

# Controls on indium mineralisation in tin-tungsten-base metal deposits of the Canadian Appalachians

Christopher R. Goeddeke<sup>1</sup>, John B. Chapman<sup>2</sup> and Iain M. Samson<sup>1</sup>

1. Department of Earth and Environmental Sciences, University of Windsor, 401 Sunset Av., Windsor, Ontario

2. Geological Survey of Canada, 625 Robson St., Vancouver, British Columbia

**Abstract:** Indium is a minor but potentially economically significant component of the ore metal tenor of many porphyry-style, stockwork and polymetallic vein-type Sn-W and Sn-base metal deposits of the Canadian Appalachians. However, indium distribution between deposits is highly uneven, and whereas some deposits contain hundreds of kilograms of the metal at grades sufficient to justify recovery, others are near-barren. In order to investigate the fundamental temperature, mineralogical, spatial and chemical controls on indium mineralisation in the district, this study has taken samples from indium rich and poor occurrences at 10 drilled prospects in southern New Brunswick and southwest Nova Scotia, as well as from the past-producing East Kemptville Mine in Nova Scotia.

Detailed mineralogical characterization of these materials has shown that, contrary to existing models, within this district indium is commonly introduced early in the deposit paragenesis, presumably as a component of the initial, high-temperature magmatic-hydrothermal fluids. During this phase of mineralisation, indium is dominantly precipitated within copper-rich sphalerite, and it is the distribution of this mineral phase that primarily governs the presence or absence of indium within a mineralised body. During later cooling of the deposit a proportion of the indium is exsolved from sphalerite during recrystallization, and forms lamellae of a sulphide mineral that resembles sakuraiite in the core zones of many individual sphalerite.

## Introduction

Indium has seen a dramatic rise in demand in recent years due to the variety of industrial and technology applications it can be put to, particularly in electronics. Devices such as touch screens, superconductors and solar panels incorporate significant quantities of indium, and at present there is no practicable or cost-effective substitute available.

Within the provinces of New Brunswick and Nova Scotia, rocks of the Appalachian Orogen (Fig. 1) contain numerous porphyry- and granitoid-related tin, tungsten and base metal deposits that are variably enriched with indium, particularly in the vicinity of the past-producing Mount Pleasant mine in Charlotte County, NB (Fig. 2), and East Kemptville mine near Yarmouth, NS (Fig. 3). In many cases, indium content within a deposit may be only slightly enriched above regional background levels and does not contribute significantly to the economic potential of the deposit. However, at other deposits indium can be present in quantities great enough that it comprises a significant proportion of the economic ore tenor. At almost 1000 tonnes combined indicated and inferred contained metal (McCutcheon et al., 2013), the porphyry tungsten-tin-base metal deposits of the Mount Pleasant mine represent possibly the largest documented global indium reserve (Sinclair et al., 2006).

These documented occurrences represent an opportunity to study the mechanisms and controls on indium deposition in known indium enriched and barren ore forming systems of otherwise similar genesis. The objective of the work described herein is to characterize these processes in order to provide improved genetic context and exploration targeting criteria. Samples recovered from archival diamond drill

core taken at a variety of deposits across the region were used to characterize the mineralogy and paragenesis of indium-rich and indium-poor ore assemblages, to determine the mineralogical controls on indium distribution, and to characterize possible mechanisms controlling the transport and concentration of indium into viable ore deposits.

## Geology, geochemistry and mineralogy of indium

### Geochemistry

Indium, in its native form, is a soft, lustrous metal that is highly malleable and ductile. In the natural environment, however, the most common oxidation state of indium is +3, where its outer valence shell comprises a full complement of ten d-orbital electrons. This electron configuration leads to a greater degree of covalent bonding and greater stability when forming chloride complexes than other elements in the same periodic group (Wood and Samson, 2005). The high charge and moderate ionic radius of the  $\text{In}^{3+}$  ion make it a hard acid, that should preferentially form complexes with hard bases (e.g.,  $\text{OH}^-$ ,  $\text{F}^-$ ) and organic ligands bonding through oxygen (Wood and Samson, 2005). The  $\text{In}^{3+}$  ion is larger than similar cations of like charge, which results in greater tendency to form complexes with chloride and bisulfide (Wood and Samson, 2005).

Indium is not found in significant quantities in common natural waters as strong complexation or highly acidic conditions are required to solubilize indium at low temperatures (Wood and Samson, 2005); for example, indium concentrations are less than 1.7 parts per trillion in Japanese freshwater systems that have been exposed to significant anthropogenic indium (Nozaki et al., 2000). Higher concentrations of

Corresponding author: John Chapman (jchapman@nrcan.gc.ca)

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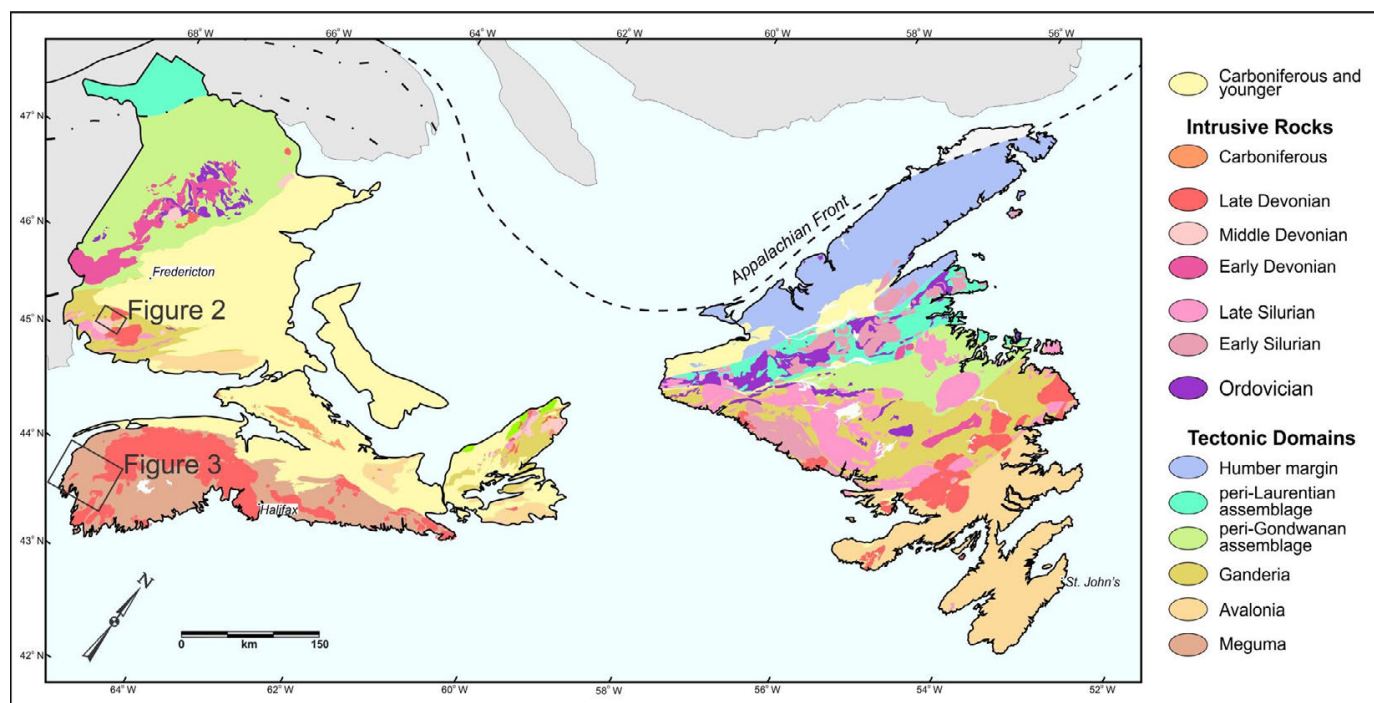


