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Notes on the chemical composition of zirconolite with thorutite inclusions from Walaweduwa, Sri Lanka

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ZIRCONOLITE and its polymorph zirkelite are rare in natural rocks, and have been found as accessory minerals mostly in carbonatites and ultrabasic intrusive rocks (see Williams and Gieré, 1996, for a recent review). The chemical formula of zirconolite is essentially $\text{CaZrTi}_2\text{O}_7$, but a wide range of substitutions exists, which makes it suitable for use in SYNROC, a potential storage material of radioactive waste (Ringwood *et al.*, 1979).

Zirconolites from Sri Lanka, found associated with 'gem gravels' in alluvial deposits were collected at the beginning of the century and are now incorporated in various museum collections around the world. However, to the best of our knowledge, their source rock is still unknown. Among these zirconolite samples, a variety from Walaweduwa, first described as zirkelite by Blake and Smith (1913), is of specific interest because of its unusually high concentrations of Th and U. This characteristic provides information on the resistance of the mineral to radiation damage (Sinclair and Ringwood, 1981), and on the chemical substitutions that stabilize the crystal structure. The reported analyses (Blake and Smith, 1913; Sinclair and Ringwood, 1981, and Lumpkin *et al.*, 1986) do not include all minor and trace elements. Here we report the results of detailed electron microprobe analyses of a zirconolite crystal from Walaweduwa. In the course of this study inclusions of the extremely rare mineral thorutite, ThTi_2O_6 , were found, the composition of which is also reported.

Experimental

Electron microprobe analyses were made using a Jeol X-8600 Superprobe, fitted with wavelength (WDS) and energy (EDS) dispersive spectrometers, and operated at an acceleration voltage of 15 kV, a specimen current of 25 nA, and a beam diameter of

1 μm . All element concentrations were measured with WDS, using the EDS only for qualitative scans. Pure metals (for Zr, Mn, W, Zn, Ta, Nb, Ni, Cr, Zn, Mo, Sc, Ti), glass standards (for rare earth elements (*REE*) and Y; Drake and Weill, 1972) and natural minerals (for the remaining elements) were used as standards. The elements Gd, Pr, and Dy were determined on the $L\beta_1$ peaks (instead of $L\alpha$) to avoid interference with other *REE* peaks. Two positions for background determinations were selected on both sides of each peak, based on wavelength spectra of the natural mineral. Corrections for interferences on net peak signals were applied to Gd (with $\text{Ho-L}\alpha_1$), Eu (with $\text{Pr-L}\beta_{2,15}$ and $\text{Nd-L}\beta_3$) and W (with $\text{Zr-L}\lambda$). A data collection time of 200 s for both peak and backgrounds was used for Gd, Dy, Sm, Er, Yb, Eu, Hf, Ba, W, Pb and Ta, 100 s for Fe, La, Mn, Na, Nb, Nd, Pr, Sc, Sr, U and Mo, and 10–60 s for the remaining elements. Reported detection limits are based on three times the standard deviation of the background at the peak position. A Tracor Northern ZAF program was used for matrix corrections.

Results and discussion

Zirconolite. The specimen studied was obtained from the mineral collection in the Faculty of Earth Sciences, Utrecht University, which contains several zirconolite grains labelled 'Zirkelit, Walaweduwa, Ceylon' and numbered 75.1912. The collector of these specimens is unknown. The 5–10 mm dark brown crystals show well developed crystal faces. On breaking they display a conchoidal surface with a metallic lustre.

