SOLID PYROBITUMEN IN VEINS, PANEL MINE, ELLIOT LAKE DISTRICT, ONTARIO

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ABSTRACT
Globular blebs of solid pyrobitumen (thucholite of older reports) are found in veins exposed in open stopes and drifts in the Panel mine in the Elliot Lake uranium district, Ontario. The veins fill fractures in the 2.2-2.4 Ga Matinenda Formation. The blebs are small (1-10 mm) and vary in shape from round to discoid, twisted or elongate. Their surfaces are shiny and permeated with vesicles. The blebs are composed predominantly of carbon with a H/C ratio of 0.57, a reflectivity (Rm) of 0.9%, and a δ13C value of -33‰ (PDB). Pyrobitumen formed early in the veins. The paragenetic sequence of minerals and pyrobitumen is: quartz, pyrite I, pyrobitumen, sepiolite, pyrite II, pyrrhotite and galena, and finally calcite. The pyrobitumen blebs in the Panel mine are the result of natural migration and maturation of Precambrian petroleum. Petroleum migrated into fractures, and, with time and increased temperature, polymerized into tarry masses that matured into blebs of solid pyrobitumen.

Keywords: pyrobitumen, kerogen, thucholite, Elliot Lake district, Ontario, Huronian Supergroup, Precambrian petroleum, organic geochemistry.

SOMMAIRE
Des globules de pyrobitume solide (la “thucholite” des rapports antérieurs) ont été découverts dans des fissures exposées le long des galeries de la mine Panel, dans le camp minier uranifère de Elliot Lake, en Ontario. Les fissures se trouvent dans la Formation de Matinenda, dont l’âge est fixé à 2.2-2.4 Ga. Les globules sont petits (1-10 mm), ronds à discoides, et tordus ou allongés. Leur surface possède un éclat brillant et révèle un réseau de cavités. Ils contiennent surtout du carbone; le rapport H/C a une valeur de 0.57, la réflectivité (Rm) de 0.9%, et δ13C, -33‰ (PDB). Le pyrobitume s’est formé à un stade précoce dans les fissures. La séquence paragénétique de l’association minéraux-pyrobitume serait: quartz, pyrite I, pyrobitume, sepiolite, pyrite II, pyrrhotite et galène, et enfin calcite. Les globules de la mine Panel sont le résultat de la migration naturelle et de la maturation d’un pétrole précambrien. Le pétrole a d’abord migré dans les fissures; avec le temps et une température plus élevée, il est devenu polymérisé en masses goudronneuses qui ont évolué en globules de pyrobitume solide.

(Mots-clés: pyrobitume, kérogène, “thucholite”, district de Elliot Lake, Ontario, Supergroupe Huronien, pétrole précambrien, géochimie organique.)

INTRODUCTION
In the Panel mine of the Elliot Lake uranium district, Ontario, globular carbonaceous blebs occur in veins that cut the Matinenda Formation. Kaiman & Horwood (1976) described similar material from the nearby Milliken mine and concluded that the carbonaceous blebs, termed “thucholite”, were formed by the agglomeration and polymerization of carbon particles from the exhaust of diesel mining equipment. We propose that the carbonaceous blebs (pyrobitumen) in veins in the Panel mine resulted from natural migration and maturation of petroleum derived from Proterozoic kerogen.

Thucholite, an acronym for Th, U, C, H, and O (Ellsworth 1928), has been used in reference to carbonaceous material in the radioactive conglomerates of the Elliot Lake district. Pyrobitumen, as defined by Hunt (1979), is black to dark brown bitumen that is infusible and <2% soluble in carbon disulfide. The carbonaceous blebs in the Panel mine contain less than 0.5 ppm of thorium and uranium and are <2% soluble in carbon disulfide; therefore, the term pyrobitumen is preferred. Willingham et al. (1985) described the occurrence of stratiform and dispersed kerogens (insoluble organic solid that does not migrate following sedimentation) in the Matinenda Formation from the Stanleigh and Denison mines. They suggested that dispersed globular particles were derived from this kerogen.

