



Indium mineralisation in SW England: Host parageneses and mineralogical relations



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ABSTRACT

The SW England ore region contains significant amounts of indium (In) in Early Permian granite-related skarn and lode parageneses and, to a lesser extent, Triassic epithermal “crosscourse” veins. Ore parageneses that pre-date granite emplacement (Devonian and Lower Carboniferous sedimentary exhalative and vein parageneses) are largely devoid of In. Cadmium (Cd) and gallium (Ga) 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 across the region. Magnetite-silicate skarns and quartz-tourmaline lodes 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. Surprisingly, chalcopyrite accounts for the majority of the In budget throughout the region, although concentrations are highest in sphalerite and stannite group minerals. Sphalerite locally contains up to 1.42 wt% In, chalcopyrite has up to 2200 ppm and stannite group minerals up to 6800 ppm. 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. Roquesite and possibly dzhaldindite or native In formed locally where In-bearing chalcopyrite or sphalerite has been replaced by bornite and quartz. The In partitioning between sphalerite and chalcopyrite varies broadly between 1:1 and 10:1.

Sporadic In was included in Triassic crosscourse veins as a result of interactions between migrating CaCl₂-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 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 CaCl₂-rich basinal brines in a similar manner as In-bearing veins in the West Shropshire ore field.

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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. Irrespective of economics, however, a much expanded circulation and use of In in the modern society requires a greater understanding of its geological distribution, not only to allow

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for new resources to be located, but also to better predict and mitigate a potential increase in environmental effects.

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; Valkama et al., 2016). 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 occurs 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 lithophile element during crustal differentiation (van Westrenen et al., 1999; Jenner and O'Neill, 2012).

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, CuIn_2S_2 which is isostructural with chalcopyrite, CuFeS_2 . Other minerals reported from granite-related systems include dzhalindite $\text{In}(\text{OH})_3$; indite FeIn_2S_4 ; native In; petrukite $(\text{Cu}, \text{Fe}, \text{Zn}, \text{Ag})_3(\text{Sn}, \text{In})\text{S}_4$; and sakuraiite $(\text{Cu}, \text{Zn}, \text{Fe})_3(\text{In}, \text{Sn})\text{S}_4$ (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 Rheohercynian 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 Rheohercynian 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 Rheohercynian 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 Rheohercynian 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 toward their base (Edwards et al., 1997). Lamprophyre dykes with similar Early Permian ages are hosted throughout the Variscan-deformed Devonian and

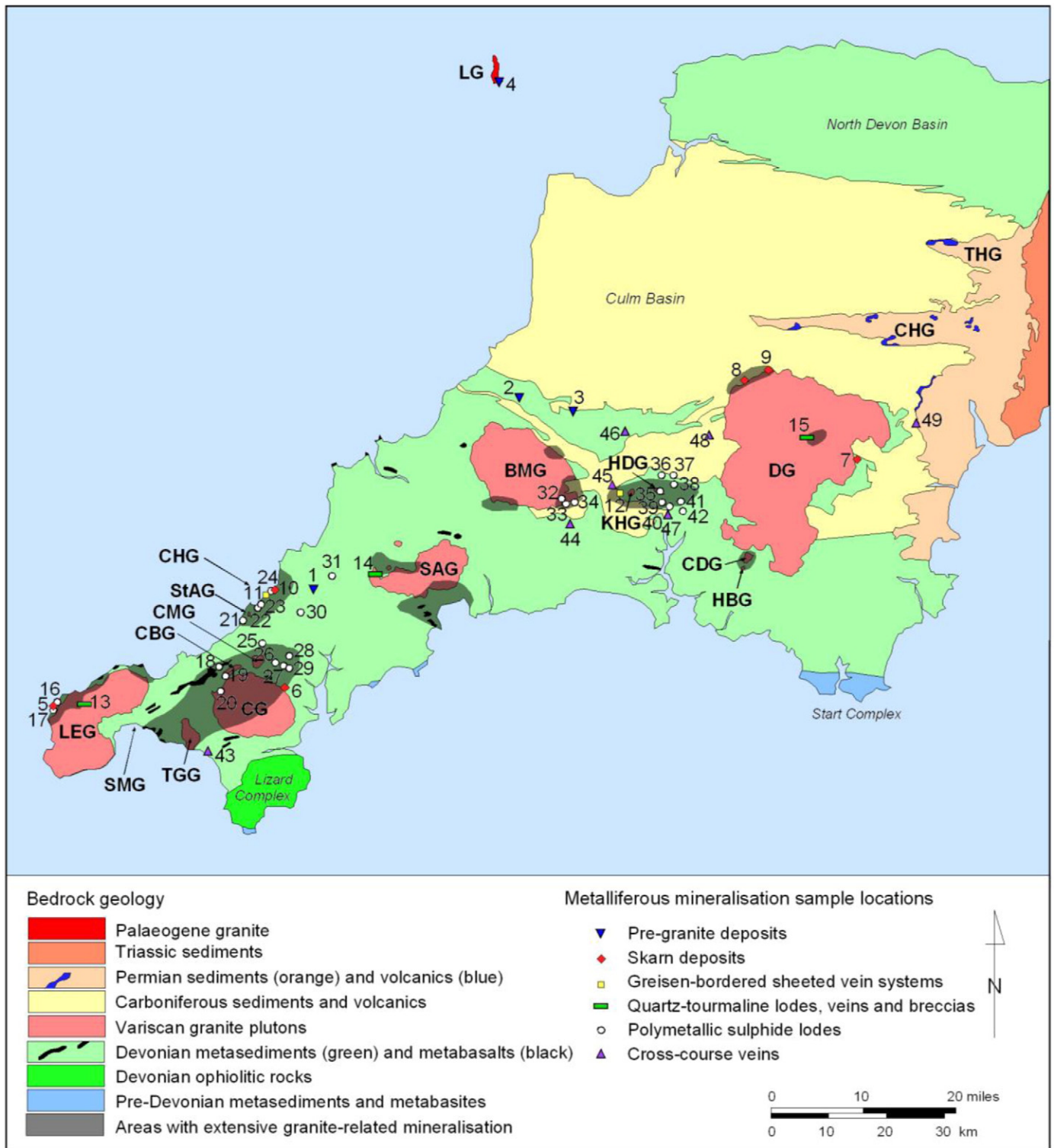


Fig. 1. Geological map of SW England (e.g., Leveridge and Hartley, 2006; Shail and Leveridge, 2009). The Variscan granites include the Land's End (LEG), St Michaels Mount (SMG), Tregonning-Godolphin (TGG), Carnmenellis (CG), Carn Brea (CBG), Carn Marth (CMG), St Agnes (StAG) Cligga Head (CHG), St Austell (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 2.

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 (Dartmoor, Bodmin Moor, St Austell, Carnmenellis, Tregonning-Godolphin, Land's End, and 40 km further west, Isles of Scilly) and several stocks (Crownhill

Down, Hemerdon Ball, Hingston Down, Kit Hill, Belowda Beacon, Cligga Head, St. Agnes, Carn Marth, Carn Brea and St. Michael's Mount 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 to 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, 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

4.2.1. 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 (50.718°N, –3.534°W), the Teign Valley (50.642°N, 3.627°W), Milton Abbot (50.602°N, –4.234°W) and Brentor (50.603640°N, 4.162°W) (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).

4.2.2. 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 (50.517°N, 4.835°W) 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 (50.325°N, 3.802°W, Stanley et al., 1990b). Inclusion fluid and textural studies on veins from the

Table 1

Overview of mineralisation styles in the SW England ore field.

Pre-granite mineralisation
1) Rifting and passive margin development (<i>Early Devonian–Early Carboniferous</i>)
Sedimentary-exhalative (SedEx) mineralisation
2) Variscan convergence and continental collision (<i>Late Devonian–Carboniferous</i>)
Shear zone hosted Au-Sb + base metal mineralisation
Granite-related mineralisation
3) Early post-Variscan extension and magmatism (<i>Early Permian</i>)
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 (<i>Late Permian – Cenozoic</i>)
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