Figure 1 – Simplified lithotectonic map of the Appalachian Orogen in Canada. Positions of Figures 2 and 3 are indicated by solid boxes. Modified after Hibbard et al. (2006), van Staal et al. (2009), Rogers et al. (2014) and references therein.

indium, reaching several hundred parts per million, have been documented from active undersea vent fluids, however (Schwarz-Schampera and Herzig, 2002). In acidic, fluoride-rich solutions, indium fluoride complexes may play role in the hydrothermal transport of indium, but this may be limited by the low solubility of fluorite and topaz (Wood and Samson, 2005). Experimental investigations have indicated that the only indium chloride species present in a 0.1 mol HCl solution at 350°C is the tetrahedrally coordinated  $\text{InCl}_4^-$  ion (Seward et al., 2000; Wood and Samson, 2005). The existence of hydrothermal enrichments of indium demonstrate that conditions exist under which the element is relatively soluble, but at present these are only sparsely documented in nature.

### Mineralogy

Indium can be contained within a variety of minerals, either as a major structural constituent or as a trace element substitution (Tables 1 and 2; Schwarz-Schampera and Herzig, 2002). Minerals within which indium is an essential, structural element are rarely found in substantial quantities, and indium most commonly occurs in base metal sulphides such as sphalerite, chalcopyrite, stannite and stannoidite through a range of elemental substitutions. Sphalerite is the most economically significant source of indium, with indium-rich sphalerite occurs in various types of deposits around the world (Schwarz-Schampera and Herzig, 2002). The bulk of indium production at present is achieved as a by-product of the mining of zinc-rich volcanogenic massive sulphide (VMS) deposits, such as at the giant Kidd Creek deposit in Ontario (Cook et al., 2011a). Other deposits within which indium occurs in economically viable quantities also contain sphalerite, and indium generally shows a positive grade correlation with zinc and copper in bulk analyses (Schwarz-Schampera and Herzig, 2002), and a possible negative correlation with iron (Cook et al., 2009) consistent with the bulk of the indium residing within sphalerite

Table 1 – Minerals into which indium displays significant natural substitution

Mineral	Ideal formula	Dominant substitution
Sphalerite	$(\text{Zn,Fe})\text{S}$	Zn, Fe
Stannite	$\text{Cu}_2\text{FeSnS}_4$	Sn, Fe
Kesterite	$\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4$	Sn
Mawsonite	$\text{Cu}_6\text{Fe}_2\text{SnS}_8$	Sn, Fe
Stannoidite	$\text{Cu}_6^+\text{Cu}_2^{2+}(\text{Fe}^{2+},\text{Zn})_3\text{Sn}_2\text{S}_{12}$	Sn, Zn, Fe
Cassiterite	$\text{SnO}_2$	(Sn), Fe
Digenite	$\text{Cu}_9\text{S}_5$	Cu
Enargite	$\text{Cu}_3\text{AsS}_4$	Cu, As
Tetrahedrite	$(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$	Cu, Sb, (As)
Tennantite	$(\text{Cu,Ag,Fe,Zn})_{12}\text{As}_4\text{S}_{13}$	Cu, As, (Sb)

Table 2 – Indium minerals

Mineral	Ideal formula	Common association
Roquestite	$\text{CuInS}_2$	Sphalerite, chalcopyrite
Sakuraiite	$(\text{Cu,Zn,Fe})_3(\text{In,Sn})\text{S}_4$	Sphalerite, chalcopyrite
Dzhalindite	$\text{In}(\text{OH})_3$	Sphalerite
Indite	$\text{FeIn}_2\text{S}_4$	Linnaeite
Laforetite	$\text{AgInS}_2$	Chalcopyrite
Petrunkite	$(\text{Cu,Fe,Zn,Ag})_3(\text{Sn,In})\text{S}_4$	Stannite
Ishiharite	$(\text{Cu,Ga,Fe,In,Zn})\text{S}$	Sphalerite

