

# Composition of zircons from the Cornubian Batholith of SW England and comparison with zircons from other European Variscan rare-metal granites

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## ABSTRACT

Zircon from 14 representative granite samples of the late-Variscan Cornubian Batholith in SW England was analysed for W, P, As, Nb, Ta, Si, Ti, Zr, Hf, Th, U, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb, Al, Sc, Bi, Mn, Fe, Ca, Pb, Cu, S and F using electron probe microanalyses. Zircons from the biotite and tourmaline granites are poor in minor and trace elements, usually containing 1.0–1.5 wt.% HfO<sub>2</sub>, <0.5 wt.% UO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>, <0.25 wt.% Y<sub>2</sub>O<sub>3</sub>, <0.2 wt.% Sc<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> and <0.1 wt.% ThO<sub>2</sub>. Zircon from topaz granites from the St. Austell Pluton, Meldon Aplite and Megiliggarr Rocks are slightly enriched in Hf (up to 4 wt.% HfO<sub>2</sub>), U (1–3.5 wt.% UO<sub>2</sub>) and Sc (0.5–1 wt.% Sc<sub>2</sub>O<sub>3</sub>). Scarce metamictized zircon grains are somewhat enriched in Al, Ca, Fe and Mn. The decrease of the zircon Zr/Hf ratio, a reliable magma fractionation index, from 110–60 in the biotite granites to 30–10 in the most evolved topaz granites (Meldon Aplite and Megiliggarr Rocks), supports a comagmatic origin of the biotite and topaz granites via long-lasting fractionation of common peraluminous crustal magma. In comparison with other European rare-metal provinces, the overall contents of trace elements in Cornubian zircons are low and the Zr/Hf and U/Th ratios show lower degrees of fractionation of the parental melt.

**KEYWORDS:** zircon, chemical composition, Cornwall, rare-metal granite.

## Introduction

ZIRCON is one of the most common accessory minerals in granites and is commonly used as a petrogenetic indicator (Wark and Miller, 1993; Hoskin and Schaltegger, 2003; Hanchar and Watson, 2003; Gagnevin *et al.*, 2010), in provenance studies (Hoskin and Ireland, 2000; Belousova *et al.*, 2002; Grimes *et al.*, 2007) and for geochronology (Davis *et al.*, 2003; Crowley *et al.*, 2008). Regardless of an apparently simple composition (ZrSiO<sub>4</sub>), the zircon lattice is able to accommodate

substantial amounts of several minor and many trace elements. Such substitutions are influenced by the: (1) evolving composition of the crystallizing melt, in particular the content of fluxing elements (F, Cl, P) and *P-T* conditions (Bea *et al.*, 1994; Sano *et al.*, 2002; Thomas *et al.*, 2002; Nardi *et al.*, 2013); (2) trace-element composition of the source (Hoskin and Ireland, 2000; Belousova *et al.*, 2002); and (3) geotectonic setting (e.g. A- vs. S-type granites, Breiter *et al.*, 2014).

The Cornubian Batholith of SW England is a classic location for the study of rare-metal granites (e.g. Černý *et al.*, 2005) and has been studied extensively (e.g. Manning and Exley, 1984; Stone and Exley, 1985; Charoy, 1986; Willis-Richards and Jackson, 1989; Jackson *et al.*, 1989; Chappell

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and Hine, 2006; Müller *et al.*, 2006 and references therein). However, accessory mineral compositional data is relatively scarce: tourmaline (London and Manning, 1995), topaz (Manning and Exley, 1984), radioactive minerals (Jefferies, 1984, Ward *et al.*, 1992), Nb-Ta minerals (Scott *et al.*, 1998) and rare-earth element (*REE*) minerals (Jefferies, 1985). As far as zircon is concerned, the only published analyses are those from the Land's End pluton where Müller *et al.* (2006) reported Zr/Hf = 29–46 and variable contents of Th, U, Y, *REE* and Fe, but without any systematic trend.

The purpose of this article is: (1) to describe and interpret the minor and trace-element mineral chemistry of zircons from different granites of the Cornubian Batholith; and (2) to compare the compositions of these zircons with those from other European rare-metal granites.

### The Cornubian Batholith

The Cornubian Batholith of SW England is a WSW–ENE trending, 250 km long  $\times$  20–40 km wide composite granite intrusion extending from the Isles of Scilly in the west to Dartmoor in the east (Willis-Richards and Jackson, 1989). Modelling of gravity anomaly data suggests a minimum batholith thickness of *c.* 6–7 km and implies that  $>40,000 \text{ km}^3$  of magma was generated and emplaced over a 25 Ma period in the Early–Mid Permian (295–270 Ma) (Willis-Richards and Jackson, 1989; Chen *et al.*, 1993; Chesley *et al.*, 1993; Taylor, 2007). Granite magmatism occurred in the footwall of the Variscan Rhenohercynian / Rheic suture, was approximately contemporaneous with mantle-derived lamprophyres and high-K basalts (e.g. Leat *et al.* 1987; Stimac *et al.*, 1995; Dupuis *et al.*, 2015), and strongly influenced by a transtensional tectonic regime established following Variscan convergence (Shail and Leveridge, 2009).

At the current exposure level, the batholith comprises (vol.%)  $>90\%$  biotite granite,  $>3\%$  tourmaline granite and  $>1\%$  topaz granite with minor aplites and pegmatites (Hawkes and Dangerfield, 1978; Willis-Richards and Jackson, 1989; Manning *et al.*, 1996). Six major plutons crop out from east to west on the Cornubian mainland: the Dartmoor, Bodmin Moor, St Austell, Carnmenellis, Tregonning-Godolphin and Land's End granites (Fig. 1). The seventh pluton is situated further to the west on the Isles of Scilly,  $\sim 40 \text{ km}$  WSW of the Land's End Granite. Other expressions of magmatism

include granite stocks, rhyolite / microgranite dykes locally termed 'elvans' and rare rhyolite lavas.

### Biotite granites

The biotite granites are commonly porphyritic, and are mainly monzogranites with subordinate syenogranites (Willis-Richards and Jackson, 1989; data from Exley and Stone, 1964). They are classified as S-type granites (sense Chappell and White, 1974), usually containing K-feldspar phenocrysts,  $\sim 5$  to 10 modal% biotite (mol. Fe/Fe + Mg  $\approx 0.68$ ), up to 4 modal% muscovite, 1 modal% tourmaline and a wide variety of accessory minerals including andalusite, sillimanite, zircon, monazite, uraninite, xenotime, apatite, ilmenite, rutile, anatase, brookite, spinel, fluorite, topaz and garnet (Exley and Stone, 1964, 1982; Jefferies, 1984, 1985; Charoy, 1986; Stimac *et al.*, 1995; Chappell and Hine, 2006). The granites are peraluminous with an aluminium saturation index (ASI) of 1.1–1.4 (Willis-Richards and Jackson, 1989) and silica-rich with a limited range of compositions ( $\text{SiO}_2 = 70\text{--}76 \text{ wt.}\%$ ; Darbyshire and Shepherd, 1985, 1987), with an average of 72.35 wt.% ( $n = 54$ ; Chappell and Hine, 2006). They contain elevated As, B, Be, Co, Cs, F, Ga, Li, P, Pb, Rb, Sn, Ta, U and Zn.

A textural distinction can be made between the older ( $>290 \text{ Ma}$ ) biotite granites of the Isles of Scilly, Carnmenellis and Bodmin plutons, which comprise mainly small phenocryst, coarse-grained granite  $\pm$  variably porphyritic medium-grained granite, and the younger ( $<286 \text{ Ma}$ ) biotite granites of the Land's End, Dartmoor and St Austell plutons that are characterized by variably porphyritic, larger phenocryst, coarse-grained granite (Fig. 1). The older biotite granites also have sparse or absent microgranitoid enclaves, more aluminous compositions, lower femic elements, steeper *REE* patterns, more negative  $\epsilon\text{Nd}$ , higher  $\text{NH}_4^+$  and biotite/muscovite ratio  $<1$  (Stone, 1997, 2000).

### Tourmaline granites

The tourmaline granites are characterized by tourmaline rather than biotite as the dominant ferromagnesian mineral; they are usually monzogranites and syenogranites and contain either K-feldspar or quartz phenocrysts. Detailed descriptions of the mineralogical and textural variations exhibited by the tourmaline granites are provided by Manning *et al.* (1996). Tourmaline granites occur widely as minor dykes and sills, hosted by

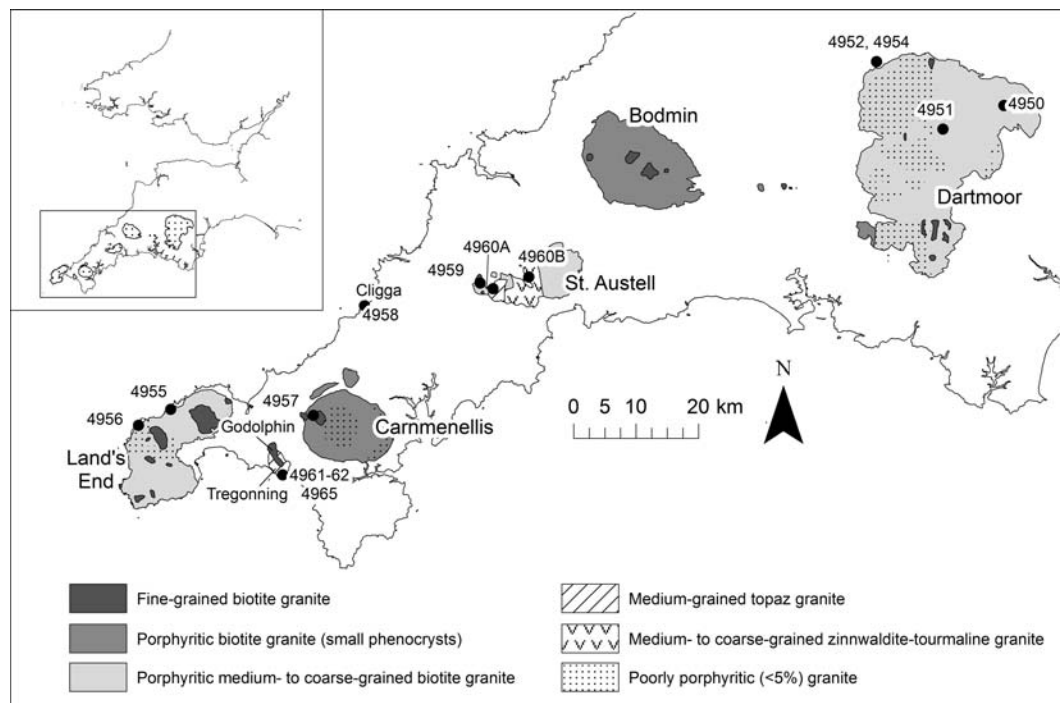


FIG. 1. Geological sketch map of studied granite plutons. Summarized from Dangerfield and Hawkes (1981), Manning *et al.* (1996) and British Geological Survey mapping.

