Organic matter and clay anomalies associated with base-metal sulfide deposits

Yvon Héroux, André Chagnon, Martine Savard

Québec Geosciences Center 2700, rue Einstein, C.P. 7500, Sainte-Foy, Québec, Canada, G1V 4C7

Received 1 July 1994; accepted 15 September 1995

Abstract

Organic matter and clay mineral anomalies surround the Polaris, Gays River and Gaspé Mines base-metal sulfide deposits. The Polaris mine, in the Canadian Arctic, is an MVT deposit formed by low temperature solutions (homogenization temperatures, $T_h$: 105–120°C) and is characterized by a zone of pure illite above a kaolinite envelope surrounding the deposit. These clay mineral assemblages are laterally replaced by kaolinite-illite and chlorite-corrensite zones, while the background assemblage in the host rocks is illite-interstratified illite/smectite-chlorite. The organic matter reflectance ($R_o$) shows two trends depending on the permeability and chemical reactivity of the host rock: (1) an increase with depth above the ore zones in the overlying impermeable shaly cap rock. $R_o$ reaches a maximum value of 1.3% above the ore, compared to 0.8% in equivalent country rocks; (2) an anomalous decrease with depth in the mineralized carbonate horizon that hosts the deposit. The Gays River mine, Nova Scotia, is a medium temperature ($T_h$: 250°C) carbonate-hosted deposit associated with the replacement of well-crystallized detrital illite and chlorite by smectite forming a halo around the main ore zone and by kaolinite and chlorite-corrensite within the ore zone. Reflectance and its absolute variability increase in the host rocks toward the ore zone adjacent to the deposit (0.8 to 1.88%) and shows a relatively low $R_o$ in the ore. The economic mineralization at Gaspé Mines, Québec, is a typical high-temperature skarn and porphyry-copper deposit with the concomitant clay mineral alteration assemblages: chlorite-corrensite-illite, smectite-chlorite-illite and almost pure illite with traces of chlorite. The first assemblage is observed within the ore zone and extends slightly outside the porcellanite halo. Smectite is also found near the mineralization, but its limit of occurrence is wider than the chlorite assemblage. The illite assemblage is found outside the chlorite zone and is present as irregular tongues. $R_o$ increases (1.2 to 15%) approaching ore over a lateral distance of 60 km. In the bleached zone, the organic matter exhibits mosaic and degasification textures and isotropic alteration rims with very low $R_o$.

These three deposits, as well as others studied by the authors, are centrally located within thermal aureoles whose size and intensity correlate directly with increasing temperature of formation. The decreasing values of $R_o$ in the ore zones of these deposits and the associated authigenic clay minerals reflect changes in chemical conditions due to precipitation of sulfides and to reaction of the ore and post-ore fluids with host rocks.

1. Introduction

Clay minerals and organic matter disseminated in sedimentary host rocks are reactive components intimately involved in the various thermal and chemical alteration processes affecting the entire sedimentary sequence. Aside from their possible active role in the transportation and precipitation of metals, organic matter and clay minerals are good indicators of the nature of metallogenic events. The thermochemical
reactions leading to the formation of ore alter the chemical equilibrium of the host rock-system within the ore zone and as spent ore fluids move away from the ore zone they react with the host rock to produce zoned alteration halos of the organic matter and clay mineral assemblages. This alteration of organic matter and these clay minerals have been observed within, and around, all base metal sulfides deposits studied by the authors of this paper (Fig. 1): Yava Pb-deposit, Nova Scotia (Héraux et al., 1989); St-Lawrence Lowlands Pb–Zn, Ba showings, Québec (Héraux and Tassé, 1990); Viburnum Trend Pb–Zn district, Missouri (Henry et al., 1992); Reboul Cu, Pb, Zn, Ag, Au showing, Québec (Malo et al., 1990); Acton Vale (Cu) and Upton Cu, Ba, Québec (Chagnon et al., 1992); Pine Point Pb–Zn deposits, Northwest Territories (Héraux and Chagnon, 1994); Gays River Zn–Pb deposit, Nova Scotia (Héraux et al., 1994); Polaris Zn–Pb mine, Northwest Territories (Randell, 1994); Beddiane Zn–Pb deposit, District of Touissit–Bou Beker, Morocco (Bouabdellah, 1994).

The objective of this paper is to show that the nature and the size of the altered zones, defined by organic matter and clay mineral assemblages, are not only of primary geological importance for the modelling of ore-forming processes, but also form easily identifiable targets for exploration purposes that are much larger than the deposits themselves and of the porcellanite-skarn bleached zones and, locally, the dolomite previously used as a guide in the discovery of these three deposits.

2. Geological settings

The choice of the three case studies is based on the occurrences of spectacular anomalies outlined by the organic matter and clay mineral assemblages, in spite of the differences in their geological settings,
their mineralization models and, most particularly, their thermal regimes (Fig. 2).