Blebs of similar morphology and occurrence have been reported from veins in the Cambrian Bonneterre Formation from the Magmont mine on the Viburnum Trend, Missouri (Marikos et al. 1986) and the Ordovician Trenton Formation in Wyandot County, Ohio (Haefner et al. 1988). Both are considered to have been formed from locally derived oil that was polymerized in fractures.
THE CANADIAN MINERALOGIST

GEOLoGICAL SETTING

The Huronian Supergroup consists of a southward-thickening wedge of coarse clastic sediments with local basal volcanic units and minor chemical sediments (Colvine 1981, Mossman & Harren 1984, Robinson & Spooner 1984). The lowermost group of the Huronian Supergroup is the Elliot Lake Group, which rests disconformably on Archean gneisses and greenstones (Frarey 1977, Fralick & Miall 1981, Young 1983). The Elliot Lake Group has been described by Card et al. (1977) as an interfin-gering sequence of feldspathic quartzites and conglomerates of various types, that include the ura-niferous quartz pebble conglomerate (Matinenda Formation), and a westward-thickening wedge of siltstones, argillites and greywackes (McKim Formation). The overlying Hough Lake, Quirke Lake, and Cobalt Groups represent major sedimentary sequences consisting of conglomerates, sandstones, siltstones, and carbonate formations (Pienaar 1963).

The Matinenda Formation is subdivided into two lithofacies: lower coarse sandstones with interbedded conglomerates and upper fine-to coarse-grained, poorly sorted subarkoses, lithic arkoses, and lithic subarkosic wackes (Pienaar 1963). The uraniferous conglomerates are found in the lower sandstone lithofacies. Conglomerate deposition appears to have been controlled by basement topography (Fralick & Miall 1981, Young 1983). The depositional model postulated for the Matinenda Formation, interpreted from sedimentary structures such as cross bedding, scour and fill, mud drapes, and imbrication, is a braided stream environment (Fralick & Miall 1981, Pienaar 1963). Intruded into the rocks of the Huronian Supergroup are swarms of Nipissing Diabase sills and dikes (Potter 1987, Frarey 1977).

The age of the Elliot Lake Group is 2.2 to 2.4 Ga. This estimate falls between the ages of 2.11 ± 0.08 for the Nipissing Diabase (Van Schmus 1965, Fairbairn et al. 1969), and 2.333 ± 0.002 Ga (Frarey et al. 1982) and 2.388 ± 0.002 Ga (Krogh et al. 1984) for the Creighton and Murray granites, which intrude the Elliot Lake Group in the Sudbury area.

<table>
<thead>
<tr>
<th>MINERAL</th>
<th>EARLY</th>
<th>LATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td>1st gen.</td>
<td>2nd gen.</td>
</tr>
<tr>
<td>Pyrobitumen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sepiolite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galena</td>
<td></td>
<td></td>
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<tr>
<td>Calcite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Paragenetic sequence of minerals and pyrobitumen in fractures in the Matinenda Formation, Panel mine.


Fig. 2. Scanning electron photomicrograph of pyrobitumen (P) on quartz (Q). Scale in millimeters.

Fig. 3. Pyrobitumen (P) on first-generation pyrite (P1). Scale in millimeters.
Pyrobitumen in Veins, Elliot Lake, Ontario

Pyrobitumen blebs in the Panel mine are found in fractures, vugs, and veins in the Matinenda Formation. Numerous generations of fractures cut the Matinenda Formation. Fracture zones range in width from <2 cm to 45 cm. Pyrobitumen is found in vugs and other openings within the fractures, but comprises <1% of the material in the fractures. Fractures that contain pyrobitumen were not observed crossing diabase dykes. The fractures strike from N 45° E to N 30° W and dip nearly vertically. Rocks along some fractures are chloritized, whereas rocks adjacent to other fractures are unaltered. Potter (1987) concluded that chloritization of the wallrocks postdated the emplacement of Nipissing Diabase but predated Penokean metamorphism.

Paragenetic Sequence

Thin and polished section petrography and scanning electron microscopy with an energy-dispersion analyzer were used to describe the morphology of the pyrobitumen and to interpret the paragenetic sequence. The paragenetic sequence of minerals and pyrobitumen in the fractures is: quartz, pyrite I, pyrobitumen, sepiolite, pyrite II, pyrrhotite and galena, and finally calcite (Fig. 1).

Quartz, the first mineral to crystallize in the fractures and vugs, lines vein walls in contact with the Matinenda Formation. Euhedral to subhedral crys-
tals range from <1 mm to 1 cm in length. Following the precipitation of quartz, a first generation of pyrite was deposited. Pyrite I occurs as etched and rounded cubes (1–5 mm across) coating euhedral and subhedral crystals of quartz.

Petroleum was introduced into the fractures after pyrite I. Tarry masses, which were free to move, attached themselves to the surfaces of quartz and first-generation pyrite (Figs. 2, 3). Subsequently, the tarry blebs polymerized into solid pyrobitumen by outgassing, water-washing, and thermal cracking.

