

MAR 19990007: STEEPBANK RIVER

Received date: Mar 19, 1999

Public release date: Mar 20, 2000

DISCLAIMER

By accessing and using the Alberta Energy website to download or otherwise obtain a scanned mineral assessment report, you ("User") agree to be bound by the following terms and conditions:

- a) Each scanned mineral assessment report that is downloaded or otherwise obtained from Alberta Energy is provided "AS IS", with no warranties or representations of any kind whatsoever from Her Majesty the Queen in Right of Alberta, as represented by the Minister of Energy ("Minister"), expressed or implied, including, but not limited to, no warranties or other representations from the Minister, regarding the content, accuracy, reliability, use or results from the use of or the integrity, completeness, quality or legibility of each such scanned mineral assessment report;
- b) To the fullest extent permitted by applicable laws, the Minister hereby expressly disclaims, and is released from, liability and responsibility for all warranties and conditions, expressed or implied, in relation to each scanned mineral assessment report shown or displayed on the Alberta Energy website including but not limited to warranties as to the satisfactory quality of or the fitness of the scanned mineral assessment report for a particular purpose and warranties as to the non-infringement or other non-violation of the proprietary rights held by any third party in respect of the scanned mineral assessment report;
- c) To the fullest extent permitted by applicable law, the Minister, and the Minister's employees and agents, exclude and disclaim liability to the User for losses and damages of whatsoever nature and howsoever arising including, without limitation, any direct, indirect, special, consequential, punitive or incidental damages, loss of use, loss of data, loss caused by a virus, loss of income or profit, claims of third parties, even if Alberta Energy have been advised of the possibility of such damages or losses, arising out of or in connection with the use of the Alberta Energy website, including the accessing or downloading of the scanned mineral assessment report and the use for any purpose of the scanned mineral assessment report so downloaded or retrieved.
- d) User agrees to indemnify and hold harmless the Minister, and the Minister's employees and agents against and from any and all third party claims, losses, liabilities, demands, actions or proceedings related to the downloading, distribution, transmissions, storage, redistribution, reproduction or exploitation of each scanned mineral assessment report obtained by the User from Alberta Energy.

MIN 9907

19990007

Steepbank River Permit

Permit no. #9396110048

ASSESSMENT REPORT

Authors:

Larry MacGougan
Debbie Puckett

March 10, 1998

Table of Contents

	Page
Introduction -----	1
Summary -----	2
Work Performed	
Dates-----	4
Fieldwork-----	5
Lab & Research-----	6
Location	
Map-----	7
Access-----	8
Geology	
Topography & Drift-----	8
Regional Geology-----	8
Expenditures	
1996-----	10
1997-----	11
1998-----	12
Conclusion -----	13
Recommendations -----	13
Declaration -----	14
Author Information -----	15
References -----	16
Geology	
Peace River Arch-----	17
Topographic-----	18
Drift-----	19
Precambrian Basement Tectonic Features-----	20
Oil, kimberlite & precious metal sites-----	21
First Bedrock-----	23
Stratigraphy -----	24
Suncor & Syncrude -----	25
Suncor Mine Map -----	26
Gold & Platinum Tests -----	27
Assays -----	28
Experimental Assays #1-----	43
Experimental Assays #3-----	46
Experimental Assays #5-----	54

Research Papers

I. The Transportation of Deposition of Gold Nature-----	82
II. The Transportation of Gold by Organic Underground Solutions.-----	98
III. Phanerozoic Analogues for Carbonaceous Matter in Witwatersrand Ore Deposits-----	106
IV. Occurrence & Distribution of Invisible Gold in a Carlin-type Gold Deposit in China-----	114
V. Behavior During Processes Connected with Magmatism-----	122
VI. Metallogeny of Heavy Oils, Natural Bitumens, and Oil Shales-----	134
Sample Location Map-----	149
Aerial Photo Maps-----	150

INTRODUCTION

One Metallic and Industrial Mineral permit, totally 9216 hectares, land description of

4-08-090: 19-21; 28-33

4-08-091: 4-9; 16-21; 28-33

4-08-092: 4-9; 16-18

was staked in northeast Alberta for the purpose of prospecting. The permit was filed and registered on November 21, 1996 as Metallic Mineral Exploration Permit # 9396110048. Anniversary date is November 21, 1998 when renewal or downsizing is mandatory.

This regional land position was staked for surface collection, causing none to minimal surface disturbance in the course of recovery and work. Its location was ideal because of where it is situated within the Western Canada Sedimentary Basin (WCSB), its close proximity to the Suncor Mine, and the feasibility of shallow overburden in comparison to other areas where it is deep and encumbersome. The principal exploration objective was to find and record anomalous values of gold, silver, platinum, PGM's, and other metals in the overlying Clearwater shales, Cretaceous sands, and Devonian limestones. In order to better understand and deal with the mineralization, it was pertinent to examine the potential source rocks and investigate the complexities of why their metals can't be assayed, through geochemical study.

The regional geology and its history were studied by reading numerous reports, studies, scientific research from Geological Survey of Canada (GSC), so to continue work from what was learned from them. To date all exploration companies have had difficulties in assaying with the standard fire assay, were gold even could be impregnated into a sample, and then they could not get it back out. Until the assay problem is resolved an economical mineral deposit is controversial, so more work needed to be assessed towards mineralogy and its chemical makeup, than geology.

By processing and assaying samples certain minerals or metals can be lost or altered, and some persist through different treatments. In nature it is much the same, some chemical evolution, alternation, or geological mechanisms can change the environment and mineralization. In this area the mineralogy and the gold are predominately in native and/or salt form, and the metals have been enriched by some process to form a deposit. It is postulated low temperature saline brines flowed up along the fault systems precipitating out the mineral assemblage from solution when encountering an reducing environment. The reducing zones were in areas of high carbon content such as shales, bitumen-rich rocks, and in the overlying limestones. Working with the Au/Ag/Pt mineralization in the sedimentary rocks helped with the study in relationships between gold and discharging brines, gold brines and hydrocarbons.

