Indicator mineral fingerprints in surficial sediments near Cu-Au deposits of the porphyry-epithermal-volcanogenic suite

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An indicator mineral, in the sense used herein, is a mineral whose dispersed grains in surficial sediments are of practical use for detecting, from afar, a specific type of rock, mineralized zone, or hydrothermal alteration zone. To detect the intended target from afar, the minerals must be visually discernible at concentrations as low as 5 grains per billion. Therefore the grains must be of a sufficient specific gravity — generally >3.2 g/cm^3 — to be further concentrated by heavy mineral separation, and also generally coarser than 0.25 mm. However, gold and a few other minerals are sufficiently dense and visually distinctive that grains of any size can be used.

Cu-Au deposits of the porphyry-epithermal-volcanogenic suite are a source of many potential indicator minerals but the utility of some of these minerals depends on climate (both past and present), depth of sampling, and the degree of interference from visually similar background heavy minerals. This will be illustrated using examples from glaciated Cu, Cu-Au, and Au deposits in the metamorphosed Archean craton and younger, unmetamorphosed Western Cordillera of Canada and Alaska, as well as unglaciated deposits in the southern hemisphere.

GENETIC RELATIONSHIPS BETWEEN PORPHYRY Cu, EPITHERMAL Au AND VOLCANOGENIC Au DEPOSITS

Porphyry Cu (and Cu-Au), epithermal Au and volcanogenic Au deposits are genetically related, being differentiated mainly on their depth of formation (Fig. 1) and thus, indirectly, on the temperatures and compositions of their associated hydrothermal fluids. Porphyry deposits are the deepest, forming ~5 km below surface within or adjacent to high-level porphyritic intrusions of a felsic to intermediate composition in terrestrial volcanic belts. Most preserved porphyry deposits are geologically young, either of Mesozoic or Cenozoic age, and occur in areas of recent uplift because older terrestrial belts tend to be so deeply eroded that any former porphyry deposits have been erased. Epithermal deposits form in the overlying volcanic rocks at crustal depths sufficiently shallow to allow boiling of hydrothermal fluids, typically <1 km. Volcanogenic Au deposits, in contrast, are mainly submarine. They form either directly on the seafloor or in permeable volcaniclastic rocks below the seafloor, with an underlying porphyry intrusion commonly providing the heat source to drive subsurface circulation of metal-scavenging seawater. Being better protected from erosion than terrestrial deposits, they are preserved in volcanic belts of all ages, with known occurrences in Canada ranging from the Archean deposits at Bousquet, Quebec (Dubé *et al.* 2007b) and Rainy River, Ontario (Averill 2013) in the Canadian Shield to the Cretaceous Blackwater deposit (Simpson *et al.* 2012) in the interior of British Columbia in the Western Cordillera (Fig. 2).

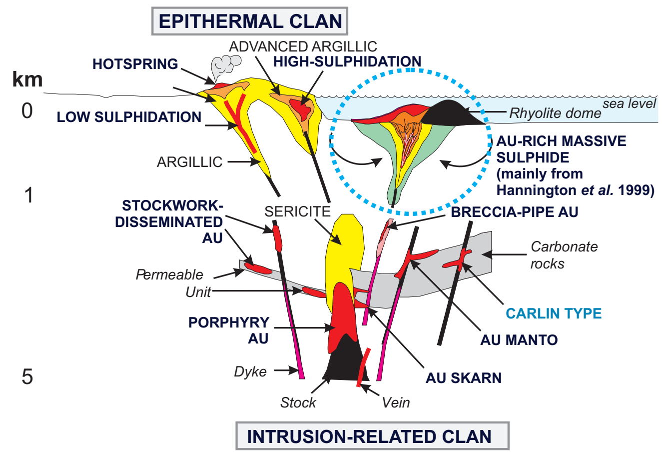

Fig. 1. Inferred crustal levels of gold deposition in porphyry, epithermal, volcanogenic. and other related deposits. Modified from Dubé *et al.* (2007a) and Sillitoe & Bonham (1990).

RANGE OF INDICATOR MINERALS

Each of the above deposits is a source of visually recognizable and deposit-specific heavy minerals coarser than 0.25 mm, many of which form useful indicator minerals under favourable conditions. All but the porphyry Cu deposits are also a source of gold grains. While most gold grains are much finer than 0.25 mm, with ~90% being silt-sized or <0.063 mm (Averill 2001), the grains are visually distinct and their high specific gravity of ~19 g/cm^3 permits their separation from the other heavy minerals in the concentrate. Consequently each recovered gold grain, no matter how small, can be physically identified and studied.

GOLD AS AN INDICATOR MINERAL

A key feature of gold grains is their ability to survive both physical transport and post-depositional weathering. Only a few other heavy minerals — principally ilmenite, rutile, zircon, chromite, kyanite, and staurolite commonly found in residual soils and heavy mineral sands — have this capability. In the deeply weathered Cenozoic colluvial cover at the Big Spring and Ellendale olivine lamproite fields in arid Western Australia, for example, chromite and picroilmenite are often the only durable kimberlite/lamproite indicator minerals. Most or all grains of olivine and other silicate indicator minerals, including the key Cr-pyrope garnet grains that are needed to assess diamond prospectivity, have been degraded (Jaques *et al.* 1986). To the east in the more tropical Northern Territory, Hutchison (2013) notes that a "large majority" of the surviving grains are chromite and in many cases diamond is the most abundant mineral present even though in kimberlite and lamproite it is

