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Indium mineralisation in SW England: host parageneses and mineralogical relations

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ABSTRACT

The SW England ore region contains significant indium (In) in Early Permian granite-related skarn and lode parageneses and, to a lesser extent, Triassic epithermal “crosscourse” veins. Ore parageneses that predate granite emplacement (Devonian and Lower Carboniferous sedimentary exhalative and vein parageneses) are largely devoid of In. Cadmium (Cd) and gallium (Ga), in contrast, occur widely in all sulphide-bearing parageneses across the region with sphalerite concentrations locally reaching 1.74 wt% Cd and 1750 ppm Ga.

Indium displays a strong affinity to sulphide-bearing magmatic-hydrothermal parageneses. It occurs in silicate-sulphide skarns, polymetallic sulphide lodes and sulphide-bearing portions of greisen-bordered sheeted vein systems and quartz-tourmaline lodes, veins and breccias across the region. Magnetite-silicate skarns and quartz-tourmaline lodes, veins and breccias that are devoid of sulphide, in contrast, were comparatively unfavourable for In precipitation. The highest In concentrations are found in mineral lodes associated with the Carnmenellis and St Agnes granites, which are the districts that had the highest historical production of Sn. Total In concentrations in these areas locally exceed 430 ppm, while concentrations elsewhere are systematically below 200 ppm.

The principal In hosts are chalcopyrite, sphalerite and stannite group minerals with local concentrations within cassiterite and tennantite. No In was detected in löllingite, arsenopyrite, rutile, haematite, magnetite, tourmaline, biotite, chlorite, galena, bornite, chalcocite or pyrrhotite. Scattered concentrations in pyrite relate to impurities rather than incorporation by solid solution. Sphalerite locally contains up to 1.42 wt% In, chalcopyrite has up to 2200 ppm and stannite group minerals up to 6800 ppm. Although In concentrations are highest in sphalerite and stannite group minerals, chalcopyrite accounts for the majority of the In budget throughout most of the region. Roquesite and possibly dzhalindite or native In formed locally where In-bearing chalcopyrite or sphalerite have been replaced by bornite and quartz. The In partitioning between sphalerite and chalcopyrite varies broadly between 1:1 and 10:1.

In the granite-related parageneses, the In deportment varies across the different parageneses, and this variation is systematically related to different sphalerite morphologies. Chalcopyrite contains most of the In budget within parageneses that have large, unzoned sphalerite grains with chalcopyrite disease or only sparse, minute grains of sphalerite. In contrast, zoned sphalerite without chalcopyrite disease carries the majority of the In budget.
in the evolved parts of the polymetallic sulphide lodes. Although chalcopyrite is also abundant here, it is much less significant as a host.

Sporadic In was included in Triassic crosscourse veins as a result of interactions between migrating CaCl$_2$-rich basinal brines and earlier formed granite-related parageneses. The interactions involved at least two distinct components: 1) Incorporation of clasts of magmatic-hydrothermal veins in crosscourse veins during faulting, and 2) Dissolution and re-precipitation of magmatic-hydrothermal vein minerals in crosscourse fluids. Local concentrations reach 140 ppm In.

The region-wide dominance of chalcopyrite as an In host is unexpected and appears to be at variance with magmatic-hydrothermal parageneses elsewhere. This suggests that processing strategies that focus exclusively on sphalerite are likely to have little success. Detailed mineral deportment assessments must be a pre-requisite for the design of successful processing strategies in the region. Interestingly, we have no reason to believe that SW England is different to other regions with granite-related magmatic-hydrothermal parageneses, and it is possible that the global potential for In recovery from chalcopyrite has been underestimated.

The magmatic-hydrothermal parageneses in SW England are comparable to the South China Tin Belt, Mount Pleasant, as well as Erzgebirge/Krušné Hory. Magmatic-hydrothermal fluids associated with peraluminous granites have developed a variety of skarn, greisen, lode and veins parageneses by interactions with their host rocks and contained fluids. Crosscourse epithermal mineralisation occurred as In was transported by CaCl$_2$-rich basinal brines in a similar manner as In-bearing veins in the West Shropshire ore field.

1. INTRODUCTION

Indium (In) has over the last decade become a highly priced commodity used in mobile telephones, solar panels, flat screen computer monitors and televisions. Demand has more than tripled since 2001 and it is considered to be particularly vulnerable to supply risks (British Geological Survey, 2011). Dominant uses include indium-tin oxide thin films for colour liquid crystal displays (LCD), lead-free solders (considered as environmentally friendly alternatives to traditional solders), and cadmium-indium-gallium-selenide (CIGS) crystals in photovoltaic cells. Indium is currently extracted exclusively as a by-product of zinc.
processing, and hence the commercial availability of In is entirely dependent upon zinc mining (Alfantazi and Moskalyk 2003). It is thus difficult to increase In production during periods of economic downturn and reduced Zn demand. In order to secure future supply, it may be necessary to identify new resources where In is the dominant economic focus.

Indium concentrations are particularly high in some granite-related polymetallic vein systems, such as those in Yunnan, China (Ishihara et al. 2008; 2011); at Freiberg, Germany (Seifert and Sandmann 2006); Mount Pleasant, Canada (Sinclair et al. 2006); and the Wiborg batholith, Finland (Cook et al. 2011c). SW England, with nearly 2000 historical metal mines (Dines 1956) overwhelmingly related to granite-related mineralisation, is one of the most important polymetallic mining regions in Europe. Archaeological investigations confirm that Sn and Cu have been extracted since the Bronze Age (Christie 1986). Peak mining during the 18th to 20th centuries saw the production of a much wider range of metals and metalloids including Ag, As, Au, Bi, Co, Fe, Mn, Ni, Pb, S, Sb, U, W and Zn (Dines 1956; Burt 1998). Studies of the ores and mine waste have revealed that many more metals and metalloids are present in high concentrations including Cd, In, Li, Nb, Rb, REE and Ta (e.g., Beer et al. 1978; Scott et al. 1998; LeBoutillier et al. 2003; Andersen 2008; Andersen et al. 2009). Although these elements were never commercially extracted, many are now in high demand for specialist environmental and technological applications, and they present a new facet to exploration in this historic mining area.

Metalliferous mining in SW England declined before demand for In increased and, since In is not routinely analysed in geochemical studies, very little is known about its regional distribution or the factors that contribute to its concentration. We present here the results of the first province-wide investigation of the occurrence of In and related metals (Ga, Cd) within the SW England ore-field. Emphasis is placed on the principal parageneses associated with granite-related mineralisation but we also evaluate the role of pre- and post-granite mineralisation episodes in controlling In distribution. The purpose is to demonstrate the mineralogical hosts and associations for In and the most prospective mineralisation styles.

2. MINERALOGY AND GEOCHEMISTRY OF INDIUM

The continental crust is estimated to carry 0.05 ppm and the oceanic crust 0.072 ppm In (Taylor and McLennan 1985). The mantle concentration is estimated to 18±3 ppb
(Witt-Eickschen et al. 2009). Indium is considered to be chalcophile and occur exclusively as In$^{3+}$ in the Earth’s mantle and crust (e.g., Smith et al. 1978). When sulphide is absent, the metal can be expected to behave as a small REE (van Westrenen et al. 1999; Jenner and O’Neill 2012) and concentrate in similar ways as lithophile trace elements during processes of crustal differentiation.

In most rocks, In is carried exclusively as a trace element that substitutes into sphalerite and Cu-Fe-Sn sulphides. Commercial production is principally from acid treatment of residues from sphalerite ores (Alfantazi and Moskalyk 2003). Eighteen discrete In minerals are known, and these are found only in very In-rich systems. The most important is roquesite, CuInS$_2$ which is isostructural with chalcopyrite, CuFeS$_2$. Other minerals reported from granite-related systems include dzhalindite In(OH)$_3$; indite FeIn$_2$S$_4$; native In; petrukite (Cu,Fe,Zn,Ag)$_3$(Sn,In)S$_4$; and sakuraiite (Cu,Zn,Fe)$_3$(In,Sn)S$_4$ (Schwarz-Schampera and Herzig, 2002).

3. REGIONAL GEOLOGICAL EVOLUTION

SW England is an Upper Palaeozoic Variscan massif, comprising low-grade regionally metamorphosed Devonian and Carboniferous sedimentary and igneous rocks that host the Early Permian Cornubian Batholith (Fig. 1). It is unconformably overlain to the east, and in surrounding offshore sedimentary basins, by post-orogenic Permian and younger successions. SW England is correlated with the Rhenohercynian Zone of the Variscan orogen, interpreted as a short-lived marginal or successor basin formed during or after the closure of the Rheic Ocean (e.g. Franke 2000; Shail and Leveridge 2009). Although pre-Devonian basement is not exposed, an Avalonian provenance is assumed due to a location north of the Rheic suture (Shail and Leveridge 2009).

The regional geological evolution and associated mineralisation reflects four broad tectonic regimes: (1) rifting and passive margin development (Early Devonian – Early Carboniferous), (2) Variscan convergence and continental collision (Late Devonian – Carboniferous), (3) early post-Variscan extension and magmatism (Early Permian) and (4) episodic intraplate rifting and inversion (late Permian – Cenozoic).

3.1 Rifting and passive margin development (Early Devonian-Early Carboniferous)
Devonian-Carboniferous successions were deposited in a series of E-W trending graben and half-graben sedimentary basins that formed during progressive rifting and development of the southwards-facing Rhenohercynian passive margin (Leveridge and Hartley 2006; Shail and Leveridge 2009). The successions are dominated by siliciclastic sedimentary rocks, primarily mudstones, siltstones and sandstones, with locally significant occurrences of limestones and cherts; rift-related mafic igneous rocks, mostly basalt lavas and basalt-gabbro sills, are common (Leveridge and Hartley 2006). The southwards transition, to highly attenuated continental lithosphere of the distal passive margin, is recorded in allochthonous units of the Gramscatho Basin and Start Complex; oceanic lithosphere preserved in the Lizard ophiolite had formed by the Middle Devonian (Shail and Leveridge 2009).

3.2 Variscan convergence and continental collision (Late Devonian-Carboniferous)

Variscan convergence brought about closure of the Rhenohercynian marginal / successor basin and continental collision during which SW England occupied a lower plate position (Shail and Leveridge 2009). The orogenic wedge, comprising the upper plate and frontally accreted elements of the distal passive margin (Gramscatho Basin / Lizard ophiolite) collided with the continental slope in the earliest Carboniferous (Holder and Leveridge 1986). Shortening migrated northwards through the passive margin and was accommodated by the ‘thick-skinned’ inversion of sedimentary basins and pre-rift basement above a mid-crustal décollement (Leveridge and Hartley 2006; Shail and Leveridge 2009). Deformation is represented by thrusts, cleavage and close to isoclinal folds, that are usually compatible with a top-sense-of-shear to the NNW; dextral slip on NNW-SSE striking, steeply-inclined, transfer faults occurred throughout the convergence history (Shail and Leveridge 2009). The youngest successions that experienced Variscan deformation are preserved in the Culm Basin and are late Carboniferous (Moscovian) in age (Edwards et al. 1997). All successions have undergone epizone-anchizone very low grade regional metamorphism (Warr et al. 1991).

3.3 Early post-Variscan extension and magmatism (Early Permian)

Variscan convergence ended in the latest Carboniferous and, in common with most of Western Europe, was replaced by a dextral transtensional regime (Ziegler and Dèzes 2006). In SW England, this was manifested by the latest Carboniferous to Early Permian reactivation of Variscan thrusts, and development of new fault systems, during NNW-SSE lithospheric extension (Alexander and Shail 1995, Shail and Leveridge 2009). Thinning and
exhumation of lower plate SW England, during extensional reactivation of the Rhenohercynian suture, was accompanied by the development of ‘red-bed’ sedimentary basins, bimodal post-collisional magmatism and associated magmatic-hydrothermal mineralisation (Shail and Wilkinson 1994).

The Crediton and Tiverton half-grabens (Fig. 1) had initiated by the earliest Permian and host red beds of the Exeter Group that include Early Permian lamprophyre and basalt lavas towards their base (Edwards et al. 1997). Lamprophyre dykes with similar Early Permian ages are hosted throughout the Variscan-deformed Devonian and Carboniferous successions (Dupuis et al. 2015). Offshore to the south of the peninsula, substantial thicknesses of Early Permian sedimentary and volcanic rocks are preserved in sedimentary basins developed during subsidence of the former upper plate during extensional reactivation of the suture (Evans 1990).

The Cornubian Batholith is the dominant expression of post-Variscan magmatism in SW England. It comprises strongly peraluminous monzogranites and syenogranites exposed in seven major plutons (Isles of Scilly, Land’s End, Tregonning-Godolphin, Carmmenellis, St Austell, Bodmin Moor and Dartmoor granites) and several stocks (St Michael’s Mount, Carn Brea, Carn Marth, St. Agnes, Cigga Head, Belowda Beacon, Kit Hill, Hingston Down, Crownhill Down and Hemerdon Ball granites) (Fig. 1). Gravity anomaly data indicate that the batholith is continuous at depth (Bott et al. 1958) with a thickness of 10 km in the vicinity of the Dartmoor pluton but possibly 5-6 km further west (Taylor 2007).

The batholith is composite and displays considerable mineralogical and textural variation. Biotite granites, all of which are two-mica granites, are dominant with subordinate tourmaline and topaz granites contributing <10% at the present exposure level (Dangerfield and Hawkes 1981; Manning et al. 1996; Müller et al. 2006; Scrivener 2006). Field relations consistently show that all granites post-date host rock structures developed during Variscan convergence and largely post-date those attributable to post-Variscan extensional reactivation (Alexander and Shail 1995). Quartz-porphyry and microgranite dykes (locally called ‘elvans’) are hosted by faults developed in the older granites and their adjacent country rocks during ongoing NNW-SSE extension (Shail and Wilkinson 1994). The Kingsand Rhyolite Formation (Leveridge et al. 2002) in SE Cornwall provides the only in situ evidence for felsic volcanism. However, the abundance of rhyolite clasts in Permian sedimentary successions indicates that felsic volcanism was extensive but subsequently eroded (Awad et al. 1996; Edwards et al. 1997).
Monazite and xenotime U-Pb ages indicate batholith emplacement occurred over a period of at least 20 Ma in the Early Permian, from 294-274 Ma (Chen et al. 1993; Chesley et al. 1993). The oldest granites (Isles of Scilly, Carnmenellis, Bodmin Moor) have similar ages (>290 Ma) to the oldest lamprophyre lavas and dykes (Dupuis et al. 2015).