An X-ray diffraction pattern of the powdered sample did not show crystalline structures, which suggests that the crystal is completely metamict. This is consistent with the observation of Blake and Smith (1913) that "minute fragments are isotropic, as seems

TABLE 1. Composition of the Walaweduwa zirconolite based on the average of two runs of five analyses. Elements marked with an asterisk were analysed in only one run. For calculation of the average concentration, analyses below the detection limit were replaced by half the value of the detection limit. The elements concerned are reported between brackets

	Average wt.% (n=10)	Average error ($\pm 1\sigma$)	Concentration range		# cations (based on 7O)	
			Min.	Max.		
ZrO ₂	29.53	± 0.15	28.78	30.03	Zr	0.966
HfO ₂	0.61	± 0.05	0.51	0.67	Hf	0.012
					$\Sigma(\text{Zr})$	0.978
TiO ₂	27.46	± 0.14	26.88	28.20	Ti	1.386
FeO	3.32	± 0.05	3.00	3.53	Fe	0.186
MgO	2.62	± 0.02	2.38	2.92	Mg	0.262
Al ₂ O ₃	0.64	± 0.01	0.59	0.89	Al	0.051
SiO ₂	<0.008			<0.008	Si	—
Nb ₂ O ₅	3.85	± 0.07	3.29	4.33	Nb	0.117
Ta ₂ O ₅	0.26	± 0.05	0.19	0.34	Ta	0.005
WO ₃ *	0.07	± 0.01	0.05	0.09	W	0.001
					$\Sigma(\text{Ti})$	2.008
CaO	7.98	± 0.05	7.79	8.35	Ca	0.573
MnO*	(0.03)	± 0.02	<0.03	0.03	Mn	(0.002)
ThO ₂	19.71	± 0.15	18.60	20.90	Th	0.301
UO ₂	2.04	± 0.04	1.94	2.14	U	0.031
PbO*	0.63	± 0.02	0.52	1.00	Pb	0.014
Y ₂ O ₃	0.29	± 0.02	0.25	0.33	Y	0.011
Sc ₂ O ₃ *	(0.01)	± 0.01	<0.01	0.01	Sc	(0.001)
La ₂ O ₃	(0.06)	± 0.01	<0.039	0.11	La	(0.002)
Ce ₂ O ₃	0.68	± 0.03	0.62	0.75	Ce	0.017
Pr ₂ O ₃	(0.07)	± 0.03	<0.069	0.08	Pr	(0.002)
Nd ₂ O ₃	0.41	± 0.05	0.31	0.48	Nd	0.010
Sm ₂ O ₃ *	(0.09)	± 0.02	<0.048	0.16	Sm	(0.002)
Eu ₂ O ₃ *	(0.04)	± 0.03	<0.054	0.06	Eu	(0.001)
Gd ₂ O ₃ *	(0.09)	± 0.03	<0.097	0.18	Gd	(0.002)
Dy ₂ O ₃ *	(0.08)	± 0.02	<0.10	0.14	Dy	(0.002)
Er ₂ O ₃	(0.04)	± 0.02	<0.055	0.10	Er	(0.001)
Yb ₂ O ₃	(0.05)	± 0.02	<0.061	0.07	Yb	(0.001)
Na ₂ O	0.08	± 0.01	0.05	0.12	Na	0.010
K ₂ O	(0.03)	± 0.01	<0.01	0.04	K	(0.002)
SrO*	0.18	± 0.02	0.16	0.20	Sr	0.007
BaO	0.12	± 0.01	0.06	0.19	Ba	0.003
P ₂ O ₅ *	0.08	± 0.01	0.07	0.10	P	0.005
					$\Sigma(\text{Ca})$	1.000
Cr ₂ O ₃ *	<0.03			<0.03	Cr	—
Mo ₂ O ₃ *	<0.05			<0.05	Mo	—
NiO*	<0.04			<0.04	Ni	—
ZnO*	<0.06			<0.06	Zn	—
Total	101.16					3.986
Th/U	9.9	Zr/Hf	82	Nb/Ta	25	

The numbers of analyses below detection limits are: MnO: 3 (of 5); Sc₂O₃: 3 (of 5); La₂O₃: 4 (of 10); Pr₂O₃: 6 (of 10); Sm₂O₃: 2 (of 10); Eu₂O₃: 3 (of 5); Gd₂O₃: 5 (of 10); Dy₂O₃: 3 (of 5); Er₂O₃: 7 (of 10); Yb₂O₃: 9 (of 10); and K₂O: 5 (of 10). All Fe as FeO, all Eu as Eu₂O₃, all U as UO₂. Th/U, Zr/Hf and Nb/Ta are cation ratios.

