The geological setting of the indium-rich Baal Gammon and Isabel Sn-Cu-Zn deposits in the Herberton Mineral Field, Queensland, Australia

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ARTICLE INFO
Keywords:
Herberton Mineral Field
Critical Metals
Indium
Tin
Mossman Orogen

ABSTRACT
Base metal mineralization at the Baal Gammon and Isabel deposits of the Herberton Mineral Field (HMF) is hosted in metamorphosed greywacke beds in the Hodgkinson Formation, which were intruded by granite, porphyry dykes and overlain by volcanic rocks of the Kennedy Igneous Association during the Carboniferous and Permian. The tin mineralization at the Baal Gammon deposit is hosted by a silicified, chlorite-altered, quartz-feldspar porphyry (UNA Porphyry). The tin mineralization at the Isabel deposit is in polymetallic veins hosting disseminated cassiterite. Polymetallic sulfides (Cu-Zn) and indium (In) mineralization at both deposits overprint the tin mineralization. Chalcopyrite, sphalerite, and stannite host indium in the polymetallic sulfide assemblage at both deposits. Based on overprinting relationships, the timing of tin mineralization is related to the magmatic activity at ca. 320 Ma, whereas the sulfide and indium mineralization are most likely associated with the replacement of porphyry dykes at ca. 290 Ma. The overall magmatic activity in the HMF spreads between ca. 365 and 280 Ma, with peaks at ca. 337, 322, 305, and 285 Ma. The change from tin mineralization at ca. 320 Ma to sulfide and indium mineralization at ca. 290 Ma indicates a transition from a compressive to an extensional tectonic regime.

1. Introduction

Indium is one of the critical metals with a substantial increase in demand over the last two decades, because of its increased usage in the production of flat panel displays, touchscreens, photovoltaic cells, and fiber optic technology (Fontana et al., 2021). Economic concentrations of In mineralization are found in various types of deposits, including volcanogenic massive sulfide (VMS), sediment-hosted base-metal, epithermal, skarn, porphyry, and granite-related deposits (Schwarz-Schampera and Herzig, 2002; Werner et al., 2017). Polymetallic tin deposits, particularly those with a magmatic-hydrothermal origin that host base-metal mineralization, can be significantly enriched in In (Korges et al., 2020; Voudouris et al., 2022).

The HMF forms the northern part of multiple tin provinces situated along the Tasman Fold Belt (or the Tasmanides of Walshe et al., 2011). The occurrence of tin in the mineral field is associated with polymetallic mineralization that contains high-grade In. Tin, base-metals, and In mineralization are commonly associated with fractionated granites in the fold belt (Walshe et al., 2011).

Three major tin fields have been described from the Tasman Fold Belt, including the cassiterite (SnO2) deposits in Tasmania (Collins and Williams, 1986), the Ardlethan tin field in New South Wales (Ren et al., 1995), and the HMF in Queensland (Pollard, 1988). Cassiterite from the Tasmanian tin field has yielded U-Pb mineralization ages of ca. 391 and 359 Ma (Denholm et al., 2021), whereas cassiterite from the New South Wales tin field has yielded a younger U-Pb mineralization age of ca. 246 Ma (Carr et al., 2020). The U-Pb zircon ages from granites in both tin fields are similar to the related U-Pb cassiterite ages (Carr et al., 2020; Schaltegger et al., 2005), thus zircon ages can provide good estimates of tin mineralization related to particular magmatic activities. There is limited age data available from HMF and consequently the relationship between tin, polymetallic veins and In mineralization is unclear.

Tin was discovered in the HMF in 1875, and mining began around 1880 (Dash et al., 1991). By 1971, most mining companies in the HMF were exploring for polymetallic systems containing Zn, Pb, Au, Ag, Bi, Cu, Ag, In, and Cd (Kositcin et al., 2009; Clarke and Chang, 2017). These polymetallic deposits are associated with microgranites, pegmatite veins, greisen, skarn, volcanic rocks, and meta-basalt (Clarke and Chang, 2017). The Baal Gammon and Isabel deposits within the HMF are the only deposits with a defined In resource and are the focus of this paper.

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https://doi.org/10.1016/j.oregeorev.2022.105095
Received 7 April 2022; Received in revised form 1 September 2022; Accepted 3 September 2022
Available online 6 September 2022
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The deposits are ~5 km apart and located northwest of the Herberton township (Fig. 1). This paper provides a geological framework for the Baal Gammon and Isabel deposits, age estimates for mineralization events, and further improves the tectonic setting for HMF from Cheng et al. (2018) and Champion (2016).
2. Geological setting

The northeast margin of the Tasmanides formed via accretion during the Cambrian to the Triassic. It contains important metallogenic domains that host base, precious, and critical metals (Edgar et al., 2022a,b; Glen, 2005, 2013; Rosenbaum, 2018). In northeast Australia, the Tasmanides comprise the Phanerozoic Mossman and Thomson Orogens which are separated from the Mesoproterozoic Georgetown inlet by the Palmerville Fault (Fergusson et al., 2007; Murgulov et al., 2007; Rosenbaum, 2018; Fig. 1). Devonian to Carboniferous sedimentary sequences over most of the Thompson Orogen (Fergusson et al., 2013) and, together with the adjacent North Australia Craton, was intruded by Silurian to Devonian granites included in the Pama Igneous Association. The suite consists predominantly of I-type granites emplaced between ca. 434 and 382 Ma (Bain and Draper, 1997; Henderson et al., 2013).