Contact metamorphism of Devonian-Carboniferous sedimentary and volcanic successions and their mafic intrusive rocks overprints low-grade regional metamorphic assemblages and is recognisable in the field up to 1 km from the batholith. Slates typically exhibit spotting defined by biotite, cordierite, chlorite ± andalusite that is consistent with low pressure amphibolite (hornblende hornfels) facies. Exotic cordierite–anthophyllite assemblages in the proximal aureole of the Land’s End Granite indicate peak contact metamorphic conditions of 1.5 ± 1.0 kbar and 615 ± 50 °C (Pownall et al. 2012).

3.4 Episodic intraplate rifting and inversion (late Permian – Cenozoic).

Evidence for multiple low extension rift episodes occurs in the late Permian to Early Cretaceous sedimentary basins that surround the SW England massif (Evans 1990). Mid-Triassic ENE-WSW orientated extension (Chadwick and Evans 1995) brought about extensional reactivation of the NNW-SSE transfer faults, and formation of similar orientated new faults, in both host rocks and granites (Shail and Alexander 1997). Latest Jurassic – Early Cretaceous rifting was associated with substantial exhumation and likely erosional unroofing of Permian and Triassic cover rocks from the SW England massif followed by subsidence and marine deposition of the Chalk (Evans 1990).

The onset of North Atlantic opening in the latest Cretaceous – earliest Palaeogene brought about renewed exhumation and erosion of the previously deposited Chalk, once more exposing the SW England Massif. Further reactivation of NNW-SSE faults occurred during the Oligocene-Miocene intraplate shortening (Holloway and Chadwick 1986) that was a component of a complex Cenozoic inversion and exhumation history (Holford et al. 2009).

4. MINERALISATION IN SW ENGLAND

4.1 Overview

A wide variety of metals (Sn, Cu, W, Fe, Zn, Pb, Ag, Ba, U, Sb, Bi, Ni, Co, Bi) and As have historically been mined in SW England (Dines 1956; Burt 2014) and reflect four broad mineralisation episodes controlled by the changing regional tectonic regime (Table 1).
Production has been dominated by Sn and Cu from magmatic-hydrothermal vein systems associated with the Cornubian Batholith (episode 3). There has been subordinate Pb (+Ag), Zn and Fe production from post-granite ‘cross-course’ epithermal vein systems (episode 4). The production of all other metals has been minor and mineralisation episodes 1 and 2 have only been worked very locally. The character of each mineralisation episode is summarised below.

4.2 Pre-granite mineralisation

Episode 1 - Sedimentary exhalative (SedEx) mineralisation (Devonian-Carboniferous)

Exhalative Fe-Cu-Pb-Zn sulphides (Fig. 2a) are associated with the Upper Devonian sedimentary succession of the North Devon Basin (Scrivener and Bennett 1980) and on Lundy Island (Edmonds et al. 1979), and the Lower Carboniferous volcano-sedimentary successions of the Tavy Basin that crop out along the northern margins of the Dartmoor and Bodmin Moor granites (e.g., at Wilsey Down and Egloskerry; Benham et al. 2004). Stratiform low-grade Mn ores are found around Exeter, the Teign Valley, Milton Abbot and Brentor (Beer and Scrivener 1982).

The Perran Iron Lode is a NW-SE trending, paragenetically, complex calcite-siderite-hematite breccia zone up to 30 m in width that hosts Fe, Zn and Pb mineralisation. The earliest paragenesis is represented by banded siderite, calcite and sphalerite that pre-dates Variscan deformation and has been interpreted as sedimentary exhalative (SedEx) or volcanic-exhalative mineralisation contemporaneous with deposition of the Devonian host rocks (Henley 1971; Scrivener et al. 2006). Small quantities of Sn reported by Goode and Merriman (1977) indicate that it was subsequently overprinted by magmatic-hydrothermal fluids (episode 3); it is also cut by epithermal cross-course veins (episode 4) (Scrivener et al. 2006).

Episode 2 - Orogenic shear zone hosted Au-Sb + base metal mineralisation (Carboniferous)

NW-SE to N-S trending steeply inclined strike-slip shear zones, active as transfer faults during Variscan thrusting, cut the Devonian-Carboniferous successions and are locally associated with Au-Sb and base metal mineralisation (Stanley et al. 1990b). These have not been sampled for this study but exhibit some characteristics of orogenic gold deposits. Two occurrences associated with historical metal production have been described in detail. Quartz-carbonate veins in the Tavy Basin succession around Wadebridge carry Au, As, Ba,
Cu, Fe, Pb, Sb, and Zn (Clayton et al. 1990; Clayton and Spiro 2000). A broadly similar association is hosted by quartz-carbonate veins in the Looe Basin succession near Loddiswell (Stanley et al. 1990b). Inclusion fluid and textural studies on veins from the Wadebridge area indicate quartz-Au-Sb was early and precipitated from CO$_2$-rich metamorphic fluids with Th 315-280 °C and was post-dated by fluids with Th 210-180 °C responsible for Pb-Zn-Ag mineralisation (Clayton et al. 1990). These assemblages have the potential to be overprinted during selective reactivation of NW-SE to N-S trending fault zones during late Permian to Cenozoic rifting and inversion (Stanley et al. 1990b).

4.3 Episode 3 - Granite-related mineralisation (Early Permian)

The progressive emplacement of the Cornubian Batholith, over a 20 Ma period in the Early Permian, was associated with the release of huge volumes of magmatic-hydrothermal fluids (Chen et al. 1993; Chesley et al. 1993). Fluid migration through both the granites and their overlying host rocks was primarily controlled by fault and joint systems developed in the contemporaneous post-Variscan extensional regime (Shail and Wilkinson 1994). The variety of granite-related mineralisation styles reflect the complex interplay between magmatic-hydrothermal, meteoric, metamorphic and basinal fluids during variable mixing and unmixing, cooling, mineral deposition, and fluid-rock equilibration (Jackson et al. 1989; Alderton 1993; Scrivener and Shepherd 1998; Scrivener 2006).

Several parageneses formed by magmatic-hydrothermal mineralisation during and after the granite emplacement. Although described as discrete types, these parageneses should be considered as a continuum in evolution from high-temperature parageneses formed largely from magmatic-derived fluids, to lower temperature parageneses formed from magmatic fluids that were substantially diluted with other crustal fluids. Skarns formed where the granite-related fluids came into contact with metabasalts and metacarbonates. The development of vapor-saturated carapaces led to hydraulic fracturing of the host and the formation of greisen-bordered sheeted vein systems, quartz-tourmaline lodes, veins and breccias. Leveridge et al. (1990) suggested that these two parageneses formed by unmixing of magmatic fluids into low-salinity and hypersaline components.

Quartz-tourmaline lodes, veins and breccias and polymetallic sulphide lodes developed as magmatic fluids migrated along fault zones in the outer parts of the granite and their surrounding host rocks. The lodes are commonly strongly zoned with B, Sn, W and As precipitating in quartz ± tourmaline gangue assemblages, within or close to the granites, from fluids that were almost entirely magmatic-hydrothermal in origin. Cooling and
increasing mixing with meteoric fluids controlled the precipitation, primarily in the metamorphic host rocks, of Sn, W, As, Cu and then Pb and Zn in a quartz-chlorite ± fluorite gangue (Dines 1956; Hosking, 1969; Scivener 2006).

The granite-related parageneses in SW England are considered as classical examples of zoning in magmatic-hydrothermal mineral deposits, and this is most clearly expressed in the polymetallic lodes. Very similar systems have developed elsewhere in the World, notably the San Rafael Lode in Peru (Kontak et al. 2002) and the Yankee Lode associated with the Mole Granite in Australia (Audétat et al. 2000).

**Pegmatites**

Pegmatites and aplites (not illustrated) are occasionally mineralised, particularly those associated with topaz granites, although they have not been commercially exploited for metals. Pegmatite-aplite sheets at Megiliggar Rocks in the roof zone of the Tregonning Granite, for example, are banded assemblages of very coarse grained and fine grained successions of feldspar, quartz, tourmaline and mica (muscovite or Li-mica) with minor apatite and topaz, and host löllingite, arsenopyrite, molybdenite, bismuth and wolframite with traces of columbite, Sn-bearing rutile, cassiterite and uraninite (Bromley 1989). A similar assemblage occurs in the Goonbarrow Pegmatite of the St Austell Granite. The Carnmenellis Granite hosts internal pegmatites that comprise quartz, albite, microcline, orthoclase, tourmaline, muscovite, Li-mica, topaz, apatite, fluorite and betrandite (Be₄Si₂O₇(OH)₂), but which also include cassiterite, stokesite (CaSnSi₃O₉•2H₂O), sphalerite, pyrite and galena (Hosking, 1954, 1969). A wide variety of minerals, many of them rare, have also been identified in the Meldon Aplite (Edmonds et al., 1968), and Embrey (1953) reported beryl from pegmatites at the New Consols Mine at Stoke Climsland.

**Skarns**

Skarn deposits (not illustrated) evolved in metabasalts and calc-silicate bearing metasedimentary rocks across the region. The deposits can be broadly classified into two types: magnetite-silicate skarns (MSK) that have variable assemblages of garnet, magnetite, cassiterite, tourmaline, pyroxene, hornblende, and biotite; and sulphide-silicate skarns (SSK) that carry cassiterite, arsenopyrite, löllingite, chalcopyrite, sphalerite, pyrrhotite and/or pyrite along with garnet, tourmaline, malayaite and chlorite. Magnetite-silicate skarns occur across the region and include Grylls Bunny at Botallack (Jackson 1974; van Marcke de Lummen 1985; Goode and Taylor 1988), Magdalen Mine at Ponsanooth (Scrivener 2006).
and the Haytor Vale Mine near Bovey Tracey (Scrivener et al. 1987). Sulphide-silicate skarns developed locally in the Meldon Chert Formation along the northern margin of the Dartmoor granite (Beer et al. 1989) and include the Belstone Consols, Ramsley, Forest and Red-a-Ven Mines near Okehampton (el-Sharkawi and Dearman 1966; Beer et al. 1989). Fluid inclusions indicate that the skarns encompass an early silicate assemblage (garnet-pyroxene-magnetite) formed at temperatures in excess of 600°C from saline (10-20 wt% NaCl eq) fluids with a later Sn-B-As-Cu-Zn silicate-sulphide assemblage formed from hypersaline (30-50 wt% NaCl eq.) brines at 350–460°C (Peng and Bromley 1992).

**Greisen-bordered sheeted veins (GBSV)**

Greisen-bordered sheeted vein complexes (Fig. 2b) developed in the apical parts of the granite (endogranitic) and the overlying metasedimentary rocks (exogranitic) in several locations across the region. The veins are 1 – 10 cm in width and extend to a distance of 100 m away from the granite contacts. The sheeted vein complexes at St Michael’s Mount and Cligga Head are both examples of endogranitic greisen systems and comprise hundreds of closely spaced, steeply dipping sub-parallel quartz veins. Further vein-complexes include Goonbarrow and Hensbarrow near St Austell, Bostraze and Balleswidden in Penwith, and Hemerdon in Devon. Exogranitic greisen-bordered veins occur at Redmoor and Hemerdon (cf., Goode and Taylor 1988). The greisen-bordered veins at Hemerdon show significant mineralogical differences across the granite contact (R. Scrivener, personal communication, 2009), indicating that host rock interactions are significant in their evolution.

The greisen-bordered veins show little or no brecciation, are infilled with quartz and tourmaline and carry cassiterite, wolframite, stannite group minerals (we do not differentiate here between stannite, stannoidite, kësterite and ferrokësterite), chalcopyrite, sphalerite, bismuthinite, löllingite and arsenopyrite. Bromley (1989) suggested that mineralisation in W-As-Sn was associated with the primary emplacement, while the Cu-Zn sulphide assemblage was introduced through subsequent re-fracturing of the original veins. Minor gangue minerals include topaz, beryl, apatite and fluorite (cf., Goode and Taylor 1988). Endogranitic veins are surrounded by 5 – 20 cm wide strongly silicified zones where feldspars were replaced by muscovite and quartz. Kaolinization of the granite host is particularly well developed at Goonbarrow and Cligga Head. Exogranitic veins, in contrast, have 2 – 5 mm wide borders of muscovite, and the metasedimentary host rocks typically carry significant disseminated tourmaline and cassiterite.
Fluid inclusions indicate that the greisen-bordered veins were precipitated over a wide range of temperatures. Inclusions in topaz, cassiterite and wolframite homogenize between 300ºC and >500ºC (Campbell and Panter 1990; Williamson et al. 1997), while quartz inclusions homogenize between 250ºC and 350ºC (Campbell and Panter 1990). Campbell and Panter (1990) found that inclusions in cassiterite and wolframite from Cligga Head and St Michaels Mount were generally low salinity fluids (3-9 wt% eq.), while Williamson et al. (1997) found that inclusions within topaz from Hensbarrow had much higher salinities (23–30 wt% NaCl eq.).

Quartz-tourmaline lodes, veins and breccias (QTL)

Quartz-tourmaline (-cassiterite) lodes, veins and breccias (Fig. 2c) developed within and immediately adjacent to the granites. These bodies have no mineral borders but are commonly associated with tourmalinisation of their host rocks. Primary white feldspars are replaced by tourmaline and secondary red-pink feldspars (e.g., Lister 1978), and biotite is commonly replaced by tourmaline and/or chlorite (Scrivener and Shepherd 1998). Quartz-tourmaline lodes, veins and breccias are locally deficient in sulphides but appear widely as early manifestations of systems that evolved to polymetallic sulphide lodes. Quartz-tourmaline lodes at Ding Dong Mine and Birch Tor and Vitifer Mine (Goode and Taylor 1988; Bromley 1989) carry cassiterite and haematite, while the Wheal Remfry Breccia pipe has little cassiterite or wolframite but carries Sn and W in rutile (Müller and Halls 2005). Fluid inclusions indicate temperatures of formation of 400-230ºC and salinities of 5-15 wt% NaCl eq. (Alderton and Harmon 1991).

Polymetallic sulphide lodes (PSL)

Polymetallic sulphide lodes (Fig. 2d) carry W, Sn, As, Cu, Zn and Pb and represent the most extensive mineralisation across the region. They were the dominant targets for mining in the 18th and early half of the 19th century, and continued to be economically significant until the mine closures of Geevor in 1990, Mount Wellington in 1991, Wheal Jane in 1992 and South Crofty in 1998. Some of the richest mines in the region were: 1) Dolcoath (Camborne-Redruth district), the most productive mine in Cornwall developed to a depth of more than a kilometre and in continuous operation from the late 18th century to 1919 (Harris 1974). 2) Fowey Consols, the largest Cu mine in the St Austell district, in operation until 1870 (Dines 1956). 3) South Caradon, the deepest and richest Cu mine in the Caradon district, which at one stage was the third largest producer of Cu in Cornwall (Dines 1956);
and 4) Devon Great Consols, thought to be Europe’s richest Cu mine between 1844 and 1870, which continued to supply half of the World’s As in the 1920s (Booker 1967).