TABLE 2. Mineral chemistry of Walaweduwa zirconolites from this study compared with previous data. Asterisk indicates that the amount of FeO is recalculated from Fe₂O₃ in the original publication

	This study	Blake and Smith (1913) no. II	Blake and Smith (1913) no. III	Sinclair and Ringwood (1981) B20392	Lumpkin <i>et al.</i> (1986)
ZrO ₂	29.53	30.73	32.56	30.9	28.2
TiO ₂	27.46	29.50	30.95	28.0	29.6
FeO	3.32	4.07	4.42	3.1	2.59*
CaO	7.98	6.87	6.78	7.9	8.46
ThO ₂	19.71	20.44	18.78	20.5	18.8
UO ₂	2.04	1.06	0.65	2.1	1.74
Nb ₂ O ₅	3.85	—	—	3.6	2.58
Al ₂ O ₃	0.64	—	—	—	0.74
Y ₂ O ₃	0.29	1.08	0.40	—	0.29
REE ₂ O ₃	1.61	2.68	1.40	—	1.04
MgO	2.62	2.34	3.04	2.4	2.38
MnO	<0.03	0.03	—	—	0.06
PbO	0.63	0.38	—	—	0.44
Total	99.68	99.18	98.98	98.5	96.92

to be generally the case with crystallised minerals containing rare earths whatever the morphological symmetry," although they also noted that "the minerals have undoubtedly hexagonal or lower symmetry." Sinclair and Ringwood (1981) suggested that, as electron micrographs revealed that the grains were composed of small crystalline domains, a large degree of short range order still exists in their samples. Following the scheme of Bayliss *et al.* (1989), this non-crystalline mineral should be referred to as zirconolite.

The results of our electron microprobe analyses of the zirconolite crystal are given in Table 1. As shown in Table 2, they are consistent with literature data on other specimens from Walaweduwa. Analyses II–III from Blake and Smith's (1913) description of Sri Lanka zirconolites represent material from the Bambarabotuwa District of the Sabaragamuwa province. Sinclair and Ringwood (1981) determined lead and uranium ages, which averaged to 561 ± 4 Ma.

The Walaweduwa zirconolite has relatively high Th+U and low REE concentrations compared to those from other natural environments, which adds to the observation that zirconolites are commonly enriched either in REE or in Th+U (Fig. 1). Although some variations in composition exist, no systematic chemical zoning was observed on a micrometre-scale. Concentrations of the major elements range from 4% relative for Zr to 10% relative for Th+U. Our results show that ~20

elements have concentrations >0.1 wt.%. The chondrite-normalized REE pattern of the Walaweduwa zirconolite is shown in Fig. 2. The zirconolite crystal prefers the heavier LREE (Ce–Sm), similar to many other zirconolites from the literature.

The simplified chemical formula of the Walaweduwa zirconolite deduced from our data is: $[\text{Ca}_{0.55}\text{REE}_{0.10}(\text{Th},\text{U})_{0.35}]\text{Zr}_{1.00}[\text{Ti}_{1.45}\text{Mg}_{0.25}\text{Fe}_{0.20}\text{Nb}_{0.10}]\text{O}_7$. Based on charge balance calculations, iron is present in its divalent state. The main inferred element substitutions are:

- 1 Coupled substitution at the Ti-site:
 $3 \text{Ti}^{4+} = 2 \text{Nb}^{5+} + (\text{Mg},\text{Fe})^{2+}$
- 2 Coupled substitution between the Ca and Ti-sites:
 $\text{Ti}^{4+} + \text{Ca}^{2+} = (\text{Mg},\text{Fe})^{2+} + \text{Th}^{4+}$
 $\text{Ti}^{4+} + 2 \text{Ca}^{2+} = (\text{Mg},\text{Fe})^{2+} + 2 \text{REE}^{3+}$

These substitutions are comparable to exchange vectors #1 and #3 described by Gieré and Williams (1992). As emphasized by our data, high activities of small divalent cations, like Mg²⁺ and Fe²⁺, may be needed to allow for the incorporation of large amounts of actinide elements.