biotite granite and immediately adjacent host rocks. Larger bodies have been recognized in the St Austell, Dartmoor and Land's End plutons (Hill and Manning, 1987; Knox and Jackson, 1990; Manning *et al.*, 1996; Müller *et al.*, 2006). The mineralogy of the tourmaline granites is broadly similar, with quartz, alkali feldspar, plagioclase (typically  $\leq An_7$ ), biotite and tourmaline (Stone *et al.*, 1988; Henderson *et al.*, 1989). Accessory minerals usually consist of apatite, monazite, zircon, topaz and Nb-rich rutile.

### Topaz granites

The topaz granites are typically medium-grained, equigranular and aphyric, and characterized by euhedral-subhedral topaz contents of up to 3% and lithium-rich micas (Manning and Hill, 1990; Stone, 1992; Manning *et al.*, 1996). They are classified as alkali feldspar granites due to their plagioclase composition ( $< An_5$ ). Topaz granites occur principally in the Tregonning Granite and the Nanpean and Hensbarrow stocks within the St Austell Granite where they are commonly associated with

topaz-rich aplites and pegmatites. At Megiliggarr Rocks, a series of sub-horizontal topaz granite sheets hosted by slates occur in the roof zone of the Tregonning Granite (Stone, 1975, 1992). The Meldon Aplite is a 3.5 km long, 15–20 m thick, fine-grained topaz granite dyke that crops out in the north-western aureole of the Dartmoor Granite (Edmonds *et al.*, 1968). Plagioclase, commonly euhedral and unzoned, is almost pure albite ( $An_{1-4}$ ). Lithium micas are zinnwaldite and lepidolite (Stone *et al.*, 1988; Henderson *et al.* 1989); tourmaline is normally schorl, but includes a substantial component of the Li-rich end-member elbaite (London and Manning, 1995). The diverse accessory mineral assemblage variably includes apatite, amblygonite, zircon, ilmenorutile, Mn-ilmenite, Nb-Ta rutile, columbite-tantalite and cassiterite (Manning, 1983; Manning *et al.*, 1996; Scott *et al.*, 1998; Stone and George, 1985).

### Samples and analytical methods

Fourteen zircon-bearing samples of granite were obtained from all the plutons of the Cornubian

TABLE 1. Locations of the zircons investigated.

No.	Locality	Description	Minor minerals	UK Grid Reference
4950	Dartmoor Granite	Coarse-grained porphyritic biotite granite	Zircon, apatite, uraninite	SX 7865 8560
4951	Dartmoor Granite, near the Warren House Inn	Fine-grained tourmaline-biotite granite	Zircon, monazite, xenotime, apatite, uraninite	SX 6763 8095
4952, 4954	Meldon Aplite	Fine-grained topaz aplite-pegmatite dykes	Zircon, apatite, fluorite, uraninite, columbite, thorite, monazite	SX 5707 9204
4955	Land's End Granite, Porthmeor Cove	Fine-grained biotite granite	Zircon, apatite, rutile, monazite	SW 4252 3764
4956	Land's End Granite, Geevor mine	Coarse-grained porphyritic biotite granite	Zircon, apatite, fluorite, monazite	SW 3754 3456
4957	Carmenellis Granite, Holman's Test mine	Coarse-grained (small phenocryst) biotite granite	Zircon, apatite, monazite, rutile, uraninite	SW 6569 3668
4958	Cligga Head Granite	Fine-grained biotite granite, locally kaolinized	Zircon, apatite, rutile, monazite, xenotime, columbite	SW 7386 5367
4959	St. Austell Granite, Wheal Remfry	Porphyritic medium-grained biotite granite	Zircon, apatite, monazite, rutile, fluorite	SW 9268 5699
4960A	St. Austell Granite, Treviscoe	Leucocratic medium-grained Li-biotite granite (topaz granite)	Zircon, apatite, topaz, rutile, columbite	SW 9462 5560
4960B	St. Austell Granite, Goonbarrow	Leucocratic medium-grained zinnwaldite granite (topaz granite)	Zircon, topaz, apatite, columbite, thorite	SX 0095 5848
4961	Legereath Zawn Elvan, Megilggar Rocks	Elvan ('Legereath granite porphyry') of Stone (1975), granite porphyry with orthoclase phenocryst and fine-grained groundmass	Zircon, ilmenite, gahnite, arsenopyrite, monazite	SW 6076 2676
4962	Tregonning Granite roof complex sills, Megilggar Rocks	Medium-grained two-mica granite (topaz granite)	Zircon, apatite, monazite, topaz, xenotime	SW 6081 2671
4965	Tregonning Granite roof complex sills, Megilggar Rocks	Layered tourmaline aplite/pegmatite	Zircon, apatite, tourmaline, Bi, columbite, pyrite, monazite, rutile, ixiolite, cassiterite	SW 6081 2671

Batholith except the Isles of Scilly and Bodmin Moor plutons (Fig. 1, Table 1). Minor intrusions sampled were the Meldon Aplite, Cligga Head Granite, Megilggar Rocks intrusive sheets (Tregonning Granite roof complex) and an elvan dyke, termed here the Legereath Zawn Elvan, that pre-dates the Tregonning Granite and has been interpreted as a possible expression of the Godolphin Granite, the 'Legereath granite porphyry' of Stone (1975).

Polished thin sections were made from all samples in order to establish the relations between the zircons and rock-forming minerals. Back-scattered electron (BSE) images were taken, prior to analysis, to study the internal zoning of individual mineral grains and their relative position

to rock-forming minerals. Zircon and associated minerals such as monazite, xenotime and uraninite were analysed using an identical protocol to include all of the elements identified in at least one of the above-mentioned minerals. Elemental abundances of W, P, As, Nb, Ta, Si, Ti, Zr, Hf, Th, U, Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb, Al, Sc, Bi, Mn, Fe, Ca, Pb, Cu, S and F in oxide minerals were determined using a CAMECA SX100 electron probe micro-analyser, equipped with five wavelength-dispersive spectrometers, hosted by Masaryk University and the Czech Geological Survey, Brno. Minerals were analysed at an accelerating voltage and beam current of 15 keV and 40 nA, respectively, and with a beam diameter ranging from 2 to 5  $\mu\text{m}$ . The following