2.1. Polaris mine

The Polaris mine is located on Little Cornwallis Island in the Canadian Arctic, 133 km east of the North magnetic pole (Fig. 3A). The orebody is a Mississippi Valley-type deposit of 22 million tonnes of 14% Zn and 4% Pb with dimensions of approximately 300 m by 800 m in plan by 40–150 m thick. It is hosted by Middle to Upper Ordovician platform carbonates of the Thumb Mountain Formation (Fig. 3B). The host rocks are dolomitized and form an envelope of up to 100 m around the orebody. Sphalerite occurs as colloform masses suggesting a low temperature regime with fluid inclusion that give temperatures ranging from 105 to 125°C (Anderson and Randell, 1994; Randell, 1994). Stratigraphic reconstruction indicates a maximum depth of burial during mineralization of about 1500 m corresponding to a burial temperature of 60°C, thus, the mineralization must have represented a significant thermal anomaly. Paleomagnetic work (Symons and Sangster, 1992) indicates a Late Devonian age of mineralization. The orebody lies within the N–S-trending Cornwallis fold belt in which early to mid-Paleozoic rocks are folded as a result of basement deformation which produced the boothia Arch (Fig. 3A). Part of this deformation of the overlying Paleozoic rocks is attributed to salt tectonics (Anderson and Randell, 1994; Randell, 1994).

2.2. The Gays River Mine

The Gays River Mine is located 55 km northeast of Halifax, in central Nova Scotia (Figs. 1 and 4A). The orebody contains 2.4 million tonnes of 8.6% Zn and 6.3% Pb. It mainly occupies the northwest flank of a dolomitized carbonate bank that unconformably overlies a basement ridge of the metasedimentary lower Paleozoic Meguma Group. The orebody consists of stratabound sphalerite–galena–barite filling primary pores of the dolostone (low-grade ore) or totally replacing the carbonates (high-grade ore). The Gays River dolostones are overlain by the evaporites of the Carrolls Corner Formation (Visean; Fig. 4B).

The isotopic geochemistry (δ18O, δ13C, 87Sr/86Sr) and fluid inclusion microthermometry suggest mixing of two or more fluids during mineralization, one of which was high temperature (< 250°C) and saline (< 25–30 wt% eq. NaCl) (Kontak, 1992; Savard, 1992; Kontak et al., 1993; Savard and Kontak, 1994; Savard et al., 1994). Dating methods such as apatite fission track analysis (Arne et al., 1990), paleomagnetism (Symons and Sangster, 1992), and K/Ar analyses of micas from basement rock (Kontak et al., 1996) all suggest a broad “apparent” age of ca. 300 Ma (Fig. 2).

The basement ridge that separates the Shubenacadie and Musquodoboit sub-basins (Fig. 4A and 4B) may have partly controlled the nature of the organic matter assemblage; a type III organic matter is particularly abundant in the studied samples from the Gays River area. The vitrinite reflectance values range from 0.8 to 1.31% (Héroux et al., 1994) which corresponds to temperatures in the range 130 to 230°C (calculated from the expression: ln(Ro) = 0.0081Tb − 1.26; Barker and Goldstein, 1990), which is similar to the homogenization temperatures of syn- to post-ore calcites and sphalerite (140–250°C).

2.3. The Gaspé mines

The Gaspé ores are high-temperature skarn and porphyry-copper deposits located near Murdochville, about 600 km northeast ofQuébec City (Figs. 1 and 5A). Combined production and reserves of the skarn
Not all dolostones contain orebody!
Fig. 4. Geological setting of the Gays River mine at the margin of the Shubenacadie and Musquodoboit sub-basins: (A) geological map with the locations of the sampled diamond drill holes (⊕); (B) major stratigraphic units of the sub-basins (after Giles and Boehner (1982)).

orebodies, all zones included, is estimated to be 54 million tonnes with an average grade ranging from 0.7% to 2.95% Cu and from 0.02% to 0.03% Mo. The porphyry orebody contains 230 million tonnes of sulfide ore averaging 0.4% Cu and 0.02% Mo and 34 million tonnes of oxide ore averaging 0.045% Cu (Procyshyn and Bernard, 1990). The deposits are hosted by a Devonian carbonate sequence, the Upper

Fig. 3. Geological setting of the Polaris orebody. (A) Geological map showing the major structural unit, Parry Island fold belt and the Cornwallis fold belt overlying the Boothia Uplift. The mining district shows the location of the orebody, projected at the surface and the diamond drill holes sampled and studied by Randell (1994). (B) Schematic cross-section of the orebody and of the dolostones forming an envelope around the orebody up to about 100 m in width (adapted from Randell and Anderson (1990)).
Gaspé Limestones (Fig. 5B). They are surrounded by a bleached limestone zone and exhibit hydrothermal characteristics typical of porphyry and skarn type deposits. The thermal regime, probably related to plutonic activity in Late Devonian–Early Mississippian time, is estimated to be characterized by temperatures from 370°C to 570°C (Allcock, 1982).