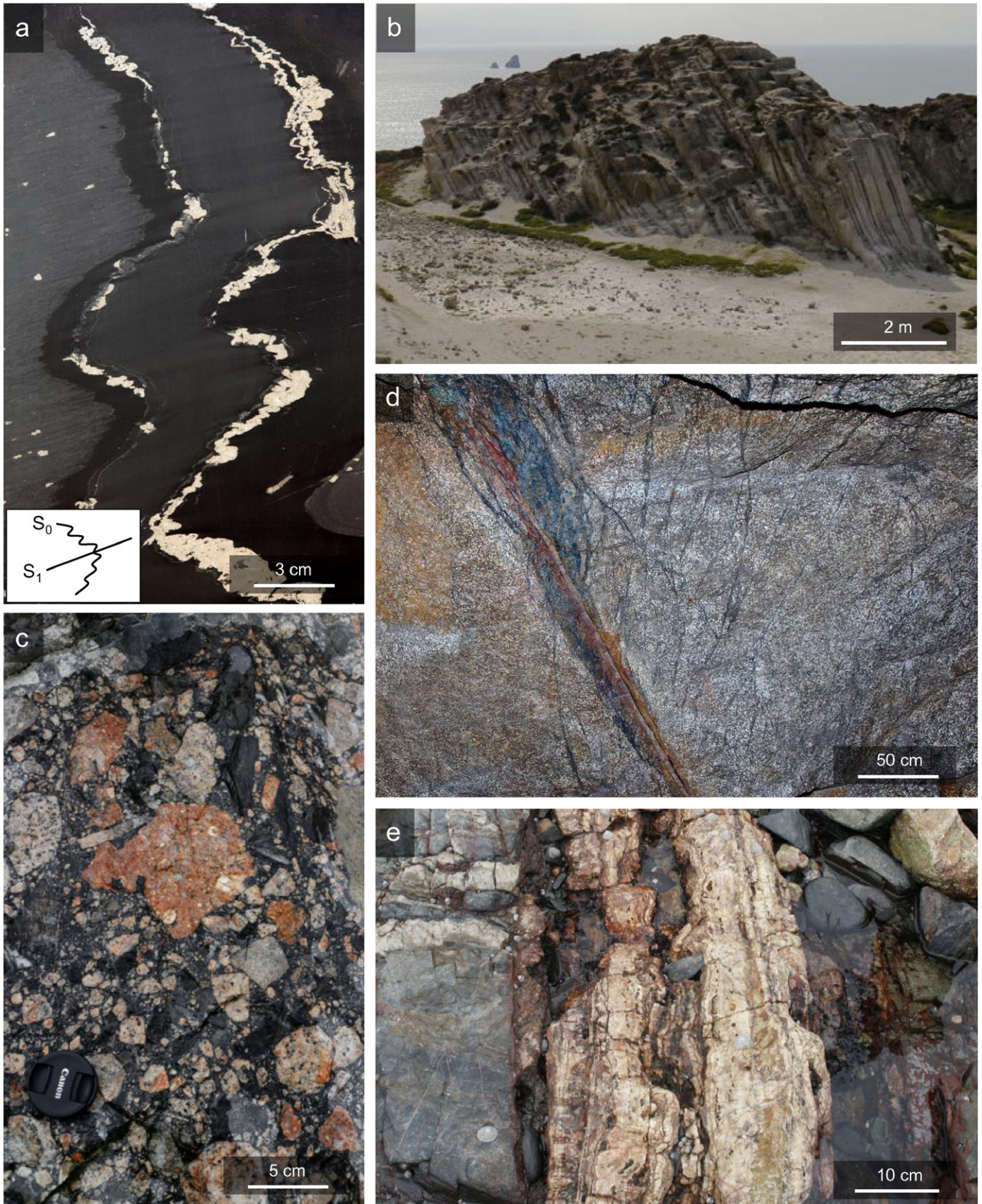


Fig. 2. Examples of mineralisation styles from SW England. a. Stratiform sulphide bands in Lower Carboniferous folded black shale at Wilsey Down. The insert shows the two prominent structural directions, the primary bedding, S_0 , and the tectonic overprint, S_1 . b. Greisen-bordered quartz veins cross-cutting 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 Carmmenellis granite at Holman's test mine. f. Banded quartz-hematite crosscourse vein from Megilligar on the Cornish south coast.

Wadebridge area indicate quartz–Au–Sb was early and precipitated from CO₂-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, they 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 and 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; Scrivener, 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 and Clark, 2002) and the Yankee Lode associated with the Mole Granite in Australia (Audétat et al., 2000).

4.3.1. Pegmatites

Pegmatites and aplites are occasionally mineralised, particularly those associated with topaz granites, although they have not been commercially exploited for metals. Pegmatite-aplite sheets at Megiliggarr Rocks (50.091°N, 5.341°W) 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 (50.389°N, 4.791°W) 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 bertrandite (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 (50.709°N, 4.032°W, Edmonds et al., 1968), and Embrey (1953) reported beryl from pegmatites at the New Consols Mine at Stoke Climsland (50.546°N, 4.316°W).

4.3.2. Skarns

Skarn deposits 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).

4.3.3. 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, extend to a distance of 100 m away from the granite contacts, and are characterised by the development of greisen assemblages at their margins. 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, 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, kesterite and ferrokesterite), 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 amounts of 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 300 °C and >500 °C

(Campbell and Panter, 1990; Williamson et al., 1997), while quartz inclusions homogenize between 250 °C and 350 °C (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.).

4.3.4. Quartz-tourmaline lodes, veins and breccias (QTL)

Quartz-tourmaline (-cassiterite) lodes, veins and breccias (Fig. 2c) developed within and immediately adjacent to the granites. In contrast to the greisen-bordered sheeted veins, these bodies have no reactive mineral development along their borders, although they 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 400–230 °C and salinities of 5–15 wt% NaCl eq. (Alderton and Harmon, 1991).

4.3.5. 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, the most productive mine in

■	Arsenopyrite	Apy
■	Löllingite	Lö
■	Sphalerite	Sp
■	Pyrite	Py
■	Pyrrhotite	Po
■	Chalcopyrite	Ccp
■	Galena	Gn
■	Cassiterite	Cst
■	Stannite group	Stn
■	Wolframite	Wf
■	Tennantite	Tnt
■	Haematite/magnetite	Hem/Mag
■	Quartz	Qz
■	K-feldspar	Ksp
■	Plagioclase	Pl
■	Muscovite	Ms
■	Biotite	Bt
■	Chlorite	Chl
■	Tourmaline	Tur
■	Epidote/garnet	Ep/Grt
■	Calcite	Cc
■	Fluorite	Fl

Fig. 4. Key to the QEMSCAN false-colour mineral distribution maps in Figs. 5–8.

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 associated with the St Austell Granite, in operation until 1870 (Dines, 1956), and 3) South Caradon, the deepest and richest Cu mine associated with the Bodmin Moor Granites, 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 albitization, 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 220 °C 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, Cammenellis 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 are dominated by 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

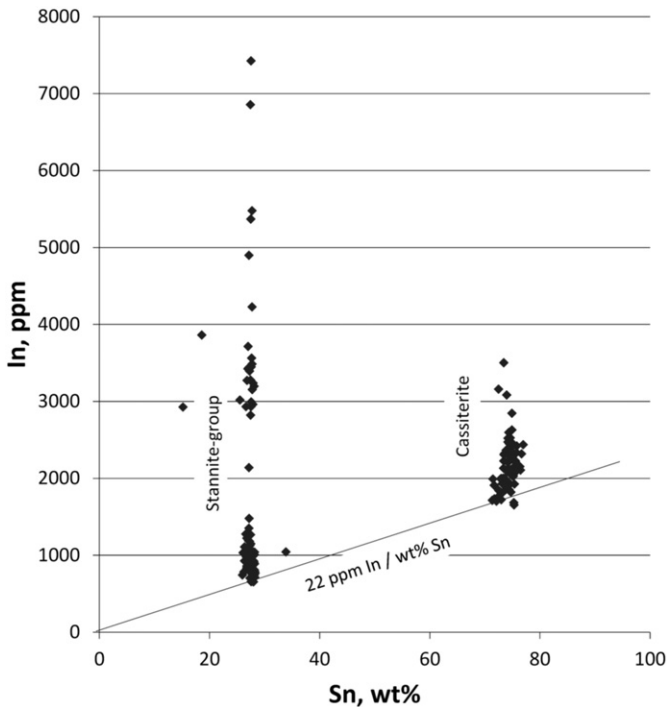


Fig. 3. Interference correction for Sn on In. The interference is calculated from the minimum measured signal for In-K α for stannite group minerals and cassiterite and approximates 22 ppm In for 1 wt% Sn.

Table 2
Sample locations, mineralisation styles, ore and gangue minerals. Location information is recorded by GPS or by Google Earth, numbers refer to Fig. 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, qtv = 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.

