.026	0.031	0.027	0.037	0.028	0.042
Sm ³⁺	0.007	0.007	0.004	0.005	0.005	0.005
Gd ³⁺	0.005	0.005	0.008	0.008	0.007	0.007
Dv^{3+}	0.000	0.000	0.000	0.004	0.000	0.000
Pb ²⁺	0.001	0.001	0.000	0.004	0.000	0.000
Th ⁴⁺	0.033	0.020	0.037	0.017	0.063	0.062
\hat{U}^{4+}	0.009	0.008	0.016	0.006	0.008	0.005
Sum Ca	1.033	1.016	0.988	1.022	1.013	1.000

TABLE 1. Representative microprobe analyses of zirconolite

20 kV accelerating voltage and 20 nA current measured on a Faraday cup. Standards used were a combination of well-characterized minerals, synthetic compounds and pure metals.

Zirconolite is a relatively rare accessory mineral which occurs in a wide variety of rock types, of which carbonatites are the most commonly reported (Williams and Gieré, 1996). Although essentially $CaZrTi_2O_7$ in composition, zirconolite can accom-

modate many other cations within its structure. The major substitutions are the rare earth elements (*REE*) and actinide elements (Th and U) for Ca, and Fe, Nb (and Ta) for Ti (e.g. Gieré and Williams, 1992). In the zirconolite described here, both Nb and Ta have significantly high concentrations (Table 1) and are among the highest values reported for these elements: the mean for Nb₂O₅ of 18 analyses is 18.64 wt.% (range 13.97 to 21.21 wt.%), and for Ta₂O₅ the mean

TABLE	1.	(contd.)
-------	----	----------

	1	2	3	4	5	6
Zr ⁴⁺	0.988	0.997	0.991	0.986	0.964	0.974
Hf⁴+	0.012	0.012	0.013	0.014	0.011	0.010
Sum Zr	1.000	1.008	1.004	1.000	0.975	0.985
Ti ²⁺	1.174	1.160	1.133	0.938	0.857	0.867
Ti^{2+} Si ⁴⁺ Mg ²⁺ Fe ²⁺ Al ³⁺ Nb ⁵⁺ Ta ⁵⁺	0.000	0.000	0.000	0.000	0.000	0.000
Mg ²⁺	0.027	0.026	0.030	0.058	0.061	0.066
Mn ²⁺	0.006	0.003	0.019	0.011	0.016	0.015
Fe ²⁺	0.375	0.389	0.376	0.428	0.420	0.434
Al ³⁺	0.000	0.000	0.000	0.000	0.000	0.000
Nb ⁵⁺	0.417	0.431	0.433	0.551	0.652	0.617
Ta ⁵⁺	0.030	0.030	0.050	0.059	0.030	0.041
W ⁶⁺	0.000	0.000	0.000	0.000	0.000	0.000
Sum Ti	2.028	2.039	2.041	2.044	2.036	2.040
Total	4.061	4.063	4.033	4.067	4.024	4.025
Zɪ/Hf	40.6	43.9	40.0	36.7	45.3	47.6
Nb/Ta	7.0	7.5	4.4	4.8	11.2	7.8
Th/U	3.5	2.4	2.3	2.7	8.0	11.4

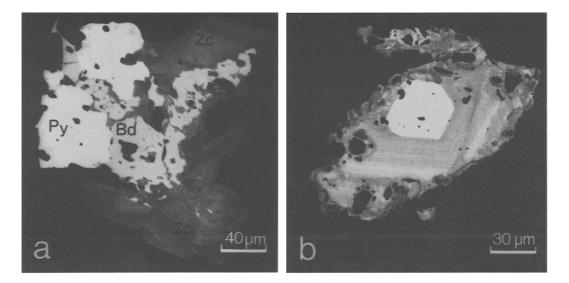


FIG. 1.(a) Backscattered electron image (BEI) of pyrochlore (Py), baddeleyite (Bd) and zirconolite (Zc). The zirconolite has better developed crystal forms than the other two minerals, and partly replaces them. The zoning in zirconolite is largely a result of changes in the Nb/Ta ratio. The darker zones are depleted in Nb and enriched in Ta relative to the lighter zones. (b) BEI of pyrochlore. The lighter cuhedral core (analysis 1, Table 2) is enriched in Ta (and depleted in Nb) relative to the outer region. Within this outer region, the lighter zone (analysis 3, Table 2) is enriched in U (and depleted in Nb) relative to the darker region (analysis 2, Table 2). Note the corrosion and embayment of the pyrochlore grain. The dark inclusions are apatite.