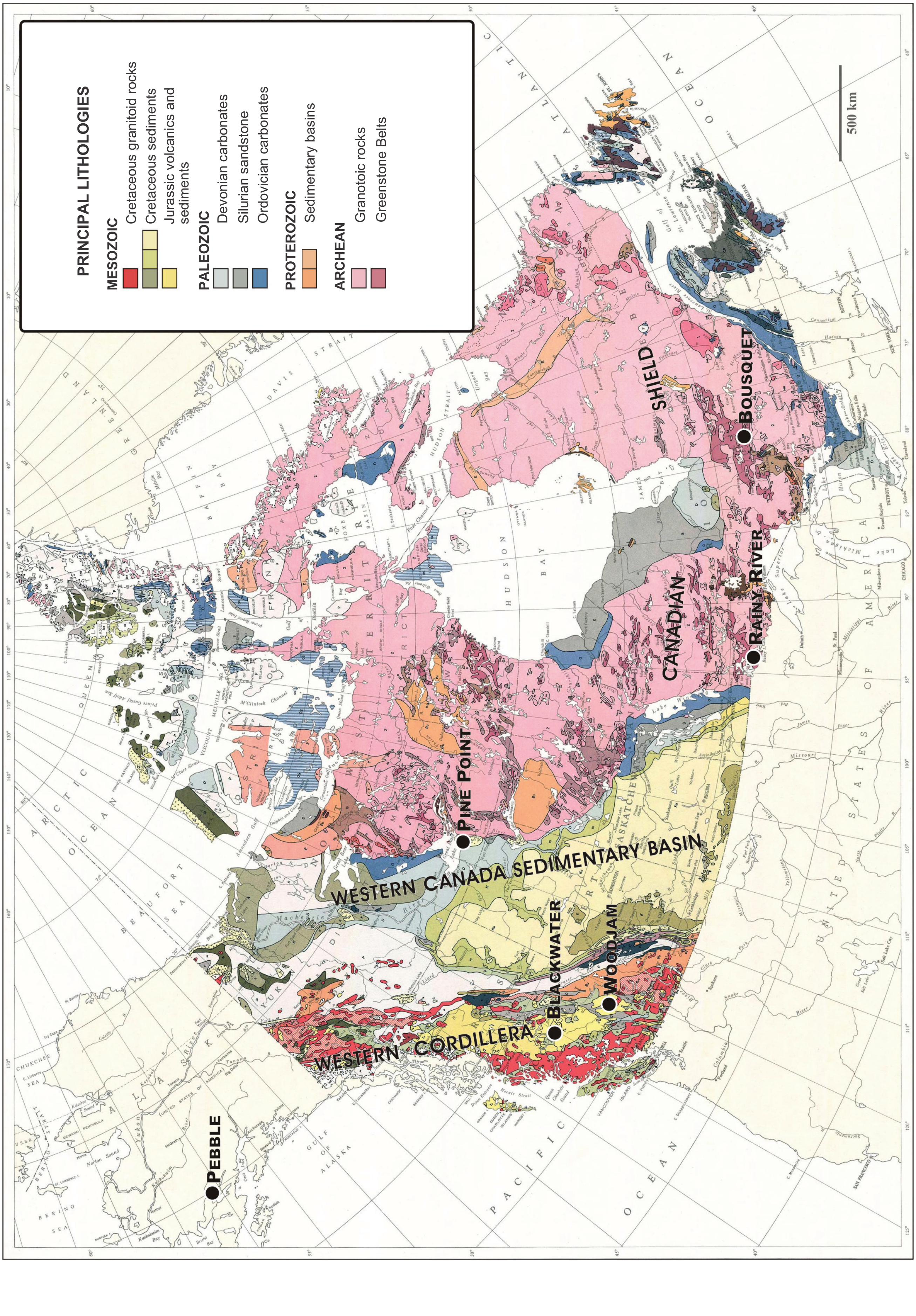

Fig.e 2. Geological setting of Canadian and Alaskan mineral deposits discussed in the text. Map source: Geological Survey of Canada (1957).

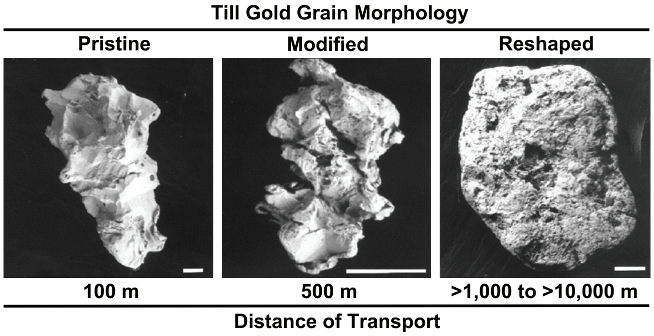

Fig. 3. Backscatter electron images of gold grains from till illustrating the relationship between grain wear and distance of transport. The wear processes are compressional (infolding and compaction) and do not reduce the mass of the gold grain. Scale bars = 50 μm. Source: Averill (2001).

several orders of magnitude less abundant than the other indicator minerals.

The physical resistance of gold is a result of its malleability. This property also results in the grains being moulded systematically during transport, a feature that can be used to gauge their distance of transport as exemplified by the progressive modification and eventual reshaping of pristine grains during glacial transport (Fig. 3; Averill 2001).

Throughout the glaciated regions of Canada (Fig. 4), exposed till sections are significantly oxidized to a depth of 2 to 3 m (Fig. 5), below which drilling has consistently shown that the till is as fresh as when it was deposited 10,000 to 15,000 years ago (Fig. 6). All gold grains from the oxidized zone of the till that have been analyzed by the author and his associates at Overburden Drilling Management (ODM) have been found to completely retain their primary, alloyed silver whereas grains from the cold-