The Massman Orogen largely consists of the Hodgkinson Group that is intruded by granites of the Kennedy Igneous Association (Henderson et al., 2013; Fig. 1). The group consists of shallow-marine limestone (Chillagoe Formation) and turbidites intercalated with melange deposits (Barron-Palmer Formation, Withnall and Henderson, 2012), which in the western part of the group were interpreted as being deposited on an abyssal fan (Henderson et al., 2013). The maximum depositional age of the group has been variably estimated at ca. 482, 463, 454, and 370 Ma, based on the age of detrital zircons (Henderson et al., 2013; Kositcin and Bultitude, 2015), but its minimum age is constrained by the age of the Kennedy Igneous Association.

The Kennedy Igneous Association is composed of Carboniferous to Permian granites, high-level intrusive, and volcanic rocks. The granites have been grouped in suites and supersuites, based on petrological similarities (White et al., 2001). This grouping of the granites is based on various assumptions, and most batholiths are composites of multiple intrusions. Supersuites identified in the HMF include, from oldest to youngest, the O’Brien Creek, Ootan and Almaden supersuites (Fig. 1). Volcanic units near the study site consist of the Featherbed and Koolmoon volcanics.

The O’Brien Creek Supersuite is highly fractionated, and includes the Herberton Hill and Jumna granites (Champion, 1991; Fig. 1). The supersuite typically consists of pink to yellow alkali feldspar granite associated with granophyre, microgranite, topaz-bearing aplite and silexite, which reflects the fractionated nature of this unit (Johnston and Black, 1986). Dating by Cheng et al. (2018) has constrained the age of this unit to ca. 335–317 Ma.

The Ootann Supersuite is widespread in HMF (Champion, 1991), and is represented by the Carboniferous (ca. 310–302 Ma) Watsonville Granite in the study area (Cheng et al., 2018; Fig. 1). The granite is medium- to coarse-grained and commonly contains veins of aplite and patches of pegmatite (Blake, 1972).

The Almaden Supersuite consists of granodiorite with minor diorite, and it includes the Kalunga Granodiorite south of the Isabel deposit (Fig. 1). The granodiorite is not mineralized and contains medium-grained quartz, zoned oligoclase-andesine, turbid orthoclase, and biotite that defines a hydridiomorph granular texture (Sheraton and Labonne, 1978).

The Featherbed Volcanics have been divided into the Old and Young Featherbeds. The Old Featherbed Volcanics yield ages of ca. 325–317 Ma (Cheng et al., 2018), which consists of dacite to rhyolitic ignimbrite and minor andesitic tuff (Cheng et al., 2018; Mackenzie, 1993). The age of the Young Featherbed Volcanic unit has been constrained at ca. 310–275 Ma (Cheng et al., 2018). The unit consists of porphyritic rhyolite, rhyolitic ignimbrite, volcanic breccia, microgranite, and minor dacite (Cheng et al., 2018; Sheraton and Labonne, 1978).

The Koolmoon Volcanic Group consists of the Walsh Bluff, Glen Gordon, and Slaughter Yard Creek Volcanics (Donchak and Bultitude, 1998). The group consists of tuff, tuffaceous sandstone and siltstone, felsic lava flows, and agglomerate (Blake, 1972). Despite being grouped

<table>
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<th>Sample #</th>
<th>Unit</th>
<th>206Pb/238U Weights</th>
<th>Mean age/MDA* (Ma, and error as 2σ)</th>
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3. Methods

Indium-rich sulfides ore at the Baal Gammon and Isabel deposits were identified from diamond-drill core assay data. Eleven Baal
Gammon and eleven Isabel quarter diamond-drill cores from the identified In-rich zones were obtained from the Geological Survey of Queensland for petrographic, SEM, and LA-ICP-MS analyses. Petrography was conducted on all the samples; SEM on four Baal Gammon, and three Isabel samples; and LA-ICP-MS on two Baal Gammon, and two Isabel samples.

The petrographic analyses and interpreted mineral paragenesis are based on transmitted and reflected light microscope, and scanning electron microscopy. A Hitachi SU5000 SEM, at the Advanced Analytical Centre of the James Cook University, was used for imaging by
backscatter electron (BSE), and mineral identification and composi-
tional mapping by energy dispersive spectroscopy (EDS).

Spot analyses for elements concentration on sulfide phases were
conducted on a Thermo iCap-TQ ICP-MS instrument coupled to an An-
alyte G2 Excimer Laser Ablation system with the parameters: 2 J/cm
laser energy density; 5 Hz laser repetition rate; and 40 µm laser spot size.
The standards, NIST610, MASS-1, and GSE-1, were analysed, and the
data was reduced using the Iolite software (Paton et al., 2011). Sum-
maries of the results are presented in Tables 1 and 2.

Twelve samples consisting of intrusive dykes, meta-sedimentary,
granitic, and volcanic rocks were selected for U-Pb zircon dating
(Table. 3). From the Baal Gammon deposit (Fig. 3), samples were taken
from the UNA Porphyry (BGOT009), quartz-feldspar porphyry (BG01),
medium-grained porphyry (BG02) and shallow-level intrusive rhyolitic
dyke (BGW03). From the Isabel deposit, samples were taken from non-
mineralized brecciated meta-sedimentary rock (ISOT04), and from a
quartz-feldspar porphyry dyke (QFPI) that intrudes the meta-
sedimentary rocks next to the deposit (ISOT09). From the regional
granite intrusions, samples were taken from the Herberton Hill Granite
(HBH01), Jumna Granite (JM05), Kalunga Granodiorite (KG06), and
Watsonville Granite (WT03). In addition, two samples were collected
from the Slaughter Yard Creek Volcanics (GGV01 and GGV02).