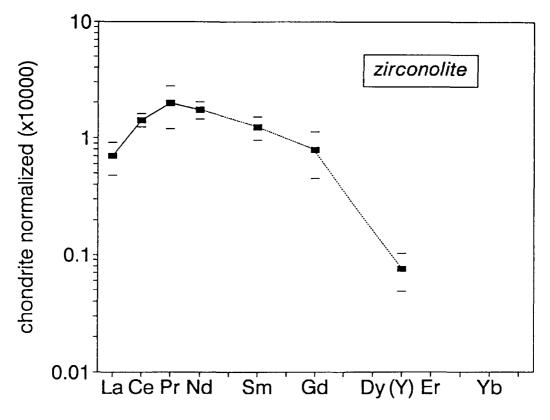


FIG. 2. Chondrite-normalized *REE* plot for the mean and one standard deviation of zirconolite (from 18 microprobe analyses).

is 2.51 wt.% (range 1.58 to 4.97 wt.%). These high levels of Nb and Ta are consistent with those previously published chemical analyses of zirconolite crystals separated from the Kovdor carbonatite (Kapustin, 1980). Up to 32% of the Ti site is occupied by Nb, thus confirming the niobian species.

Previous reports of niobozirconolite from Koydor (Kukharenko et al., 1965; Kapustin, 1980) refer only to analyses and morphological descriptions of separated mineral grains, and thus did not describe any fine-scale textural or chemical variations. In this study, the use of backscattered electron imaging was essential in revealing detailed fine-scale compositional zoning within the zirconolite, and textural relationships between zirconolite and the other accessory minerals. All the grains examined possessed some degree of compositional zoning, and a typical example of its complexity is illustrated in Fig. 1a. The compositional differences revealed are primarily due to changes in the Nb/Ti ratio. The darker (lower mean atomic number) zones in the oscillatory and sector zoned crystal in Fig. 1a have a

lower Nb₂O₅ (and higher TiO₂) value than the lighter zones which are richer in Nb₂O₅ (and poorer in TiO₂): compare analyses 1 and 4 of Table 1 which correspond with the darker and lighter zones respectively on Fig. 1a. This type of zoning and elemental correlation has also been observed in zirconolites from the carbonatite at Schryburt Lake, Ontario, Canada (Williams and Platt, in prep.). Zoning of this complex nature is being increasingly reported from other Ti, Zr, Nb, REE and actinide minerals, e.g. in titanite (Paterson et al., 1989), zircon (Rubin et al., 1993), aeschynite-(Ce) - a REE, Ti, Nb oxide - and zirconolite (Gieré and Williams, 1992). The zonation patterns reflect minor fluctuations in the composition (and/or temperature) of the magmatic or metasomatic fluids during crystallization of the mineral.

Of other elements in zirconolite, the *REE* show little variation from grain to grain, or between zones with a mean $\Sigma REE_2O_3 = 4.22$ wt.% (range from 2.46 to 5.23 wt.%). The chondrite normalized pattern is convex upwards and similar to that of zirconolites

from other carbonatites, with a maximum at the position of Pr and Nd (Fig. 2).

Of the actinide elements, Th is more abundant than U (mean ThO₂ = 3.10 wt.%, range 1.09 to 6.26 wt.%; mean UO₂ = 0.46 wt.%, range 0.13 to 1.07 wt.%). There is no correlation between either of these elements and the observed zoning.