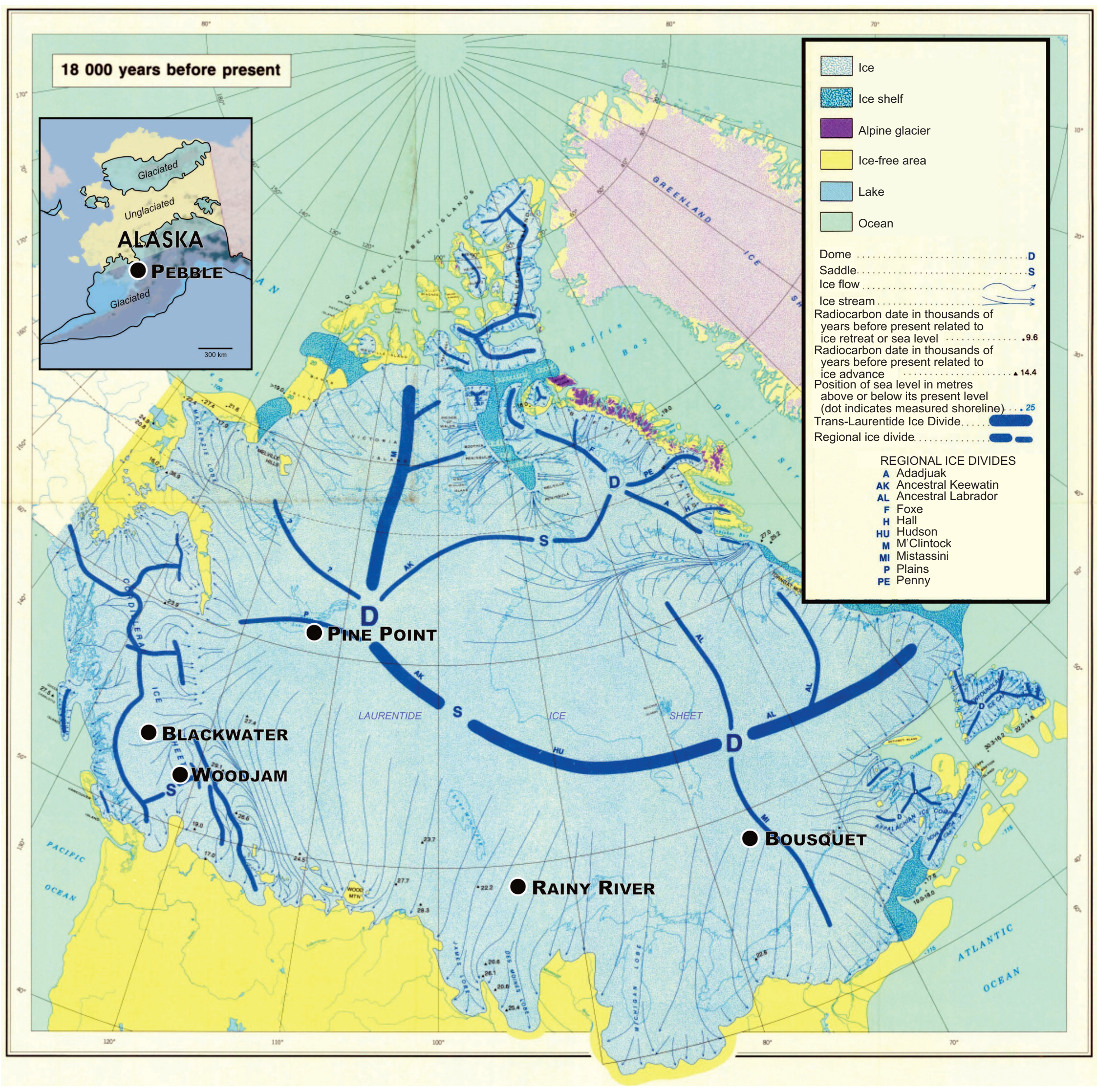

Fig. 4. Locations of the Canadian and Alaskan mineral deposits discussed in the text in relation to the Laurentide and Cordilleran ice sheets during glaciation approximately 18,000 years ago. Map source: Dyke & Prest (1987).

Fig. 5. Typical sample pit in oxidized till in Canada. Till excavated from the B- and C-horizons of the overprinted soil profile has been piled separately to illustrate their different oxidization states. Ideally, the sample is obtained from the weakly oxidized, pale yellow-ochre C-horizon below the highly oxidized, dark red-ochre B-horizon, generally at a depth of 0.5 to 1 m. The insert shows the heavy mineral fraction of the till in which most of the original sulphide grains have been consumed by oxidation.

climate alluvial placers of the Klondike have Ag-depleted rims (Knight *et al.* 1999) and those from more mature placers elsewhere are depleted to the core (Desborough *et al.* 1970). In French Guiana, where most placers contain only fully Ag-depleted gold grains, Kelley (2007) used remnant alloyed silver and small sulphide inclusions to identify a less mature, actively forming placer having a potentially significant lode source. This example raises the further possibility that the types of sulphide inclusions present in gold grains might be used to distinguish porphyry, epithermal, and volcanogenic gold sources

LIMITATIONS OF SULPHIDES AS INDICATOR MINERALS

The coarse, >0.25 mm heavy minerals in most porphyry, epithermal, and volcanogenic Au deposits that have not been affected by supergene alteration include at least one primary sulphide mineral in addition to pyrite. The sulphide species vary with deposit type, with porphyry deposits typically containing chalcopyrite and possibly also bornite and molybdenite, epithermal deposits containing As sulphides such as realgar, and volcanogenic deposits containing chalcopyrite, sphalerite, and possibly galena.

In till samples collected in Canada by reverse circulation or rotasonic drilling below the 2 to 3 m depth of post-glacial weathering, all sulphide mineral grains are perfectly preserved (Fig. 6). In areas of thick till cover, therefore, most base metal anomalies obtained from surface soil geochemistry surveys simply reflect leaching of glacially dispersed sulphide minerals from the top 2 to 3 m of the till, regardless of the analytical method employed, and are not indicative of mineralization in the subjacent bedrock.

In the top 2 to 3 m of non-calcareous till, such as that found over the Canadian Shield, grains of only two sulphide minerals, molybdenite and chalcopyrite, are significantly resistant to oxidation (Table 1). The rate of molybdenite survival appears to be 100 percent as no transported grains with visibly leached

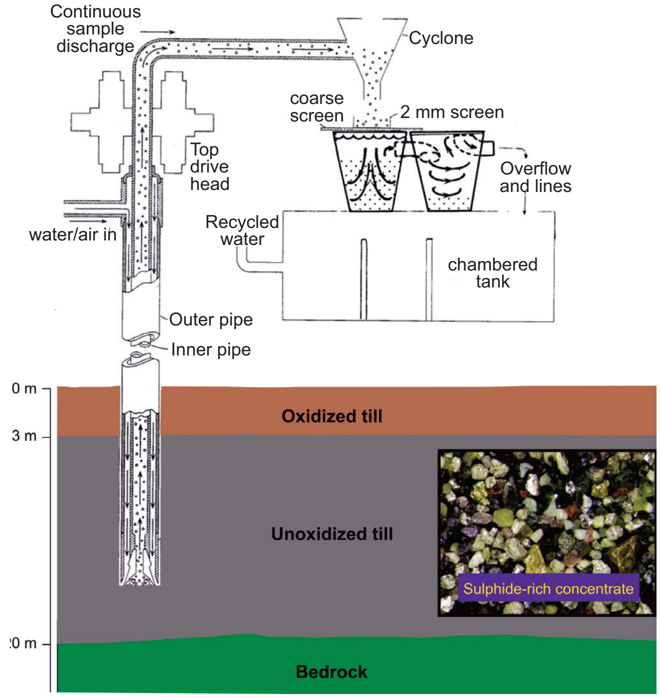

Fig. 6. Schematic diagram of a typical reverse circulation rotary drill specifically designed for sampling thick till in Canada. In holes drilled by these and other drill rigs, fresh, unoxidized till is typically encountered below a depth of 2 to 3 m. As illustrated in the inset, this fresh till retains all of its original sulphide mineral grains, precluding mobility of metals from or through the till to the overlying soil.

