The Canadian Mineralogist
Vol. 35, pp. 23-34 (1997)

IODARGYRITE AS AN INDICATOR OF ARID CLIMATIC CONDITIONS AND ITS ASSOCIATION WITH GOLD-BEARING GLACIAL TILLS OF THE CHIBOUGAMAU – CHAPAIS AREA, QUEBEC*

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ABSTRACT

The Ag halide mineral, iodargyrite, together with associated minerals chlorargyrite, bromargyrite, and "embolite", form a group of secondary minerals that, in terrigenous supergene environments worldwide, are exclusively confined to oxidized sulfide zones formed in arid and semi-arid climates. The presence of iodargyrite in gold-bearing glacial sediments of the Chibougamau – Chapais area of Quebec (first recorded occurrence of this mineral in Canada), together with other indicators of an arid climate, provides cogent evidence of a past arid climate in this region. These indicators include: a) the existence of a deep water table during sulfide ore oxidation of Chibougamau copper deposits, b) the abundance of "limonite dice" in glacial tills, indicative of the pseudomorphic replacement of pyrite grains in bedrock formations under arid conditions, c) the abundance of spongy and corroded grains of gold typical of lateritic terranes, and d) the abundance of possibly desert-derived quartzofeldspathic sand formations. The period of aridity is conjectural at this time owing to lack of definitive dating media, but the nature and preservation of weathered profiles in the region strongly suggest a period of aridity in the Tertiary. Arid climatic conditions in this region may coincide with a known global warming period in late Eocene to middle Oligocene times, when the Earth experienced some of its warmest temperatures. However, possible Pliocene arid conditions preceding onset of glacial events cannot be ruled out.

Keywords: iodargyrite, Ag halides, climatic mineral indicators, arid climate, gold, weathering, heavy minerals, Tertiary, glacial tills, Chibougamau, Quebec.

SOMMAIRE

Le halogénure de Ag, l'iodargyrite, ainsi que les minéraux qui lui sont associés, comme chlorargyrite, bromargyrite et "embolite", constituent un groupe de phases secondaires qui sont, dans les milieux supergènes partout au monde, exclusivement retrouvés dans les zones oxydées d'amas de sulfures sujets à un climat aride ou semi-aride. La présence d'iodargyrite dans les sédiments aurifères provenant des glaciers dans la région de Chibougamau – Chapais, au Québec (le premier exemple de ce minéral connu au Canada), considérée à la lumière d'autres indicateurs d'un climat aride, fournit une indication concluante de la présence d'un climat aride dans cette région par le passé. Parmi ces indicateurs, on trouve a) l'existence de nappes d'eau profondes lors de l'oxydation du minerai sulfuré des gisements de cuivre de la région de Chibougamau, b) l'abondance de "dés de limonite" dans les tills glaciaires, indicatifs du remplacement par pseudomorphose de grains de pyrite dans les formations du socle en milieux arides, c) l'abondance de particules d'or spongieuses et corrodées, typiques de séquences latéritiques, et d) la présence d'amas de sable quartzofeldspathique, possiblement d'origine désertique. Il n'y a encore aucune donnée radiométrique apte à préciser la période d'aridité, faute de matériaux datables, mais la nature et le degré de préservation des profils météorisés de la région font soupçonner le Tertiaire. Les conditions climatiques arides dans cette région pourraient coïncider avec une période de réchauffement à l'échelle du globe vers la fin de l'Eocène jusqu'au milieu de l'Oligocène, à une époque où la Terre a subi les climats les plus tempérés. Il est toutefois possible que c'est au Pliocène que cette période aride a eu lieu, comme prélude aux stades de glaciation.

(Traduit par la Rédaction)

Mots-clés: iodargyrite, halogénures d'Ag, indicateurs climatiques, climat aride, or, météorisation, minéraux lourds, Tertiaire, tills glaciaires, Chibougamau, Québec.

INTRODUCTION

> "Over a large part of the arid region of the west, lying between the Rocky Mountains and the Sierra Nevada, ores containing chloride of silver (cerargyrite) are abundant, and sometimes the bromides and iodides also occur; ....it seems probable that their abundance can be traced to the effect of the peculiar climatic conditions which have prevailed in that region in late geologic times."
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> Penrose (1894, p. 314)

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* Geological Survey of Canada contribution number 1996447.

> "The silver halides include chlorargyrite (cerargyrite), bromargyrite (bromyrite), miersite, and iodargyrite (iodyrite). They are comparatively common supergene minerals in arid regions or where aridity prevailed in the past."
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> Boyle (1968, p. 26)

The use of minerals as indicators of past climates has seen a constant increase in application since the turn of the century. In this respect, certain minerals, as characterized by their physical form, chemical composition, or relative abundance, can be used to describe climatic constraints at the time of their formation. The present work attempts to show that a particular group of chemically precipitated minerals, namely the silver halides, and in particular iodargyrite (AgI), can be used, along with other climatic indicators, to confirm the existence of past aridity in certain geological and geographical environments. Recently, the author has discovered concentrations of iodargyrite associated with large concentrations of gold grains and other products of weathering in glacial tills in the Chibougamau – Chapais region of north-central Quebec. This is the first recorded occurrence of this mineral in Canada, but more importantly, it is a "marker" of a period of preglacial aridity that probably persisted for some time in the Tertiary in this region.