3. Methods

3.1. Sampling

At Polaris, nearly 700 samples distributed over 125 diamond drill holes and outcrops have been analyzed for their organic matter and clay minerals content. The samples are restricted from an area no more than a few kilometers in diameter around the Polaris mine as shown in Randell (1994) (Fig. 3A and 3B). The samples are from the overlying fine siliciclastics of the Cape Phillips Formation down to the carbonate and shaly units of the Bay Fiord Formation, with most taken from the nodular carbonates of the Upper Thumb Mountain Formation. At Gays River, 61 samples from fifteen localities, extending 25 km westward and 35 km eastward from the orebody were used (Fig. 4A). This sampling was performed as part of a regional study of diagenesis (Savard, 1992). The samples are from the carbonate mounds of the Gays River Formation which is composed of algal bindstones, coralgal bafflestones (calcarenites/calcirudites) with mollusc packstone and wackestone textures. In the Murdochville area, 96 samples from nine diamond drill holes located within and around the Gaspé Mines deposits were studied (Fig. 5C). They are from the Upper Gaspé Limestones including Indian Point, Shiphead and Forillon Formations. These formations mainly comprise limestones, cherty limestones and calcareous mudstones and siltstones. Skarn and porcellanite (baked silicified limestone) samples were also analyzed.
3.2. Analytical techniques

Three major categories of data were used in this study: organic matter petrography, organic geochemistry and clay mineralogy. The procedure used in this study for obtaining organic matter concentrates, polishing the transparent strewn slide mounts of kerogen and conducting the $R_o$ measurements are de-
scribed by Henry et al. (1992). Polished slabs of rock and polished standard petrographic thin sections were also prepared to examine the relationship between solid bitumen and ore. Fossils with organic skeletons (zooclasts) are the major components of kerogen in the pre-Carboniferous host rocks and can be used for $R_o$ studies (Bertrand, 1990). All of the reflectance values at the Polaris mine and part of the reflectance values at Gaspé Mines are measured on zooclasts and solid bitumen. The reflectance values of zooclasts can be converted to vitrinite reflectance equivalents (Bertrand, 1990). Only the measured and calculated values of vitrinite reflectance are used in this paper. Although solid bitumen can be used for $R_o$ studies, the limitations of its use have to be taken into account (Bertrand, 1993).

Clay mineral assemblages were identified by X-ray diffraction and scanning electron microscopy (SEM) using methods described in Héroux and Chagnon (1994) and Chagnon and Desjardins (1991). These assemblages were determined in the same samples used for organic matter studies as well as other samples having no organic matter.

4. Results

4.1. Polaris mine

Data from 8 diamond drill holes, out of the 125 mentioned above, were chosen for the study presented in this paper. From these 8 diamond drill holes a cross-section of the orebody extending 1 km south of the mine was constructed and is shown in Fig. 6A. The clay mineral assemblages are strongly zoned around the Polaris orebody (Fig. 6A, 6B). Six clay mineral assemblages have been detected: (1) the assemblage illite > interstratified illite/smectite > chlorite is observed mainly in the Cape Phillips Formation. This is most probably a normal, unaltered sedimentary assemblage because it is found where no other signs of alteration are observed and it is locally replaced, in part, by other assemblages or by silica; (2) the assemblage illite > chlorite > interstratified illite/chlorite is restricted to the Thumb Mountain Formation and is likely the background clay mineral assemblage for this unit; (3) the assemblage (chlorite + corrensite + chlorite/smectite mixed layer) > illite > interstratified illite/smectite referred to as the chlorite–corrensite assemblage, is found predominantly in the Irene Bay Formation and less commonly in the upper part of the Upper Thumb Mountain Formation and Cliff Member at the base of Cape Phillips Formation. Corrensite and most of the chlorite are authigenic minerals in these units; (4) the pure illite clay facies can also show traces of chlorite but in this assemblage the illite is always well crystallized and contains few swelling layers. It has been found only over the main orebody in the Cliff Member, Irene Bay Formation, and upper part of the Upper Thumb Mountain Formation; (5) the fine kaolinite assemblage contains illite and kaolinite with, locally, traces of chlorite. The illite to kaolinite ratio is about the same in the less than 2 micron fraction as in the 2–16 micron fraction. It is most common in the Thumb Mountain Formation, but it is also observed in Bay Fiord, Cape Phillips and Irene Bay Formations; (6) the coarse kaolinite assemblage is the richest in kaolinite. It contains kaolinite and illite, with some traces of chlorite but usually in lesser amounts than in the fine kaolinite assemblage. The kaolinite to illite ratio is always much higher in the 2–16 micron fraction. Scanning electronic microscopy reveals that this kaolinite is present as large vermicules filling the pore spaces in the dolostones. It is found in the Thumb Mountain Formation, adjacent to the mineralization.

