Possible Role of Petroliferous Materials in Sulfide Precipitation at the Frank R. Millikan Mine, Southeast Missouri

Clark Alan Niewendorp
Western Michigan University

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POSSIBLE ROLE OF PETROLIFEROUS MATERIALS IN SULFIDE PRECIPITATION AT THE FRANK R. MILLIKAN MINE, SOUTHEAST MISSOURI

by

Clark Alan Niewendorp

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Science
Department of Geology

Western Michigan University
Kalamazoo Michigan
August 1987
The Millikan Mine's ore body contains ubiquitous amounts of petroliferous materials occurring as blebs, coal-like pods and veinlets, and seeps coating mine stope walls. Emplacement of hydrocarbons into the ore occurred before the final episode of mineralization ceased, based on growth of dendritic galena in some coal-like bitumen and other paragenetic relationships. Growth of dendritic galena in a hydrocarbon substance suggests that hydrocarbons provided sulfur for galena mineralization by either abiogenetic reduction of sulfate or thermochemical evolution of organic sulfur. Texturally, it also suggests that the presence of hydrocarbons may have been responsible for some zones of rapid precipitate mineralization. One possible source for the petroliferous materials could be the ore-hosting rocks, based on the host rock's enrichment of organic carbon and its association with bituminous seeps. Hydrocarbons may also have been a source for nickel, cobalt, and cadmium.
ACKNOWLEDGEMENTS

I would like to thank Mr. H. A. Krueger, Vice-President of Underground Mine Operations for Kennecott Minerals Company, and Mr. M. C. Young, General Manager of Ozark Lead Company's Frank R. Millikan Mine, for permission to conduct this study.

I wish to thank my advisor, Dr. J. Grace, and committee members, Dr. T. Straw and Dr. W. Harrison, for their reviews. A portion of the laboratory work was supported by a grant from The Graduate College of Western Michigan University, which is gratefully acknowledged. The Ozark Lead Company also underwrote some of the laboratory and photographic print expense.

There is no way to express my thanks to Mr. K. G. Larsen, Chief Geologist/Technical Supervisor, and Mr. C. W. Clendenin, former Senior Mine Geologist at the Millikan Mine, to whom I owe a special debt for the conception of this work, his sustained interest, constructive criticism, and advice. I am proud and honored to have worked with you and for you. Thanks are owed to John Boyle and Jim Barnett for their help.

Use of Dr. G. R. Lowell's ore microscope at Southeast Missouri State University and his helpful discussion of microscopic results is greatly appreciated.
Electron Microprobe results used in this work were carried out in the laboratory of Claudia Garparrini, Mininel Scientific Ltd., Toronto, Ontario. Organic carbon and trace metal analysis was conducted by Rinehart Laboratories, Inc., Arvada, Colorado.

Thanks, Dr. Grace for running X-Ray powder diffraction.

Of all the people who have contributed to this work, my wife, Joyce, deserves the most thanks. If not for her encouragement and support, this work would not be possible. I dedicate this work to Joyce.

Clark Alan Niewendorp
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CHAPTER I

INTRODUCTION

Purpose

The purpose of this study is to determine the influence of petroliferous materials on the physicochemical character of lead-zinc-copper minerals and formation of the ore body at the Millikan Mine, southeast Missouri. First, the approach was to establish a special and temporal relationship of petroliferous materials to the sequence of mineralization by hand samples and microscopic examination. This involved a systematic field investigation to collect and to classify type of petroliferous material in the ore body.

Second, a possible chemical inter-relationship between the petroliferous materials and physicochemical parameters of the ore solutions was examined. This involved a chemical analysis to determine if the petroliferous materials contain sulfur and/or metals, nickel cobalt, and cadmium, and to determine if they were spacially related to nickel, cobalt, and cadmium found in the ore.

Third, a study was conducted to evaluate the Bonneterre Formation in and around the Millikan Mine as a
possible organic carbon source.

Location, History, and Production

The Frank R. Millikan Mine and Mill operated by Ozark Lead Company, a division of Kennecott Mineral Company, is the southernmost mine along the 45-mile long north-south trend called the New Lead Belt or Viburnum Trend (Figure 1). The mine is located in Reynolds County in the State of Missouri, approximately 100 miles southwest of St. Louis.

Active lead mining began in the southern Missouri region as early as the eighteenth century in the "Old Lead Belt." In the 1930s, St. Joe Minerals Company began acquiring many small mines and developed new ones in this area (Kisvarsanyi & Grant, 1982; Wharton, 1975). This aggressive acquisition policy soon made St. Joe the only mine operator in the district. St. Joe suspended operations in the "Old Lead Belt" in October 1972, after 108 years of mining (Kisvarsanyi & Grant, 1982).

However, St. Joe remained very active in exploration for new lead deposits outside the old district. Their prospecting spread westward, according to Kisvarsanyi and Grant (1982), and quick success came with the discovery of the Indian Creek ore bodies in north-central Washington County (Figure 1). St. Joe's prospect drilling continued
Figure 1. Location Map of Major Lead Deposits and Mining Operations in Southeast Missouri (After Wharton, 1975).
south down the western flank of the St. Francois Mountains and several lead deposits were discovered near the town Viburnum in September 1955, and this has subsequently given the trend its name (Kisvarsanyi & Grant, 1982).

Meanwhile, Bear Creek, the exploration subsidiary of Kennecott Mineral Company, started an exploration program near Eminence, Missouri, about 50 miles south of St. Joe's discoveries. Bear Creek's prospect drilling moved north along the western flank of the St. Francois Mountains. The ore body at Sweetwater in Reynolds County was discovered in January 1962, and mining operations at the Frank R. Millikan Mine, originally named the Sweetwater Mine, began in June 1968.

The Millikan Mine-Mill's design production capacity of combined lead and zinc is 8000 tons of ore per day, at grades of 6.0 percent lead and 0.5 percent zinc. Due to a depressed lead market, the Millikan Mine suspended mining operations indefinitely in March of 1982.

Previous Work

Although there is considerable literature dealing with the character of the ores in the New Lead Belt deposits, literature available on petroliferous materials in these deposits and amounts of organic carbon in the Bonneterre Formation is limited to a few articles.
Clendenin (1977) first mentioned the presence of bitumen blebs with lead ores at the Millikan Mine. He indicated that the bitumen is associated with remobilized ores ponded below the Sullivan Siltstone Member in the mine. Clendenin regarded the bitumen in this type of ore as both a buffering agent that may have suppressed white secondary dolomite formation and a "hydrocarbon-rich liquid" that could have supplied reduced sulfur to the site of ore deposition.

Beales and Hardy (1980) obtained a sample of "sticky residual oil" from the Millikan Mine. Its location in the ore body is presumably from the upper ore horizons (65-zone below the Sullivan Siltstone Member's contact). Analysis of the oil revealed that the oil is a "normal" mature paleozoic-type oil and badly biodegraded.

Rickman (1981) reported that four types of bitumen are present in the mine workings. He felt that each type of bitumen, based primarily on physical appearances, represented various maturation ranges of oil from a motor oil-like substance to coal-like material. In addition, Rickman's study reported several observations regarding organic matter in the dark brown, burrow-mottled, wacke-stones that host the stratiform ore. He noted that an "oily" substance was removed from the rock during acid digestion. Further, carbonaceous material was also
thermally removed from similar rocks during an initial hydrothermal bomb experiment conducted at approximately 150°C. Larsen, Clendenin, Mouat, and Niewendorp (1982) described field relationships of bitumen blebs and a bituminous material they called "anthraxolite" at the Millikan Mine. They indicated that bituminous blebs occur as "coating sulfides and secondary dolomite . . . commonly found at the base of the Sullivan Silt," and anthraxolite occurs as "veinlets and pods . . . in a breccia collapse area closely associated with both galena and chalcopyrite" (p. 112).

In the Buick Mine, approximately 30 miles north of the Millikan Mine, Rogers and Davis (1977) reported that the Lamotte Sandstone contains local patches of bitumen. The Lamotte Sandstone is stratigraphically below the ore body. In addition, Rogers and Davis (1977) and Sverjensky (1981) indicated that fluid inclusions in dark-colored sphalerite crystals are commonly filled with hydrocarbons at the Buick Mine.

Rothbard (1982) found amber-colored organic material or "pyrobitumen" in the Lamotte-Bonneterre dolomitic transition zone in a borehole just north of the Indian Creek ore deposits approximately 55 miles north of the Millikan Mine. The amber-colored carbonaceous material occurred as stains and inclusions in hydrothermal
dolomite.

Sverjensky (1981) examined five Bonneterre dolostones for organic carbon in and adjacent to the Buick Mine. Two brown dolostones within the ore body contained 0.19 wt percent TOC and 0.37 wt percent TOC. The three other samples were collected outside the ore body, and they contained significantly less amounts of organic carbon: 0.05 wt percent TOC, 0.07 wt percent TOC, and 0.04 wt percent TOC.

Veits, Mosier, and Erickson (1983) found that organic carbon showed similar distribution in core holes of the Bonneterre Formation that transected the Viburnum Trend north of the Buick Mine. They suggested that a relationship may exist between sulfide distribution and organic carbon.

Skinner (1967) first suggested that organic matter might possibly be a source of nickel, cobalt, cadmium, and sulfur in the ores of some Mississippi Valley-type deposits after trace metal analysis of bitumen from the Gordon Mine, Oklahoma in the Tri-State district, 200 miles west of the study area. Sverjensky, Rye, and Doe (1979) also considered the possibility that organic matter may have provided a source for those elements in the ores of the Viburnum Trend.