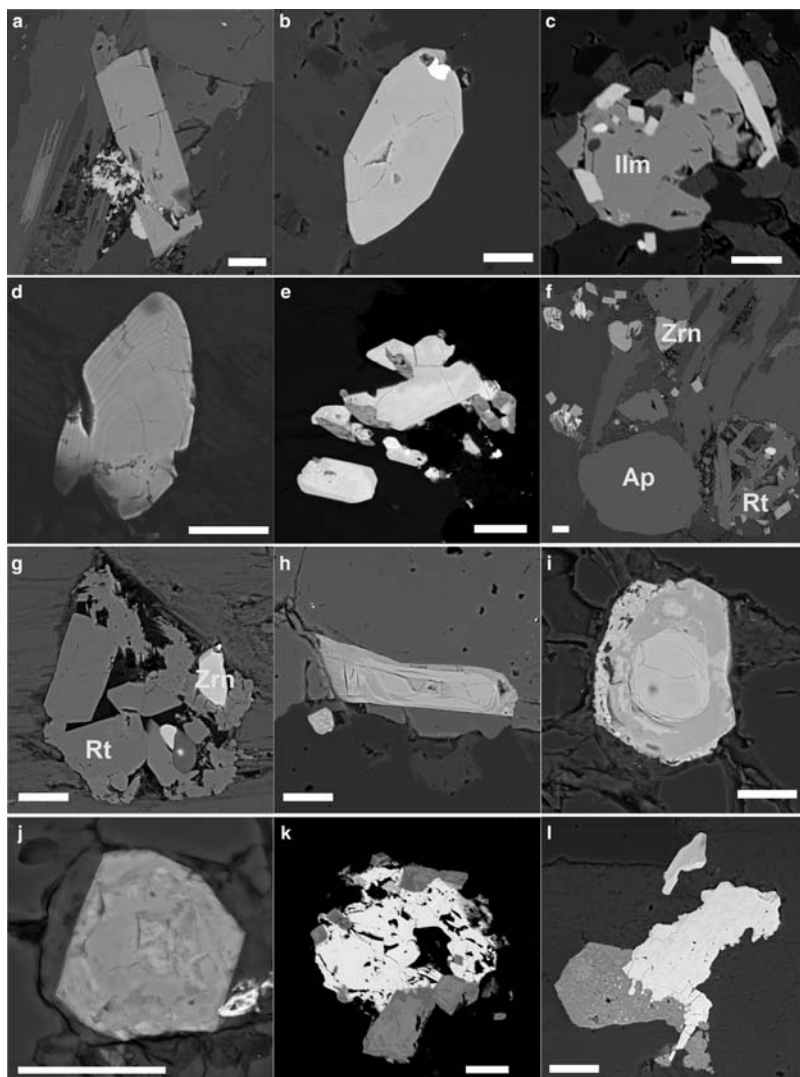


FIG. 2. BSE-images of typical zircon grains and associated minerals (scale bar in all cases 20  $\mu\text{m}$ ): (a) broken homogeneous columnar zircon crystal (grey) with attached monazite aggregates (bright), sample #4957, coarse-grained biotite granite of the Cammenellis pluton; (b) crystal of zircon (light grey) with inclusion of monazite (bright), #4959, porphyritic medium-grained biotite granite of the St. Austell pluton; (c) homogeneous zircon crystal (bright) associated with ilmenite (grey), #4961, Legereath Zawn elvan, Megilggar Rocks; (d) oscillatory zoned zircon crystal (grey), #4950, coarse-grained biotite granite of the Dartmoor pluton; (e) large slightly zoned xenotime crystals (bright) with several associated small zircon grains (grey), #4951, fine-grained biotite granite of the Dartmoor pluton; (f) small grains of zircon (light grey) associated with monazite (bright), large isometric grain of apatite (Ap) and aggregate of columnar rutile (Rt), #4957, coarse-grained biotite granite of the Cammenellis pluton; (g) zircon (bright) associated with columnar rutile (Rt), #4955, fine-grained biotite granite of the Land's End pluton; (h) zoned crystal of zircon, core is near the ideal zircon composition (compare anal. 28, Table 2), while rim is enriched in P, Y and F (anal. 29, Table 2), #4959, porphyritic medium-grained biotite granite of the St. Austell pluton; (i) zoned zircon crystal with bright core (anal. 37, Table 2) and darker metamictized U, Al, Sc, F-enriched rim (anal. 38, Table 2), #4960A, medium-grained topaz granite of the St. Austell pluton; (j) patchy metamictized zircon, #4960B, medium-grained topaz granite of the St. Austell pluton; (k) monazite (bright) with associate zircon crystals (grey), #4962, fine-grained two-mica granite, Megilggar Rocks; (l) patchy metamictized zircon (grey) associated with columbite (bright), #4952, topaz aplite, Meldon quarry.

TABLE 2. Representative compositions of zircon (wt.%) and empirical formulae (in atoms per formula unit) based on 4 O atoms. Contents of Ta, La and Cu were in all cases under the detection limits of EMPA (u.d.l.).

Anal.No. Sample Locality	44 Dm	36 Dm	2 Mn	4952	5 Mn	4954	28core 4959 St.A	29rim 4959 St.A	37core 4960A St.A	38rim 4960A St.A	41 4960B St.A	24 4957 HTM	21 4958 CH	30 4955 LE	3 4956 LE	11 4961 LZ	10 4962 Mg	15 4965 Mg	
WO <sub>3</sub>	u.d.l.	0.30	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.47	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.
P <sub>2</sub> O <sub>5</sub>	0.35	1.57	0.75	0.30	0.59	0.30	0.30	5.25	0.30	1.07	5.48	0.41	0.10	0.85	0.39	0.38	0.66	0.92	0.92
As <sub>2</sub> O <sub>5</sub>	0.06	0.12	0.29	0.04	0.11	0.04	0.06	0.30	0.06	0.19	0.46	0.07	0.07	0.09	0.05	0.05	0.16	0.15	0.15
Nb <sub>2</sub> O <sub>5</sub>	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.55	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.
SiO <sub>2</sub>	31.83	22.95	27.35	31.01	31.01	31.60	31.60	22.78	31.60	25.37	21.91	32.18	32.18	29.65	31.92	31.88	30.84	30.87	30.87
TiO <sub>2</sub>	0.01	u.d.l.	0.02	0.06	0.06	u.d.l.	u.d.l.	0.03	u.d.l.	u.d.l.	0.09	u.d.l.	0.24	0.06	0.07	0.50	0.13	u.d.l.	u.d.l.
ZrO <sub>2</sub>	63.67	43.37	50.87	60.60	60.60	64.22	63.86	52.19	63.86	49.17	50.50	64.66	64.56	59.20	64.44	63.52	61.91	59.84	59.84
HfO <sub>2</sub>	1.65	1.79	7.35	3.87	3.87	1.47	1.42	2.17	1.42	2.12	2.76	1.59	1.84	1.42	1.41	1.18	1.62	3.56	3.56
ThO <sub>2</sub>	u.d.l.	3.17	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.12	u.d.l.	u.d.l.	u.d.l.	0.56	0.11	u.d.l.	0.13	u.d.l.	u.d.l.
UO <sub>2</sub>	0.50	1.68	1.52	0.66	0.66	0.13	0.13	0.75	0.13	3.60	1.50	0.23	0.21	0.70	0.40	0.29	1.03	1.04	1.04
Y <sub>2</sub> O <sub>3</sub>	0.30	3.02	0.55	u.d.l.	u.d.l.	0.13	0.08	1.85	0.08	u.d.l.	u.d.l.	0.20	u.d.l.	1.23	0.28	0.22	0.41	0.27	0.27
Ce <sub>2</sub> O <sub>3</sub>	u.d.l.	0.12	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.15	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.11	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.
Pr <sub>2</sub> O <sub>3</sub>	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.07	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.08	0.06	u.d.l.	u.d.l.	u.d.l.	u.d.l.
Nd <sub>2</sub> O <sub>3</sub>	u.d.l.	0.11	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.20	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.11	0.02	0.10	0.05	u.d.l.	u.d.l.
Sm <sub>2</sub> O <sub>3</sub>	u.d.l.	0.11	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.14	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.07	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.
Gd <sub>2</sub> O <sub>3</sub>	u.d.l.	0.18	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.22	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.13	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.
Dy <sub>2</sub> O <sub>3</sub>	u.d.l.	0.42	0.18	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.25	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.18	u.d.l.	0.06	0.10	u.d.l.	u.d.l.
Er <sub>2</sub> O <sub>3</sub>	0.11	0.35	0.14	0.06	0.06	0.06	0.06	0.32	0.08	u.d.l.	u.d.l.	u.d.l.	0.06	0.16	0.07	u.d.l.	0.09	0.11	0.11
Yb <sub>2</sub> O <sub>3</sub>	0.18	0.47	0.27	0.10	0.10	u.d.l.	0.06	0.32	0.06	0.09	u.d.l.	0.06	u.d.l.	0.21	u.d.l.	0.09	0.17	0.21	0.21
Al <sub>2</sub> O <sub>3</sub>	u.d.l.	1.20	0.48	0.13	0.13	u.d.l.	u.d.l.	1.00	u.d.l.	1.22	1.04	u.d.l.	u.d.l.	0.49	u.d.l.	u.d.l.	u.d.l.	0.59	0.59
Sc <sub>2</sub> O <sub>3</sub>	0.05	0.03	0.30	0.31	0.31	0.08	0.06	0.18	0.06	1.14	1.52	0.12	0.04	0.15	0.10	0.11	0.21	0.54	0.54
Bi <sub>2</sub> O <sub>3</sub>	0.13	0.19	u.d.l.	0.18	0.18	u.d.l.	u.d.l.	0.47	u.d.l.	u.d.l.	0.55	u.d.l.	0.16	u.d.l.	u.d.l.	0.13	u.d.l.	u.d.l.	u.d.l.
MnO	u.d.l.	0.09	0.47	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.10	u.d.l.	0.17	0.11	u.d.l.	u.d.l.	0.07	u.d.l.	u.d.l.	0.04	u.d.l.	u.d.l.
FeO	0.72	4.08	0.72	u.d.l.	u.d.l.	u.d.l.	u.d.l.	1.09	u.d.l.	1.09	0.88	0.34	0.07	1.17	0.48	0.73	0.48	0.12	0.12
CaO	u.d.l.	1.08	1.31	0.33	0.33	0.14	u.d.l.	1.82	u.d.l.	1.15	1.35	0.04	u.d.l.	0.46	0.04	u.d.l.	0.18	0.07	0.07
PbO	u.d.l.	0.13	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.
MgO	u.d.l.	0.05	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.07	0.05	u.d.l.	u.d.l.	0.08	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.
SO <sub>3</sub>	u.d.l.	0.04	u.d.l.	0.09	0.09	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.04	u.d.l.	u.d.l.	0.05	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.
F	u.d.l.	0.74	0.19	u.d.l.	u.d.l.	u.d.l.	u.d.l.	1.59	u.d.l.	0.74	1.03	u.d.l.	u.d.l.	0.08	u.d.l.	u.d.l.	0.08	u.d.l.	u.d.l.
Total	99.79	87.34	92.94	0.000	98.31	98.44	97.95	93.36	97.95	87.53	90.44	100.18	99.70	97.45	100.03	99.45	98.45	98.53	98.53
W	0.000	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
P	0.009	0.050	0.022	0.008	0.016	0.008	0.008	0.152	0.008	0.033	0.161	0.011	0.003	0.023	0.010	0.010	0.018	0.024	0.024
As	0.001	0.002	0.005	0.001	0.002	0.001	0.001	0.005	0.001	0.004	0.008	0.001	0.001	0.002	0.001	0.001	0.003	0.003	0.003