The samples were crushed to obtain fresh chips that were milled and
sieved to grain sizes of ≤500 µm. Heavy minerals were separated from
the sieved samples using standard magnetic, and heavy liquid separation
techniques. Zircons were hand-picked from the heavy mineral separates,
mounted in epoxy resin, and polished to near mid-section exposure. To
illustrate zoning patterns, the polished zircons were imaged with a
cathodoluminescence detector attached to a Jeol JSM5410LV scanning
electron microscope.

The zircons were analysed for U-Pb isotopes with an Analyte G2
Excimer Laser Ablation system coupled to a Thermo iCap-RQ ICP-MS
instrument. The ablation was carried out with a laser with an energy
density of 2 J/cm² at a rate of 5 Hz on a spot size of 30 µm. All the
samples were imaged and dated at the Advanced Analytical Centre,
James Cook University, Townsville.

Isotope data were reduced using the Iolite software (Fisher et al.,
2017), and age calculations were done with IsoplotR (vermeesch, 2018).
The weighted average ages were calculated using the 206Pb/238U isotope
system. For igneous samples, 50 to 60 zircon spots were analysed and
only analyses with <5% discordance were used for age calculations.
Only analyses with <10% discordance were used to determine the
maximum depositional age of detrital zircons. The Plesovice zircon
(ID-TIMS 206Pb/238U age of 337.13 ± 0.37 Ma; Slama et al., 2008) was used
as the primary standard for downhole fractionation corrections. The
secondary zircon standards used are Zircon GJ-1 (ID-TIMS 206Pb/206Pb
age of 608 ± 2 Ma and 206Pb/238U age of 602 ± 0.4 Ma; Jackson et al.,
2004; Horstwood et al., 2016), and 91500 (207Pb/206Pb age of 1072 ±
1.5 Ma and 206Pb/238U age of 1064 ± 0.65 Ma; Wiedenbeck et al., 1995;
Horstwood et al., 2016). The GJ1 and 91500 zircons yielded a weighted
mean 206Pb/238U age of 605 ± 1 Ma (n = 182) and 1072 ± 1 Ma (n =
182), respectively. The calculated concordia ages for the secondary

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**Fig. 3.** Field photographs (a-c), diamond-drill core
(d) and microscope images (e-f) of samples from the
Baal Gammon deposit: (a) the contact between MGPD
and QFP; (b) low level rhyolite intrusion; (c) sulfide-
altered meta-sandstone in contact with a QFP dyke;
(d) diamond-drillhole core showing sulfide vein
crosscutting the UNA Porphyry; (e) sericite alteration
of feldspar (Fsp) in the UNA Porphyry (crossed-nicols
polarized light photomicrograph); and (f) embayed
quartz (Qz) in the UNA Porphyry (crossed-nicols
polarized light photomicrograph).
zircon standards were 604 ± 1 Ma (GJI, n = 182) and 1071 ± 1 Ma (91500, n = 182). A summary of the results is presented in Table 3 with errors reported at 2σ.

4. The geology of the Baal Gammon and Isabel deposits

4.1. The Baal Gammon deposit

4.1.1. The host rocks

The Baal Gammon Sn-Cu-Zn-In deposit is located at the contact between meta-sandstone assigned to the Hodgkinson Formation and the UNA Porphyry (Fraser, 1972; Fig. 2). The formation constitutes the oldest geological unit in the area, and consists of cross-bedded fine- to coarse-grained meta-sandstone that dips gently (~20°) towards the south to southwest. The formation is intruded and hydrothermally altered by the tin-bearing, UNA Porphyry, barren quartz veins, and quartz-feldspar porphyry dykes mapped as the Slaughter Yard Creek Volcanics (Donchak and Bultitude, 1998). Fraser (1972) has observed the presence of andalusite in the meta-sandstone near the UNA Porphyry, but no andalusite was identified during this study. The meta-sandstone in the open pit at Baal Gammon is strongly jointed and fractured, altered, and silicified, with muscovite growth parallel to joints and fractures.

4.1.2. Intrusive rocks

The UNA Porphyry is granitic in composition, and intrudes the Hodgkinson Formation as an irregularly shaped dyke dipping shallowly to moderately south (Fig. 2b). Its patchy appearance in outcrop is due to its irregular shape, and an orientation that is subparallel to the topography. The porphyry and Hodgkinson Formation are crosscut by a series of veins of biotite, chlorite, muscovite and garnet, and a series of steeply dipping, NNW trending faults. The UNA Porphyry at the Baal Gammon open pit surrounding hills is highly altered, and has a vuggy texture. The less altered section of the porphyry is composed of quartz (50%), alkali feldspar (10%), plagioclase (5%), biotite, chlorite, garnet, and sulfides, with a granophytic groundmass. The subhedral, porphyritic quartz crystals have embayments of fine-grained material similar in composition to the surrounding matrix, and commonly display a spongy texture (Fig. 3). The embayment textures may have formed during decompression and ascent of the porphyritic body, when the quartz crystals were partially dissolved (Chang and Meinert, 2004). Most of the plagioclase and alkali feldspar are altered to sericite, and biotite is partly altered to chlorite.