REVIEW OF PREVIOUS WORK

Mineral climatic indicators can include the physical form and relative abundance of quartz grains in sediments (Dal 1968, D'Orsay & van de Poll 1985), feldspar stabilities and abundances (Todd 1968), clay:quartz ratios (Bonatti & Gartner 1973), types, chemical compositions, and abundances of clay minerals (Singer 1984, Mizota & van Reeuwijk 1989, Chamley 1990), relative abundances of heavy minerals in recent and ancient sediments (Kurze & Roth 1977), specific types of carbonate accumulations in soils and sediments (Quigley & Dreimanis 1966), the relative abundances of chemically precipitated minerals (Usdowski & Knoke 1970, Chafetz 1980, Semeniuk 1986), and the use of isotope ratios in minerals, particularly those of oxygen and carbon, to map climatic trends (Bowen 1966, Stuiver 1970, Savin 1991, Winograd *et al.* 1992).

For Canadian geological environments, elucidation of Cenozoic, and in particular, Tertiary climatic conditions is obscured by thick glacial deposits and the lack of complete Cenozoic continental stratigraphic sections. Nevertheless, partial stratigraphic sections or weathered profiles have been used to describe possible preglacial climatic events over the Shield, Appalachian, and Arctic platform regions. Boyle (1995) and Symons *et al.* (1996) have used paleomagnetic surveys and the absence of certain minerals that occur in massive sulfide gossans formed in semi-arid to arid climates to indicate that gossan deposits in the Bathurst base-metal metallogenic province of northern New Brunswick formed in a predominantly warm, humid, temperate climate during the Pliocene. Saprolite profiles over Grenville rocks along the north shore of the St. Lawrence River (Lasalle *et al.* 1983, de Kimpe *et al.* 1985), saprolite and laterite soil profiles over rocks of central Gaspé region (David & Bédard 1986, Cloutier & Corbeil 1986), and Tertiary gold-bearing placer deposits in the Eastern Townships region of Quebec (Shilts & Smith 1986, Smith & Shilts 1987) also signify the existence of a preglacial hotter and more humid climate during the Tertiary than exists in these regions today. In the Arctic platform region of Canada, extensive research on the late Tertiary sedimentary rocks, notably by Wolfe & Poore (1982), Wolfe (1985), and Matthews & Ovenden (1990), indicates that the Tertiary forests of this region formed in a warm temperate climate similar to that of southern Canada today. Placing the above-mentioned Tertiary climatic regions in today's climatic context, the Eastern Maritimes and St. Lawrence Lowlands regions would be located in the southeastern to south-central portion of the United States, and the Arctic platform would be located in the Oregon to south-central British Columbia region. In between these two regions are areas that experience hot temperate, alpine (including arid alpine), cool temperate, and semi-arid to arid climates. Unfortunately, because of extensive glaciation, geoscientists know very little about the Tertiary climatic conditions that prevailed in the large region that extends from the Maritimes to the high Arctic. This region is much larger in size than the entire United States, and we can surmise, therefore, that the variety of climates that prevail over the U.S. subcontinent today also occurred over the Canadian landmass during the Tertiary.

REVIEW OF OCCURRENCES OF SILVER HALIDES AND THEIR CLIMATIC SETTINGS

Many economic geologists have recognized the relationship between the formation of Ag halide minerals in oxidized sulfide deposits and periods of aridity. In addition to the quoted references at the beginning of this paper, the confinement of Ag halide minerals to arid regions of the world has been noted by Burgess (1911, p. 13), Emmons (1917, p. 255–304), Lindgren (1933, p. 860–868), and Guilbert & Park (1986, p. 89). Some of these investigators noted the presence of chlorargyrite in regions with slightly moister climates than semi-arid conditions, but occurrences of the much less soluble bromide, iodide, and bromide–iodide minerals are almost exclusively confined to arid and semi-arid regions.

A survey of the relative proportions of halide minerals in metallogenic provinces shows that the bromide and iodide minerals are concentrated in deposits restricted to extremely arid environments [*e.g.*, the

Sleeper (Saunders 1993), Tonopah (Burgess 1911), and Wonder (Burgess 1917, Young 1918, Lindgren 1918) deposits in the Nevada desert; the Dusty Mac deposit (Western Miner 1981) and Exposed Treasure mine (Emmons 1917) in the Mohave desert, California, the Lake Valley deposits (Genth & von Rath 1885) of New Mexico, the Chanarcillo (Whitehead 1919) and Caracoles (Boyle 1968) mining districts in the Atacama desert, Chile, the Djelambet, Dzhezkazgan, and Maikain deposits (Chukhrov 1940) in central Kazakhstan desert region, the Gai pyrite deposits of the southern Urals, Russia (Sergeev *et al.* 1994), and the Broken Hill (Mason 1976), Teutonic Bore (Nickel 1984), and Cobar (Rayner 1969) deposits in the arid interior of Australia]. Most of these have been developed primarily as bonanza secondary Ag halide – native Ag deposits, the primary ores generally being of much lesser economic importance. Surrounding these extremely dry regions, oxidized ore deposits in semi-arid fringes generally contain mostly chlorargyrite, with few occurrences of Ag bromide–iodide minerals. In contrast, for temperate climatic areas surrounding Ag halide provinces, such as the Great Basin region of North America, the oxidized sulfide deposits generally contain only native silver, Ag sulfosalts, and secondary argentite as the Ag ore minerals (Emmons 1917, Lindgren 1918, Guilbert & Park 1986). This is also true of mineral deposits in small alpine regions within the arid Great Basin (Emmons 1917), where relatively moist alpine climates have existed.

The Ag halide minerals, mainly chlorargyrite, form in high-altitude arid regions such as the Potosi Sn–Ag metallogenic province of Bolivia and the Tintic polymetallic province of Utah (Emmons 1917).

