

Chemical and textural interpretation of late-stage coffinite and brannerite from the Olympic Dam IOCG-Ag-U deposit

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ABSTRACT

The Olympic Dam iron-oxide copper-gold-silver-uranium deposit, South Australia, contains three dominant U minerals: uraninite; coffinite; and brannerite. Microanalytical and petrographic observations provide evidence for an interpretation in which brannerite and coffinite essentially represent the products of U mineralizing events after initial deposit formation at 1.6 Ga. Marked compositional and textural differences between the various types of brannerite and coffinite highlight the role of multiple stages of U dissolution and reprecipitation.

On the basis of petrography (size, habit, textures and mineral associations) and compositional variation, brannerites are divided into four distinct groups (brannerite-A, -B, -C and -D), and coffinite into three groups (coffinite-A, -B and -C). Brannerite-A ranges in composition from what is effectively uraniferous rutile to stoichiometric brannerite, and has elevated (Mg + Mn + Na + K) and (Fe + Al) compared to other brannerite types. It displays the most diverse range of morphologies, including complex irregular-shaped aggregates, replacement bands, and discrete elongate seams. The internal structure of brannerite-A consists of randomly-oriented hair-like needles and blades. Brannerite-B (<5 µm in size) is generally prismatic and typically associated with baryte and REY minerals ($REE + Y = REY$). Brannerite-C and -D are both associated with Cu-(Fe)-sulfides and are typically composed of irregular masses and blebs (10–50 µm in size) with a more uniform or massive internal structure. Brannerite-D is distinct from -C and always contains inclusions of galena. Brannerite-B to -D all contain elevated ΣREY , with brannerite-B and -C having elevated As, and brannerite-D having elevated Nb.

All coffinite is typically globular (each globule is 2–10 µm in size) to collomorphic in appearance. Coffinite-A ranges from discrete globules to collomorphic bands completely encompassing quartz. Coffinite-B is always found with uraninite, and includes collomorphic coffinite enveloped by massive uraninite, as well as aureoles of coffinite on the margins of uraninite crystals. Coffinite-C is associated with brannerite and REY minerals. The majority of coffinite is heterogeneous.

Brannerite and coffinite have probably precipitated as part of a late-stage hydrothermal U-event, which might have involved the dissolution and/or reprecipitation of earlier precipitated uraninite, or could represent the products of a later U mineralizing event. Evidence which supports formation of late-stage coffinite and brannerite includes: (1) low-Pb contents of both minerals; (2) coffinite is commonly found on the edges of uraninite, implying later deposition; and (3) coffinite is often found on the edge of brannerite aggregates, suggestive of brannerite precipitation occurred before coffinite. Moreover, there are many features (e.g. banding, scalloped edges, alteration rinds, variable compositions etc.) indicative of hydrothermal alteration processes.

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Introduction

THE most important U^{4+} minerals found in nature, based on abundance and economic value, are uraninite [UO_2], coffinite [$USiO_4$] and brannerite [UTi_2O_6] (Finch and Murakami, 1999). Although most U^{4+} minerals occur as accessory minerals in granitic, pegmatitic or aluminous metamorphic rocks, coffinite and brannerite appear largely restricted to systems where uranium has been mobilized and subsequently reprecipitated as these minerals.

Transport of U can occur in both reducing and oxidizing environments (Finch and Murakami, 1999). Under reducing conditions, U can be transported typically only fractions of a centimetre, however if either F^- or Cl^- ligands are available, these can stabilize the U^{4+} in solution, and the transport distance may be much further (Keppler and Wyllie, 1990). In contrast, under oxidizing conditions, the uranyl ion (UO_2^{2+}) and related complexes can permit U migration up to many kilometres from source until the solution chemistry changes sufficiently to allow for precipitation of U minerals (Finch and Murakami, 1999). When the uranyl ion encounters more reducing conditions such as organic matter or sulfides, U is subsequently reduced and may result in precipitation of other U minerals. Coffinite, for example, is usually only found in deposits formed by low-temperature processes, and is typically an alteration product of an earlier uraninite which has been altered under reducing conditions (Janeczek and Ewing, 1992; Plant *et al.*, 1999). Alternatively, coffinite may be multi-generational, in which a primary coffinite has been sequentially exposed to both reducing and oxidizing conditions, producing compositionally distinct coffinites (e.g. coffinites associated with organic matter from the Grants uranium region, New Mexico; Deditius *et al.*, 2008). Thus, in some cases U minerals may already have precipitated within a deposit from an earlier mineralizing event, and if exposed to later fluids, the U may be remobilized and then reprecipitated as the same or different U mineral(s).

A 'recycling' of uranium minerals is considered applicable to the Olympic Dam deposit, South Australia, the World's largest uranium resource. There are three dominant U minerals at Olympic Dam: uraninite, coffinite and brannerite; and petrographic study provides extensive evidence of multiple stages of U dissolution and reprecipitation (e.g. Reeve *et al.*, 1990; Ehrig *et al.*, 2012; Kirchenbaur *et al.*, 2016; Macmillan *et al.*, 2016).

There have been at least two uraninite mineralizing events at Olympic Dam, an early one at ~ 1590 Ma, and a superimposed, younger event. Both events generated texturally and chemically distinct uraninites (Macmillan *et al.*, 2016). The presence of brannerite and coffinite at Olympic Dam has long been acknowledged, but no mineralogical study has been published before now. The key objectives here are therefore to determine the chemical and textural variability of brannerite and coffinite at Olympic Dam, and to suggest possible mechanisms of formation and alteration of these minerals.

Background and geological context

Both brannerite and coffinite are texturally diverse and display wide compositional ranges, as a result of formation in wide-ranging geological settings. The key crystal chemical features of both minerals are discussed below, followed by a brief introduction to uranium mineralogy at Olympic Dam.

Brannerite

The ideal chemical formula of brannerite is UTi_2O_6 . The mineral crystallizes in the monoclinic system, with space group $C2/m$ (Szymanski and Scott, 1982) and is isostructural with thorutite, $ThTi_2O_6$ (Ruh and Wadsley, 1966). Stoichiometric brannerite theoretically contains 62.8 wt.% UO_2 and 37.2 wt.% TiO_2 (Fron del, 1958). In common with many uranium minerals, brannerite is commonly non-stoichiometric, and has been shown to have a complex and variable composition (e.g. Fron del, 1958; Ferris and Ruud, 1971; Szymanski and Scott, 1982; Saager and Stupp, 1983; Smith, 1984; Lumpkin *et al.*, 2012). The general formula is best described to be AB_2O_6 , where A is U and commonly also Pb, Ca, Fe, Th, REE + Y (hereafter, ΣREY), and B typically contains Ti, which can be replaced by Si, Al, or Fe. Brannerite has also been reported to contain Ba, Sr, Ni, Bi, Sn, Ta, Nb, Sc, P, He and Zr (Saager and Stupp, 1983 and references therein). The A site is octahedral (six-coordinated), and the B site is also octahedral, but the octahedra share corners and/or edges to form a structural framework (Szymanski and Scott, 1982). One attempt at a more accurate formula is given by Szymanski and Scott (1982): $(U, Pb, Ca)_{0.6x}Ti_x(Si, Fe, Al, V)_{3.36-1.65x}O_6$, where $1.2 < x < 1.8$. Brannerite is also typically oxidized, and typically contains both U^{4+} and U^{6+} (Finch and Murakami, 1999). The related mineral orthobrannerite is

hydrated and has the formula $(U^{4+}, U^{6+})(Ti, Fe)_2O_6(OH)$ (Singh *et al.*, 1990; Gaines *et al.*, 1997).

All natural brannerite is metamict (Smith, 1984), and due to radioactive decay via α -particle emission, is typically amorphous (Lumpkin *et al.*, 2014). The metamict nature of brannerite may explain why it is able to incorporate large amounts of impurities into its structure, including Pb from the radioactive decay of U. Brannerite is found in a number of different geological environments, including placer deposits, veins, metasomatic-hydrothermal veins and replacements, pegmatites, and in disseminated copper and molybdenum deposits (Ferris and Ruud, 1971). The first detailed description and photomicrographs of brannerite were provided by Ramdohr (1957), who describes the typically delicate and complex internal network of blades and intergrowths of brannerite aggregates.

Coffinite

Coffinite, nominally $USiO_4$, space group $I4_1/amd$ and $Z=4$, is a tetragonal orthosilicate with U^{4+} coordinated by eight O atoms in the form of a distorted cube-like polyhedron (Fuchs and Gebert, 1958). Ideal anhydrous coffinite contains 81.80 wt.% UO_2 and 18.20 wt.% SiO_2 , whereas ideal hydrated coffinite contains 73.75 wt.% UO_2 , 16.41 wt.% SiO_2 and 9.84 wt.% H_2O (Janeczek and Ewing, 1992, 1996). There are a large number of possible element substitutions: U^{6+} , Zr^{4+} , Th^{4+} , Hf^{4+} , Ca^{2+} , Fe^{2+} and REY^{3+} in the A site (U^{4+}); and P^{5+} , As^{5+} , V^{5+} , W^{6+} and S^{6+} in the B site (Si^{4+}) (Stieff *et al.*, 1956; Pointer *et al.*, 1988; Hansley and Fitzpatrick, 1989; Janeczek and Ewing, 1992; Förster, 2006). Furthermore, there can also be potential vacancies in the tetrahedral site. An extensive range of limited or complete solid solutions between coffinite and isostructural minerals are thus possible. These include, but are not restricted to, the relatively common solid solutions between coffinite [$USiO_4$], zircon [$ZrSiO_4$], thorite [$ThSiO_4$] and xenotime [$(Y, REE)PO_4$] (e.g. Speer, 1980; Pointer *et al.*, 1988; Finch and Hanchar, 2003; Förster, 2006). Hansley and Fitzpatrick (1989) and Janeczek and Ewing (1996) show coffinite-xenotime solid solution is complete and widespread in natural samples. With respect to some of the extended range of elements reported in coffinite, some may clearly be contained as fine-grained intergrowths or inclusions within coffinite rather than incorporated within the lattice. The typically fine-grained ($<10\ \mu m$) and intergrown

character of coffinite can make accurate and unambiguous microanalysis difficult (Hansley and Fitzpatrick, 1989; Finch and Murakami, 1999).

Coffinite occurs in a variety of different uranium deposit types, including granitic systems and those where uranium has been remobilized via hydrothermal or meteoric waters. It is commonly associated with sandstone uranium and/or low-temperature U deposits (Stieff *et al.*, 1956; Dahlkamp, 1978; Ludwig and Grauch, 1980). Coffinite can also be formed in reducing conditions via alteration of uraninite in Si-rich systems (Janeczek and Ewing, 1992), from hydrothermal and supergene processes in granitic environments (Leroy and Turpin, 1988; Förster, 2006), and may be associated with reductants such as organic matter which act initially as reducing agents and subsequently preserve the coffinite even in the presence of oxidizing fluids (Deditius *et al.*, 2008). Smits (1989) described coffinite as a component of the Witwatersrand gold deposits, South Africa, where it occurs in paleoplacer conglomerates and replaces detrital uraninite grains through uptake of silica.

Geological context

The Olympic Dam iron-oxide copper-gold (IOCG)-silver-uranium deposit is located 520 km NNW of Adelaide, South Australia. The geological setting and mineralogy of the Olympic Dam deposit have been described in detail elsewhere (e.g. Reeve *et al.*, 1990; Ehrig *et al.*, 2012), so only specific features pertaining to the U minerals are discussed here. IOCG deposits typically contain significant amounts of U, including Olympic Dam (Reeve *et al.*, 1990) and Ernest Henry, east of Mt. Isa, Queensland (Ryan, 1998), but little mineralogical data has been published about the textural and compositional variation of the U minerals within these deposits. Initial U mineral work at Olympic Dam focused predominantly in the higher-grade, central parts of the deposit where massive uraninite textures are typical (Trueman *et al.*, 1986; Oreskes and Einaudi, 1990; Johnson, 1993). More recently, due to the improved geological knowledge from the extensive drillhole and mineralogical database, a greater awareness of the U mineral variability and mineral association has been ascertained. Ehrig *et al.* (2012) describe how the proportion of uraninite relative to coffinite and brannerite increases with total Fe content throughout the deposit. The average relative proportions of

brannerite, coffinite and uraninite across the entire deposit are 31, 56 and 13 wt.%, respectively; however local mineralogical variation throughout the deposit controls which U mineral is most abundant. Typically, uraninite is associated more strongly with hematite and sulfides, but coffinite and brannerite tend to be associated more closely with gangue (quartz, sericite, chlorite, or hematite).

Macmillan *et al.* (2016) outline uraninite mineralogy at Olympic Dam, and identify at least two main uraninite mineralizing events with evidence of multiple stages of U dissolution and reprecipitation. There are crystalline and sparsely preserved early uraninites, and late uraninites which tend to be stringer-like, massive, or aphanitic. Textural and compositional differences between these uraninites, as well as differences in the Pb/U ratios (based on electron microprobe analyses), distinguish the two types. Both show evidence of hydrothermal alteration, but there may also have been additional influxes of U-bearing fluids which allowed precipitation of brannerite and coffinite. It has been proposed (e.g. Oreskes and Einaudi, 1992; Ehrig *et al.*, 2012; Kirchenbaur *et al.*, 2016) that the uranium minerals have a complex history with repeated cycles of precipitation, dissolution and reprecipitation. Kirchenbaur *et al.* (2016) suggest that the uranium is probably sourced from upper crustal lithologies; the $\delta^{238}\text{U}$ values are consistent with those of hydrothermal deposits with U sourced from high-temperature granitoid/volcanic/volcanogenic rocks. These authors did not observe any high- $\delta^{238}\text{U}$ signatures, and thus concluded that low-temperature reworking of earlier precipitated U minerals did not play a significant role in the formation of the U mineralization at Olympic Dam. It is, however, possible that post- or re-depositional processes destroyed any evidence of high- $\delta^{238}\text{U}$ values, or that the depositional mechanisms involved minimal isotopic fractionation of U. Moreover, these authors identified a lack of fission fragment contributions, and this was explained by more recent U deposition (i.e. post the initial ~1.6 Ga age of mineralization), or episodic development of the U ores with repeated fractionation of U. Thus, the results presented by Kirchenbaur *et al.* (2016) support the notion of a gradual addition of U in several stages over >1000 Ma which occurred at elevated temperatures during mineralization, and highlights the prolonged and complex processes involved in U mineral formation at Olympic Dam. The objectives of this study are to document the compositions and textural variability of both coffinite and brannerite, and to

interpret the results to refine further our understanding of the protracted U mineralization processes involved in formation of the Olympic Dam deposit.

Analytical methods

A total of 23 representative samples were analysed, and polished thin-sections examined by scanning electron microscopy (SEM), using a Quanta 450 field emission gun (FEG) SEM with silicon-drift detector (Adelaide Microscopy, University of Adelaide). Qualitative variation in chemistry of the U minerals was determined using SEM-energy dispersive spectroscopy (EDS).

Assays were measured to determine the bulk concentration of various elements in each sample (Macmillan *et al.*, 2016); U_3O_8 values (Table 1) are of significance here. Samples selected for this study contained a range of U_3O_8 grades, as it was thought this provided the best chance of obtaining variation in the relative abundances of U minerals. Subsequent characterization of modal mineralogy using a Mineral Liberation Analyser (MLA) system (ALS Mineralogy, Brisbane; Appendix and Table A1) was conducted (Macmillan *et al.*, 2016). Bulk modal mineralogy was measured using the X-ray modal (MLA XMOD) technique. Sparse phase liberation mapping (MLA SPL Lite) was used to specifically target U minerals and provide information on the relative abundances of uraninite, coffinite and brannerite (Table 1), as well as details of all minerals found in contact with U mineral grains (Table A2).

Quantitative compositional data for both brannerite and coffinite were obtained using a Cameca SX-Five electron probe micro-analyser (EPMA) equipped with five tuneable wavelength-dispersive spectrometers (Adelaide Microscopy, University of Adelaide). Operating conditions were 15 keV accelerating voltage, 100 nA beam current, 40° takeoff angle, with 0.5–1 μm -sized beam. A total of 28 elements were measured: U, Pb, Th, Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, Fe, Cu, As, Zr, Nb, Y, Ce, La, Pr, Nd, Sm, Gd, Sr, Ba and Te. *Probe for EPMA* software (Donovan, 2014) was used for data processing. Standards, X-ray lines, count times, mean precision and typical minimum detection limits (mdl) are reported in the Appendix.

Petrography

Samples were selected to ensure coverage of the broadest possible range of U mineral associations

TABLE 1 Sample details (ID, depth, U₃O₈ grade) with summary of coffinite and brannerite textures and relative proportions of U minerals in each sample.

Sample ID	Sample no.	Hole ID	Depth (m)	U ₃ O ₈ Grade (ppm)	U mineral Relative abundance (wt.%) [*]			Breccia type [†]	Brannerite group	Coffinite group	Coffinite/brannerite texture description
					Uraninite	Coffinite	Brannerite				
S1 [‡]	RX7253	RD1303	471.9	21,326	6	91	3	GRNH	–	A1 & B	Coffinite (collomorphic) rimming quartz, typically enveloped by massive uraninite; coffinite has variable P/Y, Si, Ca (speckled); laths of bornite sometimes protrude into coffinite globules
S2 [‡]	RX7254	RD1304	890.1	781	36	23	41	HEMH	C	A1	Brannerite associated with chalcopyrite and hematite; coffinite globules typically discrete
S3 [§]	RX7255	RD1305	691.0	364	2	16	82	GRNL	A	A1	Needle-like brannerite typically as an overgrowth on rutile grains and intergrown with fluorite/sericite/chlorite; disseminated globules of coffinite associated with siderite/hematite/quartz, in some cases these coffinite globules nucleate on chalcopyrite into quartz grains
S4 [§]	RX7256	RD1988	880.8	6914	96	0	4	HEMH	A & B	–	Bladed brannerite found surrounding rutile within sericite; blebs of brannerite with baryte often found near <i>REY</i> minerals (zircon/monazite)
S5	RX7257	RD1988	1618.9	597	93	7	0	HEM	–	B	Coffinitization of uraninite crystals; fine grained ‘dusting’ of U minerals (in hematite)
S6	RX7258	RD1988	1768.8	408	91	8	1	HEM	–	B	Coffinitization of uraninite crystals; fine grained ‘dusting’ of U minerals (in hematite)
S7	RX7259	RD1988	1808.9	369	83	14	3	HEM	–	A1 & C2	Coffinite globules found on edges of xenotime and as discrete globules nucleating on hematite in quartz; fine grained ‘dusting’ of U minerals (in hematite)

(continued)

TABLE 1 (*contd.*)

Sample ID	Sample no.	Hole ID	Depth (m)	U ₃ O ₈ Grade (ppm)	U mineral Relative abundance (wt.%)*			Breccia type [†]	Brannerite group	Coffinite group	Coffinite/brannerite texture description
					Uraninite	Coffinite	Brannerite				
S8 [‡]	RX7260	RD2080	479.7	1686	91	3	6	GRNL	A	A1 & C2 & C3	Coffinite globules typically rimming quartz, some contain bright banding and globules typically very mottled in appearance; Brannerite with sericite and hematite
S9 ^{‡,§}	RX7261	RD3000W1	936.3	387	1	5	94	HEMH	A & C	A1 & C1	Mixture of needle-like to bladed brannerite masses in sericite and brannerite blebs associated with bornite/chalcocite/hematite; coffinite globules found on rims of brannerite masses and as discrete globules on the edge of quartz grains
S10 ^{‡,§}	RX7262	RD3000W1	948.2	382	1	5	94	HEMH	A	C1 & C2	Needle-like to bladed brannerite masses and irregular aggregates with replacement bands; minor coffinite on edges brannerite masses; coffinite intergrown with <i>REY</i> minerals
S11	RX7264	RD3002	472.4	119	89	11	0	HEM	—	A1	Fine-grained discrete coffinite globules on edge quartz grains and ‘dusting’ of U minerals in hematite
S12	RX7265	RD3022	921.6	2244	5	13	82	HEM	A	C1	Coffinite and brannerite intimately intergrown with sericite/chlorite
S13 [‡]	RX7266	RD3022	968.2	731	4	84	12	HEM	A	A1 & A2	Coffinite globules and collomorphic textures rimming quartz; in some cases galena crystals found near coffinite; some coffinite display radiating growth pattern; brannerite disseminated and associated with quartz, hematite and siderite
S14	RX7267	RD3035	675.5	1293	89	8	3	HEMH	—	A1 & B	Coffinitization of uraninite crystals; some discrete coffinite globules on rims quartz grains in hematite

S15	RX7268	RD3035	876.8	638	8	18	74	HEM	A	A1 & C1	Coffinite rimming quartz, appears altered and is usually within sericite; disseminated coffinite globules and irregular masses of brannerite in sericite/quartz/hematite/fluorite bands
S16	RX7269	RD3035	970.5	1605	70	17	13	HEMF	A	B	Coffinitization of uraninite crystals; brannerite in sericite/quartz/hematite/fluorite bands
S17	RX7270	RD3307	1092.8	1153	59	17	24	HEM	A	B	Coffinitization of uraninite crystals; brannerite in sericite/quartz/hematite/fluorite bands
S18 [‡]	RX7271	RD3554	455.9	424	0	44	56	GRNH	A & C	A1 & A2 & C1	Disseminated coffinite globules in quartz/sericite, sometimes associated with chalcopryrite or galena; minor coffinite globules on edges brannerite masses; needle-like to bladed brannerite masses associated with hematite and sericite; some brannerite blebs in chalcopryrite
S19 [‡]	RX7272	RD3554	494.4	425	6	49	45	GRNH	A	A1 & C1	Coffinite globules in sericite/fluorite/carbonates, typically nucleating on the edge of bornite and/or quartz; coffinite and brannerite intergrowths; fine grained <i>REY</i> -phosphates commonly near coffinite
S20	RX7273	RD3554	498.2	139	1	46	53	GRNH	C	A1	Disseminated coffinite in hematite, bornite and sericite; irregular, patches of brannerite in bornite; fine grained 'dusting' of U minerals in hematite
S21 [§]	RX7274	RD3560	716.3	11,259	83	0	17	GRNL	A & D	—	Brannerite blebs in hematite containing galena, hematite, bornite/chalcocite and anatase (?); some brannerite in sericite/quartz/hematite bands
S22	RX7275	RD3560	719.6	494	24	1	75	GRNL	A & D	—	Brannerite masses in sericite/quartz/hematite/fluorite bands; some brannerite blebs inside bornite

(continued)

TABLE 1 (contd.)