Clendenin (1981) submitted some of the Millikan
Mine's bitumen blebs to Kennecott Mineral Research Center for trace metal analysis and infrared spectrophotometry characterization of the bitumen. The bitumen blebs contained 30 ppm, nickel; <10 ppm, cobalt; and 0.19 %, sulfur (Table 1).

Table 1

<table>
<thead>
<tr>
<th>Analysis of Trace Metals in Bitumen Blebs</th>
</tr>
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<tbody>
<tr>
<td>Ag &lt;1.0 ppm</td>
</tr>
<tr>
<td>Al 5.0 ppm</td>
</tr>
<tr>
<td>As &lt;10.0 ppm</td>
</tr>
<tr>
<td>Au N.D.</td>
</tr>
<tr>
<td>B 10.0 ppm</td>
</tr>
<tr>
<td>Ba 30.0 ppm</td>
</tr>
<tr>
<td>Be 0.6 ppm</td>
</tr>
<tr>
<td>Bi N.D.</td>
</tr>
<tr>
<td>Pb 0.1 %</td>
</tr>
<tr>
<td>Sb N.D</td>
</tr>
<tr>
<td>Sn N.D.</td>
</tr>
<tr>
<td>Te N.D.</td>
</tr>
<tr>
<td>Tl N.D.</td>
</tr>
<tr>
<td>Y N.D.</td>
</tr>
<tr>
<td>S 0.19 %</td>
</tr>
</tbody>
</table>

Note. N.D. = Not Detected.

As shown in Table 2, the amounts of nickel, cobalt, and sulfur in the bitumen blebs are consistent with those
metals found in some crude oils (Ball, 1960; Ball & Wenger, 1960; Erickson, Myers, & Horr, 1954; Swanson, 1963; Yen, 1975; Valkovic, 1978).

Table 2
Trace Element Content of Some Crude Oils

<table>
<thead>
<tr>
<th>Crude Oils</th>
<th>Ni</th>
<th>ppm</th>
<th>Cd</th>
<th>Sulfur (%)</th>
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</thead>
<tbody>
<tr>
<td>California</td>
<td>9.84</td>
<td>13.5</td>
<td>0.004</td>
<td>-</td>
</tr>
<tr>
<td>Libya</td>
<td>49.1</td>
<td>0.032</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Venezuela</td>
<td>117.0</td>
<td>0.178</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>Pamuco Mexico</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.2</td>
</tr>
<tr>
<td>Oklahoma City</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>West Texas</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.55</td>
</tr>
<tr>
<td>Gulf Coast</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.15</td>
</tr>
</tbody>
</table>

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CHAPTER II

STRATIGRAPHY

Regional

Rocks present in the New Lead Belt range from upper Cambrian to lower Ordovician in age (Figure 2). Although Devonian and Mississippian strata are thought to have once been deposited in the area, erosion has apparently removed such strata from much of south-central Missouri (McCraken, 1971).

Lead-zinc mineralization occurs locally within favorable horizons in the Cambrian age Bonnerterre Formation in both the Old and New Lead Belts. The Bonnerterre Formation lies conformably between the Lamotte Sandstone and Davis Shale Formation (Figure 2).

In the New Lead Belt, the Bonnerterre contains a dolostone-limestone interface, and dolostones can be further divided into a white rock-brown rock interface (Lyle, 1973, 1977). The white rock-brown rock interface of the dolostone portion is characterized by:

1. A white to light tan coarsely crystalline dolostone that lies east of the mineralized trend, and pinches out against the St. Francois Mountains. Secondary dolomitization has subsequently destroyed the rock's original
Figure 2. Generalized Stratigraphic Column Showing the PreCambrian to Ordovician Rocks in Southeast Missouri (After Thacker & Anderson, 1977).
limestone fabric and has altered the rock’s color to sparry white (Howe, 1968).

2. A finely crystalline brown dolostone is present in areas surrounding the mineralized trend. These dolostones have retained their original brown rock color and fabric, although they contain secondary sparry dolomite locally.

The grey limestone portion of the Bonneterre Formation lies to the west of the mineralized trend.

Mine Stratigraphy

Interpretation of the Bonneterre's stratigraphy in the mine area used in this thesis follows that of Gerde-mann and Myers (1972), Lyle (1973, 1977), and especially that of Larsen (1975, 1977).

There are four distinct facies in the Bonneterre (Larsen, 1975, 1977) and principle lithologies encountered in the four facies are as follows: grey-green, shales and mudstones (micrite and shale facies); grey-brown, burrow-mottled, oolitic wackestone-packstone and tan-brown, oolitic grainstone (oolitic facies); grey-brown, digitate stromatolite boundstone (stacked and laterally linked hemispheriods and oncolites) (digitate stromatolite facies); and tan-brown, planar stromatolite and burrowed lime mudstone (planar stromatolite and burrowed lime
mudstone facies). Rocks of the oolitic and digitate stromatolite facies are predominant in the Millikan Mine area (Mouat and Clendenin, 1977). Figure 3 shows the facies patterns of the Bonneterre Formation as described above.

Figure 3. Facies of the Bonneterre Formation for the Millikan Mine (After Larsen, 1977).
Depositional Models

Two major interpretations for the depositional environment of the Bonneterre Formation have been forwarded. Larsen (1977) interpreted the carbonate facies of the Bonneterre as having been deposited on a gently, westerly dipping platform (planar stromatolite and burrowed lime mudstone facies), platform margin (digitate stromatolite facies), slope into the basin (oolitic facies), and intracratonic basin (micrite and shale facies) reflecting subtidal and below wave base to supratidal sedimentation.

Using the results of regional core logging in south-central Missouri, Clendenin (1984) has expanded Larsen's (1977) earlier interpretation by suggesting that the Bonneterre's facies were deposited on a carbonate ramp represented by three lithotopes: basin, ramp, and peritidal platform. Rocks of the micrite and shale facies define the basinal lithotope. The ramp lithotope is represented by the oolitic facies, and the peritidal platform lithotopes can be seen by both the digitate stromatolite-planar stromatolite and burrowed lime mudstone facies. Figure 4 illustrates the depositional models proposed for the Bonneterre facies in the Millikan Mine area.
<table>
<thead>
<tr>
<th>SUBTIDAL</th>
<th>INTERTIDAL TO SUPRATIDAL</th>
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</thead>
<tbody>
<tr>
<td>BASINAL LITHOTYPE</td>
<td>RAMP LITHOTYPE</td>
</tr>
<tr>
<td>INTRACRATONIC BASIN</td>
<td>SLOPE INTO BASIN</td>
</tr>
<tr>
<td>INTRACRATONIC BASIN</td>
<td>PLATFORM MARGIN</td>
</tr>
<tr>
<td>WEST</td>
<td>PLATFORM MARGIN</td>
</tr>
<tr>
<td>SEA LEVEL</td>
<td>EAST</td>
</tr>
<tr>
<td>WAVE BASE</td>
<td>BIOSTOMES OUTWARD GROWTH</td>
</tr>
</tbody>
</table>

- PLANAR STROMATOLITE & BURROWED LIME MUDSTONE FACIES
- DIGITATE STROMATOLITE BOUNDSTONE FACIES
- OOLITIC FACIES (grainstone-packstone-wackestone)

Figure 4. Schematic Cross Section of the Depositional Model for the Bonne-terre's Facies in the Millikan Mine Area.
Depositional Framework

Two different sedimentary cycles have been recognized in the Bonneterre of the study area: a regressive and transgressive event, separated from each other by a unconformity (Larsen, 1975, 1977). The unconformity is the boundary between the lower and middle Bonneterre in the mine area and separates the regressive from the transgressive cycles. Carbonate sedimentation is regressive below the unconformity, and it is overlapped by transgressive sedimentation above the unconformity (Figure 3).

The lower Bonneterre sedimentary sequence prograded westward or basinward (Figure 3). This general progradation is best illustrated by the digitate stromatolite facies outbuilding as biostromes (Larsen, 1977). As shown in Figure 3, the biostromal buildup retreated (transgressed) approximately 6000 feet to the east over the unconformity (Larsen, 1977), and the oolitic facies spread across the peritidal platform area in the mine, which now is devoid of the digitate stromatolite facies.

A distinct wedge of calcareous siltstone serves as the stratigraphic marker for the lower boundary of the upper Bonneterre in the mine area (Figure 3) and is called the Sullivan Siltstone Member (Kurtz, Thacker, Anderson, & Gerdemann, 1975). It is basinal in nature and a
transgressive wedge that eventually pinches out just north and east of the Viburnum Trend.

**Host Rocks**

The dark brown, burrow-mottled, wackestone-packstone "Q" beds (oolitic facies), as shown in the detailed stratigraphic column of the Bonneterre in Figure 5, are the host rocks for the stratiform ores. The host rocks are found above the intraformational unconformity in various locations within the middle Bonneterre. These wackestone-packstone beds are usually 1 to 5 feet thick, interbedded with oolitic grainstones, and structurally deformed in the ore zones. These rocks have been solutionally attacked, causing the development of the breccia (described in the next section).