Further evidence of the restriction of the Ag halide minerals to arid regions can be gleaned from examination of oxidized sulfide zones located in regions where Tertiary climates are known or suspected of being temperate or tropical, with varying degrees of rainfall. Supergene deposits formed over sulfide deposits in temperate regions are largely devoid of Ag halide minerals, most certainly so in tropical climates. Thus, in the rich Ag–Pb veins of Keno Hill – Galena Hill, Yukon, where oxidation exceeds depths of 100 meters and the late Tertiary climate was largely temperate (Tarnocai & Schweger 1991), many secondary minerals of Ag, Pb, As, and Sb are developed, but no Ag halides (Boyle 1965). The Teutonic Bore gossan deposit in the Central Arid Basin of Australia (Nickel 1984) and the Murray Brook deposit in the Bathurst region of New Brunswick (Boyle 1995) are both massive sulfide Cu–Pb–Zn–Ag deposits with very similar primary mineralogy and geology, but their oxide zones have formed under contrasting climatic conditions. The Murray Brook oxide zone formed under warm, moist temperate conditions (Symons *et al.* 1996, Boyle 1995), whereas the Teutonic Bore deposit formed under a prolonged period of aridity (Quilty 1984). The Teutonic Bore deposit contains the full complement of Ag halide minerals, and is especially rich in iodargyrite; the Murray Brook oxide zone is devoid of any Ag halide minerals or other secondary minerals (carbonates, silicates) commonly associated with dry climates.

Although there are Ag halides in oxidized zones of polymetallic deposits in the Harz and Erzgebirge regions of Germany (Maqua 1983, von Hoppe & Damaschun 1986) and the Krusne Hory region of the Czech Republic (Boyle 1968), their occurrence in metallogenic provinces of central Europe is very rare. Oxidized sulfide zones in Germany and Czech Republic are most likely preglacial in origin. Studies of Tertiary regoliths and sediments in this region (*e.g.*, along the Rhine and Loire valleys) indicate a general overall subtropical climate, with distinct periods of aridity in the Eocene and Pliocene (Wang 1951, Schwarzbach 1968, Staeblein 1972). Given the extreme diversification in climatic zones (tropical to desert) that can occur over a landmass largely characterized as subtropical (*e.g.*, central Africa today; Tertiary central Europe), it is highly probable that arid microclimatic regions existed locally over central Europe during the Tertiary. One such region in Europe that is arid even today is the silver deposit region of Hiendelaencina, Spain (Calvo & Sevillano 1992). Here, the full complement of Ag halide minerals (chlorargyrite: "plata cornea – horn silver"; bromargyrite: "plata verde – green silver"; and iodargyrite) occur with many other secondary minerals, mostly Ag–As–Sb–S and Cu–S compounds. The relative abundance of the Ag halide minerals at Hiendelaencina decreases significantly in the order presented above, indicating that extreme periods of aridity, such as occurred in parts of central U.S. and the Atacama Desert region of Chile, where iodargyrite is relatively more abundant, did not occur in central Spain during oxidation of the Hiendelaencina deposits.

In the deep-sea marine environment, chlorargyrite, associated with atacamite and complex Cu–Pb–Ag sulfosalts, has been discovered in the oxidized portions of black smoker sulfide deposits on the Axial Sea Mount and Explorer Ridge (I. Jonasson, pers. comm.; Hannington 1993). Iodyargyrite has not yet been found in this environment. The solutions in these deposits are probably supersaturated with respect to Ag and Cl (and possibly Br and I), and formation of Ag halides can be expected. It is highly unlikely that these minerals would survive later diagenetic processes, since primary Ag halide minerals have never been found in sulfide deposits.

FORMATION AND HABIT OF SILVER HALIDE MINERALS

Silver forms three end-member minerals with the halides Cl, Br, and I: chlorargyrite (AgCl, formerly cerargyrite), bromargyrite (AgBr, formerly bromyrite), and iodargyrite (AgI, formerly iodyrite). There is no F equivalent, since AgF is extremely soluble. There would appear to be complete solid-solution between chlorargyrite and bromargyrite, and limited solid-solution between chlorargyrite and iodargyrite, and between bromargyrite and iodargyrite, resulting in a confusing array of minerals under the generic name "embolite" with prefixes chlor-, iod-, and brom-. Boyle (1968) has indicated that the Ag halide group of minerals should more appropriately be given names such as bromian iodian chlorargyrite, chlorian bromian bromargyrite, *etc.*

'Silver iodide crystallizes in both the hexagonal (iodargyrite: common) and isometric (miersite: very rare) systems. Miersite has been found only in the Broken Hill (Australia) and Bisbee (Arizona) deposits, and is metastable unless it contains a small proportion of Cu ions (Williams 1990). Three other non-Ag-bearing halide minerals are commonly found with the Ag halides, namely marshite, CuI, which forms a solid-solution series with miersite, nantokite, CuCl, and calomel, HgCl. Like the Ag halides, all three are found only in oxidized zones formed in arid climates.

The approximate solubilities of the Ag halide minerals are as follows: AgCl (8.9×10^{-4} g/L), AgBr (8.4×10^{-5} g/L), and AgI (2.8×10^{-6} g/L). Despite these observed solubilities (in deionized water), the order of precipitation of the Ag halide minerals, as deduced from various zoning relationships in deposits (Burgess 1911, 1917, Whitehead 1919, Lindgren 1933), is reversed (AgCl > AgBr > AgI). Three main factors account for this unexpected reversal: a) chloride is much more abundant than Br and I, and the solubility of AgCl increases more rapidly than AgBr and AgI with increasing temperature; thus after initial infiltration, warm, near-surface waters will become saturated with AgCl, and with further descent, chlorargyrite will precipitate owing to lowering of groundwater temperatures and oversaturation, b) both AgBr and AgI are more soluble in alkali chloride solutions, thus requiring more Br and I to enter solution to reach solubility limits for bromargyrite and iodargyrite (Emmons 1917), and c) the ferric ion exerts a much stronger oxidizing effect on Br^- and I^- (with formation of Br_2 and I_2) than Cl^-, thus lowering the concentration of bromide and iodide ions that can complex with Ag (Knopf 1918).