Inconsistencies between assay methods are related to the presence of dispersed organic (hydrocarbons) material or bitumen in the rocks and the search for a reliable gold analysis of these organic-rich rocks has been a long and diligent hunt. With the salts vaporizing at about 600

degrees C, some of the gold, especially if it is in salt form, will vaporize during the fire assay process; and secondly when there is bitumen present and the samples are being crushed for assay, the gold could be selectively screened out or could vaporize with the bitumen, or even go into the slag, during the assay. So either way it explains why it could be lost.

Every mineral and metal being a chemical element, the use of chemicals was an essential and necessary tool in changing the composition of the ore, ridding certain unhomogeneous material by dissolving them, to make it more assayable. To further an attempt in understanding the chemistry of ore deposition carried out in nature, in determining the host mineralogy of the metals (sulphides, organic or clay?) or whatever rock or layer the fluids went through, in terms of alternation.

SUMMARY

In 1996 this Steepbank River permit was acquired for the purpose to collect and process samples for the potential of gold, platinum-group minerals, and for any other precious or base metal occurrences. This assessment report is mainly technical because of the many assay procedures involved, and the costs incurred are due to fieldwork, processing rocks, with follow-ups of extensive microinvestigative, analytical and mineral concentration testwork. The scope of fieldwork comprised of reconnaissance prospecting, stream sediment and glacier till sampling, orientation surveys of the land that has virtually been unexplored by mining companies and previous owners. Selective rock grabs of limestones with disseminated and veinlets of mineralization, bitumen-stained or sulfur-stained, and any other alternations were taken for leaching and roasting in the lab or interpretation. With many return visits to the area of primary interest for follow-up sampling and re-testing.

Stream sediments collected for panning showed no visible gold other than a few fine specks, with some specimens in the water floating, possibly gold coated with oil or carbon. The mineralization here doesn't seem to be as related to the faulting as it does to the carbons and hydrocarbons. Towards the north of the property there is more sulfurous (rusty) shale and green decalcified rock, and fewer pyrites.

The history of gold in the Fort McMurray and Athabasca area is it is found in microdisseminated, sediment-hosted deposits; and its gold grains can be scanned by a scanning electron microscope (SEM), but it can't be assayed. One of the biggest reasons gold doesn't assay properly is because it doesn't want to go into metallic form. The metal doesn't form into a metallic bead when certain other bonding elements are present, and in the instances where tellurium, sodium, sulfur, arsenic are involved the metal won't change unless they are removed. This is also complicated by the deterrence of carbon, iron and organic matter.

The interfering constituents have to be eliminated firstly either chemically and/or burned off prior to assaying. There are also probably many other metals besides them that could interfere, alter or hinder. Certain elements bond together and by being together it prevents a complete

recovery by conventional extraction techniques. With the gold and platinum, it was hard to get out of solution, it won't gather together and volatilizes easily. Native metals and complex alloys were commonly encountered. Another theory why the assaying is problematic is because gold is in a salt form or because it is finely disseminated in organic and carbonaceous material. Or just for the simple reason disseminated gold can't be assayed.

Extensive study, time and expense was allocated to the investigation of platinum and the platinum group, after Birch Mountain Mineral's impressive results of 2.21 and 4.94 grams per tonne over a 1.6 metre interval on Township 96, Range 10, W4. After many trips to the library searching for information regarding this precious metal, only scarce material would prove to be useful. Very little exploration and independent studies have been done strictly on platinum and the platinum group in Alberta, and the metal is usually found in placer deposits, not microdisseminated like the gold. When there are iron impurities present platinum can be weakly magnetic and it is almost always alloyed with iron, which poses the same problem of assaying as with the gold. When platinum is bonded with tellurium and sulfur it is not metallic and will not form into a lead bead. The reason for this is it might be in a salt form or perhaps it can't even go into metallic form. It inhibits the solid solution and in a complex solid solution high temperatures (in a hydrogen atmosphere) are needed to extract metal.

A standard lead fire assay is a method for collecting all the precious metals into a lead bead by oxidizing the base metals, semi-conductors and salts, etc. off, and then compelling and oxidizing the lead off without losing the metal. Platinum by itself could be assayed this way, but it can't be with the platinum group, and platinum always contains other members of its chemical group. All six metals (ruthenium, rhodium, palladium "light" specific gravities; osmium, iridium, platinum "heavy") with various molecules combined in the same metal act differently than platinum by itself. An example being rhodium and palladium alone join 1 to 1 with iron when firing, therefore the separation is hard. Not being fully separated, detection devices such as ICP and AA are distorted by the iron.

Unless the standard is changed platinum-group minerals are near impossible to assay accurately because of the many bonds they create with alternation. In assaying they either oxidize or volatile off; too much oxygen it either volatiles off or goes into the slag (it won't form a bead) PGM's need to break their bond, they're extremely easy to oxidize, readily more than gold and platinum by itself. When roasting to remove sulfur, arsenic, cerium, etc. PGM metals probably volatile off because their oxygen state changed or because of atmospheric conditions, or should of been done under reducing (direct flame) conditions and not oxidizing conditions (electric kiln). Over numerous chemical methods and metallurgical testwork by reducing organic matter the platinum was lost by roasting it too high, changing it to an oxide. Roasting samples over several hours resulted in increases in Au/Pt content due to breakdown, and likely to favorable atmospheric conditions. For the most part PGM's are chemically inert, have high electrical conductivity and serve as catalysts in many chemical reactions.

WORK PERFORMED

DATES

1996

Winter trips:

Dec 1-3; 3 days

Dec 7-9; 3 days

1997

Winter trips:

Jan 7-8; 2 days

Jan 18-20; 2 days

Feb 1-3; 3 days

Feb 16-18; 3 days

Mar 4-5; 2 days

Summer trips:

June 25-30; 6 days

July 1-3; 3 days

July 9-12; 4 days

July 17-21; 5 days

Aug 1-7; 7 days

Spring trips:

Mar 24-29; 6 days

April 2-4; 3 days

April 30-May 2; 3 days

May 5-9; 5 days

May 15-18; 4 days

May 23-28; 6 days

June 10-14; 5 days

Sept 7-9; 3 days

Fall trips:

Sept 23-26; 4 days

Oct 5-6; 2 days

Oct 11-14; 4 days

Nov 3-4; 2 days

In 1996 there was a total of 2 trips & 6 days to the field. All trips and days are divided in half for each permit.(Permit no.# 9396110048 with 1 trip/3 days. Permit no. #9396110050 with 1 trip/3 days.)