The polymetallic sulphide lodes occupy faults that extend for several kilometres away from the granites and show evidence for open-space deposition accompanied by variable wall-rock alteration. Primary silicates are variably replaced by sericite, tourmaline and chlorite, locally with albitionization, silicification, and/or kaolinisation as well as the introduction of disseminated cassiterite and arsenopyrite. The lodes may themselves locally include greisen and/or quartz-tourmaline components (cf., Scrivener and Shepherd 1998). The polymetallic sulphide lodes generally trend ENE-WSW or E-W, consistent with their formation Early Permian NNW-SSE crustal extension (Shail and Wilkinson 1994). Individual polymetallic lodes can be up to several meters wide, are structurally complex, and strongly zoned. Textures of successive deposition and replacement are evidence for multistage emplacement and evolution. The lodes typically exhibit early assemblages of cassiterite, arsenopyrite, wolframite and pyrite in a quartz and tourmaline gangue (locally with muscovite). This stage is followed by deposition of base metal sulphides (chalcopyrite, sphalerite, stannite, pyrite) associated with quartz and chlorite gangue; which further is succeeded by pyrite, chalcopyrite, sphalerite and galena (locally with Sb minerals) in a fluorite-siderite gangue. Fluid inclusions from the polymetallic sulphide lodes indicate temperatures of formation between 300 and 220ºC and salinities below 8 wt% NaCl eq. (Alderton and Harmon 1991).

The composition of lode systems varies systematically across the region. The parageneses associated with the Land’s End, Carnmenellis and St Agnes granites are much richer in Sn and Zn than the systems associated with the St Austell, Bodmin Moor and Dartmoor granites, which were mostly mined for Cu (cf., Dines 1956; Willis-Richards and Jackson 1989).

Individual lodes are also strongly zoned with respect to the distribution of different metals and minerals (called telescoping by Hosking, 1969). A high-temperature arsenopyrite-cassiterite-wolframite assemblage in a quartz ± tourmaline gangue is commonly followed by an assemblage of arsenopyrite and chalcopyrite with minor stannite in a gangue of quartz and chlorite, which in turn is followed by a zone with sphalerite and pyrite in a siderite-calcite-fluorite gangue. This mineralogical variation is commonly expressed up-dip and along strike in individual lodes, away from the source of the magmatic-hydrothermal fluids. However, many lodes show much more complex internal structures reflecting changes in mineral deposition during evolution as well as successive
episodes of re-fracturing, dissolution and re-precipitation, re-crystallisation and alteration. Polymetallic lodes commonly form a continuum in deposition with quartz-tourmaline vein assemblages (observed at Dolcoath), and more rarely, greisen-bordered veins such as at Wheal Jane (Bromley and Holl 1986) and at depth in the Devon Great Consols Mine (R. C. Scrivener, personal communication, 2012).

4.4. Episode 4 - Post-granite mineralisation (Triassic)

The main post-granite mineralisation led to the sub-vertical, NW-SE trending epithermal crosscourse veins (Scrivener et al. 1994) (Fig. 2e). The veins are typically up to metre wide, infilled with quartz, chalcedony, chlorite and hematite and locally carry significant Pb, Zn, Cu, Ag, Ba and F. They cross-cut the polymetallic W-Sn-As-Cu-Zn lodes and are commonly associated with dextral fault slip of up to 100 m. The crosscourse veins were mined primarily for Pb and Ag with Cu and Zn as by-products. The richest deposits were found in the Bere Alston area to the north of Plymouth, where silver was already being extracted by the late 13th century (Rippon et al. 2009). The dominant vein assemblages formed from low temperature (100-170°C), high salinity (19-27 wt% NaCl eq.), CaCl₂-rich fluids that are thought to have originated in Permo-Triassic ‘red-bed’ sedimentary basins (Scrivener et al. 1994; Gleeson et al. 2001). The deposition of argentian galena and sphalerite in a quartz-fluorite-siderite gangue is attributed to the mixing of these highly saline basinal fluids with connate waters. Further carbonate-Au-Sb-Se mineralisation at Hope’s Nose (Stanley et al. 1990a) formed at 65-120°C from fluids with similar salinities and compositions (Scrivener et al. 1982).

5. ANALYTICAL METHODS

Mineral compositions were determined with the JEOL JXA-8200 electron-probe microanalyzer at Camborne School of Mines, University of Exeter, using a 180 nA electron beam accelerated to 15 kV and focused to a diameter of 1-5 µm. Analyses were collected by the use of wavelength dispersive spectrometers, calibrated to pure metal, alloy and sulphide standards, and were corrected for matrix effects with the CITZAF v. 3.50 routine (Armstrong 1995) implemented by P. Carpenter. Major element signals were counted over 20 s, while minor elements were analysed for 60-120 s. Indium, gallium and cadmium were measured at the Lα lines on JEOL XCE-type spectrometers (for high spectral resolution) using a PET crystal for In-Lα and Cd-Lα, and a TAP crystal for Ga-Lα.
The Sn-L\eta (\lambda = 3.789 Å) interference on the In-L\alpha (\lambda = 3.772 Å) intensity (cf., Benzaazoua et al. 2003) was determined to contribute 22 ppm In per 1 wt% Sn by linear approximation to the minimum measured In concentrations in stannite and cassiterite (Fig. 3). A further minor correction for the 3rd order In-L\alpha reflection (\lambda = 11.316 Å) on the Ga-L\alpha intensity (\lambda = 11.292 Å) amounted to 500 ppm Ga per 1 wt% In measured on InAs. For silicate minerals, the K-K\alpha (\lambda = 3.741 Å) interference on the In-L\alpha amounted to 49 ppm In (59 ppm In$_2$O$_3$) per 1 wt% K$_2$O.

In the absence of spectral interferences, analytical lower limit of detections for In, Ga and Cd are estimated to 50 ppm. However, in minerals with significant Sn (stannite group minerals, cassiterite), the lower limit of detection for In is closer to 100 ppm.

Major and trace mineral abundances were determined by the QEMSCAN 4300 at Camborne School of Mines, University of Exeter. The instrument is a scanning electron microscope with fully automated electron beam and stage controls, energy-dispersive X-ray spectrum acquisition and computer-based spectral classification to allow for the rapid determination of the spatial distribution of minerals on polished sample surfaces. The spatially resolved X-ray spectra allow for the precise determination of modal abundances, particle size distributions, and mineral associations. The system has routines for trace mineral searches as well as scans of entire surfaces (fieldscans) of polished blocks and thin sections. Detailed information on the methodology and specific analytical modes are reviewed by Gottlieb et al. (2000) and Pirrie et al. (2004).

Bulk mineral abundances determined by fieldscans are based on 1000 X-ray counts per spectrum. Typically more than 1 million points were collected at 10 µm spacing and classified into mineral groups (Fig. 4) according to the diagnostic X-ray signals by use of a customized species identification protocol (SIP) based on the Intellection LCU5 SIP. Roquesite was located by a trace mineral search with the introduction of tightly defined upper and lower threshold limits on the electron backscattering coefficient. While most minerals and mineral groups are very tightly constrained, some of the more sensitive discriminations may result in misclassifications of minerals with very similar X-ray spectra (such as kaolinite and topaz; tourmaline and chlorite; and complex fine-grained mixtures of clays, micas and feldspar). Results were verified optically for these assemblages.

6. RESULTS
Samples from 50 locations across the region have been used to characterise pre-, syn- and post-granite mineralisation styles (Fig. 1, Supplementary data A1). Sample location details are included in Table 2, along with a summary of the style of mineralisation and the observed mineral assemblages. Many specimens are polished blocks and thin sections from archive collections, for which whole-rock geochemical analyses are not available. Textures of the different mineralisation styles are represented in Figs. 4-8. Data on mineral abundances from the QEMSCAN analysis are included as supplementary data file A2. Summaries of mineral analyses are included as Tables 3-5, and the full analytical data are included in the supplementary data file A3. Mineral compositional relations are presented in Figs. 9-12. Indium partitioned into cassiterite, stannite group minerals, chalcopyrite and sphalerite with local occurrences as roquesite and within tennantite. Sphalerite is the only Ga-bearing sulphide, while Cd is found in sphalerite and tennantite. Indium was not detected in wolframite, löllingite, arsenopyrite, pyrite, pyrrhotite, bornite, chalcocite, galena, rutile, magnetite, haematite, garnet, tourmaline, malayaite or biotite.

6.1 Pre-granite sulphide mineral occurrences

Stratiform sulphide parageneses at Wilsey Down (Fig. 5a-b) and Egloskerry (Fig. 5c-k) are associated with Lower Carboniferous carbonaceous black slate of the Teign Valley Group. Two sulphide-rich bedding-parallel layers sampled from the Wilsey Down borehole core (approximately 250 m depth, McKeown et al. 1973) are up to 20 mm thick and intensely folded (Fig. 5a). A prominent axial planar cleavage penetrates the sample but is not associated with sulphide redistribution. The host mudrocks also contain disseminated sulphides. Pyrite and pyrrhotite dominate with minor chalcopyrite and sphalerite and traces of galena (Fig. 5b). The sphalerite carries up to 1 wt% Cd and 1000 ppm Ga, but In concentrations are systematically below the lower limit of detection. Chalcopyrite carries no detectable In.

Drill core samples from Egloskerry are slates with interbedded metasiltstones, metacarbonate rocks and metavolcanic rocks (Fig. 5c-k). Galena, sphalerite and pyrite are disseminated throughout and locally form interbedded lenses and bands (Fig. 5d-f). Chalcopyrite and pyrrhotite are very rare, but a single sample (Fig. 5j) carries 4 vol% arsenopyrite. The sulphides are predominantly stratabound (Fig. 5d-e) with occasional breccias (Fig. 5f), but have been partially redistributed along with quartz and locally calcite into tensile fractures, Riedel shears (Fig. 5g-h) and transgressive veins (Fig. 5i-j). One sample includes an undeformed quartz vein with hematite, sphalerite and minor galena,
which appears to be texturally and mineralogically similar to crosscourse mineralisation (Fig. 5k). The sphalerite has 3-4 wt% Fe and carries significant Cd (up to 2150 ppm) and Ga (up to 1050 ppm) but In is generally below the lower limit of detection with a couple of outliers up to 100 ppm.

Rare sulphide lenses are interbedded with slates of the Lametry peninsula on Lundy Island that are correlated with the Upper Devonian succession of the North Devon Basin (Edmonds et al. 1979; Leveridge and Hartley 2006). Pyrite and sphalerite dominate with small amounts of pyrrhotite and traces of chalcopyrite and galena in a gangue of calcite and quartz. The sphalerite has chalcopyrite disease (Barton and Bethke 1987) and carries 1.5 - 3 wt% Fe, up to 1.4 wt% Cd and 1080 ppm Ga. In concentrations are mostly below the lower limit of detection with a couple of scattered outliers up to 240 ppm. The galena carries 0.66 – 0.92 wt% Ag.

A single sample from the Duchy Peru Mine on the Perran Iron Lode (Fig. 5l) has angular inclusions of quartz, feldspar and slate in a matrix of iron-oxides, chlorite, apatite and calcite. Chalcopyrite forms large amoeboidal grains, while pyrite and sphalerite are disseminated in the matrix as well as included within quartz clasts. Minor galena is associated with the sphalerite. Chalcocite rims the chalcopyrite and is dispersed as smaller particles in the matrix. Two minute grains of cassiterite (<15 µm), one of which is hosted in a quartz clast, suggest that the breccia may have been influenced by granite-related fluids. Indium is below the lower limit of detection in the sphalerite and chalcopyrite. The sphalerite is Fe-poor (< 6 wt%) and carries significant Cd (900 - 7000 ppm) and Ga (380 - 590 ppm) but no In. Chalcopyrite carries traces of Zn (200-720 ppm) and pyrite up to 0.66 wt% As.

6.2 Skarn deposits

The Red-a-Ven and Ramsley mines at Okehampton worked sulphide-bearing skarns hosted by calc-silicate hornfels in the Meldon Chert Formation adjacent to the Dartmoor Granite. The ores are massive or crudely banded assemblages (Fig. 6a-c) of löllingite, pyrite, pyrrhotite, chalcopyrite and sphalerite with minor arsenopyrite in a gangue of tin and/or boron bearing silicates (axinite, datolite, malayaite, grossular and andradite), pyroxene, hornblende, chlorite, quartz and fluorite. The sulphides generally form the matrix between the silicate minerals. Frequent inclusions of löllingite in the garnet porphyroblasts indicate simultaneous crystallisation and growth, while sphalerite is only included in the outermost garnet margins (Fig. 6a). The matrix consists of domains of pyrrhotite-löllingite, sphalerite-löllingite and axinite-malayaite. Sphalerite and chalcopyrite are mostly interstitial
to the silicates and also occur in fractures within the silicates (Fig. 6b) as well as the various matrix assemblages (Fig. 6c). Epidote locally occurs in late stage fractures, while pyrite commonly rims pyrrhotite. Fluorite is locally abundant in the matrix.

Sphalerite has chalcopyrite disease and contains 500-1250 ppm In (average of 890 ppm), 4300-4800 ppm Cd and 100-395 ppm Ga. Chalcopyrite has up to 443 ppm In and up to 0.25 wt% Zn with scattered higher values probably representing microinclusions of sphalerite. Pyrrhotite carries up to 220 ppm As. Whole-rock In concentrations calculated by mineral deportment reach 193 ppm and the In is almost exclusively hosted in sphalerite.

The Ashton Shale (Teign Valley Group) at the Haytor Vale Mine hosts disseminated arsenopyrite, pyrite, chalcopyrite and sphalerite within a quartz, feldspar, biotite, muscovite and chlorite matrix. Sphalerite has on average 4 wt% Fe and 0.6 wt% Cu, up to 1300 ppm In (average 540 ppm), around 2400 ppm Cd and 1000 ppm Ga. Chalcopyrite carries trace Zn (0.13 wt%) but In is close to the lower limit of detection.