surfaces have been observed by ODM in many years of study. The rate of chalcopyrite survival is much lower, apparently just a few percent, and most of the surviving grains are of a dull bronze colour with deeply furrowed surfaces (Fig. 7A). With pyrite normally being much more abundant than chalcopyrite even in significant Cu deposits, pyrite grains were correspondingly more abundant in the till before it was oxidized. Due to the lag in chalcopyrite degradation relative to pyrite degradation, the survival of just a few tens to hundreds of chalcopyrite grains unaccompanied by pyrite grains indicates a once-stronger and potentially significant chalcopyrite anomaly. Sphalerite and galena grains have been found to survive to a significant extent only in carbonate-rich, sulphide-buffering till such as that found over the Western Canada Sedimentary Basin (Fig. 2), where they form a significant dispersal train glacially down-ice from the Mississippi Valley-type Zn-Pb deposit at Pine Point (Oviatt *et al.* 2013).

In the deeply weathered lateritic soils of the tropics and the thick, mature colluvium/alluvium covering ancient, low-relief landscapes in arid regions such as Western Australia, sulphide leaching is normally complete, precluding the use of any sulphide minerals as indicator minerals. In geologically younger,

Table 1. Relative stabilities of sulphide and arsenide mineral grains in oxidized till in Canada. Stabilities were determined by comparing grain abundances in shallow, oxidized till samples to those in deeper, unoxidized samples. Modified from Averill (2011).

Stable	Unstable	Parastable
Molybdenite	Pyrrhotite	Chalcopyrite
Cinnabar	Pyrite	Sphalerite } in carbonate-rich till
Sperrylite	Pentlandite	Galena } in carbonate-rich till
Loellingite	Arsenopyrite	

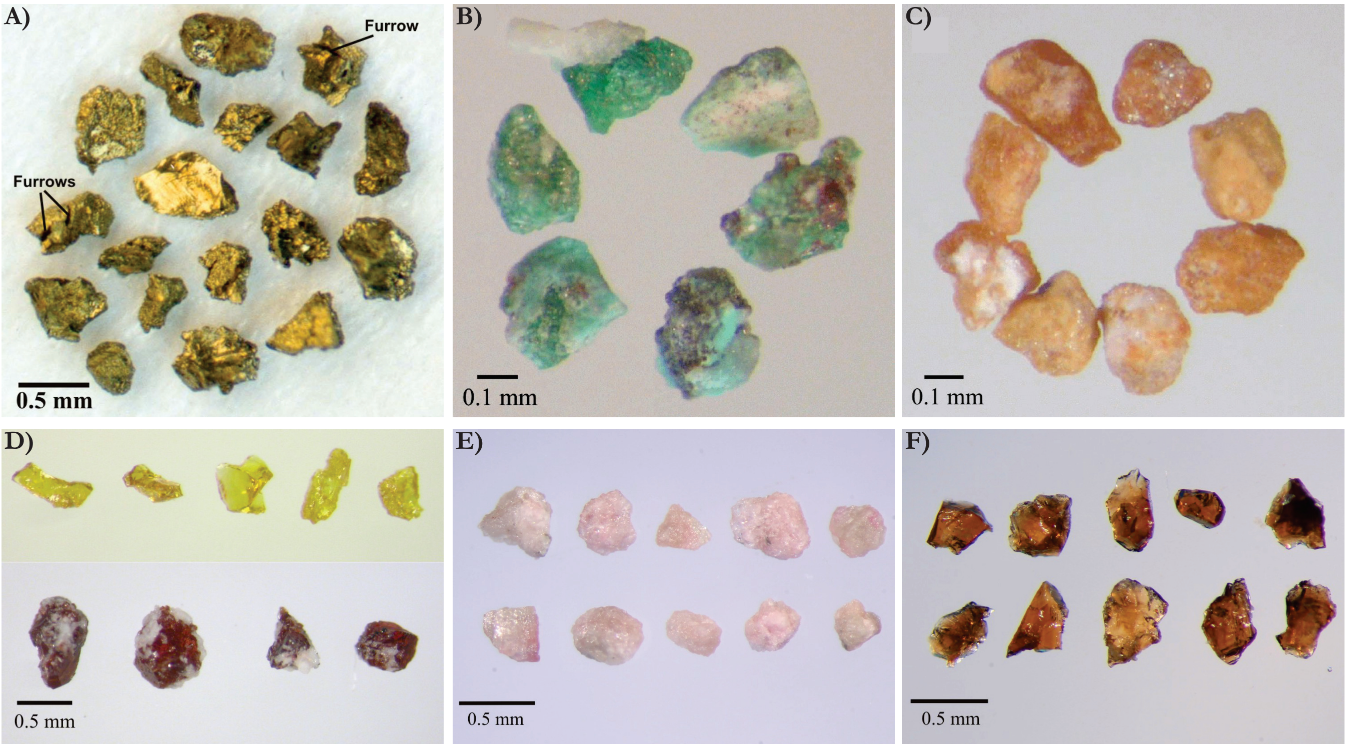

Fig. 7. Examples of transported indicator mineral grains recovered from oxidized surficial sediments near porphyry Cu and volcanogenic Au deposits. **A)** Surviving chalcopyrite grains from a shallow till sample in Canada. The original bright metallic surfaces have been oxidized to a dull bronze colour and deep furrows have developed along some cleavage planes. **B)** Atacamite grains from sheet wash gravel, Chile. **C)** Jarosite grains from sheet wash gravel, Chile. **D)** Andradite garnet grains from alluvium, Arizona porphyry Cu belt, USA. The colour of the grains ranges from yellow-orange (top row) to red-orange (lower row; garnet is intergrown with finer grained quartz alteration) or orange-brown. **E)** Ruby-pink Mn-epidote grains from a shallow till sample, Woodjam porphyry Cu district, British Columbia, Canada. **F)** Orange-brown spessartine garnet grains from a shallow till sample, Blackwater volcanogenic Au district, British Columbia, Canada. All photos by Overburden Drilling Management Limited.