In 1997 there was a total of 22 trips & 84 days to the field.(Permit no. #9396110048 with 11 trips/24 days. Permit no. #9396110050 with 11 trips/24 days)

1998

Winter trips:

Feb 11-13; 3 days

Spring trips:

April 26-30; 5 days

May 5-8; 4 days

May 23-28; 6 days

Summer trips:

June 13-16; 4 days

June 21-27; 7 days

Aug 12-17; 6 days

Aug 20-25; 5 days

Aug 31-Sept 1; 2 days

Sept 12-15; 4 days

In 1998 there was a total of 10 trips & 46 days in the field. (Permit no. #9396110048 with 5 trips/23 days. Permit no. #9396110050 with 5 trips/23 days.)

1996 FIELDWORK

The first two trips to the area were to get an orientation to the geological setting; ground work for which areas held better potential for a mineral deposit. Initial exploratory work was mainly done by foot traverse and only a few samples were taken at this time.

1997 FIELDWORK

Winter & Spring Work:

The roads were passable for as long as the frost was in the ground and still freezing at night. Access was sometimes gained by skidoo. During this period sample collecting sites were chosen and an area reconnaissance was done on both permits. Also several regional surface samplings. Samples were obtained by either a shovel or a hand auger and anywhere there was an open pit or soil moved by a pipeline crossing.

Summer & Fall Work:

Roads weren't passable because of the muskeg. To get to the location of sites was either done by foot traverse or quad, depending on distance and weather conditions.

While in the field, rock samples and panned concentrates were collected. Those samples were later processed and assayed for gold and platinum. With the aid of a microscope, to detect mineralization of interest, it was important to examine and identify the accompanying heavy minerals. Samples of oddity, staining, mineralization and weight were all selectively chosen.

1998 FIELDWORK

Winter & Spring Work:

More trips were taken to the permits and surrounding areas to find rocks of the same type and texture. All rocks were put in a pail and tagged, smaller samples were bagged and labeled according to area and surface coordinates. Most of the work performed was surface soil sampling and collecting.

Summer Work:

Grab samples were taken from various spots along the rivers and streams. To evacuate deeper a hand auger (with an extension adjustment) was used, boring holes from six to sixteen feet deep depending on the density of the rock and soil beneath the vegetation and peat moss. Any oddity of land was sampled, in a search for outcroppings. Many of the rivers and streams were panned, their concentrates studied on a microscope, later dried and bottled.

LAB AND RESEARCH LABOUR

With 136 days (Nov 21/96 - Nov 21/98) in total in the field (68 days on permit no. #9396110048), the rest of the time was dedicated to lab work and research. A total of 190 days (95 days) was claimed for assessment.

After each trip to Fort McMurray and/or Fort McKay, the samples were taken back to Edmonton, where a small lab was sent up to process and test them. Many hours were spent on exploratory laboratory work, first with simple chemical tests to more complicated procedures, using various chemicals. Working on concentration and leaching equipments, searching for a method and answers to why the metals won't assay consistently, extreme care taken in not to expose samples to sources of metallic contamination prior to process, assay and examination.

A kiln was purchased to roast samples. Prior to that a torch was used.

Experimental and unexperimental samples were couriered to different labs to be assayed.

While results were awaited, time was utilized in the library (Alberta Energy) doing research or going to the university for assistance. Research information gathering consisted of map searches (faults, overburden, geology) theories on gold deposition, geochemistry of gold and platinum, Alberta Geological Survey material on Prairie-type sedimentary Au-Ag-Pt., etc. At the University of Alberta instrumental analysis were performed.

STEEP BANK RIVER PERMIT

27TH BASE LINE

25TH BASE LINE

24TH BASE LINE

23RD BASE LINE

THICKWOOD

Fort McMurray

Gregory Lake Prov. Park

Permit # 9396110048

A map of Gregoire Lake Provincial Park. The lake is centrally located and labeled 'Gregoire Lake'. To the north is 'GREGOIRE LAKE PROV. PARK'. To the east is 'Anzac'. Roads are shown with labels 'Hwy. 100' and 'Hwy. 1'. A road segment is labeled 'L.R. 176B'. Another road segment is labeled 'L.R. 176A'.

LOCATION

The Steepbank River permit, totalling an aggregated area of 23,010 acres, portions on Townships 90-91-92, Range 8, West of the 4th, is bounded by a 56 latitude and 111 longitude. It is situated northeast of the town of Fort McMurray and Highway 63 by approximately six miles. There are several cutline and seismic trails throughout the property. The Steepbank River runs north and southwesterly through Township 91-92; and McLean Creek runs through a portion of Township 90, dipping south and east. The permit's one township is in the south portion of the Athabasca Basin and in the Alberta Oil Sands, and the Suncor Mine site overlaps the western portion of the permitted area.

GEOLOGY

TOPOGRAPHY AND DRIFT :

The land on this permit is mostly a low-lying region and is drained by the Athabasca River directly west of it. There are several intermittent streams and creeks. The rocks east of the Athabasca River are carbonaceous Devonian to lower Cretaceous. This particular area is also known for brinial activity proximal to bituminous coals.

Sample specimens contained:

- i) reddish ironstone
- ii) siliceous sand, partially clay
- iii) limestone till
- iv) green and blackish green shale
- v) rusty clay and sand

There is allegedly a broad zone of northeasterly faulting; and structural disturbances overlying the mineralized sources. No bedrock exposure was found. The overburden deepness is very shallow, < 50 feet.

REGIONAL GEOLOGY:

The area of Fort McMurray contains a diversity of rock types, including exposures of Precambrian Shield, Paleozoic carbonates and Cretaceous clastic sedimentary rocks and is situated on the edge of a significant subsurface brine basin (AGS, Dufresne & Henderson). Most of the area is underlain by rocks of Devonian and Cretaceous ages.