The coarse kaolinite facies is restricted to within 250 meters of the ore at the mine property. This is overlain by a pure illite facies which ends abruptly against the impermeable shales of the Cape Phillips Formation, which contain an illite–illite/smectite facies assumed to be a normal, sedimentary clay assemblage. The clay mineral assemblages in the carbonate host rock crosscut lithostratigraphic units. Away from Polaris mine, the Irene Bay Formation and the upper part of the Thumb Mountain Formation are characterized by a chlorite–corrensite assemblage, which thickens away from the mine, cutting across the Irene Bay/Thumb Mountain lithological contact. Most of the Thumb Mountain Formation contains a fine kaolinite for at least 1 km away from the orebody.

The organic matter in the Cape Phillips, Irene Bay and Upper Thumb Mountain Formations consists

primarily of solid bitumen and zooclasts. Graptolites are most abundant in the Cape Phillips Formation, chitinozoans and scolecodonts predominate in the Irene Bay Formation and the top of the Upper Thumb Mountain Formation, while hydrozoans mainly occur in the Upper Thumb Mountain Formation. Well structured alginate occurs in the Vr-marker near the contact between the Upper and the Lower Thumb Mountain Formation. Kerogen in the Tetradium Zone of the Upper Thumb Mountain Formation and the Lower Thumb Mountain and Bay Fiord formations mainly consists of amorphous organic matter. This organic matter does not give reliable reflectance results.

The $R_\theta$ curves near the ore typically show higher values in the impermeable Cape Phillips and Irene Bay formations than in the permeable Cliff Member and Thumb Mountain Formation (Fig. 6A, 6B). Above the orebody, the organic matter of the Cape Phillips Formation exhibits an $R_\theta$ value of 1.35%, which is twice as high as the expected background value ($R_\theta = 0.7\%$) for this lithostratigraphic unit in the remote diamond drill hole 1 km south of the orebody (Fig. 6A). The $R_\theta$ values from the Irene Bay Formation are also higher, by about 50%, above the ore zone, with decreasing values away from the ore. On the other hand, within the ore deposit, the $R_\theta$ data from the Upper Thumb Mountain Formation shows values that are 0.3% lower than the expected $R_\theta$ background (Fig. 6A, 6B). This apparent “suppressive” effect is also outlined by decreasing $R_\theta$ values down the diamond drill hole. The difference between the lowest and the highest $R_\theta$ values, occurring respectively near the bottom and the top of a same diamond drill hole, is twice the lowest value. This behavior of $R_\theta$ is illustrated by the two curves in Fig. 6B showing the evolution of $R_\theta$ at the base of the Cape Phillips Formation and at the base of the Upper Thumb Mountain Formation. In the impermeable Cape Phillips Formation, the increasing $R_\theta$ values are very likely the result of the thermal event related to the mineralizing fluid and, in part, related to the exothermic sulfate reduction by organic matter present in the underlying permeable carbonate rocks which hosts the ore. In this latter unit, the fluids resulting from sulfate reduction and sulfide formation ($CH_4 + M^{2+} + SO_4^{2-} \rightleftharpoons MS + H^+ + HCO_3^- + H_2O$), may have caused hydrogenation of the organic matter and a decrease in $R_\theta$ values. The increasing distance between the two $R_\theta$ curves respectively at the base of the Cape Phillips and at the base of the Upper Thumb Mountain formations (Fig. 6B) indicates a more effective alteration process of the organic matter towards the ore. This anomaly is manifested in two ways: (1) an increase in $R_\theta$ values in the impermeable Irene Bay and Cape Phillips formations, above the ore, with a maximum $R_\theta$ of 1.3% compared to 0.7% for equivalent unaltered country rocks and (2) a decrease in $R_\theta$ for organic matter in the mineralized portion of the permeable Thumb Mountain Formation, with a minimum $R_\theta$ of 0.5% compared to 0.8% for its equivalent unaltered country rocks. High $R_\theta$ values outline a thermal anomaly at Polaris which is 2 km in diameter and extending at least 100 m into the Cape Phillips Formation.

The relationships between clay mineral assemblages, $R_\theta$ anomalies, and mineralization at Polaris show that organic matter and clay minerals are very likely related to Zn–Pb mineralization. The superposition of organic matter and clay mineral aureoles around the orebody implies that organic matter alteration and clay mineral zoning can be used as a tool for exploration. The size of the alteration halos defined by these techniques are much larger than that outlined by the dolostone alteration surrounding the ore zone (Fig. 6A, 6B). The illite cap is restricted to the orebody and the dolostone extends only 100 m from the orebody but the edge of the coarse kaolinite and that of the organic matter alteration are respectively, about 500 m and 1000 m in width.