Thorutite. The Walaweduwa zirconolite studied contains several subrounded inclusions of a non-Zr oxide, which are randomly distributed without any preferential orientation. Their maximum size is 30 µm. The composition of one of the inclusions is very similar to thorutite, a mineral known from an unspecified locality in the former USSR (Gotman

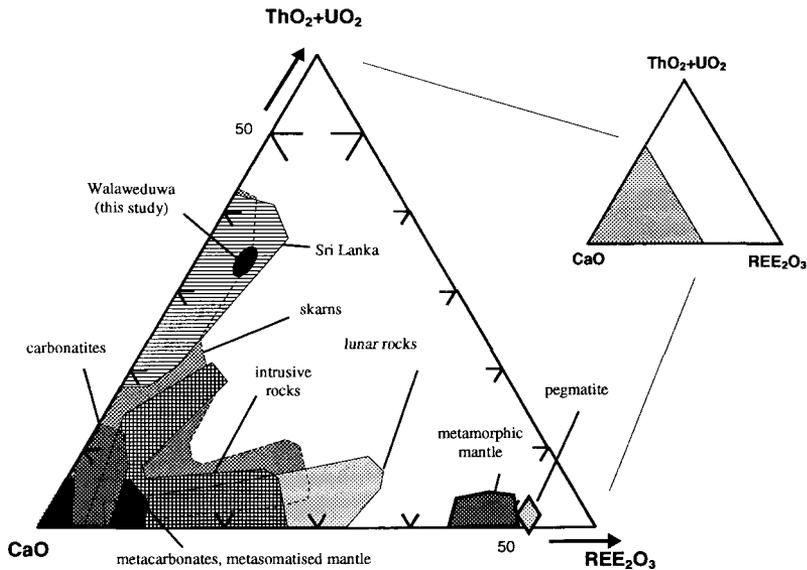


FIG. 1. $\text{CaO}-\text{REE}_2\text{O}_3-(\text{Th,U})\text{O}_2$ diagram showing the compositional variation of natural zirconolites. Data from this study, Williams and Gieré (1996) and references therein.

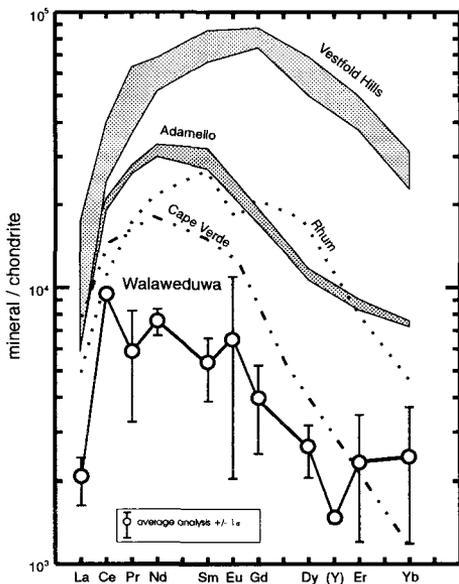


FIG. 2. Chondrite-normalized REE -patterns of the Walaweduwa zirconolite and some natural zirconolites. Note that Y is plotted in the place of Ho. Data from this study, Williams and Gieré (1996) and references therein. Chondrite values from Sun and McDonough (1989).

and Khapaev, 1958) (Table 3). These authors proposed the generalized formula $2(\text{Ca,U,Th})\text{O}_2 \cdot 4\text{TiO}_2 \cdot \text{H}_2\text{O}$. Our microprobe results correspond to $\text{A}_1\text{Ti}_2\text{O}_6$, where $\text{A} = (\text{Th}^{4+}, \text{U}^{4+}, \text{Nb}^{5+}, \text{REE}^{3+})$, with Th as major cation (79 atom%). The oxide total suggests that thorutite may not necessarily contain crystal-water.