A distinct vertical zonation of Ag halide minerals has been noted for those deposits that have been studied in detail. For the Tonopah deposit in Nevada (Burgess 1911) and the Chanarcillo silver camp of Chile (Whitehead 1919), chlorargyrite is located near the surface, and gives way with depth to bromargyrite and, finally, to iodargyrite. Transitional "embolite"-type minerals [Ag(Cl,Br,I)] form throughout the oxidized zones. The Ag halide minerals can persist in oxidized sulfide zones to well over 500 meters in depth.

Perhaps the most cogent indicator linking the formation of Ag halide minerals to arid regions that have experienced high rates of evaporation and salination is the relationship between sources of the halides and the precipitating environment. Penrose (1894), Burgess (1911, 1917), and Emmons (1917) have noted the close proximity between the Ag halide oxide deposits and the formation through time of salt lakes in regions of New Mexico, Nevada, Utah, and Arizona. These areas were once covered during the early Tertiary by numerous large bodies of water, which gradually dried up, resulting in a large supply of halide ions to groundwater oxidation systems. For the Chanarcillo Ag halide deposits in the Atacama Desert, Chile, Whitehead (1919) suggested a windborne source off the Pacific Ocean for the halides, with evaporative concentration at the surface. Presumably these salts would move down into the supergene zone during the few periods of precipitation in this region to form concentrated alkali salt solutions containing dissolved Ag. The Ag halide minerals associated with Australian deposits such as Broken Hill, Teutonic Bore, and Cobar also are located in areas of extensive development of saline basins and a long period of Tertiary aridity.

OCCURRENCE OF IODARGYRITE IN TILLS OF THE CHIBOUGAMAU – CHAPAIS REGION

Iodargyrite has been found in heavy-mineral concentrates collected during a till exploration program covering a large shear-zone structure south of Chapais, Quebec (Fig. 1). Till cover in this region is quite thick (up to 40 m), and no *in situ* remnants of the preglacial weathered zone have been found. Three main areas where the mineral is concentrated within the survey region have been outlined (areas 1–3, Fig. 1). Approximately 1200 heavy-mineral samples have been obtained from the tills of this area using tabling, super panning, and heavy liquid separation. Portions of half of these heavy mineral separates, distributed over the entire area, were mounted on stubs and examined using secondary and back-scatter techniques with a scanning electron microscope (SEM). Approximately 10% of the samples contain iodargyrite. Owing to the small grain-size of the iodargyrite (<10 μm) and its friable nature, attempts to obtain polished mounts in epoxy for quantitative chemical analysis were unsuccessful. However, slow counting of flat crystal faces of some the larger iodargyrite grains allowed reasonable semiquantitative analyses with regard to Cl and Br contents.

Iodargyrite occurs as: a) single and aggregate crystals on surfaces and in voids of gold grains (Fig. 2a), b) encrustations on gold grains (Fig. 2b), and rarely, on limonite grains, and c) individual loose grains within the heavy-mineral concentrates. The gold grains with which the mineral is associated are commonly "amoeboid" in form, typical of hydrosol grains of gold formed in laterites or gossans over auriferous mineralization (Fig. 3a). The mineral may be present as rosettes on highly corroded grains of gold (Fig. 3b), but generally it is present as dispersed individual hexagonal crystals attached to (Fig. 3c) and "impregnating" gold (Fig. 3d). Crystals of secondary gold are occasionally found precipitated on individual grains of iodargyrite (Fig. 3c). Goethite commonly forms as crusts on crystals and encrustations of iodargyrite. Loose crystals of iodargyrite in the concentrates generally display a