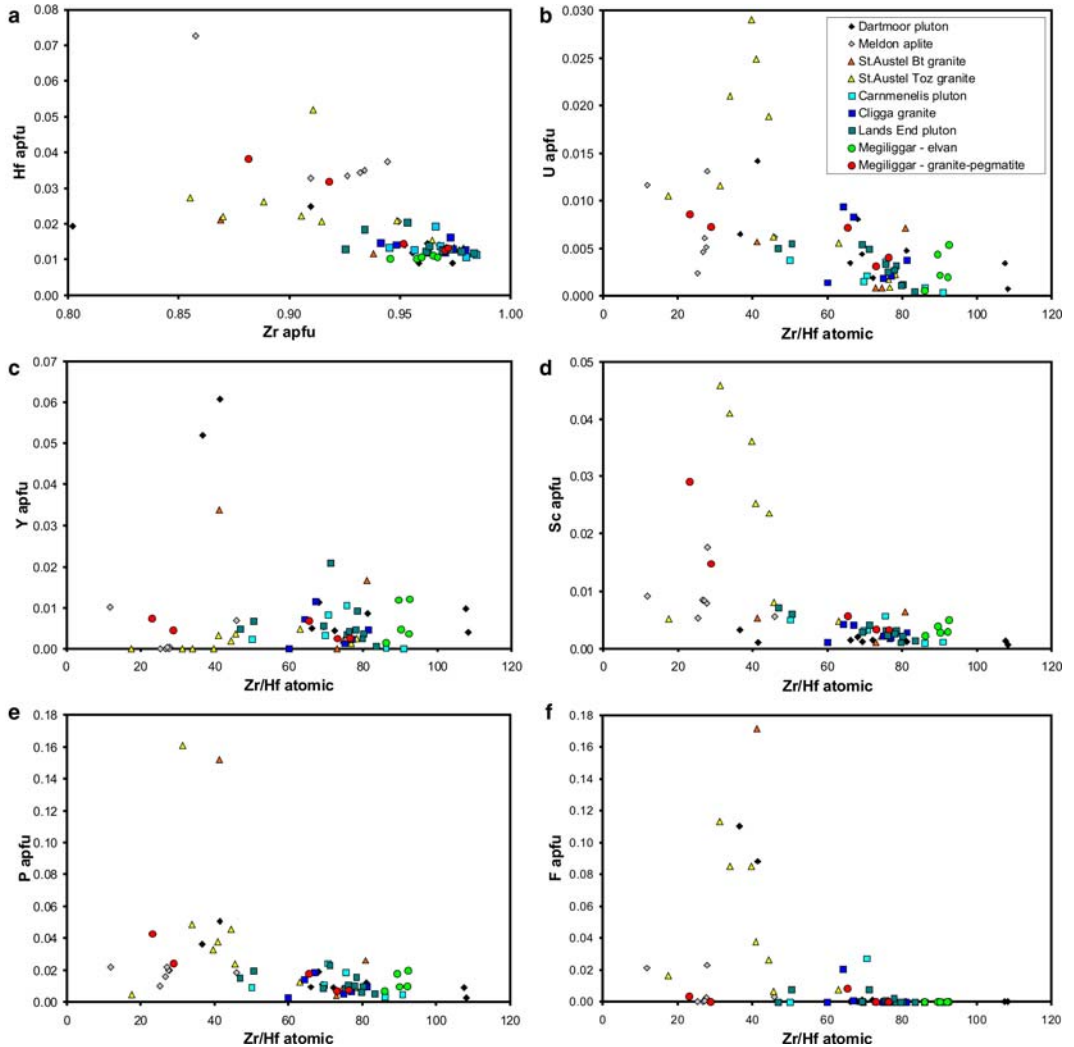


FIG. 3. Composition of zircon from Cornubian granites (in atoms per formula unit): (a) Zr vs. Hf; (b) Zr/Hf vs. U; (c) Zr/Hf vs. Y; (d) Zr/Hf vs. Sc; (e) Zr/Hf vs. P; (f) Zr/Hf vs. F.

standards were used: U – metallic U, Pb – PbSe, Th – ThO<sub>2</sub>, P – fluorapatite, Y – YAG, La – LaB<sub>6</sub>, Ce – CeAl<sub>2</sub>, Pr – PrF<sub>3</sub>, Nd – NdF<sub>3</sub>, Sm – SmF<sub>3</sub>, Gd – GdF<sub>3</sub>, Dy – DyP<sub>5</sub>O<sub>14</sub>, Er – YErAG, Yb – YbP<sub>5</sub>O<sub>14</sub>, Al – almandine, Si, Ca, Fe – andradite, Mn – rhodonite, W – scheelite, S – barite, F – topaz, As, Cu – lammerite, Nb – columbite, Ta – CrTa<sub>2</sub>O<sub>6</sub>, Ti – titanite, Zr – zircon; Hf – metallic Hf; Bi – metallic Bi; mg – mgAL<sub>2</sub>O<sub>4</sub> and Sc – ScVO<sub>4</sub>. Empirical formulae of zircon were calculated on the basis of four atoms of oxygen in a formula unit (4 O apfu).

## Results

### Zircon crystal morphology

Zircon from the biotite granites and Legereath Zawn Elvan forms mostly columnar crystals, internally homogeneous (Fig. 2a, b, c) or with fine oscillatory zoning (Fig. 2d). It is usually located within, or at the surface of, mica flakes and is associated typically with xenotime (Fig. 2e) or monazite (Fig. 2a). In the Legereath Zawn Elvan, and in the coarse-grained biotite granite from



## ZIRCON FROM CORNUBIAN GRANITES

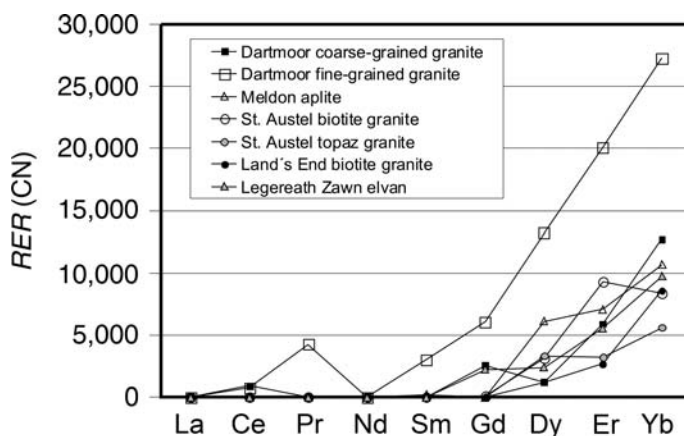


FIG. 4. Chondrite normalized (CN) distribution of *REE* (McDonough and Sun, 1995) in selected zircon grains.

Carmenellis and Land's End plutons, zircon forms aggregates with rutile (Fig. 2*c, f, g*).

Strongly zoned zircons with a light core and a darker rim are typical for the biotite and topaz granites of the St. Austell pluton (Fig. 2*h, i*). The rims of these crystals are enriched in Hf and U but, due to strong metamictization, have low analytical totals which result in a darker colour in back-scattered electron images (compare Nasdala *et al.*, 2009).

The most differentiated topaz granites contain mainly patchy zoned and metamict zircons (St. Austell, Fig. 2*j*) associated typically with monazite (Megilggar Rocks, Fig. 2*k*) or columbite (Meldon Aplite, Fig. 2*l*).

### Zircon composition

Altogether, 68 analyses of zircon were obtained from 14 thin sections (Appendix 1, deposited with the Principal Editor of *Mineralogical Magazine* and available from [http://www.minersoc.org/pages/e\\_journals/dep\\_mat\\_mm.html](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html)). Representative compositions are given in Table 2.

Zircon ( $\text{ZrSiO}_4$ ) ideally contains 67.3 wt.%  $\text{ZrO}_2$  and 32.7 wt.%  $\text{SiO}_2$ . In reality, the content of both elements decreases due to variable substitution by a wide range of minor and trace elements. In the samples studied,  $\text{ZrO}_2$  was as low as 43.4 wt.% (0.80 apfu Zr) and  $\text{SiO}_2$  as low as 21.9 wt.% (0.76 Si apfu).

Hafnium is crystallochemically similar to zirconium and so there is substantial substitution in zircon from all rock types. Zircon from the biotite and tourmaline granites analysed usually contains

1.0–1.5 wt.%  $\text{HfO}_2$  (0.01–0.015 apfu Hf) but this increases to 2.0–3.5 wt.%  $\text{HfO}_2$  (0.02–0.035 apfu Hf) in the topaz granites, reaching a maximum of 7.35 wt.%  $\text{HfO}_2$  (0.073 apfu Hf) in the Meldon Aplite.

The Zr/Hf ratio in zircon is, in general, considered a reliable indicator of magma fractionation (e.g. Linnen and Keppler, 2002) and therefore was chosen as the index against which to compare variations in all other elements. The atomic Zr/Hf ratio ranges from 110–60 in the biotite granites to 30–10 in the Meldon Aplite and Megilggar Rocks topaz granite. Nevertheless, the Zr/Hf ratios vary considerably, not only among different granite types, but also among single zircon grains in the same thin section (Fig. 3).

The radioactive elements thorium and uranium are ubiquitous components. The U content usually varies from <0.1 to 1.0 wt.%  $\text{UO}_2$  (0.0005–0.007 apfu U). The highest contents, up to 3.6 wt.%  $\text{UO}_2$  (0.029 apfu U), were found in the St. Austell topaz granites. The Th content is usually lower than 0.1 wt.%  $\text{ThO}_2$  (0.0005 apfu Th) and high concentrations were found only rarely with a maximum at 3.17 wt.%  $\text{ThO}_2$  (0.027 apfu Th) in a fine-grained biotite granite from the Dartmoor pluton. Atomic U/Th ratios usually range between 3 and 15, but in the fine-grained Dartmoor biotite granite and St. Austell topaz granite commonly exceed 100.

Yttrium and heavy *REE* (*HREE*) are also generally common in granitic zircon due to isostructural mixing between zircon and xenotime,  $\text{ZrSiO}_4 \leftrightarrow \text{YPO}_4$ . The content of Y is usually lower than 0.4 wt.%, only rarely exceeding 0.5 wt.%  $\text{Y}_2\text{O}_3$ . The highest values, up to 3.0 wt.%  $\text{Y}_2\text{O}_3$

TABLE 3. Representative compositions of monazite, xenotime and uraninite (wt.%) and empirical formulae (in atoms per formula unit) based on 4 O atoms for phosphates and 2 O atoms for uraninite. Contents of W, As, Nb, Ta, Hf, Al, Cu and S were in all cases under the detection limits of EMPA (u.d.l.).