recently uplifted, high-relief regions with similarly arid climates such as the Atacama Desert and Arizona in the Western Cordillera of the Americas, however, most porphyry Cu and Cu-Au deposits have a supergene blanket in which the original chalcopyrite has been transformed into secondary sulphide minerals such as chalcocite and "oxide" minerals such as turquoise ($CuAl_6(PO_4)_4(OH)_8{\cdot}5H_2O$) and atacamite ($Cu_2Cl(OH)_3$; Fig. 7B). Exploration samples collected from the thin, dry soil or *chusca* developed on alluvial gravel downslope from porphyry Cu deposits in Chile and Arizona and tested by ODM have consistently shown high survival of dispersed grains of supergene Cu-oxide minerals whereas supergene Cu-sulphides are absent. For example, a distinct turquoise anomaly, defined by sampling at a density of ~1 sample per km^2 (Fig. 8), is present

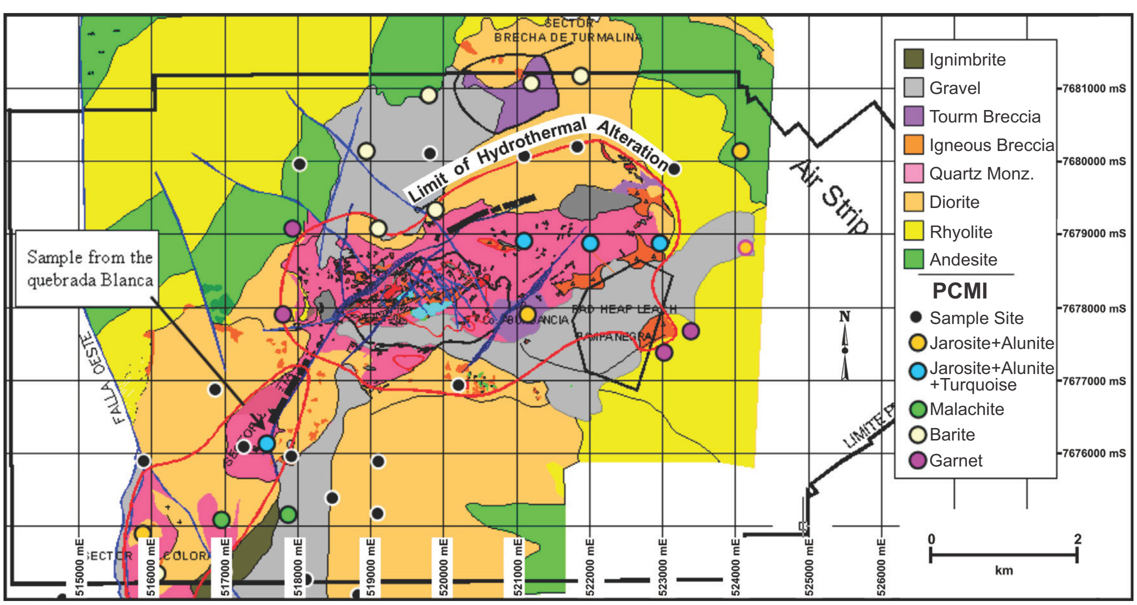

Fig. 8. Distribution of porphyry Cu indicator minerals in weathered alluvium near the Quebrada Blanca deposit, Chile. Source: Averill (2011).

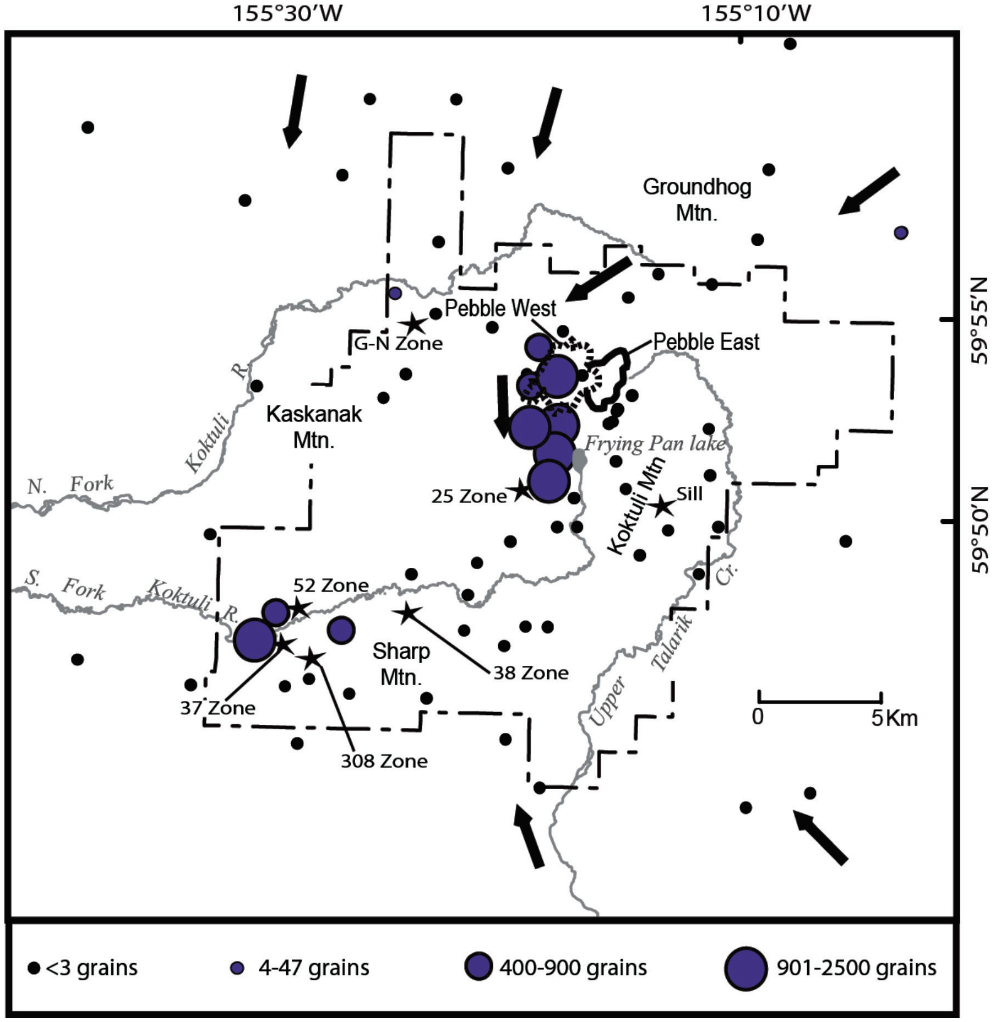

Fig. 9. Jarosite abundance in the 0.25 to 0.5 mm heavy mineral fraction of 10 kg till samples collected near the Pebble porphyry Cu-Au deposit, Alaska. The direction of glacial ice flow is shown by the black arrows. Source: Kelley *et al.* (2011).