A skarn sample (Fig. 6d) from Ken Hosking’s collection (e.g. Hosking 1969) was attributed to the Perran St George Mine near Perranporth. However, as there are no published records of skarns or their usual hosts (metabasalts, calc-silicate rocks) in the vicinity of this mine the provenance is unconfirmed. The sample carries cassiterite, pyrrhotite, pyrite and chalcopyrite with minor arsenopyrite and traces of sphalerite in a gangue of quartz and hornblende with minor fluorite and traces of chlorite and sphene. Pyrite envelops pyrrhotite, while sphalerite occurs only as minute inclusions in chalcopyrite. In contrast to Red-a-Ven and Ramsley, there is no axinite, datolite, malayaite or tin-bearing garnet. Sphalerite contains 5.5-7.2 wt% Fe, up to 1.2 wt% In, 1140-1898 ppm Cd and 328-677 ppm Ga. Chalcopyrite contains up to 1246 ppm In and up to 0.1 wt% Zn. The sample also carries rare, minute grains of roquesite (CuInS₂). Whole-rock In concentrations reach 320 ppm and are predominantly hosted in chalcopyrite.

Samples of silicate-oxide skarns from Grylls Bunny (Fig. 6e-f) and Magdalen Mine (Fig. 6g) are predominantly assemblages of magnetite, garnet and tourmaline with variable pyroxene, hornblende, biotite, chlorite, quartz and fluorite. The skarn samples are mineralogically and texturally very variable. While they locally carry cassiterite (Fig. 6f), sulphides are generally confined to cross-cutting veins. Whole rock In concentrations determined by ICP-MS locally reach 5 ppm and display a broad correlation with Sn but not with Cu or Zn.
6.3 Greisen-bordered sheeted vein deposits

The greisen-bordered veins at Cligga Head (samples from historic waste dumps and underground exposures) and Redmoor (samples from drill cores) carry assemblages of cassiterite, wolframite, stannite group minerals, arsenopyrite, löllingite, chalcopyrite, sphalerite and pyrite (Fig. 6h-l). At Redmoor, the sulphide assemblages also occur in polymetallic lodes that have no mineral borders.

Löllingite mostly occurs as cores or inclusions in arsenopyrite (Fig. 6j-k), although a single sample from Cligga Head also displays löllingite in cross-cutting veins (not shown). Stannite group minerals are locally abundant at both localities (Fig. 6j) as well as traces of bismuth minerals (not shown). Sphalerite has abundant inclusions of chalcopyrite and, more rarely, stannite. Fractures in cassiterite and arsenopyrite are commonly infilled by later chalcopyrite, sphalerite, pyrite, chlorite and quartz (Fig. 6l), while all sulphides are cut by veins of iron-oxides and/or fluorite (Fig. 6j-l). Bornite and chalcocite locally occur within late fractures in chalcopyrite, possibly reflecting supergene oxidation. The gangue is commonly dominated by siderite, quartz, fluorite and tourmaline with lesser chlorite.

Sphalerite from Cligga Head is Fe-poor (<1.8 wt%) while sphalerite at Redmoor contains between 5.7 and 14.9 wt% Fe. Chalcopyrite disease is widely developed and in some samples from Cligga Head accompanied by sphalerite-stannite intergrowths (Dobrovol'skaya et al. 2008). Sphalerite at Cligga Head carries up to 740 ppm In, while Ga varies from 423 to 665 ppm and Cd from 1265 to 1538 ppm. Sphalerite from Redmoor has up to 2013 ppm In, while Ga reaches 560 ppm and Cd varies between 1612 and 6911 ppm. No systematic correlations were detected between the concentrations of Fe, Cu, In, Cd, and Ga. Chalcopyrite at both Cligga Head and Redmoor carry up to 0.15 wt% Zn; scattered analyses with up to 0.4 wt% Zn are likely to represent microinclusions of sphalerite. Indium concentrations at Cligga Head locally reach 540 ppm, while Redmoor locally carries up to 939 ppm. Gallium, Cd and Sn are below the lower limit of detection in all of the chalcopyrite analyses. Stannite group minerals from Cligga Head are dominated by Zn (6 – 14 wt%) over Fe (2.5 – 7.6 wt%) and at Redmoor by Fe (11.7 – 12.4 wt%) over Zn (3.4 – 5.2 wt%). At Cligga Head, the stannite group mineral has up to 450 ppm In, while the mineral at Redmoor is barren. The stannite group minerals carry no Ga or Cd at the lower limit of detection. No In, Ga, or Cd was detected in bornite, chalcocite, pyrite, pyrrhotite, arsenopyrite, or löllingite. Whole rock In concentrations at Cligga Head and Redmoor are below 100 ppm and dominantly hosted by chalcopyrite (except for a single sample from...
Cligga Head where more than 50% is hosted in stannite group minerals. A single sample from Redmoor carries minute grains of roquesite.

6.4 Quartz-tourmaline lodes, veins and breccias

Quartz-tourmaline lodes, veins and breccias were examined from Ding Dong Mine, Holman’s Test Mine, Dolcoath, Wheal Remfrey and Vitifer Mine, as well as early stage components in the polymetallic sulphide lodes. The samples are dominated by tourmaline and quartz, and only the samples from Ding Dong and Vitifer have cassiterite. Specular hematite occurs at Vitifer, but sulphides are mostly confined to later, cross-cutting veins (Fig. 7a-b). Tourmaline, biotite and hematite had no In at the lower limit of detection; sulphides are considered to be part of the polymetallic sulphide paragenesis described below. Whole rock concentrations by ICP-MS locally reach 53 ppm In.

6.5 Polymetallic sulphide lodes

Samples from more than 20 polymetallic sulphide lodes across the region represent widely variable assemblages of cassiterite, wolframite, arsenopyrite, chalcopyrite, pyrite and sphalerite (Fig. 7c-l). Although the polymetallic sulphide lodes have no distinct mineral borders (Fig. 7c), vein margins are commonly associated with strong wall rock tourmalinisation (Fig. 7c) or chloritisation (Fig. 7d-e). Minor sulphide disseminations are common in the wall rock (Fig. 7a-c, f), and locally the sulphides appear to ‘seep’ into the wall rock (Fig. 7c). The sulphide lodes are typically associated with minor brecciation (Fig. 7f). Polymetallic sulphide lodes commonly overprint earlier quartz-tourmaline breccias, while in other places, such as Capel Tor and the deeper parts of Devon Great Consols, the sulphide lodes locally have greisen borders (Fig. 7g).

Although chalcopyrite is the most common Cu host (Fig. 7a-e, g-h), bornite is locally significant at Geevor and Dolcoath (Fig. 7i). Chalcocite is confined to rims and fractures in chalcopyrite and bornite (Fig 7j). Cassiterite is the dominant Sn mineral (Fig. 7k), but stannite group minerals are also locally abundant at Botallack, Devon Great Consols and Hingston Down. The granite-related systems carry three different morphological styles of sphalerite: Sphalerite I forms micro-inclusions in chalcopyrite and pyrite in samples that otherwise have little or no sphalerite; sphalerite II coexists with chalcopyrite as large separate unzoned grains with chalcopyrite disease; sphalerite III forms large separate grains that have no chalcopyrite inclusions but strong compositional zoning in Fe and Zn. The lodes commonly carry traces of Bi-minerals, galena, löllingite, marcasite, pyrrhotite, monazite,
rutile and tennantite. The gangue is dominated by quartz, tourmaline and chlorite, and carries minor fluorite, apatite, siderite, kaolinite and calcite.

Indium is distributed between chalcopyrite, sphalerite, stannite group minerals, cassiterite, and locally also tennantite and minute grains of discrete In minerals such as roquesite (at Geevor) and possibly dzhalindite (at Dolcoath).

Chalcopyrite locally reaches 0.22 wt% In. There is no particular discrimination between In in the different types of ores, except that concentrations are systematically low in ores with sphalerite-III.

Sphalerite I locally reaches 1.4 wt% In at Dolcoath, but the samples with the highest concentrations generally have very little sphalerite. Cadmium and Ga concentrations reach 4943 and 979 ppm respectively. Indium shows some correlation with Cu within individual samples but none with Fe, Cd or Ga.

Sphalerite II is by far the most abundant and widespread type. It has widely developed chalcopyrite disease and at Geevor also displays intergrowths with stannite. Iron-rich sphalerite (10-12 wt% Fe) dominates at Geevor, Dolcoath, Wheal Jane and Nangiles, while sphalerite in samples from the Caradon District has less than 2 wt% Fe. Sphalerite at Botallack and in the St Agnes District (Wheal Charlotte, Trevellas Coombe, Blue Hills) is intermediate with 4-8 wt% Fe. Indium concentrations are variable with averages from below the lower limit of detection at Cotehele and Tavy Consols to more than 1000 ppm at Wheal Fortune, Capel Tor, Dolcoath, Wheal Charlotte, Trevellas Coombe, and Botallack.

Sphalerite III is found in only a few samples from Geevor, Nangiles, Wheal Charlotte, Dolcoath, Wheal Jane and East Wheal Rose. This type of sphalerite appears to be associated with quartz, chlorite, chalcopyrite, pyrite, and locally with wolframite, cassiterite, arsenopyrite, pyrrhotite and galena. The sphalerite is strongly zoned with respect to Fe and free from chalcopyrite disease. Iron varies between 3.0 and 12.2 wt% and Cu locally reaches 0.46 wt%. Indium reaches 8207 ppm, while Cd varies between 1017 and 2270 ppm and Ga reaches 1092 ppm.

Stannite group minerals from Botallack have the highest In with an average of 27 analyses at 3167 ppm and the highest concentrations exceeding 6800 ppm. The zinc concentrations are variable (1.2 - 9.2 wt%), and the highest In is found in the stannite with least Zn. At Htingston Down and Devon Great Consols, In concentrations are much lower.
with averages of 220 and 410 ppm respectively and display no particular correlation with zinc.

6.6 Post-granite mineralisation

Sulphide-bearing crosscourse samples were examined from Wheal Penrose, Wrey-Ludcott United, Greystone Quarry, Wheal Betsy, Buttspill Mine, Holmbush Mine, and Wheal Exmouth. The mines operated until the late 19th century and predominantly produced silver and lead (Dines 1956).

Samples were collected from mine spoil heaps and include variable assemblages of pyrite, pyrrhotite, sphalerite, galena (locally argentian), chalcopyrite and haematite (Fig. 8). Arsenopyrite, antimony minerals and barite are locally significant at Wheal Betsy, Wheal Exmouth and Buttspill. Fluorite is abundant in the samples from Buttspill and Wrey-Ludcott United, while the gangue at Wheal Betsy, Holmbush, Wheal Penrose and Greystone Quarry is dominated by quartz. One sample from Wrey-Ludcott United has significant calcite infill, while a vein of banded haematite and apatite cuts another. Minute traces of cassiterite and tourmaline are locally found.

The samples from Greystone Quarry and Wheal Exmouth (Fig. 8a-c) carry no traces of cassiterite or tourmaline and contain no In. Minute traces of cassiterite, löllingite and/or arsenopyrite were found at Wheal Penrose, Buttspill and Holmbush mines (Fig. 8d). Of these, the Wheal Penrose sample has up to 296 ppm In within chalcopyrite, while the others were barren. Sphalerite at Greystone Quarry carries significant Cd (3600-4870 ppm) and Ga (337-597 ppm). Chalcopyrite has up to 415 ppm Zn. Galena carries up to 738 ppm Cd but no Ag.

At Wrey-Ludcott United, one sample is dominated by fluorite with calcite and minor pyrite, hematite and sphalerite (Fig. 8e). Sphalerite contains 3524 ppm Cd and 521 ppm Ga but no In. Another sample, however, carries clasts with abundant tourmaline, cassiterite and arsenopyrite (Fig. 8f) in a matrix of sphalerite, pyrite and hematite with traces of galena. Sphalerite in the matrix has chalcopyrite disease and contains around 4.2 wt% Fe. Indium reaches 1071 ppm (average 442 ppm), while Cd averages 2422 ppm and Ga 476 ppm.

Wheal Betsy contains substantial arsenopyrite and löllingite in banded ores with chalcopyrite, sphalerite, galena, pyrite and haematite (Fig. 8g-h) in a quartz gangue. Sphalerite at Wheal Betsy is relatively Fe poor (average 2 wt%) and carries up to 975 ppm In (average 106 ppm). Cadmium and Ga average 4700 ppm and 546 ppm with maximum
concentrations of 1.6 wt% Cd and 1004 ppm Ga. Chalcopyrite contains up to 285 ppm In (average 93 ppm).

7. MINERALOGICAL DISTRIBUTION OF INDIUM, GALLIUM AND CADMIUM

The most significant In hosts are sphalerite, chalcopyrite, cassiterite and stannite group minerals (Fig. 9). Minute grains of roquesite are locally significant, and sporadic In was also detected in tennantite at Geevor and Botallack. Pyrite-hosted In is erratic and probably relates to micro-inclusions of other minerals. No In was found in löllingite, arsenopyrite, pyrrhotite or galena. Although In was not detected in solid solution in bornite and chalcocite, these minerals are common hosts for roquesite.

By far the most significant In hosts across the region are sphalerite (Fig. 10-11) and chalcopyrite (Fig. 12). Where the minerals coexist, there is a broad correlation between their In contents (Fig. 13). Sphalerite carries 1-10 times more In than coexisting chalcopyrite. However, in the majority of the samples, chalcopyrite is much more abundant than sphalerite, so is usually the dominant contributor to the overall In budget.

7.1 Sphalerite

Sphalerite is the dominant carrier of Ga and Cd as well as In in the SW England ore systems (Table 3). While little In was detected in sphalerite from the pre-granite mineralisation, the mineral systematically carries In in the granite-related skarn, greisen and polymetallic sulphide lode systems. Elevated In concentrations are also found in some post-granite crosscourse veins, particularly where they carry traces of Sn- or As- minerals.

Sphalerite is most abundant in ore systems associated with the Carnmenellis, Land’s End and St Agnes granites. However, although sphalerite compositions vary significantly between, and probably within individual lodes, there appear to be no overarching regional controls on the compositional variability. All granite-related varieties of sphalerite carry In, but the concentrations correlate in very different manners with the major and trace metals (Fig. 10).

Sphalerite from the Perran St George skarn and sphalerite I from Dolcoath carry elevated Cu, which correlates negatively with (Zn+Fe) along a chalcopyrite control line (Fig. 10a). Elevated In concentrations are associated with high Cu (Fig. 10b), but the association does not define a distinct correlation. Indium concentrations correlate poorly
with Fe (Fig. 10c), although there is some evidence for a correlation with Fe+Zn (Fig. 10d), as also documented from the Freiberg region by Seifert and Sandmann (2006). This correlation approximately mirrors the correlation between In and Cu. Although In does not display a distinct correlation with Cd, high In appears to be exclusively hosted in sphalerite with low Cd (Fig. 10e). Indium shows perhaps a very weak positive correlation with Ga in the skarns (Fig. 10f).