Mineral Sample	Monazite 4956	Monazite 4961	Monazite 4959	Monazite 4957	Xenotime 4951	Xenotime 4962	Uraninite 4957	Uraninite 4950
P <sub>2</sub> O <sub>5</sub>	28.15	28.63	29.43	29.32	31.06	31.35	u.d.l.	u.d.l.
SiO <sub>2</sub>	0.62	u.d.l.	0.10	0.22	0.88	0.58	u.d.l.	u.d.l.
TiO <sub>2</sub>	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.39	u.d.l.	u.d.l.
ZrO <sub>2</sub>	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.44	u.d.l.	u.d.l.
ThO <sub>2</sub>	3.31	0.17	9.93	7.99	1.39	0.33	1.53	2.60
UO <sub>2</sub>	u.d.l.	u.d.l.	2.26	0.46	2.26	3.39	94.37	91.73
Y <sub>2</sub> O <sub>3</sub>	0.36	0.74	2.12	0.89	38.54	39.75	0.18	0.34
La <sub>2</sub> O <sub>3</sub>	13.51	14.86	10.16	12.60	u.d.l.	0.08	u.d.l.	u.d.l.
Ce <sub>2</sub> O <sub>3</sub>	31.20	32.86	24.25	27.82	0.07	0.08	u.d.l.	0.11
Pr <sub>2</sub> O <sub>3</sub>	3.52	3.49	2.65	3.00	u.d.l.	u.d.l.	0.16	0.00
Nd <sub>2</sub> O <sub>3</sub>	12.68	11.51	9.60	10.72	0.40	0.43	u.d.l.	u.d.l.
Sm <sub>2</sub> O <sub>3</sub>	2.41	2.35	2.35	2.10	0.86	0.90	u.d.l.	u.d.l.
Gd <sub>2</sub> O <sub>3</sub>	3.58	3.66	3.22	3.29	2.36	3.02	u.d.l.	u.d.l.
Dy <sub>2</sub> O <sub>3</sub>	0.18	0.26	0.64	0.31	4.83	5.68	u.d.l.	0.16
Er <sub>2</sub> O <sub>3</sub>	0.01	0.01	0.16	0.08	3.97	3.17	u.d.l.	u.d.l.
Yb <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.02	0.02	4.47	2.85	u.d.l.	u.d.l.
Sc <sub>2</sub> O <sub>3</sub>	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.06	u.d.l.	u.d.l.
Bi <sub>2</sub> O <sub>3</sub>	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.22	0.21
MnO	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.05	u.d.l.	u.d.l.	u.d.l.
FeO	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.87	u.d.l.	0.27	u.d.l.
CaO	0.09	0.05	2.52	1.56	0.10	0.36	u.d.l.	0.03
PbO	u.d.l.	u.d.l.	0.24	0.15	0.08	0.10	3.74	3.65
F	u.d.l.	u.d.l.	u.d.l.	u.d.l.	0.11	0.05	u.d.l.	u.d.l.
Total	99.83	98.78	99.67	100.63	92.44	93.17	100.88	99.25
P	0.960	0.980	0.985	0.980	0.965	0.962	0.000	0.000
Si	0.025	0.000	0.004	0.009	0.032	0.021	0.000	0.000
Ti	0.000	0.000	0.000	0.000	0.000	0.011	0.000	0.000
Zr	0.000	0.000	0.000	0.000	0.000	0.008	0.000	0.000
Th	0.030	0.002	0.089	0.072	0.012	0.003	0.016	0.027
U	0.000	0.000	0.020	0.004	0.018	0.027	0.943	0.931
Y	0.008	0.016	0.045	0.019	0.752	0.767	0.004	0.008
La	0.201	0.222	0.148	0.183	0.000	0.001	0.000	0.000
Ce	0.460	0.487	0.351	0.402	0.001	0.001	0.000	0.002
Pr	0.052	0.051	0.038	0.043	0.000	0.000	0.003	0.000
Nd	0.182	0.166	0.136	0.151	0.005	0.006	0.000	0.000
Sm	0.034	0.033	0.032	0.029	0.011	0.011	0.000	0.000
Gd	0.048	0.049	0.042	0.043	0.029	0.036	0.000	0.000
Dy	0.002	0.003	0.008	0.004	0.057	0.066	0.000	0.002
Er	0.000	0.000	0.002	0.001	0.046	0.036	0.000	0.000
Yb	0.000	0.000	0.000	0.000	0.050	0.031	0.000	0.000
Al	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sc	0.000	0.000	0.000	0.000	0.000	0.002	0.001	0.000
Bi	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.002
Mn	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000
Fe	0.000	0.000	0.000	0.000	0.027	0.000	0.010	0.000
Ca	0.004	0.002	0.106	0.066	0.004	0.014	0.000	0.002
Pb	0.000	0.000	0.003	0.002	0.001	0.001	0.045	0.045
F	0.000	0.000	0.000	0.000	0.012	0.000	0.000	0.000

(0.06 apfu Y), were found in the fine-grained Dartmoor Granite. Ytterbium is the most common REE: usually 0.05–0.20 wt.% Yb<sub>2</sub>O<sub>3</sub>, maximally 0.7 wt.% Yb<sub>2</sub>O<sub>3</sub> (0.008 apfu Yb) (Fig. 4).

Light REE are much less compatible in the crystal lattice of zircon than HREE and their content only sporadically exceeded 0.05 wt.% of appropriate oxide (= the detection limit of microprobe).

Scandium is present in the majority of zircons, typically ~0.05–0.20 wt.% Sc<sub>2</sub>O<sub>3</sub>, but in more fractionated granites reaches more than 0.5 wt.%, and a maximum of 1.5 wt.% Sc<sub>2</sub>O<sub>3</sub> (0.046 apfu Sc) in the St. Austell topaz granite.

Bismuth is a rare element, but commonly present at ~0.10–0.15 wt.% Bi<sub>2</sub>O<sub>3</sub>. The highest content occasionally found in the St. Austell topaz granite is 0.55 wt.% Bi<sub>2</sub>O<sub>3</sub> (0.005 apfu Bi).

The content of phosphorus usually varied between 0.2–0.8 wt.% P<sub>2</sub>O<sub>5</sub> (0.005–0.02 apfu P) but, in differentiated granites, increased substantially to 5.5 wt.% P<sub>2</sub>O<sub>5</sub> (0.16 apfu P) in one grain from the St. Austell topaz granite.

The content of arsenic is lower than that of P: usually 0.05–0.10 wt.% As<sub>2</sub>O<sub>5</sub>, with a maximum of 0.46 wt.% As<sub>2</sub>O<sub>5</sub> (0.008 apfu As) in the St. Austell topaz-zinnwaldite granite.

Tungsten and Nb were found in a single strongly metamictized zircon grain from the St. Austell topaz granite (0.47 wt.% WO<sub>3</sub> and 0.55 wt.% Nb<sub>2</sub>O<sub>5</sub>).

The contents of Al, Fe, Mn and Ca is usually lower than the detection limit of electron probe microanalyses (EPMA), but each of these elements may be enriched up to >1 wt.% (Mn up to 0.4 wt.%) of the corresponding oxide in metamictized grains.

The content of fluorine is usually lower than the EPMA detection limit but, in some zircons from F-enriched topaz-bearing rocks (Meldon, St. Austell), may be enriched up to 1.6 wt.% F (0.17 apfu F).

The contents of Mg, Cu, Pb and S are negligible; Ta is in all cases lower than the detection limit.

### Associated minerals

Apatite, rutile, monazite, xenotime and uraninite occur in most samples (Table 3).

Monazite forms homogeneous isometric grains up to 100 µm in diameter. It is usually enriched in Th and U: 6–10 wt.% ThO<sub>2</sub> (0.05–0.09 apfu Th) and 0.5–2.3 wt.% UO<sub>2</sub> (0.005–0.020 apfu U). Only the monazite from the Legereath Zawn Elvan is U and Th-free. Monazite appears to be younger than zircon when in mutual contact.

Xenotime forms short columnar crystals up to 50 µm (Fig. 2b) or irregular grains, usually older than the associated zircon. As well as a significant content of Y (0.75–0.80 apfu Y), xenotime contains HREE: up to 5.7 wt.% Dy<sub>2</sub>O<sub>3</sub> (0.066 apfu Dy), 5 wt.% Yb<sub>2</sub>O<sub>3</sub> (0.055 apfu Yb), 4.0 wt.% Er<sub>2</sub>O<sub>3</sub>, 3.0 wt.% Gd<sub>2</sub>O<sub>3</sub> and 1.1 wt.% Sm<sub>2</sub>O<sub>3</sub>. The contents of thorium are lower, and uranium higher, than in the associated monazite: up to 1.5 wt.% ThO<sub>2</sub> (0.012 apfu Th) and 3.8 wt.% UO<sub>2</sub> (0.030 apfu U).

Uraninite appears as small (<20 µm) isometric late interstitial grains. It usually contains 1.5–3.7 wt.% ThO<sub>2</sub> (0.03–0.08 apfu Th) and 2.8–3.7 wt.% PbO (0.07–0.09 apfu Pb).

## Discussion

### Element substitution in zircon

The tetravalent elements Hf, Th, U and Ti substitute in the zircon crystal lattice for zirconium. The trivalent elements Y and REEs enter the zircon structure as the ‘xenotime component’ (P<sup>5+</sup> + (Y, REE)<sup>3+</sup> ↔ Si<sup>4+</sup> + Zr<sup>4+</sup>) because xenotime and zircon are isostructural and have similar lattice parameters (Speer, 1982). Also Sc and occasionally Bi, substitute in zircon as their respective phosphate components ScPO<sub>4</sub> (pretulite) and BiPO<sub>4</sub> (ximengite) (Bernhard *et al.*, 1998; Shi, 1989). Positive correlation between P and the sum of REE + Y + Sc + Bi, with the ratio P/M<sup>3+</sup> close to 1, supports this interpretation (Fig. 5). Trivalent Al is present only in metamictized zircons with a partially destructed and hydrated structure and probably substitutes for Si: (AlOH)<sup>2+</sup> ↔ (SiO)<sup>2+</sup> (Geisler *et al.*, 2003; Nasdala *et al.*, 2009).