Sample ID	Sample no.	Hole ID	Depth (m)	U ₃ O ₈ Grade (ppm)	U mineral Relative abundance (wt.%) [*]			Breccia type [†]	Brannerite group	Coffinite group	Coffinite/brannerite texture description
					Uraninite	Coffinite	Brannerite				
S23	RX7276	RD3560	726.7	408	56	0	44	GRNL	A & B & D	–	Brannerite masses in sericite/quartz/hematite/fluorite bands; some brannerite blebs inside bornite; brannerite blebs found along rutile lamellae in hematite (with REY minerals i.e. bastnäsite)

Where <5% relative abundance of a U mineral was identified by MLA, it was not possible to assign the U mineral to a textural group as counting statistics were too low. ^{*}Relative proportions of coffinite/brannerite/uraninite as determined from MLA sparse phase liberation mapping (SPL_Lite) data. [†]Breccia types: GRNH = Roxby Downs Granite (RDG; 90–70%) with some hematite (10–30%) breccia, matrix contains hematized sericite, quartz; GRNL = RDG (70–40%) with hematite (30–60%) breccia, granitic clasts with hematite-rich matrix; HEMH = Hematite (60–90%) with RDG (40–10%) breccia, hematite-rich matrix supported breccia with hematitic clasts; HEM = Hematite (>90%) with RDG (<10%) breccia, hematite-rich matrix and clasts with extensive hematite alteration; HEMF = Hematite with GRV clasts, typically porphyritic with chloritized phenocrysts. [‡]EPMA data for this sample used for compositional range estimates of coffinite (Tables 3 and 4). [§]EPMA data for this sample used for compositional range estimates of brannerite (Table 2).

throughout the deposit, and thus targeted a range of U₃O₈ grades and mineralogies. The samples analysed are the same as those described in Macmillan *et al.* (2016).

The heterogeneous nature of brannerite and variability in U and Ti content, has led to the interchangeable use of the terms uraniferous anatase, -rutile, -leucoxene (and variants thereof, including uraniferous titanite and -ilmenite) by some authors (e.g. Saager and Stupp, 1983). For the purposes of consistency, the terms rutile (TiO₂-rich) and uraniferous rutile (increasing U content) are used here, as without crystal structural data, it is impossible to distinguish between the TiO₂ polymorphs and other Ti-bearing phases.

Brannerite occurrence varies from complex irregularly-shaped aggregates and anastomosing bands of uraniferous rutile-brannerite with an internal structure of randomly orientated hair-like needles and blades (Fig. 1), to irregular masses and blebs of brannerite with more uniform/massive internal structure (Figs 2 and 3). Regardless of fabric, all brannerite is intimately intergrown with a mixture of rutile, hematite, Cu-(Fe)-sulfides, sericite, chlorite, fluorite, REY minerals and quartz.

Coffinite also displays a broad range of textural associations although its morphology is typically globular to collomorphic. Strictly speaking, and with the absence of nano-structural data, the term (U,Si)-phases should probably be used to represent any of the anhedral masses, which may consist of a mixture of (UO₂+x) and amorphous silica. However, for ease of comparison, the term coffinite has been used for both the more anhedral and the more prismatic forms of coffinite. In many cases, coffinite globules completely rim quartz grains (Fig. 4a–c), or are found nucleating onto sulfides (Fig. 4e,f). Coffinite is also found in association with uraninite, which may include collomorphic coffinite which rims quartz and is enveloped by massive uraninite (Fig. 5a–c); or individual early uraninite crystals which display incipient coffinitization with an aureole of coffinite/(U,Si)-phases around the uraninite (Fig. 5d). In other cases, coffinite globules occur on the edge of rutile-bornite-brannerite-sericite aggregates or are associated with REY minerals (Fig. 6a–d). Commonly, coffinite is found nucleating onto grain boundaries, particularly on the edges of quartz and/or sulfides. It is commonly associated with quartz, sericite, hematite and sulfides, as well as brannerite and uraninite.

Brannerite is here categorized into four distinct groups, and coffinite into three groups on the basis

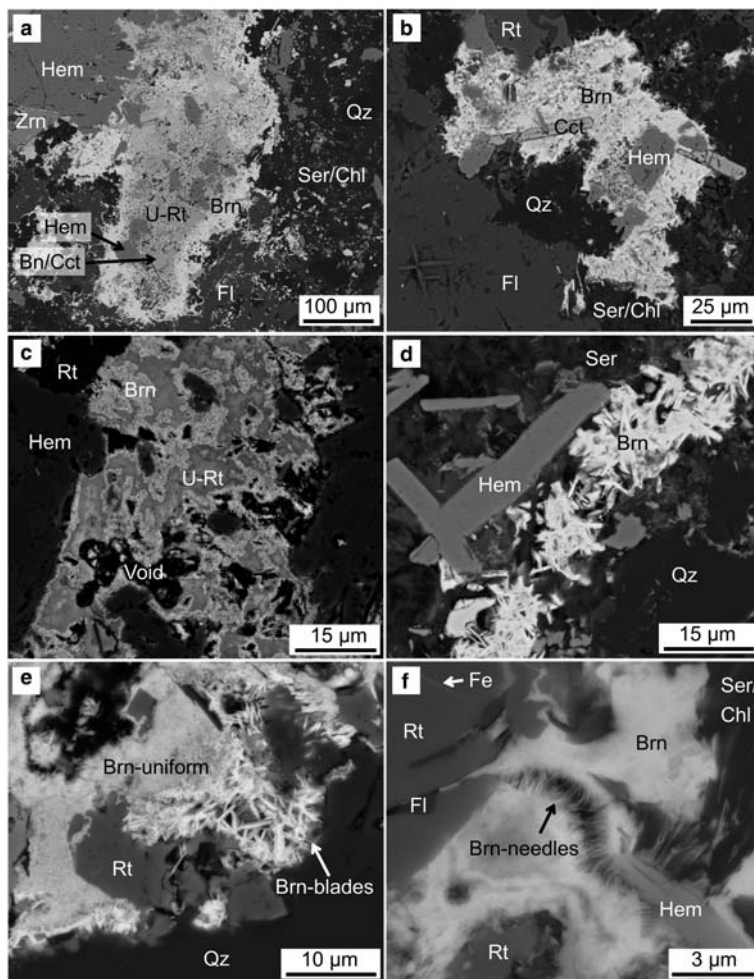


FIG. 1. Back-scatter electron (BSE) images of brannerite-A; (a) irregular aggregate of brannerite (Brn, S9.91) consisting of fine dispersions of uraniferous rutile (U-Rt; central) grading to brannerite on the rim. There is an enrichment of uranium (bright) on the periphery of the aggregate. Fine-grained rutile (Rt), fluorite (Fl), sericite (Ser) and chlorite (Chl) are intergrown within the uraniferous rutile/brannerite. Grains of chalcocite (Cct), bornite (Bn) and hematite (Hem) are contained within the aggregate. The aggregate occurs on the edge of a larger hematite mass containing fluorite and zircon (Zrn), and within a matrix of finely intergrown sericite, chlorite and fluorite and grains of quartz (Qz), hematite and bornite; (b) irregular needle- to blade-shaped network of brannerite (S9.73) containing chalcocite laths, Ti-bearing hematite (Hem) and fine-grained dispersions of rutile, fluorite, sericite and chlorite. Brannerite mass is surrounded by rutile, quartz, fluorite, sericite and chlorite; (c) anastomosing band of uraniferous rutile-brannerite (S9.61) replacing Ti-bearing hematite which contains fine-grained sericite, chlorite and Fe-Ti phases and some unfilled cavities/holes. The reduced brightness and contrast displays a mottled U-concentration gradient, with rims of higher U content (light grey) surrounding zones of lower U content (dark grey); (d) network of randomly orientated needle- to blade-shaped brannerite (S9.30) within a matrix of fine-grained sericite, quartz and hematite, and some larger hematite laths and quartz grains; (e) needle- to blade-shaped network of brannerite (S9.79) grading into more massive brannerite, typically found on edges of irregular brannerite aggregates (such as (a)); (f) fine hair-like needles of brannerite (S3.24) growing into a void on the edge of an Fe-bearing rutile grain. Brannerite is intimately intergrown with fluorite, sericite, chlorite and hematite.

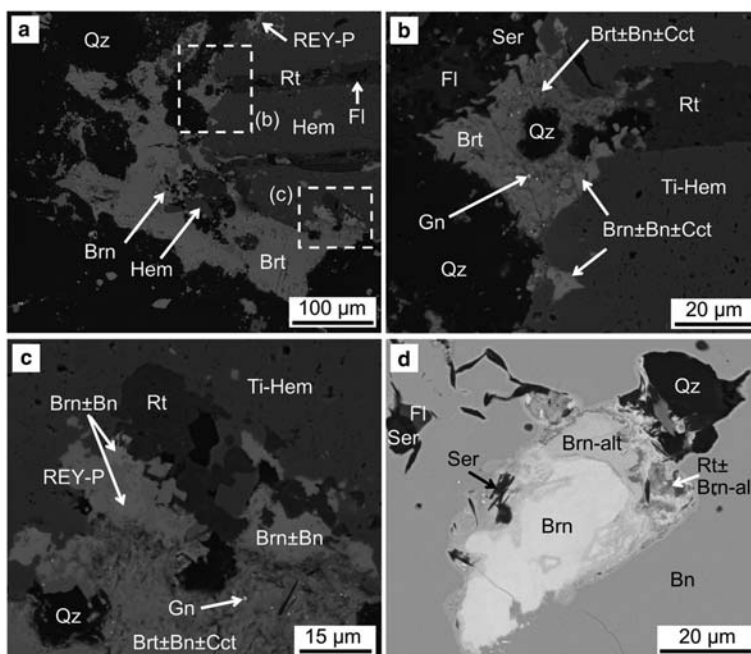


FIG. 2. BSE images of brannerite-B and -C; (a) fine-grained blebs of brannerite-B (Brn, S4.33) intergrown with baryte (Brt) on the edge of a hematite (Hem) grain containing rutile (Rt) lamellae. Areas outlined by white dotted boxes are enlarged in (b, c); (b) blebs of brannerite-B (S4.44) growing on margins of Ti-rich hematite (Ti-Hem) and rutile lamellae. Brannerite is intergrown with baryte, bornite (Bn) and chalcocite (Cct), and there is a fine dusting of galena (Gn); (c) blebs of brannerite-B (S4.53) intergrown with a *REY*-phosphate (*REY*-P; florencite/crandallite) on the edge of prismatic-grained rutile clusters. The morphology of brannerite appears to mimic the prismatic shape of some individual rutile grains. Adjacent baryte contains a fine-grained dusting of Cu-(Fe)-sulfides and galena (based on EDS spectra); (d) irregular-shaped bleb of brannerite-C (S9.23) contained within a mass of bornite/chalcocite. Cracks containing fine-grained sericite, fluorite, chlorite and quartz are found within bornite/chalcocite. An alteration rim (Brn-alt) surrounds more uniform central brannerite, where brannerite contains elevated amounts of Si, Fe, Cu and S (based on SEM-EDS spectra).

of petrographic characteristics (size, habit, textures and mineral associations), as well as differences in composition.

Brannerite petrography and textural classes

Brannerite is classified into four texturally distinct groups (hereafter, brannerite-A, -B, -C and -D). The first, brannerite-A, is variable in size (tens to hundreds of micrometres) and ranges in composition from what is effectively uraniferous rutile to stoichiometric brannerite. Brannerite-A displays a diverse range of morphology, including complex irregular-shaped aggregates (Fig. 1a,b), replacement bands (Fig. 1c) and discrete elongate seams (Fig. 1d). The internal structure of brannerite-A ranges from randomly-orientated hair-like needles

and blades to a mix of massive or bleb-like irregular masses (Fig. 1d-f). In some instances, hematite and rutile are replaced by an anastomosing band of uraniferous rutile-brannerite (e.g. Fig. 1c). A U-concentration gradient may be observed, with rims containing more U surrounding zones of lower U content. Similarly, some irregular aggregates of brannerite (Fig. 1a) have fine dispersions of uraniferous rutile in the centre with lower U content grading into U-rich brannerite on the rim. Fine-grained minerals commonly intergrown with brannerite-A include rutile, hematite, sericite, chlorite, fluorite and quartz (e.g. Fig. 1). Cu-(Fe)-sulfides, hematite and rutile are commonly dispersed throughout the brannerite aggregates (Fig. 1b).

Brannerite-B is generally finer grained (<5 µm) and associated intimately with baryte and *REY*

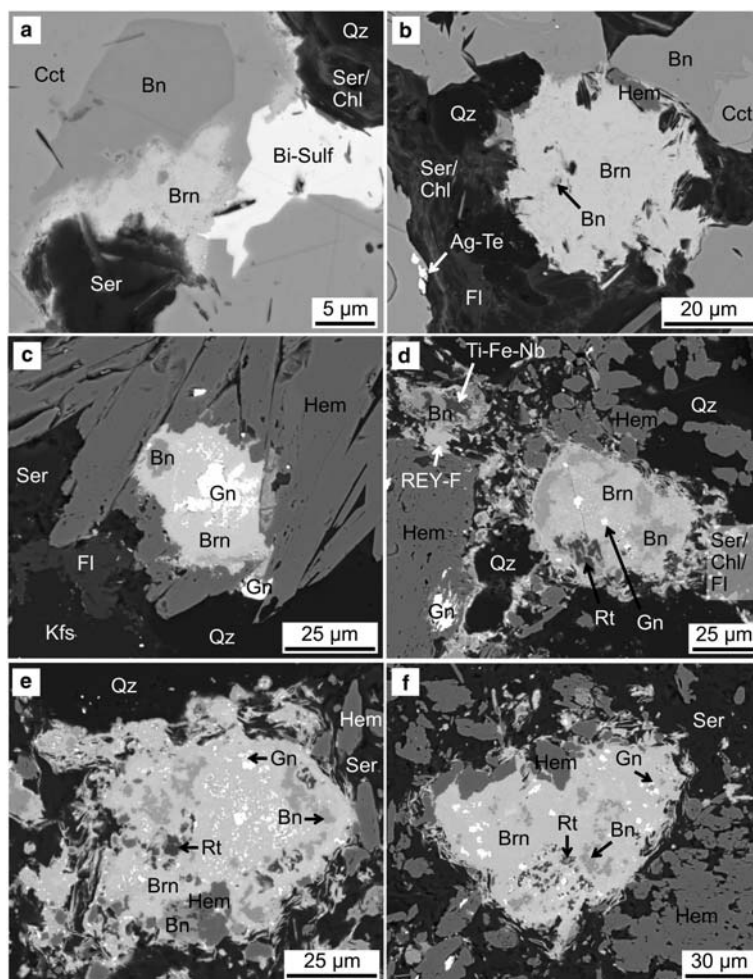


FIG. 3. BSE images of brannerite-C and -D; (a) irregular-shaped bleb of brannerite-C (Brn, S9.6) found within a mass of bornite/chalcocite (Bn/Cct) and adjacent to a Bi-bearing sulfide (Bi-Sulf). The edges of brannerite appear altered (mottled appearance) and is again associated with a sericite/chlorite (Ser/Chl) mass; (b) irregular-shaped mass of brannerite-C (S9.15) growing on the edge of a bornite/chalcocite grain. Brannerite is within a fine-grained sericite, chlorite, fluorite (Fl) matrix which contains quartz (Qz) grains. Silver-tellurides (Ag-Te) are also found nearby; (c) irregular-shaped bleb of brannerite-D (S21.92) within aggregated laths of hematite (Hem). Brannerite-D contains inclusions of galena (Gn) and bornite. Galena is also observed within the hematite laths. Surrounding minerals include: sericite, fluorite, K-feldspar (Kfs) and quartz; (d) irregular-blebs of brannerite-D (S21.110) found within a band of intergrown sericite, chlorite and fluorite. Brannerite contains rutile and hematite clusters, as well as patches of bornite. There are numerous patches and specks of galena within both the brannerite and neighbouring hematite; (e) an irregular-bleb of brannerite-D (S21.114) containing peripheral bornite and hematite grains. Galena is present in the form of larger inclusions and as a fine-dusting within the brannerite. Rutile clusters (possibly anatase) and patches of bornite can also be seen within brannerite. The edges of the larger brannerite mass consist of more lath-like brannerite which is intimately intergrown with sericite/chlorite; (f) irregular mass of brannerite-D (S21.98) again containing patches of bornite, rutile clusters and inclusions of galena. The edges of the main brannerite mass consist of lath-like brannerite which is intergrown with chlorite/sericite, and there are some larger grains of hematite.

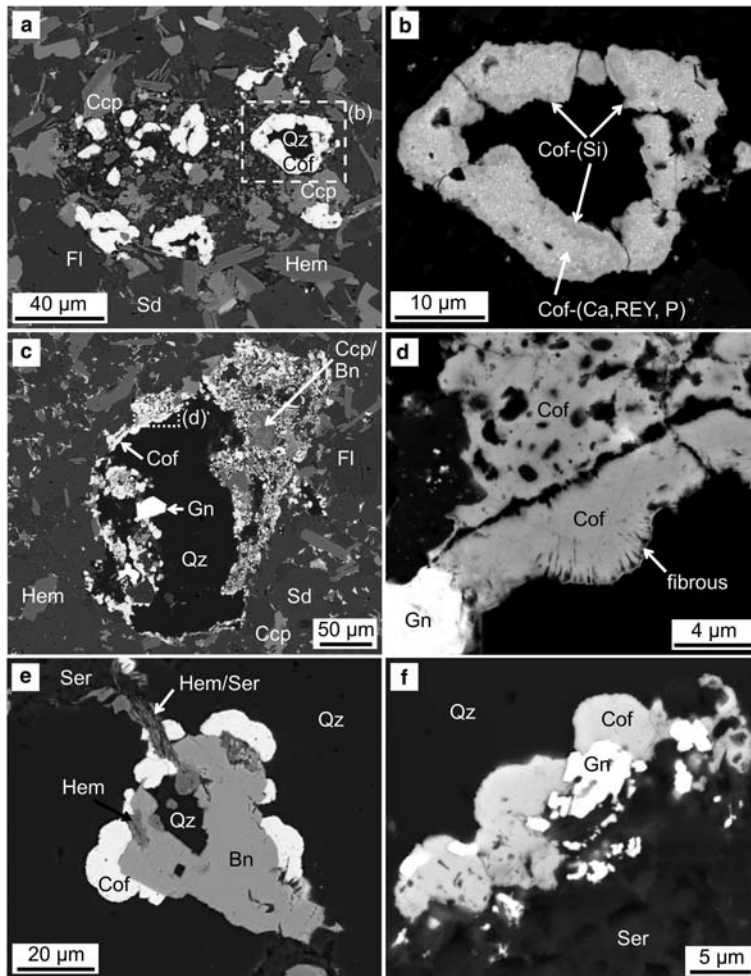


FIG. 4. BSE images of coffinite-A subtypes; (a) coffinite-A1 (Cof; S13.8) rimming quartz (Qz) in a matrix of siderite (Sd), fluorite (Fl), chalcopyrite (Ccp) and hematite (Hem). Area outlined by white dotted box is enlarged in (b); (b) coffinite-A1 (S13.9) rimming quartz with reduced brightness and contrast to display chemical heterogeneity (mottled appearance) within coffinite globules and Si-rich coffinite (Cof-(Si); duller) closest to quartz grain and Ca/REY/P-rich coffinite [Cof-(Ca,REY,P); brighter]; (c) coffinite-A2 (S13.15) globules and dendrites with galena (Gn), hematite and chalcopyrite grains rimming quartz. Surrounding minerals include: fluorite, siderite and hematite. Area outlined by white dotted box is enlarged in (d); (d) enlargement of coffinite-A2 globules (S13.29) and galena grains with reduced brightness and contrast to display more uniform appearance of coffinite and radiating-fibrous internal structure of individual coffinite grain. It appears that growth of coffinite has occurred into the quartz grain; (e) globules of coffinite-A1 (S19.105) nucleating onto the edges of a bornite grain into quartz. Some fine-grained brannerite-sericite is contained on the edges of a bornite grain. The flattened edge of the coffinite-A1 globules on the periphery of the bornite grain implies nucleation onto the sulfide, and growth into the quartz grain; (f) coffinite-A2 globules associated with galena (S18.43) growing along the boundary of quartz-sericite (Ser).

minerals (e.g. florencite, crandallite and monazite). The baryte typically contains fine disseminations of Cu-(Fe)-sulfides and also a fine dusting of galena. Blebs of brannerite-B can be found on the margins

of Ti-rich hematite and TiO_2 lamellae (Fig. 2a–c). In some examples, the brannerite has a prismatic shape similar to that of individual rutile prisms, suggesting pseudomorphic replacement (Fig. 2c).

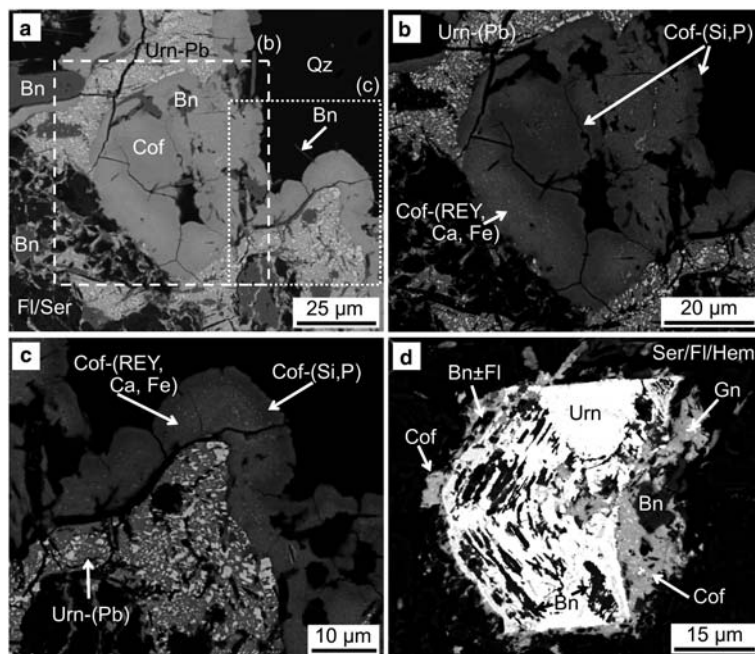


FIG. 5. BSE images of coffinite-B; (a) collomorphic coffinite-B (Cof; S1.5) rimming quartz (Qz) grains. Coffinite-B is encompassed by massive uraninite enriched in Pb (Urn-Pb)). Bornite (Bn) needles and grains found within both coffinite and uraninite. The small gaps/spaces (<1 μm) evident around the bornite contained in the coffinite globules may be indicative that the surfaces of these sulfides acted as reductants, thus allowing reduction of uranyl species from solution and subsequent coffinite precipitation. Matrix material consists of fluorite (Fl), siderite (Sd) and sericite (Ser). Areas outlined by white dotted boxes are enlarged in (b, c); (b) close-up of collomorphic coffinite-B (S1.6) with reduced brightness and contrast to display compositional variability within coffinite-B and uraninite. Bright regions in uraninite are Pb-rich. Darker, more uniform zones within coffinite are unusually enriched in Si and P (Cof-(Si,P)). Some of the brighter coffinite (Cof-(REY,Ca,Fe)) is more mottled in appearance and has higher ΣREY , Ca and Fe than the Si-rich coffinite; (c) close-up of collomorphic coffinite-B (S1.9) again with reduced brightness and contrast to highlight that the coffinite enriched in Si and P (darker) generally occurs along the rims of quartz grains and where the coffinite is cracked; (d) aureole of coffinite-B around uraninite-bornite crystal (S17.37) contained in a matrix of hematite (Hem), quartz and sericite grains. Coffinite appears mottled in appearance and contains some specks of galena (Gn).