Sepiolite formed after the initial hardening of the petroleum. It occurs as fibrous and lath-shaped crystals <2 mm in length. The blebs of pyrobitumen are, in places, encased in “cocoons” of sepiolite (Figs. 4, 5). The crystals were identified as sepiolite by energy-dispersion and X-ray-diffraction analyses.

Subsequent to sepiolite crystallization, second-generation pyrite began to crystallize. It occurs as cubes that range in size from (1 mm to 1.5 cm across, with clean faces and sharp edges. Crystals of pyrite II form a yellow crust on the sepiolite fibers. Large cubes of pyrite (1.5 cm) in places enclose pyrobitumen blebs. Where pyrobitumen has been removed from large pyrite crystals, imprints of sepiolite and pyrobitumen remain (Fig. 6).

Pyrrhotite and galena deposition occurred with pyrite II. The limited number of samples containing pyrrhotite and galena make interpretation of the paragenetic relationships somewhat speculative; however, it appears that pyrrhotite, galena, and pyrite II were penecontemporaneous. Galena occurs as cubes (1 cm across, and pyrrhotite occurs as small hexagonal crystals <5 mm in length. Blebs of pyrobitumen are partly encased in galena and pyrrhotite.

**TABLE 1. COMPOSITION OF PYROBITUMEN AND BITUMEN**

<table>
<thead>
<tr>
<th>Element</th>
<th>Panel Mine</th>
<th>Trenton Formation</th>
<th>Bannister Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>&lt;0.5</td>
<td>2</td>
<td>nd</td>
</tr>
<tr>
<td>Th</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>nd</td>
</tr>
<tr>
<td>Ni</td>
<td>20</td>
<td>15</td>
<td>nd</td>
</tr>
<tr>
<td>Fe</td>
<td>300</td>
<td>M</td>
<td>nd</td>
</tr>
<tr>
<td>Ca</td>
<td>10</td>
<td>M</td>
<td>200</td>
</tr>
<tr>
<td>Mg</td>
<td>A</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Mn</td>
<td>1</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>Ca</td>
<td>1</td>
<td>0.6</td>
<td>30</td>
</tr>
<tr>
<td>Pb</td>
<td>1</td>
<td>2</td>
<td>150</td>
</tr>
<tr>
<td>Zn</td>
<td>5</td>
<td>2</td>
<td>1000</td>
</tr>
<tr>
<td>S</td>
<td>M</td>
<td>M</td>
<td>N.K.O.</td>
</tr>
<tr>
<td>Na</td>
<td>20</td>
<td>50</td>
<td>nd</td>
</tr>
<tr>
<td>K</td>
<td>2</td>
<td>70</td>
<td>nd</td>
</tr>
<tr>
<td>Si</td>
<td>1</td>
<td>50</td>
<td>nd</td>
</tr>
<tr>
<td>Al</td>
<td>0.5</td>
<td>10</td>
<td>nd</td>
</tr>
</tbody>
</table>


Calcite was the last mineral to crystallize in the veins. It occurs as clear, euhedral crystals up to 2 cm in length that surround and enclose quartz, pyrobitumen, sepiolite and pyrite II.

**ANALYSES OF PYROBITUMEN**

Pyrobitumen forms small black blebs up to 10 mm in diameter. The shapes vary widely from round to discoid, kidney to saddle, twisted or elongate (Fig. 7). The surface of the pyrobitumen is shiny and permeated with vesicles. The blebs are brittle and display a conchoidal fracture where broken. The pyrobitumen is amorphous to X rays, indicating that it does not have a well-defined crystalline structure and is, therefore, not graphite. Multiple samples of pyrobitumen and associated minerals were collected from nine vein locations in the mine, including several newly opened stops that had not been previously exposed to mining equipment exhaust.

**Elemental analysis**

Blebs of pyrobitumen were analyzed commercially by LeDoux & Company using spark mass spectroscopy (Table 1). The results of the analyses show the blebs to contain <0.5 ppb uranium and thorium. Sulfur is a major constituent (>1000 ppm), and iron is present at a concentration of 300 ppm. Nickel and sodium are each 20 ppm, and calcium is 10 ppm. Other elements are 5 ppm or less.

