

## Zirconolite from the Glen Dessarry syenite; a comparison with other Scottish zirconolites

ZIRCONOLITE, a rarely reported Ca, Zr, Ti oxide has been identified during a fission-track and electron probe investigation of the Glen Dessarry syenite, Inverness-shire (Fowler, 1981, 1985). Here we give details of its mineralogical relationships and chemistry—including data for the REE, uranium, and thorium—and compare these with new and published chemical data of other natural examples from Scotland and elsewhere.

Problems over nomenclature have not been fully resolved, with two names, zirconolite and zirkelite, in use for chemically identical minerals. Structurally, zirconolite is monoclinic and zirkelite trigonal (Mazzi and Munno, 1983; White, 1984) but structural information is frequently difficult or impossible to obtain because of the small grain-size and metamict nature of the material. Unfortunately, this was the case for the Glen Dessarry examples, and those of the other Scottish occurrences. In this note, the mineral has been named zirconolite following the usage by Williams (1978)

on material first described from Scotland, although positive structural identification has not been possible.

To date, natural terrestrial zirconolite has been described from only ten localities, with a wide variety of host rock types (see Purtscheller and Tessadri, 1985, for a comprehensive list). Accounts of lunar material are detailed in Frondel (1975) and a review of synthetic zirconolites from the SYNROC studies has been presented by Ringwood (1985). Zirconolite from the Glen Dessarry syenite most commonly occurs as small (less than 10  $\mu\text{m}$ ), euhedral inclusions in alkali-feldspar phenocrysts, and has a deep orange-brown colour in thin section. Other associated accessory minerals include Fe-Ti oxides, sphene, allanite, apatite, and zircon. The rock-forming minerals of the syenite are aegirine-augite, edenitic amphibole, hypersolvus alkali-feldspar, orthoclase ( $\text{Or}_{85}$ ), plagioclase ( $\text{Ab}_{93}$ ), and biotite.

Three grains of zirconolite were analysed quan-

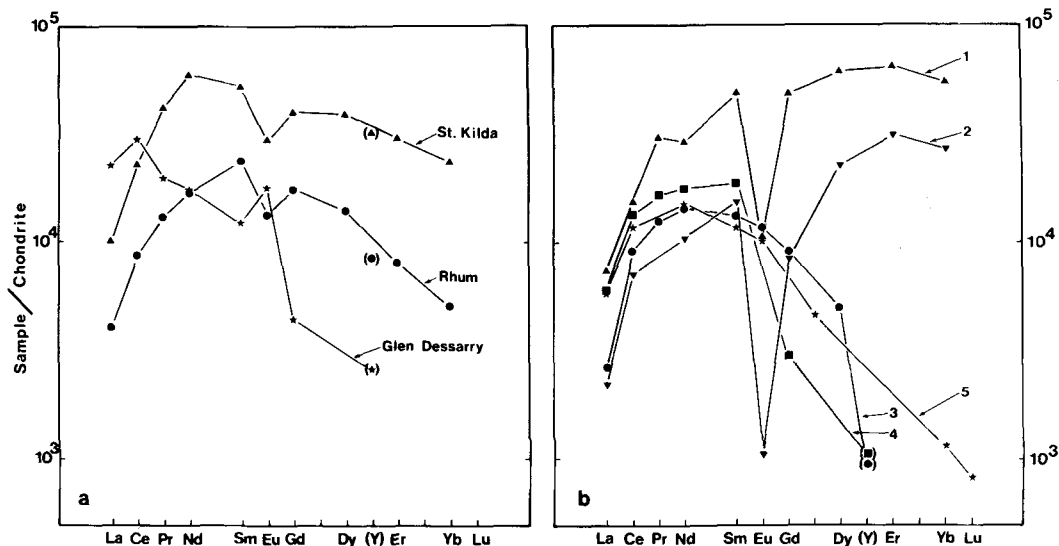


FIG. 1. (a) Chondrite-normalized REE plots of zirconolites from Scottish localities (values from Wakita *et al.*, 1971). (b) Chondrite-normalized REE plots of some other terrestrial and lunar zirconolites. 1 = Apollo 10 Mare basalt, 2 = Apollo 15 Mare basalt, 3 = Brazil pyroxenite (BM 81042), 4 = USSR (BM 1970, 39), 5 = Cape Verde carbonatite. Data for lunar samples are microprobe analyses from Wark *et al.* (1973); others are unpublished microprobe (3 and 4) and INAA (5) data by C. T. Williams. Y values are normalized to a chondritic value of 2 ppm and plotted at the atomic number of Ho based on ionic criteria, Eby (1975).