4.1.3. Volcanic rocks

The Slaughter Yard Creek Volcanics near the Baal Gammon deposit forms shallow level dykes of variable thickness (Fig. 2), which are sub-vertical and trend NW. Three different dyke phases were identified based on texture, composition, and overprinting relationships. The oldest phase consists of a coarse-grained, quartz-feldspar porphyry (QFP) trending eastward (Fig. 3). The quartz-feldspar porphyry varies in thickness from a few meters in the western wall of the pit to almost ten meters in the eastern wall of the pit. It consists of up to 20 mm large phenocrysts of plagioclase and quartz, in a fine-grained groundmass of quartz, plagioclase, K-feldspar and minor biotite. The quartz phenocrysts have an irregular shape and are commonly embayed. The second phase consists of a medium-grained porphyritic dyke (MGPD; Fig. 3a) composed of plagioclase, quartz, K-feldspar, biotite, and chlorite. Near contacts, the MGPD contains small fragments of phenocrysts of coarse-grained quartz and plagioclase like that in the QFP. This suggests that the MGPD postdated the QFP, and fragments of the QFP were incorporated in the MGPD during emplacement. The MGPD is exposed only on the eastern side in the pit where it trends SE. Biotite and chlorite are secondary alteration products in the groundmass. The youngest phase of the Slaughter Yard Creek Volcanics consists of shallow intrusive rhyolite dykes in the northeastern part of the deposit (Fig. 3b).
4.1.4. Structures

The meta-sedimentary rocks in the Baal Gammon area dip to the SW and are open folded with a fold axis that plunges gently towards 220\(^\circ\) (Fig. 4). Apart from bedding, no tectonic foliation was recognized. The UNA Porphyry is displaced by a series of moderately eastward dipping and NNW trending reverse faults (Fig. 5). In addition, the meta-sedimentary rocks are affected by bedding-parallel fractures and shears that dip 20–40\(^\circ\) SW (Fig. 4). All rock units display these fractures and shears, which are accompanied by a set of conjugate sub-vertical joints trending NE and NW.

4.1.5. Mineralization and distribution of indium at the Baal Gammon deposit

Based on crosscutting relationships and alteration characteristics, the primary mineralization in the Baal Gammon deposit can be subdivided into an early, tin oxide stage (stage I), and a later massive sulfide stage (stage II). Stage I is characterized by strong silicification of the meta-sandstone developed as a silica cap surrounding the UNA Porphyry, and in deeper parts of the UNA Porphyry (Fig. 5), sericite alteration (Fig. 3e), and cassiterite precipitation in the UNA Porphyry. The feldspar in the porphyry is sericite-altered (Fig. 3e), and cassiterite grains within the porphyry occur as 100–600 \(\mu\)m, zoned, euhedral crystals. Stage II mineralization is characterized by massive sulfides, sulfide veins (Fig. 3d), and breccia infill. Massive sulfides and mineralized brecciated meta-sandstone are present along the contact with the UNA Porphyry. The porphyry and the meta-sandstone are also crosscut by sulfide veins (Fig. 3d).

A supergene alteration cap can be observed in the open pit and the surrounding rocks (Fig. 5). The supergene cap has a wedge shape and developed above the mineralized meta-sandstone. It is dominated by iron oxides and silica, with an infill of malachite and azurite in a vuggy to honeycomb texture. Fine-grained covellite occurs as infill surrounding azurite. Near the deposit, the supergene mineralization is positioned above an east dipping fault (Fig. 5).

The distribution of In in the Baal Gammon deposit is closely related to the UNA Porphyry and the massive sulfide mineralization. The highest grades were recorded in semi-massive sulfide veins within the porphyry, or along the contact between the porphyry and the Hodgkinson Formation (Fig. 2b). The resource models indicate an average grade of \(~63\) ppm In. Element-element correlations of ore analysed from diamond-drill core at Baal Gammon (Fig. 6) show a strong positive correlation between In and Cu (\(r = 0.9\)) and Ag (\(r = 0.8\)) and a moderate correlation with Fe (\(r = 0.6\)), Bi (\(r = 0.5\)) and Zn (\(r = 0.4\)). The Cu-rich parts of the deposit (\(>0.1\%\) Cu) have an average grade of \(~40\) ppm In reaching up to 1140 ppm In in sulfides along the UNA Porphyry and Hodgkinson Formation contact. High-grade (\(~50\) ppm) Ag ore contains an average of \(~110\) ppm In, and the highest In grades were observed within the porphyry or at the contact of the meta-sediments with the porphyry. Indium displayed a weak positive correlation with Au (\(r = 0.3\)), As (\(r = 0.2\)), Pb (\(r = 0.2\)), Sb (\(r = 0.3\)), Sn (\(r = 0.3\)), W (\(r = 0.3\)), and Cd (\(r = 0.3\)). Apart from Sn, most of these metals are limited in tonnage and grade. For example, W forms high-grade thin (\(<10\) mm) quartz veins within a vertical shear zone developed in the porphyry.

4.2. The Isabel deposit

4.2.1. Country rocks

Igneous rocks near the Isabel deposit consist of the Herberton Hill Granite, Slaughter Yard Creek Volcanics, and porphyry dykes. The contact between the Herberton Hill Granite and country rocks trends NE, which are intruded by shallow level porphyry dykes assigned to the Slaughter Yard Creek Volcanics. The best exposed phase of the Herberton Hill Granite is a coarse-grained, pink, leucocratic monzogranite with traces of primary biotite and mica. The monzogranite is exposed at the southeastern end of the Isabel deposit (Fig. 7a), where it is moderately weathered with plagioclase and K-feldspar altered to clay, and iron oxides have formed at the boundary of quartz grains.