Brannerite-C and -D represent more irregular masses and blebs, are generally 10–50 μm in size and tend to have a more uniform or massive internal structure. These are distinct from each other but both display some association with Cu-(Fe)-sulfides. Brannerite-C is generally massive and surrounded by an alteration rim where brannerite contains elevated Si, Fe, Cu and S (based on SEM-EDS spectra; Fig. 2d). These are either contained completely within Cu-(Fe)-sulfides (Figs 2d and 3a), or are found on the edges of Cu-(Fe)-sulfide grains (Fig. 3b). Some Bi-sulfides (Fig. 3a) and Ag-tellurides (Fig. 3b) have been identified in close proximity to brannerite-C. In all cases, brannerite-C is found in association with fine-grained sericite, fluorite, chlorite and quartz (Figs 2d and 3a,b).

Brannerite-D is distinct in that it is the only brannerite which contains visible inclusions of galena (Fig. 3c–f). Neighbouring hematite may, in some cases, also contain galena (Fig. 3c,d). Irregular-shaped blebs of brannerite-D typically contain rutile clusters (possibly anatase), patches of bornite, and hematite grains. The edges of the larger brannerite-D masses consist of more lath-like brannerite intimately intergrown with sericite/chlorite (Fig. 3e,f).

Coffinite petrography and textural classes

Coffinite and any (U,Si)-phases are classified into three distinct groups (hereafter, coffinite-A, -B and

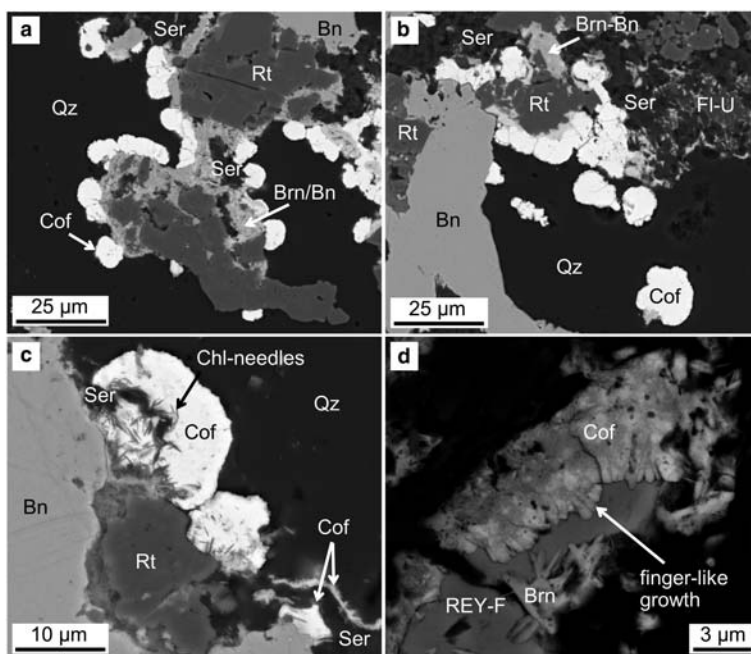


FIG. 6. BSE images of coffinite-C subtypes; (a) discrete coffinite-C1 globules (Cof, S19.103) growing between the edge of a rutile-bornite-brannerite-sericite (Rt-Bn-Brn-Ser) aggregate and quartz (Qz) grain; (b) coffinite-C1 globules (S19.96) nucleating onto brannerite-rutile aggregates, bornite and holes within quartz. Brannerite is intimately intergrown with bornite $\pm$ fluorite (Fl) $\pm$ sericite; (c) close-up of an individual coffinite-C1 globule (S19.97) nucleating onto bornite-brannerite-rutile-sericite aggregate. Needles of chlorite (Chl) and/or sericite are enclosed within the coffinite-C1 globule; (d) coffinite-C2 globules (S10.40) intimately associated with a REY-fluoride mineral (REY-F; bastnäsite/synchysite). Reduced brightness and contrast reveals internal chemical heterogeneity and radiating finger-like structure.

-C). There are a number of distinct mineral association and textural differences within these broader groups. These are identified in the following by a numbered suffix (i.e. A1, A2, C1, C2 and C3). All coffinite is found in association with quartz (i.e. typically grows on the periphery of quartz) and hematite, and is typically globular to collomorphic in appearance.

The majority of coffinite identified belong to groups A and B. Coffinite-A ranges from discrete globules to collomorphic bands which completely encompass quartz grains (Fig. 4a–c). Individual coffinite-A globules are 2–10 μm in size, and the collective collomorphic coffinite-A + quartz aggregates range in size from 20 to 100 μm (Fig. 4a–c). The coffinite-A1 subtype is always associated with, or nucleating onto, Cu-(Fe)-sulfides (Fig. 4e), whereas subtype A2 is found with galena (Fig. 4c,d,f). Globules of coffinite-A are compositionally heterogeneous (mottled appearance) and

usually contain Si-rich bands in the coffinite closest to adjacent quartz grains (Fig. 4b).

Coffinite-B is always found in association with uraninite, and includes collomorph coffinite rimming quartz, which is in turn, enveloped by massive uraninite (Fig. 5a–c), and also aureoles of coffinite/(U,Si)-phases surrounding individual uraninite crystals with incipient coffinitization (Fig. 5d). Collomorph coffinite-uraninite intergrowths are typically hundreds of micrometres in size, with individual coffinite globules 2–10 μm in diameter. The enveloping massive uraninite typically is speckled with high-Pb uraninite (Fig. 5b,c). Bornite needles and grains can be found within both coffinite and uraninite. Coffinite-B displays compositional heterogeneity; darker (on back-scatter electron (BSE) images), more uniform, (Si $\pm$ P)-enriched zones generally occurring along the rims of quartz grains and where the coffinite is fractured. The brighter coffinite-B is more mottled

in appearance than the Si-rich coffinite; the higher U content considered responsible for this difference in contrast. The other main sub-type of coffinite-B is found on the edges of uraninite crystals where incipient coffinitization has occurred (Fig. 5d). This form is probably better referred to as a mixture of (U,Si)-phases rather than coffinite, but for ease of comparison has hereafter been referred to as coffinite-B. It is usually found in patches or as an aureole on the rim of the uraninite-bornite grains.

Coffinite-C includes three subtypes C1, C2 and C3. Broadly, coffinite-C is defined as being associated with brannerite or *REY* minerals, with individual globules typically 2–10 μm in diameter. In some cases, coffinite-C globules coalesce forming a string of almost collomorphic coffinite (Fig. 6a). Coffinite-C1 is defined as being associated with, or nucleating onto brannerite, and grows between the edge of rutile-bornite-brannerite-sericite aggregates and quartz (Fig. 6a,b). Globules of coffinite-C1 typically contain needles of chlorite and/or sericite (Fig. 6c). In some cases, discrete globules of coffinite-C1 are found at the peripheries of larger brannerite-A aggregates (Fig. 1a). Coffinite-C2 and -C3 are both associated with *REY* minerals (Fig. 6d), with C2 typically exhibiting finger-like growth into *REY* minerals, whereas C3 contains distinct bright banding when the brightness and contrast of the BSE image are reduced.

Generally, the rounded edge of individual coffinite grains is typically found within quartz, and the flattened edge of the globule is always found along the grain boundary of quartz or any mineral (i.e. sulfide, brannerite, or uraninite) onto which the coffinite nucleates (e.g. Figs 4d,e and 5c). The Cu-(Fe)-sulfides, brannerite and/or uraninite, as well as the quartz found in contact with the coffinite, typically display evidence of corrosion expressed by embayed margins, and in some cases the presence cracks/gaps (e.g. Fig. 5a) between these minerals and the coffinite. Moreover, individual coffinite globules typically appear to have a radiating-fibrous internal structure, and growth appears to occur into quartz grains (Fig. 4d).

Associations and distribution of coffinite and brannerite

A total of 23 samples were analysed in this study; each sample contains different relative abundances of uraninite, coffinite and brannerite (Table 1). Samples which contained the most brannerite

(94%) relative to all U minerals were dominated typically by brannerite-A. The latter was identified in 15 samples, whereas brannerite-B, -C and -D were found in only 2, 4 and 3 samples, respectively. Thus, brannerite-A occurs within the broadest range of samples in terms of depth, rock type and grade (Table 1). Comparatively, the most coffinite contained in any one sample was 91% of all U minerals, with coffinite-A being dominant (occurs within 13 samples). Coffinite-C1 and -B were found in six samples each, with coffinite-C2 and C3 only occurring in a minority of samples.

Mineral liberation analyser data can be used to understand what minerals are found in association with either brannerite or coffinite. For example, where a wt.% value is given for mineral-A found in association with brannerite, this represents the wt.% of mineral-A found in association with the total surface wt.% of brannerite. Overall, the minerals found in direct contact with either brannerite or coffinite do not change among the sample suite, but the relative proportions of individual components within the associations can be used to highlight some differences between the different groupings (Figs 7 and 8; Table A2). The dominant minerals found in association with brannerite are hematite (29–38 wt.%), sericite/chlorite (21–31 wt.%) and quartz (10–24 wt.%). Brannerite-A is also associated commonly with carbonate, fluorite, Ti minerals and sulfides (5 wt.% each). Brannerite-B has the highest association with quartz and sericite/chlorite (combined total of 55 wt.%) of all brannerite groups. The highest association of any brannerite group with sulfides is for brannerite-C (24 wt.%), and brannerite-D has the highest association (7 wt.%) with Pb minerals (dominantly galena but also minor cerussite, clausthalite and altaite). The relative proportion of other U minerals (coffinite and uraninite) found in contact with brannerite grains is usually fairly low (up to 1.5 wt.%).

Coffinite was predominantly associated with hematite (28–45 wt.%), quartz (12–30 wt.%) and sericite/chlorite (9–22 wt.%). The association of coffinite with sulfides is reasonably consistent between groups (~4–7 wt.%). Coffinite-B has the highest relative association with fluorite (13 wt.%) and K-feldspar (7 wt.%) of any coffinite group, and coffinite-A has the highest association with carbonates (7 wt.%). The relative proportion of other U minerals (brannerite and uraninite) found in contact with coffinite is frequently high (up to 5 wt.% brannerite and 2 wt.% uraninite), highlighting the observation that coffinite is often found peripheral to, and replacing, other U minerals.

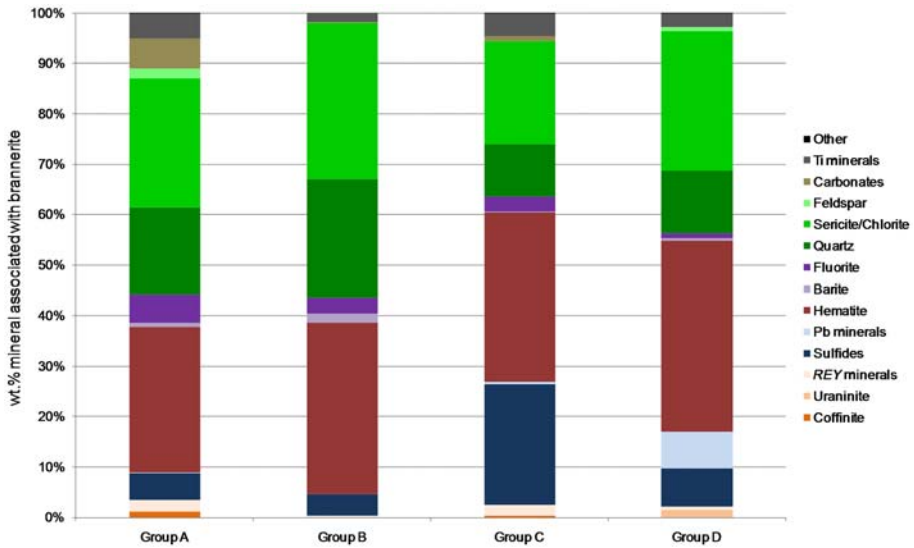


FIG. 7. Column chart displaying wt.% of various minerals in association with brannerite (MLA data; Table A2). The association data for each brannerite group have been averaged for all samples containing that particular brannerite as identified in Table 1.

The distribution of brannerite and coffinite shows no discernible zonation trend with lithology or sulfide zoning. Both minerals can be found at any depth within the deposit (i.e. brannerite/

coffinite can be found in both shallow and deep samples; Table 1). They can be found within a single drillhole, but their abundance and type does vary with depth. For example, in one of the deepest

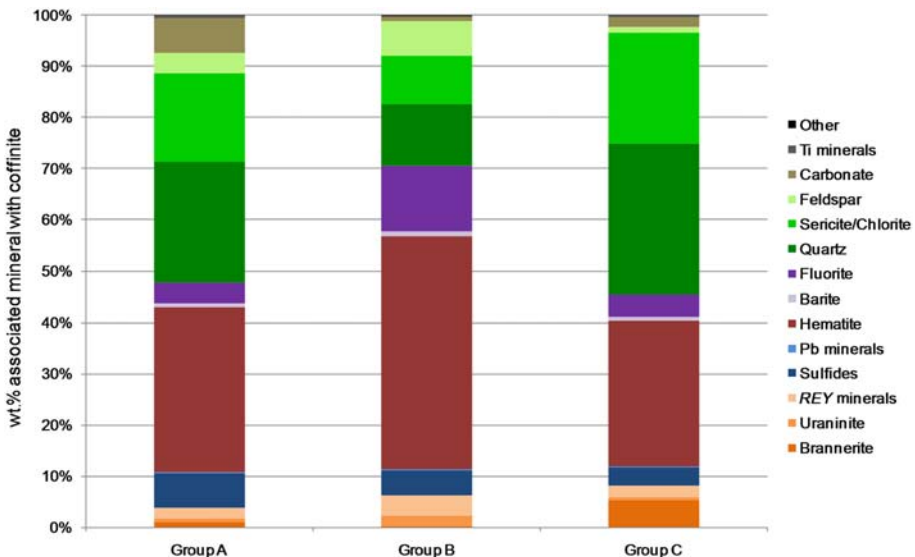


FIG. 8. Column chart displaying wt.% of various minerals in association with coffinite (MLA data; Table A2). The association data for each coffinite group have been averaged for all samples containing the particular coffinite as identified in Table 1.

drillholes (RD1988; Table 1), brannerite-A and -B is found in the shallowest sample (S4, ~880 m), coffinite-B is found at depths between 1620 to 1770 m (S5 and S6) and coffinite-A1 and -C2 are found in the deepest (~1800 m) sample (S7). In another drillhole (RD3035), coffinite-A1 and -B are found at a depth of ~375 m (S14), and the two deeper samples (S15 and S16) contain both brannerite-A and a mixture of coffinite-A1, -B and -C1.

Compositional data

Data presentation and formulae calculation

All 23 samples were analysed by SEM and EPMA. Data filtering was undertaken to remove individual analyses which did not correspond to compositionally homogenous brannerite or coffinite. For brannerite, points which had >50 wt.% TiO₂, >10 wt.% Fe₂O₃ or SiO₂, >5 wt.% CaO, >4 wt.% Cu₂O and >2 wt.% ZrO₂, BaO, SO₃, PbO or P₂O₅ were excluded, as were those with <25 wt.% TiO₂ or <30 wt.% UO₂. A similar filtering process was used for coffinite analyses, where points which had >25 wt.% SiO₂, >10 wt.% Fe₂O₃, >5 wt.% CaO, >4 wt.% Cu₂O, BaO or SO₃, >2 wt.% PbO or Al₂O₃ and >1 wt.% TiO₂, were excluded, as were those with <45 wt.% UO₂ or <10 wt.% SiO₂. Anomalous concentrations of these components are attributable to mineral impurities and fine-grained intergrowths or inclusions with various minerals.

Clean spot analysis proved difficult to obtain. The main factors contributing to data rejection were: (1) brannerite and/or coffinite was too fine-grained; (2) brannerite and coffinite were finely intergrown; (3) brannerite/coffinite grains contained inclusions of *REY* minerals, galena, hematite, rutile, Cu-(Fe)-sulfides, baryte or various silicates; and (4) grains had incipient branneritization or coffinitization, or had partially altered rims. Grains displaying one or more of these features yielded poor analytical totals (typically <85%), and these analyses were rejected. Moreover, for both brannerite and coffinite, variability in analytical totals is probably due to a combination of metamictization, amorphization and/or hydration (Lumpkin *et al.*, 2012). A total of 395 brannerite analyses and 380 coffinite analyses were however deemed acceptable. Means, standard deviations and minimum/maximum values are reported in Tables 2 3 and 4.

Selection of compositionally homogeneous areas for EPMA proved difficult, not only due to the fine-grained nature of the minerals themselves but also as there is chemical heterogeneity within individual grains. This heterogeneity is highlighted by significant variation in grey-scale within brannerite (Figs 1a,c and 2d) and coffinite (Figs 4b and 5b,c).

A variety of different methods were employed to discriminate between different brannerite/coffinite groups, and included comparison based solely on composition, where cluster analysis was used to distinguish different groups. Although this proved moderately successful, it did not take any of the valuable textural data into account. Thus, discrimination of different groups of brannerite and coffinite was made on the basis of their mode of occurrence (habit, associated minerals etc.) and any key distinguishing features (e.g. internal banding). EPMA data has been reported as mean analyses (Tables 2–4) for the entire population, and also as mean analyses for key identified textural groups. As each group occupies a compositional range, minimum, maximum and standard deviation values are included in the tables. In some cases, concentrations of one or more elements were <mdl in individual spot analyses. A value of half the individual spot analysis mdl was utilized for calculation of the mean for all subsequent statistical analysis, calculations of atoms per formula unit (apfu) and data plotting.

The apfu calculations for brannerite require several critical assumptions: (1) a basis of 6 O atoms and AB₂O₆ stoichiometry; (2) cation valencies and site allocations (*A* vs. *B*) given in Table 2 are correct; (3) S⁶⁺, Cu⁺, P⁵⁺ are omitted as these elements are probably restricted to nanoscale inclusions; (4) 74% of U is present as U⁶⁺ (see below); (5) Fe, As are present in oxidized form i.e. as Fe³⁺ and As⁵⁺; (6) Fe³⁺ and REY³⁺ are assumed to be contained in brannerite and no correction has been made for any Fe present within Cu-(Fe)-sulfide inclusions or *REY* hosted by *REY* mineral inclusions; and (7) any anion substitution (e.g. F⁻, (OH)⁻ or (CO₃)²⁻ for O²⁻) is insignificant. To highlight the compositional variability between brannerite groups, total cations, as well as *A*- and *B*-site cation totals have been included in the tables.

For coffinite, the key apfu calculation assumptions included: (1) a basis of 4 O atoms and a mineral stoichiometry of ABO₄; (2) cation valencies and site allocations (*A* vs. *B*) given in Tables 3 and 4 are correct; (3) omitting Cu⁺ as it is probably restricted to nanoscale inclusions of Cu-(Fe)-sulfides;

TABLE 2 Compositional data from electron probe microanalyses for brannerite.