**TABLE 2. ANALYTICAL DATA - PYROBITUMEN AND BITUMEN**

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Reflectance</th>
<th>δ13C (PDB)</th>
<th>H/C</th>
<th>C</th>
<th>XRD</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrobitumen</td>
<td>0.91% (MSD 0.02)</td>
<td>-33%</td>
<td>0.57</td>
<td>75.88%</td>
<td>Amorphous</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Carbon Blebs</td>
<td>-24%</td>
<td>80.0%</td>
<td>Amorphous</td>
<td>nd</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bannister Mine</td>
<td>nd</td>
<td>1.41</td>
<td>86.6%</td>
<td>nd</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrobitumen</td>
<td>&gt;2.0%</td>
<td>-34%</td>
<td>0.53</td>
<td>nd</td>
<td>Amorphous</td>
<td>&lt;2%</td>
</tr>
</tbody>
</table>

fur, iron, calcium, nickel, and sodium were enriched in both environments.

Marikos et al. (1986) reported metals and sulfur in blebs of bitumen from the Cambrian Bonneterre Formation in Missouri. They concluded that the high level of metals and sulfur in blebs of insoluble bitumen probably indicates that the blebs were semiliquid when they encountered metal-containing solutions. A similar conclusion could be drawn for the enrichment of some of the metals and sulfur in the pyrobitumen from the Panel mine and the bitumen from the Trenton Limestone.

**Hydrogen/carbon ratio**

The hydrogen/carbon atomic ratio (H/C) is a sensitive indicator of thermal alteration. Decreasing H/C values result from polymerization and carbon-condensing reactions of thermal cracking processes and from dehydrogenation following deasphalting (Rogers et al. 1974). A H/C value of less than 0.53 is common for pyrobitumen (Hunt 1979). The hydrogen-to-carbon ratio for pyrobitumen from the Panel mine is 0.57 (Table 2). Thermal alteration to the catagenesis stage of petroleum maturation generates H/C values from 0.5 to 1.5 (Tissot & Welte 1984, Hayes et al. 1983).

**Carbon isotopes**

The blebs of pyrobitumen from the Panel mine have δ13C values averaging -32.61‰ (PDB) (Mancuso et al. 1989) (Table 2). The greatest cause of fractionation of carbon isotopes is biological activity (Tissot & Welte 1984, Schopf 1983). Marine organisms that utilize carbon dioxide rather than HCO3- to build cellular material produce a significant deficiency in δ13C through photosynthesis (Hunt 1979, Schidlowski et al. 1983). Hayes et al. (1983) concluded that it is unlikely that an inorganic process would produce such a large fractionation; therefore, a deficiency of δ13C in the range of -25 to -35‰ (PDB) highly suggests a photosynthetic origin. Also, the δ13C value compares favorably with published δ13C values of Phanerozoic reservoirs of natural carbon and, therefore, is consistent with our conclusion that the blebs were formed by the maturation and destruction of petroleum after it migrated into the fractures.

**Scanning electron microscopy**

Kaiman & Horwood (1976) reported the presence of low-level radiation in the outer margins of carbonaceous blebs from the Milliken mine using autoradiography. Dot maps for U and Th in the blebs of pyrobitumen from the Panel mine made with the KEVEX energy-dispersion analyzer failed to reveal the presence of these elements. Back-scatter imagery also failed to show the presence of any elements of high atomic number in freshly broken blebs.

**Infrared absorption spectroscopy**

Pyrobitumen from the Panel mine and bitumen from the Ordovician Trenton Limestone were analyzed by infrared absorption spectrophotometry. Their absorption spectra are compared to a standard bitumen (Fig. 8). The infrared absorption spectrum for the pyrobitumen from the Panel mine does not resemble that of bitumen from the Trenton Limestone or the standard. LeDoux & Company (1986, written comm.) reported that spectra of the Panel mine pyrobitumen do not seem to indicate organic structures but may be more consistent with a mixture of metal oxides and carbon.
Reflectance

Reflectance is one of the most useful measures of maturation and metamorphism of organic matter (Tissot & Welte 1984, Waples 1980, Hood et al. 1975). It is directly applicable to the study of thermal history of petroleum and provides a continuous numerical scale that measures the process of maturation and metamorphism. The maximum temperature reached can be estimated provided the elapsed effective heating time is known (Barker 1983). The principal type of maceral used in reflectance studies is vitrinite. Coaly material, however, which produces vitrinite, does not occur in Precambrian rocks; therefore, pyrobitumen or kerogen is used in reflectance studies on these older rocks (Duba & Williams-Jones 1983). The relationships among reflectance, time, and temperature for pyrobitumen have not been firmly established, but are estimated to be comparable to those of vitrinite (Robert 1980).