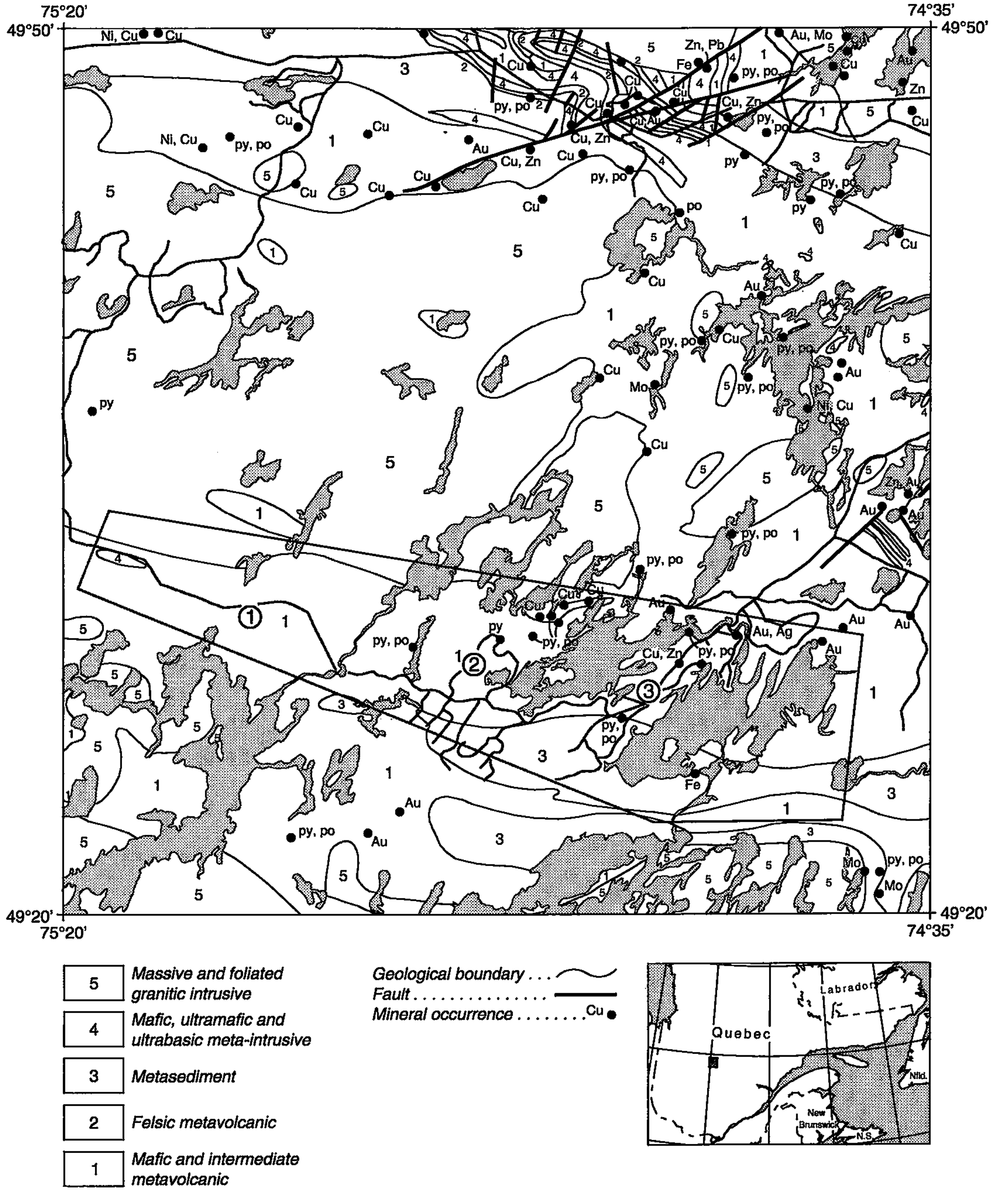

FIG. 1. Location and geology of till-prospecting survey in the Chibougamau – Chapais area of central Quebec. Locations 1, 2 and 3 represent sites in the survey area where iodargyrite has been found, associated with gold in tills.

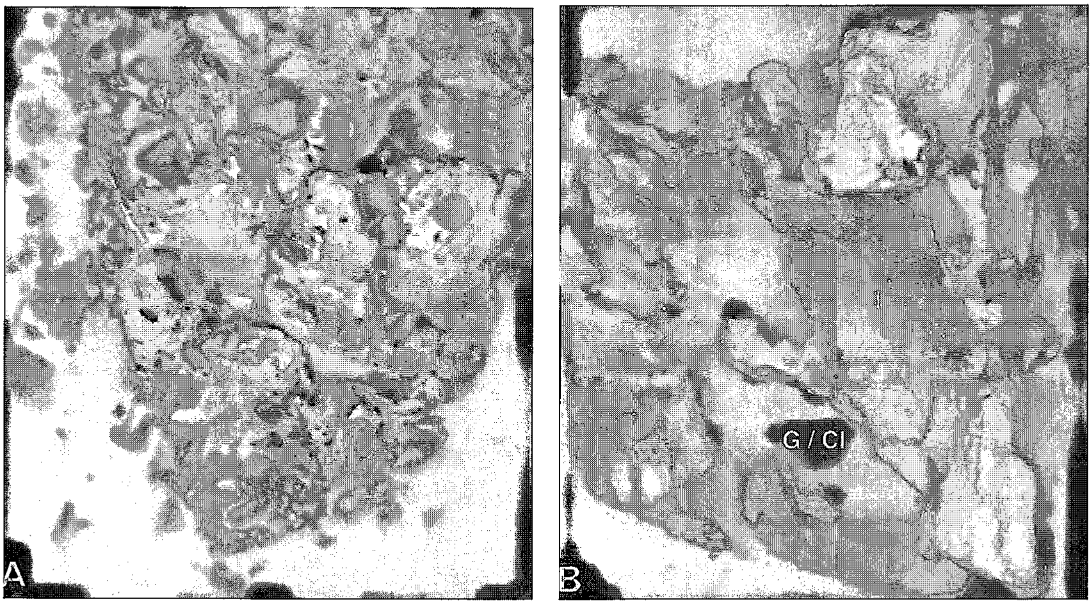

FIG. 2. Two main forms of iodargyrite associated with gold grains in tills of the Chibougamau – Chapais region: A) single and aggregate crystals on surfaces and in voids of gold grains, B) encrustations (aggregates of fine crystals) of iodargyrite (I) on gold grains with associated goethite (G) and clay (Cl) minerals. Scales: 1 cm = 4 µm in A, 6 µm in B.

hexagonal tabular habit, with the pronounced hemimorphism characteristic of this mineral (Kraus & Cook 1909). Individual crystals rarely exceed 10 µm in size.

Chemically, all of the grains examined display an almost pure AgI composition on energy-dispersion spectra. It is possible, however, that Ag(I,Br) minerals may be present, since fine till fractions rich in gold are also anomalous in bromine.