Type	All data				A				B				C				D			
Valid <i>N</i> (analyses) (wt.%)	395				250				22				9				114			
	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD
UO ₂	41.13	30.50	48.74	4.44	41.58	30.50	48.74	5.16	43.11	40.19	44.28	0.93	43.83	36.38	45.98	3.34	39.54	35.05	43.97	2.20
TiO ₂	34.34	25.95	49.94	3.91	34.79	25.95	49.94	4.84	33.25	32.49	33.92	0.35	33.41	32.57	35.11	0.77	33.66	31.07	35.23	0.72
Na ₂ O	0.69	0.05	1.88	0.45	0.96	0.26	1.88	0.33	0.33	0.09	0.83	0.17	0.35	0.06	0.62	0.22	0.19	0.05	0.50	0.09
MgO	0.11	<mdl	1.37	0.15	0.16	0.03	1.37	0.17	0.03	0.02	0.04	–	0.07	<mdl	0.13	0.05	0.02	<mdl	0.04	–
Al ₂ O ₃	0.35	0.05	2.08	0.26	0.38	0.14	2.08	0.31	0.11	0.05	0.25	0.05	0.25	0.12	0.73	0.18	0.34	0.20	0.86	0.07
SiO ₂	4.14	2.01	8.40	1.07	4.01	2.46	8.26	0.96	3.11	2.01	5.69	0.88	3.99	2.01	6.80	1.49	4.65	3.07	8.40	1.08
P ₂ O ₅	0.08	<mdl	1.70	0.15	0.13	<mdl	1.70	0.17	<mdl	<mdl	<mdl	–	0.05	<mdl	0.11	0.04	<mdl	<mdl	0.09	–
SO ₃	0.09	<mdl	1.76	0.18	0.05	<mdl	1.00	0.11	0.39	<mdl	1.76	0.50	<mdl	<mdl	0.10	0.03	0.12	<mdl	0.78	0.12
K ₂ O	0.13	<mdl	0.78	0.12	0.18	0.05	0.78	0.12	0.03	<mdl	0.09	0.02	0.08	<mdl	0.12	0.05	0.03	<mdl	0.10	0.02
CaO	1.96	0.59	4.81	0.75	1.85	0.66	4.81	0.83	2.34	1.21	3.00	0.37	1.70	0.59	2.44	0.57	2.15	0.80	3.33	0.56
MnO	0.21	0.05	0.48	0.06	0.20	0.06	0.48	0.05	0.25	0.16	0.31	0.04	0.21	0.14	0.27	0.04	0.23	0.05	0.41	0.07
Fe ₂ O ₃	4.83	2.39	9.89	1.30	5.41	2.39	9.89	1.25	4.12	2.79	7.23	1.03	4.45	3.36	6.07	0.77	3.74	3.10	4.84	0.37
Cu ₂ O	1.21	<mdl	3.77	0.85	1.56	0.24	3.77	0.79	0.91	0.29	1.67	0.31	2.17	1.06	3.22	0.89	0.44	<mdl	2.43	0.38
As ₂ O ₅	0.28	<mdl	1.21	0.25	0.30	<mdl	1.21	0.17	0.99	0.67	1.19	0.11	0.55	0.31	1.03	0.30	0.10	<mdl	0.18	–
SrO	0.13	<mdl	0.42	0.09	0.08	<mdl	0.42	0.04	0.10	0.06	0.30	0.05	0.05	<mdl	0.07	–	0.24	0.09	0.36	0.06
ZrO ₂	0.49	0.10	1.96	0.28	0.45	0.10	1.96	0.24	0.30	0.20	0.37	0.04	0.47	0.16	0.79	0.29	0.60	0.18	1.53	0.35
Nb ₂ O ₅	0.77	0.30	1.65	0.33	0.58	0.41	1.20	0.14	0.50	0.30	0.58	–	0.51	0.39	0.60	–	1.23	0.87	1.65	0.12
BaO	0.40	<mdl	1.99	0.34	0.20	<mdl	1.99	0.15	0.44	0.26	1.29	0.23	0.56	0.13	1.30	0.44	0.83	0.51	1.55	0.22
Y ₂ O ₃	1.22	0.36	3.75	0.95	0.76	0.36	3.29	0.58	0.93	0.84	1.02	–	0.91	0.48	2.08	0.48	2.30	1.11	3.75	0.86
La ₂ O ₃	0.17	0.11	0.79	–	0.16	0.11	0.79	–	0.23	0.19	0.27	–	0.15	0.12	0.18	–	0.18	0.15	0.25	–
Ce ₂ O ₃	0.63	0.23	1.49	0.26	0.46	0.23	1.24	0.10	1.05	0.86	1.47	0.14	0.59	0.50	0.74	0.09	0.93	0.74	1.49	0.14
Pr ₂ O ₃	<mdl	<mdl	0.23	–	<mdl	<mdl	<mdl	–	<mdl	<mdl	0.19	–	<mdl	<mdl	<mdl	–	<mdl	<mdl	0.23	–
Nd ₂ O ₃	0.38	<mdl	1.07	0.26	0.22	<mdl	0.63	–	0.44	0.34	0.55	–	0.33	<mdl	0.71	–	0.72	0.39	1.07	–
Sm ₂ O ₃	0.15	<mdl	0.60	0.16	<mdl	<mdl	0.33	–	<mdl	<mdl	0.19	–	<mdl	<mdl	0.39	–	0.36	<mdl	0.60	–
Gd ₂ O ₃	0.30	<mdl	1.13	0.32	<mdl	<mdl	1.13	0.19	<mdl	<mdl	0.24	–	0.23	<mdl	0.80	0.22	0.65	0.19	1.12	0.31
PbO	0.40	<mdl	1.93	0.50	0.08	<mdl	0.14	–	0.42	0.28	0.79	0.12	0.28	0.13	0.72	0.19	1.11	0.47	1.93	0.34
ThO ₂	0.22	<mdl	1.38	0.17	0.22	<mdl	1.38	0.21	0.12	0.10	0.17	–	0.21	0.12	0.36	0.07	0.23	0.05	0.34	0.05
Σ Ox	94.90	85.09	99.90	2.17	95.03	85.09	99.90	2.61	93.87	92.65	96.72	1.15	95.63	94.47	96.63	0.82	94.74	92.68	97.44	0.92

Brannerite formula (apfu) – based on 6 O

U ⁴⁺	0.146	0.096	0.184	0.019	0.147	0.096	0.184	0.022	0.158	0.146	0.164	0.005	0.158	0.126	0.170	0.016	0.140	0.118	0.156	0.008
U ⁶⁺	0.415	0.275	0.524	0.054	0.418	0.275	0.524	0.063	0.449	0.416	0.466	0.013	0.449	0.358	0.483	0.045	0.399	0.335	0.444	0.023
Ca ²⁺	0.129	0.037	0.320	0.050	0.121	0.040	0.320	0.055	0.159	0.079	0.203	0.026	0.114	0.037	0.167	0.039	0.141	0.051	0.222	0.038
Sr ²⁺	0.004	0.000	0.015	0.003	0.003	0.000	0.015	0.001	0.004	0.002	0.011	0.002	0.002	0.000	0.003	0.001	0.009	0.003	0.013	0.002
Ba ²⁺	0.010	0.000	0.045	0.008	0.005	0.000	0.045	0.004	0.011	0.007	0.032	0.006	0.014	0.003	0.030	0.011	0.020	0.012	0.036	0.005
Y ³⁺	0.040	0.010	0.122	0.031	0.025	0.010	0.108	0.019	0.031	0.028	0.034	0.002	0.030	0.015	0.066	0.015	0.075	0.036	0.122	0.028
La ³⁺	0.004	0.002	0.019	0.001	0.004	0.002	0.019	0.001	0.005	0.005	0.006	0.000	0.004	0.003	0.004	0.000	0.004	0.003	0.005	0.000
Ce ³⁺	0.014	0.005	0.034	0.006	0.010	0.005	0.029	0.002	0.024	0.020	0.034	0.003	0.013	0.012	0.017	0.002	0.021	0.017	0.032	0.003
Pr ³⁺	0.002	0.001	0.005	0.001	0.001	0.001	0.004	0.001	0.003	0.001	0.004	0.001	0.002	0.001	0.003	0.001	0.003	0.001	0.005	0.001
Nd ³⁺	0.008	0.001	0.024	0.006	0.005	0.001	0.013	0.002	0.010	0.008	0.012	0.001	0.007	0.004	0.015	0.003	0.016	0.009	0.024	0.004
Sm ³⁺	0.003	0.000	0.013	0.003	0.001	0.000	0.007	0.001	0.002	0.001	0.004	0.001	0.003	0.001	0.008	0.002	0.008	0.003	0.013	0.003
Gd ³⁺	0.006	0.001	0.024	0.006	0.003	0.001	0.024	0.004	0.003	0.002	0.005	0.001	0.005	0.001	0.016	0.004	0.013	0.004	0.023	0.006
Pb ²⁺	0.003	0.000	0.016	0.004	0.001	0.000	0.001	0.000	0.004	0.002	0.007	0.001	0.002	0.001	0.006	0.002	0.009	0.004	0.016	0.003
Th ⁴⁺	0.003	0.000	0.019	0.002	0.003	0.000	0.019	0.003	0.002	0.001	0.002	0.000	0.003	0.002	0.005	0.001	0.003	0.001	0.005	0.001
ΣA-site cations	0.787	0.459	1.010	0.104	0.745	0.459	1.010	0.107	0.864	0.779	0.904	0.032	0.805	0.647	0.918	0.085	0.861	0.727	0.928	0.043
(excl. U)	0.226	0.076	0.462	0.088	0.181	0.076	0.462	0.068	0.258	0.188	0.329	0.027	0.198	0.125	0.265	0.054	0.322	0.199	0.390	0.050
Ti ⁴⁺	1.574	1.230	2.042	0.133	1.584	1.230	2.042	0.163	1.582	1.529	1.619	0.027	1.561	1.521	1.587	0.020	1.551	1.392	1.615	0.040
Si ⁴⁺	0.253	0.128	0.516	0.064	0.244	0.134	0.516	0.059	0.196	0.128	0.347	0.053	0.246	0.128	0.406	0.084	0.284	0.191	0.501	0.062
Na ⁺	0.082	0.006	0.232	0.054	0.114	0.029	0.232	0.041	0.040	0.011	0.098	0.021	0.042	0.008	0.075	0.027	0.023	0.006	0.057	0.010
Mg ²⁺	0.010	0.000	0.120	0.013	0.014	0.003	0.120	0.015	0.003	0.002	0.004	0.000	0.007	0.000	0.012	0.005	0.001	0.000	0.004	0.001
Al ³⁺	0.025	0.004	0.133	0.018	0.027	0.010	0.133	0.022	0.008	0.004	0.018	0.004	0.018	0.009	0.050	0.012	0.024	0.015	0.061	0.005
K ⁺	0.010	0.000	0.060	0.009	0.014	0.004	0.060	0.009	0.003	0.001	0.007	0.002	0.006	0.000	0.009	0.004	0.002	0.000	0.008	0.002
Mn ²⁺	0.011	0.003	0.024	0.003	0.010	0.003	0.024	0.003	0.014	0.008	0.017	0.002	0.011	0.007	0.015	0.002	0.012	0.003	0.022	0.004
Fe ³⁺	0.221	0.126	0.434	0.056	0.246	0.126	0.434	0.053	0.196	0.128	0.334	0.047	0.207	0.160	0.268	0.030	0.172	0.142	0.224	0.017
As ⁵⁺	0.009	0.000	0.041	0.008	0.009	0.000	0.041	0.006	0.033	0.022	0.040	0.004	0.018	0.010	0.034	0.010	0.003	0.000	0.006	0.001
Zr ⁴⁺	0.015	0.003	0.058	0.008	0.013	0.003	0.058	0.007	0.009	0.006	0.011	0.001	0.014	0.005	0.024	0.009	0.018	0.005	0.046	0.010
Nb ⁵⁺	0.021	0.009	0.043	0.009	0.016	0.011	0.031	0.004	0.014	0.009	0.016	0.002	0.014	0.011	0.016	0.002	0.034	0.024	0.043	0.003
ΣB-site cations	2.230	2.009	2.582	0.125	2.293	2.075	2.582	0.112	2.096	2.052	2.184	0.042	2.144	2.009	2.307	0.105	2.125	2.061	2.281	0.038
(excl. Ti)	0.656	0.422	1.163	0.131	0.709	0.463	1.163	0.127	0.515	0.436	0.653	0.065	0.584	0.422	0.759	0.116	0.574	0.468	0.802	0.069
Σcations	3.017	2.920	3.301	0.055	3.038	2.929	3.301	0.057	2.961	2.939	3.006	0.021	2.949	2.920	3.014	0.028	2.985	2.932	3.021	0.022

Average minimum detection limit (mdl) per element for 99% confidence interval (wt.%): U ≈ 0.03, Pb ≈ 0.03, Th ≈ 0.03, Na ≈ 0.02, Mg ≈ 0.01, Al ≈ 0.01, Si ≈ 0.01, P ≈ 0.01, S ≈ 0.01, K ≈ 0.01, Ca ≈ 0.005, Ti ≈ 0.01, Mn ≈ 0.03, Fe ≈ 0.02, Cu ≈ 0.03, As ≈ 0.02, Zr ≈ 0.02, Nb ≈ 0.03, Y ≈ 0.02, Ce ≈ 0.02, La ≈ 0.02, Pr ≈ 0.07, Nd ≈ 0.08, Sm ≈ 0.06, Gd ≈ 0.07, Sr ≈ 0.02, Ba ≈ 0.02.

TABLE 3 Compositional data from electron probe microanalyses for coffinite-A and -B.

Type	All data				A1				A2				B			
Valid <i>N</i> (analyses)	380				122				180				52			
(wt.%)	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD
UO ₂	58.44	45.14	70.02	5.66	57.06	47.57	69.00	5.33	58.45	49.35	65.64	3.48	66.41	58.53	70.02	2.44
SiO ₂	15.79	10.38	24.69	2.78	16.35	10.89	24.69	2.66	16.32	11.45	24.47	2.28	13.09	10.58	21.37	2.18
Na ₂ O	0.34	<mdl	1.20	0.25	0.37	<mdl	1.08	0.24	0.30	<mdl	1.20	0.27	0.42	0.19	1.00	0.16
MgO	0.10	0.01	2.14	0.15	0.05	0.02	0.18	0.02	0.09	0.01	0.73	0.09	0.12	0.09	0.26	0.03
Al ₂ O ₃	0.55	<mdl	1.86	0.35	0.53	0.06	1.73	0.25	0.62	0.18	1.81	0.39	0.32	0.21	0.55	0.07
P ₂ O ₅	3.05	0.63	11.43	1.82	3.27	1.54	5.39	0.88	2.55	0.63	6.18	1.03	2.04	1.37	3.75	0.45
SO ₃	0.34	<mdl	3.31	0.61	0.14	<mdl	3.31	0.41	0.25	<mdl	3.23	0.50	0.72	0.09	2.10	0.44
K ₂ O	0.11	<mdl	0.74	0.10	0.14	<mdl	0.62	0.11	0.08	<mdl	0.74	0.09	0.07	0.04	0.17	0.02
CaO	2.19	0.57	4.59	0.90	1.70	0.62	3.40	0.71	2.12	0.80	4.59	0.75	3.36	2.96	3.80	0.19
TiO ₂	0.13	<mdl	0.90	0.11	0.14	<mdl	0.90	0.11	0.14	0.07	0.41	0.04	0.03	<mdl	0.28	0.05
MnO	0.09	<mdl	0.51	0.10	0.05	<mdl	0.39	0.07	0.06	<mdl	0.51	0.06	0.26	0.08	0.41	0.09
FeO	1.81	0.22	8.41	1.57	0.96	0.22	5.18	0.80	2.72	0.36	8.41	1.77	0.94	0.51	1.68	0.21
Cu ₂ O	0.36	<mdl	3.78	0.41	0.41	<mdl	3.78	0.55	0.33	<mdl	1.67	0.31	0.44	<mdl	1.70	0.34
As ₂ O ₅	0.11	<mdl	1.05	0.17	0.09	<mdl	0.65	0.17	0.14	<mdl	0.56	0.14	<mdl	<mdl	<mdl	–
SrO	<mdl	<mdl	0.18	–	<mdl	<mdl	0.10	–	0.03	<mdl	0.18	0.03	<mdl	<mdl	0.04	–
ZrO ₂	0.21	<mdl	1.44	0.19	0.24	<mdl	1.44	0.28	0.20	<mdl	0.75	0.10	0.15	0.05	0.29	0.05
Nb ₂ O ₅	0.84	<mdl	6.11	0.96	0.16	<mdl	0.93	0.21	1.65	<mdl	6.11	0.82	<mdl	<mdl	<mdl	–
BaO	0.20	<mdl	0.62	0.15	0.15	<mdl	0.49	0.11	0.30	0.04	0.62	0.11	<mdl	<mdl	<mdl	–
Y ₂ O ₃	4.78	0.37	15.60	3.06	7.05	1.12	11.94	2.75	3.30	0.37	7.66	1.45	2.09	1.48	2.53	0.30
La ₂ O ₃	0.27	0.16	2.30	0.16	0.24	0.17	0.39	–	0.26	0.16	2.30	0.22	0.40	0.32	0.53	0.06
Ce ₂ O ₃	1.12	0.30	5.06	0.44	0.94	0.30	1.38	0.24	1.27	0.84	5.06	0.53	1.23	1.01	1.79	0.19
Pr ₂ O ₃	0.22	<mdl	0.70	–	<mdl	<mdl	0.32	–	0.26	<mdl	0.70	–	0.21	<mdl	0.34	–
Nd ₂ O ₃	1.29	0.33	2.76	0.42	1.00	0.33	1.82	0.29	1.66	1.24	2.76	0.21	0.99	0.73	1.31	–
Sm ₂ O ₃	0.48	<mdl	0.86	0.18	0.37	<mdl	0.74	–	0.62	0.27	0.86	–	0.29	0.16	0.41	–
Gd ₂ O ₃	0.81	0.19	1.82	0.29	0.87	0.31	1.26	0.20	0.81	0.19	1.02	–	0.36	0.19	0.51	–
PbO	0.20	<mdl	1.97	0.30	0.11	<mdl	1.03	0.20	0.24	<mdl	1.97	0.37	0.31	0.14	0.84	0.17
ThO ₂	0.12	<mdl	3.61	0.37	0.30	<mdl	3.61	0.61	<mdl	<mdl	0.52	0.08	<mdl	<mdl	<mdl	–
Σ Ox	93.99	86.28	100.00	2.16	92.88	86.51	100.00	2.58	94.84	90.92	99.06	1.39	94.34	93.24	96.21	0.77

Coffinite formula (apfu) – based on 4 O

U ⁴⁺	0.354	0.218	0.477	0.054	0.345	0.262	0.466	0.048	0.349	0.254	0.431	0.035	0.430	0.316	0.477	0.036
U ⁶⁺	0.273	0.168	0.369	0.042	0.267	0.203	0.360	0.037	0.270	0.196	0.334	0.027	0.333	0.244	0.369	0.028
Th ⁴⁺	0.001	0.000	0.039	0.004	0.003	0.000	0.039	0.006	0.000	0.000	0.005	0.001	0.000	0.000	0.000	0.000
Zr ⁴⁺	0.005	0.000	0.032	0.004	0.005	0.000	0.032	0.006	0.005	0.000	0.017	0.002	0.004	0.001	0.007	0.001
Mg ²⁺	0.007	0.001	0.138	0.010	0.004	0.002	0.012	0.002	0.007	0.001	0.049	0.006	0.009	0.006	0.017	0.002
Ca ²⁺	0.114	0.030	0.234	0.050	0.089	0.030	0.194	0.043	0.109	0.038	0.234	0.041	0.186	0.141	0.220	0.018
Mn ²⁺	0.004	0.000	0.019	0.004	0.002	0.000	0.018	0.003	0.003	0.000	0.019	0.003	0.012	0.003	0.019	0.004
Fe ²⁺	0.072	0.009	0.334	0.061	0.039	0.009	0.205	0.031	0.107	0.013	0.334	0.068	0.041	0.020	0.072	0.010
Sr ²⁺	0.001	0.000	0.005	0.001	0.001	0.000	0.003	0.001	0.001	0.000	0.005	0.001	0.000	0.000	0.001	0.000
Pb ²⁺	0.003	0.000	0.024	0.004	0.001	0.000	0.014	0.003	0.003	0.000	0.024	0.005	0.004	0.002	0.012	0.002
Ba ²⁺	0.004	0.000	0.012	0.003	0.003	0.000	0.010	0.002	0.006	0.001	0.012	0.002	0.000	0.000	0.000	0.000
Y ³⁺	0.120	0.009	0.377	0.075	0.178	0.032	0.300	0.070	0.083	0.009	0.180	0.033	0.058	0.036	0.071	0.010
La ³⁺	0.005	0.002	0.041	0.003	0.004	0.003	0.008	0.001	0.005	0.002	0.041	0.004	0.008	0.006	0.010	0.001
Ce ³⁺	0.020	0.005	0.089	0.008	0.017	0.005	0.026	0.004	0.022	0.013	0.089	0.009	0.023	0.020	0.030	0.003
Pr ³⁺	0.004	0.001	0.012	0.001	0.003	0.001	0.006	0.001	0.005	0.002	0.012	0.001	0.004	0.002	0.006	0.001
Nd ³⁺	0.022	0.005	0.047	0.007	0.017	0.005	0.035	0.006	0.028	0.019	0.047	0.004	0.018	0.014	0.022	0.002
Sm ³⁺	0.008	0.002	0.014	0.003	0.006	0.002	0.014	0.002	0.010	0.004	0.014	0.002	0.005	0.002	0.007	0.001
Gd ³⁺	0.013	0.003	0.026	0.004	0.014	0.006	0.020	0.003	0.013	0.003	0.016	0.002	0.006	0.003	0.009	0.001
Na ⁺	0.032	0.001	0.103	0.023	0.034	0.001	0.101	0.022	0.027	0.001	0.103	0.024	0.042	0.017	0.102	0.016
K ⁺	0.006	0.000	0.042	0.006	0.008	0.000	0.033	0.006	0.005	0.000	0.042	0.005	0.005	0.003	0.011	0.002
ΣA-site cations (excl. U)	1.066	0.790	1.301	0.101	1.041	0.813	1.277	0.092	1.056	0.885	1.279	0.081	1.187	0.911	1.301	0.095
Si ⁴⁺	0.439	0.291	0.744	0.068	0.429	0.291	0.604	0.049	0.437	0.296	0.744	0.076	0.424	0.340	0.494	0.036
Ti ⁴⁺	0.752	0.437	1.032	0.104	0.779	0.584	1.032	0.092	0.771	0.601	1.022	0.080	0.669	0.572	0.918	0.073
P ⁵⁺	0.005	0.000	0.033	0.004	0.005	0.000	0.033	0.004	0.005	0.002	0.016	0.002	0.001	0.000	0.011	0.002
As ⁵⁺	0.121	0.027	0.410	0.064	0.132	0.068	0.211	0.032	0.102	0.027	0.231	0.039	0.088	0.063	0.145	0.015
Nb ⁵⁺	0.003	0.000	0.023	0.004	0.002	0.000	0.018	0.005	0.004	0.000	0.015	0.004	0.000	0.000	0.001	0.000
Al ³⁺	0.018	0.000	0.138	0.021	0.004	0.000	0.022	0.005	0.035	0.001	0.138	0.018	0.001	0.000	0.001	0.000
S ⁶⁺	0.031	0.001	0.098	0.018	0.030	0.003	0.086	0.013	0.034	0.011	0.098	0.020	0.019	0.013	0.034	0.003
ΣB-site cations (excl. Si)	0.012	0.000	0.112	0.021	0.005	0.000	0.112	0.014	0.009	0.000	0.109	0.017	0.027	0.004	0.080	0.016
Σcations	0.942	0.698	1.202	0.101	0.957	0.726	1.161	0.093	0.960	0.769	1.176	0.076	0.806	0.698	1.090	0.089
A/B	0.190	0.096	0.544	0.068	0.178	0.111	0.283	0.034	0.189	0.129	0.324	0.030	0.137	0.096	0.216	0.026
ΣREY	2.007	1.940	2.205	0.042	1.998	1.951	2.076	0.025	2.016	1.940	2.205	0.053	1.994	1.966	2.048	0.015
P+As+Nb	1.157	0.658	1.865	0.246	1.110	0.700	1.753	0.226	1.112	0.758	1.639	0.169	1.500	0.836	1.865	0.257
	0.191	0.081	0.421	0.066	0.240	0.115	0.356	0.063	0.165	0.081	0.250	0.031	0.122	0.095	0.140	0.010
	0.142	0.050	0.411	0.060	0.138	0.068	0.226	0.032	0.141	0.085	0.233	0.030	0.089	0.064	0.146	0.015

Average minimum detection limit (mdl) per element for 99% confidence interval (wt.%): U $\approx$ 0.03, Si $\approx$ 0.007, Na $\approx$ 0.02, Mg $\approx$ 0.008, Al $\approx$ 0.006, P $\approx$ 0.009, S $\approx$ 0.01, K $\approx$ 0.007, Ca $\approx$ 0.005, Ti $\approx$ 0.007, Mn $\approx$ 0.03, Fe $\approx$ 0.02, Cu $\approx$ 0.03, As $\approx$ 0.02, Sr $\approx$ 0.02, Y $\approx$ 0.04, Zr $\approx$ 0.03, Nb $\approx$ 0.04, Ba $\approx$ 0.03, La $\approx$ 0.02, Ce $\approx$ 0.02, Pr $\approx$ 0.08, Nd $\approx$ 0.09, Sm $\approx$ 0.07, Gd $\approx$ 0.07, Pb $\approx$ 0.03, Th $\approx$ 0.04.

TABLE 4 Compositional data from electron probe microanalyses for coffinite-C.