### Fractionation of the Cornubian granites

The Zr/Hf ratio in zircon is a good indicator of granite fractionation (Linnen and Keppler, 2002). Breiter *et al.* (2014) compared the zircon atomic Zr/Hf ratio with the grade of fractionation of parental granites and were able to divide granites into three groups: common granites containing zircon with Zr/Hf > 55, evolved granites containing zircon with Zr/Hf = 25–55, and strongly evolved granites with zircon with Zr/Hf < 25. According to this classification, the coarse-grained biotite granites from Dartmoor, Carnmenellis, Cligga Head, Land’s End and St. Austell plutons and the Legereath Zawn Elvan are ‘common granites’, whilst the Dartmoor fine-grained biotite-tourmaline granite, St. Austell

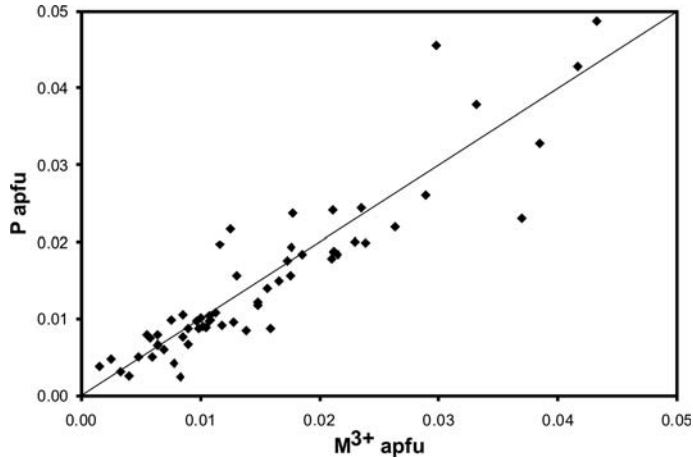


FIG. 5. Xenotime-type substitution  $P^{5+} + (Y, REE, Sc, Bi)^{3+} \leftrightarrow Si^{4+} + Zr^{4+}$  in Cornubian zircons.

topaz granites, Meldon Aplite and Megilgar topaz aplite/pegmatite are 'evolved granites'. This is in good agreement with generally accepted petrological/geochemical classification of the Cornubian Batholith as comprising, at the current exposure level, predominantly less-evolved biotite ( $\pm$ tourmaline) granites and minor more-evolved topaz granites (Manning and Hill, 1990).

The genetic relationship between biotite granites and topaz granites in SW England remains controversial. The topaz granites have been interpreted variably as the: (1) result of progressive fractionation of the biotite granite magma (Stone, 1975; Taylor and Fallick, 1997); (2) product of partial melting of lower crustal residues after generation and extraction of previous biotite granite magmas (Manning and Hill, 1990); or (3) product of partial melting of metasomatically enriched lower crust (Stone, 1992).

When evaluating these models, the approximately coeval ( $<1$  Ma) emplacement of biotite (Godolphin) and topaz (Tregonning) granites in the same area (Clark *et al.*, 1994) must also be considered.

Melting of a crustal residuum, as proposed by Manning and Hill (1990), is unlikely because such melting will produce a subaluminous, P-poor, A-type melt (Eby, 1990; Bonin, 2007) and not a strongly peraluminous P-rich melt required to form the topaz granites.

Enrichment of the lower crust with F- and Li-bearing fluid during the short period between production of both principal types of granites is highly speculative; moreover the topaz granites are enriched not only in F and Li, but also in Sn, Nb, Ta,

W, etc. The Cornubian biotite and topaz granites are chemically and mineralogically similar to late-Variscan composite plutons in Massif Central, France and Western Erzgebirge, Germany/Czech Republic, where the direct link between the less differentiated biotite granites and spatially associated Li-mica-topaz granites is well established (Raimbault *et al.*, 1995; Förster *et al.*, 1999; Breiter, 2012). Therefore, the origin of the topaz granites via pronounced fractionation of the biotite granite-magma seems to be the most probable.

The Cornubian biotite granites contain 66–169 ppm Zr (Chappell and Hine, 2006) and the topaz granites less than 30 ppm Zr (Manning and Hill, 1990). Assuming melting temperature at or slightly above 800°C, the biotite granites were Zr-saturated, and the topaz granites strongly under saturated at the source (Watson and Harrison, 1983). This implies no Zr/Hf fractionation during partial melting. All aforementioned models assume generation of both granite types from a similar protolith, i.e. the biotite granite-magma and the topaz granite-magma started their evolution with the same Zr/Hf ratios (identical with the protolith). The substantially lower Zr/Hf in the topaz granites, in comparison with those in the 'common' biotite granites, documents a comparatively longer/more intensive fractionation path of the former. However, this is not a proof that topaz granites in the St. Austell and Tregonning plutons originated via fractionation of a magma batch that formed the immediately adjacent biotite granites. The less-evolved members of the topaz granite suite, with lower contents of volatiles and thus more viscous, may be present at deeper levels in the batholith and

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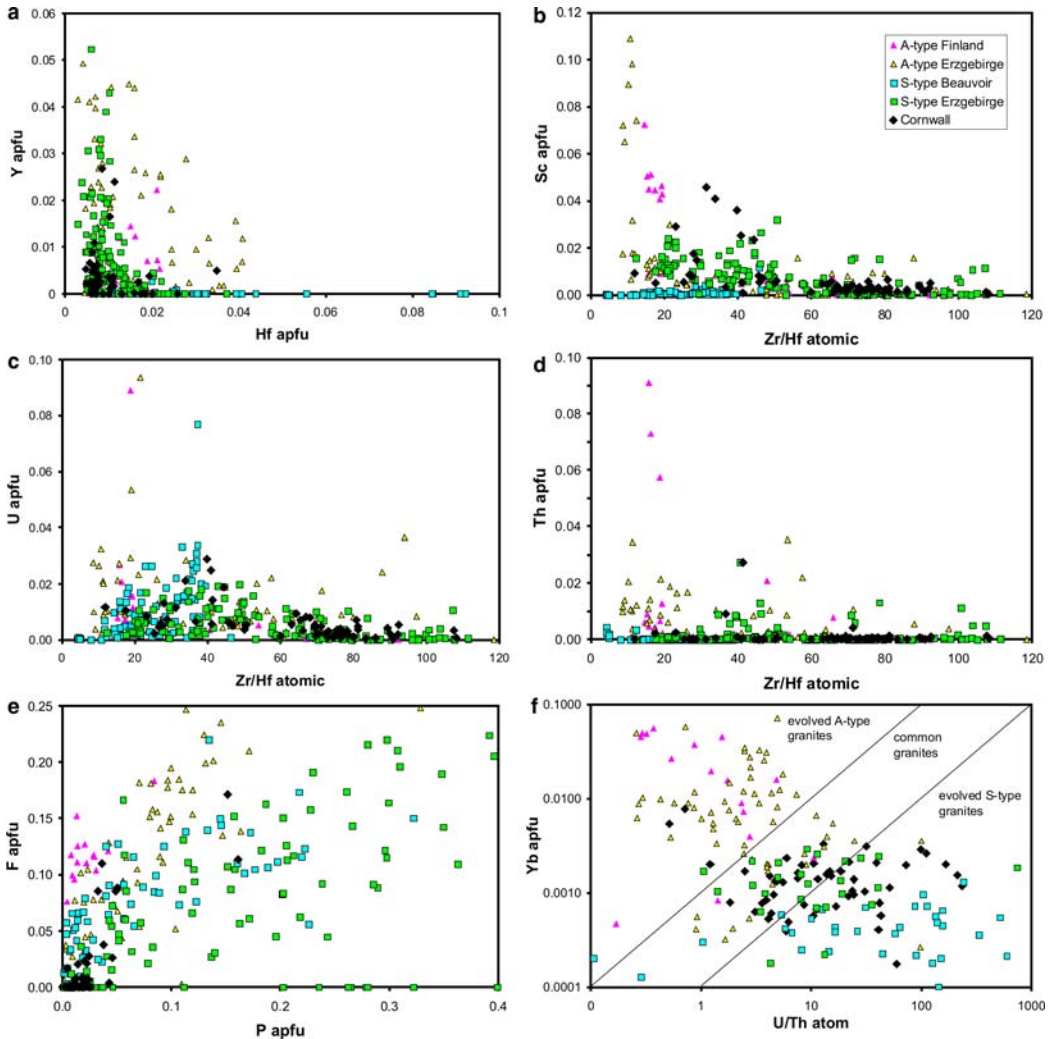


FIG. 6. Comparison of the contents of minor elements in zircons from SW England and other European rare-metal granites (in atoms per formula unit): (a) Hf vs. Y; (b) Zr/Hf vs. Sc; (c) Zr/Hf vs. U; (d) Zr/Hf vs. Th; (e) P vs. F; (f) U/Th vs. Yb.

may not have any surface expression. Such superposition of the more- and less-fractionated portions of a pluton are described in detail in rare-metal granites from Beauvoir, France and Cínovec, Erzgebirge (Raimbault *et al.*, 1995; Breiter and Škoda, 2012).

*Comparison with zircon from other European rare-metal granites*

The association of minor and trace elements in granitic zircon is highly variable and principally

reflects three factors: (1) composition of the melted source rocks; (2) *P-T* conditions of melting; and (3) degree of fractionation of the granitic melt. The first two factors result in higher contents of Th, Y and *HREE* in zircon from A-type granites than in zircon from peraluminous S-type granites (Breiter *et al.*, 2014). The granites of the Cornubian Batholith are differentiated, as represented by their enrichment in volatile agents and some ore elements (e.g. Sn, W, Cu), commonly termed as ‘rare metal-’ or ‘tin-’ granites (Černý *et al.*, 2005). Strongly differentiated rare-metal granites occur widely in Europe.

Examples include the distinctly peraluminous (S-type) late Variscan granites of the Western Erzgebirge (Germany/Czech Republic, Förster *et al.*, 1999; Breiter, 2012) and Massif Central (France, Raimbault *et al.*, 1995), the slightly peraluminous to subaluminous (A-type) late Variscan granites of the Eastern Erzgebirge (Förster *et al.*, 1999; Breiter, 2012) and the Proterozoic Wiborg Batholith in Finland (Haapala, 1995).