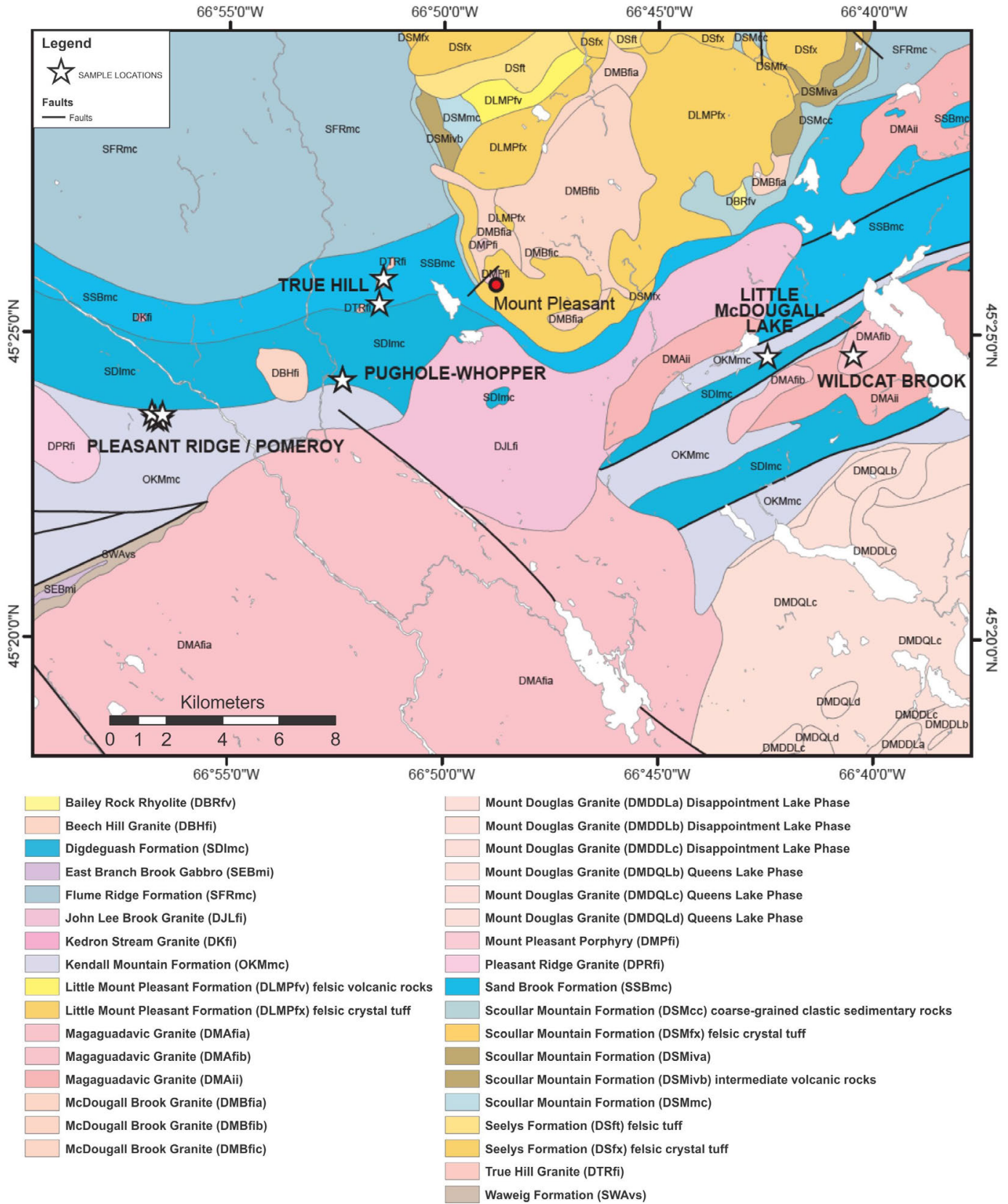


Figure 2 – Sample location map of the Mount Pleasant tin-tungsten district, Charlotte County, New Brunswick. Bedrock geology after McLeod et al. (2005).



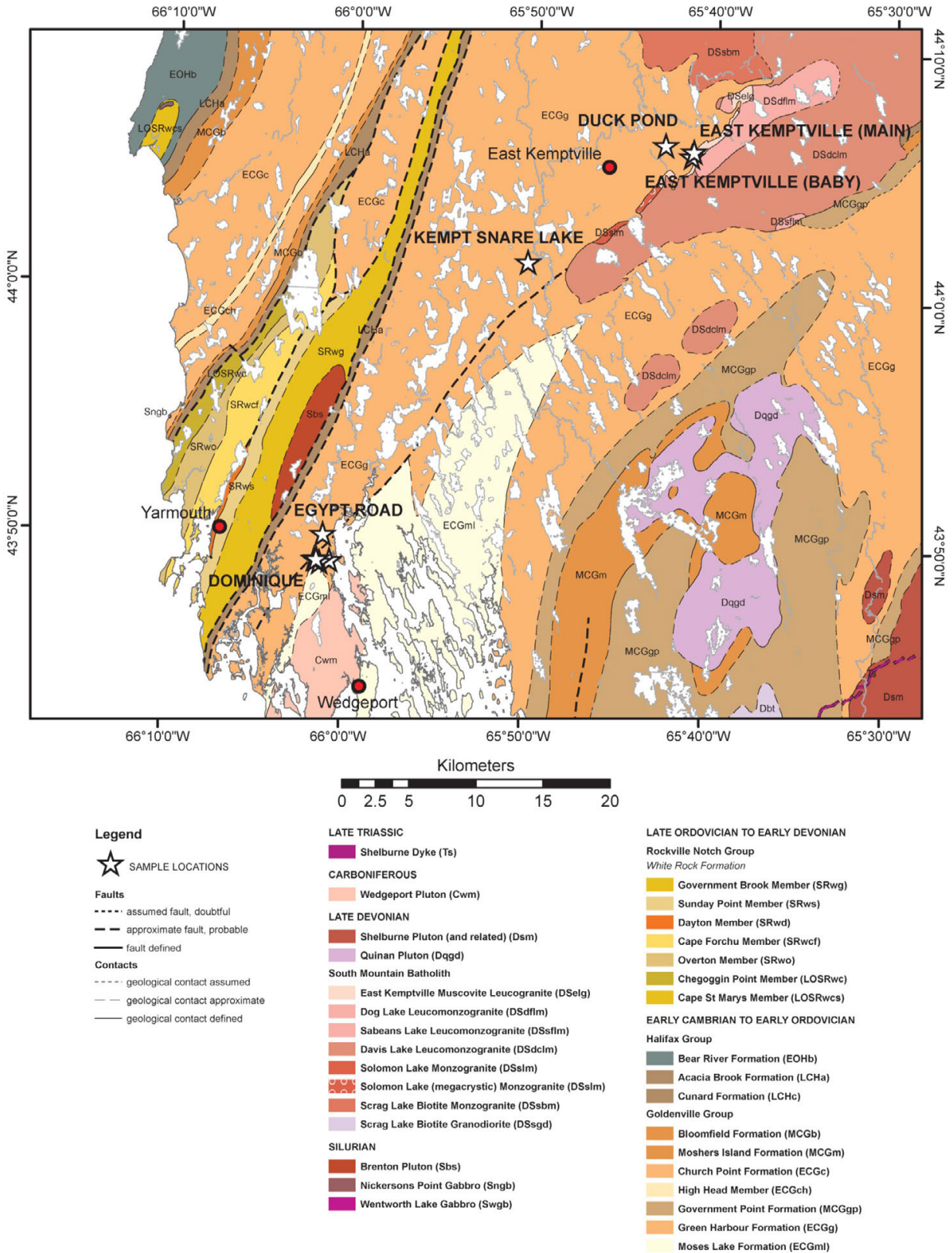


Figure 3 – Sample location map of the southwest Nova Scotia tin domain, Yarmouth County, Nova Scotia. Bedrock geology after White et al. (2012).

and copper sulphide minerals. This distribution is observed at the Mount Pleasant deposits, where sphalerite is the most important indium host, with chalcopyrite the second most significant host (Sinclair et al., 2006).