The high concentrations of Cu (4-7 wt%) in sphalerite from these systems by far exceeds the solubility limit, or the relationship expected by solid solution with a roquesite component. Although the Cu can be explained by a chalcopyrite component, such a component cannot explain the high In concentrations. Similar Cu and In characteristics were reported from Mount Pleasant by Boorman and Abbott (1967) and Sinclair et al. (2006).

Sphalerite from Red-a-Ven and Ramsley mines, along with the remaining sphalerite I, sphalerite II and sphalerite in greisen-bordered vein systems do not show any particular association of In with Cu. Concentrations of both metals are generally lower with In mostly below 2000 ppm.

In contrast, In in sphalerite III displays a well-defined atomic correlation with Cu (Fig. 11). The dominant 1Cu:1In atomic ratio indicates that In is predominantly incorporated into sphalerite as a roquesite solid solution component. However, although less abundant, the sphalerite also locally includes zones with a 3Cu:1In atomic ratio. These zones also carry traces of Sn and are consistent with a sakuraiite component.

7.2 Chalcopyrite

Chalcopyrite carries significant indium in the granite-related mineralisation systems (Table 4). Similar to the sphalerite, no In was detected in the pre-granite parageneses, but sporadic concentrations were found in crosscourse veins. Although no particular correlations are apparent with the major elements (Fig. 12a) or Zn (Fig. 12b), the highest In concentrations appear to be associated with stoichiometric chalcopyrite that has a (Cu+Fe)/S (atomic) of 0.95–1.00. The high In in chalcopyrite from the Perran St George skarn is consistent with high In in sphalerite (Fig. 10a). Chalcopyrite from Red-a-Ven and Ramsley mines has much lower In and is comparable with the concentrations in greisen-bordered sheeted veins and polymetallic sulphide lodes. Chalcopyrite from polymetallic sulphide lodes with sphalerite I and sphalerite II cannot be systematically distinguished from chalcopyrite in greisen-bordered sheeted veins. However, polymetallic sulphide lodes with
In-rich sphalerite III carry very little In in chalcopyrite. Although In does not display a distinct negative correlation with Zn, the highest In concentrations are invariably found in chalcopyrite with low Zn.

7.3 Stannite group minerals

Stannite group minerals are not widely distributed or abundant, but are locally significant indium hosts (Table 5). All of the analysed grains carry Zn, but Zn/Fe is very variable. The very high indium concentrations at Botallack are associated with a Zn-poor, Fe-rich member of the group, while the indium contents at Geevor, Cligga Head, Hingston Down, Redmoor and Devon Great Consols are variable and show no particular correlation with Zn or Fe. We do not currently have enough analyses to provide a full assessment of indium incorporation into these minerals.

7.4 Cassiterite

Cassiterite is locally a significant indium host, but concentrations appear to be less systematic than in sphalerite and chalcopyrite (Table 5). However, X-ray spectral interferences prevent the reliable quantitative determination of In using standard electron microbeam analysis, and consequently, our analyses are indicative only. Significant concentrations at Geevor, Dolcoath and Wheal Fortune locally reach 1000-2000 ppm. However, with an interference correction as high as 1650 ppm, concentrations in the region of 200-800 ppm cannot be considered to be reliable. There is no apparent correlation between Fe and In in cassiterite.

7.5 Discrete indium minerals

Roquesite is locally significant at Perran St George, Redmoor and Geevor. We only found roquesite in samples that carry bornite, and it generally forms inclusions within bornite and neighbouring chalcopyrite. The intimate association suggests that roquesite formation is intimately linked to the evolution of the copper sulphides. The bornite is generally devoid of In, consistent with the conclusion of Cook et al (2011a) that bornite is a poor indium host. We suggest that the roquesite formed during the replacement of In-bearing chalcopyrite with In-free bornite. Although this could be an effect of the sulphur fugacity of the primary mineralisation system, such replacement is a common result of oxidation, for example, during supergene alteration.
At Dolcoath, minute grains of an In-rich mineral, possibly dzhalindite (In(OH)$_3$) or native In are locally abundant in distinct growth zones within quartz crystals that are in contact with sphalerite (Fig. 14). The growth structure suggests that the grains formed during the replacement of In-bearing sphalerite with quartz. Although we were unable to get fully quantitative analyses of these inclusions, elemental mapping confirms that they carry no As, Cu, Fe, S or Zn, which, apart from the unlikely occurrence of Pt-Pd-bearing minerals, is consistent with dzhalindite or native In.

7.6 Other minerals

Tennantite (and other sulfosalts) locally carry In at Geevor and Botallack but is barren elsewhere (Wheal Charlotte). We do not have enough analytical data to establish the controls on In incorporation into the sulfosalts.

Although pyrite is not generally a host for In, it does exhibit sporadic concentrations that display a positive correlation with other impurities such as Cu and Zn. This indicates that In is likely to be hosted in sub-microscopic inclusions of chalcopyrite and sphalerite.

Rutile has been considered to host In at La Châtaigneraie, in the French Massif Central (Lerouge et al. 2007), and we tested In in rutile from greisen-bordered sheeted veins at Cligga Head and from the tourmaline-quartz breccia at Wheal Remfry. Although the rutile systematically carries Nb, Sn, W and V (cf., Müller and Halls 2005), In was consistently below the lower limit of detection.

8. ORIGIN AND TIMING OF INDIUM MINERALISATION

8.1 General considerations

Our study suggests that there is very little In in the pre-granite parageneses, and that it is primarily associated with granite-related mineralisation systems where it is overwhelmingly occurs with sulphides and to a lesser extent cassiterite. The primary parageneses hosting In are the sulphide-bearing skarns, greisen-bordered sheeted vein complexes and polymetallic W-Sn-As-Cu-Zn sulphide lode systems. Silicate-oxide skarns and quartz-tourmaline lodes, veins and breccias are comparatively poor in In. There is some In associated with post-granite mineralisation, although concentrations are lower than in the granite-related parageneses.
Indium therefore appears to have been introduced and/or concentrated in the SW England upper crust during granite magmatism associated with Early Permian post-Variscan extension. It was concentrated in granite-related magmatic-hydrothermal fluids and precipitated during fracture-controlled fluid flow by wall-rock reactions and mixing with meteoric ± Early Permian basinal fluids within the Devonian-Carboniferous host rocks and upper parts of granite plutons.

Host rock compositions were likely to be critical for the deposition of In in sulphide-bearing skarns (Red-a-Ven, Ramsley) whilst variable fluid mixing between magmatic-hydrothermal and meteoric fluids resulted in precipitation in polymetallic sulphide lodes and similar assemblages overprinting greisen-bordered sheeted veins and tourmaline-quartz veins. Unsurprisingly, considering the temporal, spatial, and compositional complexity of the fluid-rock and fluid-fluid interactions, there is extreme variability between the deposits across the region, and even between samples from individual parageneses. Nevertheless, the precipitation of chalcopyrite, sphalerite and stannite group minerals appears to be a prerequisite for In deposition. The associations with different types of sphalerite suggest that depositional mechanisms varied within and between the parageneses.

Apart from the granite related systems, In is recorded sporadically in post-granite crosscourse parageneses at Wheal Betsy and Wrey-Ludcott United. Samples from these locations are different from other crosscourse samples in their abundance of minerals that are associated with the granite related parageneses. These differences suggest that the crosscourse fluids in these places interacted either with granite-related fluids or granite-related mineral veins at depth.

8.2 Controls on indium in skarns

The complex deportment of In between the different mineral hosts (Fig. 9) indicates that the metal was subject to several different depositional controls in the different mineralisation styles. The coarse-grained nature and complex paragenetic evolution of the ore systems invariably lead to some sampling variability. However, it is clear that the In mineralisation can be divided into two overarching styles; the chalcopyrite-dominant and the less abundant sphalerite-dominant.

The skarns in SW England formed where granite-derived magmatic-hydrothermal fluids entered carbonate-rich country rocks (at the northern margin of the Dartmoor granite) or metabasic igneous rocks (around the Carnmenellis and Land’s End granites). It is clear
from the fluid inclusion studies (Peng and Bromley 1992), that they represent the highest temperature environments of mineralisation associated with the granites. Peng and Bromley (1992) suggested that the silicate assemblage (garnet-pyroxene) formed at temperatures in excess of 600°C, while the later silicate-sulphide assemblage formed at 350–460°C. However, we have not observed a distinct transition between the chalcopyrite- and sphalerite-dominant assemblages and suggest that they represent a progressive evolution rather than separate mineralisation events.

In the sulphide-bearing skarn environments, In preferentially entered sphalerite (as at Red-a-Ven and Ramsley). However, where sphalerite was unavailable, chalcopyrite became the dominant host (as at Perran St George). Indium did not precipitate effectively in the silicate-oxide skarns, although some In is likely to have been incorporated into cassiterite (at Grylls Bunny and Magdalen Mine). The strong association of In with high Cu in sphalerite at Perran St George (Fig. 10b) parallels relations at Mount Pleasant (Sinclair et al. 2006), in the Freiberg region (Seifert and Sandmann 2006), and at Toyoha (Cook et al. 2009). Kieft and Damman (1990) reported sphalerite with extreme Cu and In substitution (up to 15 wt%) from Bergslagen, Sweden, and suggested that sphalerite can display extensive solid solution with roquesite and chalcopyrite. At Perran St George, high Cu and In relates to very small sphalerite inclusions in chalcopyrite, and we consider it likely that they developed their compositions by high temperature equilibrium with their In-bearing chalcopyrite host.

8.3 Controls on indium in granite-related polymetallic vein systems

The greisen-bordered sheeted veins and tourmaline-quartz veins and breccias are considered to have formed at lower temperatures than the skarns from fluids that are primarily granite derived (Alderton and Harmon 1991). Leveridge et al. (1990) considered the different styles to have formed in response to unmixing of low-density, low-salinity, CO₂-bearing fluids (responsible for the greisen-bordered veins) from high-density, highly saline fluids (responsible for the tourmaline-quartz veins and breccias). The high-temperature deposition of quartz and tourmaline with cassiterite and wolframite (and löllingite or arsenopyrite) in these systems is followed by later sulphide assemblages, which for both types are considered to have formed as the granite-derived fluids mixed with connate and meteoric water (Scrivener 2006).

At the resolution of this study, we are unable to distinguish differences in the sulphide assemblages of greisen-bordered sheeted veins, tourmaline-quartz breccias and
veins, and the polymetallic sulphide lodes. The deportment suggests two distinct principal associations:

1) Chalcopyrite-dominated. Although sphalerite consistently carries higher In concentrations, chalcopyrite is much more abundant and so carries the majority of the In. This association includes all greisen-bordered quartz-veins as well as the polymetallic sulphide lodes that carry sphalerite I and II.

2) Sphalerite-dominated. This association is much rarer and includes the polymetallic sulphide lodes with sphalerite III. Although we cannot be conclusive in our assessment, these appear to be the more distal parts of the polymetallic sulphide lodes (with less cassiterite, wolframite and arsenopyrite). Indium in this association appears to be strongly controlled by the solid solution of roquesite and, to a lesser extent sakuraiite, into the sphalerite structure.

8.4 Controls on indium in crosscourse veins

The crosscourse paragenesis postdates the cooling and hydrothermal alteration of the granites and is thought to have formed primarily through the migration of basinal brines from the Permo-Triassic ‘red-bed’ sedimentary basins at much lower temperatures (100-170°C) (Scrivener et al. 1994; Gleeson et al. 2001). Indium in this environment appears to be related to the interaction of these fluids with granite-related mineralisation or fluids. Although at the surface, many of these systems are distant from granite-related magmatic-hydrothermal vein systems, the inclusion of tourmaline-cassiterite-arsenopyrite bearing clasts at Wrey-Ludcott United, as well as trace Sn- and As-minerals at Buttspill, Wheal Penrose and Holmbush, indicate that unexposed granite-related veins may be widespread at depth beneath these areas. Indium within this environment appears to be dominantly hosted by sphalerite, although chalcopyrite was also locally found to be significant. The possible range of interactions includes:

1) Incorporation of clasts of Early-Mid Permian magmatic-hydrothermal veins in crosscourse veins during Mid-Triassic faulting,

2) Dissolution and re-precipitation of magmatic-hydrothermal vein minerals in cross-course vein systems, and

3) Contemporaneous availability of Early-Mid Permian magmatic-hydrothermal and basinal brine fluids in the manner suggested by Scrivener et al. (1986).
The clasts at Wrey-Ludcott United are unequivocal evidence for the inclusion of granite-derived vein material, as they include cassiterite, arsenopyrite and tourmaline. The minute inclusions of cassiterite and tourmaline found more widespread across the region (Buttspill, Wheal Penrose) may also have been clasts. However, sphalerite with elevated In at Wrey-Ludcott United is clearly part of the crosscourse matrix, which is suggestive of dissolution and re-precipitation from crosscourse fluids. The paragenesis at Wheal Betsy, where sphalerite is associated with growth zones in the banded ore, is also suggestive for dissolution and re-precipitation. Radiometric dating suggests that granite-related mineralisation was complete before the main episode of crosscourse mineralisation occurred, suggesting that little fluid mixing took place (cf. Chen et al. 1993; Chesley et al. 1993; Scrivener et al. 1994).

9. EXPLORATION AND RECOVERY POTENTIAL

Within the individual magmatic-hydrothermal systems, In is shared between chalcopyrite and sphalerite with minor contributions from stannite group minerals, roquesite and cassiterite. The most surprising result of our investigation is the overall dominance of chalcopyrite over sphalerite as the In host. This contrasts to the assessment by Schwarz-Schampera and Herzig (2002) that sphalerite is likely to account for more than 75% of the In in granite-related vein deposits. Cook et al (2011b) concluded similarly that chalcopyrite is only likely to be a major host in parageneses with very little sphalerite. Very few of the parageneses in SW England conform to these assessments.

All samples with more than 200 ppm In were derived from vein systems associated with the Carnmenellis and St Agnes Granites in West Cornwall (Fig. 9). These are also the areas that were historically richest in tin (Willis-Richards and Jackson 1989) and suggests that the prospectivities for these metals are tightly linked within the region. Although there could be many explanations for this, a recent study by Simons (2015) indicates a granite protolith control related to the partial melting of muscovite-bearing metamudstone at depth.