Location	Name	Lat. (°N)	Long. (°W)	Type	Oxide and sulphide minerals	Associated gangue	Notes
<i>Pre-granite</i>							
1	Duchy Peru	50.358	5.103	bv	1: Cst 2: Py, Ccp, Sp, Hem, Gn 3: Cct	1: Qz, Bt, Chl, Ms., Ksp 2: Cc, Chl, Sd	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
2	Wilsey Down	50.671	4.577	sts	Py, Po, Ccp, Sp, Gn	Cc, Qz, Chl, Bt	Metapelite/metapsammite with folded stratiform sulphides in calcareous black shale
3	Egloskerry	50.641	4.430	sts	1: Gn, Sp, Py, (Apy), Hem 2: Gn, Py 3: Sp	Qz, Chl, Bt, Ms., Ksp, Cc	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.
4	Lundy	51.163	4.658	sts	Py, Po, Sp (Ccp)	Cc, Qz, Chl	Sulphide-bearing metacarbonate interbedded with Upper Devonian metapelites and metapsammites. Sphalerite has exsolved chalcopyrite, but chalcopyrite has not been observed as a discrete mineral.
<i>Granite related</i>							
5	Grylls Bunny	50.142	5.691	msk	Mt, Cst	Grt, Tur	Banded magnetite-garnet and tourmaline skarns in contact-metamorphic succession of Devonian metapelite and metabasalt of the Mylor Slate Formation
6	Magdalen Mine	50.196	5.132	msk	Mt, Cst	Hbl, Bt	Magnetite-silicate skarn associated with metabasalt and metapelite of the Mylor Slate Formation.
7	Haytor Vale	50.583	3.737	msk	Mt, Apy, Py, Ccp, Sp	Qz, Chl, Bt, Ms., Ksp	Sulphide-bearing metapelite of the Crackington Formation (Ashton Shale equivalent) associated with magnetite-skarn
8	Red-a-Ven	50.707	4.027	ssk	Po, Py, Lo, Ccp, (Sp), (Apy)	Grt, Mly, Chl, Cpx, Fl, (Qz)	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
9	Ramsley	50.721	3.914	ssk	Po, Ccp	Grt, Mly, Chl, Cpx, Fl, (Qz)	Silicate-sulphide skarn in calc-silicate bearing metasediment of the Meldon Chert Formation.
10	Perran St George	50.339	5.176	ssk	Cst, Ccp, Py, Po, (Sp), (Apy)	Grt, cpx, Qz, Fl, Ap, (Chl)	Pyrrhotite cores surrounded by pyrite in matrix of chalcopyrite. Cassiterite as <1 mm large crystals. Sphalerite as minute grains in chalcopyrite. Provenanced in collection to Perran St George, but location unverified.
11	Cligga Head	50.339	5.179	gbsv (psl)	Apy, Ccp, Wf, Cst, Stn, Cct, Py, Ttr, (Lo)	Ms, Qz, Tur, Kln, Chl	Greisen-bordered veins with polymetallic sulphides in kaolinised biotite granite
12	Redmoor	50.517	4.319	gbsv - psl	Apy, Lo, Wf, Cst, Stn, Ccp, Sp, Py, Cst, Hem	Ms, Qz, Tur, Kln, Chl	Greisen-bordered veins with polymetallic sulphides in folded succession of metapelite and metapsammite
13	Ding Dong	50.154	5.593	qtv	Cst, Hem	Qz, Tur	Cassiterite bearing quartz-tourmaline (–hematite) veins cross-cutting megacrystic biotite granite
14	Wheal Remfry	50.381	4.920	qtv	Rt, Cst	Qz, Tur	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)
15	Vitifer Mine	50.613	3.865	qtv	Cst, Hem	Qz, Tur	Cassiterite bearing quartz-tourmaline (–hematite) veins cross-cutting megacrystic biotite granite
16	Geevor	50.154	5.678	psl	Apy, Cst, Ccp, Bn, Sp-III, Py, (Gn), (Cct)	Qz, Chl, Ksp, (Bt), (Cc)	Polymetallic sulphide lodes with quartz and chlorite cross-cutting granite, hornfels, slate and metabasalt
17	Botallack	50.138	5.692	psl	Cst, Apy, Py, Ccp, Sp-II, Stn, Gn	Qz, Tur, Chl, Ksp, (Ms)	Polymetallic sulphide lodes with quartz and chlorite cross-cutting granite, hornfels, slate and metabasalt
18	Dolcoath	50.217	5.281	psl	Cst, Wf, Apy, Ccp, Sp-II, Sp-III, (Bn), (Lo)	Qz, (Tur), Chl, Fl, Ms	Very variable and complex polymetallic sulphide lode system developed at the northern contact of the Cammenellis granite. Locally showing skarn development in metabasites.
19	Great Condurow	50.207	5.280	psl	Sp-I, Ccp, Py, Apy, Cst, Wf, Bn, Fe-ox	Qz, Chl, Ms	Quartz-chlorite lodes with sulphide minerals. Löllingite 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.
20	Holmans Test Mine	50.184	5.283	qtv - psl	Rt, Cst, Apy, Py, Ccp, Sp-II	Qz, Tur, Chl, Fl	Polymetallic sulphides in quartz-tourmaline breccia veins and quartz-chlorite lodes cross-cutting megacrystic biotite granite
21	Wheal Charlotte	50.297	5.234	psl	Sp-III, Ccp, Py, Apy, Bm, (Po), Fe-ox	Qz, Chl	Polymetallic sulphide lode with quartz and chlorite cross cutting metapelites of the Porthtowan Formation
22	Blue Hills	50.321	5.197	psl	Py, Cst, (Ccp)	Qz, Chl, Bt	Polymetallic sulphide lode with quartz and chlorite cross cutting metapelites of the Porthtowan Formation
23	Trevellas Coombe	50.322	5.193	psl	Py, Ccp, Sp-I, Sp-II, (Gn), (Bm), (Cct)	Qz, Chl	Polymetallic sulphide lode with quartz and chlorite cross cutting metapelites of the Porthtowan Formation
24	Perran St George	50.339	5.176	psl	Py, Rt	Qz, Chl, (Bt)	Polymetallic sulphides in quartz-chlorite lode
25	Wheal Concord	50.271	5.190	psl	Apy, Cst, Sp-II, Ccp, Py, (Gn)	Qz, Chl	Polymetallic sulphides in quartz-chlorite lode cross cutting metapelite
26	Creegbrawse	50.248	5.164	psl	Apy, Ccp, Sp-II, (Py), (Gn)	Qz, Tur, Chl, (Bt), (Ms)	Polymetallic sulphide lode with quartz and tourmaline gangue cross cutting metapelites
27	Wheal Fortune	50.237	5.149	psl	Ccp, Py, Sp-I, (Apy), (Gn)	Qz, Chl, (Ms), (Bt)	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.

Table 2 (continued)

Location	Name	Lat. (°N)	Long. (°W)	Type	Oxide and sulphide minerals	Associated gangue	Notes
28	Wheal Jane	50.238	5.126	psl	Apy, Py, Cpy, Sp-I, Sp-II, Cst	Qz, Tur, Chl	Polymetallic sulphide lode cross cutting the Devonian Mylor Slate Formation.
29	Nangiles	50.235	5.137	psl	Py, Sp-II, Ccp, Apy, Wf	Qz, Chl	Polymetallic sulphide lode cross cutting the Devonian Mylor Slate Formation.
30	West Chiverton	50.318	5.101	psl	Py, Sp	Qz, Ms., Ksp	Polymetallic sulphide lode cross cutting the Devonian slates of the Ladock Beds.
31	East Wheal Rose	50.362	5.041	psl	Sp, Py, (Po), (Ccp), (Gn)	Qz	Polymetallic sulphide lode cross cutting the Lower Devonian calcareous slates of the Meadfoot Beds.
32	Gonamena	50.508	4.453	psl	Apy, Ccp, Cst, Py, Cob, (Cct), (Lo)	Qz, Chl, (Ms), (Bt)	Polymetallic sulphide lode cross cutting the Bodmin Moor biotite granite to the west of Caradon Hill
33	South Caradon	50.504	4.450	psl	Apy, Ccp, Cst, (Py), (Lo), (Bm)	Qz, Chl, Fl, (Bt)	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.
34	East Caradon	50.503	4.435	psl	Apy, Ccp, Cst, Py, (Cct), (Cob), (Bm)	Qz, Chl, (Bt)	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.
35	Hingston Down	50.526	4.245	psl	1: Apy, Py, Ccp, Cst, Stn, Wf, Ttr 2: Bn, Cct	Qz, Ms., Tpz	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
36	Capel Tor	50.547	4.246	qtv - psl	Apy, Cst, Ccp, Py, Sp-I, (Lo)	Tur, Qz, Ms., (Bt)	Complex ore paragenesis with early tourmaline-quartz breccias cross cut by polymetallic sulphides. Some localised development of greisen borders
37	Great Sheba Consols	50.540	4.298	psl	Sp-II, Py, Apy, Ccp, (Gn)	Qz, Tur, Kln	Polymetallic sulphide lodes cross-cutting metapelites and metapsammities of the Upper Devonian Kate Brook Slate Formation.
38	Devon Great Consols	50.540	4.222	qtv - psl	Apy, Ccp, Cst, Stn, Py, Fe-ox, (Lo), (Gn)	Tur, Ms., Ksp, Bt, Qz, Fl	Polymetallic sulphide lodes cross-cutting metapelites and metapsammities of the Upper Devonian Kate Brook Slate Formation. Localised greisen development at depth.
39	Cotehele Consols	50.503	4.225	psl	Apy, Cst, Ccp, Py, Sp-II	Qz Chl, Fl, (Bt)	Polymetallic sulphide lodes cross-cutting metapelites and metapsammities of the Upper Devonian Kate Brook Slate Formation.
40	Okeltor	50.500	4.193	psl	Apy, Cst, Ccp, Py, Sp-II, Fe-ox	Qz, Chl, Tur, Kln	Polymetallic sulphide lodes cross-cutting metapelites and metapsammities of the Upper Devonian Kate Brook Slate Formation.
41	William and Mary	50.510	4.169	psl	Ccp, Py, Sp-II	Qz, Ksp, Bt, Chl, Ms	Polymetallic sulphide lodes cross-cutting metapelites and metapsammities of the Upper Devonian Kate Brook Slate Formation.
42	Tavy Consols	50.498	4.160	psl	Apy, Cst, Ccp, Sp-II, (Sp-I), Py	Qz, Chl, Tur, Fl, (Ms)	Polymetallic sulphide lodes cross-cutting metapelites and metapsammities of the Upper Devonian Kate Brook Slate Formation.
<i>Post-granite</i>							
43	Wheal Penrose	50.077	5.305	ccv	Ccp, Py, Gn, Hem, (Apy)	Qz, Ksp, Mnz	N-S trending vein of banded hematite and quartz cross-cutting metapelite of the Mylor Slate Formation.
44	Wrey-Ludcott United	50.469	4.399	ccv	1: Cst, Apy, 2: Sp, Py, Fe-ox, (Ccp), (Gn)	1: Qz, Tur, Ksp, Chl 2: Fl, Cc, Ap	Two N–S trending crosscourse veins crosscutting the Upper Devonian Burraton and Saltash Formations and historically mined for Pb and Ag.
45	Holmbush Mine	50.525	4.318	ccv	Ga, Sp, Fe-ox, (Py)	Qz, Ms., Ksp	N-S trending crosscourse vein emplaced into the Kate Brook Slate formation and intersecting the greisen-bordered sheeted vein complex at Redmoor.
46	Greystone Quarry	50.601	4.314	ccv	Py, Gn, Ccp, Sp, (Po)	Qz, Ms., Ksp	Crosscourse vein in Lower Carboniferous metapelite and metadolerite with interbedded chert.
47	Buttspill Mine	50.490	4.204	ccv	Ccp, Gn, Sp, Py, Cob, (Fe-ox), (Lo)	Qz, Fl, Ksp	N-S trending crosscourse vein originally mined for Ag and cross cutting the Lower Carboniferous Kate Brook Slate and Cotehele Sandstone Formations
48	Wheal Betsy	50.613	4.107	ccv - (psl)	Apy, Lo, Ccp, Sp, Py, Gn, Sd, Hem	Qz, Chl, Bt, Ksp	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.
49	Wheal Exmouth	50.635	3.640	ccv	Gn, Sp, Py, Apy, Ccp	Qz, Chl, Ms., Kln	N-S trending crosscourse vein cutting the Lower Carboniferous Combe Shale and Teign Chert Formations.

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.