Mineralization is also developed along bedding planes, shale partings, and contacts between different lithologies (Mouat & Clendenin, 1977).
<table>
<thead>
<tr>
<th>Layer</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>J2</td>
<td>BROWN MARKER</td>
</tr>
<tr>
<td>J1</td>
<td>GREY MARKER</td>
</tr>
<tr>
<td>M</td>
<td>SULLIVAN SILTSTONE</td>
</tr>
<tr>
<td></td>
<td>MOTTLED UNIT</td>
</tr>
<tr>
<td>P</td>
<td>&quot;GREY BEDS&quot;</td>
</tr>
<tr>
<td>Q3</td>
<td></td>
</tr>
<tr>
<td>Q2</td>
<td></td>
</tr>
<tr>
<td>Q1</td>
<td>UNCONFORMITY</td>
</tr>
<tr>
<td>R2</td>
<td>GLF (GREY LONG FINGERS)</td>
</tr>
<tr>
<td>R1</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>ASH MARKER</td>
</tr>
<tr>
<td>T</td>
<td></td>
</tr>
</tbody>
</table>

**BROWN MUDSTONE**
- BROWN AND GREY WACKESTONE AND MUDSTONE
- GLAUCONITE WITH INTERBEDDED SHALE
- GREY WACKESTONE AND GRAINSTONE

**BROWN WACKESTONE AND MUDSTONE**
- THIN BEDDED GREY QUARTZ SILT
- BROWN OOLITIC GRAINSTONE
- BROWN MOTTLED WACKESTONE WITH SHALE PARTINGS
- BROWN OOLITIC GRAINSTONE

**GREY MUDSTONE BEDS**
- BROWN GRAINSTONE AND WACKESTONE
- BROWN DIGITATE BOUNDSTONE/GRAINSTONE

**BROWN WACKESTONE AND OOLITIC PACKSTONE**
- BROWN AND GREY DIGITATE AND PLANAR BOUNDSTONE WITH INTERBEDDED GRAINSTONE AND WACKESTONE
- GREY-BROWN DIGITATE BOUNDSTONE

**BROWN DIGITATE BOUNDSTONE WITH INTERBEDDED GRAINSTONE, WACKESTONE, AND LOCAL MUDSTONES**
- MUDSTONE AND WACKESTONE WITH THIN BEDS OF LIGHT GREY MUDSTONE
- SANDY WACKESTONE AND GRAINSTONE

Figure 5. Generalized Stratigraphic Column of the Frank R. Millikan Mine (After Mouat & Clendenin, 1975).
CHAPTER III

STRUCTURE

Regional

The Ozark Uplift is the dominant structural feature in south-central Missouri. This Uplift is expressed as a deeply eroded dome with its structural axis located in the St. Francois Mountains (McCra...
Figure 6. Structural Features of Southeast Missouri (After Wharton, 1975).
northwest-trending Sweetwater Fault displaces ore-bearing rocks with a left-lateral dip-slip component (Larsen et al., 1982).

Other structural features several miles north of the study area are post-Silurian Furance Creek and Crooked Creek volcanic vents. In addition, a subsurface volcanic vent located approximately 30 miles northeast of the Millikan Mine is known from drill core data and is called the Bee Fork structure. This vent has been suggested as the source of the ash marker found in the lower Bonneterre at both the Buick Mine and Millikan Mine (Lyle, 1973, 1977; Mouat & Clendenin, 1977).

For more complete details on the structural features of Missouri, the reader is referred to Heyl (1972), Kane et al. (1981), Kisvarsanyi and Grant (1982), Snyder and Gerdemann (1965), Thacker and Anderson (1977), and Zoback, Hamilton, Crone, Russ, McKeown, and Brockman (1980).

Mine Structure

Two significant structural styles define almost all of the structural ore controls in the Millikan Mine. These two primary styles are gravity sliding and wrench fault structures. Subsequent breccia collapse structures and/or related response structures developed in association with gravity slides and wrench faults and define
secondary ground preparation for mineralization.

Gravity Sliding

Gravity sliding in the Millikan Mine is characterized by "singular and multiple overthrusts, horizontal slickensides, rectilinear shearing, and folding" through incompetent layers of dark brown, burrow-mottled, wackestone-packstone beds (Larsen et al., 1982). Boundaries of slide zones are distinct and are made up of an updip cusp-shaped listric normal fault, and a down-dip "toe" structure (an asymmetrical fold) with outward thrust faulting through its crest (Figure 7).

Wrench Faulting

The ground preparation for mineralization produced by wrench faulting is almost entirely restricted to the Q1 horizon in the northwestern portion of the mine. A left-lateral strike-slip ground movement defined by en echelon asymmetrical folding and dilation brecciation has prepared the ground for mineralization in the northwestern portion of the westernmost workings of the mine (Larsen et al., 1982). Field observations indicate that gravity sliding has overprinted and masked wrench fault structures in gravity sliding zones in other portions of the mine (Larsen et al., 1982).
Figure 7. Schematic Cross Section of a Typical Gravity Slide Zone.
Solution-Induced Brecciation

Significant permeability and porosity was created by the invasion of undersaturated solutions into favorable strata (i.e., wackestone-packstone bedded ore hosts) or structurally prepared ground (Clendenin, 1977; Larsen et al., 1982; Mouat & Clendenin, 1977). The structures that resulted were formed in response to solutional thinning (as much as 10 to 20 percent) along the gravity slides under the mottled unit (Figure 8). The grey beds were let down into the solutionally thinned Q3 horizons at the breccia limits (Larsen et al., 1982; Mouat & Clendenin, 1977). It is interesting to note that, in the northwestern portion of the mine, undersaturated solutions "seismically pumped" (Sibson, Moore, & Rankin, 1975) through faults has produced zones of light, grey-green K-feldspar alteration and thinning of the Q1 which has allowed bedding stratigraphically higher to collapse into the attacked zones. Small zones of similar alteration also occur in solutionally induced brecciation along the gravity slide zone in other portions of the mine. This suggests to the writer that the alteration process may be a precursor to solution-induced brecciation.

Bedding stratigraphically higher but adjacent to the solutional thinned Q3 detached and moved towards a
Figure 8. Schematic Cross Section of the Bonneterre Showing some of the Typical Breccia Structures in the Mine.
developing void. This response structure was referred to as the marginal break zone by Mouat and Clendenin (1977), and shown in Figure 8. Solutionally induced collapse also accompanies the marginal break zone, because the marginal break zones served to detour solutions from the breccia pile (Mouat & Clendenin, 1977).

Lateral stresses were produced as the response gravity slide block or marginal break zone detached and moved towards the developing breccia void (Larsen et al., 1982). These stresses were deflected upon collusion with the breccia edge or passive roll and resulted in upward stepping thrust planes (Figure 8) that propagated into the upper Bonneterre (Larsen et al., 1982; Mouat & Clendenin, 1977). The thrust structures became active and enlarged solutional channelways and controlled the breccia configuration associated with the Sullivan Siltstone Member (Figure 8) in the upper Bonneterre (Mouat & Clendenin, 1977).
CHAPTER IV

MINERALOGY AND PARAGENETIC RELATIONSHIPS

The dominant sulfides in the Millikan Mine are galena and sphalerite, and they occur in approximately a 6:1 ratio, respectively (Mouat & Clendenin, 1977). Galena crystallizes as octahedrons, cubes, and combination of these forms; other less common varieties include leached, distorted, twinned octahedrons, colloform masses, and dendrites (Clendenin, 1977; Rickman, 1981).

Sphalerite, along with galena, occurs mostly as bedded rock replacement ore, although small vug-filling sphalerite crystals are common and widespread throughout the ore body.

Chalcopyrite is volumetrically minor and occurs as several discrete bodies of stratiform lenses, up to 6 feet thick, one of which contains small bornite pods (Clendenin, 1977; Rickman, 1981; Woolverton, 1975) and small vug-filling crystals.

The mineralogy, textural relationships and distribution of rare minerals containing nickel and cobalt was described by Jessey (1981) and Rickman (1981).

The complex paragenesis of ores and associated gangue minerals (Rickman, 1981) is summarized in Figure 9. The paragenetic sequence begins with copper-rich solutions.
<table>
<thead>
<tr>
<th>PERIOD</th>
<th>REPLACEMENT</th>
<th>OCTAHEDRAL</th>
<th>CUBIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>PYRITE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MARCASITE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHALCOPYRITE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GALENA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCTAHEDRAL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CUBIC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COLLOFORM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPHALERITE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIEGENITE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOLOMITE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CALCITE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>QUARTZ</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RELATIVE TIME</th>
<th>OLDER</th>
<th>YOUNGER</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 9. Paragenetic Diagram for Vug-Filling Mineralization in the Millikan Mine (Modified After Rickman, 1981).
depositing the discrete copper bodies over several stratigraphic/structural highs in the lower and middle Bonneterre. This early copper mineralization was followed by bedded rock replacement zinc-lead mineralization which lies on either side and above the copper bodies (Clendenin, 1982).

Zinc mineralization appears to have been deposited prior to lead mineralization when the two occur together. There are two varieties of bedded rock replacement sphalerite based on color. A bedded rock replacement, yellow sphalerite is probably earlier than more common, olive-green variety, because the olive-green sphalerite spatially separates yellow sphalerite from galena.

Galena mineralization is often found lying above and adjacent to the earlier zinc zones in the bedded ore hosts. At least four periods of octahedral galena, a minimum of one period of colloform galena, and at least three periods of cubic-form galena can be recognized in the depositional sequence of lead mineralization (Clendenin, 1982). According to Clendenin (1977), octahedral galena, which the writer believes may constitute 85 percent or more of lead mineralization at the Millikan Mine, was deposited prior to cubic galena. The bulk of cubic galena occurs in the upper ore zones. Iron sulfides, vug-filling chalcopyrite, and secondary dolomite
precipitation marks depositional breaks in the zinc-lead periods.