Assessments of In recovery would have to deal with the complex deportment of In on a prospect by prospect basis. Our study highlights the importance for detailed mineralogical studies before an evaluation of the recovery can be determined. A successful processing strategy would have to be closely tailored to the variability of the individual prospects.
Processing strategies that focus exclusively on the recovery of In from sphalerite (Alfantazi and Moskalyk 2003) are likely to be unsuccessful in SW England. More than 70% of our samples have chalcopyrite as the dominant In host. The samples that have sphalerite as the dominant host are not confined to specific sites, and a mixing of the two types during extraction is highly likely. Although In appears to be recoverable during the processing of chalcopyrite (Smith et al. 1978; Ke et al. 1984), we are unaware of any current operations that involves such processing.

The complex deportment suggests that the use of geochemistry (from hand-held XRF or whole-rock assays) will not sufficiently characterise In in these types of ores. An a priori assumption that In resides in sphalerite may lead to poorly designed processing strategies and subsequent losses. The geochemistry alone will not provide a unique solution to the deportment of In between chalcopyrite, sphalerite, stannite and cassiterite. Mineralogical studies must be an integral part of the evaluation of In resources associated with granitic systems.

10. COMPARISON OF THE SW ENGLAND ORE FIELD TO OTHER INDIUM-BEARING PROVINCES

The diversity of In parageneses in the SW England region bear similarities to other provinces around the World. However, the diversity of occurrences is unprecedented in other single regions. The link to evolved peraluminous granites is shared with the dominant In deposits in China (Ishihara et al. 2008; 2011), the Erzgebirge / Krušné Hory mountains of Germany and the Czech Republic (Seifert and Sandmann 2006), the Massif Central of France (Lerouge et al. 2007) and Mount Pleasant in Canada (Sinclair et al. 2006). The crosscourse paragenesis, in contrast, bear close resemblance to In-bearing epithermal veins in the West Shropshire orefield (Pattrick and Bowell 1991). As the paragenesis formed largely from basinal brines, comparisons may also be made with feeder zones beneath sedimentary exhalative parageneses at, for example, Rammelsberg, Germany (Large and Walcher, 1999) and Långban, Sweden (Burke and Kieft 1980).

The majority of the World’s In is produced in China, where deposits are located in two different geological regions. Deposits in South China cover a strike length of >1000 km from South Sichuan across the provinces of Yunnan and Guangxi to Guangdong and include the large Sn-Cu skarn and vein deposits at Dachang, Dulong and Gejiu, which combined are
estimated to carry in excess of 10,000 tons In (Ishihara et al. 2011). In North China, vein deposits associated with granite and dacite porphyries in the Da Hinggan Mountains (Anle, Dajing and Meng’entaolegai, Zhang et al. 2006; Ishihara et al. 2008) are estimated to carry some 1,200 tons of contained In. Although the SW England ore field is not as extensive as the South China province, In occurrences are nevertheless found systematically along a >200 km strike length. The SW England ore region shares many characteristics with the deposits in South China, particularly the close association of In with Sn and tourmaline, as well as the spatial association of In-bearing mineral veins with two-mica granites (Cheng and Mao 2010).

Indium has been reported from other Variscan terranes in Europe, including the Erzgebirge (Pöhla-Globenstein, Hösel 2002; the Freiberg region, Seifert and Sandmann 2006) and Krušné Hory mountains (Cinovec, Novák et al. 1991; 1995 as cited by Schwarz-Schampera and Herzig 2002), and the Massif Central of France (Charrier, Picot and Pierrot 1963; La Châtaigneraie, Lerouge et al. 2007). Mount Pleasant in New Brunswick, Canada, although now an ocean apart, shares the provenance to Avalonian crust with SW England and may represent a westward extension to the European Variscan terranes.

The Erzgebirge / Krušné Hory host significant resources at Pöhla-Globenstein, which is inferred to contain 1,427 tons In (Hösel 2002), and neighbouring properties at Hämmerlein, Dreiberg and Zweibach, which are estimated to carry a further 2,149 tons (Treliver Minerals Ltd. 2015). Further In is expected at Breitenbrunn and Zlaty Kopec (R. Seltmann, pers. comm. 2015). The deposits in the Erzgebirge and Krušné Hory mountains are predominantly skarns and massive greisens (Hösel 2002), while vein deposits dominate in the Freiberg district (Seifert and Sandmann 2006). At Mount Pleasant, the North Zone and Upper Deep Tin Zones are considered to contain 1,096 tons of In (Sinclair et al. 2006) associated with replacement bodies, greisens, breccias and polymetallic chlorite-sulphide lodes.

We consider that the differences in parageneses between these areas and SW England relate primarily to differences in the composition and properties of the host, as well as different source melting and crystallisation histories. Carbonate-rocks are rare in SW England, providing fewer opportunities for skarn formation than in the Erzgebirge / Krušné Hory. Rather than massive greisens formed within the granites, for example at Cinovec, the granite-related fluids associated with the Cornubian batholith were able to escape more
easily into faults and fractures, leading to the sheeted vein paragenesis as well as the much more extensive quartz-tourmaline and polymetallic sulphide lodes.

The mineral assemblages in the crosscourse environment are similar to Pb-Zn-Ba-Ag-Cu epithermal veins in the West Shropshire ore field (Pattrick and Bowell 1991). In contrast to other epithermal systems listed by Schwarz-Schampera and Herzig (2002), which mostly are reported from volcanic terranes, these veins were not influenced by magmatic fluids. Instead, the principal fluids are considered to be basinal brines. As in SW England, In-bearing sphalerite from the West Shropshire Ore Field is associated with CaCl$_2$-rich fluid inclusions (Pattrick and Bowell 1991). In SW England there appears to be a distinct connection between In and granite-related components in the crosscourse assemblage, which suggests that the metal was remobilised from granite-related parageneses at depth. In contrast, the West Shropshire mineralisation was likely to have formed from fluids derived from the Cheshire Basin, which hosts red-bed sediments that are contemporary with the Permo-Triassic succession in SW England. However, the Cheshire Basin did not experience magmatic activity (Naylor et al. 1989), and the fluids must therefore have tapped a different In source.

11. CONCLUSIONS

- Indium concentration in the upper crust of SW England is primarily associated with voluminous Early-Permian peraluminous granite magmatism. Cadmium and Ga were abundantly available prior to the emplacement of the granites.

- Magmatic-hydrothermal activity led to the transport of In into granite-related skarn and vein systems, where it deposited primarily in the sulphide-dominated portions. The highest In concentrations are associated with the Carnmenellis and St Agnes plutons in the western part of the region, and in this respect the metal appears to follow Sn.

- The majority of In is hosted by chalcopyrite and sphalerite with lesser amounts in cassiterite and stannite group minerals. Roquesite and other discrete In minerals formed where In-bearing chalcopyrite and sphalerite have been replaced, either during the complex evolution of the ore systems, or by later supergene alteration. Tennantite is locally an In host.

- Indium was not detected in löllingite, arsenopyrite, rutile, haematite, magnetite, tourmaline, biotite, chlorite, galena, bornite, chalcocite or pyrrhotite. Scattered concentrations in pyrite relate to impurities rather than incorporation by solid solution.
The In deportment varies between granite-related parageneses with different sphalerite morphologies. The In budget is predominantly in chalcopyrite in parageneses that have little sphalerite or large, unzoned sphalerite with chalcopyrite disease.

Sphalerite in calc-silicate hosted skarns and sphalerite I in polymetallic sulphide lodes are Cu-rich and have elevated In, however Cu and In do not correlate in the expected manner for a solid solution component. Sphalerite II displays no correlation between Cu and In, while the variations in sphalerite III are consistent with solid solution of roquesite, and to a lesser extent sakuraiite into the sphalerite lattice.

Remobilisation of In from granite-related parageneses led to localised concentration into Triassic crosscourse veins. This involved the inclusion of clasts into the crosscourse veins as well as dissolution and re-precipitation of In into sphalerite in the crosscourse matrix.

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TABLES

Table 1. Overview of mineralisation styles in the SW England ore field.

Table 2. Sample locations, mineralisation styles, ore and gangue minerals. Location information is recorded by GPS or by Google Earth (GE) with reference to the WGS84 datum. Mineralisation styles are sts = stratiform sulphides, bv = breccia vein, msk = magnetite-silicate skarn, ssk = sulphide-silicate skarn, gbsv = greisen-bordered sheeted vein, QTL = quartz-tourmaline breccia, psl = polymetallic sulphide lode and ccv = crosscourse vein. Mineral abbreviations follow the recommendations of Whitney and Evans (2010). Additional minerals include cob = cobaltite; bi = bismuthinite; mly = malayaite; stn = stannite group minerals; Fe-ox = unspecified iron oxide, oxyhydroxide, and carbonate minerals; wf = wolframite.

Table 3. Summary of compositions of In-bearing sphalerite. The full analytical dataset can be found in the electronic supplement.

Table 4. Summary of compositions of chalcopyrite. The full analytical dataset can be found in the electronic supplement.

Table 5. Summary of compositions of stannite group minerals and cassiterite. The full analytical dataset can be found in the electronic supplement.
**FIGURES**

**Figure 1.** Geological map of SW England (e.g., Leveridge and Hartley 2006; Shail and Leveridge 2009). The Variscan granites include the Land’s End (LEG), St Michaels Mount (SMG), Tregonning-Godolphin (TGG), Carnmenellis (CG), Carn Brea (CBG), Carn Marth (CMG), St Agnes (StAG) Cligga Head (CHG), St Austell (SAG), Bodmin Moor (BMG), Kit Hill (KHG), Hingston Down (HDG), Dartmoor (DG), Crownhill Down (CDG), and Hemerdon Ball (HBG). The Crediton and Tiverton Half-Grabens are marked CHG and THG respectively; and the Palaeogene Lundy Granite with LG. Sample locations are listed in Table 1.

**Figure 2.** Examples of mineralisation styles from SW England. **a.** Stratiform sulphide bands in Lower Carboniferous folded black shale at Wilsey Down. The insert shows the two prominent structural directions, the primary bedding, \( s_0 \), and the tectonic overprint, \( s_1 \). **b.** Greisen-bordered quartz veins cross-cutting kaolinised granite at Cligga Head. **c.** Tourmaline-quartz breccia with granite fragments from Wheal Remfry in the St. Austell granite. **d.** Polymetallic sulphide lode cross-cutting the Carnmenellis granite at Holman’s test mine. **f.** Banded quartz-hematite crosscourse vein from Megilligar on the Cornish south coast.

**Figure 3.** Interference correction for Sn on In. The interference is calculated from the minimum measured signal for In-K\( \alpha \) for stannite group minerals and cassiterite.

**Figure 4.** Key to the QEMSCAN false-colour mineral distribution maps in figures 5-8.

**Figure 5.** Examples of textures (QEMSCAN mineral maps) of pre-granite mineralisation styles from the Wilsey Down borehole (**a-b**), Egloskerry (**c-k**), and the Perran Iron Lode (**l**). Mineral acronyms are apy = arsenopyrite, ax = axinite, bt = biotite, cc = calcite, ccp = chalcopyrite, cct = chalcocite, chl = chlorite, cst = cassiterite, fl = fluorite, gn = galena, grt = garnet, hem = hematite, ksp = alkali feldspar, lo = löllingite, ms = muscovite, mt = magnetite, po = pyrrhotite, py = pyrite, qz = quartz, sp = sphalerite, stn = stannite group minerals, tur = tourmaline, wf = wolframite.

**a-b.** Bedding parallel sulphide layers from Wilsey Down. **c-k.** Sulphide occurrences from Egloskerry. **l.** Hematite breccia with quartz and slate (sl) fragments from the Duchy Peru Mine on the Perran Iron Lode. Sulphide minerals include pyrite, chalcopyrite and sphalerite. Chalcocite (and bornite) rims the chalcopyrite.
Figure 6. Examples of textures (QEMSCAN mineral maps) of skarns and greisen-bordered veins (mineral abbreviations as in Fig. 5). Sulphide-bearing skarns from Red-a-Ven (a-c) and Perran St George (d); silicate-oxide skarns from Grylls Bunny (e-f) and Magdalen Mine (g); greisen-bordered sheeted veins with polymetallic sulphides from Cligga Head (h) and Redmoor (i – l).

Figure 7. Examples of textures (QEMSCAN mineral maps) of quartz-tourmaline veins and polymetallic sulphide lodes (mineral abbreviations as in Fig. 5). a-b. Quartz-tourmaline lodes, veins and breccias cross-cut by polymetallic sulphides at Capel Tor. c. Polymetallic sulphide lode with tourmalinisation of metapelitic host from Capel Tor. d-e. Lodes associated with chloritisation of metapelitic hosts at William and Mary Mine and Cotehele Consols. f-g. Lodes associated with intensely tourmalinised host rocks at Great Sheba Consols and Capel Tor. The vein at Capel Tor also has associated muscovite. h. Lode dominated by chalcopyrite and pyrite with associated chlorite, tourmaline and hematite alteration from Okeltor. i. Chalcopyrite-bornite assemblage at Geevor. j. Chalcopyrite with chalcocite replacement along margins and within fractures at Dolcoath. k. Cassiterite associated with quartz and alkali feldspar at Geevor. l. Chalcopyrite and sphalerite III associated with pyrite in quartz gangue with traces of chlorite from Wheal Charlotte.

Figure 8. Examples of textures (QEMSCAN mineral maps) of crosscourse veins (mineral abbreviations as in Fig. 5) from Wheal Exmouth (a-c), Buttspill (d), Wrey-Ludcott United (e-f), and Wheal Betsy (g-h).

Figure 9. The mineralogical distribution (deportment) of In in the studied samples. Absolute concentrations of In are calculated from the abundances of In-bearing minerals (from QEMSCAN analysis) and the average concentrations of In within each of these minerals (from EPMA analysis). CH = Cligga Head, PSG = Perran St George, RaV = Red-a-Ven.

Figure 10. Compositional variations in sphalerite. The two highlighted groups are skarns from Perran St George (1) and Red-a-Ven (2). a. Against Zn+Fe, copper appears to follow a chalcopyrite (ccp) control. b. Cu versus In. c. Fe versus In. d. Zn+Fe versus In. e. Cd versus In. f. Ga versus In.

Figure 11. Correlation between Cu and In in sphalerite III from East Wheal Rose. Diamonds are analyses with no detected Sn, open squares are analyses with traces of Sn. The CuIn control line reflects the metal proportions in a roquesite component, while Cu$_3$In reflects the proportions in sakuraiite.
**Figure 12.** Compositional variations in chalcopyrite. Like for sphalerite, the chalcopyrite from skarn deposits define two distinct groups. Group 1 is Perran St George while group 2 is Red-a-Ven. **a.** Atomic (Cu+Fe)/S versus In reflecting minor variability from the ideal stoichiometry. **b.** Zn versus In.