Formation of indium-rich sphalerite may occur as part of primary mineralisation or may be part of later alteration, with a possible positive correlation between high temperatures of formation or alteration and indium content within sphalerite (Cook et al., 2011b). Indium-rich sphalerite has been associated with elevated copper content. Secondary alteration processes, such as those associated with 'chalcopyrite disease', have been associated with the formation of iron rich and indium-bearing sphalerite (Barton and Bethke, 1987; Eldridge et al., 1988; Schwarz-Schampera and Herzig, 2002). Incomplete or 'disordered' solid solution series have been suggested between sphalerite and roquesite [ $\text{CuInS}_2$ ], and between sphalerite and stannite [ $\text{Cu}_2(\text{Fe,Zn})\text{SnS}_4$ ] (Sinclair et al., 2006; Cook et al., 2011b). The solid solution between sphalerite and stannite encompasses the stannite-group mineral sakuraiite [ $(\text{Cu,Fe,Zn})_2(\text{Sn,In})\text{S}_4$ ].

Indium substitutes for either zinc or iron in the lattice of sphalerite, usually in conjunction with copper through a charge-balanced coupled substitution mechanism. This substitution requires that  $\text{Cu}^{2+} + \text{In}^{3+}$  replaces  $2(\text{Zn}^{2+}, \text{Fe}^{2+})$ . Replacement zones in experimentally synthesized sphalerite crystals indicate that iron was preferentially replaced by indium, rather than zinc (Bente and Doering 1995). How this process varies as a function of temperature is not fully understood, although it has been theorized that indium substitution occurs in sphalerite over the relatively narrow temperature range of 350–400°C (Cook et al., 2011b).

Chalcopyrite can also host significant indium, and in some occurrences has higher indium content than coexisting sphalerite (Schwarz-Schampera and Herzig, 2002). Stannite and stannoidite have also been documented as hosts for indium, as have tennantite-tetrahedrite, cassiterite, and a variety of other minerals (Table 1; Cook et al., 2011b). The formation of roquesite, and other minerals within which indium is a required structural component, has been interpreted to occur only where the availability of minerals containing indium-replaceable elements (e.g., iron in sphalerite) is limited (Cook et al., 2011b).

## Deposit associations

Indium is commonly associated with zinc-rich sulphide deposits such as VMS, sedimentary exhalative (SEDEX) and skarn types, but is also concentrated in tin porphyry, stockwork vein, and epithermal systems (Schwarz-Schampera and Herzig, 2002). The average crustal abundance of indium is ca. 0.1 ppm, but concentrations within known deposits can range up to ca. 3000 ppm (reported from polymetallic veins; Murao et al., 2008). The majority of present global production is from zinc-rich VMS deposits, whereby indium is recovered as a by-product of zinc processing. However, the majority of known indium reserves reside in porphyry-related deposits such as that those found at the Mount Pleasant mine in New Brunswick (Jorgenson and George, 2004). Previous models for the formation of the Mount Pleasant deposits suggested that indium-bearing mineral assemblages were superimposed on earlier tungsten-iron-tin-molybdenum or zinc-bearing assemblages at temperatures in excess of 350°C (Schwarz-Schampera and Herzig, 2002). However, in light of recent detailed studies of indium mineralogy and inter-mineral partitioning by Cook et al. (2011b), observations of coexisting indium-poor sphalerite and roquesite within the North Zone at Mount Pleasant suggest that indium introduction was not solely a late stage phenomenon.

## Deposit geology

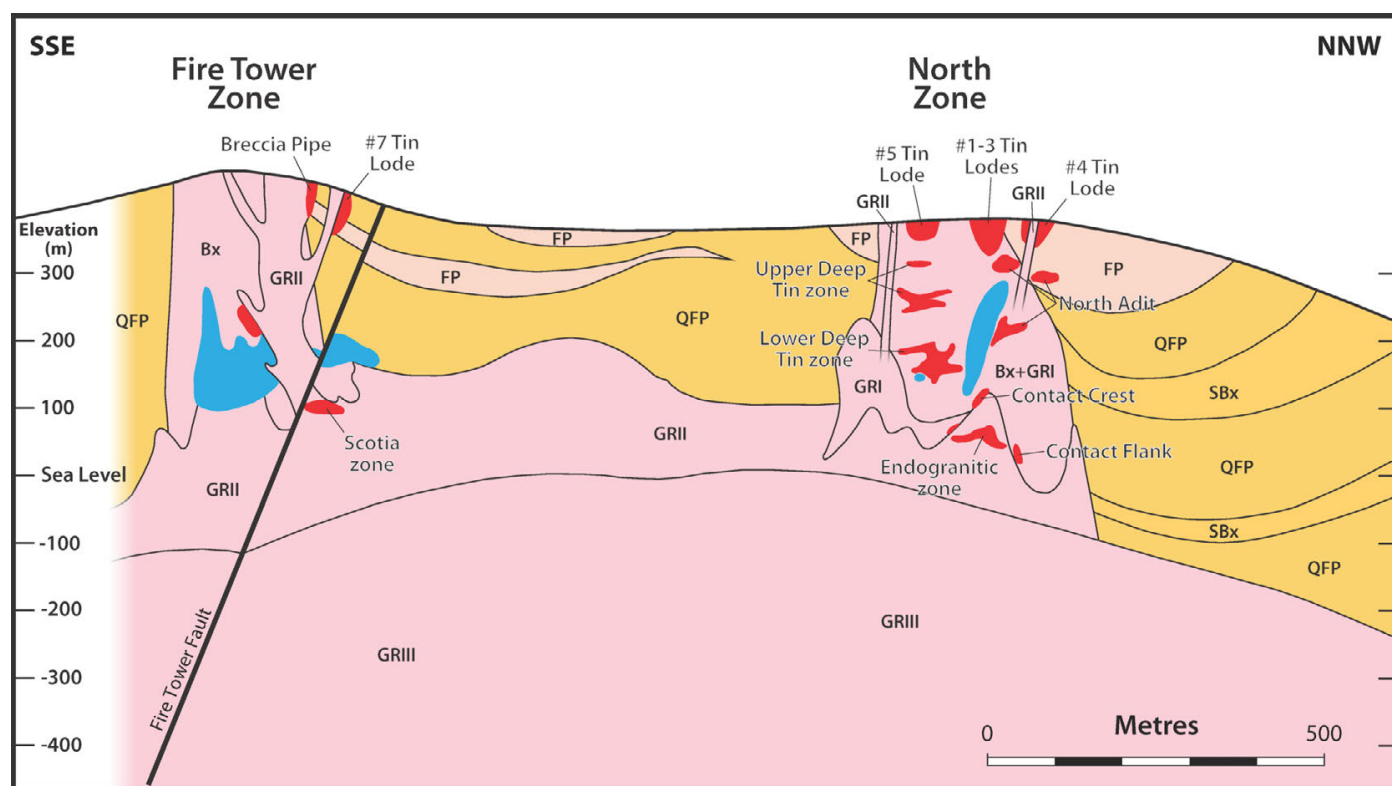
Within the Canadian Appalachian region a number of different ore deposit styles occur that contain significant indium, including porphyry, stockwork vein, and epithermal types and many of the VMS deposits of the Bathurst Mining Camp in New Brunswick contain extractable indium (e.g., Brunswick #12). Assay data from the porphyry and stockwork deposits at Mount Pleasant, Pleasant Ridge/Pomeroy, Pughole and True Hill in New Brunswick (Fig. 2) indicate enrichments of indium of potentially economic significance. The largest of these is 620 tonnes of contained indium metal identified within the Mount Pleasant deposits (Sinclair et al., 2006). In Nova Scotia, the East Kemptville, Dominique, Duck Pond and Egypt Road deposits (Fig. 3) have also been identified as potential indium resources. During the late 1970s and early 1980s, extensive diamond drilling of these deposits was carried out and recovered drill core from many were assayed for indium at that time. Technology-driven demand for indium in more recent times has led to reassessment of these materials and their potential at providing a means to resolve the mode of occurrence and controls on indium endowment within these provinces.