Type	C1				C2				C3			
Valid <i>N</i> (analyses)	11				9				6			
(wt.%)	Mean	Min	Max	SD	Mean	Min	Max	SD	Mean	Min	Max	SD
UO ₂	47.98	45.14	50.64	1.82	48.21	45.48	50.60	1.73	51.74	46.32	64.87	6.91
SiO ₂	17.03	12.25	22.36	3.91	12.22	10.38	15.03	1.55	15.12	10.55	22.32	4.93
Na ₂ O	0.50	0.31	0.90	0.18	0.37	0.05	0.77	0.25	0.29	<mdl	1.01	0.37
MgO	0.06	0.02	0.09	0.02	0.65	0.10	2.14	0.62	0.51	0.24	0.66	0.18
Al ₂ O ₃	0.56	<mdl	1.56	0.52	0.69	0.07	1.86	0.67	0.84	0.30	1.43	0.42
P ₂ O ₅	5.16	1.26	10.58	4.33	9.93	7.71	11.43	1.26	7.96	3.38	10.12	2.61
SO ₃	<mdl	<mdl	0.05	–	1.98	<mdl	2.82	0.81	2.21	1.02	2.80	0.65
K ₂ O	0.10	0.02	0.31	0.08	0.19	0.07	0.36	0.12	0.29	0.10	0.50	0.15
CaO	1.47	0.57	2.38	0.80	3.44	1.49	3.98	0.75	3.33	2.75	3.83	0.45
TiO ₂	0.34	0.11	0.87	0.25	0.15	0.01	0.86	0.27	0.13	<mdl	0.26	0.11
MnO	<mdl	<mdl	0.08	–	0.08	<mdl	0.13	–	0.14	0.09	0.28	0.07
FeO	1.12	0.32	2.98	0.77	1.21	0.56	3.44	1.02	1.10	0.60	1.87	0.48
Cu ₂ O	0.41	0.13	0.98	0.26	<mdl	<mdl	0.12	–	0.14	<mdl	0.47	0.16
As ₂ O ₅	0.12	<mdl	0.26	0.12	0.13	<mdl	0.57	0.17	0.55	<mdl	1.05	0.42
SrO	<mdl	<mdl	<mdl	–	<mdl	<mdl	<mdl	–	<mdl	<mdl	0.05	–
ZrO ₂	0.23	0.04	0.71	0.21	0.33	0.08	0.84	0.28	0.37	0.19	0.69	0.21
Nb ₂ O ₅	<mdl	<mdl	<mdl	–	<mdl	<mdl	<mdl	–	<mdl	<mdl	<mdl	–
BaO	0.18	0.14	0.23	0.03	0.04	<mdl	0.18	0.05	<mdl	<mdl	0.03	–
Y ₂ O ₃	11.47	7.84	14.90	2.55	9.59	6.99	15.60	2.42	6.60	2.46	8.18	2.08
La ₂ O ₃	0.18	0.16	0.21	–	0.24	0.21	0.28	–	0.28	0.23	0.38	0.05
Ce ₂ O ₃	0.50	0.47	0.55	–	0.87	0.49	1.05	0.16	1.05	0.92	1.16	0.08
Pr ₂ O ₃	<mdl	<mdl	<mdl	–	<mdl	<mdl	0.21	–	<mdl	<mdl	0.19	–
Nd ₂ O ₃	0.54	0.47	0.65	–	0.83	0.37	0.97	–	0.86	0.60	0.95	–
Sm ₂ O ₃	0.24	0.17	0.30	–	0.53	0.19	0.67	–	0.49	0.27	0.56	–
Gd ₂ O ₃	1.30	0.82	1.72	0.34	1.65	1.40	1.82	–	1.33	0.55	1.63	0.39
PbO	<mdl	<mdl	<mdl	–	0.25	<mdl	0.81	0.29	0.15	<mdl	0.77	0.30
ThO ₂	0.20	<mdl	0.83	0.26	0.06	<mdl	0.24	0.08	<mdl	<mdl	<mdl	–
ΣOx	89.85	86.28	93.64	2.69	93.85	91.35	95.84	1.33	95.67	93.87	97.79	1.80

Coffinite formula (apfu) – based on 4 O

U ⁴⁺	0.279	0.229	0.319	0.027	0.257	0.237	0.268	0.009	0.276	0.218	0.416	0.072
U ⁶⁺	0.216	0.177	0.247	0.021	0.199	0.184	0.207	0.007	0.213	0.168	0.322	0.056
Th ⁴⁺	0.002	0.000	0.009	0.003	0.001	0.000	0.003	0.001	0.000	0.000	0.000	0.000
Zr ⁴⁺	0.005	0.001	0.017	0.005	0.007	0.002	0.017	0.006	0.008	0.003	0.014	0.005
Mg ²⁺	0.004	0.001	0.006	0.001	0.041	0.007	0.138	0.040	0.031	0.014	0.042	0.010
Ca ²⁺	0.071	0.031	0.115	0.036	0.156	0.072	0.179	0.033	0.149	0.118	0.173	0.023
Mn ²⁺	0.001	0.000	0.003	0.001	0.003	0.001	0.005	0.001	0.005	0.003	0.012	0.003
Fe ²⁺	0.043	0.013	0.119	0.030	0.043	0.020	0.124	0.038	0.039	0.021	0.064	0.019
Sr ²⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
Pb ²⁺	0.000	0.000	0.000	0.000	0.003	0.000	0.009	0.003	0.002	0.000	0.008	0.003
Ba ²⁺	0.003	0.002	0.005	0.001	0.001	0.000	0.003	0.001	0.000	0.000	0.000	0.000
Y ³⁺	0.280	0.191	0.350	0.053	0.218	0.160	0.377	0.063	0.144	0.067	0.184	0.041
La ³⁺	0.003	0.003	0.004	0.000	0.004	0.003	0.004	0.000	0.004	0.003	0.006	0.001
Ce ³⁺	0.009	0.007	0.010	0.001	0.013	0.008	0.017	0.002	0.016	0.013	0.020	0.002
Pr ³⁺	0.001	0.001	0.002	0.001	0.002	0.001	0.003	0.001	0.002	0.001	0.003	0.001
Nd ³⁺	0.009	0.007	0.011	0.001	0.013	0.006	0.015	0.003	0.013	0.011	0.014	0.001
Sm ³⁺	0.004	0.003	0.005	0.001	0.008	0.003	0.010	0.002	0.007	0.005	0.008	0.001
Gd ³⁺	0.020	0.012	0.025	0.004	0.023	0.020	0.026	0.002	0.018	0.009	0.022	0.005
Na ⁺	0.045	0.027	0.083	0.018	0.030	0.004	0.064	0.021	0.026	0.001	0.100	0.037
K ⁺	0.006	0.001	0.019	0.005	0.010	0.004	0.019	0.006	0.016	0.005	0.029	0.010
ΣA-site cations	1.001	0.859	1.072	0.074	1.031	0.956	1.189	0.072	0.970	0.790	1.263	0.162
. (excl.U)	0.507	0.404	0.613	0.083	0.575	0.484	0.736	0.072	0.481	0.404	0.530	0.048
Si ⁴⁺	0.789	0.542	1.022	0.195	0.519	0.437	0.617	0.067	0.621	0.445	0.829	0.157
Ti ⁴⁺	0.012	0.004	0.029	0.009	0.005	0.000	0.029	0.009	0.004	0.000	0.008	0.003
P ⁵⁺	0.194	0.050	0.396	0.159	0.356	0.296	0.410	0.040	0.277	0.146	0.359	0.083
As ⁵⁺	0.003	0.000	0.006	0.003	0.003	0.000	0.013	0.004	0.012	0.000	0.023	0.009
Nb ⁵⁺	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000
Al ³⁺	0.031	0.001	0.088	0.029	0.034	0.004	0.095	0.034	0.041	0.014	0.071	0.019
S ⁶⁺	0.000	0.000	0.002	0.001	0.063	0.001	0.090	0.026	0.068	0.039	0.089	0.018
ΣB-site cations	1.030	0.944	1.141	0.078	0.981	0.940	1.057	0.040	1.023	0.784	1.202	0.143
(excl. Si)	0.241	0.111	0.409	0.135	0.462	0.335	0.503	0.053	0.402	0.219	0.544	0.124
Σ cations	2.032	2.000	2.107	0.029	2.012	1.946	2.138	0.056	1.993	1.958	2.047	0.029
A/B	0.981	0.753	1.131	0.140	1.055	0.909	1.254	0.105	0.986	0.658	1.610	0.334
ΣREY	0.325	0.225	0.401	0.057	0.281	0.224	0.421	0.057	0.204	0.118	0.248	0.046
P + As + Nb	0.198	0.050	0.403	0.162	0.360	0.300	0.411	0.038	0.289	0.149	0.377	0.091

Average minimum detection limit (mdl) per element for 99% confidence interval (wt.%): U ≈ 0.03, Si ≈ 0.007, Na ≈ 0.02, Mg ≈ 0.008, Al ≈ 0.006, P ≈ 0.009, S ≈ 0.01, K ≈ 0.007, Ca ≈ 0.005, Ti ≈ 0.007, Mn ≈ 0.03, Fe ≈ 0.02, Cu ≈ 0.03, As ≈ 0.02, Sr ≈ 0.02, Y ≈ 0.04, Zr ≈ 0.03, Nb ≈ 0.04, Ba ≈ 0.03, La ≈ 0.02, Ce ≈ 0.02, Pr ≈ 0.08, Nd ≈ 0.09, Sm ≈ 0.07, Gd ≈ 0.07, Pb ≈ 0.03, Th ≈ 0.04.

(4) 43.6% of U present as U^{6+} (see below); (5) Fe present as Fe^{2+} as it probably occupies the *A*-site and there are known charge balance mechanisms which use Fe^{2+} rather than Fe^{3+} (see below); (6) S^{6+} and Fe^{2+} assumed to be contained in coffinite, with no correction made for any S or Fe contained within Cu-(Fe)-sulfides; and (7) any anion substitution (e.g. F^- , $(OH)^-$ or CO_3^{2-} for O^{2-}) considered insignificant. To highlight the chemical variability between coffinite groups, in addition to the total cations and *A*- and *B*-site cation totals, values for *A/B*, ΣREY and $(P + As + Nb)$ are included in the tables. When discussing compositional variability of brannerite or coffinite hereafter, Y is combined with the other *REE* (ΣREY), but in the case of coffinite, where Y is typically much higher, the contents of *REE* and Y have sometimes been separated.

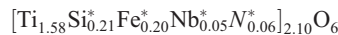
Composition of brannerite

The means and compositional ranges for each brannerite class are given in Table 2. The mean composition for all brannerite analysed in this study ($n = 395$) is 41.13 wt.% UO_2 , 34.34 wt.% TiO_2 , 4.14 wt.% SiO_2 , 1.96 wt.% CaO , 4.83 wt.% Fe_2O_3 , 0.69 wt.% Na_2O , 0.77 wt.% Nb_2O_5 , 2.85 wt.% ΣREY_2O_3 and 0.40 wt.% PbO , with a mean analytical total of 94.90 wt.%.

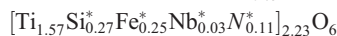
Calculated formulae were derived initially by normalization to 6 O atoms, but cation totals typically ranged from 2.85–3.24, rather than the ideal 3.0. Only 122 of 395 analyses had a cation total in the range 2.95–3.05. A method was thus devised to see whether allocation, by iteration, of some U^{4+} to U^{6+} might improve these cation totals. It was found that if 74% of total U was assumed to be U^{6+} , then 73% of analyses (291 of 395) would have cation totals within an acceptable range. This assumption seems plausible given that brannerite compositional analyses by wet chemical methods (e.g. Pabst, 1954; Whittle, 1954) yield ~75% U as UO_3 , with the remainder as UO_2 . More recently, multiple U valencies (U^{4+} , U^{5+} and U^{6+}) have been identified in brannerite (e.g. Finnie *et al.*, 2003; Vance *et al.*, 2015), further supporting the validity of the multiple U valence assumption.

In terms of site occupancy for brannerite, the *A*-site typically contains 0.37–0.71 apfu $U^{4+} + U^{6+}$, and up to 0.46 apfu other cations, which includes a maximum of 0.32 apfu Ca^{2+} and 0.24 apfu ΣREY^{3+} (Table 2). Similarly, the *B*-site typically contains 1.23–2.04 apfu Ti^{4+} , and up to 1.16 apfu other *B*-site cations, including a maximum of 0.52 apfu Si^{4+} ,

0.43 apfu Fe^{3+} , 0.23 apfu Na^+ , 0.13 apfu Al^{3+} and 0.12 apfu Mg^{2+} . The *A*-site cation totals range between 0.46–1.01 apfu, with a mean of 0.79 apfu; whereas the *B*-site cation totals range between 2.01–2.58 apfu, with a mean of 2.23 apfu. However, total cations (*A* + *B*) tend to range between 2.92–3.30 apfu, with a mean of 3.02. The marked deviation from ideal 1.0 apfu *A*-site and 2.0 apfu *B*-site totals indicates there is significant replacement within both sites, with charge compensation and possibly, also vacancies (see below). For each brannerite class, an empirical formula can be given based on mean composition (Table 2):



where $M^* = \Sigma(Sr, Ba, Pb, Th)$, $Si^* = \Sigma(Si, Zr)$, $Fe^* = \Sigma(Fe, Al)$, $Nb^* = \Sigma(Nb, As)$ and $N^* = \Sigma(Mg, Mn, K, Na)$. The mean formula for all analyses can be given as:



In comparison with this average, brannerite-B and -C (Figs 2 and 3*a,b*) contain the largest amounts of U (0.61 apfu). The highest M^* and ΣREY values of 0.04 and 0.14 apfu, respectively, are noted for brannerite-D (Fig. 3*c-f*). The amount of Ca is highest in brannerite-B (0.16 apfu; Fig. 2*a-c*). Thus, brannerite-B and -D have the highest *A*-site totals (both 0.86 apfu). The ideal *A*-site total is 1.0 apfu, therefore these low *A*-site totals highlight a deficiency in *A*-site cations. All brannerite types have similar Ti contents (1.55–1.58 apfu), with the highest Si^* content for brannerite-D (0.30 apfu), and lowest for brannerite-B (0.21 apfu). All other *B*-site cations for the different brannerite types contain variable amounts of other impurities; Fe^* and N^* are highest in brannerite-A (0.27 and 0.15 apfu, respectively), and Nb^* the highest for brannerite-B (0.05 apfu). *B*-site totals deviate from the ideal 2.0, ranging from 2.10 (brannerite-B) to 2.29 (brannerite-A), highlighting that *B*-site cation totals are commonly in excess.

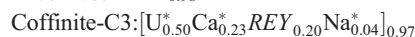
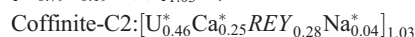
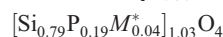
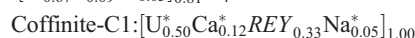
Composition of coffinite

The mean and compositional range for each coffinite group are given in Tables 3 and 4. The mean composition for all analysed coffinite ($n = 380$) is 58.44 wt.% UO_2 , 15.79 wt.% SiO_2 , 3.05 wt.% P_2O_5 , 2.19 wt.% CaO , 1.81 wt.% FeO , 0.11 wt.% As_2O_5 , 4.78 wt.% Y_2O_3 , 0.84 wt.% Nb_2O_5 , 4.20 wt.% $\Sigma\text{REE}_2\text{O}_3$, with a mean analytical total of 93.99 wt.%.

Initially, the formula of coffinite was calculated by normalization to 4.00 O atoms, but cation totals were all above the ideal 2.0 (2.05–2.34). Using a similar method to that derived for brannerite, we varied the amount of U^{4+} and U^{6+} to see if this could improve the cation totals to a more acceptable range (1.95–2.05). It was found that if 43.6% of total U was assumed to be U^{6+} , then 85% (i.e. 296/380) of analyses had cation totals in the acceptable range. As with brannerite, the U content of coffinite in most published work is reported as a single oxide, but U^{6+} has been recognized in some natural coffinite (e.g. Goldhaber *et al.*, 1987). The likelihood that both U^{4+} and U^{6+} are present within natural coffinite may be strengthened by the possible substitution of Ca^{2+} , which involves both U cations (see below). The addition of H^+ (protons) in the form of H_2O , or $(\text{OH})^-$ in lieu of, or in addition to the presence of U^{6+} could also aid charge balance, thus providing another mechanism to support the presence of U^{6+} . However, the presence of both U^{6+} and structural water (OH^- or H_2O) has not been confirmed for natural crystals, and some recent spectroscopic studies of synthetic coffinite (e.g. Clavier *et al.*, 2014) have shown that coffinite contains neither U^{6+} (in the form of UO_2^{2+}) nor structural water (either OH^- or H_2O). This observation may hold true for synthetic coffinites, but for natural samples the effects of hydrothermal alteration and/or the degradation caused by metamictization may allow for the presence of UO_2^{2+} and/or $(\text{OH}^-)/\text{H}_2\text{O}$ within coffinite.

For coffinite of the form ABO_4 , the A site typically contains 0.39–0.85 apfu $\text{U}^{4+} + \text{U}^{6+}$, and up to 0.74 apfu other A-site cations, including a maximum of 0.23 apfu Ca^{2+} , 0.33 apfu Fe^{2+} , 0.14 apfu Mg^{2+} , 0.10 apfu Na^+ and 0.61 apfu ΣREY^{3+} (Tables 3 and 4). Similarly, the B-site typically contains 0.44–1.03 apfu Si^{4+} , and up to 0.54 apfu other B-site cations, including a maximum of 0.41 apfu P^{5+} , 0.14 apfu Nb^{5+} , 0.11 apfu S^{6+} , 0.10 apfu Al^{3+} . The A-site cation totals range between 0.79–1.30 apfu, with a mean

of 1.07 apfu; whereas the B-site cation totals range between 0.70–1.20 apfu, with a mean of 0.94 apfu. Cation totals tend to range between 1.94–2.21 apfu, with a mean of 2.01. The deviations from the ideal 1.0 apfu A- and B-site totals indicates there is some replacement within both the A- and B-sites of coffinite; exchange mechanisms are discussed below. The A/B ratios are mostly >1 (ranging from 0.66 to 1.87) and with a mean of 1.16 for all coffinite data. Typically, $A > B$ for all coffinite groups except coffinite-C1 and -C3. For each coffinite grouping an estimate of the chemical formula based on the mean composition (Tables 3 and 4) can therefore be made:



where $\text{U}^* = \Sigma(\text{U}, \text{Th}, \text{Zr})$, $\text{Ca}^* = \Sigma(\text{Ca}, \text{Fe}, \text{Mg}, \text{Mn}, \text{Sr}, \text{Pb}, \text{Ba})$, $\text{Na}^* = \Sigma(\text{Na}, \text{K})$, $\text{Nb}^* = \Sigma(\text{Nb}, \text{As})$ and $\text{M}^* = \Sigma(\text{Ti}, \text{Al}, \text{S})$. The average formulae for coffinite (all 380 analyses) is:



From the estimated formula for the different coffinite groups compared to the average, coffinite-B (coffinite associated with uraninite; Fig. 5) contains the most U^* (0.77 apfu) and Ca^* (0.25 apfu), lowest ΣREY (0.12 apfu) and has the highest A-site totals (1.19 apfu). Conversely, it has the lowest P content (0.09 apfu) and B-site totals (0.81 apfu) of all coffinite types. Coffinite-C1 (coffinite associated with brannerite; Fig. 6a–c) has the highest ΣREY content (0.33 apfu), lowest Ca^* content (0.12 apfu), an A-site total close to parity and Si content (0.79 apfu) the highest of all coffinite. Some brannerite is found in close proximity to REY-bearing minerals (i.e. Fig. 2a–c) and typically contains some ΣREY . Coffinite-C2 and

-C3 have the highest M^* content; 0.10 and 0.11, respectively. Coffinite-A does not contain a unique concentration of any particular element, but represents the majority of coffinite analysed, although coffinite-A2 does have the highest Nb* content (0.04 apfu), albeit this value is low compared to the more dominant substituents.

Discussion

Compositional trends for brannerite

Compositional variability in terms of substitution at the *A* and *B* sites is summarized in Figs 9 and 10. Potential *A*-site substituents are plotted against total U (Fig. 9), and for the total *A*-site cations excluding U (Fig. 9a) no clear trend is discernible. However, if selected *A*-site substituents are plotted individually, several trends are evident. There is a strong negative correlation between ΣREY and total U for brannerite with elevated ΣREY (brannerite-B to -D), with a slope of -0.92 for the line of best fit. Plotting Pb against total U (Fig. 9c) gives the same strong negative correlation for brannerite-B to -D. Brannerite-A has the least ΣREY , Pb and other *A*-site substituents when compared to other brannerite groups. Addition of other divalent cations (Ca, Sr and Ba) to Pb does not change the negative correlation with U (Fig. 9d). Although Ca is the second most abundant *A*-site cation (0.13 apfu for all analyses), there is no discernible relationship when plotted against U (Fig. 9d). Thus, as suggested by Lumpkin *et al.* (2012), coupled substitutions involving Ca and *B*-site cations, or oxygen and hydroxyl groups may explain the observed patterns.

A plot of *B*-site substitutions vs. Ti is shown in Fig. 10. In most cases, a negative correlation between a particular element and Ti is observed, indicative of substitution for that element. The same negative correlation is seen between total *B*-site cations (excluding Ti) with Ti (Fig. 10a). There are, however, two distinct trends, with brannerite-A typically having a broader range of both Ti values and total *B*-site cation contents than brannerite-B to -D. The slope of the trend for brannerite-A is also shallower (cf. -0.57 vs. -1.68). The total *B*-site occupancies for brannerite-B to -D are also closer to the ideal (2.0) than brannerite-A, highlighting the observation that brannerite-A has greater levels of *B*-site substitution than the other groups, or that brannerite-B to -D represents purer examples of brannerite.

Considering the key elements involved in *B*-site substitution, the trends for total *B* site (excluding

Ti) vs. Ti (Fig. 10a) and for Si vs. Ti (Fig. 10b), are similar. Brannerite-A displays a shallower slope (-0.57 and -0.24 , respectively) than the trend for brannerite-B to -D (-1.68 and -1.54 , respectively). All brannerite shows a broad range of Si content (0.13–0.52 apfu). The role of Si in brannerite is unclear. Lumpkin *et al.* (2012) suggest it occupies the *B* site, but admit this is questionable as they only found a weak correlation between Si and Ti.

The divalent cations Mg and Mn are combined with monovalent Na and K apfu contents and plotted against Ti (Fig. 10c). The trends are analogous if each element is plotted individually. These four elements typically reflect lower temperature hydrothermal alteration, and are thus sensibly combined onto a single plot. The (Mg + Mn + Na + K) content of brannerite-A varies (slope of -0.19 for line of best fit), but has a negative trend; whereas for brannerite-B to -D, there is no apparent trend and the data cluster together. Brannerite-A contains more (Mg + Mn + Na + K) than the other brannerite groups.