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References

- Bayliss, P., Mazzi, F., Munno, R. and White, T.J. (1989) Mineral nomenclature: zirconolite. *Mineral. Mag.*, **53**, 565–9.
- Blake, G.S. and Smith, H. (1913) On varieties of zirkelite from Ceylon. *Mineral. Mag.*, **16**, 309–16.
- Drake, M.J. and Weill, D.F. (1972) New rare earth element standards for electron microprobe analysis.

TABLE 3. Composition of a Th-titanate inclusion in the Walaweduwa zirconolite (with all U as UO₂), inferred to be thorutite from the similarity in composition with the mineral reported first by Gotman and Khapaev (1958)

	Walaweduwa (this study)	Gotman and Khapaev (1958)
TiO ₂	40.78 ± 0.21	36.10
ThO ₂	52.71 ± 0.29	54.10
UO ₂	1.23* ± 0.03	1.43
UO ₃	—	0.14
Nb ₂ O ₅	2.46 ± 0.06	1.12
Al ₂ O ₃	<0.012	1.50
La ₂ O ₃	0.78 ± 0.02	—
Ce ₂ O ₃	2.20 ± 0.03	—
Nd ₂ O ₃	0.66 ± 0.06	—
Ta ₂ O ₅	<0.078	0.08
SiO ₂	<0.008	0.44
CaO	<0.020	1.07
Fe ₂ O ₃	<0.034	1.10
H ₂ O	—	0.94
LOI	—	1.72
Total	100.82	99.74
#(O.OH)	12	13
#Ti	4.060	3.921
#Th	1.588	1.778
#U ⁴⁺	0.036	0.046
#U ⁶⁺	—	0.004
#La	0.038	—
#Ce	0.107	—
#Nd	0.031	—
#Nb	0.147	0.073
#Ta	—	0.003
#Si	—	0.064
#Al	—	0.255
#Fe	—	0.120
#Ca	—	0.166
Total	6.007	6.429
#OH	—	0.905

Chem. Geol., **10**, 179–81.

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.

Gotman, Y.D. and Khapaev, I.A. (1958) Thorutite — a new mineral in the group of titanates of thorium. *Zap. Vses. Mineral. Obshch.*, **87**, 201–2.

Lumpkin, G.R., Ewing, R.C., Chakoumakos, B.C., Gregor, R.B., Lytle, F.W., Foltyn, E.M., Clinard, F.W. Jr., Boatner, L.A. and Abraham, M.M. (1986) Alpha-recoil damage in zirconolite (CaZrTi₂O₇). *J. Material Res.*, **1**, 564–76.

Ringwood, A.E., Kesson, S.E., War, N.G., Hibberson, W. and Major, A. (1979) Immobilization of high level nuclear reactor wastes in SYNROC. *Nature*, **278**, 219–23.

Sinclair, W. and Ringwood, A.E. (1981) Alpha-recoil damage in natural zirconolite and perovskite. *Geochem. J.*, **15**, 229–43.

Sun, S.S. and McDonough, W.F. (1989) Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes. In *Magmatism in the Oceanic Basins.*, Geol. Soc. London Spec. Publ. (A.D. Saunders and M.J. Norry, eds.), **42**, 315–45.

Williams, C.T. and Gieré, R. (1996) Zirconolite: a review of localities worldwide, and a compilation of its chemical compositions. *Bull. Nat. Hist. Mus. (Geol.)*, **52**, 1–24.

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