Northeast Alberta is known for its bitumen reserves in the Lower Cretaceous Mannville Group, the development of the oil sands within the McMurray Formation. The discovery of a potential for precious metals such as gold, silver and platinum in the Devonian carbonates, which

directly underlies the Cretaceous McMurray Formation, has put a new focus on the area. Between the Devonian and Cretaceous rocks there is the Beaver River sandstones (silica-rich) which outcrops in the Fort McMurray area. The McMurray Formation contains hydrocarbons, providing the necessary reducing environment.

The potential deposit types to explore for include:

- (a) Brine - and/or hydrocarbon related gold deposits.
- (b) Archean shear zone hosted gold deposits.
- (c) Mississippi Valley type lead-zinc deposits.
- (d) sediment hosted base metal deposits with one or more of zinc, lead, copper, nickel, silver and gold.
- (e) granitoid-related uranium and/or rare earth element, precious metal or base metal deposits.
- (f) sandstone-hosted or vein-type uranium deposits.
- (g) diamondiferous kimberlite or lamproite diatremes.
- (h) various types of placer or paleoplacer deposits, with the important metals/minerals being gold, diamonds, titanium or other heavy minerals. (AGS- Dufresne & Henderson)

EXPENDITURES

Currently two permits have reached the end of their 1st assessment period of November 21, 1998, and their assessment reports need to be submitted so the land can be kept for another two year term. One permit being no. #9396110048 on Township 90-91-92, Range 8, W4; the other being no. #9396110050 on Township 100, Range 11, W4. Their assessment work is general assaying, results from grab samples coming off both permits, including the expanse of area in between them. The samples assayed were rocks of the same rock type and texture, and their processing and assaying were done in duplicate, therefore the expenses will be divided equally between the two assessments.

Permit No. # 9396110048 - \$1,893.80
9396110050 - \$1,893.80

1996 EXPENDITURE STATEMENT (Nov 21- Dec 31)

	Full Total	Half Total
Office-----	\$15.00	\$7.50 <i>R</i>
Food-----	\$30.98	\$15.49 <i>P</i>
Gas (Fort McMurray)-----	\$49.60	\$24.80 <i>P</i>
Travelling expenses (mileage*)-----	\$1,200.00	\$600.00 <i>P</i>
Fieldwork labour (6 days@ #300/per day)-----	\$1,800.00	\$900.00 <i>S</i>
Fuel (Edmonton)-----	\$305.02	\$152.51 <i>P</i>
Equipment (microscope)-----	\$387.00	\$193.50 <i>V</i>
	\$3,787.60	\$1,893.80
Total expenses:	\$3,787.60	\$1,893.80

*Mileage - 1996 GMC 4x4: 2400 kms x \$.50

A total of \$69,592.52 was spent in 1997:

Permit no. #9396110048 - \$34,796.26

#9396110050 - \$34,796.26

1997 EXPENDITURE STATEMENT

	Full Total	Half Total
Office-----	\$682.14	\$341.07 <i>R</i>
Warranty (oxygen & acetylene)-----	\$90.00	\$45.00 <i>P</i>
Lodging-----	\$1,544.38	\$772.19 <i>P</i>
Food-----	\$328.56	\$164.28 <i>P</i>
Gas (Fort McMurray)-----	\$536.64	\$268.32 <i>P</i>
Travelling expenses (mileage*)-----	\$13,200.00	\$6,600.00 <i>P</i>
Fieldwork labour (46 days @ \$300/per day)-----	\$25,200.00	\$12,600.00 <i>S</i>
Transportation (plane)-----	\$300.00	\$150.00 <i>P</i>
Fuel (Edmonton)-----	\$2,597.90	\$1,298.95 <i>P</i>
Lab & Research labour (180 days @ \$100/per day)-----	\$18,000.00	\$9,000.00 <i>P</i>
Lab chemicals & supplies-----	\$4,000.52	\$2,000.26 <i>P</i>
Courier services-----	\$310.38	\$155.19 <i>R</i>
Assaying-----	\$1,659.00	\$829.50 <i>A</i>
Camping supplies-----	\$1,143.00	\$571.50 <i>P</i>
	<hr/>	<hr/>
Total Expenses:	\$69,592.52	\$34,796.26

* Mileage - 1996 GMC 4x4: 26,400 kms x \$.50

A total of \$59,545.36 was spent in 1998:

Permit no.#9396110048 - \$29,772.68
#9396110050 - \$29,772.68

1998 EXPENDITURE STATEMENT

	Full Total	Half Total
Office-----	\$1648.08	\$824.04 <i>R</i>
Warranty (oxygen & acetylene)-----	\$90.00	\$45.00 <i>P</i>
Lodging-----	\$529.90	\$264.95 <i>P</i>
Food-----	\$802.66	\$401.33 <i>P</i>
Gas (Fort McMurray)-----	\$576.38	\$288.19 <i>P</i>
Travelling expenses (mileage*)-----	\$6,000.00	\$3,000.00 <i>P</i>
Fieldwork labour (46 days @ \$300/per day)-----	\$13,800.00	\$6,900.00 <i>S</i>
Fuel (Edmonton)-----	\$1,549.08	\$774.54 <i>P</i>
Lab & Research labour (200 days @ \$100/per day)-----	\$20,000.00	\$10,000.00 <i>P</i>
Lab chemicals & supplies-----	\$2,138.14	\$1,069.07 <i>A</i>
Courier services-----	\$277.48	\$138.74 <i>R</i>
Assaying-----	\$2,605.92	\$1,302.96 <i>A</i>
Equip. purchases (kiln)-----	\$2,009.22	\$1,004.61 <i>P</i>
Consulting fees-----	\$2,500.00	\$1,250.00 <i>R</i>
Computer lease-----	\$2,018.50	\$1,009.25 <i>R</i>
Assessment report preparation-----	\$2,000.00	\$1,000.00 <i>A</i>
Helper (5 days @ \$200/per day)-----	\$1,000.00	\$500.00 <i>R</i>
Total Expenses:	\$59,545.36	\$29,772.68

*Mileage - 1996 GMC 4x4: 12,000 kms x .50

From the period, November 21, 1996 to November 21, 1998, a total of \$132,925.48 was spent on expenditures. Claiming \$66,462.74 on Permit no.# 9396110048
\$66,462.74 on Permit no.# 9396110050

CONCLUSION

This report is a preliminary assessment of the potential for metallic mineral deposits in the tar sands and surrounding areas of N.E. Alberta. Although there has been extensive scientific research done on this area, there has been doubt and minimal exploration work done with the metallogeny of heavy oil in comparison to other parts of the world, such as Russia (Report on Metallogeny of Heavy Oils, Natural Bitumens & Oil Shales; Goldberg)

This compilation of assessment work summarizes the results of two years of research, by physically testing and assaying samples and rocks from beginning to end. By working with the mineralization of this nature it is quickly learned procedural and metallurgical problems first have to be addressed, and not ignored, before any assaying can be accurate or truthful to what actual values of minerals and metals exist.