Pyrochlore, a relatively common accessory mineral in carbonatites (e.g. Hogarth, 1989), is also capable of accommodating a wide variety of cations. In the Kovdor carbonatite described here, the compositional range of the pyrochlore was determined from 26 microprobe analyses of several grains, of which representative analyses are given in Table 2. Large compositional variations were observed in the major oxides CaO (range 8.0-11.9 wt.%); TiO₂ (3.7-8.5 wt.%); Nb₂O₅ (36.5-46.2 wt.%); ThO₂ (0.8-3.8 wt.%) and UO₂ (14.5-20.4 wt.%). Of note are the relative abundances of Th and U. The mean ThO₂ value of 2.18 wt.% is markedly lower than the mean UO₂ value of 17.46 wt.% and is the converse of that for zirconolite. Of the REE, only Ce is present at concentration levels above the microprobe detection limits. Of note also, is the detectable level of ZrO_2 which ranges from 0.7 to 4.1 wt.%.

The compositional variations observed correspond essentially to three different zones identified from backscattered electron images. These zones are illustrated in Fig. 1b where the pyrochlore crystal has a clearly defined Ta-rich core (analysis 1, Table 2) enclosed by a zone of lower Ta composition (analysis 2, Table 2), in which there is a marginal discontinuous (?) zone relatively enriched in U (analysis 3, Table 2).

These compositions are in general agreement with those reported by Lebedova *et al.* (1973) from the Kovdor carbonatite, who also described the presence of Ta-rich cores and U-rich rims. Similar compositions are reported in pyrochlores separated from a calcite-rich tuff at Ndale (Hogarth and Horne, 1989), and also in a magnetite-apatite-rich late-stage sövite from Qaqarssuk, W. Greenland (Knudsen, 1989).

From the formulae calculated on the basis of Bsite cations = 2.0, the A-site values are generally close to 2, Table 2. This, together with a lack of any patchy zonation features, often seen in altered pyrochlores, indicates that those from the Kovdor carbonatite have not been subject to any significant degree of sub-solidus cation leaching and hydration. However, the subhedral nature of the pyrochlore and existence of embayed edges (Fig. 1b), clearly indicates that some degree of dissolution and corrosion has occurred.

Baddeleyite. This mineral was initially described from Kovdor by Bubnova *et al.* (1973). In the sample analysed here, several small grains of baddeleyite (essentially ZrO_2) were observed often intergrown with zirconolite and pyrochlore. Representative microprobe analyses are given in Table 3. The Fe and Ti concentrations are amongst the lowest, and Nb and Ta the highest reported from terrestrial baddeleyite (compare with analyses in Heaman and LeCheminant, 1993).

Discussion

The textural information indicates that zirconolite crystallized later than, and in some cases replaces, pyrochlore and baddeleyite. The crystallization sequence of Zr minerals in carbonatites is discussed by Bulakh and Ivanikov (1984). They describe zirconolite ('zirkelite') as usually crystallizing after the silicate minerals, perovskite, magnetite, baddelevite and calzirtite and early generations of pyrochlore. It crystallizes before the carbonate minerals, titanite and partly before late generations of pyrochlore. Pojazitskaja and Samoilov (1972) in a review of carbonatites from Eastern Siberia, report also that baddeleyite is the major Zr-bearing mineral and that zirconolite (and calzirtite) crystallize after the formation of baddeleyite. Calzirtite (essentially $CaZr_{3}TiO_{9}$) was not observed in the sample studied here, but does occur in the Kovdor carbonatite (A. Bulakh, pers. comm., 1995).

Of interest is a comparison of the incompatible element ratios Zr/Hf, Nb/Ta and Th/U in the three accessory minerals zirconolite, pyrochlore and baddeleyite. Although mass balance calculations have not been made, because of the heterogeneous distribution of these minerals in the carbonatite, it is probable that they are the major hosts for the incompatible elements. In pyrochlore, the Nb/Ta ratio increases from the Ta-rich cores to the Ta-poor rims (core = 2.3, rim = 4.1, analyses 1 and 2, Table 2). This change reflects the late-stage differentiation of magmas of both alkaline (e.g. Gerasimovsky, 1974) and carbonatitic (e.g. Knudsen, 1989) affinities. The Nb/Ta ratio of baddelevite is similar to that of the pyrochlore cores, but in zirconolite this ratio is significantly higher and more variable.