in the alluvium over and downslope from the Quebrada Blanca porphyry Cu deposit (Averill 2011). Similarly, the primary realgar and other As-bearing sulphides of epithermal Au deposits have been partly transformed to the more stable and useful As-oxide mineral scorodite ($FeAsO_4 \cdot 2H_2O$). Some of the oxide minerals have a specific gravity of <3.2 g/cm^3 and thus become useful indicator minerals only if a lower density separation is performed to recover them (Averill 2011).

The hyperarid weathering in Chile has been beneficial not only in transforming hypogene chalcopyrite and realgar into stable secondary oxide minerals that can be used effectively as indicator minerals; it has also transformed pyrite into jarosite ($KFe_3(SO_4)_2(OH)6$; Fig. 7C), which is similarly stable and distinctly anomalous in the *chusca* at Quebrada Blanca (Fig. 8). While an arid climate combined with a recently uplifted terrane such as the Western Cordillera of the Americas is necessary for the formation of secondary sulphurous minerals such as jarosite, today's climate need not be arid in order for these minerals to be used as indicator minerals. For example, the Pebble porphyry Cu-Au deposit occurs in an area of Alaska that has been glaciated (Fig. 3) and presently has a subarctic climate but the preglacial climate was arid and glaciation was sufficiently light that part of the supergene blanket of the deposit is preserved. Recognizing this, Kelley *et al.* (2011) performed an indicator mineral survey at Pebble specifically directed at recovering both gold grains and a Chilean-type suite of porphyry Cu-Au indicator minerals and successfully identified a strong, 5 km long jarosite dispersal train leading directly down-ice from the Pebble deposit (Fig. 9). The jarosite content of the anomalous samples ranged up to 2500 grains per 10 kg till sample versus background of just 0 to 3 grains per sample

ALTERATION INDICATOR MINERALS

The very limited survival of sulphide mineral grains in surficial sediments near sulphide-rich mineral deposits greatly increases the dependence of indicator mineral surveys on more chemically stable minerals derived from the hydrothermal alteration zones of these deposits. The alteration systems associated with porphyry Cu and Cu-Au deposits tend to be concentrically zoned (Lowell & Guilbert 1970) and, as shown by Averill (2011) and summarized in Table 2, at least one hypogene mineral from each alteration zone can be used as an indicator mineral. The most useful minerals identified to date include diaspore and magnesian tourmaline (dravite), derived from the highly aluminous, advanced argillic core of the alteration system, and andradite garnet, derived from the outer propylitic zone, as illustrated by the central tourmaline and peripheral andradite anomalies at Quebrada Blanca (Fig. 8). If, as at Quebrada Blanca, the porphyry mineralization grades upward to epithermal mineralization, significant barite can also be expected.

Table 2. Principal hypogene porphyry Cu and epithermal Au indicator minerals found in oxidized surficial sediments in recently uplifted arid regions of the Western Cordillera of the Americas. Modified from Averill (2011).

Mineral	Composition	Principal Provenance (alteration zone)				
		Potassic	Argillic	Phyllic	Propylitic	Epithermal Au
Diaspore	$AlO(OH)$		—			
Alunite	$KAl_3(SO_4)_2(OH)_6$	—	—			
Dravite	$NaMg_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$		—			
Andradite	$Ca_3Fe_2(SiO_4)_3$				—	
Barite	$BaSO_4$					—

The chemical composition of andradite ($CaFe_2(SiO_4)_3$) reflects the Ca+Fe metasomatism that is characteristic of propylitic alteration. This metasomatism is further indicated by the presence within propylitic zones of other, more abundant Ca and/or Fe-rich minerals, principally calcite, epidote ($Ca_2(Al,Fe)_3(Si_3O_{12})(OH)$), and pyrite (Lowell & Guilbert 1970). While epidote is sufficiently heavy and resistant to weathering to be a potential indicator mineral, the surficial sediments near most porphyry deposits contain abundant epidote derived from unaltered intrusive and volcanic rocks, impeding the recognition of any propylitic epidote grains. In the glaciated Woodjam porphyry district (Fig. 2) in the Western Cordillera of Canada, however, the unaltered rocks contain minimal epidote and Plouffe *et al.* (2013) have shown that the propylitic alteration zones of the porphyry deposits are reflected by a significant increase in the overall epidote content of the till (Fig. 10). Some of the epidote grains contain sufficient manganese to change their colour from the usual pistachio green to ruby pink (Fig. 7E) but overall epidote abundance rather than epidote colour is the best indicator of propylitic alteration at Woodjam.

The hydrothermal alteration envelopes of the volcanogenic gold deposits in the Bousquet, Rainy River, and Blackwater districts in Canada also contain garnet but of a spessartine ($MnFe_2(SiO_4)_3$) rather than andradite composition, reflecting Mn enrichment in the fluids associated with the formation of volcanogenic deposits. Spessartine is abundant at each deposit but is a useful indicator mineral only in the Blackwater district. Blackwater is located in the Western Cordillera (Fig. 2) where the till contains no almandine garnet to impede identification of the spessartine grains, which are of a rather bland orange-brown colour (Fig. 7F). The absence of almandine in the till is due to (a) the underlying volcanic rocks being unmetamorphosed; and (b) the Blackwater area, during glaciation, being only 100 km down-ice form the ice divide in the high mountains of the Coast Range to the west (Fig. 3) and most of the intervening rock formations also being unmetamorphosed.