The porphyry dykes comprise feldspar porphyry, quartz-feldspar porphyry, and dolerite dykes. Only the quartz-feldspar porphyry (QFPI) and dolerite dykes are exposed at the ground surface. The QFPI consists of plagioclase altered to sericite and embayed quartz. The altered feldspar is surrounded by muscovite, and locally contains carbonates in vugs. The groundmass consists of fine-grained quartz, plagioclase and chlorite, and opaque minerals replacing feldspar and the groundmass. The groundmass has a granophyric texture and consists of quartz, altered feldspar and chlorite. The dolerite dyke is fine-grained and chlorite-sericite altered. It contains veins and late infill of vugs by fine-grained quartz, plagioclase, and carbonates; pyroxene and plagioclase have been altered to chlorite.
4.2.3. Structural setting

The Hodgkinson Formation at the Isabel deposit dips 75° east, where it is faulted and intruded by porphyry and dolerite dykes. Robinson (1983) has recognized four sets of lineaments, interpreted as faults, striking at 327° (first generation), 45° (second generation), 275° (third generation), and 300° (fourth generation). The quartz feldspar porphyry and dolerite dykes are parallel to the first generation of lineaments (Fig. 7a). The second generation of lineaments are parallel to the contact between the monzogranite and host rocks. This lineament orientation correlates with the orientation of tin mineralization near the Isabel deposit. The areas of intersection between the first and fourth lineament generations is characterized by intense brecciation, and the deposition of lead–zinc sulfides ore (Robinson, 1983).

4.2.4. Mineralization and distribution of indium at Isabel

The Pb-Zn-Ag mineralization at Isabel consists of polymetallic veins and breccia hosted by the Hodgkinson Formation. Based on the composition of the sulfide minerals, the polymetallic veins recognized are here referred to as the Type I and Type II vein sets. The Type I veins consisting of disseminated cassiterite and sphalerite containing chalcopyrite inclusions, and are crosscut by chalcopyrite-pyrrohotite veins. The cassiterite grains are fractured and show early stages of alteration (Fig. 7e). The Type II veins consist of sphalerite, galena, and stannite. The galena forms idiomorphic crystals and shows triangular pits under reflected light. The sphalerite and quartz veins crosscut the galena, and the sphalerite contains stannite inclusions.

Resource models for the Isabel deposit indicate an average In grade of ~370 ppm (Red River Resources Limited., ASX announcements, 2020). The Sn- and Cu-rich parts of the deposit (>1% Cu, and >0.2% Sn) have an average In concentration of ~1140 ppm, with a maximum recorded concentration of up to 2030 ppm. The In concentration in the Zn ore zones locally reaches 3170 ppm. Element-element correlations (Fig. 8) based on geochemical assay results in diamond-drillholes from the Isabel deposit indicate that In has a strong positive correlation with Cu (r = 0.7), Sn (r = 0.6), and Zn (r = 0.6), and a weak positive correlation with Ag (r = 0.4; Fig. 8).

5. Results

5.1. Petrography and mineral paragenesis

A simplified mineral paragenesis sequence of the ore mineralogy is presented in Fig. 9 for the Baal Gammon and Isabel deposits. Chalcopyrite containing inclusions of sphalerite is the most abundant sulfide mineral at the Baal Gammon deposit, and is in association with pyrrhotite forming massive sulfides. The early cassiterite phase has altered to In-rich stannite in the massive sulfides (Fig. 10a-b). Element composition maps indicate that the stannite is rich in Zn, Sn, and In (Fig. 10c-e). At the Isabel deposit, sphalerite is the dominant sulfide and contains inclusions of chalcopyrite (Fig. 11a). The early cassiterite in the Type I veins were partially replaced by chalcopyrite, giving it a slightly porous texture (Fig. 7e and Fig. 11a). Complete cassiterite alteration was not observed in the Isabel deposit and only dissolution and replacement textures are present (Fig. 7e). Stannite was observed in the Type II veins at the Isabel deposit (Fig. 11b) along the boundary of sphalerite and galena, but mostly in sphalerite.

5.2. Indium content of sphalerite, chalcopyrite and pyrrhotite

The LA-ICP-MS analyses indicate that the main host for In is sphalerite and chalcopyrite. The In content of sphalerite from the Baal Gammon deposit varies between 3009 and 6795 ppm (Table 1), whereas the In content of sphalerite from the Isabel deposit varies between 1303 and 1565 ppm (Table 2). The Sn and Cu content of sphalerite from both deposits are highly variable (Fig. 12), indicating the presence of micro-inclusions of chalcopyrite and cassiterite-stannite. The In content of
Fig. 7. Maps and photographs showing: (a) geological map of the Isabel area; (b) cross-section showing mineralization and crosscutting units at the deposit; (c) mineralized hydrothermal breccia; (d) unit QFPI; and (e) reflected light photomicrograph of cassiterite (Cst) in sphalerite (Sp) and chalcopyrite (Ccp) vein.
chalcopyrite from the Baal Gammon deposit varies between 1071 and 1727 ppm (Table 1), whereas the In content of chalcopyrite from the Isabel deposit varies between 573 and 857 ppm (Table 2). The Zn content of chalcopyrite from the Baal Gammon deposit varies between 727 and 1896 ppm, whereas the Sn content varies between 1323 and 2354 ppm (Table 1). For the Isabel deposit, the Zn and Sn content of chalcopyrite (Table 2; Fig. 12) is highly variable indicating the presence of several micro-inclusions of sphalerite and cassiterite-stannite. Pyrrhotite commonly does not incorporate large amounts of In, Sn and Zn in its crystal structure, and large variability observed in the concentration of these elements indicates the presence of several micro-inclusions (Fig. 12).

5.3. Zircon geochronology

5.3.1. The Baal Gammon deposit

Zircon grains extracted from sample BGOT009 from the UNA Porphyry at the northern part of the Baal Gammon pit have low luminescence, are elongated and euhedral with only few subhedral crystals (Figs. 2 and 13a). Fifty-seven spots on these zircons were analysed, yielding two distinct age populations. The younger population consists of 21 concordant analyses yielding a 206Pb/238U weighted mean age of 333 ± 2 Ma and an identical concordia age (Fig. 14a). The older population consists of 36 concordant analyses yielding a 206Pb/238U weighted mean age of 363 ± 1 Ma and an identical concordia age (Fig. 14a). The younger population is interpreted as the emplacement age for the UNA Porphyry whereas the older population is interpreted as zircons inheritance from the Jumna Granite.