4.2. Gays River Mine

As at the Polaris mine, the ore and the host rock at Gays River are characterized by a well defined zoning of clay mineral assemblages and a concomitant anomalous trend of $R_\theta$ values. Two composite cross-sections east/west and north/south show the behavior of $R_\theta$ and clay mineral assemblages relative to the ore deposit (Figs. 7 and 8) (Héroux et al., 1994). A much more detailed study of the alteration at Gays River is currently in progress and part of the results based on data from approximately 185 samples from 41 diamond drill holes and 5 outcrops have been presented by Saint-Antoine et al. (1994).
Four clay mineral assemblages have been identified at Gays River: (1) the assemblage illite > chlorite in which these minerals show a very high degree of crystallinity. It is more abundant outside the ore zone and is most probably a detrital unaltered clay mineral assemblage; (2) the assemblage smectite-interstratified illite/smectite-illite is referred to as the smectite zone. Although smectite is not always the dominant mineral, it is always present. It is most abundant at the rim of the ore zone (Fig. 7) and under the scanning electron microscope it shows morphologies and textures typical of its authigenic origin ("corn flakes" morphology); (3) the assemblage illite > kaolinite is found only in the ore zone and is referred to as the kaolinite zone; (4) the assemblage corrensite-interstratified chlorite/smectite-chlorite-illite shows various proportions of these minerals. It is only found in the ore zone. Two major observations regarding these assemblages should be noted (Fig. 7). The authigenic smectite is particularly abundant at the rim of the orebody and decreases outward and also toward the center of the most mineralized zone where kaolinite and corrensite are present. Secondly, beyond the altered areas, the clay mineral assemblage is made up of well-crystallized illite and chlorite. Such changes in clay mineral assemblages in a...
homogeneous carbonate platform can be explained neither by sedimentological changes in their palaeoenvironments nor by a normal burial diagenetic evolution.

The kerogen at Gays River is composed of amorphous organic matter, unidentified zooclasts, and macerals of the vitrinite and inertinite groups. Solid bitumen is also present. The amorphous organic matter exhibits lamellar structures suggesting an algal origin (lamalginite). Some unidentified zooclasts are present as empty to partly filled ball-shaped structures of organic matter a few tens of microns in diameter. The specimens nearly devoid of bitumen are similar to sporinite both in shape and $R_o$ values, whereas, the bitumen-filled specimens look like globules of organic matter. Vitrinite and spherical-shaped bodies of organic matter are abundant at the mine site and disappear eastward and westward from the ore where they are replaced by increasing amounts of amorphous organic matter. Several localities in the center of the study area are devoid of amorphous organic matter, alginite and organoclasts suggesting a change in facies toward the mine site.

The variation in $R_o$ values along two cross-sections is illustrated in Fig. 8. In each cross-section, the lower curve represents the trend in mean $R_o$ values measured on randomly oriented vitrinite and undifferentiated organoclasts-vitrinite. In each cross-section, the upper curve is the trend of higher $R_o$ values (upper limit of the range) measured for the same groups of organic matter. Because the organic matter in the area does not show significant bireflectance but an unusually high standard deviation in $R_o$, we believe that the discrepancy between these two curves reflects a local organic matter alteration process. Hence, if two vitrinite fragments from the same locality have a significantly different $R_o$, one might suspect that this is not related to thermal alteration but to chemical alteration. In this regard three aspects are worth noting: (1) apart from locality "D", the highest $R_o$ values are from the mine site; (2) the greatest absolute variability of the $R_o$ increases toward the deposit; (3) outside the mine site, apart from locality "D", the highest $R_o$ values (1.7%) are associated with mosaic textures (locality "E" in Fig. 8). This thermal alteration corresponds to temperatures near 235°C (calculated from $R_o$ using the expression: $\ln R_o = 0.0081 T_h - 1.26$; Barker and Goldstein, 1990), which are comparable to the homogenization temperature of 250°C from inclusions in sphalerite (Ravenhurst et al., 1989; Kontak, 1992). These high temperatures might be responsible for the partly dehydrated smectite from the southern area ("E" on Fig. 7).