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, chalcocopy, chlorite and hematite and locally carry significant amounts of 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; Shepherd et al., 2005) 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

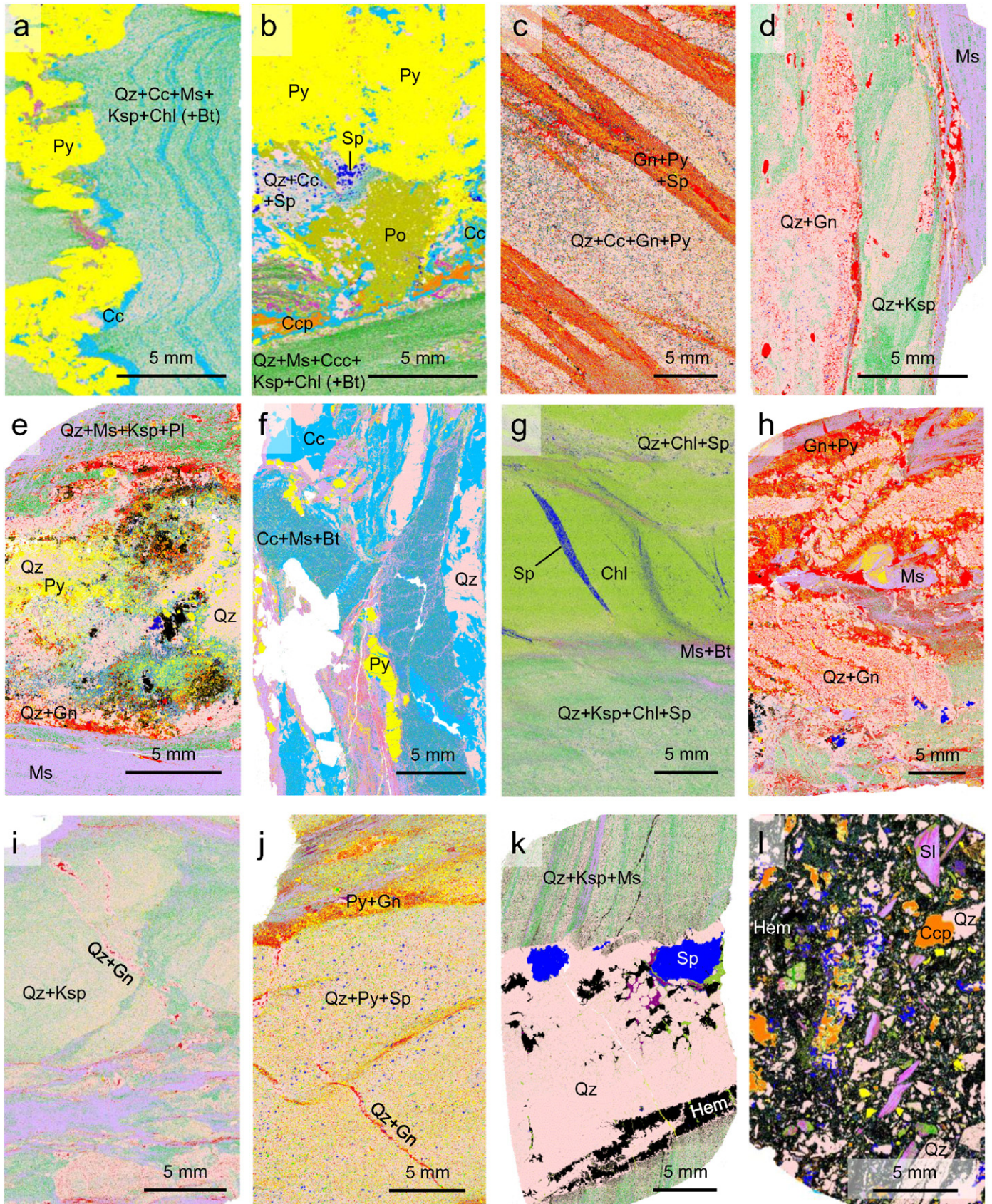


Fig. 5. Examples of textures (QEMSCAN mineral maps) of pre-granite mineralisation styles from the Wilsey Down borehole (a–b), Egloskerry (c–k) and the Perran Iron Lode (l). Mineral acronyms are apy = arsenopyrite, ax = axinite, bt = biotite, cc = calcite, ccp = chalcopyrite, cct = chalcocite, chl = chlorite, 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.

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 L α lines on JEOL XCE-type spectrometers (for high spectral resolution) using a PET crystal for In-L α and Cd-L α , and a TAP crystal for Ga-L α .

The Sn-L η ($\lambda = 3.789 \text{ \AA}$) interference on the In-L α ($\lambda = 3.772 \text{ \AA}$) 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 α reflection ($\lambda = 11.316 \text{ \AA}$) on the Ga-L α intensity ($\lambda = 11.292 \text{ \AA}$) amounted to 500 ppm Ga per 1 wt% In measured on InAs. For silicate minerals, the K-K α ($\lambda = 3.741 \text{ \AA}$) interference on the In-L α amounted to 49 ppm In (59 ppm In₂O₃) per 1 wt% K₂O.

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.

Whole-rock abundances and deportments of In were determined by mass balance by the use of Eq. (1):

$$C = \sum_{i=1}^n x_i \times C_i \quad (1)$$

where C represents the whole rock concentration, x_i the weight fraction of mineral i and C_i the In concentration in mineral i . Whole-rock concentrations for sulphide-poor parageneses were determined by the measurement of ¹¹³In and ¹¹⁵In using ICP-MS after sodium peroxide sintering and dissolution with HNO₃. Isobaric corrections were made for the ¹¹³Cd and ¹¹⁵Sn interferences and Tb was used as the internal standard.

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 data 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 analytical data 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 metasilstones, 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 stratabound (Fig. 5d–f) or in breccias (Fig. 5f), and have locally been redistributed into tensile fractures, Riedel shears (Fig. 5g–h) and transgressive quartz and calcite 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 amounts of 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 amounts of 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.

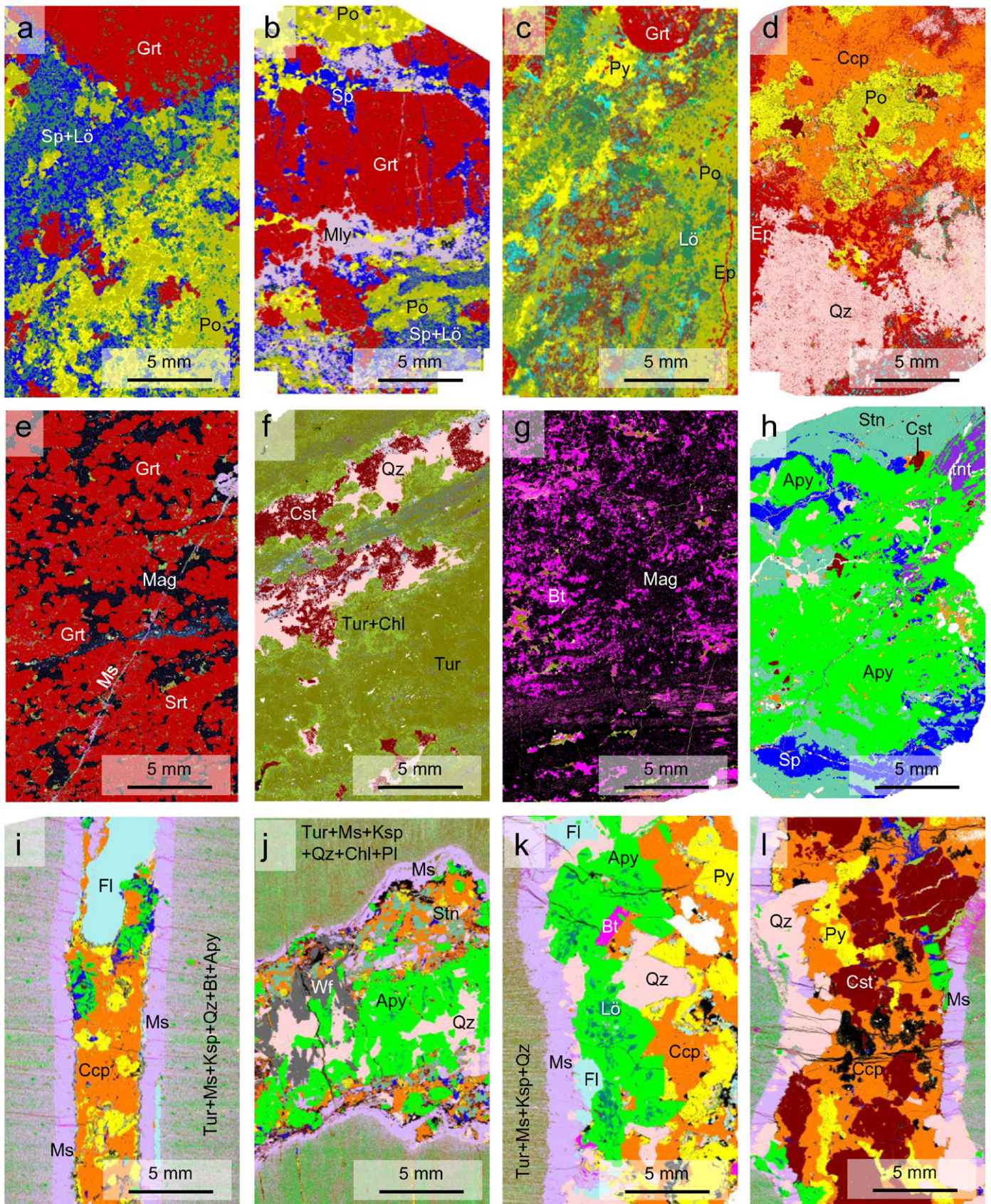


Fig. 6. Examples of textures (QEMSCAN mineral maps) of skarns and greisen-bordered veins (mineral abbreviations as in Fig. 5). Sulphide-bearing skarns from Red-a-Ven (a–c) and Perran St George (d); silicate-oxide skarns from Grylls Bunny (e–f) and Magdalen Mine (g); greisen-bordered sheeted veins with polymetallic sulphides from Cligga Head (h) and Redmoor (i–l).