Samples BG01, BG02 and BGW03 were collected from dykes mapped as the Slaughter Yard Creek Volcanics. Sample BG01 was collected from a quartz-feldspar porphyry dyke (QFP) from the western side of the deposit (Fig. 2). The zircon grains separated from this sample are elongated and euhedral with moderate luminescence and concentric zoning typical for magmatic zircons (Fig. 13b). Forty-seven concordant analyses yield a 206Pb/238U weighted mean age of 289 ± 1 Ma and an identical concordia age (Fig. 14b) interpreted as the emplacement age for the dyke. Sample BG02 was collected from a medium-grained porphyry dyke (MGPD) ~45 m NW of sample BG01. The zircon grains separated from this sample are similar in appearance to those from sample BG01. Forty-two concordant analyses yield a 206Pb/238U weighted mean age of 288 ± 1 Ma and an identical concordia age interpreted as the emplacement age for this dyke.

Sample BGW03 was collected from a shallow level intrusive rhyolite dyke that outcrops in the eastern part of the deposit (Fig. 2). The zircon grains separated from this sample are similar in appearance to those separated from samples BG01 and BG02 (Fig. 13). Thirty-four concordant analyses yield a 206Pb/238U weighted mean age of 288 ± 1 Ma and an identical concordia age interpreted as the emplacement age for the dyke (Fig. 14d).

5.3.2. Isabel deposit

A sample of brecciated meta-sandstone (ISOT04) from the Hodgkinson Formation that hosts polymetallic vein mineralization was collected from near the Isabel deposit. Some of the zircon grains extracted from this sample are brown, indicative of a high uranium content. The brown zircons have rounded edges, while most of the clear zircon grains appear euhedral and elongated. The zircon grains have variable luminescence and internal zoning. Two-hundred-eleven analyses were performed, and 161 analyses had a discordance of <10%. Individual 206Pb/238U ages range from 2989 ± 55 to 409 ± 9 Ma. Two populations can be identified on a kernel density estimate (KDE) plot (Fig. 14e). One population peaks at 1605 Ma and the other at 457 Ma. The younger age was interpreted as the maximum depositional age for the meta-sandstone sample.

Sample ISOT09 was collected from a quartz-porphyry dyke (QFP) that intruded the meta-sandstone near the Isabel deposit (Fig. 7). The zircon grains separated from the sample are elongated and euhedral with concentric zoning and moderate luminescence (Fig. 13f). Forty-three analyses yielded concordant ages with a 206Pb/238U weighted mean age of 292 ± 1 Ma and an identical concordia age (Fig. 14f), interpreted as the emplacement age for this dyke.

5.3.3. Regional granite units and volcanic rocks

Four samples (HBBH01, JM05, WT03, and KG06) were collected from granites that intruded the Hodgkinson Formation near the Baal Gammon and Isabel deposits, and two samples (GGV01 and GGV02) were collected from the Slaughter Yard Creek Volcanics near the Isabel deposit (Fig. 1e). Sample HBBH01 was collected from the Herberton Hill Granite near the Isabel deposit. The zircon grains separated from the sample are euhedral and elongated with concentric zoning and intermediate to low luminescence. Eleven analyses yielded concordant ages with a 206Pb/238U weighted mean age of 300 ± 1 Ma and an identical concordia age (Fig. 15a), interpreted as the emplacement age for the Herberton Hill Granite. Sample JM05 was collected from the Jumna Granite ~1.6 km SW of the Baal Gammon deposit (Fig. 1). The zircon grains separated from this sample are euhedral and elongated with concentric zoning and low luminescence. Nine analyses yield concordant ages with a 206Pb/238U weighted mean age of 367 ± 2 Ma with an identical
concordia age (Fig. 15b), which has been interpreted as the emplacement age for the Jumna Granite. Sample WT03 was collected from the Watsonville Granite ~1.6 km north of the Baal Gammon deposit (Fig. 1). The zircon grains separated from this sample are like the ones separated from the Jumna Granite. Nineteen analyses yielded concordant ages with a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 283 ± 1 Ma and a slightly older concordia age of 285 ± 1 Ma (Fig. 15c). The $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 283 ± 1 Ma is interpreted as the emplacement age of the Watsonville Granite. Sample KG06 was collected from the Kalunga Granodiorite ~1 km south of the Isabel deposit (Fig. 1). The zircon grains separated from this sample are elongated and euhedral with moderate luminescence and concentric zoning. Thirteen analyses yielded concordant ages with a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 314 ± 2 Ma and a similar concordia age of 316 ± 2 Ma (Fig. 15d). The former has been interpreted as the emplacement age for the Watsonville Granite. Sample KG06 was collected from the Kalunga Granodiorite ~1 km south of the Isabel deposit (Fig. 1). The zircon grains separated from this sample are elongated and euhedral with moderate luminescence and concentric zoning. Thirteen analyses yielded concordant ages with a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 314 ± 2 Ma and a similar concordia age of 316 ± 2 Ma (Fig. 15d). The former has been interpreted as the emplacement age for the Kalunga Granodiorite.

Sample GGV01 was collected from the Slaughter Yard Creek Volcanics ~600 m northwest of the Isabel deposit (Fig. 1). The zircon grains separated from the sample are elongated, euhedral with low luminescence, and most are not zoned. Twelve analyses yielded concordant ages with a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 292 ± 1 Ma and an identical concordia age (Fig. 15e), interpreted as the emplacement age. Sample GGV02 was collected from a flow-banded rhyolite in the Slaughter Yard Creek Volcanics (Fig. 1). Zircon grains separated from the sample are subhedral and have low luminescence with no visible zoning. Twenty analyses yielded concordant ages with a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age of 325 ± 1 Ma and an identical concordia age (Fig. 15f), interpreted as the emplacement age for this unit.