The Zr/Hf ratio of baddeleyite is slightly (but probably significantly) higher than that for zirconolite (the Zr/Hf ratio could not be accurately determined in the pyrochlore). Most variation however, is seen in the Th/U ratio where values for pyrochlore range from 0.04 to 0.22, which contrasts dramatically with that for zirconolite, ranging from 2.3 to 11.4 (this ratio could not be determined in the baddeleyite). Distribution coefficients for the actinide elements are not well established for either of these minerals, and the observed differences between the two minerals, or could reflect real changes in the fluid composition.

C. T. WILLIAMS

	1	2	3	4	5	6
 Na ₂ O	3.91	5.36	5.14	5.23	4.93	5.38
CaO	9.18	11.29	10.33	10.92	10.72	11.38
TiO ₂	3.82	5.14	4.66	5.03	5.90	8.44
MnŎ	< 0.05	<0.05	0.09	< 0.05	< 0.05	< 0.05
Fe ₂ O ₃	1.35	0.89	0.75	0.80	0.76	0.77
SrO	0.30	0.23	0.24	0.19	0.33	0.31
Y_2O_3	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
ZrO_2	3.09	2.51	3.02	1.88	2.02	1.90
Nb ₂ O ₅	38.57	45.32	43.20	44.68	43.34	37.95
La_2O_3	0.11	<0.1	<0.1	<0.1	<0.1	< 0.1
Ce_2O_3	0.18	0.12	0.28	0.30	0.41	0.49
Pr_2O_3	< 0.15	< 0.15	<0.15	< 0.15	<0.15	< 0.15
Nd ₂ O ₃	< 0.15	< 0.15	<0.15	<0.15	<0.15	0.26
Sm_2O_3	< 0.15	< 0.15	<0.15	< 0.15	<0.15	< 0.15
Gd ₂ O ₃	< 0.18	< 0.18	< 0.18	<0.18	<0.18	< 0.18
Ta ₂ O ₅	14.57	9.42	9.72	11.33	11.05	10.75
PbO	1.14	0.92	1.21	0.21	0.67	0.49
ThO ₂	1.81	2.10	0.83	2.16	2.26	3.79
UO ₂	20.42	15.91	18.75	16.65	16.89	17.37
F	0.47	1.02	1.03	0.48	0.35	0.59
Total	98.92	100.23	99.25	99.86	99.63	99.87
O=F	0.20	0.43	0.43	0.20	0.15	0.25
Total	98.72	99.80	98.82	99.66	99.48	99.62
	2 B-site cations					
A site					0.440	0.747
Nat	0.566	0.722	0.719	0.710	0.669	0.747
Ca ²⁺	0.734	0.840	0.799	0.819	0.803	0.873
Mn^{2+}	0.000	0.000	0.006	0.000	0.000	0.000
Sr^{2+}	0.008	0.006	0.007	0.005	0.009	0.008
La^{3+}	0.003	0.000	0.000	0.000	0.000	0.000
Ce^{3+}	0.005	0.003	0.007	0.008	0.010	0.013
Nd ³⁺	0.000	0.000	0.000	0.000	0.000	0.007
Pb^{2+}	0.023	0.017	0.024	0.004	0.013	0.009
Th ⁴⁺	0.031	0.033	0.014	0.034	0.036	0.062
U ⁴⁺	0.339	0.246	0.301	0.259	0.263	0.277
Total	1.709	1.867	1.876	1.839	1.803	1.996
B site	a - • •		0.0	0.015	0.210	A 16+
Ti^{4+} Fe ³⁺	0.214	0.268	0.253	0.265	0.310	0.454
Fe ^r	0.076	0.046	0.041	0.042	0.040	0.041
Zr^{4+}	0.112	0.085	0.106	0.064	0.069	0.066
Nb^{5+}	1.302	1.422	1.409	1.413	1.371	1.228
Ta ⁵⁺	0.296	0.178	0.191	0.216	0.210	0.209
Total	2.000	2.000	2.000	2.000	2.000	2.000
Total O	6.565	6.575	6.617	6.585	6.550	6.680
F	0.111	0.224	0.235	0.106	0.077	0.134