tatively using a Cambridge Instruments Microscan 9 wavelength dispersive electron probe at the British Museum (Natural History), using pure metals, synthetic compounds or minerals as standards. Since little chemical variation was observed between or within grains, an average analysis is presented in Table I. In order to facilitate comparisons between the three Scottish examples, zirconolites from Rhum (Williams, 1978) and St Kilda (Harding *et al.*, 1982) were reanalysed to include data for the REE, U, and Th (see Table I). Cation proportions have been recalculated on the basis of 7 oxygen atoms, and site occupancy assigned following procedures by Kesson *et al.* (1983).

It is apparent from previous work that Y, Nb, REE, Th, and U can substitute extensively in the zirconolite structure. A characteristic feature of the Glen Dessarry sample is its high U and Th content ( $UO_2 + ThO_2 = 11\%$ , compared to less than 1% in the Rhum and St Kilda specimens). However, zirconolite from St Kilda is extremely rich in Y and REE ( $Y_2O_3 + \text{total } REE_2O_3 = 24\%$ , compared to 6.6% for Rhum and 7.3% for Glen Dessarry).

In fig. 1(a) chondrite-normalized values are plotted for the Scottish zirconolite and can be compared with those for lunar and other terrestrial material in fig. 1(b). The REE patterns are similar in both lunar and terrestrial zirconolites for the light and medium REE, and show light-REE depletion with medium-REE enrichment. In addition, terrestrial zirconolites have slight heavy-REE depletion, whereas lunar zirconolites are enriched in the heavy REE. However, the pattern from Glen Dessarry is distinct in its light-REE trend, with  $(La/Sm)_{cn} > 1$ , compared to  $(La/Sm)_{cn} < 1$  for other zirconolites. At Glen Dessarry it is likely that zirconolites crystallized from a melt enriched in light REE, as demonstrated by the highly fractionated REE distribution in the syenite host rock [ $(Ce/Yb)_{cn} = 20$ ; Fowler, 1985]. This may in part explain the distinctive light-REE pattern of the Glen Dessarry zirconolites. However, such an explanation cannot apply to the U and Th abundances, since their concentrations in the syenites are low (1.1 to 2.8 ppm and 4.9 to 15 ppm respectively for the leucocratic syenite).

Terrestrial zirconolites have variable, and often non-chondritic, element ratios of Nb/Ta, Zr/Hf, and U/Th; values for the Scottish examples are given in Table I. These element pairs are generally considered to be geochemically coherent during magmatic processes, owing to the close similarity between their respective ionic radii and stable valence states (Henderson, 1982). Subtle deviations from the chondritic ratios in whole-rock samples have often been attributed to variations in source composition (e.g. Wood *et al.*, 1979; Eby, 1985).

Table I. Microprobe data for zirconolites from Scottish localities

	Glen Dessarry <sup>1</sup>	Rhum <sup>2</sup>	St Kilda <sup>3</sup>
MgO	0.07	0.35	0.06
Al <sub>2</sub> O <sub>3</sub>	0.27	0.31	0.09
SiO <sub>2</sub>	0.29	0.25	0.1
CaO	9.05	10.80	4.05
TiO <sub>2</sub>	28.80	35.76	29.03
MnO	0.15	<0.1	<0.1
FeO*	7.70	5.14	8.26
Y <sub>2</sub> O <sub>3</sub>	0.67	2.04	8.11
ZrO <sub>2</sub>	31.53	37.60	31.33
Nb <sub>2</sub> O <sub>5</sub>	2.71	0.35	1.29
BaO	0.12	-	<0.1
La <sub>2</sub> O <sub>3</sub>	0.91	0.17	0.52
Ce <sub>2</sub> O <sub>3</sub>	3.25	0.92	2.83
Pr <sub>2</sub> O <sub>3</sub>	0.28	0.19	0.63
Nd <sub>2</sub> O <sub>3</sub>	1.29	1.28	4.66
Sm <sub>2</sub> O <sub>3</sub>	0.28	0.55	1.33
Eu <sub>2</sub> O <sub>3</sub>	0.15	<0.1	0.29
Gd <sub>2</sub> O <sub>3</sub>	0.10	0.53	1.63
Dy <sub>2</sub> O <sub>3</sub>	<0.2	0.48	1.83
Er <sub>2</sub> O <sub>3</sub>	<0.1	0.18	0.96
Yb <sub>2</sub> O <sub>3</sub>	<0.1	0.13	0.87
HfO <sub>2</sub>	0.31	0.80	0.92
Ta <sub>2</sub> O <sub>5</sub>	0.26	0.23	0.16
PbO	0.29	<0.1	<0.1
ThO <sub>2</sub>	8.22	0.48	0.45
UO <sub>2</sub>	2.86	0.18	0.21
Total	99.56	98.72	99.51
**			
Zr/Hf	34.2	88.8	41.0
Nb/Ta	17.5	8.9	1.3
U/Th	0.3	0.35	0.38