The trivalent cations Fe and Al have also been combined and plotted against Ti (Fig. 10d). The negative trend is less discernible than for the above, however brannerite-A still appears to have a negative correlation (slope of -0.13 for line of best fit). On average, brannerite-A contains more (Fe + Al) than brannerite-B to -D. Observed scatter in this plot may be due to the presence of both Fe^{2+} and Fe^{3+} , or could indicate the simultaneous presence of these elements in the *A*- and *B*-sites.

Elevated Nb^{5+} occurs within brannerite-D (Fig. 10e), whereas As^{5+} is elevated within brannerite-B and -C (Fig. 10f). For both elements, the data appear to cluster rather than form a trend. However, the brannerite-A data exhibit a slight negative trend for As, even if As contents are low (usually <0.013 apfu).

Trace-element substitution into brannerite

Our results demonstrate the highly variable composition of brannerite at Olympic Dam. Uranium is clearly replaced by significant, though variable amounts of Ca and ΣREY with up to 32 and 24%, respectively, of the *A* site occupied by these substituents. These results are concordant with Lumpkin *et al.* (2012), who found that the *A* site may contain appreciable Ca, Th and ΣREY (up to 50–60% of the total *A*-site substituents). Mechanisms responsible for their incorporation into the *A*-site are poorly documented, but are most

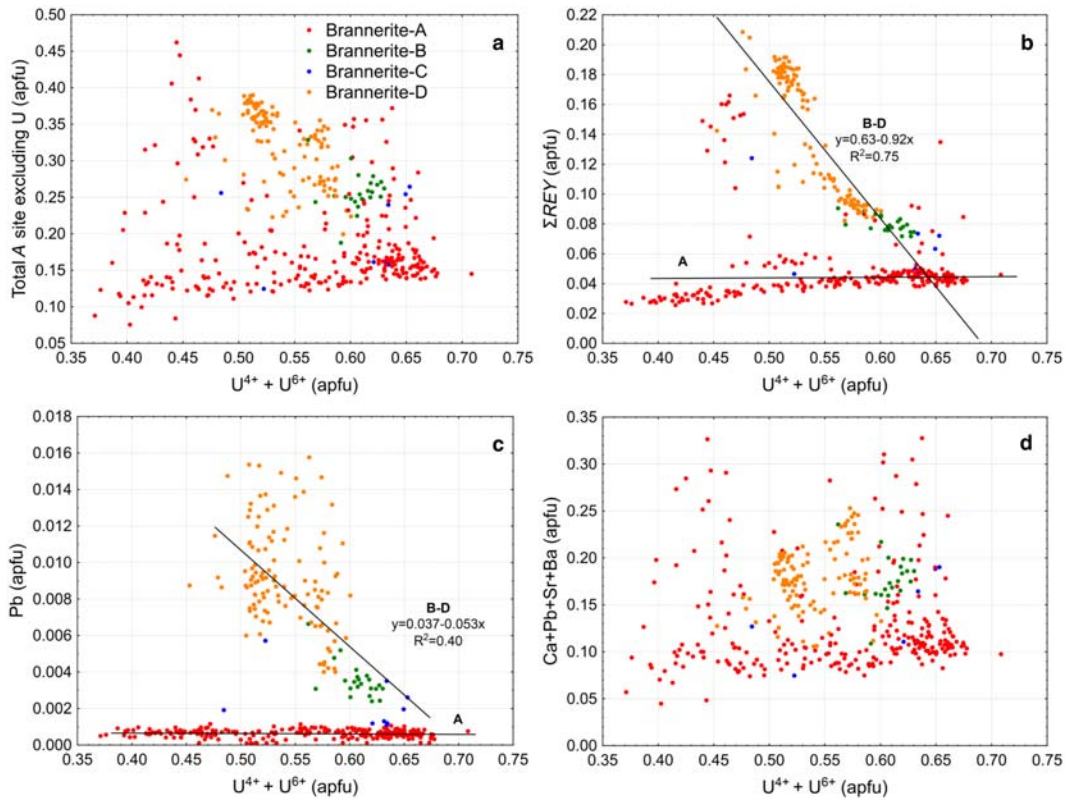
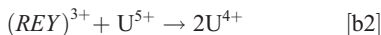


FIG. 9. Scatterplots of selected *A*-site cations vs. total U content of brannerite in atoms per formula unit (apfu); (a) Total *A*-site cations excluding U^{4+} and U^{6+} (i.e. Ca^{2+} , Sr^{2+} , Ba^{2+} , ΣREY^{3+} , Pb^{2+} , Th^{4+}) display no discernible trend with total U; (b) ΣREY show a negative correlation with total U, especially for brannerite-B to -D. Brannerite-A has a lower ΣREY content, so the line of best fit is almost horizontal; (c) Pb has a negative correlation with total U, especially for brannerite-B to -D. Again, the low-Pb content of brannerite-A yields a horizontal line of best fit; (d) the addition of Ca, Sr and Ba to Pb content causes more scatter and provides less information than that gained by (c).

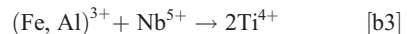
likely to be:



Both coupled substitutions are plausible and would account for the observed correlations. Other cations for which mechanism [b1] may be relevant include Sr^{2+} , Ba^{2+} and Pb^{2+} . Diffuse reflectance spectroscopy and X-ray photoelectron spectroscopy (e.g. Vance *et al.*, 2001; Finnie *et al.*, 2003), has shown that synthetic brannerite contains U^{5+} , aiding charge balance to facilitate incorporation of Ca and ΣREY .

The Ti content of brannerite also varies, but appears less variable than U, with ~20% of the *B* site occupied by substituents (Si, Fe, Na, Al, Nb, Zr,

Mn, Mg, K and As), concordant with Lumpkin *et al.* (2012). Coupled *B*-site substitution of potential applicability here is:



Niobium is, however, not always present and mechanism [b3] may only partly explain Fe and Al substitution. For Olympic Dam brannerite, As^{5+} is also present in some brannerite and could readily join Nb^{5+} in mechanism [b3]. Arsenic-for-Ti exchange is plausible, although it has not been previously documented in brannerite. Charge balance for cations with lesser valencies than $4+$ introduced into the *B*-site (i.e. Fe^{3+} , Mn^{2+} , Mg^{2+} , Na^{+} and K^{+}), could also be achieved by the addition

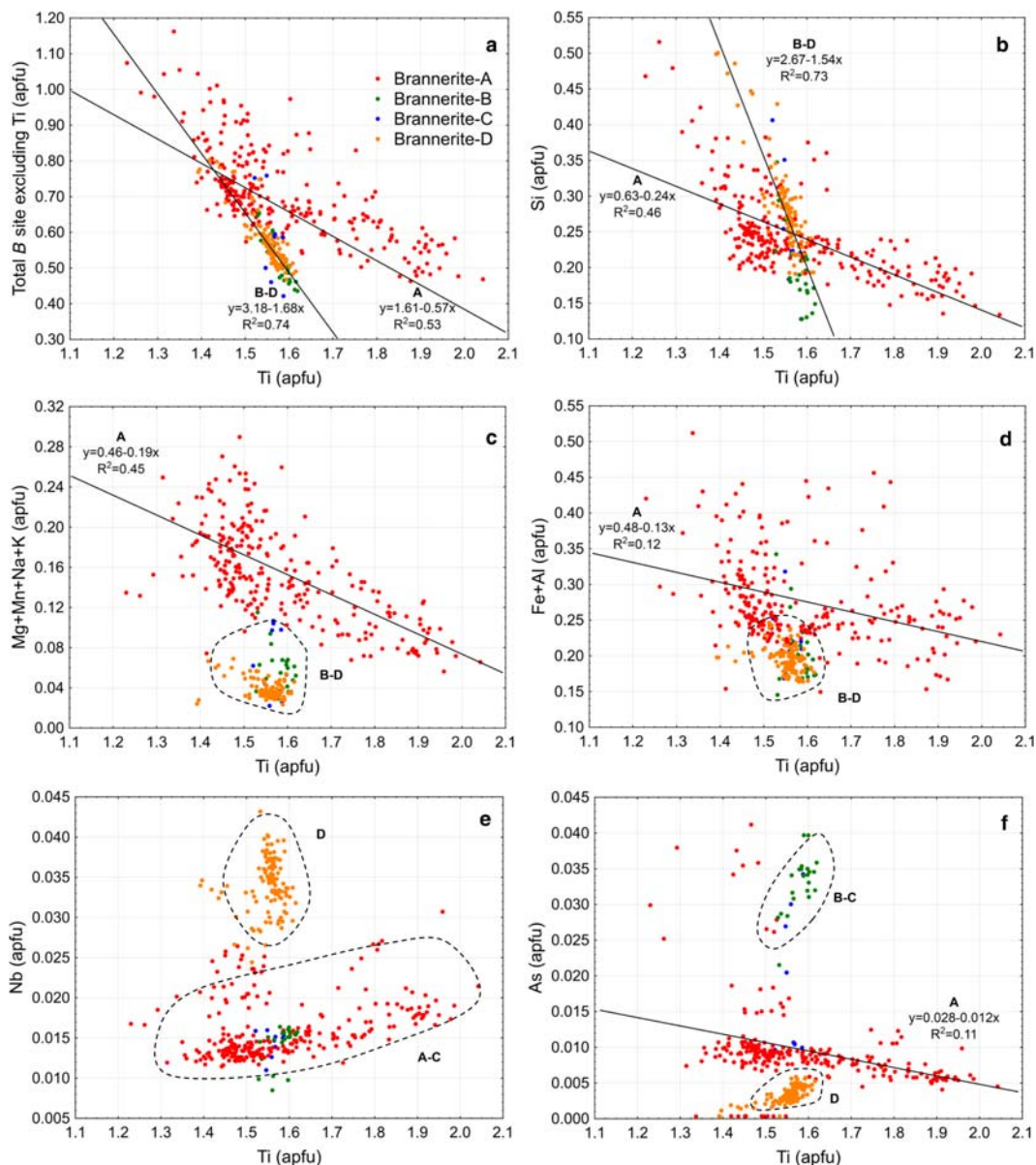


FIG. 10. Scatterplots of selected *B*-site cations vs. Ti content of brannerite (apfu); (a) total *B*-site cations excluding Ti^{4+} (i.e. Si^{4+} , Na^+ , Mg^{2+} , Al^{3+} , K^+ , Mn^{2+} , Fe^{3+} , As^{5+} , Zr^{4+} and Nb^{5+}) display two clear negative correlations. Brannerite-A appears to span a greater Si and Ti range compared to brannerite-B to -D; (b) Si has a negative correlation with Ti, again with data for brannerite-B to -D having a steeper line of best fit compared to data for brannerite-A; (c) divalent Mg and Mn with monovalent Na and K have a negative correlation with Ti, especially for brannerite-A as shown by line of best fit. Brannerite-B to -D data cluster (circled by dashed line) beneath the line of best fit; (d) trivalent Fe and Al only display a weak negative correlation with Ti. Brannerite-B to -D data cluster (circled by dashed line) beneath the line of best fit; (e) Nb data tend to cluster (circled by dashed lines) rather than form trends with Ti, with brannerite-D having the highest Nb content; (f) As data also tend to cluster (circled by dashed lines) rather than form trends with Ti. However, there is a negative correlation for brannerite-A and brannerite-B and C have the highest As contents.

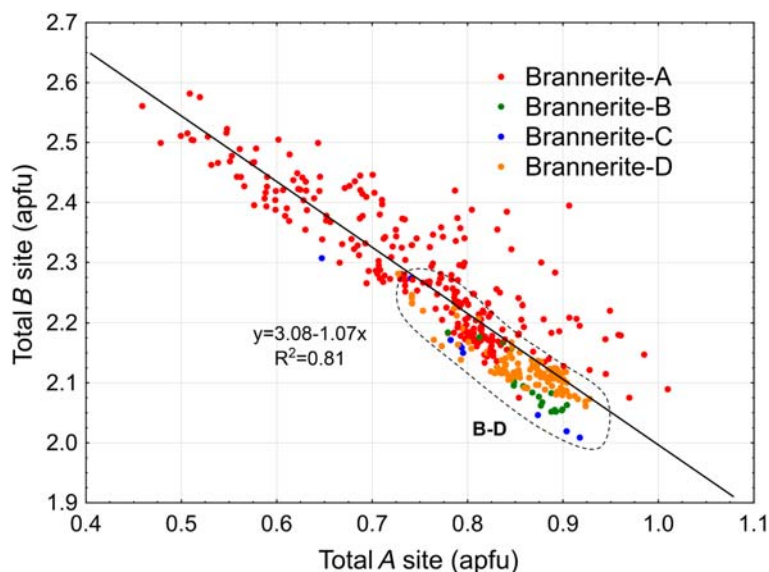
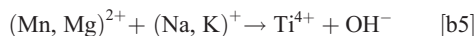


FIG. 11. Scatterplot of total *B*-site cations vs. total *A*-site cations for brannerite (apfu). There is generally a surplus of *B*-site charge (i.e. values above the ideal 2.0) and a deficit of *A*-site charge (i.e. values below the ideal 1.0). Data circled by a dashed line represent brannerite-B to -D which have totals closest to ideal.

of $(\text{OH})^-$, i.e.:



Substitutions [b4] and [b5] are, however, speculative and require confirmation by Raman infrared spectroscopy. Natural radiation-damaged brannerite can contain appreciable H_2O (up to 7.4 wt.% at Crocker's Well; Ludwig and Cooper, 1984), thus supporting charge compensation by $(\text{OH})^-$.

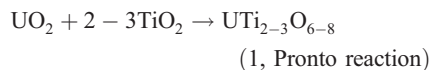
Silicon displays a negative correlation with Ti (Fig. 10b) but it is unclear whether Si can directly substitute for Ti. It is known that Si is unlikely to substitute for Ti in octahedral coordination above trace levels at low pressures, and is thus thought to occupy interstitial rather than structural sites (Lumpkin *et al.*, 2012). Detailed characterization at the nanoscale is required to ascertain whether Si is an interstitial and/or a structural component of brannerite.

Figure 11 and Table 2 clearly show there is generally a surplus of *B*-site occupancy (i.e. above ideal 2.0 apfu) and a corresponding deficit in the *A* site (i.e. below ideal 1.0 apfu). This observation supports a coupling of substitutions across the two sites. Furthermore, there is less variability of total

A- and *B*-site values for brannerite-B to -D (circled with dashed line on Fig. 11).

Brannerite formation

Formation of brannerite is generally linked to decomposition of ilmenite in the presence of U-bearing hydrothermal fluids, and the subsequent adsorption of U onto the surface of decomposing ilmenite (e.g. Ferris and Ruud, 1971). This process was originally described by Ramdohr (1957), who suggested brannerite forms *in situ* via the 'Pronto reaction' where uranium migrates to Ti-rich phases, or titanium to uraninite, forming U-titanite:



The reaction results in the formation of 'uraninite ghosts': fine-grained brannerite splinters rimming the peripheries of abraded uraninite. Brannerite thus pseudomorphs rutile laths which are, in turn, originally derived from ilmenite. The 'Pronto reaction' (1) is thought to occur under hydrothermal conditions at temperatures of $\sim 225^\circ\text{C}$ (Schidlowski, 1966).

Ramdohr (1957) and Schidlowski (1966) relate rutile to the decomposition of ilmenite but do not

directly relate brannerite textures to those of ilmenite; however, this is covered by Ferris and Ruud (1971). Ilmenite is known to alter in stages so that any given grain may contain variable stringers, lamellae, patches and rims of material which differ, both crystallographically and chemically, from the original ilmenite (Lynd, 1960). This results in a mineral aggregate which has multiple Ti-bearing phases and leads to differential uptake of U. Iron is always removed.

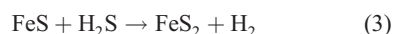
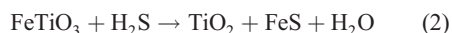
Olympic Dam brannerite commonly displays variable composition and in some cases, displays evidence of further geochemical alteration by the presence of alteration rims (Figs 2d and 3a). Incorporation of Si, Ca, Na, ΣREY , Fe, Nb, As etc., substituting for U and Ti, are all potentially sourced from interactions with hydrothermal fluid(s). The variable U content of Olympic Dam brannerite may be due to limited and/or variable supply of uranium to the sites of decomposing ilmenite, or alternatively due to oversupply of Ti and other elements. The compositional diversity observed may also reflect alteration of pre-existing brannerite. This may be particularly important for brannerite-C (Figs 2d and 3a) which shows evidence of marginal alteration. Notably, all Olympic Dam brannerite has low-Th content (<mdl–1.38 wt.% ThO₂). It is known that uraninite formed at lower temperatures (<250°C) characteristically contains less Th than if formed at >350°C (e.g. Hazen *et al.*, 2009). Sodium content is also used commonly to reflect low-temperature hydrothermal alteration. The Na content of all Olympic Dam brannerite is fairly constant (0.05–1.88 wt.% Na₂O).

A key observation for Olympic Dam brannerite is that those with the highest U, typically occur on the margins of the brannerite-rutile-hematite aggregates (e.g. Fig. 1a), and this grades into uraniferous rutile with lesser U towards the aggregate centre. Ferris and Ruud (1971) explained this phenomenon using absorption of U onto titanogels. Titanogels and titanium oxyhydroxides are known to have high sorptive capacities for weak uranium solutions (Davies *et al.*, 1964; Yermolayev, 1971). The transformation of ilmenite into various Ti-rich phases may have occurred progressively from the outside inwards, one surface layer at a time, forming a titanogel or analogous compound. Thus, as replacement progressed, rutile was formed from ilmenite in the presence of a U-bearing solution, and TiO₂ incorporated U within each crystallized layer. The rate of formation of rutile or the precursor titanogel and the concentration of U in solution would ultimately control the

composition(s) of the precipitating brannerite, and where little or no U was available, only rutile (or anatase) would form. The observed textural variability can therefore be explained by a process such as this, where within brannerite containing aggregates, there is a mix of brannerite laths, and partially replaced uraniferous rutile, all with differing U concentrations. The mix of brannerite and rutile layers can be explained in terms of fluctuating U content in the fluid.

Replacement of ilmenite by rutile in an acidic environment was explored by Janssen *et al.* (2010), invoking coupled dissolution-reprecipitation (CDR) reaction (Putnis, 2002). Janssen *et al.* (2010) found that alteration begins at the original ilmenite crystal surface and moves inwards along fractures generated by the volume changes associated with ilmenite dissolution, and there is simultaneous reprecipitation of rutile (i.e. pseudomorphic replacement of the original ilmenite with rutile). This may also be applicable to brannerite, with the key difference being the presence of U within a hydrothermal fluid. Geisler *et al.* (2005) showed clear evidence that alteration of crystalline pyrochlore-type ceramics [(Ca,Nb,Sr)₂(Ta,Nb,Ti,Si)₂O₆F)] is CDR-controlled rather than a function of diffusion-controlled leaching.

To explain the association of brannerite with sulfides, Ferris and Ruud (1971) use the work of Gruner (1959) to show that H₂S-saturated fluids will react with ilmenite to form rutile and pyrite at >220°C:



Adams *et al.* (1974) alternatively suggest that alteration of magnetite and ilmenite by O₂-deficient groundwaters can occur at Eh<–0.2 and pH<7. Pyrite and uraninite would be preserved but the reaction still allows for decomposition of both magnetite and ilmenite as temperatures decrease. This may be applicable to Olympic Dam brannerite, which typically is associated with sulfides and baryte.

Another key parameter to be considered in the formation and alteration of brannerite is the role of radiation damage. In older brannerite which displays substantial radiation damage, the Pb content is expected to be higher, assuming that lead has not migrated from the parent mineral. Lead may serve as a network modifier, particularly when accompanied by elevated Si, as the Ti–Si–O framework allows for retention of radiogenic Pb

(Lumpkin *et al.*, 2012). However, losses of significant amounts of radiogenic Pb from brannerite (~40%; Lumpkin *et al.*, 2012) have also been reported, and in these cases brannerite typically contains abundant fine galena particles. This has been attributed to local trapping of Pb, whereby brannerite has been exposed to fluids containing S (e.g. Lumpkin *et al.*, 2012 and references therein).

Overall, Olympic Dam brannerite contains low concentrations of Pb (<mdl–1.93 wt.% PbO), thus either indicating that the various types of brannerite are young (i.e. insufficient time for significant production of radiogenic Pb), or that Pb has been mobilized out of brannerite. The only brannerite at Olympic Dam found in close proximity to galena is brannerite-D. There are three possible explanations for the spatial association of galena and brannerite. Firstly, galena may be non-radiogenic and trapped within brannerite during initial mineralization, an interpretation supported by the abundant co-existing sphalerite within these samples. Alternatively, brannerite-D may represent an older generation of brannerite from which radiogenic Pb has not migrated from the parent mineral but instead formed galena. This is supported by the distinctive trace-element signature of brannerite-D, with higher ΣREY than all other brannerite types. A final possibility is that the abundance of contained galena in brannerite-D relates to decay or replacement of pre-existing uraninite.

Compositional trends for coffinite

To further understand element variability within the different coffinite groups, the most strongly correlating elements in the *A*- or *B*-sites are plotted (Figs 12 and 13). In some cases, the data for coffinite-B have distinct trend lines which differ to those of the overall coffinite dataset, highlighting key compositional differences. Firstly, some of the *A*-site substitutions are considered: Ca vs. total U (Fig. 12a); and ΣREY vs. total U (Fig. 12b). Calcium correlates positively with U whereas ΣREY shows a broadly negative correlation with U. The line of best fit for coffinite-B data (Fig. 12a) is offset to that of the bulk of the coffinite analyses, indicating that coffinite-B contains more Ca than the other coffinite types. A positive correlation between Ca and U is expected because, as shown by varying the brightness and contrast of some of the coffinite globules (Figs 4b and 5b,c), the brighter coffinite always contains more Ca and U

than the duller coffinite, which is instead elevated in Si. The ΣREY content of coffinite-B (Fig. 12b) is lower than in the majority of coffinite analyses, but there is nevertheless a slight positive correlation between ΣREY and total U for coffinite-B, contrasting with the negative correlation seen for the majority of analyses. One explanation for the observed differences between coffinite-B and other coffinite types is that coffinite-B may actually consist of a mixture of (U,Si)-phases rather than individual crystals of coffinite.