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, chalcocopyrite and sphalerite with minor arsenopyrite in a gangue of tin and/or boron bearing silicates (axinite, datolite, malayaite, grossular and

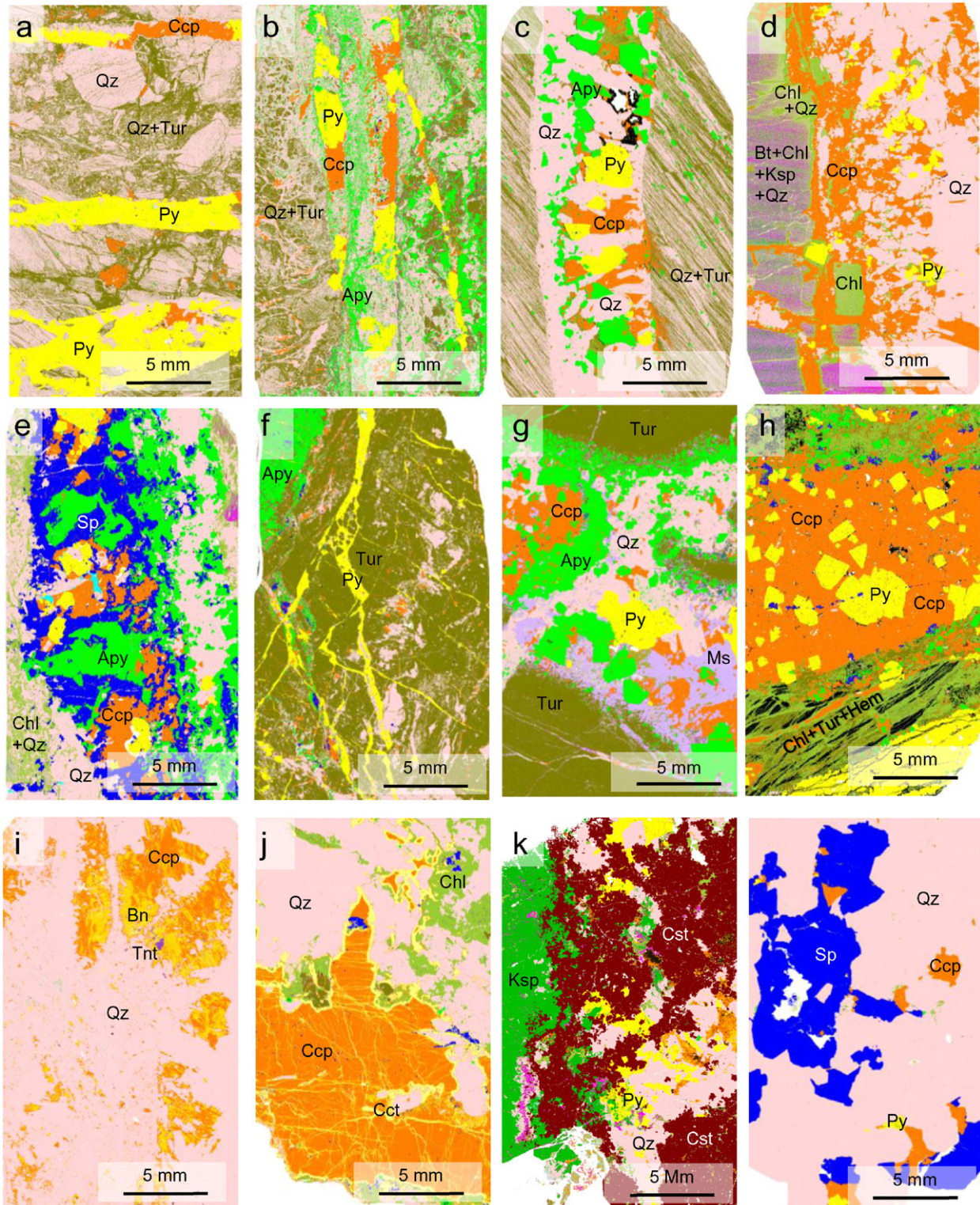


Fig. 7. Examples of textures (QEMSCAN mineral maps) of quartz-tourmaline veins and breccias cross-cut by polymetallic sulphides at Capel Tor. a–b. Quartz-tourmaline lodes, veins and breccias cross-cut by polymetallic sulphides at Capel Tor. c. Polymetallic sulphide lode with tourmalinisation of metapelitic 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 chalcocopyrite and pyrite with associated chlorite, tourmaline and hematite alteration from Okeltor. i. Chalcocopyrite-bornite assemblage at Geevor. j. Chalcocopyrite with chalcocite replacement along margins and within fractures at Dolcoath. k. Cassiterite associated with quartz and alkali feldspar at Geevor. l. Chalcocopyrite and sphalerite III associated with pyrite in quartz gangue with traces of chlorite from Wheal Charlotte.

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 displays 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 department 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. Stannite group minerals are locally abundant at both localities (Fig. 6j) as well as traces of bismuth minerals. Sphalerite has abundant inclusions of chalcopyrite and, more rarely, stannite group minerals. 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 analytical data 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 Remfry 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

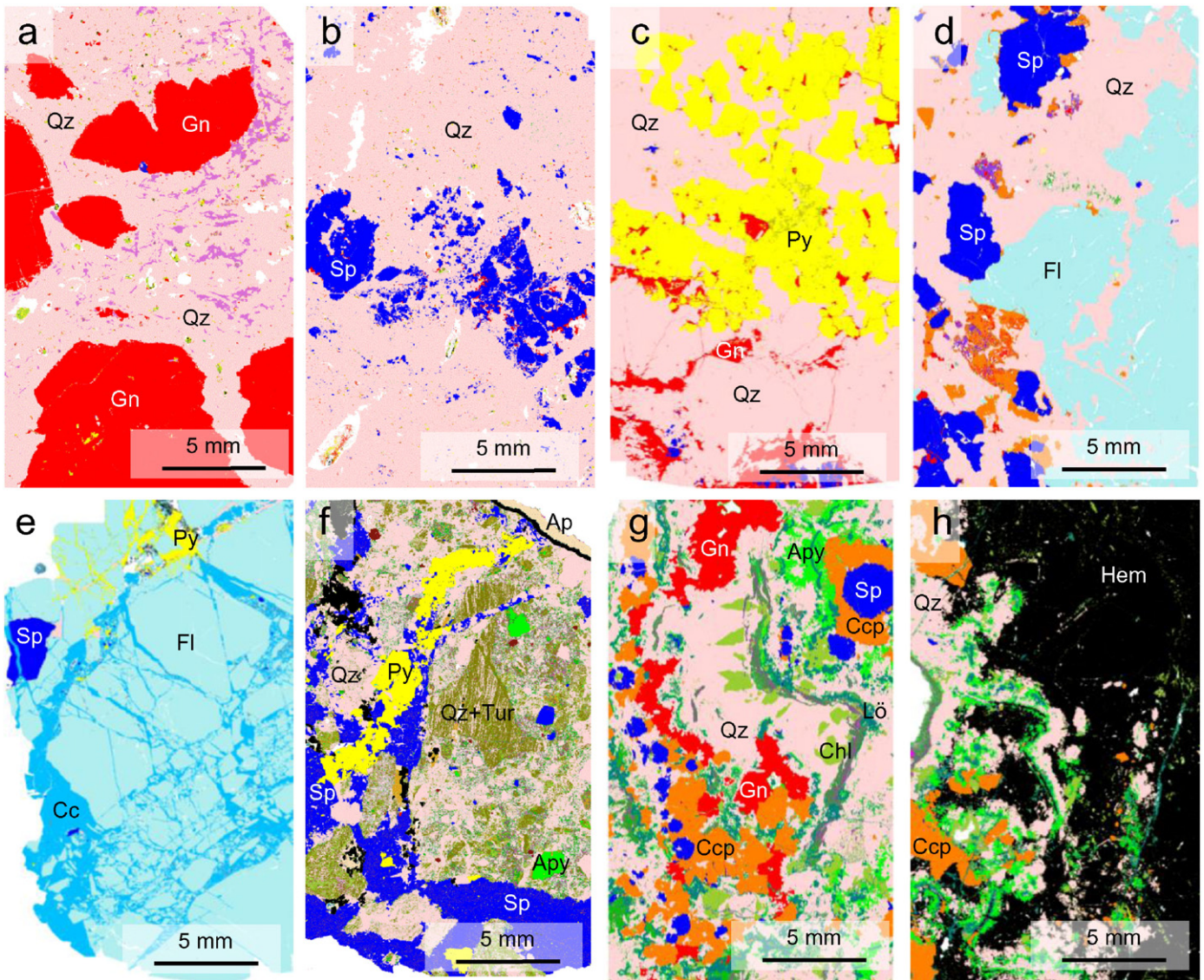


Fig. 8. Examples of textures (QEMSCAN mineral maps) of crosscourse veins (mineral abbreviations as in Fig. 5) from Wheal Exmouth (a–c), Buttspill (d), Wrey-Ludcott United (e–f), and Wheal Betsy (g–h).

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 dzhaldindite (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 displays 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 <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 analytical data 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 group mineral with least Zn. At Hingston 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.

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.