In using various various experimental methods, and analytical work at the university and labs, the work performed was successful in identifying anomalous values of several precious and base metals, showing an increase of those values with a better process and leach. Example being #1 (raw) and #2 (pre-leach) in comparison to #3 (leach residue), all the same sample; assayed and resulting differently. All the assaying completed showed you first have to separate something, so you to develop the right leach, if you want to effectively record a higher value in a difficult-to-assay rock and metal such as platinum. The results show the gold and platinum are there. Assay problems will take due diligence, because the oddity in the complexes in the mineralization are yet to be all identified. Before there is any feasibility of extraction further research and time will need to be applied to solve and combat those complexities and by understanding the origins of the gold and PGE's the answers will undoubtedly follow.

RECOMMENDATIONS:


Further evaluation and assessment is warranted with pre-assaying samples and rocks, to better define mineralized trends, to subsequently pick out drill locations.

This area is structurally perfect for a discovery of metals or diamonds, because of the uplift of the Peace River Arch and its location to the Proterozoic Taltson Arc, a strong magnetic high.

A diamond indicator mineral analysis should be done in order to assess its potential for kimberlite and diamonds, also being found close by.

DECLARATION

I, Larry MacGougan, solemnly swear all expenditures claimed on this assessment are valid and were spent on assessing the mineralogy of this permit.



AUTHOR INFORMATION:

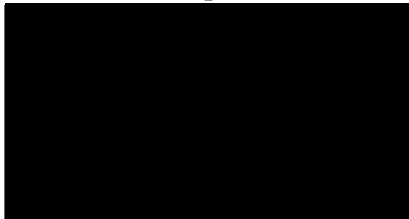
This report was prepared by Debbie Puckett. The work and results reported herein were carried out by and under the supervision of Larry MacGougan.

Larry MacGougan is the permit holder. He is a full-time prospector and files as such with Revenue Canada. He has over ten years of experience in prospecting and mining. He is also the vice- president of 374624 Alberta Limited.

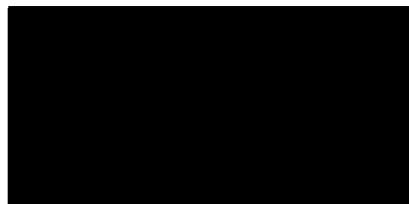
Chris Puckett was his helper in 1998 on one expedition. He worked five days.

Addresses of the above:

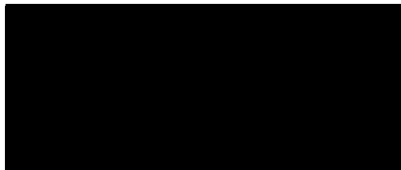
Larry MacGougan



Debbie Puckett



Chris Puckett



REFERENCES

- Abercrombie, H. & Feng R.; Disseminated Au-Ag-Cu Mineralization in the Western Canadian Sedimentary Basin, Fort McKay, NE Alberta, presented at C.I.M., Toronto, 1994.
- Dufresne, M.B. & Henderson, B.A.; The Mineral Deposits Potential of the Marguerite River and Fort McKay Areas, Northeast Alberta, Alberta Research Council, 1994.