6. Discussion

6.1. Indium distribution in the Baal Gammon and Isabel deposits

The ore mineralogy (Figs. 3, 7, 10, and 11), SEM and LA-ICP-MS analysis of sulfides, together with multielement correlation matrixes (Figs. 6 and 8) can be used to make inferences about the distribution of In at the Baal Gammon and Isabel deposits. Cassiterite and chalcopyrite are the major ore minerals at the Baal Gammon deposit, and sphalerite and galena are the major ore minerals at the Isabel deposit. Cassiterite incorporates minor amounts of In (up to 304 ppm; Pavlova et al., 2015), and it is unlikely to be a major host for In at either of the deposits. The SEM results indicate that cassiterite has altered to stannite (Fig. 10) and incorporated In content >0.5 wt%. Stannite was observed in the massive sulfides of the Baal Gammon deposit and Type II veins at the Isabel deposit.

Chalcopyrite can incorporate up to 4000 ppm In (Sinclair et al., 2006). The strong correlation between In and Cu observed at Baal
Gammon implies that chalcopyrite hosts a significant amount of In (Fig. 6; r = 0.9). In situ LA-ICP-MS analysis of chalcopyrite indicates a mean In content of 1244 ppm (Table 1). Sphalerite can incorporate >6 wt% In (Bauer et al., 2019; Murakami and Ishihara, 2013; Torro et al., 2019; Valkama et al., 2016), through a coupled substitution of In\(^{3+}\) and Cu\(^{2+}\) for two Zn\(^{2+}\) atoms (e.g. Bauer et al., 2019; Cook et al., 2012; Shaw, 1952; Xu et al., 2021). Additionally, Ag\(^{+}\), Sn\(^{4+}\), and Sb\(^{3+}\) can be involved in this substitution (Belissont et al., 2014; Schirmer et al., 2020). Even though higher In content averaging 4042 ppm was measured in sphalerite from the Baal Gammon deposit (Table 1), the moderate correlation between In and Zn (r = 0.4) and the lower density of inclusion in the massive sulfides suggests that sphalerite contributes less than chalcopyrite to the overall In budget. At the Isabel deposit, In displays moderate correlations (Fig. 8) with Zn (r = 0.6), Sn (r = 0.6) and Cu (r = 0.7). These three elements (Zn, Sn and Cu) are the primary constituents of stannite. In addition, the correlations, SEM (Fig. 11), and LA-ICP-MS analysis (Table 2; Fig. 12) indicate that chalcopyrite, sphalerite, and stannite are the major hosts for In in the Isabel deposit.

### 6.2. Timing of mineralization

The timing of mineralization at the Baal Gammon and Isabel deposits is constrained based on field relationships, and zircon geochronology. The oldest phase of the mineralization comprises disseminated cassiterite-hosted by the UNA Porphyry at Baal Gammon, and disseminated cassiterite in polymetallic veins at Isabel. The 333 ± 2 Ma (Fig. 14a) emplacement age for the UNA Porphyry constrains the maximum age for tin mineralization at Baal Gammon. The timing of tin mineralization at Isabel is constrained by Sn-bearing granites associated with the deposit. As discussed earlier, the Isabel deposit is located near the contact between the Hodgkinson Formation and the Herberton Hill Granite (Fig. 7a). Similar vein-hosted cassiterite mineralization is present throughout the Herberton Hill Granite and the Hodgkinson Formation (Fig. 1b-c; Robinson, 1983), suggesting that the mineralization hosted by the granite and host rocks are related. The Herberton Hill Granite is a composite intrusive body, which yields emplacement ages of between 339 ± 2 and 322 ± 4 Ma (Fig. 15a; Murugulov et al., 2013). Tin mineralization is present in all phases of the Herberton Hill Granite, which indicates that the maximum age for tin mineralization can be constrained by the youngest phase of the granite at 322 ± 4 Ma. This age is identical to the \(^{206}\)Pb/\(^{238}\)U cassiterite age of 318 ± 2 Ma within error obtained from the same supersuite to represent the overall timing of tin mineralization in the HMF (Cheng et al., 2018; 2019).

The cassiterite mineralization is overprinted by stannite at the Baal Gammon and Isabel deposits (Figs. 3 and 7). This indicates that the sulfide mineralization is younger than ca. 318 Ma. Direct relationships between crosscutting dykes and sulfide mineralization at the Baal Gammon and Isabel deposits can be used to constrain the minimum age of mineralization (Fig. 3c and Fig. 7a-b). The QFP dyke that crosscuts the mineralization at the Baal Gammon deposit dates at 289 ± 1 Ma, and the crosscutting dyke (QFP) at the Isabel deposit returned a similar age of 292 ± 1 Ma (Fig. 14b, f). Thus, the timing of the sulfide mineralization can be constrained between the age of the tin mineralization (ca. 318 Ma) and the age of crosscutting dykes (ca. 290 Ma). The close spatial and temporal relationship between the ca. 290 Ma porphyry dykes and the sulfide mineralization at Baal Gammon and Isabel suggest the possibility of a genetic connection. The presence of vermicular quartz and embayment textures in quartz phenocrysts from these dykes indicate a magmatic to hydrothermal transition. Porphyry dykes that display similar textures at the Empire Mine, Idaho, USA, have been linked to mineralization processes (Chang and Meinert, 2004).