Most of the deposits within the Canadian Appalachians documented as hosting economically significant indium contents (>60 ppm; Sinclair et al., 2006) were formed during the Devonian to Early Carboniferous Acadian and Neocadian orogenies (van Staal et al., 2009, and references therein). Of those indium-rich deposits linked to magmatism associated with granitoid emplacement, the Mount Pleasant in Charlotte County, south-western New Brunswick, has attracted the most detailed academic investigation. Here, indium occurs mainly in sphalerite but is also associated with chalcopyrite. The indium potential of deposits within the Southwest Nova Scotia Tin domain, including the past-producing East Kemptville mine, is less well understood. Multiple replacement and mineralisation events are common to the deposits, with mineralisation occurring as pockets in veins and along the interface between veins and their host lithologies. Greisen-style alteration is commonly associated with tin and indium deposition, but not exclusively. Not all areas subject to greisen alteration contain elevated indium, but indium-rich sphalerite is largely associated with greisen alteration (Halter et al., 1998; Sinclair et al., 2006).

## New Brunswick indium deposits

### Mount Pleasant

The Mount Pleasant deposit comprises two discrete centres of porphyry-style intrusive mineralisation, located at the south-western margin of the late Devonian Mount Pleasant Caldera Complex (Fig. 2; McCutcheon et al., 2010). These two centres, each cored by magmatic-hydrothermal breccia, are the Fire Tower Zone and the North Zone. Of these, the Sn-Zn-dominated North Zone contains most of the significant indium mineralisation (Fig. 4; Sinclair et al., 2006), while the W-Mo-Bi-rich Fire Tower Zone is less strongly enriched in indium, and its distribution within this zone is irregular. Within the Mount Pleasant deposits, indium mineralisation is strongly correlated to zinc abundance and, to a lesser extent, copper (Sinclair et al., 2006). There is also a weaker correlation between indium and tin, and little to no correlation between indium and cadmium. Indium is dominantly hosted within sphalerite (ca. 90 %) and chalcopyrite (ca. 9 %), with minor quantities contained within stannite group minerals (to ca. 1 %) and sparse indium minerals such as roquesite (<<1 %). Whole-rock indium concentrations from Mount Pleasant range from 1 to 3690 ppm, with a median value of 58 ppm (Sinclair et al., 2006).



#### Mine Terminology (Formal stratigraphic unit)

GRIII	Granite III	(Mount Pleasant Porphyry)
Bx	Hydrothermal breccia	(Mount Pleasant Porphyry)
GRII	Granite II	(Mount Pleasant Porphyry)
GRI	Granite I	(Mount Pleasant Porphyry)
FP	Feldspar porphyry	(McDougall Brook Granite)
QFP	Quartz-feldspar porphyry	(Little Mount Pleasant Fm.)
SBx	Sedimentary breccia	(Scoullar Mountain Fm.)

#### Mineralization



	W-(Mo-Bi) mineralization
	Sn-(In-Zn-Cu) mineralization

Figure 4 – Schematic cross section through the Fire Tower Zone and North Zone at the Mount Pleasant mine, New Brunswick (Fig. 2), facing southwest. Each zone comprises a cluster of W-(Mo-Bi) and Sn-(In-Zn-Cu) mineralised bodies centred on a near-vertical plug of magmatic-hydrothermal breccia associated with the second phase of intrusion of the Mount Pleasant Porphyry complex (Granite II) into older rocks of the Mount Pleasant Caldera complex. Annotation nomenclature used is the informal mine terminology, but formal unit names given in parentheses and colour scheme are per Figure 2. Modified from McCutcheon et al. (2010; 2013) and Sinclair et al. (2006).

The North Zone mineralisation is hosted within stockwork bodies contained within a cluster of breccia pipes and subvolcanic granitic plutonic bodies. The granitic phases have been subdivided into three main sequences, which from oldest to youngest are designated Granites I, II and III. These have been interpreted as representing the cooling stages of a single parent magma body (McCutcheon et al., 2010). Granite I is associated with low-grade tungsten and molybdenum mineralisation, and was brecciated and altered by fluids released during subsequent emplacement of Granite II beneath it. Individual intrusive bodies of Granite II are approximately cone-shaped, and contain breccia pipes in their upper portions. These breccia pipes are thought to be of magmatic-hydrothermal origin, caused by the exsolution of magmatic fluids from the cooling plutonic bodies. Metallic mineral precipitation was likely caused by a combination of rapid cooling and increasing pH within the magmatic fluids, as a consequence of their interaction and mixing with groundwater (Sinclair et al., 2006).