Relative to the aforementioned granites, zircons from the Cornubian Batholith are relatively poor in trace elements (Fig. 6). Figure 6a combines contents of Hf and Y: increasing Hf mirrors the increasing degree of magma fractionation while Y represents the share of the xenotime component (e.g. content of Y and HREE in melt). The Cornubian zircons are also relatively poor in both Hf and Y: Zircons from the Beauvoir pluton are more enriched in Hf, and zircons from the A-type granites much more enriched in Y (Breiter *et al.*, 2006, 2014; Breiter and Škoda, 2012).

Figures 6b, c, d show a general increase in Sc, U and Th with increasing differentiation (as shown by the decrease in the Zr/Hf ratio). The composition of the Cornubian zircons is comparable with the zircons from the S-type granites in the Western Erzgebirge. Zircons from the Beauvoir Granite, France are Sc- and Th-poor, while zircons from both A-type granite series are typically Sc-, Th- and Y-rich with common mixed compositions among zircon, thorite, xenotime and pretulite (Förster, 2006; Breiter and Škoda, 2012; Breiter *et al.*, 2014).

The elements F and P play an important role in the transport of ore elements by lowering melt viscosity and forming metal complexes (Linnen, 1998; Keppler, 1993). Figure 6e demonstrates the differences between zircons from strongly peraluminous granites (enriched simultaneously in F and P) and zircon from the A-type granites (enriched only in F). In this case, Cornubian zircons are generally poor in both F and P, which again demonstrates a relatively lower degree of differentiation in the Cornubian Batholith in comparison with granites from the Erzgebirge and Massif Central.

The Fig. 6f was proposed by Breiter *et al.* (2014) for classification of zircons from fractionated, typically ore-bearing granites. Here, the Cornubian zircons are again similar to the peraluminous granites from the Western Erzgebirge, although having somewhat lower grade of differentiation in terms of U/Th and Zr/Hf ratios.

With respect to W, Nb, Ta and Bi, their contents in Cornubian zircon are very low (W, Nb and Ta are

usually less than the detection limit of EPMA). Enrichment of these elements in order 0.X wt.%, commonly found in many rare-metal granites (Breiter *et al.* 2006, 2014) are not found in SW England.

## Conclusions

Zircons from the Cornubian granites are relatively poor in minor and trace elements.

The lower Zr/Hf ratio in zircons from the topaz granites, in comparison with those from biotite granites, implies a greater degree of fractionation if the granites shared a similar protolith. The pronounced fractionation of a primary crustal magma seems to be the most probable model of origin of the topaz granites from the St Austell and Tregonning-Godolphin plutons. Nevertheless, some of the less-evolved members of the topaz granite suites probably remained hidden under surface exposure.

Cornubian zircons exhibit a relatively lower grade of fractionation in terms of Zr/Hf and U/Th ratio in comparison with other European rare-metal granites.

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## References

- Bea, F., Pereira, M.D. and Stroh, A. (1994) Mineral/leucosome trace-element partitioning in a peraluminous migmatite (a laser ablation-ICP-MS study). *Chemical Geology*, **117**, 291–312.
- Belousova, E.A., Griffin, W.L., ÓReilly, S.Y. and Fisher, N.I. (2002) Igneous zircon: trace element composition as an indicator of source rock type. *Contributions to Mineralogy and Petrology*, **143**, 602–622.
- Bernhard, F., Walter, F., Ettinger, K., Taucher, J. and Mereiter, K. (1998) Pretulite, ScPO<sub>4</sub>, a new scandium mineral from the Styrian and Lower Austrian lazulite occurrences, Austria. *American Mineralogist*, **83**, 625–630.
- Bonin, B. (2007) A-type granites and related rocks: Evolution of a concept, problems and prospects. *Lithos*, **97**, 1–29.
- Breiter, K. (2012) Nearly contemporaneous evolution of the A- and S-type fractionated granites in the Krušné

- hory/Erzgebirge Mts., Central Europe. *Lithos*, **151**, 105–121.
- Breiter, K. and Škoda, R. (2012) Vertical zonality of fractionated granite plutons reflected in zircon chemistry: the Cínovec A-type versus the Beauvoir S-type suite. *Geologica Carpathica*, **63**, 383–398.
- Breiter, K., Förster, H.-J. and Škoda, R. (2006) Extreme P-, Bi-, Nb-, Sc-, U- and F-rich zircon from fractionated perphosphorus granites: The peraluminous Podlesí granite system, Czech Republic. *Lithos*, **88**, 15–34.
- Breiter, K., Lamarao, C.N., Borges, R.M.K. and Dal'Ágnol, R. (2014) Chemical characteristic of zircon from A-type granites and comparison to zircon of S-type granites. *Lithos*, **192–195**, 208–225.
- Černý, P., Blevin, P.L., Cuney, M. and London, D. (2005) Granite-related ore deposits. *Economic Geology 100th Anniversary volume*, 337–370.
- Chappel, B.W. and Hine, R. (2006) The Cornubian Batholith: an example of magmatic fractionation on a crustal scale. *Resource Geology*, **56**, 203–244.
- Chappel, B.W. and White, A.J.R. (1974) Two contrasting granite types. *Pacific Geology*, **8**, 173–174.
- Charoy, B. (1986) The genesis of the Cornubian Batholith (South-West England): the example of the Carrmenellis Pluton. *Journal of Petrology*, **27**, 571–604.
- Chen, Y., Clark, A.H., Farrar, E., Wasteneys, H.A.H.P., Hodgson, M.J. and Bromley, A.V. (1993) Diachronous and independent histories of plutonism and mineralization in the Cornubian batholith, southwest England. *Journal of the Geological Society, London*, **150**, 1183–1191.
- Chesley, J.T., Halliday, A.N., Snee, L.W., Mezger, K., Shepherd, T.J. and Scrivener, R.C. (1993) Thermochronology of the Cornubian batholith in southwest England: implication for pluton emplacement and protracted hydrothermal mineralization. *Geochimica and Cosmochimica Acta*, **57**, 1817–1835.
- Clark, A.H., Chen, Y., Farrar, E., Northcote, B., Wasteneys, H.A.H.P., Hodgson, M.J. and Bromley, A.V. (1994) Refinement of the time/space relationship of intrusion and hydrothermal activity in the Cornubian Batholith (abstract). *Proceedings of the Ussher Society*, **8**, 345.
- Crowley, J.L., Brown, R.L., Gervais, F. and Gibson, H.D. (2008) Assessing inheritance of zircon and monazite in granitic rocks from the Monashee complex, Canadian Cordillera. *Journal of Petrology*, **49**, 1915–1929.
- Davis, D.W., Williams, I.S. and Krogh, T.E. (2003) Historical development of zircon geochronology. Pp. 145–181 in: *Zircon* (J.M. Hanchar and P.W.O. Hoskin, editors). Reviews in Mineralogy & Geochemistry, **53**. Mineralogical Society of America and the Geochemical Society, Washington, DC.
- Dangerfield, J. and Hawkes, J.R. (1981). The Variscan granites of south-west England: additional information. *Proceedings of the Ussher Society*, **5**, 116–120.
- Darbyshire, D.P.F. and Shepherd, T.J. (1985) Chronology of granite magmatism and associated mineralization, SW England. *Journal of the Geological Society of London*, **142**, 1159–1177.
- Darbyshire, D.P.F. and Shepherd, T.J. (1987) Chronology of magmatism in south-west England. *Proceedings of the Ussher Society*, **6**, 431–438.
- Dupuis, N.E., Braid, J.A., Murphy, J.B., Shail, R.K., Nance, R.D. and Archibald D.A. (2015) <sup>40</sup>Ar/<sup>39</sup>Ar phlogopite geochronology of lamprophyre dykes in Cornwall, UK: new age constraints on Early Permian post-collisional magmatism in the Rhenohercynian Zone, SW England. *Journal of the Geological Society*, **172**, 566–575.
- Eby, G.N. (1990) The A-type granitoids: A review of their occurrence and chemical characteristics and speculations on their petrogenesis. *Lithos*, **26**, 115–134.
- Edmonds, E.A., Wright, J.E., Beer, K.E., Hawkes, J.R., Williams, M., Freshney, E.C. and Fenning, P.J. (1968) *Geology of the Country Around Okehampton*. Memoirs of the Geological Survey of Great Britain, Sheet 324 (England and Wales).
- Exley, C.S. and Stone, M. (1964) The granitic rocks of South-West England. Pp. 131–184 in: *Present View of Some Aspects of the Geology of Cornwall* (K.F.G. Hosking and G.J. Shrimpton, editors). Blackford, Truro, UK.
- Exley, C.S. and Stone, M. (1982) Hercynian intrusive rocks. Pp. 287–320 in: *Igneous rocks of the British Isles* (D.S. Sutherland, editor). Wiley, Chichester, UK.
- Förster, H.J. (2006) Composition and origin of intermediate solid solutions in the system thorite-xenotime-zircon-coffinite. *Lithos*, **88**, 35–55.
- Förster, H.J., Tischendorf, G., Trumbull, R.B. and Gottesmann, B. (1999) Late-collisional granites in the Variscan Erzgebirge, Germany. *Journal of Petrology*, **40**, 1613–1645.
- Gagnevin, D., Daly, J.S. and Kronz, A. (2010) Zircon texture and chemical composition as a guide to magmatic processes and mixing in a granitic environment and coeval volcanic system. *Contribution to Mineralogy and Petrology*, **159**, 579–596.
- Geisler, T., Pidgeon, R.T., Kurtz, R., van Bronswijk, W. and Schleicher, H. (2003) Experimental hydrothermal alteration of partially metamict zircon. *American Mineralogist*, **88**, 1496–1513.
- Grimes, C.B., John, B.E., Kelemen, P.B., Mazdab, F.K., Wooden, J.L., Cheadle, M.J., Hanghoj, K. and Schwart J.J. (2007) Trace element chemistry of zircon from oceanic crust: a method for distinguishing detrital zircon provenance. *Geology*, **35**, 643–646.
- Haapala, I. (1995) Metallogeny of the Rapakivi granites. *Mineralogy and Petrology*, **54**, 149–160.
- Hanchar, J.M. and Watson, E.B. (2003) Zircon Saturation Thermometry. Pp. 89–112 in: *Zircon* (J.M. Hanchar and P.W.O. Hoskin, editors). Reviews in Mineralogy &