	Type	n	Fe [max] wt%	Fe [ave] wt%	Cu [max] wt%	Cu [ave] wt%	In [max] ppm	In [ave] ppm	Cd [max] ppm	Cd [ave] ppm	Ga [max] ppm	Ga [ave] ppm	
<i>Pre-granite</i>													
1	Duchy Peru	bv	31	5.78	2.45	0.53	0.16	34	7	6892	2311	584	491
2	Wilsey Down	sts	9	8.82	7.69	0.22	0.06	82	16	10,700	9804	1004	866
3	Egloskerry	sts	63	4.38	3.51	0.97	0.09	107	22	2153	869	1046	880
4	Lundy	sts	18	2.86	1.54	0.02	0.00	242	86	13,900	11,556	1083	878
<i>Granite related</i>													
7	Haytor Vale	mks	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	11,900	6062	1898	1482	677	480
11	Cligga 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	14,200	1416	9474	1646	610	348
21	Wheal Charlotte	psl	64	8.35	6.24	0.72	0.08	13,600	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	Creegbrowse	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
<i>Post-granite</i>													
44	Wrey-Ludcott United	ccv	25	6.27	3.46	2.50	0.22	1071	336	4378	2687	647	487
45	Holmbush Mine	ccv	3	4.18	3.60	0.14	0.06	37	20	1727	922	950	749
46	Greystone Quarry	ccv	18	0.43	0.18	0.33	0.04	97	16	4928	4088	630	468
47	Buttspill Mine	ccv	24	1.59	0.47	2.74	0.54	42	6	17,400	5428	1366	784
48	Wheal Betsy	ccv - (psl?)	36	3.72	1.98	1.55	0.43	975	106	15,500	4700	1004	547
49	Wheal Exmouth	ccv	54	11.01	1.19	0.64	0.08	424	23	11,200	3736	925	625

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 amounts of 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 displays 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.

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.

		n	Zn [max] wt%	Zn [ave] wt%	In [max] ppm	In [ave] ppm	
<i>Pre-granite</i>							
1	Duchy Peru	bv	13	0.07	0.04	21	3
2	Wilsley Down	sts	12	0.10	0.05	42	9
<i>Granite related</i>							
7	Haytor Vale	msk	9	0.63	0.13	85	63
8	Red-a-Ven	ssk	25	0.86	0.14	438	102
10	Perran St George	ssk	21	0.10	0.04	1331	1143
11	Cligga Head	gbsv (psl)	67	0.15	0.03	539	340
12	Redmoor	gbsv - psl	132	0.41	0.07	1147	157
16	Geevor	psl	57	0.05	0.02	822	203
17	Botallack	psl	28	0.09	0.03	947	342
18	Dolcoath	psl	67	0.56	0.06	2214	648
21	Wheal Charlotte	psl	57	0.48	0.05	203	60
23	Trevellas Coombe	psl	31	0.10	0.04	685	430
25	Wheal Concord	psl	9	0.69	0.39	35	8
26	Creegbrawse	psl	16	0.36	0.08	357	149
27	Wheal Fortune	psl	63	0.59	0.06	1519	602
28	Wheal Jane	psl	21	0.08	0.04	221	109
29	Nangiles	psl	4	1.84	1.66	0	0
32	Gonamena	psl	18	0.44	0.05	249	138
33	South Caradon	psl	52	0.23	0.03	1147	273
34	East Caradon	psl	82	0.06	0.02	488	287
35	Hingston Down	psl	20	0.28	0.05	281	166
36	Capel Tor	qtv - psl (gbsv)	39	0.23	0.04	1040	444
37	Great Sheba Consols	psl	1	0.05	0.05	61	61
38	Devon Great Consols	qtv - psl	170	0.23	0.04	647	189
42	Tavy Consols	psl	6	0.11	0.06	73	30
<i>Post-granite</i>							
43	Wheal Penrose	ccv	9	0.06	0.04	296	87
46	Greystone Quarry	ccv	12	0.05	0.02	2	0
47	Buttspill Mine	ccv	35	0.32	0.06	744	179
48	Wheal Betsy	ccv - (psl?)	53	0.21	0.03	285	93
49	Wheal Exmouth	ccv	1	2.53	2.53	0	0

By far the most significant In hosts across the region are sphalerite (Figs. 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

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.

Stannite-group minerals		n	Zn [max] wt%	Zn [ave] wt%	In [max] ppm	In [ave] ppm	
11	Cligga Head	gbsv (psl)	17	13.61	8.37	660	435
12	Redmoor	gbsv - psl	7	5.16	3.99	265	229
17	Botallack	psl	27	9.20	3.11	6815	3168
35	Hingston Down	psl	16	2.87	1.65	687	253
38	Devon Great Consols	qtb - psl	13	1.82	1.06	876	410
Cassiterite		n	Fe [max] wt%	Fe [ave] wt%	In [max] ppm	In [ave] ppm	
10	Perran St George	ssk	4	0.29	0.13	235	186
11	Cligga Head	gbsv (psl)	6	0.30	0.15	426	354
12	Redmoor	gbsv - psl	6	0.26	0.09	758	585
16	Geevor	psl	18	1.32	0.31	1876	863
18	Dolcoath	psl	16	1.71	0.38	1554	507
22	Blue Hills	psl	7	0.81	0.43	496	465
26	Creegbrawse	psl	4	0.52	0.16	461	443
27	Wheal Fortune	psl	1	0.99	0.99	970	970
28	Wheal Jane	psl	2	0.30	0.17	486	447
32	Gonamena	psl	2	0.64	0.51	135	121
33	South Caradon	psl	1	0.57	0.57	697	697
34	East Caradon	psl	3	0.88	0.60	744	372
35	Hingston Down	psl	1	0.15	0.15	294	294
38	Devon Great Consols	qtb - psl	3	0.40	0.24	630	607
42	Tavy Consols	psl	2	0.92	0.57	19	3

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 amounts of In in the granite-related mineralisation systems (Table 4). Similar to the sphalerite, no In was detected in the pre-granite parageneses, but sporadic concentrations

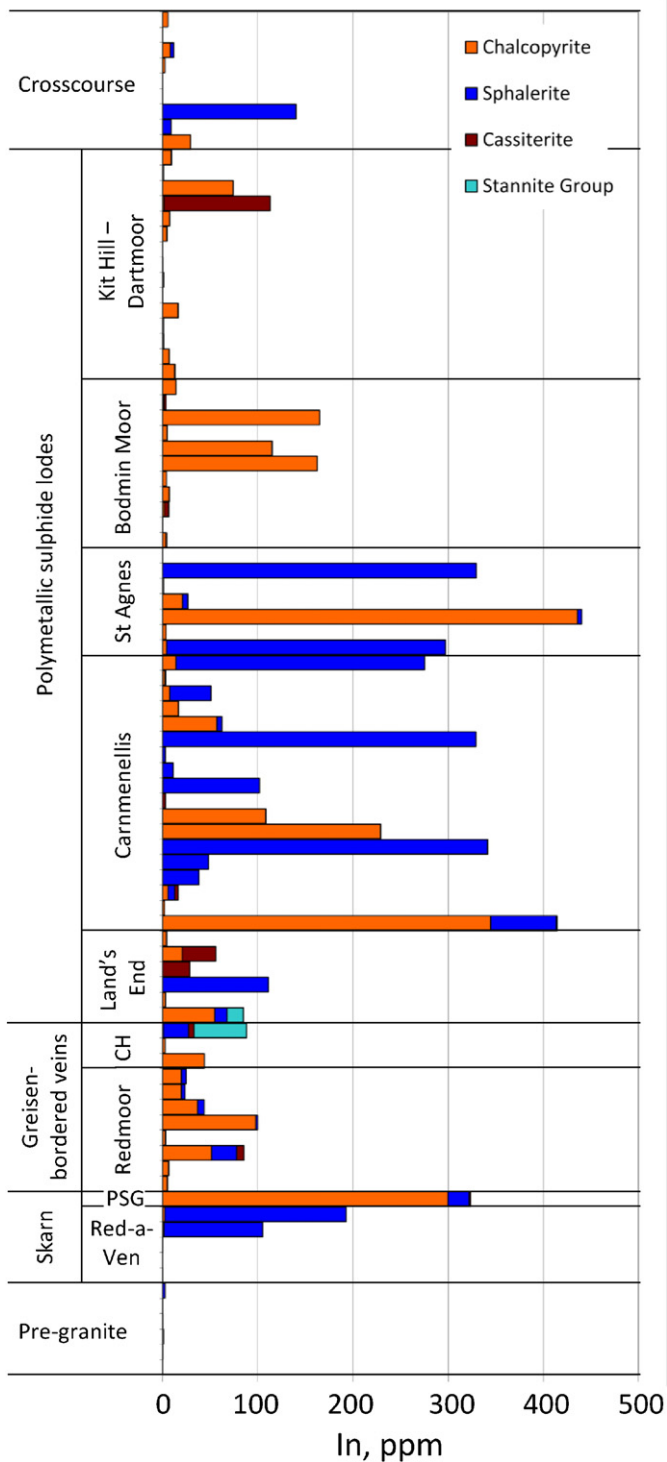


Fig. 9. The mineralogical distribution (department) of In in the studied samples. Absolute concentrations of In are calculated from the abundances of In-bearing minerals (from QEMSCAN analysis) and the average concentrations of In within each of these minerals (from EPMA analysis). CH = Cligga Head,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

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 $(\text{Cu} + \text{Fe})/\text{S}$ (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 In hosts (Table 5). All of the analysed grains carry Zn, but Zn/Fe is very variable. The very high In concentrations at Botallack are associated with a Zn-poor, Fe-rich member of the group, while the In 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 analytical data to provide a full assessment of In incorporation into these minerals.