Study of the mineral relationships also indicated that the lower bedded ore hosts (i.e., Q1 horizon) were mineralized first (Clendenin, 1977). Clendenin (1977) maintains that initial rock replacement zinc-lead mineralization, like early copper mineralization, "sealed or plugged" the lower bedded ore hosts and forced later mineralizing solutions higher into bedded ore zones in various locations in the middle Bonneterre (i.e., Q3 horizon and P-zone).

Subsequent introduction of undersaturated solutions into the higher unsealed bedded ore hosts initiated multistage brecciation and remobilization of previously existing sulfides (Clendenin, 1977). The regenerated ore solutions produced within the initial breccias were transmitted through developing marginal break ore zones and breccia structures in the upper Bonneterre, within which they reprecipitated the remobilized metals (Clendenin, 1977).
CHAPTER V

FIELD RELATIONSHIPS

Introduction

Systematic sampling and detailed field observations of the occurrence and character of organic material were conducted by the writer during the summer of 1980 and 1981. The writer identified and classified four types of petroliferous materials based on their physical properties (Figure 10). Because of the difficulties of applying a petroleum geochemical nomenclature to the petroliferous materials from the Mine, the writer will refer to them as shown below with reference to their designation in previous reports.

Bitumen A. A black film to flaky yellow-brown resinous material was designated motor oil by Rickman (1981).

Bitumen B. This bitumen closely resembles the description of the tar of Rickman (1981) and "sticky residu­al oil" of Beales et al. (1981). It occurs as tacky blebs and also as viscous globules.

Bitumen C. A black, hard, spherical material that Clendenin (1977), Larsen et al. (1982), and Rickman (1981) refer to as bituminous blebs.
<table>
<thead>
<tr>
<th>BITUMEN FORM</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>COLOR</td>
<td>BLACK</td>
<td>BLACK</td>
<td>BLACK</td>
<td>BLACK</td>
</tr>
<tr>
<td>FLUORESCENCE</td>
<td>ORANGE</td>
<td>ORANGE</td>
<td>ORANGE</td>
<td>ORANGE</td>
</tr>
<tr>
<td>STEAK</td>
<td>BROWN</td>
<td>BROWN</td>
<td>BROWN</td>
<td>BROWN</td>
</tr>
<tr>
<td>HARDNESS</td>
<td>0</td>
<td>1</td>
<td>2-2.5</td>
<td>2-2.5</td>
</tr>
<tr>
<td>APPEARANCE</td>
<td>FILM</td>
<td>GLOBULAR TO SPHERICAL</td>
<td>SPHERICAL</td>
<td>COALLIKE</td>
</tr>
<tr>
<td>LUSTER</td>
<td>DULL</td>
<td>DULL TO BRIGHT</td>
<td>BRIGHT</td>
<td>BRIGHT</td>
</tr>
<tr>
<td>FRACTURE</td>
<td>NONE</td>
<td>HACKLY TO CONCHOIDAL</td>
<td>CONCHOIDAL</td>
<td>CONCHOIDAL</td>
</tr>
</tbody>
</table>

Figure 10. Petroliferous Material Forms Physical Character.

Bitumen D. A shiny, black, coal-like material occurring as pods and veinlets. Rickman (1981) considers this bitumen to be a coal-like anthracite; Larsen et al. (1982) referred to it as anthraxolite.

Sample locations are illustrated with respect to
mine location in Figure 11 and stratigraphy in Figure 12.

Figure 11. Mine Location for the Petroliferous Materials.
<table>
<thead>
<tr>
<th>Layer</th>
<th>Zone</th>
<th>ORE ZONE</th>
<th>BITUMEN DISTRIBUTION</th>
<th>STOPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>BROWN MARKER</td>
<td>J2</td>
<td>30</td>
<td>A B &amp; C</td>
<td>X-4</td>
</tr>
<tr>
<td>SULLIVAN SILTSTONE</td>
<td>J1</td>
<td>65</td>
<td>A B &amp; C S°C</td>
<td>Y/W-2 W-7</td>
</tr>
<tr>
<td>MOTTLED UNIT</td>
<td>M2</td>
<td>80</td>
<td>S°C</td>
<td>F-5</td>
</tr>
<tr>
<td>GREY BEDS</td>
<td>P</td>
<td>120</td>
<td>A B C &amp; D S°C</td>
<td>10-3</td>
</tr>
<tr>
<td>Q3</td>
<td>145</td>
<td>A B S°C</td>
<td>F-3 10-2</td>
<td></td>
</tr>
<tr>
<td>Q2</td>
<td>175</td>
<td>A C AB S°C</td>
<td>B-26 J-17</td>
<td></td>
</tr>
<tr>
<td>Q1</td>
<td>200</td>
<td>A C &amp; D S°C</td>
<td>J-20</td>
<td></td>
</tr>
<tr>
<td>DRILL CORE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: FRACTURE/FAULT
S°C: C-SLICKENSIDE

Figure 12. Stratigraphic Distribution of the Petroliferous Materials.

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Bitumen A

Staff geologists at the Millikan Mine have continually noted a black film exuding from various open mine workings. The writer has also noted a seepage of a similar appearing substance in other mines in the district. The consensus was that this substance was made up of iron and/or manganese oxides. However, Larsen (personal communication, 1980) suggested that the black film might be composed of carbonaceous compounds. He based this assumption on the presence of similar appearing live oil found in a borehole from an interval just below the Sullivan Siltstone Member contact in the white rock portion of the Bonneterre Formation approximately one mile east of the mine (Figure 13). Two samples of bitumen A occurring in small vugs below the Sullivan Siltstone Member contact in the upper mine workings have the same general appearance as the live oil in the core from the borehole (Figure 14).

A representative sample of the black film from the mine was tested for percentage of solvent soluble organic compounds. The film yielded 4.76 percent soluble organic compounds and confirmed earlier suggestion of Larsen.

Distribution

The seeps of bitumen A are closely associated with
Figure 13. Photograph of Core Stained Black with Oil From the Vug Visible at the Top of Core.
mineralized and solutionally brecciated, dark brown, burrow-mottled, wackestone-packstone horizons in the Q1, Q3, locally below the Sullivan Siltstone Member, and grey marker. Rarely are the seeps seen above the grey mudstone beds with the exception of solutionally brecciated areas. Bitumen A seeps are occasionally associated with digitate stromatolite boundstone units in the lower Bonneterre's reef ore zones, and are usually in juxtaposition to fractures and faults.

Distribution of bitumen A appears to be most abundant
in the eastern portion of the mine in the Q3 breccia bodies, where it varies from trace amounts to large seeps coating pillars, backs (roof), and ribs (walls) (Figure 15).

Figure 15. Photograph of Black Bitumen A Coating a Q3 Breccia Stope Wall in the B-26 Stope Area. Water Droplets Cover the Bituminous Film.

The source of the seeps, such as a vug containing live or dead bitumen, has yet to be found in the mine. In all occurrences, the bitumen A seeps are always associated with fresh water; but when the advance of headings drains the open breccia structures, evaporation of seeps
leaves either a black film or a flaky, yellow-brown-colored resinous substance (Figure 16).

Figure 16. Photograph of Dried Yellow-Brown Resinous Film of Bitumen A (Arrows) at the Base of Octahedral-Form Galena Crystals From the Q3 Breccia in the B-26 Stope Area.

Bitumen B occurs as tacky to elastic blebs, ranging in size from 1 mm to 10 cm in diameter (Figure 17). Some tacky bitumen B will liquefy at room temperature (Figure 18). Bitumen B has been found in faults below the grey mudstone beds in J-17 stope area, below and in the
Figure 17. Photograph of Two Large Globular Bitumen B Blebs Coating Dolomite Crystals in an Open Space Along a Bedding Plane in the Y-2 Stope Area.
Sullivan Siltstone Member in Y-2 and W-2 stope areas, and under the grey marker in the X-4 stope area.

Bitumen B is usually found coating secondary dolomite in open spaces along bedding planes adjacent to mineralized structures (Figure 17), in small vugs lined with secondary dolomite that often contain either a crystal of cubic galena or sphalerite, or as a coating on cubic-form galena in the mineralized structure (Figure 19). Throughgoing vertical fractures extending into the Sullivan Siltstone Member often contain an interstitial...
Figure 19. Photograph of Bitumen B (Black) Coating a Cubic Galena Crystal (Dark Grey) in the Y-2 Stope Area.

filling of bitumen B - especially above mineralized structures that have not suffered extensive solution-induced brecciation (Figure 20). In addition, inclusions of bitumen B appear in calcite crystals that coat cubo-octahedral galena, and are shown in Figure 21.
Figure 20. Photograph of a Fracture Plane Containing Patches of Tacky Bitumen B (Black) on Granular Dolomite (White) in the Y-2 Stope Area.
Bitumen C

Bitumen C is in the form of hard spherical blebs 1 to 5 mm in diameter and concentrated primarily under the Sullivan Siltstone Member contact and occasionally beneath the mottled unit (Le-3 stope area) and light grey marker (X-4 stope area). This material was very abundant in the Y-2 and W-2 mine stopes and could easily be collected from the upper portion of every mineralized structure associated with a breccia edge below the Sullivan Siltstone Member contact (Figure 22).
Figure 22. Photograph of One Large and Several Smaller Blebs of Bitumen C Covering Crystals of Dolomite and Cubo-Octahedral Galena in the Y-2 Stope Area.