Steep River

Uradium
Cassell
Structure

Kimberley

MUNICIPALITY OF

WOOD BUSH

8

peace River
arch
axis

To
Peace River
by walking

PROVINCIAL PARK

7

17

Steep Bank River Land

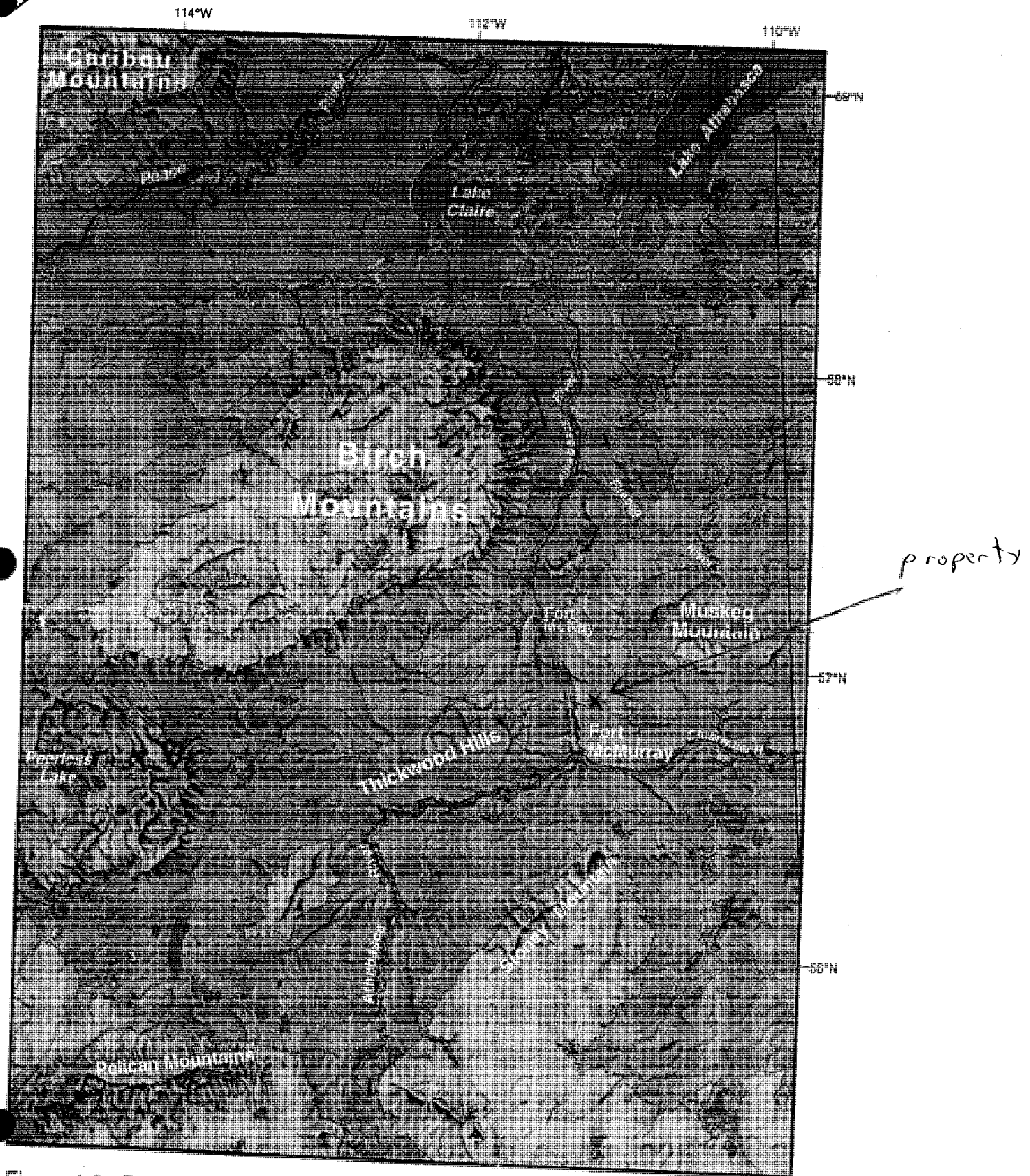
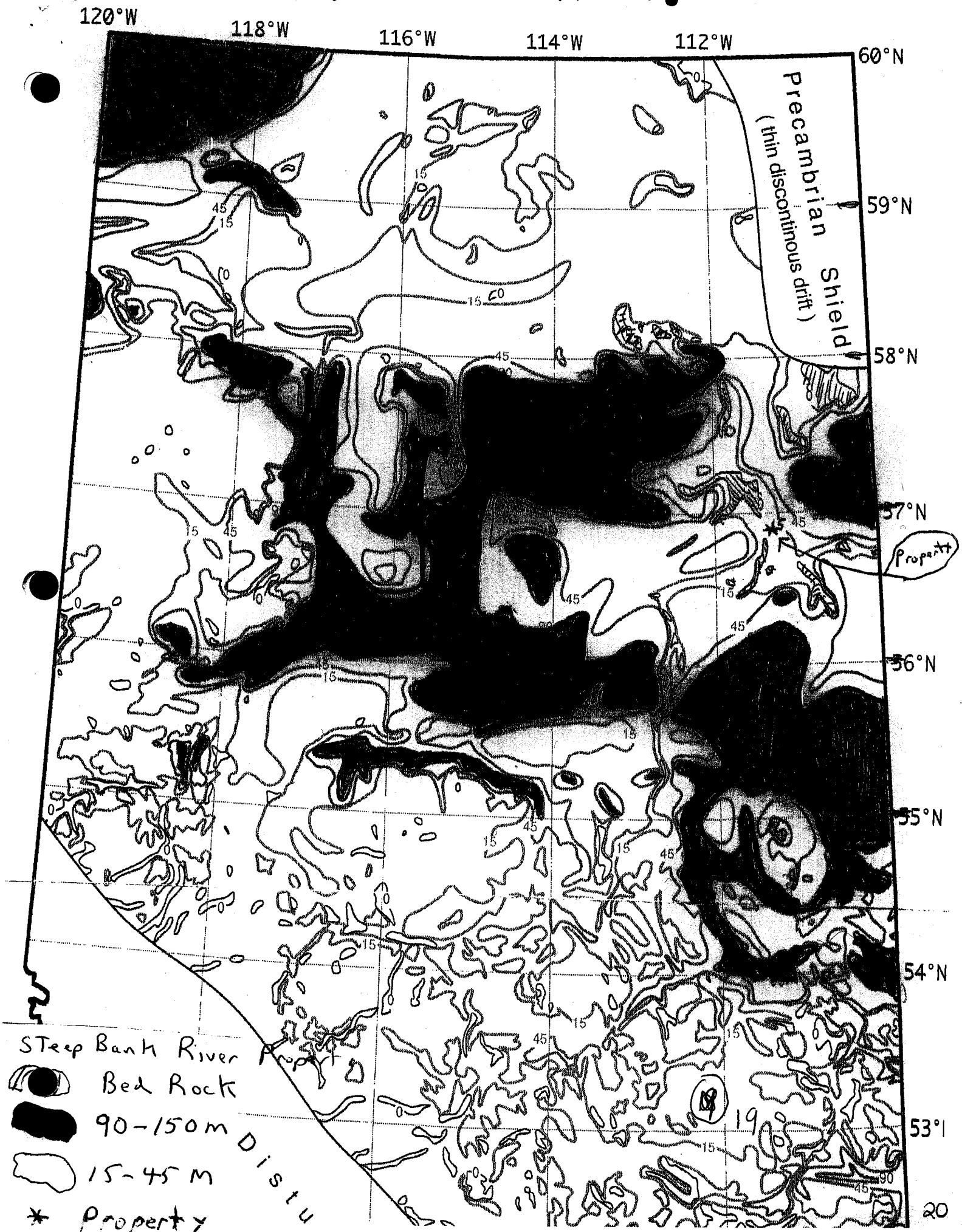
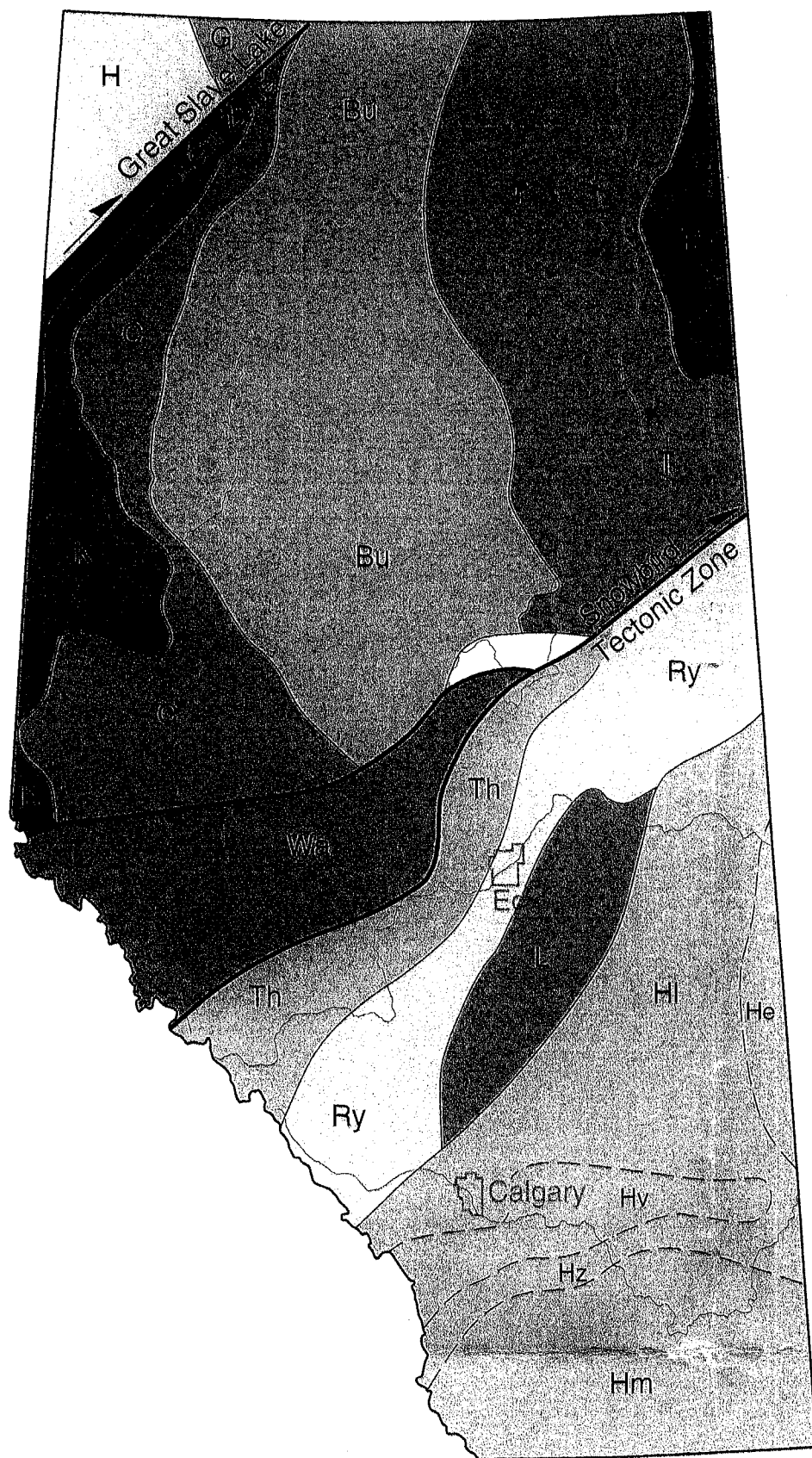