Number of Cations based on 7 oxygens

Ca	0.644	0.709	0.292
Y	0.024	0.066	0.290
Ba	0.003	-	-
La	0.023	0.004	0.013
Ce	0.079	0.021	0.070
Pr	0.007	0.005	0.016
Nd	0.031	0.028	0.112
Sm	0.006	0.012	0.031
Eu	0.003	-	0.007
Gd	0.002	0.011	0.086
Dy	-	0.010	0.040
Er	-	0.004	0.020
Yb	-	0.003	0.018
Pb	0.005	-	-
Th	0.124	0.007	0.006
U	0.042	0.003	0.003
	0.993	0.883	0.954
Zr	1.020	1.123	1.027
Hf	0.006	0.014	0.018
	1.026	1.137	1.045
Mg	0.007	0.032	0.006
Al	0.039	0.023	0.007
Si	0.041	0.016	-
Ti	1.437	1.847	1.467
Mn	0.009	-	-
Fe	0.427	0.263	0.464
Nb	0.081	0.010	0.039
Ta	0.005	0.004	0.003
	2.046	1.995	1.986
Σ	4.065	4.015	3.985

1 Glen Dessarry (Inverness-shire), slide no. 42781

2 Rhum (Inverness-shire). Unit 6, Eastern

Layered Series, slide no. R.82

3 St Kilda (Inverness-shire). Pegmatite, Glen

Bay Gabbro, slide no. S.69748A.

\* All Fe as FeO

\*\* Chondritic ratios

However, evidence (e.g. Thompson *et al.*, 1984; Wolff, 1984) is gradually accumulating that such ratios may alter systematically during post-magmatic processes, generally as a result of crystal-liquid equilibria involving minor or accessory phases with non-chondritic element ratios. Clearly, crystallization of zirconolite could rapidly and progressively change the existing ratios of these element pairs in a melt with which it is in equilibrium. At Glen Dessarry, extreme and variable Zr/Hf ratios have been recorded (Fowler, 1985), particularly in pegmatites formed by filter pressing, which represent an evolved melt composition (Zr/Hf = 69.4 to less than 11.8). Since the Zr/Hf ratio in zirconolite from Glen Dessarry is relatively high (88.8), the low values for the whole-rock might record the previous extraction of zirconolite, while the high values might represent its accumulation. Thus zirconolite is another example to add to a rapidly increasing list of minor phases whose potential effects during crystal fractionation should not be overlooked in petrogenetic studies, especially of 'evolved' magma types.

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## V-bearing derbylite from the Buca della Vena mine, Apuan Alps, Italy

DERBYLITE is an iron, titanium, and antimony oxide, first described by Hussak and Prior (1897). Derbylite has a closed-packed (...*chh*...) oxide structure (Moore and Araki, 1976) and has ideal crystal-chemical formula  $\text{Fe}_4^{3+}\text{Ti}_3^{4+}\text{Sb}^{3+}\text{O}_{13}\text{OH}$ .

Based on Moore and Araki's results, Mellini *et al.* (1983) interpreted the actual chemical data for derbylite by the formula  $\text{Fe}_x^{2+}\text{Fe}_{4-2x}^{3+}\text{Ti}_3^{4+}\text{Sb}^{3+}\text{O}_{13}\text{OH}$ . Several chemical variants might result from substitution of suitable octahedral cations for