### 6.3. Significance of the new age data and the tectonic setting of the Herberton Mineral Field

The age data presented in this study indicate that magmatic events dated between ca. 365 and 280 Ma have affected the HMF (Table 3; Figs. 10 and 11), which overlaps with the igneous activity related to the Kennedy Igneous Association (Fig. 16a). The U-Pb zircon ages obtained in this study, in combination with the geochronological data from Cheng et al. (2017), indicate four pulses of magmatic activity peaked at ca. 337,
The ca. 365 Ma age of the Jumna Granite is 25 Myrs older than the earliest intrusions recognized as part of the Kennedy Igneous Association (ca. 340–275 Ma; Champion and Bultitude, 2013a). Further east, the Mount Formartine Granite, which also intrudes the Hodgkinson Formation, is dated at 376 ± 3 Ma (Cross et al., 2019; Kositcin et al., 2015). It is unclear if this age indicates an earlier onset of magmatism associated with the Kennedy Igneous Association, or if it represents a late-stage magmatic activity related to the Tabberabberan Orogeny.

Two major detrital zircon populations were identified in the Hodgkinson Formation with peaks at ca. 1605 and 457 Ma, which indicate a likely provenance of these sedimentary rocks from the Thomson Orogen and Georgetown Inlier. These provinces were most likely situated to the west and south of the Mossman Orogen at the time of deposition of the Hodgkinson Formation (Henderson et al., 2013). These provinces were most likely situated to the west and south of the Mossman Orogen at the time of deposition of the Hodgkinson Formation (Henderson et al., 2013). Although, it was proposed that a small portion of the Thomson Orogen (e.g. the Barnard Province) bounds the Mossman Orogen to the east (Dirks et al., 2021), it is unlikely that these sedimentary rocks were sourced from the east as there are no known Proterozoic rocks east of the Tasman Line (Fig. 1). A younger detrital age of ca. 370 Ma reported by Kositcin and Bultitude (2015) from different parts of the Hodgkinson Formation may suggest diachronous sedimentation or multiple sediment sources.

The four magmatic events identified in this study are broadly coeval with those defined by Cheng et al. (2018) and are typically observed in the Kennedy Igneous Association of northeast Queensland (Champion and Bultitude, 2013a). The Hf and Nd isotope data from the Kennedy Igneous Association are indicative of a progressively more juvenile source that was involved in the generation of these magmas, which signifies a transition from crustal-derived melts to increased mantle input between 337 and 285 Ma (Champion and Bultitude, 2013b; Cheng et al., 2018). Accordingly, we agree with the model proposed by Cheng et al. (2018) and suggest that the tectonic setting of the magmatic activity during ca. 337 and 322 Ma compressional, whereas the magmatic activity at ca. 305 and 285 Ma was during a period of crustal thinning with an increased mantle input (Fig. 1b). The voluminous granitoids that formed during these crustal thickening and thinning episodes of the Kennedy Igneous Association were likely formed in a back-arc setting and the overall north–south trend of magmatism (Fig. 1a) was interpreted to indicate a west dipping subduction margin along the east coast of Australia (e.g. Vos et al., 2007; Withnall and Henderson, 2012).
Furthermore, these granitoids have a younging direction from south towards northeast (Cheng et al., 2017), suggesting a northerly migration of the magmatic activity along the subduction system. The switch from evolved, crust-derived magmas to juvenile magmas with higher mantle input interpreted by Cheng et al. (2018) as a transition from Sn dominated to W-Mo dominated mineralization. Our data suggest that sulfide mineralization and the associated enrichment of In postdated the Sn mineralization, and the sulfides were most likely related to the emplacement of the porphyry dykes at ca. 290 Ma. If that is the case, the In mineralization took place during a period of crustal thinning and was caused by juvenile magmas with a greater mantle input.

7. Conclusion

The Baal Gammon and Isabel deposits are the only deposits in the HMF with defined In resources. Tin mineralization, however, is overprinted by sulfides, as displayed in the two deposits, which is common throughout the HMF and linked to high-grade In mineralization. Indium mineralization appears to be predominantly hosted by the sulfide minerals chalcopyrite, sphalerite, and stannite. The timing of tin mineralization can be related to magmatic activity at ca. 320 Ma, whereas the sulfide mineralization is most likely related to the emplacement of porphyry dykes at ca. 290 Ma. The geodynamic setting of the HMF indicates deposition of tin mineralization in a compressional tectonic regime, while the sulfide and In were deposited during a period of crustal extension.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Fig. 14. $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age (top) and concordia plot (bottom) for samples from Baal Gammon (a-d), and Isabel (e-f). The KDE plot is shown for sample ISOT04.
Fig. 15. $^{206}\text{Pb}/^{238}\text{U}$ weighted mean age (top) and concordia plots (bottom) for samples: (a) WT03; (b) KG06; (c) HBH01; (d) JM05; (e) GGV01; and (f) GGV02.
Data availability

Datasets related to this article can be found at https://doi.org/10.25903/09v7-r187, an integrated data management platform hosted at Research Data JCU (Kumar and Sanislav, 2022).

Acknowledgments

The Geological Survey of Queensland supported this study as part of the New Economy Minerals Initiative. AAK was supported by a Commonwealth Research scholarship at James Cook University. We thank the Economic Geology Research Centre (EGRU) at James Cook University (Townsville), Red River Resources Ltd., and Assoc. Prof. Paul Gow from Sustainable Minerals Institute (SMI) at The University of Queensland (Brisbane) for supporting us in conducting this research.

Fig. 16. Age distribution of felsic rocks from: (a) the Kennedy Igneous Association and an illustration of granite emplacement in the Herberton Mineral Field highlighting Sn, W, Mo, and sulfide mineralization; and (b) the stratigraphy (modified after Champion, 2016). The data for the age distribution plot is from Cheng et al. (2017) in combination with data from this study.