In addition to gold, other secondary minerals associated with iodargyrite include kaolinite, massive to vesicular goethite, and "limonite dice" (pseudomorphs after pyrite). The primary heavy minerals associated with bedrock mineralization include euhedral to subhedral pyrite and, more rarely, siderite and ankerite. In a few cases, iodargyrite was found attached to grains of pyrite. Concentrations of pyrite grains in the tills represent downcutting of the supergene sulfide zone of the Tertiary oxidation profile in this region. In other oxidized deposits, such as Chanarcillo and Tonopah, iodargyrite is more concentrated in the lower oxide and underlying supergene sulfide zones, where it is present as crystal masses and coatings on supergene sulfides, mainly pyrite and Ag sulfosalts.

Chlorargyrite was not identified in any of the samples of the Chibougamau – Chapais study area, and the presence of bromargyrite is only suspected from the anomalous levels of bromine in tills associated with high concentrations of gold. Absence of chlorargyrite may be related to the depth of glacial erosion and the fact that iodargyrite is generally found at the deepest levels of the oxidation zone. The upper zones were probably subjected to cyclical advances of ice; material comprising them may have been diluted and transported farther to the south. Many of the heavy-mineral samples from this area contain large concentrations of euhedral grains of pyrite, suggesting glacial erosion down to at least the supergene sulfide zone of the weathered profile. Allard & Cimon (1974) have argued for minimal glacial erosion in the Chibougamau – Chapais region; the preservation of large concentrations of secondary minerals in tills, and other features of weathering mentioned below, support their hypothesis.

EVIDENCE FOR PREGLACIAL ARIDITY IN THE CHIBOUGAMAU – CHAPAIS REGION OF QUEBEC

A compilation of preglacial weathering profiles that have been preserved in the Quebec Precambrian and Quebec – Northern Maritime Appalachian regions shows three predominant areas where Tertiary climatic conditions can be studied: a) the Labrador Trough area (A, Fig. 4), b) the northern Appalachian – St. Lawrence River region (B, Fig. 4), and c) the Chibougamau to Val d'Or region (Abitibi Subprovince), stretching into Ontario (C, Fig. 4).