The North Zone is itself divided into several sub-zones that exhibit different alteration and mineralisation characteristics. Of particular interest for their indium content are a high-sulphide near surface zone (HSNSZ) of breccia and vein-hosted lodes, the Upper and Lower Deep Tin Zones (UDTZ and LDTZ), and the Endogranitic Zone (EZ; Sinclair et al., 2006). Within HSNSZ deposits, cassiterite, arsenopyrite, lollingite and sphalerite are the major ore minerals present, associated with lesser stannite, marcasite, pyrite, galena, wolframite, molybdenite, tennantite, chalcocite, bornite, native bismuth, bismuthinite and wittichenite. Sinclair et al. (2006) report indium grades of the #4 Lode from within this zone of up to 91 g/t. The Sn-base metal deposits of the UDTZ are associated with the highest indium tonnages, reported as 1.7 Mt of ore, grading 280 g/t indium at a cut-off grade of 60 g/t (Sinclair et al., 2006). Within veins and breccia bodies of the UDTZ, major ore minerals observed are sphalerite, chalcopyrite, arsenopyrite

and cassiterite, with minor roquesite, lollingite, tennantite, stannite, stannoidite and wittichenite. The UDTZ forms a near-horizontal to steeply dipping body of highly silicified and brecciated early Granite II, adjacent to a local cupola of a later phase of Granite II. The genetically associated LDTZ bodies are situated beneath and outward of the UDTZ mineralisation. In contrast to UDTZ bodies, the LDTZ exhibits relatively low indium concentrations, commonly assayed at between 5 and 20 g/t (Sinclair et al., 2006), and mineralisation is dominantly hosted within cassiterite and arsenopyrite veinlets within greisen (quartz-topaz) and chlorite-biotite alteration. Mineralisation within the EZ is compositionally and mineralogically similar to the LDTZ, but major mineralised interval in this zone was preceded by two additional phases of hydrothermal alteration, comprising pervasive sericitic alteration cross-cut by fracture-controlled chloritic alteration. The EZ is a large, tabular body containing 1.4 Mt of ore grading an average of 45 g/t indium.

#### *Pleasant Ridge/Pomeroy*

Although the Mount Pleasant deposits are the most studied in the area, the surrounding district contains numerous additional deposits of similar age and genetic character associated with smaller granitoid intrusive and plutonic bodies. Claim groups including True Hill and Pleasant Ridge (later Pomeroy) have been assayed and shown to contain elevated indium. Of these, the Pleasant Ridge/Pomeroy deposit in particular has significantly elevated indium concentrations, together with geological characteristics and similar zinc and copper mineral associations that appear similar in nature to the Mount Pleasant North Zone deposits (Watters and Martin, 2009).

#### *Nova Scotia indium deposits*

Southwest Nova Scotia has been subject to exploration interest for tin and tungsten deposits since the mid-1970s, following the discovery of mineralised granite and metasedimentary rocks near Wedgeport in Yarmouth County (O'Reilly, 2012). Intensive exploration has delineated a broad swathe of deposits from a zone south and east of Yarmouth itself, north-eastward along the margin of the late Devonian South Mountain Batholith, to the East Kemptville deposits, a distance of approximately 50 km. Within the Southwest Nova Scotia Tin Domain the various granite- and metasediment-hosted deposits have highly variable indium content.

#### *East Kemptville*

The East Kemptville deposit occurs along the northeast-trending East Kemptville Shear Zone at the margin of the Davis Lake Pluton of the South Mountain Batholith. The deposit is hosted partly within peraluminous granite and partly within Meguma Group metasedimentary rocks. Magmatic aqueous fluids exsolved from the cooling intrusion, enriched in tin, iron, zinc, sulphur and fluorine, were focused along fault planes and interacted with wall rocks, creating greisen-style alteration and mineralisation. Two main zones of greisen mineralisation have been defined within the East Kemptville property: the Main and Baby zones. Both are linked to leucogranite bodies of similar composition, and are dominated by greisen-style mineralisation developed both within the granites and their surrounding metasedimentary rocks.

The Main Zone deposit at East Kemptville is a well-documented example of greisen tin mineralisation, that locally has been subdivided into 'massive' and 'zoned' styles (Halter et al., 1996). Massive greisens formed from overlapping of individual alteration halos in highly fractured zones (Halter et al., 1998). Zoned greisens are confined to

individual veins that were subject to multiple stages of alteration (Halter et al., 1996). In each case, leucogranite was initially altered to a quartz-sericite greisen assemblage through the replacement of feldspars by muscovite, which in turn was altered to quartz-topaz greisen that is associated with development of significant cassiterite and sulphide mineralisation (Halter et al., 1998). Zonation developed through overprinting of alteration developed by successive pulses of fluid infiltration. The Baby Zone is centred on a separate cupola-like intrusion some 200 m to the southwest of the Main Zone, and only displays the zoned greisen mineralisation style (O'Reilly and Kontak 1992). Mineralisation within the Baby Zone is almost exclusively within quartz-topaz greisens, and is more concentrated than within the Main Zone (Halter et al., 1998).

The East Kemptville mine was developed during the 1980s as North America's first primary tin producer, based solely on the deposit's tin resource, but was forced to close in the early years of the 1990s due to the collapse of the tin price (O'Reilly, 2012). Recent re-examination of assay data taken during initial development of the property coupled with analysis of additional diamond-drill core material from recent and archived drilling programs within the East Kemptville footprint and from prospects in the immediate vicinity has revealed intervals containing indium at concentrations of up to 81 g/t (Avalon Rare Metals Inc., 2010).

#### *Duck Pond*

The Duck Pond prospect is located approximately 2 km to the west of the East Kemptville deposit, within the East Kemptville Shear Zone. Mineralisation at Duck Pond occurs in three distinct styles: strata-bound, quartz-chlorite-sulphide veins, and silicified/sericitised zones. Metallic minerals associated with this deposit occur primarily within the quartz-chlorite veins and strata-bound zones. The Duck Pond host rocks are primarily metawacke and meta-argillite sequences of the Goldenville Formation (Pitre and Richardson, 1989). The mineral hosting veins have been attributed to repeated hydrostatic fracturing of the country rocks by volatiles released from underlying magmatic intrusions. Multiple intrusive tin-porphyrries within the Duck Pond property are assumed to occur as a result of deformation associated with the formation of the East Kemptville Shear Zone (Pitre and Richardson, 1989). Although the deposits within the Duck Pond property are compositionally similar to the East Kemptville deposits, they occur in different host strata and have some significant geochemical and mineralogical differences to the larger deposit to the east. Fluorine-bearing and tin sulphide minerals are unknown at Duck Pond, whereas trace tourmaline is reported by Pitre and Richardson (1989) that is not present at East Kemptville. Iron-, copper- and arsenic-rich mineralisation occurs within zones associated with argillic alteration at Duck Pond, whereas alkalic alteration zones have associated muscovite, and chloritized zones are associated with elevated cassiterite, chalcopryrite and sphalerite (Pitre and Richardson, 1989).