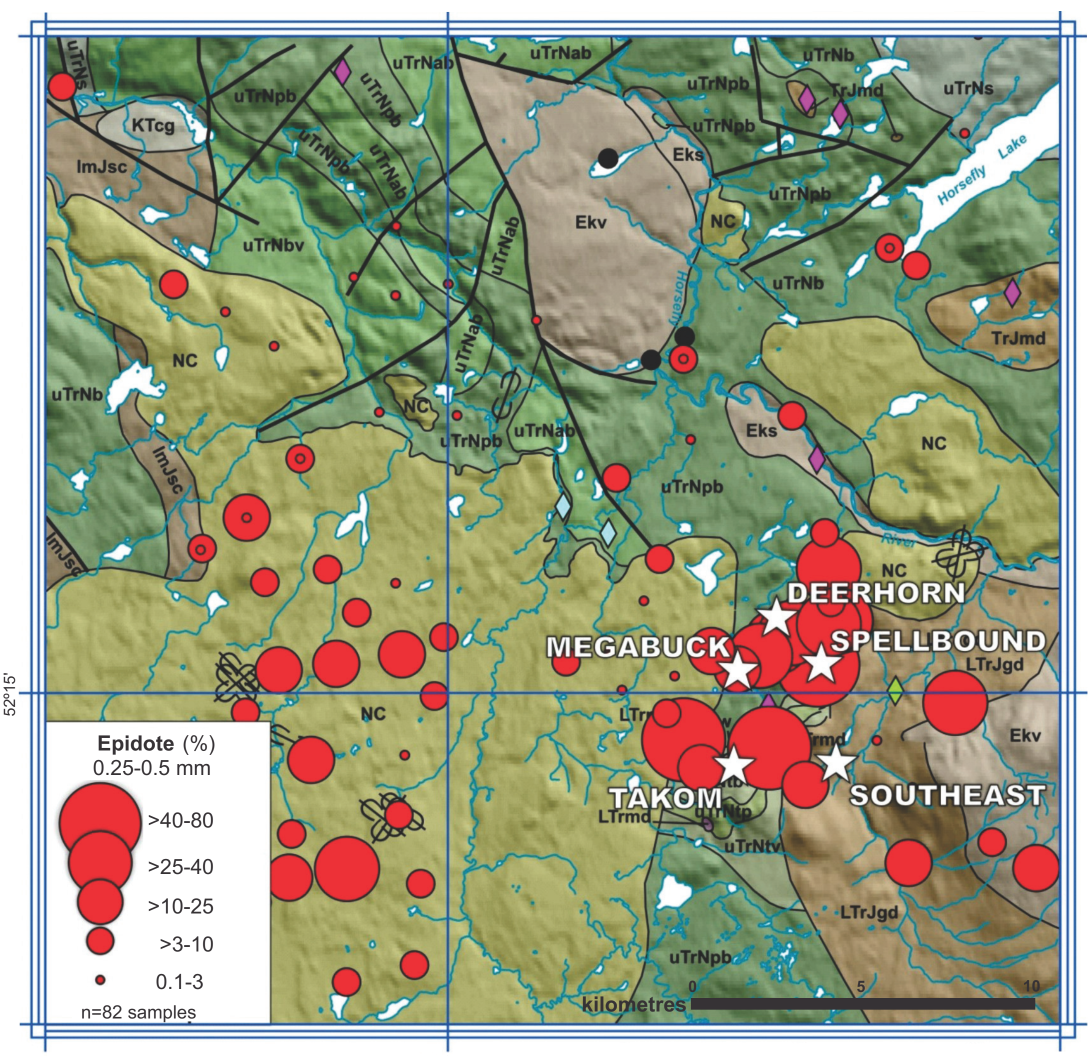

Fig. 10. Percent epidote in the 0.25 to 0.5 mm heavy mineral fraction of the till near the porphyry Cu and Cu-Au deposits of the Woodjam district, British Columbia, Canada. Source: Plouffe *et al.* (2013).

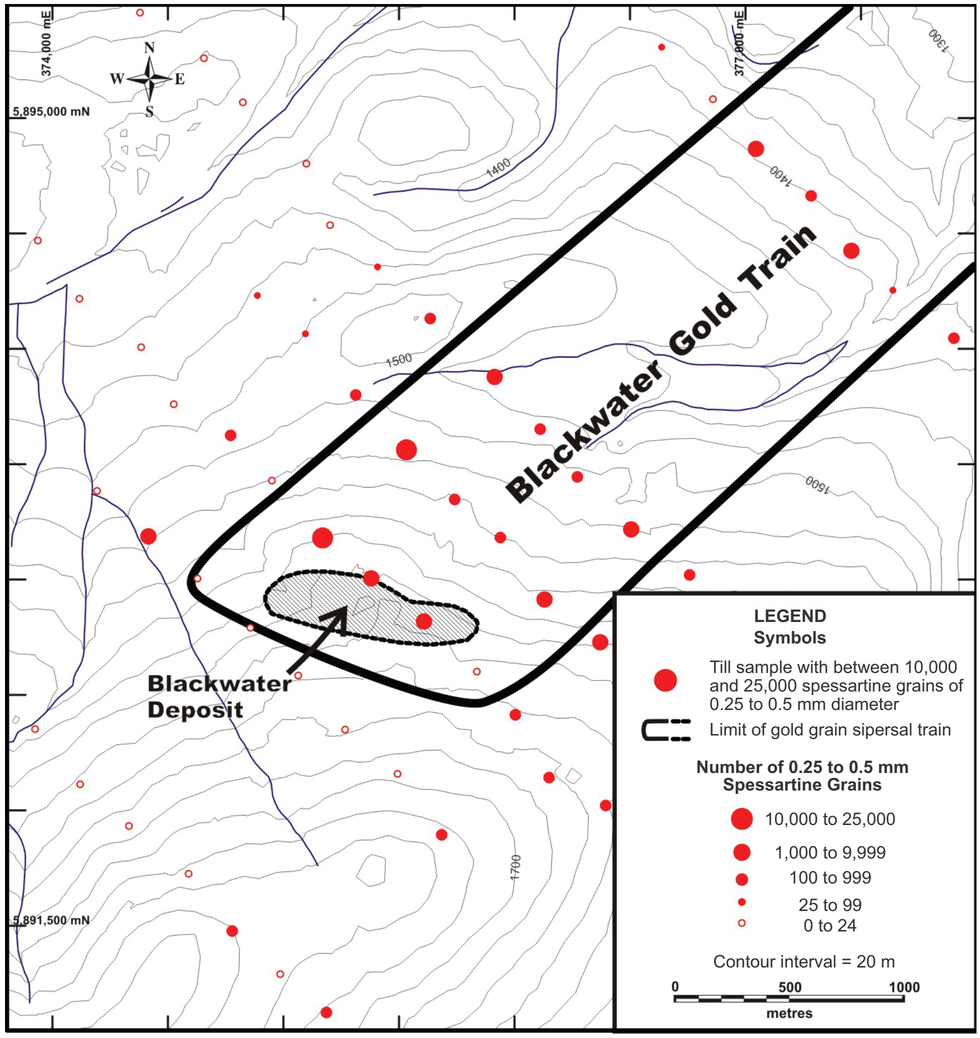

Fig. 11. Spessartine abundance in the 0.25 to 0.5 mm heavy mineral fraction of 10 kg till samples collected in the area of the Blackwater gold grain dispersal train, British Columbia. Courtesy of New Gold Inc.