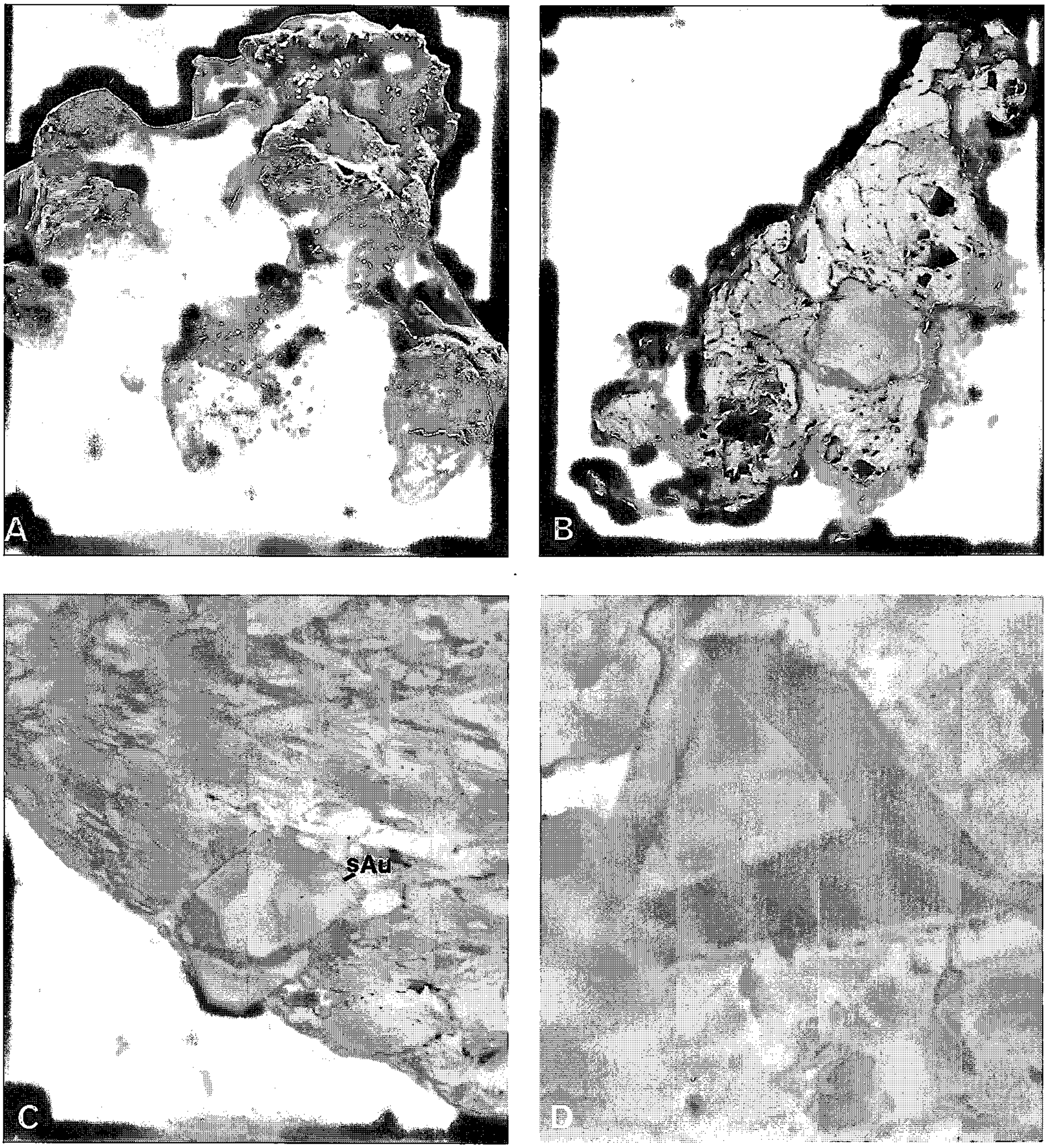

FIG. 3. Crystal habits and relationship of iodargyrite to both primary and secondary forms of gold. A) Iodargyrite crystals growing on "amoeboid" gold typical of hydrosol gold that forms in laterites or gossans over auriferous mineralization. The grain has been abraded during glacial transport. Iodargyrite crystals on abraded surfaces have been removed, whereas crystals in voids within abraded areas (*e.g.*, far left) remain. B) Rosette of iodargyrite crystals on gold grain with associated goethite. Angular voids in gold are probably pyrite casts. C) Hexagonal crystal of iodargyrite with secondary growth of gold (sAu). D) Iodargyrite crystal impregnating gold grain; overlapping gold on crystal may be secondary. Scales: 1 cm = 20 μm in A, 10 μm in B, 5 μm in C and 1.5 μm in D.

The Labrador Trough, with its rich iron-formations, has undergone weathering (silica leaching) and oxidation from at least the Cretaceous (Dorf 1959, Gross 1968). The zone of complete oxidation (and benefaction) of the iron-formation in this region exceeds 200 meters in depth. The bodies of secondary limonite–hematite display similarities to both tropically weathered iron-formation and arid weathering profiles

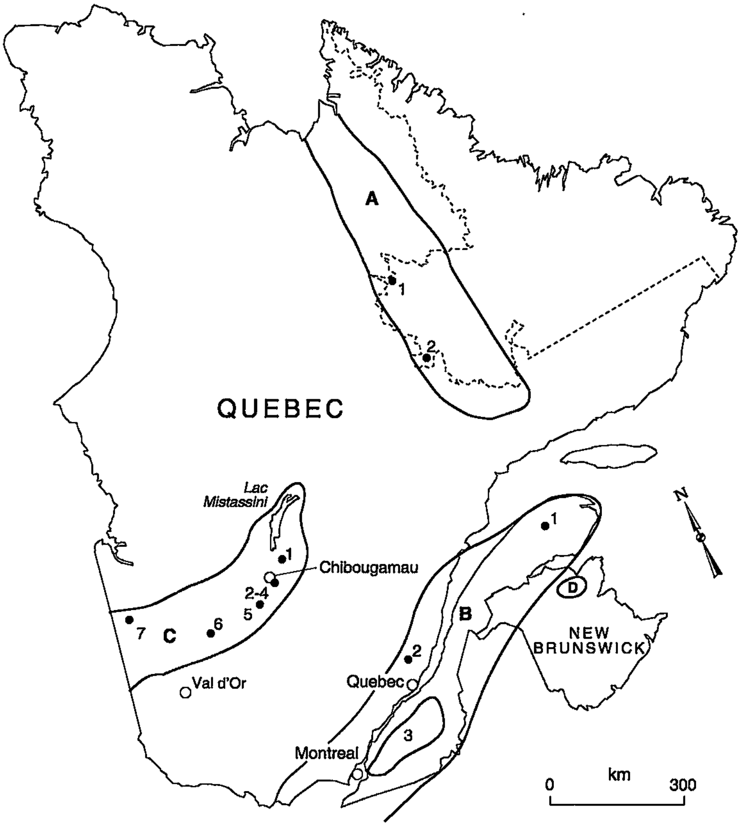

FIG. 4. Map of Quebec and northern New Brunswick outlining the main areas where preglacial weathering profiles have been discovered. (A) Labrador Trough region: 1. Schefferville, 2. Labrador City; (B) Northern Appalachians – Lower St. Lawrence region: 1. Mont Jacques-Cartier region and Gaspé Cu deposits. 2. Château-Richer and Charlesbourg regions, 3. Beauce – Chaudière River gold placer region; (C) Abitibi Subprovince: 1. Icon–Sullivan Cu deposit, 2–4. Copper Rand, Henderson, and other Cu sulfide deposits. 5. Chibougamau – Chapais till survey area (this study), 6. Lac Shortt rare-earth-enriched lateritic carbonatite, 7. Selbaie Cu (chalcocite–covellite) deposit; (D) massive sulfide gossans and Big Bald Mountain area, Bathurst region, New Brunswick.

such as the Tertiary Hammersley-type secondary iron deposits in northwestern Australia.

In the Northern Appalachian – St. Lawrence region, lateritic, saprolitic, and gossanous bedrock profiles occur near Quebec City [saprolites: Lasalle *et al.* (1983), de Kimpe *et al.* (1985)], Gaspé Peninsula [oxidized Gaspé Copper deposit: Ford (1959), saprolites: Cloutier & Corbeil (1986)], throughout the Bathurst mining camp of New Brunswick [massive sulfide gossans: Boyle (1995), saprolite and grus formations: Wang *et al.* (1981, 1982)], and in the Eastern Townships of Quebec [gold-bearing laterites: Shilts & Smith (1986), Smith & Shilts (1987)].