4.3. Gaspé Mines

The host rocks and the ore at Gaspé Mines display a complex zonation of clay mineral assemblages and a spectacular increase in $R_o$. The most striking
feature observed at Gaspé Mines is the extent of the thermal anomaly, as shown by $R_o$, that is much wider than those shown by the clay mineral assemblages and organic matter textures. The $R_o$ is measured from unidentified organic matter, vitrinite, chitinozoans, hydrozoans and solid bitumen. $R_o$ increases from 1.2 to 15% over a lateral distance of 60 km from the ore (Fig. 9). The thermal anomaly limit that is shown in Fig. 10A is the last sharp increase of $R_o$ in this trend. From 1 to 3 km from the deposits and in the visible bleached zone, the organic matter exhibits mosaic and degasification textures and isotropic alteration rims with very low $R_o$.

Five clay mineral assemblages are observed in the area:

1. The assemblage illite > chlorite is most probably chemically unaltered. It could have been heated during the mineralization process, but there is no evidence of chemical alteration. It is found away from the deposits and is laterally or vertically replaced by the other clay mineral assemblages in the mine vicinity.

2. the assemblage illite > chlorite is found along certain horizons, interbedded with the “normal” illite > chlorite assemblage. It is almost pure illite and is always observed outside the chlorite zone.

3. The assemblage chlorite–illite-interstratified chlorite/smectite and/or illite/smectite is divided into several sub-zones. It contains several types of chlorite in various proportions. The assemblage is present in the ore zone but it is also observed outside the main orebody.

Fig. 10. Distribution of clay mineral assemblages and the characteristics of organic matter at Gaspé Mines: (A) schematic cross-section; (B) schematic view in plan of the projection at surface of the clay mineral assemblages shown in Fig. 10A.
(4) The assemblage smectite-interstratified illite/smectite-illite-chlorite could also be divided
based on the proportions of clay minerals. It is referred to as the smectite assemblage; however,
smectite and illite are generally the most abundant clay phases. It is generally found at the bottom of the
sequence and also interbedded in the chlorite zone.
Its distribution is highly asymmetrical towards the north of the section (Fig. 10A, 10B).

(5) the “no-phyllosilicate” assemblage contains only quartz, feldspar and metasomatic minerals such
as tremolite, garnet, amphibole, etc. It is found in the very center of the study area with an asymmetry
similar to that of the smectite zone.

The thermal regime that accompanied the emplacement of this high-temperature skarn and por-
phyry-copper deposit is very likely responsible for the regional pattern of the \( R_0 \) values which increase
from 1.2 to 15% approaching ore over a lateral distance of 60 km. In the bleached zone, the organic
matter exhibits mosaic and degasification textures typically found in the chitinoids. The outer limit
of organic matter with mosaic textures coincides with the limit at which authigenic clay mineral as-
semblages are observed (Fig. 10A, 10B). This is most probably the outer limit of penetration by hy-
derothermal fluids in the host rock.

5. Discussion and interpretations

In the three deposits considered in this paper, authigenic clay minerals are zoned laterally and are
clearly related to the associated orebody. Changes in slope of the \( R_0 \) curves frequently coincide with
changes in the clay mineral assemblages. The conceptual model used to explain these changes assumes
that the formation of each base-metal sulfides de-
posit is the result of sulfate reduction by organic
matter as metal-bearing brines encounter gaseous
hydrocarbons (Anderson, 1991). At Polaris, several
aspects of MVT mineralization can be adequately
addressed based on the types of clay mineral assem-
blages and organic matter studies described above.
The similar \( R_0 \) evolution pathways of zooclasts and
solid bitumen indicate that these two forms of or-
ganic matter have been simultaneously altered. The
alteration occurred after the sequence had reached a
burial depth of 1–2 km, sufficient to generate oil-bit-
tumen. This conclusion is in accordance with other
studies of the Polaris deposit (Anderson and Randell,
1994) and the Gays River deposit (Savard, 1992). At
Polaris, the zonation of the clay mineral assemblages
forming a halo around the orebody results from
reactions induced by post-ore fluids circulating later-
ally under the cap rock and originating from the ore
zone. This post-ore fluid, which has a composition
different from the ore fluid, reacts with the host
rocks until a new equilibrium is reached with respect
to the mineral phases present. Fluid composition, and
hence equilibrium assemblages, will vary with dis-
tance from the ore and produce the observed zoning
of authigenic clay mineral assemblages together with
the alteration aureoles defined by the reflectance
values and the optical textures of organic matter. The
nature of specific clay mineral assemblages is con-
trolled by key parameters of the fluid, particularly
major cation activities and pH, as well as the rock-
fluid ratio. The evidence presented here suggests that
the chemical alteration occurred when fluids encoun-
tered organic matter in the more permeable units. In
the impermeable cap rock, overlying the orebody,
post-ore hydrothermal fluids did not react with or-
ganic matter and the increasing \( R_0 \) values observed
in this unit are the result of thermal heating by
conduction. The decreasing reflectance with depth
toward the orebody is most likely related to chemical
alteration. On the other hand, the higher and increas-
ing reflectance values, toward the orebody, of the
organic matter sampled at the base of the imperme-
able shaly cap rock, overlying the deposit, are very
likely related to thermal alteration (Héroux et al.,
1994). These chemical and thermal alteration pro-
cesses, tentatively illustrated hereafter, can be aug-
mented by a physi-sorption mechanism that lowers
\( R_0 \) values (Bend, 1992). One possibly significant
source of thermal energy in such an ore-forming
system is the exothermic reduction of sulfate (SO\(_4^{2-}\))
in metal-bearing fluids (M\(^{2+}\) = metals) by organic
matter, during the formation of base-metal sulfide