The till in the Bousquet and Rainy River districts of the Canadian Shield, in contrast, is very almandine rich, commonly containing hundreds of thousands of grains of >0.25 mm size per 10 kg sample even though the underlying volcanic rocks are almandine-free greenstone. This is because these districts, when glaciated by the Laurentide ice sheet, were >1000 km down-ice from the ice centre to the northeast and the intervening Archean rocks consist mainly of garnetiferous gneiss. The alteration zones of both deposits are so aluminous that they also contain kyanite (Al_2SiO_5), a mineral that would not normally be expected in greenschist-facies rocks. At the Rainy River deposit, the presence of kyanite in the alteration zone was recognized only after a kyanite dispersal train was identified in the till (Averill 2013).

At Blackwater, surface till sampling, mostly at a density of 2 to 3 samples per km^2 compared to the 1 sample per km^2 commonly used in porphyry Cu exploration programs such as Quebrada Blanca (Fig. 8), has identified a strong, 1.2 km wide gold grain dispersal train (Fig. 11) and traced it 2.5 km down-ice to the limit of sampling. Gold grain counts obtained from 10 kg till samples collected within the train ranged from tens to hundreds of grains per sample, compared to a very low background of 0 to 5 grains per sample. The same till samples yielded up to 25,000 spessartine grains compared to very low background levels of 0 to 20 grains per sample. In view of the sharp, up to 1000:1 contrast between anomalous and background spessartine values and the considerable strength of the anomaly in the most distal till samples, 2.5 km down-ice from Blackwater, the total detectable length of the train probably exceeds 10 km.

DISCUSSION AND CONCLUSION

Porphyry Cu (and Cu-Au), epithermal Au, and volcanogenic Au deposits all contain minerals that are heavy, coarse-grained, visually distinctive, and specifically indicative of these deposits. When dispersed into surficial sediments, however, not all of these minerals form useful indicator minerals in all situations. The utility of a mineral depends mainly on its susceptibility to oxidation, the degree of oxidation of the host sediments, the climate under which this oxidation occurred, and also the climate at the time the deposit was formed, as witnessed by the jarosite dispersal train in the till at Pebble, Alaska (Fig. 9). Most sulphide indicator minerals are susceptible to oxidation whereas many indicators of hydrothermal alteration zones are stable in oxidized sediments. In gold grains, which are mostly finer than the other indicator minerals and are extracted separately, only the alloyed silver is normally subject to oxidation, although Hough *et al.* (2008) have identified minute crystals of secondary gold deposited by saline groundwater in regolith at a gold deposit in Western Australia. Noble *et al.* (2013) tested various size fractions of anomalous soil samples from this region and in some samples obtained much higher Au analyses from the -0.2 μm nanoparticulate fraction than from the coarser particulate fractions, suggesting that ultrafine secondary gold particles may also be present in the soil.

In recently glaciated regions such as Canada, all indicator minerals are preserved in unoxidized till below a depth of 2 to 3 m. At this depth, every sulphide grain remains as fresh as it was when the till deposited (Fig. 6), and the specific sulphide mineral assemblage within a dispersal train can be used to distinguish the type of source. For example, a pyrite-chalcopyrite-sphalerite-galena anomaly in the >0.25 mm fraction of the till accompanied by gold grains in the finer fractions normally indicates a volcanogenic Au deposit. A consequence of the freshness of sulphides at depth is that soil surveys in areas of thick till cover primarily detect metals leached from the top 2 to 3 m of the till. Since no metals have been leached from the underlying fresh, sulphide-bearing till, no geochemical method can be expected to see into this till or through it to bedrock.

In unglaciated areas, the most complete range of indicator minerals occurs at deposits in geologically young, recently uplifted terranes with arid climates, such as those of Arizona and the Atacama Desert. In the upper parts of these deposits, supergene oxidation has transformed some of the hypogene sulphide minerals into secondary oxide minerals that, following dispersal into the surficial environment, remain resistant to further oxidation and form very useful indicator minerals. Porphyry Cu and Cu-Au deposits tend to have particularly large and diagnostic indicator mineral signatures, especially in arid regions, because (1) both the deposits and their alteration envelopes are large; (2) the alteration is concentrically zoned with different indicator minerals present in each zone; and (3) being in geologically young terranes, there are no metamorphic minerals in the surficial sediments to dilute and impede the recognition of indicator minerals, such as the key andradite garnet grains derived from the propylitic alteration zone. Epithermal Au deposits associated with the porphyry deposits in arid regions of the Americas appear to have a more restricted suite of available indicator minerals, principally barite and scorodite.

In Canada, spessartine garnet is commonly present in the alteration zones of volcanogenic Au deposits but is a useful indicator mineral only for deposits such as Blackwater that are hosted by the unmetamorphosed volcanic rocks of the Western Cordillera (Fig. 2). While spessartine grains are also present in till near similar gold deposits in the Canadian Shield, such as those of the Bousquet and Rainy River districts, the spessartine signature tends to be overwhelmed by almandine garnet derived from Archean gneiss that comprises much of the shield. And in the most deeply weathered and thickly covered parts of Western Australia, most heavy mineral grains in the surficial sediments, including those of spessartine and other garnets, have been consumed by oxidation, as illustrated by the very limited lamproite indicator mineral suite in the colluvium at Big Spring and Ellendale (Jaques *et al.* 1986). In most other regions, however, indicator minerals derived from porphyry Cu (and Cu-Au) and epithermal and volcanogenic Au deposits are sufficiently diverse and abundant in the surficial environment to distinguish between and explore effectively and efficiently for these closely related types of mineral deposits.

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