Pyrobitumen from the Panel mine has a reflectance ($R_m$) of 0.99 (Mancuso et al. 1989) (Table 2), which suggests that the organic matter has not been subjected to excessive thermal alteration. Comparison of the reflectivity of pyrobitumen to the metamorphic stages of petroleum based on vitrinite reflectance suggests that pyrobitumen from the Panel mine falls within the catagenesis stage (50 to 150°C) of oil generation (Cordas & Kneller 1985, Tissot & Welte 1984, Hood et al. 1975). This inference concurs with the conclusion of Willingham et al. (1985) concerning dispersed kerogen granules in two samples from the Matinenda Formation at the Stanleigh mine that have reflectivity values of 1.1 and 1.2%, respectively.


discussion

The paragenetic relationship of pyrobitumen to the associated minerals in the vugs and veins in the Panel mine indicates that the pyrobitumen formed early in the sequence. This finding is inconsistent with the suggestion of Kaiman & Horwood (1976) that similar carbonaceous blebs from the Milliken mine formed by agglomeration and polymerization of carbon particles from the exhaust of diesel mining equipment.

The presence of sepiolite and the lack of graphite constrain the temperature conditions to which the blebs could have been subjected. Imai & Otsuka (1984) reported that sepiolite can crystallize under reducing conditions from low-temperature solutions (<100°C) that are charged with magnesium, iron, and silica. Imai & Otsuka (1984) also stated that above 300°C, sepiolite is not stable and recrystallizes to a talc-like mineral. X-ray-diffraction patterns show that the blebs are not graphite. Carbon in the blebs would have crystallized into graphite above 300°C. The reflectivity value of 0.9% ($R_m$) and the hydrogen-to-carbon ratio of 0.57 for the blebs of pyrobitumen correspond to the catagenesis region on a van Krevelen diagram (Tissot & Welte 1984, Hayes et al. 1983).

Low-grade thermal metamorphism accompanying the Penokean Orogeny (1.7–2.1 Ga; Van Schmus 1965, Sims & Peterman 1983) is a possible thermal
drive to cause the cracking of kerogen and the formation of petroleum in the Matinenda or McKim Formation. Willingham et al. (1985) reported the occurrence of stratiform and dispersed kerogens in the Matinenda Formation, and concluded that the kerogens formed from mats of cyanobacteria that were affected by diagenetic and low-grade metamorphic processes including partial remobilization. As the temperature rose into the catagenesis stage in these formations, kerogens cracked to form petroleum, which migrated into fractures and subsequently became pyrobitumen. The δ13C value of -32.26‰ (PDB) for the blebs of pyrobitumen matches values for petroleum from marine sources (Hunt 1979).

Following migration into fractures in the Matinenda Formation, the petroleum was most likely altered to pyrobitumen by a combination of water-washing and thermal cracking. The process of water-washing would remove light hydrocarbons and turn the oil into a more tarry form. As this tarry material detached from the wall, it formed spheroids that floated upward and were trapped in vuggy openings in the fractures. The fluids from which later minerals were precipitated may have been responsible for the water-washing. Marikos et al. (1986) and Haefner et al. (1988) proposed similar models for blebs of insoluble carbon in the Cambrian Bonneterre Formation from the Magmont Mining District in Missouri and the Trenton Formation in Wyandot County, Ohio. Further examination of samples from these localities revealed morphologies and modes of occurrence (Figs. 9, 10, 11) similar to those found in the Panel mine.

Alteration of the first-generation pyrite is further evidence for water-washing. Pyrite I crystals are rounded and etched by dissolution, whereas pyrite II crystals have sharp edges. The alteration of pyrite I appears to have occurred at about the same time as petroleum was being introduced into the fractures in the Matinenda Formation. Following the initial alteration by water-washing, the spheroids of tar underwent thermal alteration. The vesicles that permeate the surface of the blebs (Fig. 12) indicate that the tarry petroleum was in a semisolid state during outgassing.

CONCLUSION

Data acquired from chemical and optical analyses lead to the conclusion that blebs of pyrobitumen from veins in the Matinenda Formation in the Panel mine resulted from the natural migration and maturation of Precambrian petroleum. The blebs of pyrobitumen have solubilities, X-ray-diffraction patterns, infrared absorption spectra, reflectivity values, hydrogen/carbon values, δ13C values, and morphologies consistent with an origin by water-washing and thermal alteration of petroleum.

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