**Figure 13.** Correlations between the average In contents in coexisting sphalerite and chalcopyrite.

**Figure 14.** Compositional map showing inclusions of dzhalindite or native In in quartz (mineral abbreviations as in Fig. 5). The inclusions are confined to growth zones (marked 1 and 2) in two quartz crystals adjacent to In-bearing sphalerite. The sphalerite displays elevated In toward the grain boundaries.

**Figure 15.** Simplified conceptual model of In mineralisation in SW England. Stratiform sulphides (STS) in the pre-granite environment (Pb-Zn-Ba) were deformed prior to the granite emplacement. Granite emplacement, in this example with three successive intrusions (G1, G2, G3) led to sulphide-silicate skarn (SSK) formation where magmatic fluids entered calc-silicate rocks, while magnetite-silicate skarns (MSK) predominantly formed in metabasalts. Greisen-bordered sheeted vein complexes (GBSV) and quartz-tourmaline lodes, veins and breccias (QTL) formed in the apical parts of the granites. Polymetallic sulphide lodes (PSL) extend further away from the granite and appear in places to evolve from greisen-bordered veins or quartz-tourmaline breccias. Local telescoping of these styles as the magmatic-hydrothermal system evolved lead to complex variations between the PSL, GBSV and QTL parageneses. Triassic crosscourse veins (CCV) locally transect the granite related veins. Indium precipitated in the sulphide portions of the skarns and granite-related veins from which it has locally been remobilised into crosscourse veins.
Andersen et al. Figure 1. (full page width)
Andersen et al. Figure 3. (1 column width)
Andersen et al. Figure 4. (1 column width)
Andersen et al. Figure 5.
Andersen et al. Figure 6. (full page width)
Andersen et al. Figure 8. (full page width)
Andersen et al. Figure 9. (half page width)
Andersen et al. Figure 10.
Andersen et al. Figure 11. (1 column width)
Andersen et al. Figure 12.

(1 column width)
Andersen et al. Figure 13. (1 column width)
Andersen et al. Figure 14. (full page width)
Andersen et al. Figure 15.
**Table 1.** Overview of mineralisation styles in the SW England ore field.

---

**Pre-granite mineralisation**

1) Rifting and passive margin development (*Early Devonian-Early Carboniferous*)
   - Sedimentary-exhalative (SedEx) mineralisation

2) Variscan convergence and continental collision (*Late Devonian-Carboniferous*)
   - Shear zone hosted Au-Sb + base metal mineralisation

**Granite-related mineralisation**

3) Early post-Variscan extension and magmatism (*Early Permian*)
   - Magmatic-hydrothermal W-Sn-Cu-Zn-Pb mineralisation
     - a) Magnetite-silicate skarns developed in metabasaltic granite hosts
     - b) Sulphide-silicate skarns developed in calc-silicate granite hosts
     - c) Greisen-bordered sheeted vein complexes
     - d) Quartz-tourmaline veins and breccias
     - e) Polymetallic sulphide lodes

**Post-granite mineralisation**

4) Episodic intraplate rifting and inversion (*Late Permian – Cenozoic*)
   - a) ‘Cross-course’ epithermal Pb-Zn ± F, Ba mineralisation
   - b) Epithermal U ± Co-Ni-Bi-As-Ag mineralisation
   - c) Unconformity Mn, Cu and Fe ± minor gold (Au), palladium (Pd) and selenide
Table 2. Sample locations, mineralisation styles, ore and gangue minerals. Location information is recorded by GPS or by Google Earth, numbers refer to Figure 1. Lat = latitude, Long = longitude. Mineralisation styles are bv = breccia vein, sts = stratiform sulphides, msk = magnetite-silicate skarn, ssk = sulphide-silicate skarn, gbsv = greisen-bordered sheeted vein, qt = tourmaline-quartz vein/breccia, psl = polymetallic sulphide lode and ccv = crosscourse vein. Mineral abbreviations follow the recommendations of Whitney and Evans (2010). Additional minerals include Cob=cobaltite; Bm=bismuthinite; Mly=malayaite; Stn=stannite-group minerals; Fe-ox = unspecified iron oxide, oxyhydroxide, and carbonate minerals; Wf = wolframite.

<table>
<thead>
<tr>
<th>Location</th>
<th>Name</th>
<th>Lat. (°N)</th>
<th>Long. (°W)</th>
<th>Type</th>
<th>Oxide and sulphide minerals</th>
<th>Associated gangue</th>
<th>Notes</th>
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<tr>
<td>Pre-granite</td>
<td></td>
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<tr>
<td>1 Duchy Peru</td>
<td>50.358</td>
<td>5.103</td>
<td>bv</td>
<td>1: Cst</td>
<td>Py, Ccp, Sp, Hem, Gn</td>
<td>1: Qz, Bt, Ms, Ksp</td>
<td>Breccia vein cross-cutting metapelite of the Porthtowan formation. Clasts of qz, slate, ksp in a hematite-siderite matrix 1: clast assemblage, 2: matrix, 3: alteration</td>
</tr>
<tr>
<td></td>
<td>2 Wilsey Down</td>
<td>50.671</td>
<td>4.577</td>
<td>sts</td>
<td>Py, Po, Ccp, Sp, Gn</td>
<td>Cc, Qz, Chl, Bt</td>
<td>Metapelite / metapsammite with folded stratiform sulphides in calcareous black shale</td>
</tr>
<tr>
<td></td>
<td>3 Egloskerry</td>
<td>50.641</td>
<td>4.430</td>
<td>sts</td>
<td>1: Gn, Sp, Py, (Apy), Hem</td>
<td>Qz, Chl, Bt, Ms, Ksp, Cc</td>
<td>Stratiform sulphides in laminated shale and siltstone with interbedded carbonates and metavolcanics. Some evidence of mobilisation of sulphides into tensile fractures, Riedel shears and cross-cutting veins. Sample SSK36015 is cross-cut by an undeformed quartz-hematite (crosscourse) vein.</td>
</tr>
<tr>
<td></td>
<td>4 Lundy</td>
<td>51.163</td>
<td>4.658</td>
<td>sts</td>
<td>Py, Po, Sp (Ccp)</td>
<td>Cc, Qz, Chl</td>
<td>Sulphide-bearing metacarbonate interbedded with Upper Devonian metapelites and metapsammites. Sphalerite has exsolved chalcopyrite, but chalcopyrite has not been observed as a discrete mineral.</td>
</tr>
<tr>
<td>Granite related</td>
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<tr>
<td>5 Grylls Bunny</td>
<td>50.142</td>
<td>5.691</td>
<td>msk</td>
<td>Mt, Cst</td>
<td>Grt, Tur</td>
<td></td>
<td>Banded magnetite-garnet and tourmaline skarns in contact-metamorphic succession of Devonian metapelite and metabasalt of the Mylor Slate Formation</td>
</tr>
<tr>
<td>6 Magdalen Mine</td>
<td>50.196</td>
<td>5.132</td>
<td>msk</td>
<td>Mt, Cst</td>
<td>Hbl, Bt</td>
<td></td>
<td>Magnetite-silicate skarn associated with metabasalt and metapelite of the Mylor Slate Formation.</td>
</tr>
<tr>
<td>Site</td>
<td>Latitude</td>
<td>Longitude</td>
<td>Rgb</td>
<td>Mineralogy</td>
<td>Sulphide-bearing Metapelite of the Crackington Formation (Ashton Shale equivalent) associated with magnetite-skarn</td>
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<tr>
<td>Haytor Vale</td>
<td>50.583</td>
<td>3.737</td>
<td>msk</td>
<td>Mt, Apy, Py, Ccp, Sp</td>
<td>Silicate-sulphide skarn in calc-silicate bearing metasediment of the Meldon Chert Formation. Pyrrhotite, pyrite, sphalerite and löllingite in bands and lenses with minor chalcopyrite. Arsenopyrite, sphalerite, chalcopyrite and pyrite variably developed in transgressive veins.</td>
<td></td>
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</tr>
<tr>
<td>Red-a-Ven</td>
<td>50.707</td>
<td>4.027</td>
<td>ssk</td>
<td>Po, Py, Lo, Ccp, (Sp), (Apy)</td>
<td>Silicate-sulphide skarn in calc-silicate bearing metasediment of the Meldon Chert Formation. Pyrrhotite cores surrounded by pyrite in matrix of chalcopyrite. Cassiterite as &lt;1 mm large crystals. Sphalerite as minute grains in chalcopyrite. Provenanced in collection to Perran St George, but location unverified.</td>
<td></td>
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<tr>
<td>Ramsley</td>
<td>50.721</td>
<td>3.914</td>
<td>ssk</td>
<td>Po, Ccp</td>
<td>Greisen-bordered veins with polymetallic sulphides in kaolinsated biotite granite.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perran St George</td>
<td>50.339</td>
<td>5.176</td>
<td>ssk</td>
<td>Cst, Ccp, Py, Po, (Sp), (Apy)</td>
<td>Greisen-bordered veins with polymetallic sulphides in folded succession of metapelite and metapsammite.</td>
<td></td>
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<tr>
<td>Cligga Head</td>
<td>50.339</td>
<td>5.179</td>
<td>gbsv (psl)</td>
<td>Apy, Ccp, Wf, Cst, Stn, Cct, Py, Ttr, (Lo)</td>
<td>Cassiterite bearing quartz-tourmaline (-hematite) veins cross-cutting megacrystic biotite granite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Redmoor</td>
<td>50.517</td>
<td>4.319</td>
<td>gbsv - psl</td>
<td>Apy, Lo, Wf, Cst, Stn, Ccp, Sp, Py,</td>
<td>Extremely large (800 m diameter) tourmaline-quartz diatreme breccia with clasts of granite and metasediments. No sulphides, but with tin hosted by rutile (and sporadically cassiterite).</td>
<td></td>
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<tr>
<td>Ding Dong</td>
<td>50.154</td>
<td>5.593</td>
<td>qtv</td>
<td>Cst, Hem</td>
<td>Cassiterite bearing quartz-tourmaline (-hematite) veins cross-cutting megacrystic biotite granite</td>
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<tr>
<td>Wheal Remfry</td>
<td>50.381</td>
<td>4.920</td>
<td>qtv</td>
<td>Rt, Cst</td>
<td>Cassiterite bearing quartz-tourmaline (-hematite) veins cross-cutting megacrystic biotite granite.</td>
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<tr>
<td>Vitifer Mine</td>
<td>50.613</td>
<td>3.865</td>
<td>qtv</td>
<td>Cst, Hem</td>
<td>Polymetallic sulphide lodes with quartz and chlorite cross-cutting granite, hornfels, slate and metabasalt</td>
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<tr>
<td>Geevor</td>
<td>50.154</td>
<td>5.678</td>
<td>psl</td>
<td>Apy, Cst, Ccp, Bn, Sp-III, Py, (Gn), (Cct)</td>
<td>Polymetallic sulphide lodes with quartz and chlorite cross-cutting granite, hornfels, slate and metabasalt. Very variable and complex polymetallic sulphide lode system developed at the northern contact of the Carnmenellis granite. Locally showing skarn development in metabasites.</td>
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<td>Botallack</td>
<td>50.138</td>
<td>5.692</td>
<td>psl</td>
<td>Cst, Apy, Py, Ccp, Sp-II, Stn, Gn</td>
<td>Polymetallic sulphide lodes with quartz and chlorite cross-cutting granite, hornfels, slate and metabasalt</td>
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<tr>
<td>Dolcoath</td>
<td>50.217</td>
<td>5.281</td>
<td>psl</td>
<td>Cst, Wf, Apy, Ccp, Sp-II, Sp-III, (Bn), (Lo)</td>
<td>Polymetallic sulphide lodes with quartz and chlorite cross-cutting granite, hornfels, slate and metabasalt</td>
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<tr>
<td>Site Name</td>
<td>Latitude</td>
<td>Longitude</td>
<td>Minerals</td>
<td>Notes</td>
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<tr>
<td>Great Condurow</td>
<td>50.207</td>
<td>5.280</td>
<td>Sp-I, Ccp, Py, Apy, Cst, Wf, Bn, Fe-ox</td>
<td>Polymetallic sulphides in quartz-chlorite lodes with sulphide minerals. Lållingite and wolframite inclusions in arsenopyrite. Arsenopyrite, cassiterite and pyrite appear to be followed by chalcopyrite. Apart from separate grains, chalcopyrite rims arsenopyrite and occur in fractures in pyrite. Bornite and chalcocite locally rim chalcopyrite and are associated with kaolinite. Polymetallic sulphides in quartz-tourmaline breccia veins and quartz-chlorite lodes cross-cutting megacrystic biotite granite Polymetallic sulphide lode with quartz and chlorite cross cutting metapelites of the Porthtowan Formation Polymetallic sulphide lode with quartz and chlorite cross cutting metapelites of the Porthtowan Formation Polymetallic sulphide lode with quartz and chlorite cross cutting metapelites of the Porthtowan Formation Polymetallic sulphides in quartz-chlorite lode Polymetallic sulphides in quartz-chlorite lode cross cutting metapelite Polymetallic sulphide lode with quartz and tourmaline gangue cross cutting metapelites Polymetallic sulphide lode with quartz and chlorite cross cutting metapelites, ore dominated by chalcopyrite and pyrite in a chlorite – quartz gangue. Very fine disseminated cassiterite and sphalerite. Polymetallic sulphide lode cross cutting the Devonian Mylor Slate Formation. Polymetallic sulphide lode cross cutting the Devonian Mylor Slate Formation. Polymetallic sulphide lode cross cutting the Devonian slates of the Ladock Beds. Polymetallic sulphide lode cross cutting the Lower Devonian calcareous slates of the Meadfoot Beds.</td>
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<tr>
<td>Location</td>
<td>Coordinates</td>
<td>Metamorphic Assemblage</td>
<td>Metamorphic Phase</td>
<td>Mineralogy</td>
<td>Notes</td>
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<tr>
<td>32 Gonamena</td>
<td>50.508</td>
<td>Apy, Ccp, Cst, Py, Cob, (Cct), (Lo)</td>
<td>Qz, Chl, (Ms), (Bt)</td>
<td>Polymetallic sulphide lode cross cutting the Bodmin Moor biotite granite to the west of Caradon Hill</td>
<td></td>
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</tr>
<tr>
<td>33 South Caradon</td>
<td>50.504</td>
<td>Apy, Ccp, Cst, (Py), (Lo), (Bm)</td>
<td>Qz, Chl, Fl, (Bt)</td>
<td>Polymetallic sulphide lode at the boundary between the Bodmin Moor biotite granite and interbedded metasediments and metavolcanics of the Brendon Formation to the North of Darite.</td>
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<tr>
<td>34 East Caradon</td>
<td>50.503</td>
<td>Apy, Ccp, Cst, Py, (Cct), (Cob), (Bm)</td>
<td>Qz, Chl, (Bt)</td>
<td>Polymetallic sulphide lode at the boundary between the Bodmin Moor biotite granite and interbedded metasediments and metavolcanics of the Brendon Formation on the southern side of Caradon Hill, NE of Crow's Nest.</td>
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<tr>
<td>35 Hingston Down</td>
<td>50.526</td>
<td>1: Apy, Py, Ccp, Cst, Stn, Wf, Tr 2: Bn, Cct</td>
<td>Qz, Ms, Tpz</td>
<td>Primary sulphide assemblage in muscovite - quartz gangue, locally with topaz. No tourmaline or chlorite in the investigated samples. Bornite and chalcocite development along fractures in chalcopyrite</td>
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<tr>
<td>36 Capel Tor</td>
<td>50.547</td>
<td>Apy, Cst, Ccp, Py, Sp-I, (Lo)</td>
<td>Tur, Qz, Ms, (Bt)</td>
<td>Complex ore paragenesis with early tourmaline-quartz breccias cross cut by polymetallic sulphides. Some localised development of greisen borders</td>
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<tr>
<td>37 Great Sheba Consols</td>
<td>50.540</td>
<td>Sp-II, Py, Apy, Ccp, (Gn)</td>
<td>Qz, Tur, Kln</td>
<td>Polymetallic sulphide lodes cross-cutting metapelites and metapsammites of the Upper Devonian Kate Brook Slate Formation.</td>
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<tr>
<td>38 Devon Great Consols</td>
<td>50.540</td>
<td>Apy, Ccp, Cst, Stn, Py, Fe-ox, (Lo), (Gn)</td>
<td>Tur, Ms, Ksp, Bt, Qz, Fl</td>
<td>Polymetallic sulphide lodes cross-cutting metapelites and metapsammites of the Upper Devonian Kate Brook Slate Formation. Localised greisen development at depth.</td>
<td></td>
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<tr>
<td>39 Cotehele Consols</td>
<td>50.503</td>
<td>Apy, Cst, Ccp, Py, Sp-II</td>
<td>Qz Chl, Fl, (Bt)</td>
<td>Polymetallic sulphide lodes cross-cutting metapelites and metapsammites of the Upper Devonian Kate Brook Slate Formation.</td>
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</tr>
<tr>
<td>40 Okeltor</td>
<td>50.500</td>
<td>Apy, Cst, Ccp, Py, Sp-II, Fe-ox</td>
<td>Qz, Chl, Tur, Kln</td>
<td>Polymetallic sulphide lodes cross-cutting metapelites and metapsammites of the Upper Devonian Kate Brook Slate Formation.</td>
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</tr>
<tr>
<td>41 William and Mary</td>
<td>50.510</td>
<td>Ccp, Py, Sp-II</td>
<td>Qz, Ksp, Bt, Chl, Ms</td>
<td>Polymetallic sulphide lodes cross-cutting metapelites and metapsammites of the Upper Devonian Kate Brook Slate Formation.</td>
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</tr>
<tr>
<td>42 Tavy Consols</td>
<td>50.498</td>
<td>Apy, Cst, Ccp, Sp-II, (Sp-I), Py</td>
<td>Qz, Chl, Tur, Fl, (Ms)</td>
<td>Polymetallic sulphide lodes cross-cutting metapelites and metapsammites of the Upper Devonian Kate Brook Slate Formation.</td>
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</tbody>
</table>