Figure 23 shows that bitumen C blebs were apparently bouyant in the solutions that filled the mineralized structures. Subsequent tests with tap water proved that they were indeed bouyant. Within the structures, many blebs are asymmetrical and bent upward as if to suggest a current or flow direction.

Bitumen C blebs also occur in fracture/faults below the R2/Q1 contact and Q1 in the northwestern portion of the mine (J-20 stope area) and in the Bonneterre's dolomitic transition zone in a surface diamond drill core.
that transected the eastern portion of the mine. The majority of these blebs have been found in open cavities along fracture/faults, while a few blebs are found in fault breccia. Shapes of these blebs vary, most are stretched and bent upward, and some are spherical. Again, a strong solution flow direction is indicated by the stretched shapes of the blebs.

Slickensides

Slickensides of bitumen C have been found on bedding
planes in structures below the Sullivan Siltstone Member contact. In one notable occurrence, a non-slickensided bitumen C film coats a bitumen C slickenside on a bedding plane below the Sullivan Siltstone Member contact (Figure 24).

Figure 24. Photograph of Slickensided Bitumen C Partially Covered With a Hard Film of Bitumen C (Arrow) in the Y-2 Stope Area.

Jet black, polished, slickensided surfaces (Figure 25) are commonly found as linings on most gravity slide planes, and are suspected by the writer to be carbonaceous slickensides. An ignition test on a polished slickenside gave off a petroliferous odor suggesting to
the writer that most of the black, polished, slickensided surfaces have carbonaceous matter associated with them.

Association with Mineralization

In general, bitumen C blebs have an affinity for coating sulfides, especially galena cubo-octahedrons and occasionally marcasite, chalcopyrite, sphalerite, and dolomite crystals. A large number of blebs resting on the older generation of sulfide crystals have themselves been overgrown by a later period of mineralization.
(chalcopyrite, marcasite, and sphalerite crystals listed in order of abundance). Chalcopyrite and marcasite crystals occur as an overgrowth of single crystals sprinkled over the bleb's outer surface or commonly as clusters (Figure 26).

![Figure 26. Photograph of Blebs of Bitumen C Covered with Clusters of Marcasite and Chalcopyrite Crystals in the Y-2 Stope Area.](image)

It should be noted that chalcopyrite, marcasite, and sphalerite crystals, similar to those that have overgrown the bleb's outer surface, also occur as late vug-filling mineralization on the cubo-octahedral-form galena and
white dolomite crystals on which the overgrown blebs rest. No sulfide minerals could be observed within the blebs.

In the fracture/faults below the Q1/R2, bitumen C blebs are found in proximity to cubic galena, brown sphalerite, calcite, and chalcopyrite crystals in open spaces. As a rule, the blebs are deposited above the mineral assemblages. In other fractures, stretched blebs coat either granular dolomite or galena coating the fracture walls (Figure 27). On a fault breccia's cavity walls, bitumen C blebs were found suspended above large brown sphalerite crystals covering shiny marcasite druse.

Bitumen D

The occurrence of coal-like bitumen D are found as 1 to 4 cm wide veinlets (Figure 28) or 6 to 10 cm diameter long lenticular pods (Figure 29) in the P-zone above and adjacent to a high-grade copper body in the northernmost extension of the mine workings (Le-3 stope area). Distribution of bitumen D in the mineralization above and adjacent to the copper body appears to be controlled by feeder fractures and thrust structures associated with a north-south trending breccia. Usually, the presence of bitumen D is near and/or along a breccia edge. In addition, bitumen D has been found within a vertical
Figure 27. Photograph of a Feeder Fracture with a Stretched Bleb of Bitumen C (Arrow) Coating White Granular Dolomite under the Q1/R2 Contact in the J-20 Stope Area.
Figure 28. Photograph of Bitumen D in a Feeder Fracture Cross-Cutting Rock Replacement Galena (Grey) with Chalcopyrite Mineralization (Dull White) in the Le-3 Stope Area.
feeder zone in the upper R2. This feeder structure lies directly below the bitumen D found in this copper-rich area.

Other occurrences of bitumen D are those within open spaces in pronounced zoned chalcopyrite-galena bedded veinlets and in halos of hydrothermally altered host rocks that surround the chalcopyrite-bedded veinlets and thrust structures. Hydrothermal alteration leaves the host rocks friable, tan to pink, and heavily replaced with greenish marcasite or pyrite.
Association with Mineralization

Bitumen D is generally found in direct contact with or covering octahedral and cubic galena and white sparry dolomite crystals; but the most consistent and striking ore-related association is chalcopyrite with nearly all bitumen D accumulations. Granular chalcopyrite, about a millimeter in size, occurs in the bitumen D groundmass as open space fillings, box-work-like replacement along fractures, or forms a "halo" between the bitumen D and wall rock as shown in Figure 30. In addition, euhedral to distorted chalcopyrite crystals, 1 to 4 mm in size, occur frequently within open fractures in the bitumen D.

In addition to the chalcopyrite relationship, several millimeter-sized white dolomite rhombs and two galena cubes were found in an open cavity and appeared to be interstitial fillings in one bitumen D occurrence. This bitumen D occurrence was collected from a feeder fracture lined with cubic galena that cross-cut rock replacement chalcopyrite and galena (Figure 28). Also, minor white dickite development is associated with this particular bitumen D occurrence and others as well. The hydrocarbon around the dickite has a distinct sooty and friable character, in which euhedral and distorted chalcopyrite crystals are found. Petrographic analysis was made of
Figure 30. Photograph of Bitumen D's Relationship with Chalcopyrite. A "Halo" of Chalcopyrite Surrouns the Bitumen D (Arrows). Millimeter-Sized Chalcopyrite Crystals (Dull White Specks) Impregnate the Bitumen D Groundmass.

this bitumen D occurrence along with several bitumen C blebs as described below.

Petrographic Observations

Petrographic analysis of 3 polished thin sections was conducted on the bitumen D described above, and polished sections of 4 bitumen blebs which were collected from below the Sullivan Siltstone Member contact. Unfortunately, the physical characteristics of bitumen A and
bitumen B made them unsuitable for petrographic examination.

The groundmass of bitumen C and D is medium grey in plane-polarized, reflected light using a blue filter. Bitumen C and D are opaque in transmitted light and under crossed polars appeared isotropic. Only the bitumen D groundmass exhibited ore-related petrographic features and will be discussed below.

One of the most distinct physical properties of the bitumen D groundmass is its brittleness. Petrographically brittleness appears as splintery fractures which often contain single crystals of euhedral and distorted chalcopyrite crystals extending from the walls. Commonly these chalcopyrite crystals contain a replacement core that resemble pyrite.

In Figure 31, the bitumen D matrix material can be seen to share common grain boundaries with cubic-form galena and dolomitic wall rock in the feeder fracture. The cubic galena in contact with the bitumen D does not exhibit corrosion or etching, nor does the bitumen D seem to have formed at the expense of any of the pre-existing sulfides or wall rock dolomitization.

At higher magnification, the groundmass reveals several nearly spherical bloom-like masses (see Figure 31), composed of soft, steel-grey disseminated sulfides
Figure 31. Photomicrograph of the Bitumen D's Groundmass (Medium Grey) Sharing Common Grain Boundaries with Galena (White) and Dolomitic Wall Rock (Dark Grey). The Arrows Point to Two Dull White Blooms of Galena, and Chalcopyrite Crystals (Dull White) Fill the Splintery Fractures.

appearing as distinct dendrites (Figure 32). Two sizes of sulfide dendrites were observed: approximately 5 micron crystalline dendrites comprise the inner portion of a bloom; outer dendrites are approximately 20 microns. The two contrasting sizes of sulfide dendrites look vaguely like concentric colloform shells. In most cases, the blooms appear to be distributed near the edge of the bitumen D next to the dolomitic wall rock. It should be
Figure 32. Photomicrographs of the Dendritic Galena (White) in the Bitumen D Groundmass (Black) Taken at Magnifications of 500x (A) and 1250x (B).

noted that the polished thin sections indicated that the blooms are separate entities from the dolomitic wall rocks and the cubic-form galena filling this feeder fracture.

A qualitative microprobe analysis on several steel-grey dendrites confirmed them to be galena (see Appendix
A). Besides galena, the presence of widespread but minor chalcopyrite and pyrite floating islands was also confirmed by microprobe analysis (see Appendix A).
Trace metals and sulfur analysis was performed on a sample of bitumen B, C, and D. Unfortunately, a large enough sample of bitumen A free from serious contamination could not be obtained for analysis. The methods used to analyze the petroliferous materials for trace metals (nickel, cobalt, and cadmium) and sulfur involved solvent extraction for wet chemical analysis and spectrographic examination. The reasons for such steps are discussed below.

Sample Preparation and Laboratory Techniques

Although visible sulfides and gangue materials could be hand removed from samples, the complete removal of gangue, microscopic blooms of galena, and other intergrowths of sulfides was not possible. Hence, it was felt that the amounts of trace metals and sulfur that are present in the petroliferous materials and incorporated mineral matter could not be differentiated until the two were separated.