In the Chibougamau – Val d'Or region, major Tertiary weathering profiles are represented by: a) the Cu oxide zone over the Icon–Sullivan deposit, Lac Mistassini (Troop & Darcy 1973), b) deeply weathered (down to 500 m) Copper Rand and Henderson ore deposits of the Chibougamau mining camp, as well as other, smaller deposits (Parrish 1968, Allard & Cimon 1974, Allard 1976), c) lateritization of anorthosite in the Chibougamau area down to hundreds of meters (Allard & Cimon 1974, Allard 1976), d) rare-earth-bearing laterite and saprolite developed over the Lac Shortt carbonatite (Quirion 1989), and, d) the secondary covellite–chalcocite zone at the Selbaie copper deposit

(Sinclair & Gasparrini 1980, Bouillon 1990). Similar environments of deep oxidation in Ontario and the northeastern United States have been described by Moore (1938). In one of these areas, the Cobalt silver camp, oxidation in the Keeley mine is present down to at least 200 meters. Unfortunately, no detailed mineralogical studies were carried out on this deposit to determine presence or absence of Ag halide minerals. The deep oxidation, however, does signify the presence of a very deep water table.

Tertiary profiles in the Northern Appalachians – St. Lawrence region suggest that a subtropical "savanna-type" climate prevailed over this region. The gold-bearing laterites and derived placers are strong indicators of this type of climate. Tertiary profiles at some of the sites in the Chibougamau – Val d'Or region are more indicative of a much drier climate than existed farther to the south, in the St. Lawrence Lowlands. Depths of oxidation at the Copper Rand and Henderson deposits (500 m or more) suggest that the water table in this region was very deep. Weathering of sulfide orebodies to these depths has only been recorded in very dry regions, such as the Great Basin area of the western United States (Burgess 1911, Emmons 1917, Lindgren 1933). The very deep weathering of the Copper Rand and Henderson deposits would suggest that the period of aridity over which they formed persisted for some time. These oxidized zones are very porous, indicating that a considerable amount of material has been carried downward in solution, eventually exiting the system in deep groundwaters. There is no tectonic disturbance of the oxide mineral fabrics in these deposits, suggesting that they probably formed in Tertiary or Cretaceous times.

Further evidence of a period of aridity in the Chibougamau – Chapais region during the Tertiary lies in an explanation for the great expanse and thickness of fine quartzofeldspathic sands of this area, which stretch as far west as the Kapuskasing area in Ontario. Although reworked by glacial processes, these sands may have been derived from windblown desert materials or matrix-weathered zones in semi-arid lateritic terranes. Corestones characteristic of the lower weathering zones of laterites are commonly found in exposed sections of till within the region. In lateritic and saprolitic terranes, the matrix, or exfoliated products of weathering, of these corestone horizons usually consist of quartz grains and clays.

The two main mineralogical indicators of aridity in the Chibougamau – Chapais region are the presence of iodargyrite preserved in tills discussed above and the common occurrence of "limonite dice" in heavy-mineral concentrates. To form pseudomorphs after pyrite requires a very low water-to-rock ratio during oxidation to compensate for a reduction in unit-cell dimensions (pyrite *versus* limonite) and to maximize the retention of Fe. In addition, since the molar volume of pyrite is 23.9 cm^3 compared to 20.8 cm^3 for goethite (constant Fe basis), some introduction of Fe is required for final formation. Limonite dice are abundant in oxide zones of arid regions (Blanchard 1968). The mineralized bedrock underlying the iodargyrite-bearing tills in the Chibougamau – Chapais region contains abundant cubes of pyrite in metasediments. If tropical or temperate conditions prevailed, these formations would simply leave "pyrite casts" in the weathered rock owing to rapid dissolution and mobility of ferrous and ferric ions.

DISCUSSION

On the basis of its confined world-wide distribution in oxidized sulfide deposits formed in arid regions, the presence of iodargyrite in glacial sediments of the Chibougamau – Chapais area of Quebec, together with other indicators of an arid climate, provides cogent evidence of a past arid climate in this region. These indicators include: a) the existence of a deep water table during oxidation of sulfide ore in the Chibougamau copper deposits, b) the abundance of "limonite dice" in glacial tills, indicative of the pseudomorphic replacement of pyrite cubes in bedrock formations under arid conditions, c) the abundance of spongy and corroded grains of gold typical of lateritic terranes, and d) the abundance of possibly desert-derived quartzofeldspathic sand formations.

The exact timing of Tertiary aridity for the Chibougamau – Chapais region is highly conjectural, given the lack of suitable preglacial material for dating. It is known that on a world scale, the late Eocene to middle Oligocene was characterized by some of the warmest global temperatures observed (Shackleton 1978). If the iodargyrite was formed at this time, either aridity persisted throughout much of the late Tertiary, or else the weathering profile was protected by overlying deposition of post-Oligocene sediments that were later removed by erosion. During the Pliocene, the climate in the Canadian Arctic was largely temperate. However, because of the lack of suitable fossil materials, very little is known about Pliocene climate trends over the southern Canadian Shield. Studies of cores from the coastal Atlantic Ocean produce general climatic trends of a semiglobal nature, but these can hardly be extrapolated thousands of kilometers inland to predict regional microclimatic trends. It is conceivable, therefore, that aridity in the Chibougamau – Chapais area may have prevailed in Pliocene times.

ACKNOWLEDGEMENTS

Detailed SEM examinations of the Chibougamau – Chapais heavy-mineral concentrates were performed with the help of David Walker, Mineral Resources Division, Geological Survey of Canada. This work forms part of a broader geochemical study of till being carried out in this region by the author and Marcel

Durocher of Battle Mountain – Hemlo Inc. Reviews of an earlier draft of this paper by Yves Moëlo of the Institut des Matériaux, Université de Nantes, and E.H. Nickel of CSIRO, Division of Mineral Products, Western Australia, and an anonymous referee have helped to further elucidate the author's interpretations.

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Received May 21, 1996, revised manuscript accepted October 6, 1996.