- Geochemistry, **53**. Mineralogical Society of America and the Geochemical Society, Washington, DC.
- Hawkes, J.R. and Dangerfield, J. (1978) The Variscan granites of south-west England: a progress report. *Proceedings of the Ussher Society*, **4**, 158–171.
- Henderson, C.M.B., Martin, J.S. and Mason, R.A. (1989) Compositional relations in Li-micas from SW England and France: an ion- and electron- microprobe study. *Mineralogical Magazine*, **53**, 427–449.
- Hill, P.I. and Manning, D.A.C. (1987) Multiple intrusions and pervasive hydrothermal alteration in the St Austell Granite, Cornwall. *Proceedings of the Ussher Society*, **6**, 447–453.
- Hoskin, P.W.O. and Ireland, T.R. (2000) Rare earth element chemistry of zircon and its use as a provenance indicator. *Geology*, **28**, 627–630.
- Hoskin, P.W.O. and Schaltegger, U. (2003) The composition of zircon and igneous and metamorphic petrogenesis. Pp. 27–62 in: *Zircon* (J.M. Hancher and P.W. O. Hoskin, editors). Reviews in Mineralogy & Geochemistry, **53**. Mineralogical Society of America and the Geochemical Society, Washington, DC.
- Jackson, N.J., Willis-Richards, J., Manning, D.A.C. and Sams, M.S. (1989) Evolution of the Cornubian ore field, southwest England: Part 2. Mineral deposits and ore-forming process. *Economic Geology*, **84**, 1101–1133.
- Jefferies, N.L. (1984) The radioactive accessory mineral assemblage of the Carnmenellis granite, Cornwall. *Proceedings of the Ussher Society*, **6**, 35–41.
- Jefferies, N.L. (1985) The distribution of the rare earth elements within the Carnmenellis pluton, Cornwall. *Mineralogical Magazine*, **49**, 495–504.
- Kepler, H. (1993) Influence of fluorine on the enrichment of high field strength elements in granitic rocks. *Contributions to Mineralogy and Petrology*, **114**, 479–488.
- Knox, D.A. and Jackson, N.J. (1990) Composite granite intrusions of SW Dartmoor, Devon. *Proceedings of the Ussher Society*, **7**, 246–251.
- Leat, P.T., Thompson, R.N., Morrison, M.A., Hendry, G. L. and Trayhorn, S.C. (1987) Geodynamic significance of post-Variscan intrusive and extrusive potassic magmatism in SW England. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, **77**, 349–360.
- Linnen, R.L. (1998) The solubility of Nb-Ta-Zr-Hf-W in granitic melts with Li and Li + F: Constraints for mineralisation in rare metal granites and pegmatites. *Economic Geology*, **93**, 1013–1025.
- Linnen, R.L. and Kepler, H. (2002) Melt composition control of Zr/Hf fractionation in magmatic processes. *Geochimica et Cosmochimica Acta*, **66**, 3293–3301
- London, D. and Manning, D.A.C. (1995) Chemical variation and significance of tourmaline from south-west England. *Economic Geology*, **90**, 495–519.
- Manning, D.A.C. (1983) Disseminated tin sulphides in the St. Austell granite. *Proceedings of the Ussher Society*, **5**, 411–416.
- Manning, D.A.C. and Exley, C.S. (1984) The origins of late-stage rocks in the St. Austell granite – a reinterpretation. *Journal of the Geological Society*, **141**, 581–591.
- Manning, D.A.C. and Hill, P.I. (1990) The petrogenetic and metallogenetic significance of topaz granite from the southwest England orefield. Pp. 51–69 in: *Ore-bearing Granite Systems; Petrogenesis and Mineralizing Processes* (H.J. Stein and J.L. Hannah, editors). Geological Society of America Special paper, **246**. GSA, Boulder, Colorado, USA.
- Manning, D.A.C., Hill, P.I. and Howe, J.H. (1996) Primary lithological variation in the kaolinized St Austell Granite, Cornwall, England. *Journal of the Geological Society of London*, **153**, 827–838.
- McDonough, W.F. and Sun, S. (1995) The composition of the Earth. *Chemical Geology*, **120**, 223–253.
- Müller, A., Seltmann, R., Halls, C., Siebel, W., Dulski, P., Jeffries, T., Spratt, J. and Kronz, A. (2006) The magmatic evolution of the Land's End pluton, Cornwall, and associated pre-enrichment of metals. *Ore Geology Reviews*, **28**, 329–367.
- Nardi, L.V.S., Formoso, M.L.L., Müller, I.F., Fontana, E., Jarvis, K. and Lamarão, C. (2013) Zircon/rock partition coefficients of REEs, Y, Th, U, Nb, and Ta in granitic rocks: Uses for provenance and mineral exploration purposes. *Chemical Geology*, **335**, 1–7.
- Nasdala, L., Kronz, A., Wirth, R., Váczi, T., Pérez-Soba, C., Willner, A. and Kennedy, A.K. (2009) The phenomenon of deficient electron microprobe totals in radiation-damaged and altered zircon. *Geochimica Cosmochimica Acta*, **73**, 1637–1650.
- Raimbault, L., Cuney, M., Azencott, C., Duthou, J.L. and Joron, J.L. (1995) Geochemical evidence for a multistage magmatic genesis of Ta-Sn-Li mineralization in the granite at Beauvoir, French Massif Central. *Economic Geology*, **90**, 548–596.
- Sano, Y., Terada, K. and Fukuoka, T. (2002) High mass resolution ion microprobe analysis of rare earth elements in silicate glass, apatite and zircon: lack of matrix dependency. *Chemical Geology*, **184**, 217–230.
- Scott, P.W., Pascoe, R.D. and Hart, F.W. (1998) Columbite-tantalite, rutile and other accessory minerals from the St Austell topaz granite, Cornwall. *Geoscience in south-west England*, **9**, 165–170.
- Shail, R.K. and Leveridge, B.E. (2009) The Rhenohercynian passive margin of SW England: Development, inversion and extensional reactivation. *Comptes Rendus Geoscience*, **341**, 140–155.
- Shi, J. (1989) A new mineral – ximengite. *Chinese Journal of Geochemistry*, **8**, 385–391.



- Speer, J.A. (1982) Zircon. Pp. 67–112 in: *Orthosilicates* (R.G. Burns, editor). Reviews in Mineralogy, **5**. Mineralogical Society of America, Washington, DC.
- Stimac, J.A., Clark, A.H., Chen, Y. and Garcia, S. (1995) Enclaves and their bearing on the origin of the Cornubian batholith, southwest England. *Mineralogical Magazine*, **59**, 273–296.
- Stone, M. (1975) Structure and petrology of the Tregonning-Godolphin granite, Cornwall. *Proceedings of the Geologists' Association*, **86**, 155–170.
- Stone, M. (1992) The Tregonning granite: petrogenesis of Li-mica granites in the Cornubian batholith. *Mineralogical Magazine*, **56**, 141–155.
- Stone, M. (1997) A geochemical dichotomy in the Cornubian batholith. *Proceedings of the Ussher Society*, **9**, 206–210.
- Stone, M. (2000) Petrogenetic implications from biotite compositional variations in the Cornubian granite batholith. *Mineralogical Magazine*, **64**, 729–735.
- Stone, M. and Exley, C.S. (1985) High heat production granites of southwest England and their associated mineralization: a review. Pp. 571–593 in: *High Heat Production (HHP) Granites, Hydrothermal Circulation and Ore Genesis*. The Institution of Mining and Metallurgy, London.
- Stone, M. and George, M.C. (1985) Some phosphate minerals at the Megaliggar Rocks, Cornwall. *Proceedings of the Ussher Society*, **5**, 428–431.
- Stone, M., Exley, C.S. and George, M.C. (1988) Compositions of trioctahedral micas in the Cornubian batholith. *Mineralogical Magazine*, **52**, 175–192.
- Taylor, G.K. (2007) Pluton shapes in the Cornubian Batholith: new perspectives from gravity modelling. *Journal of the Geological Society, London*, **164**, 525–528.
- Taylor, R.P. and Fallick, A.E. (1997) The evolution of fluorine-rich felsic magma: source dichotomy, magmatic convergence and the origins of topaz granite. *Terra Nova*, **9**, 105–108.
- Thomas, J.B., Bodnar, R.J., Shimizu, N. and Sinha, A.K. (2002) Determination of zircon/melt trace element partition coefficient from SIMS analysis of melt inclusions in zircon. *Geochimica Cosmochimica Acta*, **66**, 2887–2901.
- Ward, C.D., McArthur, J.M. and Walsh, J.N. 1992. Rare earth element behaviour during evolution and alteration of the Dartmoor Granite, SW England. *Journal of Petrology*, **33**, 785–815
- Wark, D.A. and Miller, C.F. (1993) Accessory minerals behavior during differentiation of a granite suite: monazite, xenotime and zircon in the Sweetwater Wash pluton, southeastern California, U.S.A. *Chemical Geology*, **110**, 49–67.
- Watson, B.E. and Harrison, T.M. (1983) Zircon saturation revisited: temperature and composition effects in a variety of crustal magma types. *Earth and Planetary Science Letters*, **64**, 295–304.
- Willis-Richards, J. and Jackson, N.J. (1989) Evolution of the Cornubian ore field, southwest England: Part 1. Batholith modelling and ore distribution. *Economic Geology*, **84**, 1078–1100.