Plotting *A*-site Ca against *B*-site Si (Fig. 12c) reveals a negative correlation. Again, the line of best fit for coffinite-B appears offset to that of the other coffinite types, but the trends are similar. Pentavalent P, As and Nb plotted against Si (Fig. 12d) shows a broadly negative correlation, except for coffinite-B for which there is a slight positive correlation. Clear differences in brightness and contrast were observed on BSE images of individual coffinite globules of coffinite-B (Fig. 5a–c). These were attributed to higher Si and P (duller coffinite), or higher ΣREY , Ca and Fe content (brighter coffinite). The positive correlation between Si and P is unusual, and only applies to coffinite-B. An inverse relationship would be expected if Si and P contents were directly coupled.

Plotting ΣREY against $\Sigma(P,As,Nb)$ (Fig. 12e) shows a positive correlation, but if coffinite analyses with the greatest ΣREY or $\Sigma(P,As,Nb)$ contents are removed, there is no apparent relationship. This implies that these two variables alone do not control element-substitution patterns.

As expected, *B*-site Si content (Fig. 12f) has a negative correlation with *A*-site $\Sigma(U,Th,Ca)$. To achieve charge balance, coffinite with the highest U content would be expected to have the lowest Si content and *vice versa*.

Overall, a negative correlation between total *B*-site cations vs. total *A*-site cations is observed (Fig. 13a). The ideal totals for both the *A*- and *B*-site totals are 1, and hence for comparison the 1:1 line is superimposed on the figure. Our data closely fit the 1:1 relationship, although *A*-site totals commonly exceed *B*-site totals causing the slope of the line to shift slightly downwards (slope of –0.91).

All analyses for the *A*-site cations plot near the U apex on a U– ΣREY –Ca ternary plot (Fig. 13b). Two distinct trends are, however, identifiable: (1) coffinite-C appear to have elevated ΣREY ; and (2) coffinite-B contain the least ΣREY , but the most Ca. This may indicate formation of coffinite from fluids of differing local chemistries, or as mentioned

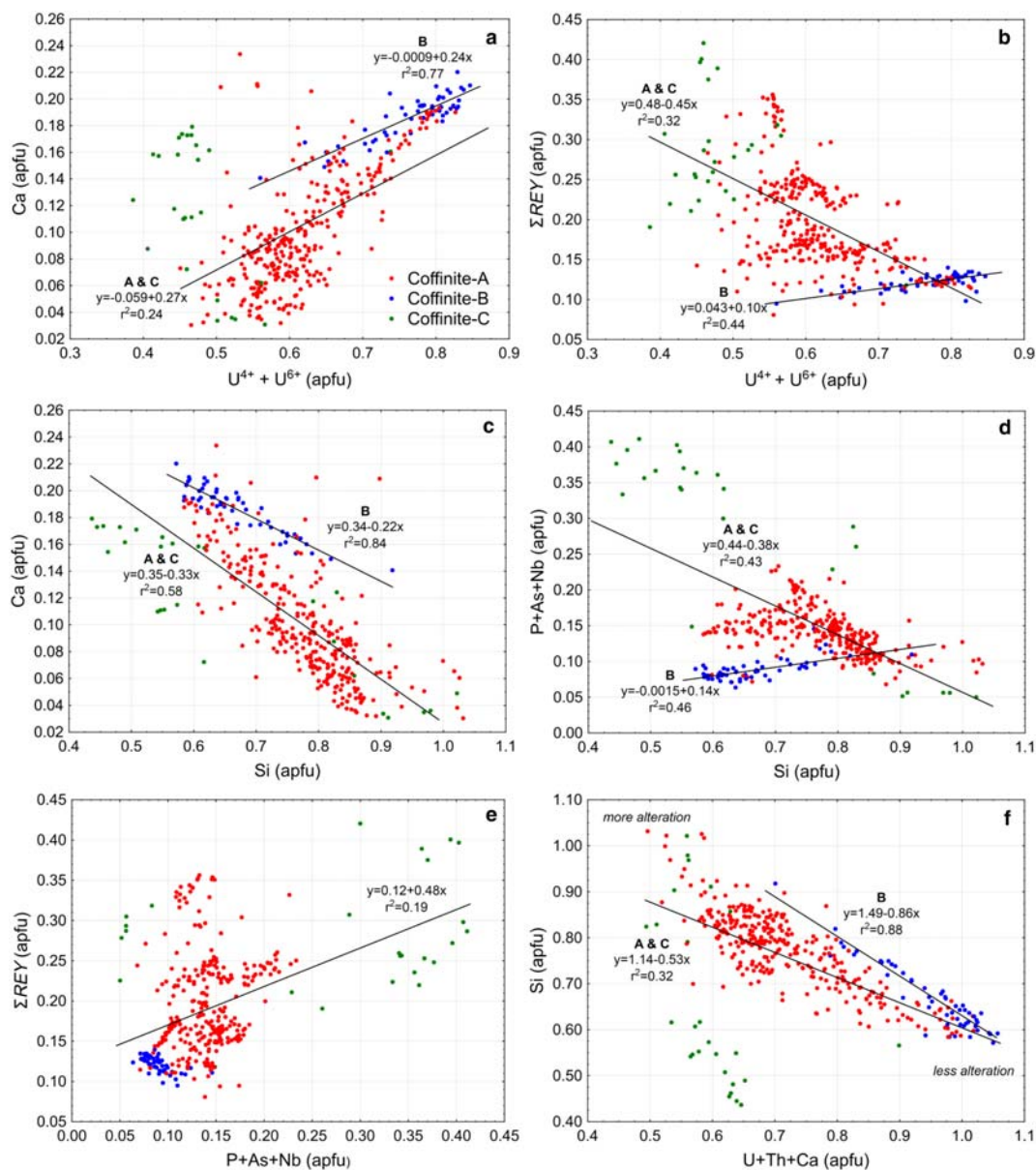


FIG. 12. Scatterplots of selected *A*- and *B*-site cations for coffinite (apfu); (a) Ca vs. total U shows a positive correlation; (b) ΣREY vs. total U has an overall negative correlation, with the low ΣREY content of coffinite-B causing the line of best fit to be almost horizontal; (c) Ca vs. Si has a negative correlation; (d) $\Sigma(P,As,Nb)$ vs. Si has a negative correlation for all coffinite types except coffinite-B; (e) ΣREY vs. $\Sigma(P,As,Nb)$ has an overall positive correlation; (f) Si vs. $\Sigma(U,Th,Ca)$ has a negative correlation.

above, may be linked to coffinite-B consisting of a mixture of (U,Si)-phases compared to the other coffinite types which are more akin to individual coffinite crystallites.

Trace element substitution into coffinite

Several substitution mechanisms are reported to occur in coffinite to balance charge (Hansley and

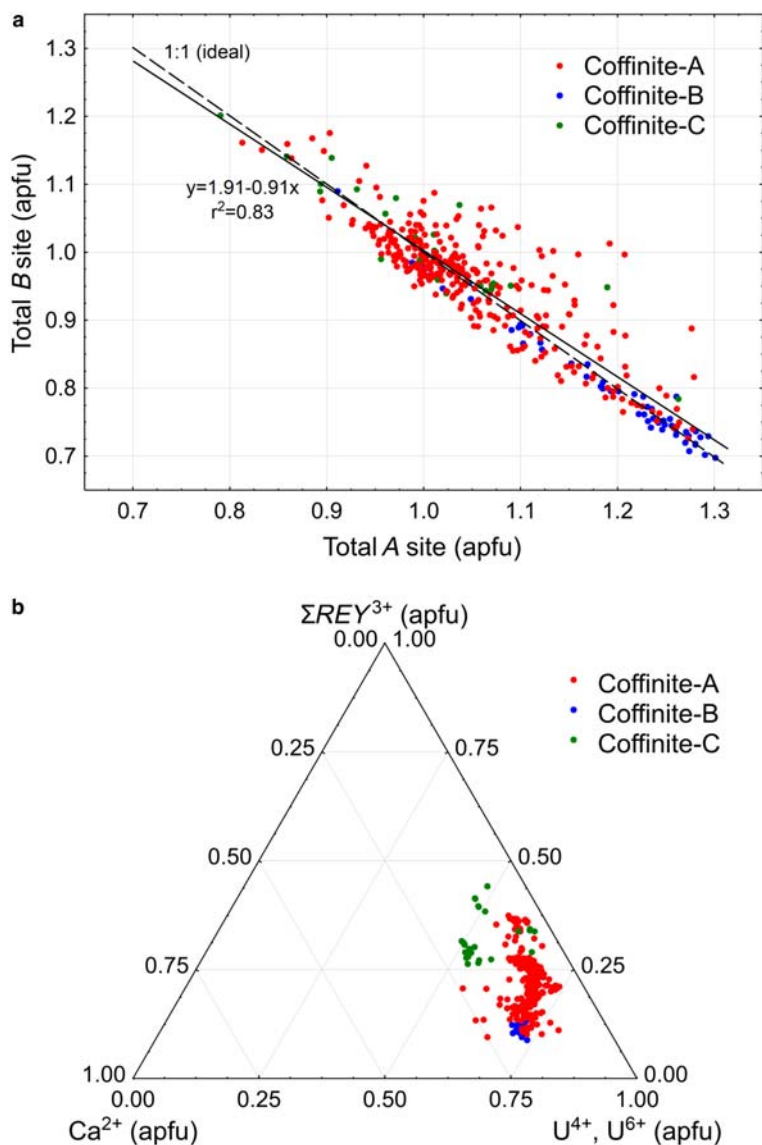
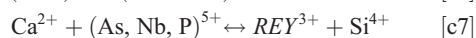
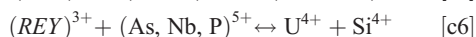
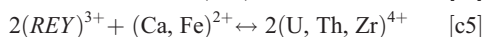
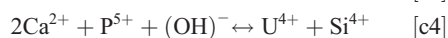
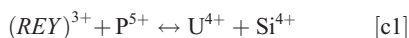
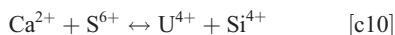
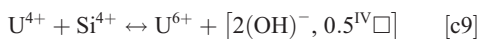
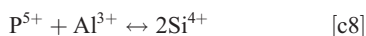


FIG. 13. (a) Scatterplot of total *B*-site cations vs. total *A*-site cations for coffinite (apfu). There is a negative correlation close to the expected 1:1; (b) Ternary plot of ΣREY^{3+} vs. $U^{4+} + U^{6+}$ and Ca^{2+} . The majority of coffinite-A and -C cluster together and form a trend toward increasing ΣREY^{3+} . Coffinite-B cluster together toward the $U^{4+} + U^{6+}$ apex, whereas coffinite-C form their own cluster with elevated ΣREY^{3+} .

Fitzpatrick, 1989; Janeczek and Ewing, 1996; Förster, 2006; Deditius *et al.*, 2008 and references therein). These include:





Mechanisms [c1] to [c5] probably all contribute to the element substitutions in Olympic Dam coffinite, although their relative roles vary from one coffinite group to the next. In terms of the marked P and Y enrichment in some coffinite, coupled xenotime-type substitution [c1] (Hansley and Fitzpatrick, 1989) involves ΣREY^{3+} incorporation into octahedral *A* sites, and charge balance via P^{5+} substitution in the tetrahedral *B* site. Janeczek and Ewing (1996), however, warn that mechanism [c1] alone cannot explain the composition of some high-Ca coffinite where the ΣREY content is too low, and P content too high. These authors explained the formation of high-Ca coffinite via limited solid solution with ningyosite, $(\text{U,Ca,Ce})(\text{PO}_4)_2 \cdot 1-2\text{H}_2\text{O}$, thereby allowing for the substitution of Ca and P for U, and Si (i.e. mechanisms [c2]–[c4]). The $^{\text{IV}}\square$ represents tetrahedral-site vacancies in the coffinite structure, which would allow for cation deficiencies in the tetrahedral site. A deficiency in silica (i.e. $A > B$) is identified in analyses of Bangombé coffinite (Janeczek and Ewing, 1996), and this deficiency is also observed for Olympic Dam coffinite. Mechanisms [c3] and [c4] may help explain this phenomenon. Substitution [c2] yields a positive correlation between Ca^{2+} and U^{6+} , whereas substitutions [c3] to [c5] would yield negative correlations between Ca^{2+} and U^{4+} . Substitution [c5] (Förster, 2006) only involves *A*-site elements and may also be important. Moreover, a similar substitution to [c1] is the substitution of As^{5+} and Nb^{5+} , in addition to P^{5+} , into the *A* site, allowing for chernovite $[\text{YAsO}_4]$ -type substitution [c6] (Janeczek and Ewing, 1996), but Ca^{2+} and ΣREY^{3+} may compete for charge compensation via [c7] (Deditius *et al.*, 2008). It is likely that P^{5+} plays an important role in coupled substitution as it is present in moderate quantities (mean 0.12 apfu). The main substituting cations in Olympic Dam coffinite are Ca^{2+} , Fe^{2+} and ΣREY^{3+} , which substitute for U^{4+} in the *A* site, and P^{5+} which substitutes for Si^{4+} in the *B* site.

Another possible substitution mechanism is Al^{3+} substitution [c8] for both the *A* and *B* sites within thorite (Förster, 2006), and this may also be applicable here. However, due to the fairly low Al content of Olympic Dam coffinite (mean

~ 0.03 apfu), and the observation that aluminosilicates have been identified within coffinite (e.g. Fig. 6c), we have decided not to consider this type of substitution any further.

As discussed above, a negative correlation between total cations in the *A* and *B* sites is observed (Fig. 13a), with the slope of the line of best fit being -0.91 (i.e. *A*-site totals typically exceed *B*-site totals). We have assumed the presence of U^{6+} when calculating structural formulae, which may explain the higher *A*-site values. To compensate for the excess positive charge from U^{6+} , either $(\text{OH})^-$, or vacancies in the Si position (mechanism [c9]) may be present, which may be in turn be linked to mechanism [c2]. Likewise, the presence of excess Ca^{2+} and ΣREY^{3+} may lead to higher *A*-site totals.

Another mechanism, [c10] that may play a significant role is S-for-Si substitution, resulting in enhanced incorporation of P and ΣREY (Jensen and Ewing, 1998; Deditius *et al.*, 2009). The presence of S reduces the number of vacancies needed in the coffinite structure, in turn aiding charge balance and allowing incorporation of less abundant elements (Tables 3 and 4). Coffinite-C2 and -C3 contain the most P (0.36 and 0.28 apfu, respectively) and also have the highest levels of S (0.063 and 0.068 apfu, respectively), inferring that mechanism [c10] is of importance, especially for the most P-rich coffinite.

The maximum Y content measured in coffinite was 15.6 wt.% Y_2O_3 (0.38 apfu), and this contributes to some of the high *A*-site totals. Yttrium is typically accommodated by elevated P levels (coffinite-xenotime solid solution [c1]; Fig. 12e). An alternative mechanism [c11] involves Y^{3+} and U^{6+} substitution for U^{4+} (Pointer *et al.*, 1988). This may also be relevant for the Olympic Dam coffinite, as to balance charge, the presence of U^{6+} has been assumed.

The key interdependencies among various cations (Figs 12 and 13) were discussed above, but in light of the different coupled substitutions, the following points should also be raised. The negative correlation between Si and Ca (Fig. 12c) and positive correlation between U and Ca (Fig. 12a) may indicate that Ca^{2+} incorporation results in Si^{4+} loss from the *B* site. A negative correlation with Si^{4+} is also generally shown by P^{5+} (Fig. 12d), thus supporting mechanisms [c3] and [c4]. The negative correlation between ΣREY and U (Fig. 12b) strongly indicates competition between ΣREY and U for *A*-site occupancy during crystallization.

Coffinite formation

Coffinite can be found in a variety of environments, but typically results from low-temperature processes. In some cases, coffinite formation involves alteration of previously precipitated uraninite through the uptake of silica (coffinitization). When this occurs, it usually happens at the margins of uraninites, or in domains that show signs of alteration (Janeczek and Ewing, 1995). Alternatively, coffinite may form as a result of changing redox, $a\text{SiO}_2$, pH, temperature, or pressure conditions, which induce coffinite precipitation. For example, the concentration of $\text{H}_4\text{SiO}_{4(\text{aq})}$ in groundwater is controlled by the presence of Al-silicates and quartz (Robit-Pointeau *et al.*, 2006). Also, in the presence of sulfides, and with sufficient Si concentration, coffinite will be precipitated in preference to uraninite (Janeczek and Ewing, 1992; Fayek *et al.*, 1997). A few studies (e.g. Guo *et al.*, 2015) have shown that coffinite is thermodynamically metastable at temperatures $<450^\circ\text{C}$, when it will decompose to a mixture of U_3O_8 and SiO_2 ; but in reduced Si-rich environments, the stability of coffinite extends to higher temperatures. Thus, if a silica-rich, aqueous solution containing dissolved U^{6+} encounters a reductant, coffinite may form.

An alternative explanation for the formation of coffinite in deposits where the alpha dose is high (e.g. those of sufficient age where significant radioactive decay has ensued) involves the radiolysis of H_2O to form H_2O_2 (Savary and Pagel, 1997; Sattonnay *et al.*, 2001). The formation of H_2O_2 causes a localized increase in the oxidation state, which may aid to dissolve earlier precipitated uraninite into the more soluble UO_2^{2+} ion (Guo *et al.*, 2015 and references therein). Then in the presence of a reducing agent such as organic matter (e.g. Deditius *et al.*, 2008) or sulfides, any UO_2^{2+} in solution may be reduced on the surface of these reductants, and provided there is sufficient dissolved silica, coffinite may be precipitated. An alternative coffinitization mechanism thus involves local oxidation of UO_2 by H_2O_2 , transport of the dissolved U^{6+} into more reducing environments that contain sufficient dissolved silica, and final precipitation of coffinite near the reductants.

To precipitate any mineral from solution, local conditions need to change to allow precipitation to take place. In terms of the precipitation of oxidized U, one possible mechanism to induce precipitation of U^{4+} minerals is the presence of a reductant. Coffinite commonly displays a close association

with sulfides or organic matter; these will retard migration and subsequently reduce U^{6+} in solution to U^{4+} (e.g. Goldhaber *et al.*, 1987; Hansley and Fitzpatrick, 1989). For both coffinite (e.g. Fig. 4e, f) and brannerite (Figs 1b, 2d and 3a–f) at Olympic Dam, the close association with Cu-(Fe)-sulfides is ubiquitous, and these are the most probable reductants. An additional observation for coffinite is the presence of chlorite inside individual coffinite globules (Fig. 6c), as well as intergrowths of chlorite and sericite with brannerite (Fig. 6a,b). Reduced Fe is present in aluminosilicates such as chlorite, and these have been shown to be the principal reductants of oxidized uranium from some hydrothermal fluids (Komninou and Sverjensky, 1996; Gregory *et al.*, 2005). Destruction of the Fe-rich silicates releases Fe^{2+} and causes reduction of solution U^{6+} . Thus, as the hydrothermal fluids interact with aluminosilicates, these begin to dissolve, releasing Si, Fe, Ti etc., which may then be incorporated into the precipitating U minerals.

One final observation is that the concentration of Th in coffinite is typically below mdl (e.g. Hansley and Fitzpatrick, 1989; Deditius *et al.*, 2008), and this is also true for Olympic Dam coffinite. Thorite precipitates at 200°C – 400°C , whereas coffinite usually precipitates at far lower temperatures (100°C – 140°C ; Goldhaber *et al.*, 1987; Janeczek and Ewing, 1992; Förster, 2006). Thus, with the absence of contained Th in coffinite, it is likely that coffinite formed as an alteration product of uraninite under Si-rich, low-temperature, reducing conditions (e.g. Janeczek and Ewing, 1992).

Evolution of brannerite and coffinite at Olympic Dam

The distinct compositions of the different brannerite groups might indicate that the local conditions that formed brannerite-A were different to those that formed brannerite-B to -D, or that they formed at different times. Brannerite-A, typically has elevated (Mg + Mn + Na + K) and (Fe + Al) concentrations (Fig. 10c,d, respectively), but lower ΣREY , Pb and other A-site substituents (Fig. 9) compared to brannerite-B to -D. There is also a difference in pentavalent B-site substitution, with elevated Nb in brannerite-D, and As in brannerite-B and -C, possibly resulting from the greater availability of these cations via breakdown of phases initially containing them. Alternatively, the low- ΣREY content of brannerite-A may suggest that ΣREY

may have precipitated into another mineral (i.e. *REY* minerals) in preference to brannerite.

On the basis of the needle- and lath-like internal structure of brannerite (especially brannerite-A), it is probable that formation involved decomposition of ilmenite/leucoxene in the presence of a Cu-U-bearing fluid. Uranium in solution combined with titania to form uraniferous rutile grading into brannerite, and the leached iron from ilmenite decomposition combined with sulfur and metals in the hydrothermal fluid to form sulfides. The presence of S may have aided alteration of ilmenite and stabilized partially leached uraninite. Brannerite-B to -D have a more massive/uniform internal structure but also show evidence of lath-like textures on their margins, suggesting formation via an analogous mechanism. These brannerite types appear to have replaced Ti-rich hematite, or rutile in close association with hematite. Irrespective of the replaced mineral, the chemistry of replacement is considered similar.

Coffinite exhibits variable composition (Figs 12 and 13); coffinite-B is especially distinct from the other groups. Coffinite-B has more Ca, but less ΣREY replacing U, and typically lower (P + As + Nb) contents than the other groups. Coffinite-C has elevated ΣREY , whereas coffinite-A shows the broadest range of substituents. In two examples (e.g. Fig. 12*b,d*) coffinite-B displays a positive trend, whereas coffinite-A and -C exhibit negative trends, further highlighting that substitution mechanisms for coffinite-B probably differ to those for coffinite-A and -C, and possibly that coffinite-B represents a mixture of (U,Si)-phases rather than true coffinite. It is typically represented by more anhedral masses instead of the more prismatic and globular forms of the other coffinite types.

As coffinite-B is associated with massive uraninite, it is likely that these formed as a result of remobilization of U from uraninite or from direct replacement of that mineral. Massive uraninites also contain significant Ca and have lower ΣREY contents than crystalline uraninites (Macmillan *et al.*, 2016). The higher ΣREY and (P + As + Nb) contents of coffinite-C (Fig. 12*b,d*, respectively), may indicate that these precipitated from fluids carrying elevated concentrations of these elements. This is not unexpected as these coffinite types are found in association with brannerite (Fig. 6*a,b*) or *REY* minerals (Fig. 6*d*), both of which contain ΣREY .

Textural observations and compositional differences allow us to conclude that brannerite and

coffinite precipitated as part of a late-stage U-event at Olympic Dam. This might have involved dissolution and/or reprecipitation of earlier uraninite, or could have involved a fresh influx of U. Key observations which support late-stage formation include: (1) low-Pb contents of both brannerite and coffinite, indicating these minerals experienced little radioactive decay and/or that radiogenic Pb was mobilized from these minerals; (2) coffinitization typically evident on the edges of uraninite crystals (Fig. 5*d*), thus implying this process occurred after uraninite deposition; (3) coffinite in contact with massive uraninite (Fig. 5*a–c*) occurring on the edges of these masses, and this uraninite containing much higher Pb than coffinite; (4) where brannerite and coffinite are found in close association (i.e. Fig. 6*a,b*), the coffinite occurring on the margins of brannerite, suggesting brannerite pre-dates coffinite.