7.4. Cassiterite

Cassiterite is locally a significant In 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 (Pavlova et al., 2015), and consequently, our analytical data 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 In 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 dzhaliindite ($\text{In}(\text{OH})_3$) 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 dzhaliindite 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

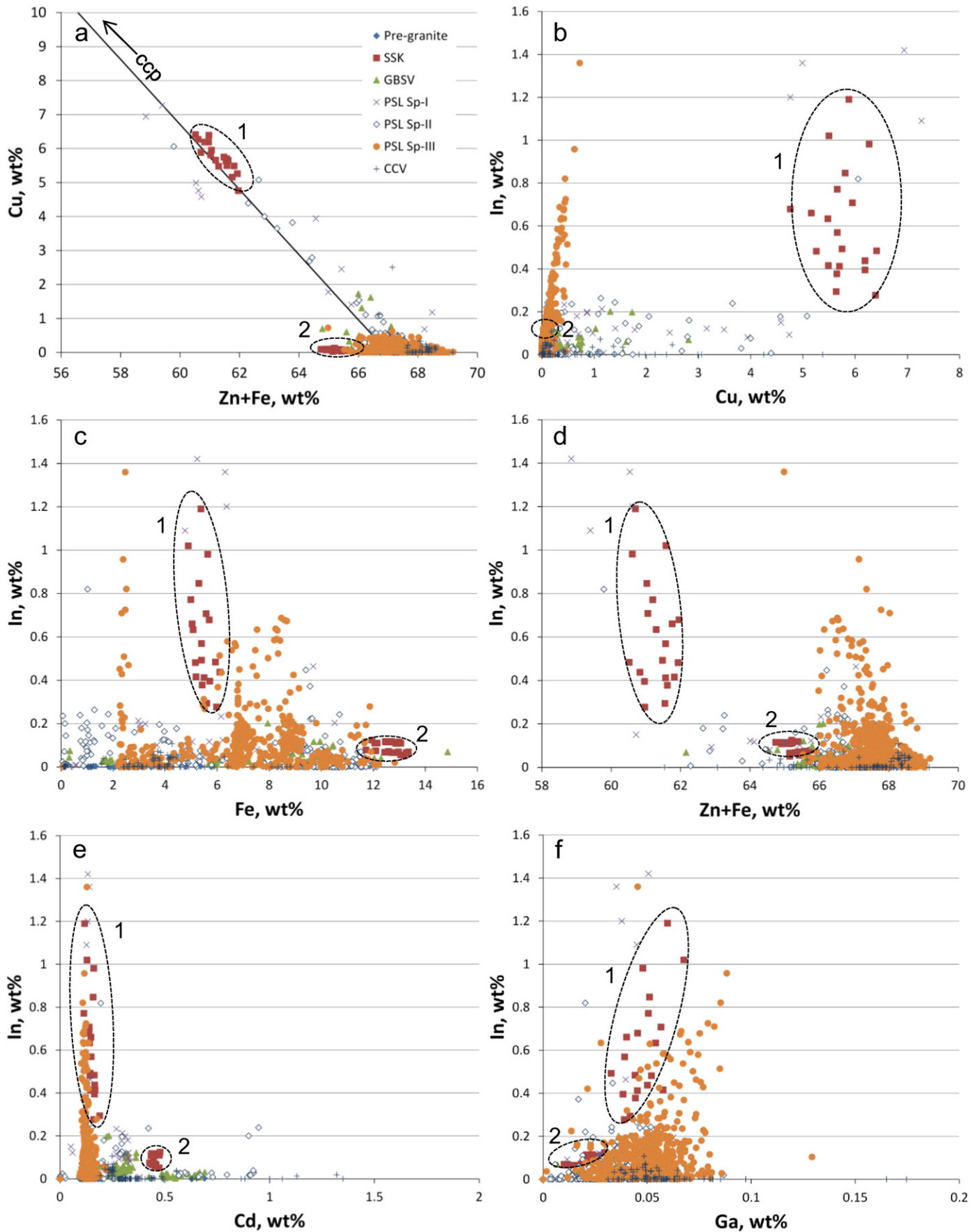


Fig. 10. Compositional variations in sphalerite. The two highlighted groups are skarns from Perran St George (1) and Red-a-Ven (2). a. Against Zn + Fe, copper appears to follow a chalcopyrite (ccp) control. b. Cu versus In. c. Fe versus In. d. Zn + Fe versus In. e. Cd versus In. f. Ga versus In.

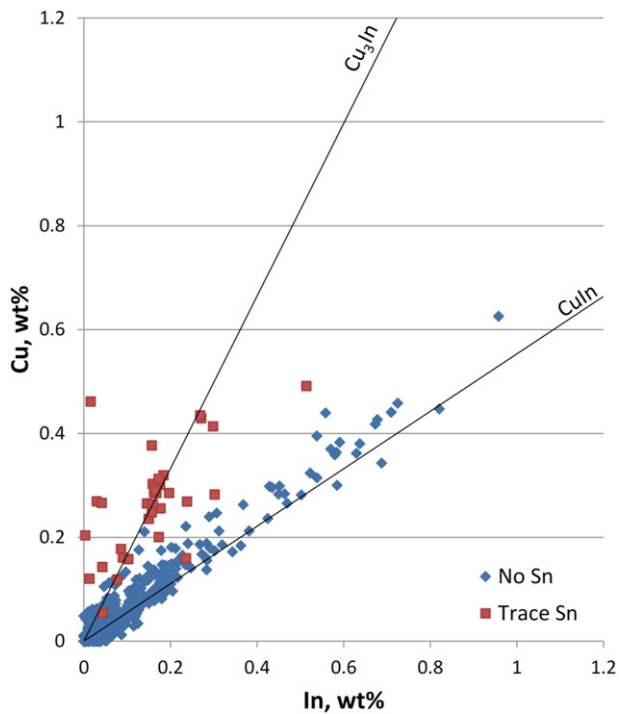


Fig. 11. Correlation between Cu and In in sphalerite III from East Wheal Rose. Diamonds are analytical data with no detected Sn, open squares are analytical data with traces of Sn. The CuIn control line reflects the metal proportions in a roquesite component, while Cu_3In reflects the proportions in sakuraiite.

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 (See Fig. 15). 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 \pm Early Permian basinal fluids within the Devonian-Carboniferous host rocks and upper parts of granite plutons. (See Fig. 15.)

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-

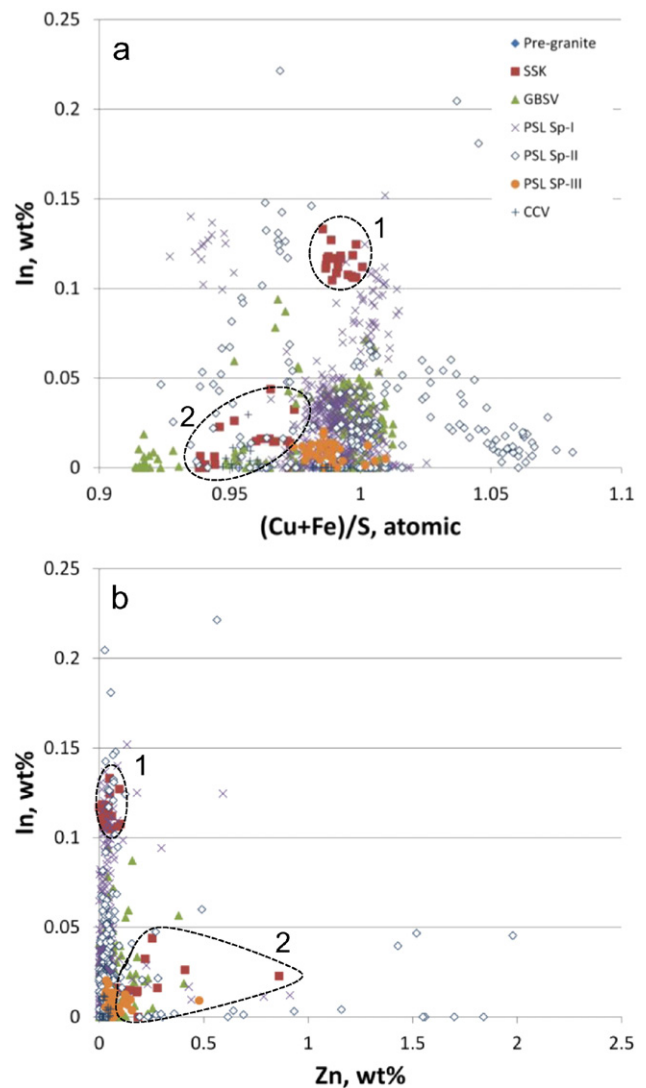


Fig. 12. Compositional variations in chalcopyrite. Like for sphalerite, the chalcopyrite from skarn deposits define two distinct groups. Group 1 is Perran St George while group 2 is Red-a-Ven. a. Atomic (Cu + Fe)/S versus In reflecting minor variability from the ideal stoichiometry. b. Zn versus In.

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 department 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

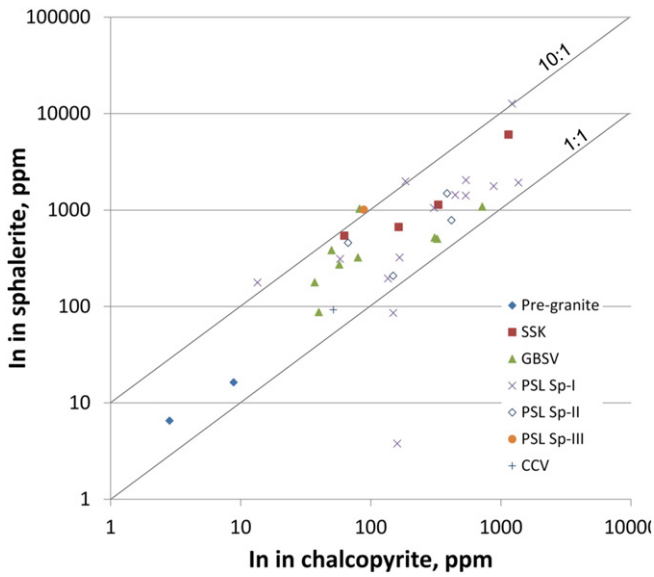


Fig. 13. Correlations between the average In contents in coexisting sphalerite and chalcopyrite.