To analyze the petroliferous materials on a
mineral-free basis, each type of bitumen was analyzed after chemical separation into an organic fraction soluble in chloroform and an insoluble fraction. A Soxhlet apparatus was used to extract and filter the soluble organic compounds from the insoluble fraction and mineral matter. The extraction process was conducted for 24 hours at room temperature.

The final step of sample preparation converted the soluble extracts into a form that can be analyzed by wet chemical and spectrographic techniques. The extracts were heated in a porcelain crucible placed in an oven for 12 hours at 60°C to force complete evaporation of the organic solvents and dryness of the samples. This process resembles low temperature ashing and was used to minimize losses of more volatile organic sulfur and organometals.

The Eschka Method was used to determine total sulfur content in the dried extracts. The procedures for Eschka determination of sulfur in petroliferous materials are discussed in detail by Campbell (1952).

The trace metals were removed from the dried extracts by an acid leaching method, as described by Hutchison (1974). The leach solution was analyzed by emission spectroscopy using a Carbon Rod Furnace.
Organic Carbon

Quantitative analysis for Total Organic Carbon (TOC) was performed on 14 samples: 6 samples were collected from mine face exposures and picked to represent the dominant rock types in the ore deposit; and 1 underground diamond drill core sample from the mine workings. The remaining 7 samples were selected from unmineralized core drilled 1 mile southwest of the present mine workings.

Sample Description and Analytical Technique

The 7 samples from the mine consisted of 3 rocks from the mineralized dark brown, burrow-mottled, wackestone-packstone beds (i.e., 2 samples from the Q1 and 1 sample from the Q3), and 4 samples of unmineralized rocks consisting of 1 grey-brown, digitate stromatolite boundstone, a tan-brown, oolitic grainstone, and a grey, burrow-mottled mudstone. The sample taken from the underground diamond drill core represented the unmineralized S-bed (a grey, burrow-mottled wackestone) which underlies the ore body. It should be noted that rocks from the planar stromatolite and burrowed lime mudstone facies were not collected and analyzed for two reasons: (1) they are not widespread in the mine exposures, and (2) they have been found to contain negligible amounts of organic carbon.
(Veits et al., 1983).

The 7 samples collected from CP-3 borehole represent the limestone interface in the lower Bonneterre to the west of the ore body. Five grey-green, shaly lime mudstone intervals were analyzed, along with 2 grey, burrow-mottled wackestone intervals that are stratigraphically equivalent to the S-bed which underlies the ore body.

A single-stage-wet-oxidation process was used to determine TOC of the rock samples. The reader is referred to Bush (1970) and Kotch, D’Itti, and Upchurch (1976) for a detailed discussion of the laboratory equipment and procedures used to determine TOC in a single-stage-wet-oxidation process. The reproductivity for the Bonneterre samples using this method ranged from 1 to 10 percent based on replicate analysis.
CHAPTER VII

RESULTS

Trace Metals and Sulfur

Table 3 shows that trace metals, nickel, cobalt, and cadmium and sulfur are present in the soluble organic extracts from bitumen B, C, and D. The range of metal values for the three petroliferous materials are: nickel, 1.45 to 16.6 ppm; cobalt, 2.6 to 147.0 ppm; and cadmium, 0.18 to 3.04 ppm. The sulfur values range from 0.2 to 7.98 wt percent.

Table 3

Results of Trace Metal and Sulfur Content of Bitumen B, C, and D

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bitumen B</th>
<th>Bitumen C</th>
<th>Bitumen D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd (ppm)</td>
<td>0.18</td>
<td>0.18</td>
<td>3.04</td>
</tr>
<tr>
<td>Ni</td>
<td>1.45</td>
<td>3.44</td>
<td>16.6</td>
</tr>
<tr>
<td>Co</td>
<td>2.6</td>
<td>18.8</td>
<td>147.0</td>
</tr>
<tr>
<td>S (wt. %)</td>
<td>3.32</td>
<td>0.2</td>
<td>7.98</td>
</tr>
<tr>
<td>Organic Compounds</td>
<td>48.24</td>
<td>7.81</td>
<td>0.86</td>
</tr>
</tbody>
</table>

In addition, the Table has values for percentage of
organic compounds extracted from the petroliferous materials. Bitumen C and D are relatively insoluble in chloroform organic solvents (7.81 percent and 0.86 percent, respectively), and bitumen B is more soluble having 48.24 percent extractable organic material.

Organic Carbon

TOC of each sample, rock type, location, and their facies association is listed in Table 4. In addition, the lower Bonneterre's stratigraphic column for CP-3 is illustrated in Figure 33. The organic carbon values are plotted adjacent to the column, so that any trend could be recognized.

In this study area, an average of 0.41 wt percent TOC characterizes the brown rocks in the ore body, compared to an average of 0.11 wt percent TOC for grey-green rocks west of the ore body. Inspection of TOC data for rocks collected in this study reveals the following distribution for organic carbon and summarized below.

1. The TOC for dark brown, burrow-mottled, wackestone-packstone beds hosting mineralization in the Millikan Mine range from 0.32 to 0.8 wt percent.

2. A much lower concentration of organic carbon appears to characterize tan-brown, oolitic grainstones that are immediately adjacent to or surround the ore
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Organic Carbon (wt. %)</th>
<th>Location</th>
<th>Facies</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLC-1*</td>
<td>0.18</td>
<td>G-10</td>
<td>Oolitic</td>
<td>Dolo, gy, bur, wacke S-bed.</td>
</tr>
<tr>
<td>OLC-2</td>
<td>0.19</td>
<td>J-18</td>
<td>Oolitic</td>
<td>Dolo, tn, oo, grain, Q2.</td>
</tr>
<tr>
<td>OLC-3</td>
<td>0.48</td>
<td>J-18</td>
<td>Digitate</td>
<td>Dolo, tn-bn, dig strom, R2.</td>
</tr>
<tr>
<td>OLC-4</td>
<td>0.32</td>
<td>J-18**</td>
<td>Oolitic</td>
<td>Dolo, dk-bn, bur m, wacke, Q1.</td>
</tr>
<tr>
<td>OLC-5</td>
<td>0.43</td>
<td>F-3**</td>
<td>Oolitic</td>
<td>Dolo, dk-bn, bur m, wacke, Q3.</td>
</tr>
<tr>
<td>OLC-6</td>
<td>0.8</td>
<td>J-18**</td>
<td>Oolitic</td>
<td>Dolo, dk-bn, bur m, wacke, Q1.</td>
</tr>
<tr>
<td>OLC-7</td>
<td>0.34</td>
<td>J-17</td>
<td>Micrite &amp; Shale</td>
<td>Dolo, gy, bur mud, grey beds.</td>
</tr>
<tr>
<td>OLC-8*</td>
<td>0.06</td>
<td>CP-3</td>
<td>Micrite &amp; Shale</td>
<td>Dolo, tn-gy, sh-mud.</td>
</tr>
<tr>
<td>OLC-9*</td>
<td>0.05</td>
<td>CP-3</td>
<td>Micrite &amp; Shale</td>
<td>Ls, gy, oo, wacke.</td>
</tr>
<tr>
<td>OLC-10*</td>
<td>0.09</td>
<td>CP-3</td>
<td>Micrite &amp; Shale</td>
<td>Ls, gy, oo, wacke.</td>
</tr>
<tr>
<td>OLC-11*</td>
<td>0.1</td>
<td>CP-3</td>
<td>Micrite &amp; Shale</td>
<td>Ls, gy, sh-mud.</td>
</tr>
</tbody>
</table>
Table 4—Continued

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Organic Carbon (wt. %)</th>
<th>Location</th>
<th>Facies</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLC-12*</td>
<td>0.13</td>
<td>CP-3</td>
<td>Micrite &amp; Shale</td>
<td>Ls, gy, sh-mud.</td>
</tr>
<tr>
<td>OLC-13*</td>
<td>0.2</td>
<td>CP-3</td>
<td>Micrite &amp; Shale</td>
<td>Ls, gy, sh-mud.</td>
</tr>
<tr>
<td>OLC-14*</td>
<td>0.1</td>
<td>CP-3</td>
<td>Micrite &amp; Shale</td>
<td>Ls, gy, sh-mud.</td>
</tr>
</tbody>
</table>

Note.  * = Each data point relating to organic carbon represents an analytical value of a 6-inch core.  ** = Mineralized Sample.
Figure 33. Stratigraphic Distribution of Organic Carbon in the Lower Bonneterre in CP-3.
hosting wackestone-packstone beds, as indicated by a 0.19 wt percent TOC.

3. A grey-brown, digitate stromatolite boundstone sample from the lower Bonneterre contained 0.48 wt percent TOC.

4. The grey, burrow-mottled mudstone from the grey beds carried 0.34 wt percent TOC.

5. The TOC for the grey, burrow-mottled wackestone sample in the S-bed below the ore body is low (0.28 wt percent) and comparable to the TOC in the stratigraphically equivalent grey, burrow-mottled wackestone intervals in CP-3 borehole 1 mile southwest of the ore body, which averages 0.1 wt percent TOC. A low TOC also characterizes the grey-green, shaly lime mudstone intervals in CP-3, as indicated by an average TOC of 0.12 wt percent.
CHAPTER VIII

DISCUSSION

Three of the crucial questions pertaining to the petroliferous materials found in the ore deposits are: (1) possible source rocks, (2) temporal relationship with mineralization, and (3) possible role in precipitation of sulfides. These three aspects of the problem are addressed in turn below.