\[
\text{CH}_4 + (\text{M}^{2+} + \text{SO}_4^{2-}) \rightarrow \text{MS} + (\text{H}^+ + \text{H}_2\text{O} + \text{HCO}_3^-) + \text{heat} \quad (1)
\]

The temperature range of the precipitation of sulfides
in MVT ores further suggests the involvement of thiosulfates ($S_2O_3^{2-}$) (Spirakis, 1991). Is such an exothermic mechanism sufficient to explain a thermal anomaly of 100°C or more, typical of MVT deposits? If sulfate–thiosulfate reduction is a viable heat source, it may modify the thermal constraints imposed by the low fluid flow velocities in the sedimentary sequence (Deming and Nunn, 1994). Although the exothermic reaction given by Eq. 1 is not necessary to explain the thermal anomaly at Polaris, the heat given off may have contributed to the maturing of the remaining kerogen, thus causing the thermal anomaly overlying the orebody. Reduction of hydrocarbons in presence of metal (Zn) in acidic fluid is schematized by the Clemmensen reduction (Eq. 2):

$$\text{CH}_3(\text{CH}_2)_5(\text{CO})\text{CH}_3 + \text{Zn}(<\text{Hg}), \text{HCl}, \Delta \rightarrow \text{CH}_3(\text{CH}_2)_5(\text{CH}_2)\text{CH}_3$$  \hspace{1cm} (2)

Let us suppose that instead of the compound represented in the Clemmensen reaction, we use kerogen (Eq. 3) which we propose contains ketones:

$$\text{R}_1(\text{CO})\text{R}_2 + \text{Zn}, \text{H}^+, \Delta \rightarrow \text{R}_1(\text{CH}_2)\text{R}_2$$  \hspace{1cm} (3)

Then, as a result of this reaction, we will have an increase in the H/C ratio which will bring about a decrease in the $R_o$ value. During this process, apparently the acid protons are incorporated into the kerogen causing decrease in $R_o$. This process could be enhanced in the presence of other catalysts, such as Mg also present in the dolomite and clay minerals at the ore deposit. This reaction is schematized by the Pinacolic reaction (Eq. 4):

$$\text{(CH}_3)_2(\text{CO}^-) + \text{(CH}_3)_2(\text{CO}^-) + \text{Mg}^{2+} \rightarrow \text{(CH}_3)_2(\text{COH}) + \text{(CH}_3)_2(\text{COH})$$  \hspace{1cm} (4)

Speculating that the organic compound of the Pinacolic could be replaced by kerogen, then the kerogen could be protonated after acidic water treatment. From Eq. 4 it is apparent that the H/C atomic ratio increases (from 2 to 2.33). Assuming that such a reaction is possible with the organic matter in the kerogen, it will result in a decrease of $R_o$. We speculate that, after catalysts are consumed and the fluid is neutralized, $R_o$ will continue to increase as a result of the thermal alteration of the kerogen and the occurrence of sulfur which will decrease the H/C atomic ratio of the kerogen (Eq. 5):

$$\text{R} - \text{C}_6\text{H}_{11} + 3\text{S} \rightarrow \text{R} - \text{C}_6\text{H}_5 + 3\text{H}_2\text{S}$$  \hspace{1cm} (5)

Eq. 5 schematizes increasing polymerization (aromatization) of asphaltenes and NSO compounds (Leventhal, 1990). The acidic conditions are partly controlled by the decay of the organic matter during dissolution of carbonates and by clay minerals which also play the role of catalyst for alteration of kerogen (Alexander et al., 1983). Based on Eq. 1, if the brine lacks dissolved ore-metals, $H^+$ production is insignificant and the thermal anomaly will not be accompanied by chemical conditions conducive to decreasing $R_o$.

At Gays River, smectite, kaolinite and corrensite are authigenic minerals related to the processes that produced the sulfide deposit. The morphology and relative chronology based on scanning electron microscopy observations indicate that smectite is authigenic and post-dolomite. The distribution of smectite, kaolinite and corrensite as observed in the Shubenacadie and Musquodoboit basins cannot be the result of normal sedimentation of detrital clay mineral assemblages, because such a mechanism tends to homogenize clay assemblages (Chamley, 1989; Weaver, 1989). Moreover, the factors controlling the nature of clay minerals that form terrigenous suites are climate, topography and lithology of the source area. It is difficult to imagine that all these conditions could have changed significantly in such a small area. Kaolinite and corrensite are present only in the ore zone, but smectite shows a distribution pattern surrounding the ore zone. These relationships lead to the conclusion that the mineralization and the authigenic clays were the result of the same hydrothermal event.