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

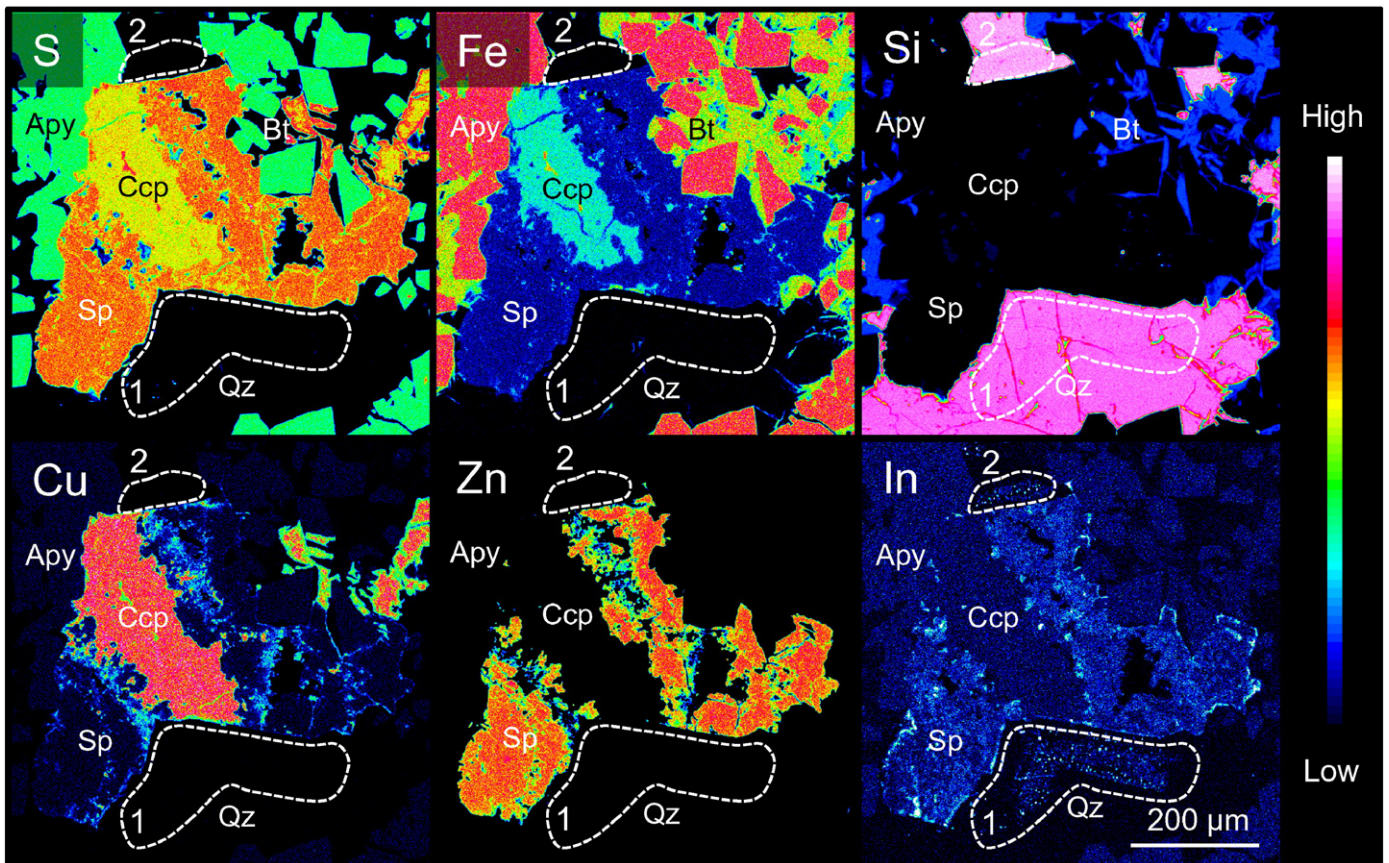


Fig. 14. Compositional map showing inclusions of dzhalindite or native In in quartz (mineral abbreviations as in Fig. 5). The inclusions are confined to growth zones (marked 1 and 2) in two quartz crystals adjacent to In-bearing sphalerite. The sphalerite displays elevated In toward the grain boundaries.

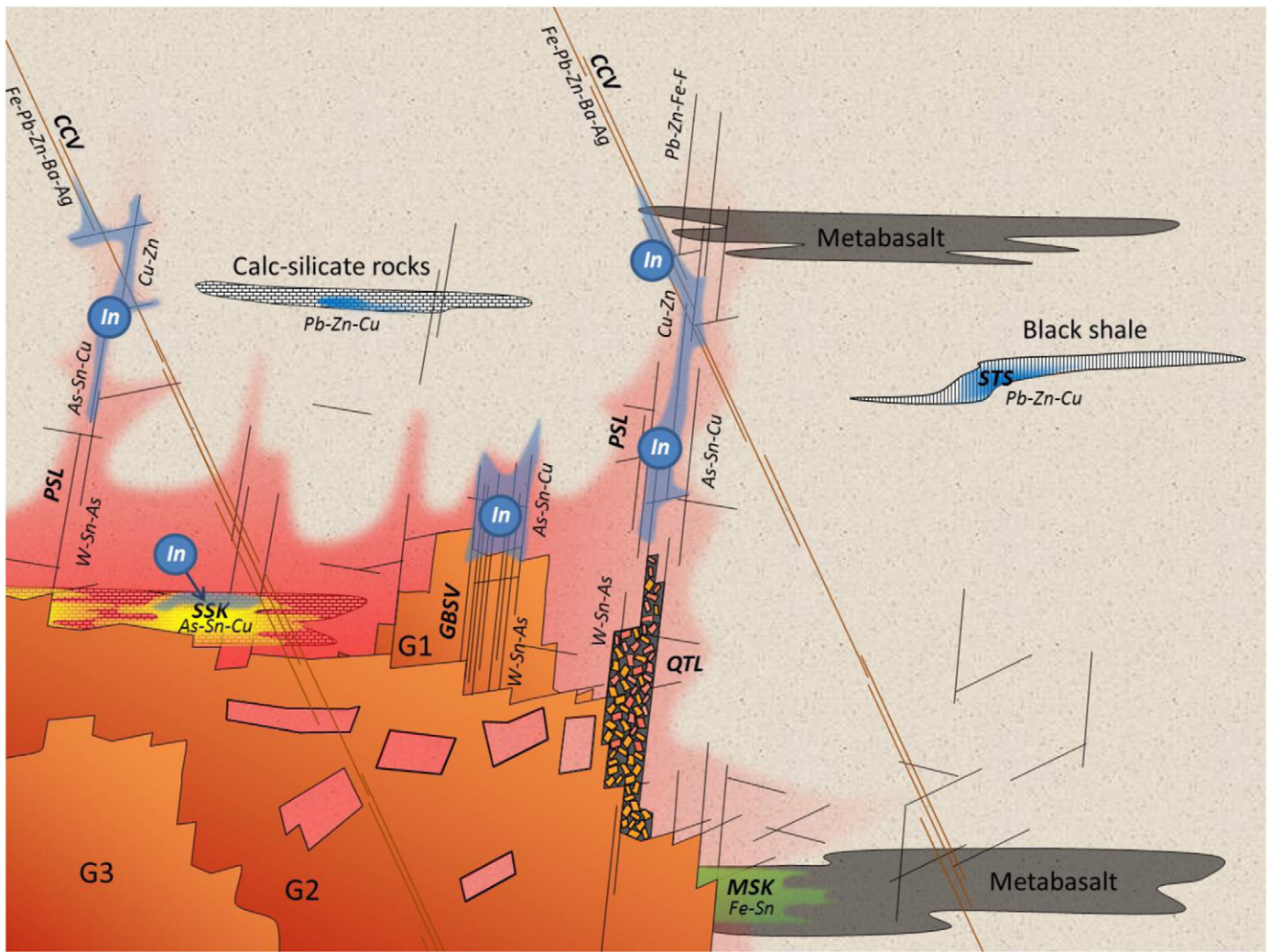


Fig. 15. Simplified conceptual model of In mineralisation in SW England. Stratiform sulphides (STS) in the pre-granite environment (Pb-Zn-Ba) were deformed prior to the granite emplacement. Granite emplacement, in this example with three successive intrusions (G1, G2, G3) led to sulphide-silicate skarn (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.

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 lodes, veins and breccias, and the polymetallic sulphide lodes. The deportment suggests two principal associations:

1) Chalcopyrite-dominated (highest temperature). 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 (lowest temperature). 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 richest in tin (Willis-Richards and Jackson, 1989) suggesting 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 department 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 department 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 department 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 (Patrick 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 (Tolcin, 2016), 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 1200 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 1427 tons In (Hösel, 2002), and neighbouring properties at Hämmerlein, Dreiberg and Zweibach, which are estimated to carry a further 2149 tons (Treliver Minerals Ltd., 2015). Further In is expected at Breitenbrunn and Zlatý Kopec. 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 1096 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 (Patrick and Howell, 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 CaCl₂-rich fluid inclusions (Patrick and Howell, 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 wolframite, löllingite, arsenopyrite, pyrrhotite, bornite, chalcocite, galena, rutile, magnetite, haematite, garnet, tourmaline, malayaite, biotite or chlorite. 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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were investigated from the archive collections of B.W. Bull and K.F.G. Hosking, M. Simpson and D. Wright guided sampling at Geevor Tin Mines. Samples from the Egloskerry drill cores were collected by T. Colman. Western United Mines sponsored samples and analyses from South Crofty and Dolcoath, while samples from Lundy were collected with the permission of the National Trust. Initial investigations for this paper were carried out as part of student projects by C.G. Butler, J. Dendle, D. Edwards, P. Hayward and S. Pearson at the University of Exeter. QEMSCAN is a registered trade mark of FEI Company. Figs. 3 and 9–13 were produced with Daniel's XL Toolbox v. 6.60 for Excel by D. Kraus. The kml file was generated with the Mapsdata online kml converter (<http://www.mapsdata.co.uk/online-file-converter/>). The authors are grateful to F. Pirajno for inviting this contribution, R. Seltmann for swift editorial handling, and K. Sundblad and one anonymous reviewer for their helpful comments and suggestions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.oregeorev.2016.02.019>. These data include Google map of the most important areas described in this article.

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