Other key observations include the observation that brannerite sometimes touches coffinite but is rarely found touching uraninite (Fig. 7). Three hypotheses may explain this: (1) brannerite formation was not the result of dissolution of earlier uraninite, but formed from another source of U; (2) brannerite did not form via direct replacement of earlier precipitated uraninite; or (3) any U that has been remobilized from earlier precipitated uraninite has been transported away from the site of initial dissolution and subsequently precipitated elsewhere as brannerite. Uraninite is chemically active, readily dissolved and mobilized in the presence of fluids. It therefore exchanges elements and reprecipitates easily during fluid circulation and mineral replacement (Grandstaff, 1976; Kotzer and Kyser, 1993; Alexandre and Kyser, 2005). The solubility of uraninite increases with temperature and with increased concentrations of F, Cl and/or CO₂ (Keppler and Wyllie, 1990). It is only sparingly soluble in reducing groundwaters under normal pH conditions (e.g. Parks and Pohl, 1988). The migration of U in reducing groundwaters is also aided by the stability of U⁴⁺-fluoride complexes at pH < 4 (Finch and Murakami, 1999). Alternatively, as suggested by Guo *et al.* (2015), the impacts of radioactive decay may have allowed for the radiolysis of H₂O, and subsequently generated a locally oxidative environment which allowed for dissolution of UO₂ and in the presence of Si-rich fluids and reductants (e.g. sulfides) allowed for the precipitation of coffinite.

Furthermore, coffinite is often found touching both uraninite and brannerite (Fig. 8), or on the periphery of these minerals. It is therefore logical

that fluids reacted with previously precipitated uraninite and/or brannerite, mobilized U from these minerals, and subsequently precipitated coffinite. The fluid must have had sufficient SiO₂ content to precipitate coffinite rather than uraninite.

At Olympic Dam, in most cases, both brannerite and coffinite are intimately associated with either sulfides, or Fe²⁺-bearing aluminosilicates (notably chlorite). There is typically a small gap/crack (<1 µm) and embayed margins around the edge of these minerals and the coffinite (e.g. Fig. 5a, small spaces around sulfides), suggesting that the surface of the sulfide (or aluminosilicate) was potentially responsible for adsorbing and reducing the uranyl species. It is thus probable that the hydrothermal fluid contained oxidized uranium, and the sulfides and/or chlorite acted as reductants, reducing uranyl species from solution. Also, both brannerite and coffinite are most strongly associated with hematite, sericite/chlorite, quartz and fluorite (Figs 7 and 8). It is common to see both brannerite and coffinite within bands of sericite, chlorite and/or fluorite. The permeability of such intervals is probably greater than those dominated by quartz or hematite. The presence of brannerite/coffinite within these bands might reflect penetration by hydrothermal fluid, and precipitation of these minerals (+ fluorite) from that fluid. From the mineral inclusions observed within brannerite and surrounding minerals, it is possible that the fluid/s contained F, Cu, Fe, S, Si and Ca, as well as Na and K derived from partial dissolution and alteration of feldspars (Kontonikas-Charos *et al.*, 2017).

Future work and concluding remarks

The evolution of uranium minerals at Olympic Dam over the past 1.6 Ga is complex and difficult to reconstruct unequivocally. Microanalytical and petrographic observations nevertheless provide evidence for an interpretation in which brannerite and coffinite largely represent the products of later U mineralizing events. Together with new data for uraninite (Macmillan *et al.*, 2016), these observations highlight the role of multiple stages of U dissolution and reprecipitation. The cyclic nature of these events is reflected in marked compositional and textural differences between the various types of brannerite and coffinite.

We suggest that dominant substitutions within brannerite include Ca²⁺ and REY³⁺ in the *A* site (replacing U⁴⁺ and/or U⁶⁺) and Si⁴⁺, Na⁺ and Fe³⁺ in the *B* site, replacing Ti⁴⁺. For coffinite, dominant

substitutions include Ca²⁺, Fe²⁺ and REY³⁺ in the *A* site (replacing U⁴⁺ and/or U⁶⁺) and P⁵⁺ in the *B* site, replacing Si⁴⁺. Further work is required to either validate these substitutions into the *A* and *B* sites of brannerite and coffinite, or to determine if these elements occur within interstitial sites. This could be done, for example, by nanoscale chemical mapping of foils prepared *in-situ* by focused ion beam SEM. The valency state of U also impacts on assumptions made for derivation of structural formulae, so attempts to ascertain whether multiple valencies of U are present, e.g. by X-ray absorption spectroscopy (XAS), are warranted. Both the presence and absence of structural water or (OH)⁻ within brannerite and coffinite has also been hypothesised in many studies, and this could be explored for natural Olympic Dam samples via Raman infrared spectroscopy.

Integrating the compositional and textural data reported here with those reported elsewhere (e.g. Kirchenbaur *et al.*, 2016; Macmillan *et al.*, 2016) expands our understanding of the sequence of events that generated the uranium mineralization at Olympic Dam. The work represents a critical step towards development of a paragenetic sequence for U mineralization and a genetic model for the deposit.

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Appendix – Analytical methods

Mineral liberation analyser (MLA)

A mineral liberation analyser (MLA) was used to provide automated mineralogy results. Measurements were conducted by staff from ALS Mineralogy, Brisbane. The MLA system consists of an automated SEM and a special software program which allows for automated mineralogy measurement. Gu (2003) has details about the available measurement modes and setup of the MLA system. For the current study, measurement modes used were X-ray modal (XMOD) and sparse phase liberation mapping (SPL_Lite). Bulk modal mineralogy was measured via the XMOD method.

Details of the mineral list used (Table A1) and bulk modal mineralogy measured via the XMOD method can be found in Macmillan *et al.* (2016). The SPL_Lite method was used to target only the U-bearing grains so that more detailed compositional and mineral association data pertaining to these grains could be attained. This method targets selected minerals (brannerite and coffinite in this case), and a measurement of the perimeter of each brannerite or coffinite grain is measured, as is the length of the boundary between any other mineral which is touching the mineral of interest. A relative proportion (in wt.%) of each mineral found in contact with the brannerite or coffinite can thus be estimated, and this is recorded as the mineral association. For the current study, the mineral

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TABLE A1. Details of mineral grouping used for MLA association data (SPL_Lite measurement technique).

Group name	Mineral name	Assumed formula
Brannerite	Brannerite	(U,Ca)(Ti,Fe) ₂ O ₆
Coffinite	Coffinite-Si ₇	(U,Y,Ca,Ce,Nd,Fe)[(Si,Al)O ₄ ,PO ₄ ,OH] ₄
	Coffinite-Si ₉ Y ₇	(U,Y,Ca,Ce,Nd,Fe)[(Si,Al)O ₄ ,PO ₄ ,OH] ₄
	Coffinite-Si ₉ Y ₉	(U,Y,Pb,Fe,Er,Dy,Nd,Ce,La,Ca,K)[SiO ₄ ,PO ₄ ,OH] ₄
	Coffinite-Si ₁₀	(U,Y,Ca,Ce,Nd,Fe)[(Si,Al)O ₄ ,PO ₄ ,OH] ₄
	Coffinite-Si ₁₀ Y ₁	(U,Y,Pb,Fe,Nd,La,Ce,Ca,K)[(Si,Al)O ₄ ,PO ₄ ,OH] ₄
	Coffinite-Si ₁₀ Y ₁₀	(U,Y,Ca,Ce,Nd,Fe)[(Si,Al)O ₄ ,PO ₄ ,OH] ₄
	Coffinite-Si ₁₂ Y ₆	(U,Y,Pb,Fe,Nd,La,Ce,Ca,K)[(Si,Al)O ₄ ,PO ₄ ,OH] ₄
	Thorite	(Th,U,Fe,Y,P,Ca,Pb)SiO ₄
Uraninite	Uranothorite	(U,Th,Y,P,Fe,Ca,Nd)SiO ₄
	Uraninite-Pb ₅	(U,Pb,Ce,Nd)O ₂
	Uraninite-Pb ₁₀	(U,Pb,Y,Ce,Nd,Fe,Cu)O ₂
	Uraninite-Pb ₁₅	(U,Pb,Ce,Nd,Sm,Gd,Y,Fe,Cu,Ca)O ₂
	Uraninite-Pb ₂₀	(U,Pb,Fe,Nd,Ce,La,K,Y)O ₂
	Uraninite_Si	(U,Fe,Nd,Ce,La,Ca,K)(SiO ₄ ,O ₂)
REY minerals	Apatite	Ca ₅ (PO ₄) ₃ F
	Bastnäsite	(Ce,La,Nd,Pr,Ca)(CO ₃)F
	Crandallite_Grp	(Ce,La,Nd,Ca,Sr)(Al,Fe) ₃ (SO ₄ ,PO ₄) ₂ (OH) ₆
	Florencite	(Ce,La,Nd,Ca,Sr)(Al,Fe) ₃ (PO ₄) ₂ (OH) ₆
	Monazite	(Ce,La,Nd,Fe,Ca)PO ₄
	Synchysite	Ca(Ce,Nd,La,Sm,Gd,Y,Fe)(CO ₃) ₂ F
	Xenotime	(Y,Yb)PO ₄
	Xenotime-U	(Y,U,Dy,Nd,Sm,Gd,Fe)[(PO ₄),(SiO ₄)]
	Zircon	ZrSiO ₄
	Zircon-U	(Zr,Hf,U,Ca,Fe,Fe,Dy,Er,Yb,Y)[(Si,Al)O ₄]
Sulfides	Bismuthinite	Bi ₂ S ₃
	Bornite	Cu ₅ FeS ₄
	Carrolite	CuCo ₂ S ₄
	Chalcocite	Cu ₂ S
	Chalcopyrite	CuFeS ₂
	Cobaltite	(Co,Fe)AsS
	Covellite	CuS
	Domeykite	(Cu,Fe) ₃ As
	Löllingite	(Fe,Co,Ni)As ₂
	Molybdenite	MoS ₂
	Native_Copper	Cu
	Pyrite	FeS ₂
	Pyrrhotite	Fe _{1-x} S (x = 0.0–0.2)
	Safflorite	(Co,Fe)(As,S) ₂
	Sphalerite	(Zn,Fe)S
	Tellurobismuthite	Bi ₂ Te ₃
	Tennantite	(Ag,Cu,Zn,Fe) ₁₂ (As,Sb) ₄ S ₁₃
Pb minerals	Altaite	PbTe
	Cerussite	PbCO ₃
	Clausthalite	PbSe
	Galena	PbS
Hematite	FeO	Fe ₂ O ₃
Baryte	Baryte	BaSO ₄
	Baryte_Sr	(Ba,Sr)SO ₄
Fluorite	Fluorite	CaF ₂
	Sellaite	MgF ₂
Quartz	Quartz	SiO ₂
Sericite/Chlorite	Sericite	K(Fe,Mg,Al) ₂ (AlSi ₃ O ₁₀)(OH,F) ₂
	Chlorite_1	(Mg,Fe,Al)3(Al,Si) ₄ O ₁₀ (OH) ₂

(continued)

TABLE A1. (*contd.*)

Group name	Mineral name	Assumed formula
Feldspar	Chlorite_2	(Fe,Al) ₃ (Al,Si) ₄ O ₁₀ (OH) ₂
	Chlorite_3	Mg ₂ (Al,Fe) ₃ Si ₃ AlO ₁₀ (OH) ₈
	Albite	NaAlSi ₃ O ₈
	Orthoclase	KAlSi ₃ O ₈
Carbonate	Ankerite	Ca(Fe,Mg,Mn)(CO ₃) ₂
	Calcite	(Ca,Mn)CO ₃
	Dolomite	Ca(Mg,Fe,Mn)(CO ₃) ₂
	Siderite	(Fe,Mn)CO ₃
	Siderite_Mn	(Fe,Mn,Ca)CO ₃
Ti minerals	Ilmenite	(Fe,Mn)TiO ₃
	Ilmenorutile	(Ti,Nb,Fe,Mn)O ₆
	Rutile	TiO ₂
	Al_Hydroxide	Al ₂ (SO ₄) ₃ ·17(H ₂ O)
Other	Anhydrite	CaSO ₄
	Corundum	(Al,Fe) ₂ O ₃
	Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄
	Scheelite	CaWO ₄
	Schorl	NaFe ₃ Al ₆ (BO ₃) ₃ Si ₆ O ₁₈ (OH) ₄
	Topaz	Al ₂ SiO ₄ (F,OH) ₂
	Unknown	Un

TABLE A2. Mineral association data for brannerite and coffinite measured by MLA using SPL_Lite method.

	Coffinite	Uraninite	REY minerals	Sulfides	Pb minerals	Hematite	Baryte
% mineral associated with brannerite							
Group A	1.2	0.0	2.3	5.3	0.2	28.9	0.8
Group B	0.0	0.0	0.4	4.3	0.0	34.0	1.7
Group C	0.4	0.0	2.2	23.9	0.6	33.4	0.1
Group D	0.0	1.5	0.7	7.6	7.3	37.8	0.4
% mineral associated with coffinite							
Group A	0.9	0.9	2.0	6.9	0.1	32.2	0.9
Group B	0.3	2.0	4.0	5.0	0.0	45.5	1.1
Group C	5.3	0.6	2.3	3.6	0.1	28.4	0.8
	Fluorite	Quartz	Sericite/Chlorite	Feldspar	Carbonate	Ti minerals	Other
% mineral associated with brannerite							
Group A	5.7	17.1	25.6	1.9	6.1	4.9	0.1
Group B	3.2	23.5	30.9	0.1	0.1	1.8	0.0
Group C	3.1	10.3	20.5	0.1	1.0	4.5	0.1
Group D	1.0	12.4	27.8	0.7	0.1	2.6	0.0
% mineral associated with coffinite							
Group A	3.9	23.6	17.4	3.8	6.9	0.5	0.1
Group B	12.7	12.2	9.4	6.7	1.0	0.0	0.1
Group C	4.4	29.4	21.7	1.1	1.8	0.4	0.0

Note: Mineral association data for brannerite/coffinite, measured by the MLA system using the SPL_Lite method. The SPL_Lite method targets selected minerals (brannerite or coffinite in this case). The perimeter of each brannerite/coffinite grain is measured, and the length of the boundary between any other mineral which is touching the brannerite/coffinite is also measured. A relative proportion (in wt.%) of each mineral found in contact with the brannerite/coffinite can thus be estimated, and this is recorded as the mineral association.

TABLE A3. Summary of EPMA set-up used for analysis of OD brannerite and coffinite.

Element X-ray line	Spectrometer/crystal	Primary standard	Count times (s)			Interference with...	Off-peak correction
			On-peak	Off-peak high	Off-peak low		
UM β	SP1 (LPET)	UO ₂	50	25	12.5	K, Th	Multi-point
PbM β	SP1 (LPET)	Pb glass - K227	60	30	30	U, Ce, S, Y	Multi-point
ThM α	SP1 (LPET)	Huttonite	50	12.5	12.5	-	Multi-point
NaK α	SP2 (TAP)	Albite	20	5	10	U	Multi-point
MgK α	SP2 (TAP)	Almandine garnet	30	15	7.5	-	Multi-point
AlK α	SP2 (TAP)	Almandine garnet	30	15	15	Ti	Multi-point
SiK α	SP2 (TAP)	Almandine garnet	30	15	7.5	Y	Multi-point
PK α	SP5 (LPET)	Apatite	30	15	7.5	Ca, Cu	Multi-point
SK α	SP5 (LPET)	Marcasite	20	10	5	Nd, La	Multi-point
KK α	SP4 (LPET)	Sanidine	20	10	10	U	Multi-point
CaK α	SP4 (LPET)	Wollastonite	30	15	15	-	Multi-point
TiK α	SP4 (LPET)	Rutile	30	15	15	U	Multi-point
MnK α	SP3 (LLIF)	Rhodonite	10	5	5	As	Slope (Hi)
FeK α	SP3 (LLIF)	Almandine garnet	20	10	10	-	Multi-point
CuK α	SP3 (LLIF)	Chalcopyrite	20	10	10	-	Multi-point
AsL α	SP2 (TAP)	Gallium arsenide	40	10	10	Sm, Nd	Multi-point
ZrL α	SP5 (LPET)	Zircon	20	20	20	Nd	Slope (Lo)
NbL α	SP5 (LPET)	Niobium	20	10	5	Mn	Linear
YL α	SP5 (LPET)	REE1	50	25	25	-	Multi-point
CeL α	SP1 (LPET)	Ce glass	30	15	15	-	Linear
LaL α	SP1 (LPET)	La glass	30	15	15	Nd	Slope (Lo)
PrL β	SP3 (LLIF)	Pr glass	30	15	7.5	U	Multi-point
NdL β	SP3 (LLIF)	Nd glass	30	7.5	7.5	-	Multi-point
SmL β	SP3 (LLIF)	Sm glass	30	15	15	-	Multi-point
GdL β	SP3 (LLIF)	Gd glass	30	15	15	U	Multi-point
SrL α	SP2 (TAP)	Celestine	30	15	7.5	-	Linear
BaL α	SP4 (LPET)	Baryte	20	10	5	Ti, U, Pr	Multi-point
TeL α	SP4 (LPET)	Silver telluride	20	10	10	Sm, U	Multi-point

association value for each sample is the average value of all measured brannerite or coffinite grains in that sample. A summary of minerals associated with both brannerite and coffinite can be found in Table A2, as well as in Figs 7 and 8.

Electron probe microanalyses (EPMA)

All U minerals that were to be compositionally analysed were first identified using the SEM, on which back-scatter electron (BSE) images (Figs 1–6) of the region being studied and the key individual U mineral grains were taken. Each image was given a unique ID (of the form Sxx.yy, where xx = sample number and yy = grain number). The locations of these regions were recorded on BSE image montages produced for each polished thin section from the MLA 650 Environmental SEM (Central Science Laboratory, University of Tasmania).

The Cameca SX-Five electron probe microanalyser (EPMA) at Adelaide Microscopy (University of Adelaide) was used to obtain quantitative compositional data. A total of 28 elements was measured. The standards used were originally published in the Appendix material of Macmillan *et al.* (2016), but are also listed here: Astimex albite for NaK α ; Astimex almandine garnet for SiK α , AlK α , MgK α , FeK α ; Astimex apatite for PK α ; Astimex baryte for BaL α ; Astimex celestite for SrL α ; Astimex marcasite for SK α ; Astimex rhodinite for MnK α ; Astimex rutile for TiK α ; Astimex sanidine for KK α ; Astimex gallium arsenide for AsL α ; chalcopyrite (P and H Developments, UK) for CuK α ; wollastonite (P and H Developments, UK) for CaK α ; silver telluride (P and H Developments, UK) for TeL α ; Astimex niobium for NbL α ; synthetic Pb glass – K227 (NIST) for PbM β ; rare-earth glass standard – REE1 (Drake and Weill, 1972) for YL α ; huttonite (David Steele) for ThM α ; UO₂ (David Steele) for UM β ; single element synthetic REE glasses for CeL α , LaL α , PrL β , NdL β , SmL β , GdL β (Edinburgh Materials and Microanalysis Centre, University of Edinburgh); zircon (C.M. Taylor Company) for ZrL α .

To identify all possible elements, minimize interferences, and to allow for accurate background point setting, high-resolution wavelength

spectrometer scans were completed. The *HREE* oxides were <mdl (identified from full wavelength spectrometer scans). Details of crystal type, count times and off-peak interference corrections can be found in Table A3. Parameters are identical to those used for the uraninite study conducted by Macmillan *et al.* (2016).

Spectrometer usage was optimized by adjusting the acquisition order so that all spectrometers had approximately equal measurement times. Also, any elements that may be affected by beam damage were measured first namely: PK α , PbM β , NaK α , MnK α , KK α ; and intensity data was corrected for Time Dependent Intensity (TDI) loss (or gain) using a self-calibrated correction for these elements. Both unknown and standard intensities were corrected for deadtime, with standard intensities also being corrected for standard drift over time.

To monitor the reproducibility of the EPMA data, a range of standards (UO₂, K227, REE1 and almandine garnet) were run as unknowns throughout each EPMA run. This showed that the probe was relatively stable, with the standard deviations (SD) for repeated analysis of these standards over a four month period being: 0.35 for U ($n = 44$), 0.41 for Pb ($n = 41$), 0.11 for Y ($n = 52$), 0.10 for Si ($n = 46$) and 0.18 for Fe ($n = 46$).

Mean mdl values for each element in both brannerite and coffinite were calculated and can be found as a footnote in Tables 2, 3 and 4. For brannerite, mean precision (wt.%) based on 1 σ , was estimated as: U $\approx$ 0.053, Pb $\approx$ 0.015, Th $\approx$ 0.015, Na $\approx$ 0.012, Mg $\approx$ 0.0036, Al $\approx$ 0.0033, Si $\approx$ 0.0068, P $\approx$ 0.0035, S $\approx$ 0.0039, K $\approx$ 0.0034, Ca $\approx$ 0.0057, Ti $\approx$ 0.019, Mn $\approx$ 0.014, Fe $\approx$ 0.020, Cu $\approx$ 0.018, As $\approx$ 0.0090, Zr $\approx$ 0.015, Nb $\approx$ 0.017, Y $\approx$ 0.017, Ce $\approx$ 0.012, La $\approx$ 0.0095, Pr $\approx$ 0.032, Nd $\approx$ 0.034, Sm $\approx$ 0.031, Gd $\approx$ 0.033, Sr $\approx$ 0.0093, Ba $\approx$ 0.011. For coffinite, mean precision (wt.%) based on 1 σ , was estimated as: U $\approx$ 0.062, Pb $\approx$ 0.015, Th $\approx$ 0.015, Na $\approx$ 0.010, Mg $\approx$ 0.0037, Al $\approx$ 0.0038, Si $\approx$ 0.012, P $\approx$ 0.010, S $\approx$ 0.0070, K $\approx$ 0.0035, Ca $\approx$ 0.0061, Ti $\approx$ 0.0034, Mn $\approx$ 0.016, Fe $\approx$ 0.015, Cu $\approx$ 0.017, As $\approx$ 0.0092, Zr $\approx$ 0.018, Nb $\approx$ 0.024, Y $\approx$ 0.035, Ce $\approx$ 0.012, La $\approx$ 0.010, Pr $\approx$ 0.037, Nd $\approx$ 0.041, Sm $\approx$ 0.034, Gd $\approx$ 0.038, Sr $\approx$ 0.0089, Ba $\approx$ 0.012.