#### *Dominique*

The Dominique deposit occurs within metasedimentary strata of the Goldenville Formation ca. 40 km southwest of the East Kemptville and Duck Pond deposits. Although the mineralisation styles are similar, the multiple granitoid intrusions in this area, such as the Early Carboniferous Wedgeport Pluton, are interpreted as significantly younger than the Late Devonian Davis Lake Pluton associated with the tin mineralisation in the vicinity of East Kemptville (McLean et al., 2003). Mineralised zones at Dominique are hosted primarily within chloritic shear zones, as replacements, and within quartz-carbonate



veins developed within altered calcareous wacke and black slate. Three separate, east-trending zones of altered and mineralised host rocks were identified during exploration by Shell Canada and Votix Corporation, and subsequent follow-up work conducted by the Nova Scotia Department of Natural Resources (O'Reilly and Kontak, 1992). Although indium distribution within the various zones of the Dominique prospect is highly variable (indium content reach ca. 90 g/t within the most northerly zone; O'Reilly and Kontak, 1992), a strong correlation with zinc content has been identified.

## Sampling and methods

Samples of mineralisation at each described location were recovered from surface outcrop locations (where available) and archival diamond-drill core materials held within the New Brunswick and Nova Scotia provincial government repositories, plus additional East Kemptville samples from recent exploration drill core from Avalon Rare Metals. Samples recovered are described in brief in Table 3. Samples were chosen to illustrate the greatest range of mineralisation and alteration associations possible from within those deposits known to be enriched in indium, or those of economic significance apparently bereft of indium. Data sources used to select core intervals for sampling include archived assay and core logs available through public records in both provinces, and those archived alongside core materials at warehousing facilities in Sussex, NB, and Stellarton, NS.

These samples were subsequently used to prepare polished sections for mineralogical analysis and geochemical investigation. Sample mineralogy and paragenesis were thoroughly characterized using a combination of optical and scanning electron microscopy techniques, including cathodoluminescence imagery, and quantitative mineral chemistry was determined using electron probe microanalysis (EPMA).

## Results and discussion

Detailed analysis of material from the Pomeroy deposit has indicated that existing models for the incorporation of indium within tungsten-base metal mineralisation likely need revisiting. Pomeroy is associated with the Pleasant Ridge Granite and contains sulphide-rich intersections (characterized by arsenopyrite, cassiterite, chalcopyrite, galena, hematite, magnetite, pyrite, and sphalerite) containing up to 15 wt% zinc and 1 wt% tin. An indium-rich phase that is tentatively interpreted as sakuraiite occurs as exsolution lamellae in sphalerite that also exhibits chalcopyrite disease (Fig. 5). Globally, indium is principally reported as a trace component in sphalerite, although indium minerals such as roquesite ( $\text{CuInS}_2$ ) and sakuraiite ( $(\text{Cu,Fe,Zn})_3(\text{In,Sn})\text{S}_4$ ) have been described from a variety of deposits (Schwarz-Schempera and Herzig, 2002). A solid solution has been proposed between both roquesite and sphalerite (Cook et al., 2009) and sakuraiite and sphalerite (Murao et al., 2008). It has been proposed that indium can either be incorporated into sphalerite during initial precipitation or through secondary alteration during interaction with copper-rich, high temperature (200–400°C) fluids, the latter being associated with the development of chalcopyrite disease.

The indium mineral lamellae at Pomeroy are restricted to the centres of sphalerite crystals (Fig. 5b, c), suggesting that the initial stages of sphalerite crystallization incorporated significant indium and copper, which were subsequently exsolved as the unknown mineral (sakuraiite?). The outer parts of the sphalerite crystals incorporated less copper and indium, presumably reflecting a decrease in the copper and indium concentrations in the fluid as a result of changes at

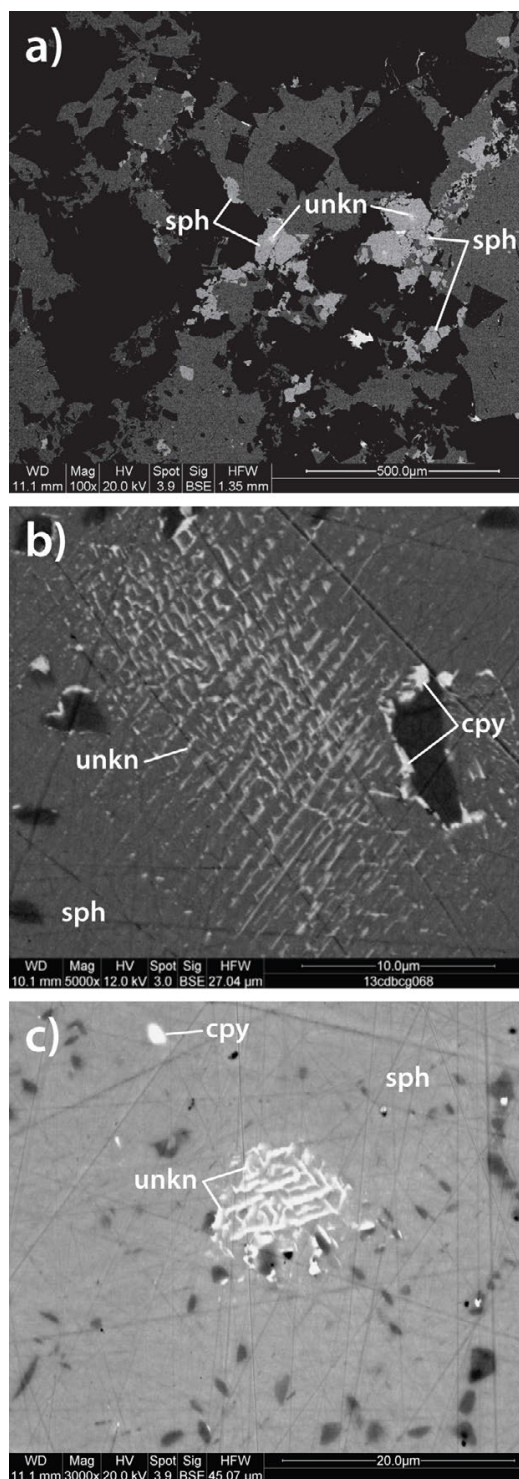


Figure 5 – Backscattered electron photomicrograph images of indium-rich sulphide assemblages from the Pomeroy deposit, New Brunswick: a) aggregate of granular sphalerite (sph) crystals with high-reflectivity cores; b) high magnification image of a high-reflectivity zone in the core of a sphalerite grain. Cross-cutting exsolution lamellae of an unknown sulphide mineral (unkn), likely sakuraiite, and associated peripheral chalcopyrite blebs; c) high magnification image of putative sakuraiite (unkn) exsolution lamellae in sphalerite, formed along three cleavage planes.