TABLE 2. Representative microprobe analyses of pyrochlore

Mg, Al, Si, and Ba are all below the detection limit (typically 0.05 wt.% oxide)

Analyses 1-3 positions are from Fig. 1(b)Analyses 4-6 are representative of other pyrochlore grains

Zr/Hf	-	-		-	-	
Nb/Ta	2.3	4.1	3.8	3.4	3.3	3.0
Th/U	0.09	0.13	0.04	0.13	0.13	0.22

NIOBIAN ZIRCONOLITE

						<u> </u>
	1	2	3	4	5	6
MgO	0.06	0.11	<0.05	<0.05	<0.05	< 0.05
CaO	< 0.05	<0.05	< 0.05	0.06	< 0.05	< 0.05
TiO ₂	0.14	0.19	0.11	0.08	0.32	0.12
MnÖ	0.05	< 0.05	< 0.05	<0.05	0.07	< 0.05
FeO	0.20	0.23	0.15	<0.05	0.11	0.10
ZrO ₂	96.31	95.52	95.91	98.31	95.67	97.99
Nb ₂ O ₅	1.40	2.51	1.34	0.37	1.02	0.80
HfO ₂	1.62	1.81	1.96	2.04	1.70	1.76
Ta ₂ O ₅	0.42	0.64	0.41	0.28	0.36	0.28
Total	100.20	101.01	99.88	101.14	99.25	101.05
Cations cal	culated to 4 oxyg	ens				
Mg^{2+} Ca ²⁺ Ti ⁴⁺ Mn ²⁺ Fe ²⁺ Zr ⁴⁺ Nb ⁵⁺ Hf ²⁺	0.004	0.007	0.000	0.000	0.000	0.000
Ca ²⁺	0.000	0.000	0.000	0.003	0.000	0.000
Ti ⁴⁺	0.004	0.006	0.003	0.002	0.010	0.004
Mn ²⁺	0.002	0.000	0.000	0.000	0.002	0.000
Fe ²⁺	0.007	0.008	0.005	0.000	0.004	0.003
Zr ⁴⁺	1.939	1.907	1.943	1.969	1.947	1.960
Nb ⁵⁺	0.026	0.046	0.025	0.007	0.019	0.015
Hf ²⁺	0.021	0.023	0.025	0.026	0.022	0.022
Ta ⁵⁺	0.005	0.007	0.005	0.003	0.004	0.003
Total	2.008	2.004	2.006	2.010	2.008	2.007
<i>REE</i> , Pb, T	h, U below detec	tion limit (typical	lly 0.1-0.15 wt.9	% oxide)		
Zr/Hf	51.9	46.1	42.7	42.1	49.1	48.6
Nb/Ta	2.8	3.3	2.8	1.1	2.4	2.4
Th/U	_	-	_	-	_	_

TABLE 3. Representative microprobe analyses of baddeleyite

Information on the evolution of the fluid composition could not be readily deduced from these ratios since the elements are essential structural constituents of the minerals and not trace components. However, integrating textural and petrographic information of accessory minerals with their incompatible element ratios, allows a fuller understanding of the role these minerals play in overall fluid/mineral interactions in carbonatites.

Acknowledgements

Frances Wall and Alan Woolley of The Natural History Museum, London are thanked for their comments which have improve the manuscript. I am also grateful to Andrei Bulakh and Lia Kogarko for detailed discussions and additional information on Russian localities. I am grateful too for the comments of an anonymous referee, which have greatly improved the paper.