**Post-granite**
<table>
<thead>
<tr>
<th>Mine Name</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Type</th>
<th>Minerals Found</th>
<th>Rock Types</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheal Penrose</td>
<td>50.077</td>
<td>-5.305</td>
<td>cv</td>
<td>Ccp, Py, Gn, Hem, (Apy)</td>
<td>Qz, Ksp, Mnz</td>
<td>N-S trending vein of banded hematite and quartz cross-cutting metapelite of the Mylor Slate Formation.</td>
</tr>
<tr>
<td>Wrey-Ludcott United</td>
<td>50.469</td>
<td>-4.399</td>
<td>cv</td>
<td>1: Cst, Apy, 2: Sp, Py, Fe-ox, (Ccp), (Gn)</td>
<td>1: Qz, Tur, Ksp, Chl, 2: Fl, Cc, Ap</td>
<td>Two N-S trending crosscourse veins crosscutting the Upper Devonian Burraton and Saltash Formations and historically mined for Pb and Ag.</td>
</tr>
<tr>
<td>Holmbush Mine</td>
<td>50.525</td>
<td>-4.318</td>
<td>cv</td>
<td>Ga, Sp, Fe-ox, (Py)</td>
<td>Qz, Ms, Ksp</td>
<td>N-S trending crosscourse vein emplaced into the Kate Brook Slate formation and intersecting the greisen-bordered sheeted vein complex at Redmoor.</td>
</tr>
<tr>
<td>Greystone Quarry</td>
<td>50.601</td>
<td>-4.314</td>
<td>cv</td>
<td>Py, Gn, Ccp, Sp, (Po)</td>
<td>Qz, Ms, Ksp</td>
<td>Crosscourse vein in Lower Carboniferous metapelite and metadolerite with interbedded chert.</td>
</tr>
<tr>
<td>Buttspill Mine</td>
<td>50.490</td>
<td>-4.204</td>
<td>cv</td>
<td>Ccp, Gn, Sp, Py, Cob, (Fe-ox), (Lo)</td>
<td>Qz, Fl, Ksp</td>
<td>N-S trending crosscourse vein originally mined for Ag and cross cutting the Lower Carboniferous Kate Brook Slate and Cotehele Sandstone Formations</td>
</tr>
<tr>
<td>Wheal Betsy</td>
<td>50.613</td>
<td>-4.107</td>
<td>(psl)</td>
<td>Apy, Lo, Ccp, Sp, Py, Gn, Sd, Hem</td>
<td>Qz, Chl, Bt, Ksp</td>
<td>N-S trending vein with complexly banded ores cross cutting the Lower Carboniferous Greystone and Bealsmill Formations and generally assumed to be of crosscourse origin. Mined for Pb and Ag.</td>
</tr>
<tr>
<td>Wheal Exmouth</td>
<td>50.635</td>
<td>-3.640</td>
<td>cv</td>
<td>Gn, Sp, Py, Apy, Ccp</td>
<td>Qz, Chl, Ms, Kln</td>
<td>N-S trending crosscourse vein cutting the Lower Carboniferous Combe Shale and Teign Chert Formations.</td>
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</table>
Table 3. Summary of compositions of indium-bearing sphalerite. Ore types are listed in table 2. The full analytical dataset can be found in the electronic supplement A3.

<table>
<thead>
<tr>
<th>Pre-granite</th>
<th>Type</th>
<th>n</th>
<th>Fe [max] wt%</th>
<th>Fe [ave] wt%</th>
<th>Cu [max] wt%</th>
<th>Cu [ave] wt%</th>
<th>In [max] ppm</th>
<th>In [ave] ppm</th>
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<th>Cd [ave] ppm</th>
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<th>Ga [ave] ppm</th>
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<td>4 Lundy</td>
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Granite related

<p>| 7 Haytor Vale        | msk  | 10 | 5.29         | 3.97         | 0.87         | 0.55         | 1311         | 541          | 2628         | 2402         | 1064         | 965          |
| 8 Red-a-Ven          | ssk  | 23 | 13.35        | 12.70        | 0.13         | 0.07         | 1241         | 891          | 4771         | 4478         | 395          | 220          |
| 10 Perran St George  | ssk  | 20 | 6.11         | 5.45         | 6.41         | 5.74         | 11900        | 6062         | 1898         | 1482         | 677          | 480          |
| 11 Cigga Head        | gbsv (psl) | 15 | 1.95         | 1.58         | 0.40         | 0.08         | 743          | 322          | 1538         | 1400         | 643          | 515          |
| 12 Redmoor           | gbsv - psl | 89 | 14.86        | 9.47         | 2.81         | 0.32         | 2013         | 407          | 6911         | 3860         | 562          | 345          |
| 16 Geevor            | psl  | 45 | 11.83        | 10.48        | 4.39         | 0.56         | 839          | 263          | 2095         | 1440         | 396          | 261          |
| 17 Botallack         | psl  | 6  | 4.14         | 3.97         | 0.62         | 0.31         | 1953         | 1410         | 2971         | 2930         | 439          | 371          |
| 18 Dolcoath          | psl  | 59 | 12.01        | 8.52         | 7.27         | 0.85         | 14200        | 1416         | 9474         | 1646         | 610          | 348          |
| 21 Wheal Charlotte   | psl  | 64 | 8.35         | 6.24         | 0.72         | 0.08         | 13600        | 1011         | 1684         | 1403         | 517          | 315          |
| 23 Trevellas Coombe  | psl  | 27 | 4.44         | 1.39         | 4.57         | 0.77         | 2632         | 1191         | 1452         | 1300         | 666          | 467          |
| 25 Wheal Concord     | psl  | 19 | 10.69        | 10.36        | 0.16         | 0.03         | 257          | 177          | 1407         | 1322         | 518          | 410          |
| 26 Creegbrawse       | psl  | 24 | 11.35        | 10.37        | 0.12         | 0.02         | 1150         | 208          | 1233         | 1110         | 427          | 279          |
| 27 Wheal Fortune     | psl  | 5  | 10.52        | 7.50         | 2.45         | 0.96         | 4634         | 1770         | 2995         | 1963         | 432          | 337          |
| 28 Wheal Jane        | psl  | 18 | 10.84        | 6.35         | 0.06         | 0.02         | 532          | 399          | 1438         | 1296         | 563          | 436          |
| 29 Nangiles          | psl  | 92 | 12.12        | 9.77         | 0.45         | 0.06         | 4468         | 290          | 2097         | 1313         | 445          | 489          |
| 30 West Chiverton    | psl  | 4  | 8.52         | 4.69         | 4.58         | 1.50         | 1494         | 703          | 1447         | 990          | 633          | 489          |
| 31 East Wheal Rose   | psl  | 19 | 12.83        | 9.58         | 0.11         | 0.03         | 2024         | 485          | 1727         | 1359         | 438          | 356          |
| 33 South Caradon     | psl  | 8  | 1.78         | 0.89         | 1.42         | 0.65         | 36           | 5            | 1526         | 1135         | 566          | 324          |
| 34 East Caradon      | psl  | 2  | 0.58         | 0.55         | 1.69         | 1.68         | 112          | 85           | 5            | 3            | 481          | 467          |
| 35 Hingston Down     | psl  | 3  | 7.53         | 2.89         | 3.94         | 1.93         | 802          | 321          | 3796         | 3215         | 435          | 387          |
| 36 Capel Tor         | qtv - psl | 10 | 6.61         | 4.35         | 4.74         | 1.70         | 2324         | 1543         | 3288         | 3071         | 626          | 447          |
| 37 Great Sheba Consols | psl | 6  | 4.10         | 3.27         | 1.74         | 0.79         | 54           | 12           | 3123         | 2916         | 478          | 385          |
| 38 Devon Great Consols | qtv - psl | 29 | 10.16        | 7.80         | 2.64         | 0.79         | 3294         | 899          | 4943         | 3072         | 565          | 360          |
| 39 Cotehele Consols  | psl  | 20 | 7.88         | 6.01         | 1.28         | 0.08         | 14           | 1            | 4638         | 4466         | 979          | 663          |
| 42 Tavy Consols      | psl  | 21 | 8.26         | 7.14         | 1.13         | 0.11         | 29           | 6            | 4055         | 3573         | 554          | 371          |</p>
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<thead>
<tr>
<th></th>
<th>Mine Name</th>
<th>Age</th>
<th>ToM</th>
<th>ToB</th>
<th>ToC</th>
<th>ToD</th>
<th>ToE</th>
<th>ToF</th>
<th>ToG</th>
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Table 4. Summary of compositions of chalcopyrite. Ore types are listed in table 2. The full analytical dataset can be found in the electronic supplement A3.

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<tr>
<th>Pre-granite</th>
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<th>Zn [ave] wt%</th>
<th>In [max] ppm</th>
<th>In [ave] ppm</th>
</tr>
</thead>
<tbody>
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<table>
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<tr>
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<th>Zn [ave] wt%</th>
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<td>11 Cigga Head gbsv (psl)</td>
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Table 5. Summary of compositions of stannite-group minerals and cassiterite. Ore types are listed in table 2. The full analytical dataset can be found in the electronic supplement A3.

<table>
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<th>Stannite-group minerals</th>
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</table>
Andersen et al.  

Graphical abstract
Andersen et al.  

Highlights

- This is the first time that indium mineralisation has been systematically documented in SW England.

- Indium concentration in the upper crust of SW England is primarily associated with voluminous Early-Permian peraluminous granite magmatism. Cadmium and Ga were abundantly available prior to the emplacement of the granites.

- Magmatic-hydrothermal activity led to the transport of In into granite-related skarn and vein systems, where it deposited primarily in the sulphide-dominated portions. The highest In concentrations are associated with the Carnmenellis and St Agnes plutons in the western part of the region, and in this respect the metal appears to follow Sn.

- Surprisingly, the majority of the indium budget is hosted by chalcopyrite in the granite-related magmatic-hydrothermal parageneses across the ore region.

- Indium is hosted by chalcopyrite and sphalerite with lesser amounts in cassiterite and stannite group minerals. Roquesite and other discrete In minerals formed where In-bearing chalcopyrite and sphalerite have been replaced, either during the complex evolution of the ore systems, or by later supergene alteration. Tennantite is locally an In host.

- Indium was not detected in löllingite, arsenopyrite, rutile, haematite, magnetite, tourmaline, biotite, chlorite, galena, bornite, chalcocite or pyrrhotite. Scattered concentrations in pyrite relate to impurities rather than incorporation by solid solution.

- The In deportment varies between granite-related parageneses with different sphalerite morphologies. The In budget is predominantly in chalcopyrite in parageneses that have little sphalerite or large, unzoned sphalerite with chalcopyrite disease.

- Sphalerite in calc-silicate hosted skarns and sphalerite I in polymetallic sulphide lodes are Cu-rich and have elevated In, however Cu and In do not correlate in the expected manner for a solid solution component. Sphalerite II displays no correlation between Cu and In, while the variations in sphalerite III are consistent with solid solution of roquesite, and to a lesser extent sakuraiite into the sphalerite lattice.
• Remobilisation of In from granite-related parageneses led to localised concentration into Triassic crosscourse veins. This involved the inclusion of clasts into the crosscourse veins as well as dissolution and re-precipitation of In into sphalerite in the crosscourse matrix.