Potential Source Rocks

Organic carbon analysis of the ore hosts and rocks adjacent to mineralization ranges from 0.19 to 0.8 wt percent TOC and is enriched up to four times relative to grey rocks west of the ore body, the TOC of which averages 0.11 wt percent. This enrichment of organic carbon in rocks in the ore body (averaging 0.41 wt percent TOC) exceeds the 0.3 wt percent TOC which is considered the minimum amount of TOC a carbonate rock needs if it is to be considered as a potential source rock (Tissot & Welte, 1978).

The following observations suggest that the host rock's organic carbon has generated hydrocarbons: (a) the ore-hosting rocks can release hydrocarbon substances during acid digestion and (b) upon heating in a hydrothermal
bomb at approximately 150°C (Rickman, 1981). The fact that hydrocarbon substances can be liberated from the ore-hosting rocks strongly suggests that the bitumen A seeps seen bleeding from the ore-hosting rocks, especially those in the wackestone-packstone bedded ore zones, represent a portion of hydrocarbons generated from the organic carbon in the host rocks.

Therefore, the ore-hosting rocks, particularly those in the wackestone-packstone bedded ore zones, could be potential source rocks for at least some of the petrolierous materials found in the ore hosts, based on their organic carbon content (greater than 0.3 wt percent TOC) and association with bitumen A seeps. Since bitumen A has not been observed bleeding from cores, the bitumen A seeps bleeding from pillars, ribs, and backs may be due to blasting during mining. The blasting would propagate microfractures through the rocks in the pillars, ribs, and backs and the bitumen could escape due to either water flushing or pressure differential created between the rock and open stope.

However, there is evidence that points to the possibility that some of the petrolierous materials in the ore body might have originated from another source. In view of local patches of bitumen noted in the Lamotte Sandstone (Rogers & Davis, 1977; Rothbard, 1982) and the
bitumen C blebs in a fracture/fault in the Bonneterre-Lamotte transition zone in the eastern portion of the mine, the hydrocarbon-rich fluid may have migrated through the Lamotte Sandstone and reached the ore body in the Bonneterre Formation through fractures and faults. This points to the possibility that the bitumen C blebs in fractures and faults below the R2/Q1 contact in the western portion of the mine and bitumen D in the R2 below the copper body in the northernmost extension of the mine were derived from the hydrocarbon-rich fluid that may have migrated through the Lamotte. However, the digitate stromatolite boundstone in the R2 and R1 as their source cannot be excluded since a digitate stromatolite boundstone contained 0.48 wt percent TOC.

Relationship with Mineralization

The evidence suggests that the generation of the bitumen A seen bleeding from the ore-hosting rocks was caused by mineralization which, for the most part, cracked the organic carbon in the ore-hosting rocks and evolved hydrocarbons. Evidence for this is the obvious lack of bitumen A seeps bleeding from non-mineralized rocks. It appears that repeated sulfide replacement of the host rocks, often in proportions of nearly 1 to 1 in the wackestone-packstone bedded ore zones (Clendenin, 1977)
and solutional thinning of the bedded ore hosts combined to generate and flush hydrocarbons into developing breccia structures.

Texturally, evidence for the relative timing of hydrocarbon generation and emplacement with mineralization can be seen by the blooms of dendritic galena in the bitumen D. Emplacement of bitumen D's original hydrocarbon compounds appears to correspond to a period of cubic galena mineralization in the ore body based on two observations: (1) the two small cubes of galena found within an open cavity in the bitumen D, and (2) the overall spatial relationship between the bitumen D and cubic galena lining the walls of the feeder fracture. The above observations also suggest that the blooms of dendritic galena in the bitumen D are related to the cubic stage of mineralization as well.

In addition, the following ore relationships and field observations of the petroliferous materials indicate that hydrocarbons were emplaced before the final episode of mineralization ceased as illustrated in Figure 34.

First, chalcopyrite mineralization associated with nearly all bitumen D accumulations represents either chalcopyrite deposited between hiatuses in the sequence of galena mineralization or chalcopyrite deposited after most other sulfides in the mine.
Figure 34. Paragenetic Diagram of Vug-Filling Mineralization in the Millikan Mine Showing the Relative Time of Emplacement for the Petroliferous Materials (Modified After Rickman, 1981).
Second, overgrowths of chalcopyrite, marcasite, and sphalerite deposited on both the cubo-octahedral galena and dolomite and bitumen C blebs are related to late vug-filling mineralization in the upper mining levels.

Third, the calcite crystals in which bitumen B is included were deposited after deposition of sulfides in the upper ore zones.

Finally, the bitumen C slickensides on bedding planes in response to gravity slide zones suggest that hydrocarbon-rich liquids were among the fluids that developed the ore-hosting breccia structures in the upper Bonneterre.

It is interesting to consider why the petroliferous materials, for the most part, appear to be emplaced late in the paragenetic sequence of mineralization. This relationship may be due to the fact that the petroliferous materials are buoyant. It might be argued that the petroliferous materials' original hydrocarbon compounds floated in the ore-forming fluids near the tops of structures. Sulfides and the roofs of ore-hosting structures were coated with the petroliferous materials when the spent ore-fluid were expelled.

In this context, the only reasonable explanation for bitumen C's and bitumen D's insolubility in organic solvents is that the petroliferous materials represent carbonized remains of hydrocarbons left behind after
thermochemical interaction with the hot ore-forming solutions. This situation is somewhat analogous to that described by Macqueen and Powell (1983) for the insoluble forms of bitumen in the Pine Point lead-zinc ore fields, Northwest Territory, Canada.

The extent to which bitumen C and bitumen D may have become altered is indicated by their isotropic optical property (Kharvari-Khorosani & Murichson, 1978), their extremely low solubilities in organic solvents (Macqueen & Powell, 1983), and their crystallographic reflections on X-Ray patterns as described below. An interlayer spacing (d) of 4.55 Å and 3.49 Å for bitumen C and 3.11 Å for bitumen D suggests that they have been partially carbonized (see Appendix B). A d-spacing of approximately 3.473 Å is characteristic of graphite (Kharavari-Khorosani & Murichson, 1978). It could be inferred from the above that bitumen C and bitumen D have some structural similarities to graphitic substances.

A close connection between bitumen C's and bitumen D's apparent alteration states and prolonged exposure to temperatures of mineralization would appear to be indicated. Temperatures of 150°C to 200°C are needed for hydrocarbon substances to advance towards graphitic materials (Hood, Gutjahr, & Heacock, 1975; Hunt, 1978; Powell & Mckirdy, 1973), and those temperatures are equivalent to...
the upper temperature range of mineral deposition in the New Lead Belt as determined by fluid inclusion studies (Roedder, 1977; Sverjensky, 1981).

Based on its 48.24 percent solubility in organic solvents, bitumen B may be an intermediate case between extremely insoluble bitumen C and bitumen D and a completely soluble hydrocarbon substance.

Role in Precipitation

The recognition that hydrocarbon generation and emplacement corresponds to mineralization suggest that sulfur present in galena mineralization in the Millikan Mine could have been supplied by organic materials in the host rocks and ore-hosting structures. Again, the growth of blooms of dendritic galena in the bitumen D points to this hypothesis. The sulfide sulfur needed to cause the growth of the blooms of dendritic galena in bitumen D's parent material could have been generated two ways: (1) thermochemical degradation of the hydrocarbon substance and release of volatile organic sulfur compounds (Skinner, 1967), or (2) reduction of sulfate in the ore brines by hydrocarbon with or without the aid of bacteria (Barton, 1967). Unfortunately, with present data, neither process of sulfur generation can be clearly eliminated, but information obtained from the geochemical data on bitumen B,
C, and D suggests that the petroliferous materials could yield organic sulfur compounds (Table 3).

Two observations suggest that thermochemical degradation of the petroliferous materials' original hydrocarbons supplied sulfur to cubic galena mineralization: (1) similarities between cubic galena's sulfur isotope ratios ($\delta^{34}S$ values of +0.00 to +10.0 per mil) and those found in petroleum (Monster, 1972; Orr, 1974; Sverjensky, 1981; Sverjensky et al., 1979; Thode, 1981), and (2) the likelihood that the blooms of dendritic galena in the bitumen D are cubic in habit.

Consideration of the above has yet another important implication. The thermochemical breakdown of the organic matter in the host rocks could have provided catalysts, such as methane and organic sulfur, to start and sustain the reduction of sulfate (Orr, 1974). Indeed, the most acceptable means of accounting for the isotopically heavy sulfur ($\delta^{34}S$ values of +10.0 to +22.0 per mil) in the octahedral galena mineralization is by the reduction of sulfate or possibly partly oxidized sulfur species in the ore fluid or some other brine (Spirakis, 1983) by organic matter encountered at the site of deposition.

The geochemical data on bitumen B, C, and D also suggests that the organic matter in the host rocks could be a possible source for some nickel, cobalt, and cadmium
found as trace metals in the ore.

In summary, the solutions depositing galena mineralization in the Millikan Mine acquired sulfur from at least two sources. In an interrelated complex fashion, reduced sulfur for precipitation of octahedral galena mineralization was supplied through reduction of sulfate or partly oxidized sulfur species by organic matter encountered at the site of deposition. The data reported in this thesis are consistent with, and would suggest that latter cubic galena mineralization incorporated H₂S (organic) from thermochemical degradation of the organic materials in the host rocks. The sulfur isotopic disequilibrium between octahedral galena and cubic galena mineralization, $\delta^{34}S$ values of +0.00 to +10.0 per mil and $\delta^{34}S$ values of +10.0 to +22.0 per mil, respectively, might then be explained as resulting from varying proportion of the two sulfur species co-existing together and type of ore-fluids at the site of deposition.