References

- Bubnova, M.I., Kochurova, T.L., Rimskaya-Korsakov, O.M. and Filatov, S.K. (1973) Structural typomorphic properties of baddeleyite of the Kovdor Massif. *Leningrad Univ.*, Vestn., Geol. Geogr., 18, 56-61 (in Russian).
- Bulakh, A.G. and Ivanikov, V.V. (1984) The problems of mineralogy and petrology of carbonatites. Leningrad University Printing House, Leningrad, (in Russian), 230 pp.
- Gerasimovsky, V.I. (1974) Trace elements in selected groups of alkaline rocks. In: *The Alkaline Rocks* (H. Sørensen, ed), John Wiley & Sons, London, 402-12.
- Gieré, R. and Williams, C.T. (1992) *REE*-bearing minerals in a Ti-rich vein from the Adamello contact aureole (Italy). *Contrib. Mineral. Petrol.*, **112**, 83-100.
- Heaman, L.M. and LeCheminant, A.N. (1993) Paragenesis and U-Pb systematics of baddeleyite.

Chem. Geol., 110, 95–126.

- Hogarth, D.D. (1989) Pyrochlore, apatite and amphibole: distinctive minerals in carbonatite. In: *Carbonatites* (K. Bell, ed), Unwin Hyman, London, 105-48.
- Hogarth, D.D. and Horne, J.E.T. (1989) Non-metamict uranoan pyrochlore and uranpyrochlore from tuff near Ndale, Fort Portal area, Uganda. *Mineral. Mag.*, 53, 257-62.
- Kapustin, Yu.L. (1980) Mineralogy of carbonatites. Amerind Publishing Company Pvt. Ltd., New Dehli, 259 pp. (translated from Mineralogiya Karbonatitov. Nauka Publ. Moscow, 1971).
- Kogarko, L.N., Kononova, V.A., Orlava, M.P. and Woolley, A.R. (1995) Alkaline rocks and carbonatites of the World Part 2: Former USSR. Chapman and Hall, London, 226 pp.
- Kukharenko, A.A., Orlaova, M.P., Bulakh, A.G., Bagdasarov, E.A., Rimskaya-Korsakova, O.M., Nephedov, E.I., Il'inskii, G.A., Ergeev, A.S. and Abakumova, N.B. (1965) The Caledonian complex of ultrabasic rocks and carbonatites of the Kola Peninsula and north Karelia. Nedra, Moscow, 772 pp (in Russian).
- Knudsen, C. (1989) Pyrochlore group minerals from the Qaqarssuk carbonatite complex. In: Lanthanides, Tantalum and Niobium, (P. Möller, P. Černý and F.

Saupé, eds). Springer-Verlag Berlin, Heidelberg, 80--99.

- Lebedova, S.I, Bytov, V.P., Dubakina, L.S., and Yurkina, K.V. (1973) Microprobe determination of the mode of deposition of trace elements in zirconbearing pyrochlores and hatchettolites. In: *Issledovaniya v oblasti rudno mineralogii* (M.S. Bezsmertnaya, ed), Nauka Publ. Moscow, (in Russian), 133-45.
- Paterson, B.A., Stephens, W.E. and Herd, D.A. (1989) Zoning in granitoid accessory minerals as revealed by backscattered electron imagery. *Mineral. Mag.*, 53, 55-62.
- Pojazitskaja, L.B. and Samoilov, V.S. (1972) Petrology, mineralogy and geochemistry of carbonatites of the Eastern Siberia. Moscow, (in Russian) 265 pp.
- Rubin, J.N., Henry, C.D. and Price, J.G. (1993) The mobility of zirconium and other "immobile" elements during hydrothermal alteration. *Chem. Geol.*, 110, 29–47.
- Williams, C.T. and Gieré, R. (1996). Zirconolite: a review of localities worldwide, and a compilation of its chemical composition. *Bull. Nat. Hist. Mus.* (*Geol*), **52**, 1–24.

[Manuscript received 3 October 1994: revised 1 August 1995]