Table 3 – Summary of deposits included in this study

Name	Province	Type	Host rocks	Max. indium assay (ppm)	Dominant metallic minerals
Dominique	NS	Polymetallic vein	Greywacke, argillite	120	Pyrite, sphalerite, chalcopyrite
Duck Pond	NS	Polymetallic vein	Argillite, quartzite	n/a	Sphalerite, pyrite, cassiterite
East Kemptville	NS	Polymetallic vein, stockwork	Greywacke, brecciated greywacke, greisenized granit	81	Cassiterite, disseminated sphalerite
Egypt Road	NS	Polymetallic vein in boulders	Metasediment	38	Sphalerite
Kempt Snare Lake	NS	Polymetallic vein	Graphite-bearing greisenized leucogranite	n/a	Sphalerite, galena
Little McDougall Lk.	NB	Polymetallic vein, skarn	Hornfelsed wacke	n/a	Pyrite
Pleasant Ridge	NB	Polymetallic vein	Feldspathic wacke, mudstone, black shale	1000	Sphalerite, magnetite, cassiterite
Pomeroy	NB	Polymetallic vein	Quartzose arenite	1520	Sphalerite, magnetite, cassiterite
Pughole	NB	Polymetallic vein, stockwork	Shale, lithic and feldspathic wacke, silty mudstone	356	Sphalerite, galena, chalcopyrite
True Hill	NB	Sn-porphyry	Feldspathic wacke, silty mudstone	59	Sphalerite, galena
Wilcat Brook	NB	Vein/disseminated, float boulders	Greisenized wacke, argillite	n/a	Molybdenite, wolframite

source, or locally due to the incorporation of these elements into early-formed sphalerite. Regardless, these observations demonstrate that late addition of indium (and copper) to sphalerite is not a viable model for this assemblage at Pomeroy.

Elemental analysis of all the major phases present in the Pomeroy mineralisation was conducted by EPMA. Copper, Fe, Zn, In and Sn data are summarized as a ternary plot in Figure 6. This plot displays an evident solid solution straight line array between sphalerite and the unknown exsolution mineral. Although the grain sizes of the lamellae are too small to allow unambiguous mineralogical determinations, the trend of the solid solution is toward the stoichiometric composition of sakuraiite, reinforcing the postulated initial mineralogical interpretation. In addition, analyses of grains more certainly known to be sakuraiite show that there is a significant excess of copper within their composition, relative to the stoichiometric ideal composition of that

mineral. This may be a simple substitution rather than a solid solution relationship between sakuraiite and chalcopyrite, as the scatter in these data within the ternary plot do not vector toward the chalcopyrite stoichiometric composition. Solid solution between sakuraiite and another, more copper-rich, sulphide phase (possibly bornite; Fig. 6) cannot be discounted but the data herein are not sufficient to confirm the existence of this relationship at present.

## Conclusions

Detailed mineralogical characterization of these materials has shown that within this district indium is commonly introduced early in the deposit paragenesis, presumably as a component of the initial, high-temperature magmatic-hydrothermal fluids. During this phase of mineralisation, indium is dominantly precipitated within copper-rich sphalerite, and it is the distribution of this mineral phase the primarily governs the presence or absence of indium within a mineralised body. During later cooling of the deposit a proportion of the indium is exsolved from sphalerite during recrystallization, and forms lamellae of a sulphide mineral that resembles sakuraiite in the core zones of many individual sphalerite crystals.

The identification of indium as a part of the initial, high-temperature, magmatic-hydrothermal ore fluid composition, and the trapping mechanism suggested by the presence of the putative sakuraiite lamellae within sphalerite, all indicate that indium concentration should be maximised closest to the centre of hydrothermal activity. Hence, although apparently unpredictable, indium content may be a useful indicator of and vector toward the position of porphyry and granite intrusion cupolas.

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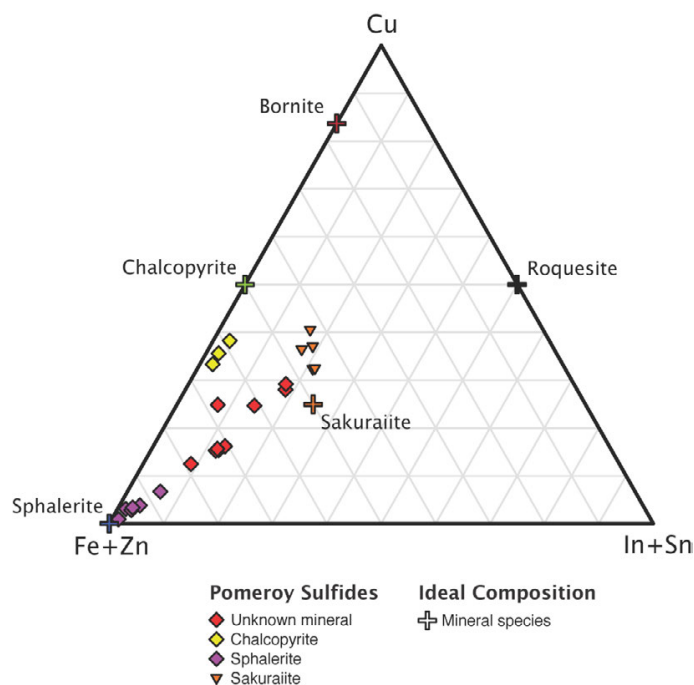


Figure 6 – Cu–(Fe+Zn)–(In+Sn) ternary plot of sulphide compositions for samples taken from the Pomeroy deposit, New Brunswick, determined by electron probe microanalysis.

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## **Appendix I:**

### **TGI 4 – Intrusion Related Mineralisation Project field trip guidebooks**

*Compiled by*

*Neil Rogers*