Another implication of the growth of blooms of dendritic galena in the bitumen D is that hydrocarbons could have influenced the rates of precipitation of some sulfides in the Millikan Mine. The growth of galena in the bitumen D is here attributed to rapid precipitation which is indicated by the dendritic texture of the galena (Anderson, 1975; Clendenin, 1977; Rickman, 1981). Previous studies
on galena's crystal habits, as illustrated in Figure 35, show that dendritic galena is developed under disequilibrium conditions caused by increasing the degree of supersaturation of the precipitating solution (Anderson, 1975).

Figure 35. Relationship of Crystal Habits of Galena to the Processes of Supersaturation and Undersaturation (After Rickman, 1981).
Several changes in the physicochemical parameters of an ore fluid at the site of deposition can cause conditions of supersaturation, and these changes are: temperature fluctuation, pH change, pressure drop, and an increase in sulfur activity (Anderson, 1975; Barton, Bethke, & Toulman, 1963). After considering the above possibilities, the writer believes that a steady or sudden supply of reduced sulfur to the ore fluids offers the only reasonably explanation for conditions of supersaturation under which the dendritic galena grew in the bitumen D's parent material.

Applying this idea to the ore body, one can envision an ore-forming process in which organic materials in the host rocks, being catalysts for sulfate reduction and/or a source of organic sulfur, locally increased the degree of supersaturation of the ore fluids passing through the ore hosts. Thus, a sudden or steady supply of reduced sulfur involving the reaction between the ore fluids and organic materials in the ore hosts may be the cause for precipitation of some massive chalcopyrite lenses in the copper bodies over local structural highs and some zones of dendritic galena and fine-grained sphalerite in the host rocks.
CHAPTER IX

CONCLUSION

Even though the exact timing of the introduction of petroliferous materials with mineralization cannot be clearly defined, its relative timing with respect to mineralization can be. Ore relationships for the petroliferous materials indicate that they were emplaced in the ore before the final episode of mineralization ceased in the Millikan Mine. One period of hydrocarbon emplacement into the ore (a bitumen D stage that contains the blooms of dendritic galena) is thought to coincide with precipitation of a cubic stage of galena mineralization.

The growth of dendritic galena in the bitumen D's parent material implies that hydrocarbon substances may have supplied sulfur to the ore fluids. The potential of the petroliferous materials as a source of sulfur is believed to be demonstrated by its present sulfur content. Although it is difficult to draw more than a tentative conclusion, much of the cubic galena mineralization in the Millikan Mine may have acquired its sulfide sulfur (as organic sulfur) from thermochemical degradation of organic matter in the ore hosts. The correlation of heavier isotopic sulfur with octahedral galena mineralization,
together with the presence of organic matter in the host rocks and petrolierous materials in the ore, is consistent with the theory that hydrocarbons were active catalysts for reduction of sulfate or partly oxidized sulfur species, which would be the precipitant for octahedral galena mineralization. The petrolierous materials in the ore are probably a product of these reactions.

It is inferred from the presence of dendritic galena in the bitumen D that organic matter could increase the states of supersaturation of the ore fluids by increasing the activity of sulfur. Variable concentrations of organic matter, being catalysts for sulfate reduction and/or direct source of sulfur, could be one cause for precipitation of the massive chalcopyrite lenses in the copper bodies over local structural/stratigraphic highs and some zones of fine-grained sphalerite and dendritic galena in the bedded ore hosts.

Organic carbon analysis of the Bonneterre Formation, particularly the dark brown, burrow-mottled, wackestone-packstone bedded ore hosts, some of the mineralized digitate stromatolite boundstone beds, and grey beds shows that they have source potential. Taken together, the organic carbon evidence and bitumen A seeps associated with the above rock types, particularly those in the wackestone-packstone bedded ore hosts, suggest that some
of the petroliferous materials in the ore may have been generated from within them by mineralization. There is field evidence, however, that points to the possibility that some of the petroliferous materials in the ore may have migrated through the Lamotte Sandstone and "seismically pumped" through the Bonneterre Formation into the developing ore body.

Either at the termination of mineralization or in association with it, it is proposed that hydrocarbon substances migrated from the ore-hosting rocks into the initial breccia bodies. As the breccia bodies developed and response structures formed, hydrocarbon-rich liquids along with ore fluids, or separately, were forced into the upper Bonneterre's ore hosts. Surges in the pumping system deposited hydrocarbon droplets against sulfide crystals and/or dolomite crystals lining solution channelways and roofs below the Sullivan Siltstone contact. Deposition of bituminous blebs on the sulfides and roofs of structures suggests that they were buoyant in the ore-forming fluids.

The Sullivan Siltstone Member is thought to have acted as a semi-permeable barrier that allowed escape of spent ore-solutions but trapped hydrocarbons and mineralization in structures beneath the barrier. In the North Mine, where bitumen D is found, it is presumed to have been trapped in the mineralization beneath the mottled
Suggestions for Further Research

Several ideas for further research based on the data presented in this study are suggested below.

1. The presence of dendritic galena in the bitumen D indicates that a sulfur isotopic analysis could yield significant information. Such a study of both the dendritic galena and the hosting bitumen D groundmass is needed to help clarify the role of the petroliferous materials with mineralization in the Millikan Mine. The organic sulfur in other types of petroliferous materials should also be included in this study along with sulfide sulfur in associated mineralization.

2. A logical follow-up to this study would be to initiate a detailed organic geochemical investigation of the petroliferous materials. Such a study would be helpful in deciphering the source of the petroliferous materials, their mode of occurrence and their maturation history in relation to mineralization.

3. A thorough study should be conducted on the distribution of organic carbon within the ore-hosting rocks, especially in the wackestone-packstone bedded ore hosts, to determine the relationship between organic carbon and mineralization.
4. A comprehensive investigation should be conducted on the content of nickel, cobalt, cadmium, and sulfur in the petroliferous materials and the solvent extract of organic matter from the host rocks. This expanded study could be used to better evaluate the petroliferous materials' potential as a source for those elements found in the ore.
APPENDICES
Appendix A

Operating Conditions for Electron Microprobe
The two sizes of galena in the bitumen D were analyzed qualitatively by electron microprobe using a X-Ray energy-dispersive technique. This technique involved the collection of X-Ray spectra showing peaks at the energy positions of all elements present in the analyzed microareas in amounts greater than approximately 0.1 percent. Figure 36 shows the electron microprobe X-Ray spectra data from the two sizes of galena, chalcopyrite, and pyrite found in the bitumen D.

Figure 36. Electron Microprobe X-Ray Spectra of Galena, Chalcopyrite, and Pyrite.
Appendix B

Operating Conditions for X-Ray Diffraction
Samples of bitumen C and bitumen D were run on a Philips X-Ray powder diffractometer to see if they possessed any crystallographic reflections.

Bitumen D was prepared by grinding to a fine powder and centrifuged to remove most sulfides or other rock material. Bitumen C was also powdered, but was not centrifuged because upon visual inspection the sample appeared free of any foreign impurities.

The goniometer was run from 5 to 60 degrees at one degree two-theta per minute with a strip chart set at one-half inch per minute. The copper tube voltage was set at 35 KV with a current of 25 milliamps, and the detector voltage was set at 1450 V. Strip charts of bitumen C's and bitumen D's X-Ray pattern is shown in Figure 37.

Heating experiments on bitumen C and bitumen D samples were made to see if temperature would change their X-Ray pattern. The response was used as an indication of their possible temperature history (i.e., geothermometer). It was found that heating bitumen C to 200°C had considerable effect on the sharpness of the 3.49 Å and 4.55 Å peaks compared with the X-Ray pattern of the unheated bitumen C. The X-Ray pattern of bitumen D didn't show much change at 200°C and 300°C from the X-Ray pattern of the fresh bitumen D, but reflections did change at 400°C. Many peaks disappeared and a color
Figure 37. X-Ray Spectra for Fresh Bitumen D (A) and Bitumen C (B).
change occurred from black to medium grey. The results of these experiments are tabulated in Table 5 and strip charts in Figure 38.

Table 5  
Results of X-Ray Diffraction Analysis

<table>
<thead>
<tr>
<th>d-spacing (Angstroms)</th>
<th>Fresh</th>
<th>200°C</th>
<th>400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bitumen C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.55*</td>
<td>4.55*</td>
<td>N/O</td>
<td></td>
</tr>
<tr>
<td>3.49*</td>
<td>3.49*</td>
<td>N/O</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>2.875</td>
<td>N/O</td>
<td></td>
</tr>
<tr>
<td>Bitumen D</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.11</td>
<td>3.11</td>
<td>4.55</td>
<td></td>
</tr>
<tr>
<td>3.015</td>
<td>3.015</td>
<td>3.532</td>
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<td>3.016</td>
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<tr>
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<td>2.696</td>
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<td>-</td>
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<tr>
<td>-</td>
<td>-</td>
<td>1.784</td>
<td></td>
</tr>
</tbody>
</table>

Note. N/O = None observed. * = Approximate (very broad).
Figure 38. X-Ray Spectra for Heated Bitumen D at 400°C (A) and Bitumen C at 200°C (B).
BIBLIOGRAPHY


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