At Gaspé Mines, individual halos around the deposits are defined by a thermal dome, alteration textures in organic matter and specific alteration clay mineral assemblages. These halos are related to the mineralization processes. However, the sequence of alteration-forming events at Gaspé Mines is more complex and ambiguous compared to the alteration processes at Polaris and Gays River. The mineralizing fluids were probably not basinal brines but mainly magmatic. The mosaic and degasification textures of
the organic matter must have been produced by early hot fluids that invaded the sequence when it was still at a low maturation level or not deeply buried. On the other hand, the presence of smectite indicates that fluids were still circulating in the system after the temperature had returned to lower levels and that the burial depth never reached the oil-window level after precipitation of smectite.

There is no sign of fluid circulation outside the outer limit of the illite zone, which more or less coincides with that of mosaic and degasification textures. From the outer limit of the illite zone to the outer limit of the thermal anomaly, abnormally high temperatures were produced by conductive heating. Another interesting point to note at Murdochville is the asymmetry in the position of the aureole-limits with respect to the mineralization. The alteration-halos are much wider at the north end of the deposit and their limits extend a great distance from the mines.

6. Conclusions

The observations of organic matter reflectivity and clay mineral assemblages at the Polaris mine, Gays River deposit and Gaspé Mines suggest that the organic matter and clay mineral assemblage anomalies result from post-ore hydrothermal alteration intimately associated with the ore-forming processes. The decreasing $R_o$ of the organic matter in the ore zones and the authigenic clay mineral halos surrounding these deposits are the result of the precipitation of sulfides and the subsequent reaction between the host rocks and the post-ore fluids. Acidic fluids enhance the formation of kaolinite and the alteration of organic matter (hydrogenation). Sulfate and thiosulfate also promote organic matter alteration as a result of either oxidation or oxygenation.

Research is ongoing to further support the theory proposed in this article. Clay mineral assemblages and $R_o$ anomalies are much greater in size than the dolostone at Polaris and the porcellanite aureole anomalies at Gaspé Mines. In general, these tools enhance the ability to identify a target area; allowing large areas to be covered quickly at relatively low cost.

These three case studies, as well as other deposits investigated by the authors, support the aforementioned working hypotheses, that mapping of $R_o$ anomalies and mapping of clay mineral assemblage anomalies are good exploration tools for a variety of epigenetic sediment-hosted hydrothermal deposits. These deposits are often surrounded by organic matter and clay mineral alteration aureoles whose size and intensity correlate with temperatures of ore formation and/or with the volume of ore-fluids responsible for ore deposition.

Acknowledgements

We acknowledge, with fond memories, our friend and colleague Michel Desjardins who died in the Fall 1992. Michel was Director of our Research Group from 1972 to 1980 and performed the scanning electron microscopy analyses for this research. His intellectual curiosity, enthusiasm and warm friendship have created a real dynamic research team. He is greatly missed. We wish to thank those who assisted in obtaining drill cores and hand specimens, especially Rod Randell (University of Toronto), Bob Sharp and Christian Sainte-Marie (Polaris Operations), Pierre Bernard (Mines Gaspé) and Pierre Saint-Antoine (Centre géoscifentifique de Québec, CGQ) and to Westminer Canada Ltd (Gays River mine). This research benefited from the insight and enthusiasm of Greg Anderson (University of Toronto) and Don Sangster (Geological Survey of Canada) and Rudolf Bertrand who developed the method used for the determination of zooclasts reflectance. René Dessureault, Glenna Gosselin, André Hébert and Yvon Houde of Institut national de la recherche scientifique (INRS-Géoressources) produced, respectively, clay mineral preparations, diffractograms, polished sections of organic matter concentrates and the figures for this paper. We acknowledge Esther Asselin of Centre géoscifentifique de Québec (CGQ), Rod Randell and the geological staff of the mines studied who provided expert advise on the palynology and associated coloration, sedimentology and the many other geologic aspects of the deposits. The manuscript has greatly benefited from the extensive editing of Thomas H. Giordano and Greg Anderson and from comments of Joel S. Leventhal, D. Kettler and Harry R. Rose. The research was funded by the
Natural Sciences and Engineering Research Council (OGP 4251, CRD 661-052/89), Geological Survey of Canada (project 90017), and contracts from Polarls Operations and Gaspé Mines.

References


Randell, R.N., 1994. Geology of the Polaris Zn–Pb Mississippi...