Figure 1.3. Physiographic map of northeastern Alberta showing location of major topographic features (from Alberta Transportation, 1978).

Drift thickness



Precambrian Basement Tectonic Features



LOWER PROTEROZOIC (1.8 - 2.5 Ga)

CONTINENTAL MARGIN

MAGMATIC ARCS (1.78 - 1.98 Ga)

Ry	Rimbey
G	Great Bear
T	Taltson
K	Ksituan

ACCRETED TERRANES (2.0 - 2.4 Ga)

H	Hottah
Bu	Buffalo Head
C	Chinchaga
Th	Thorsby

METAVOLCANIC - METASEDIMENTARY ROCK

L	Lacombe Domain
---	----------------

MYLONITIC ROCK ALONG SNOWBIRD TECTONIC ZONE

W	Wabamun Domain
---	----------------

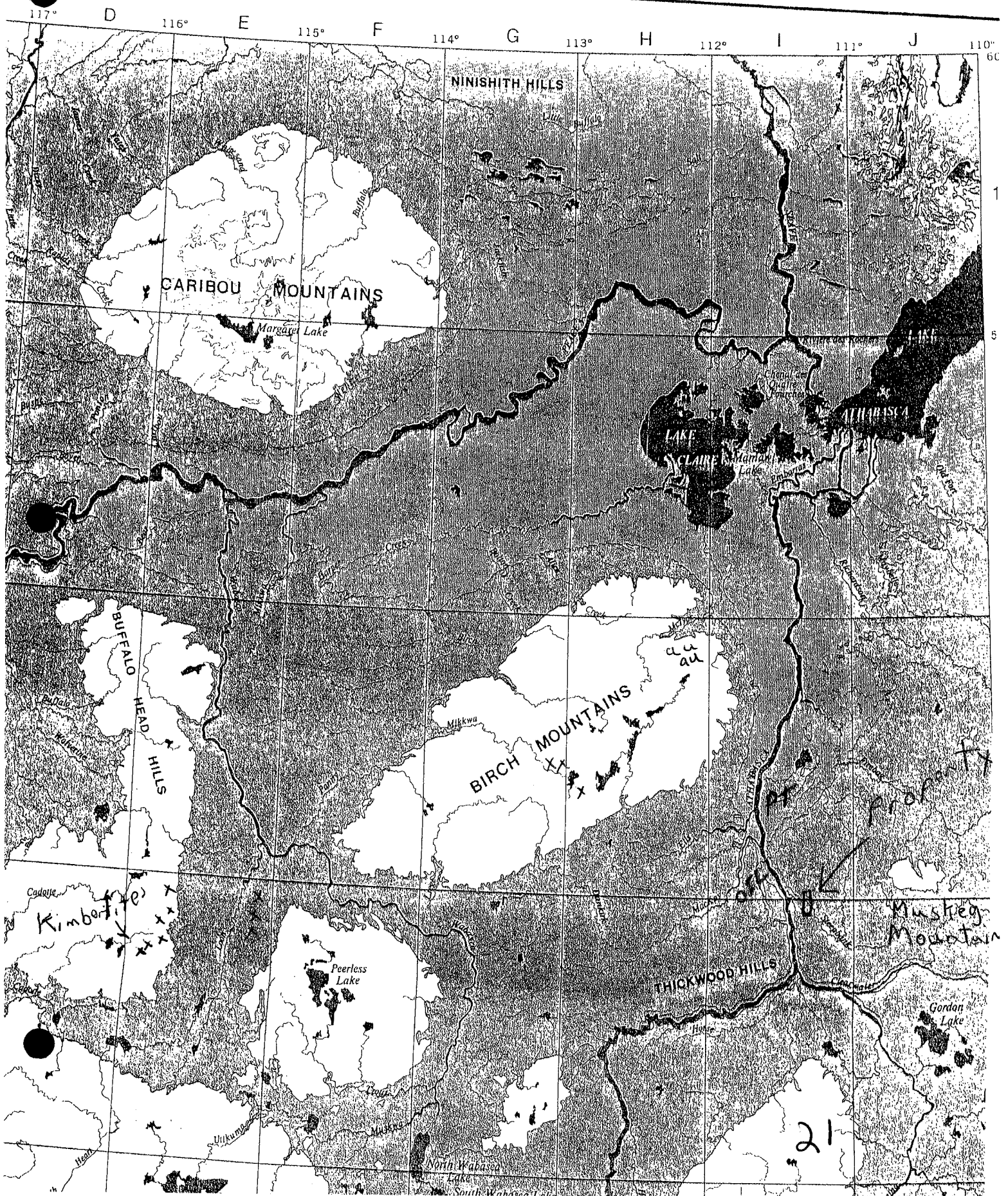
ARCHEAN PROVINCES (>2.5 Ga)

HEARNE

H ₁	Medicine Hat Block (Hm); Vulcan Low (Hv); Matzhiwin High (Hz); Eyehill High (He); Loverna Block (Hl)
R	Rae
S	Slave?
	Age unknown

From *Geological Survey of Canada*

Steep Bank Land



CRETACEOUS

UPPER AND LOWER CRETACEOUS



LABICHE FORMATION: dark grey shale and silty shale; ironstone partings and concretions; silty fish-scale bearing beds in lower part; marine

LOWER CRETACEOUS



PELICAN FORMATION: fine-grained quartzose sandstone, silty and glauconitic in lower part; marine



JOLI FOU FORMATION: dark grey fossiliferous shale, silty interbeds in upper part; marine



GRAND RAPIDS FORMATION: fine-grained quartzose and feldspathic sandstone, laminated siltstone and silty shale; thin coal beds; shoreline complex



CLEARWATER FORMATION: dark grey, fossiliferous, silty shale; laminated siltstone and fine-grained cherty sandstone; glauconitic sandstone (**Wabiskaw Member**) near base; marine



McMURRAY FORMATION: thick-bedded quartzose sandstone and siltstone; oil-impregnated; grey silty shale interbeds in upper part; nonmarine to deltaic

DEVONIAN

UPPER DEVONIAN



WATERWAYS FORMATION: grey and greenish grey shale and argillaceous limestone interbedded with grey and greyish brown, fine-grained to coarse clastic limestone; marine

MIDDLE DEVONIAN



SLAVE POINT FORMATION: grey and brown fine- to medium-grained limestone and dolomitic limestone; minor shale, gypsum; marine



FORT VERMILION FORMATION: white and grey gypsum, argillaceous and dolomitic gypsum; minor anhydrite; some fine-grained limestone, dolomitic limestone and green shale; evaporitic



MUSKEG FORMATION: white and grey gypsum, anhydrite; minor dolomite, salt and shale; evaporitic



KEG RIVER FORMATION: grey and brown fine- to medium-grained limestone, thin- to thick-bedded, locally richly fossiliferous and coarse grained; grey medium-grained dolomite, locally vuggy (upper member); fine-grained brown dolomite and laminated dolomite, locally vuggy; minor limestone; unit locally much brecciated and cemented (lower member); marine



CHINCHAGA FORMATION: white and grey gypsum, argillaceous and dolomitic gypsum and anhydrite; some dolomite, dolomitic limestone, red and green shale; some salt in subsurface; evaporitic



FITZGERALD FORMATION: grey and brown fine- to medium-grained dolomite to sandy dolomite and dolomitic limestone, locally vuggy, grading down into sandstone, arkose and breccia (**La Loche Formation**); marine



MIDDLE DEVONIAN (undivided): arkosic sandstone (**La Loche Formation**); grey-green and sandy shale, reddish shale; dolomite; minor anhydrite (**McLean River Formation**); br and buff, massive, porous dolomite; brown to grey thin-bedded dolomite; dolomitic limestone (**Methy Formation**); gypsum; anhydrite; grey-green silty and dolomitic shale; minor dolomite (**beached Prairie Evaporite Formation**); marine to evaporitic

Note: McLean River, Methy and Prairie Evaporite Formations are equivalents of Chinle, Keg River and Muskeg Formations respectively, the Prairie Evaporite including a thick succession of salt beds in subsurface

HELIKIAN

ATHABASCA GROUP

HELIKIAN

ATHABASCA GROUP



OTHERSIDE FORMATION: sandstone with minor siltstone; nonmarine



LOCKER LAKE FORMATION: massively bedded pebbly sandstone and sandstone; nonmarine



WOLVERINE POINT FORMATION:

Hw-u: upper Wolverine Point - altered vitric and ash-flow tuffs, interbedded with medium-grained, clay-rich, friable sandstones; marine-pyroclastic
Hw-l: lower Wolverine Point - medium-grained sandstone, with minor interbedded siltstone; nonmarine-marine



MANITOU FALLS FORMATION: medium-grained pebbly sandstone and sandstone; abundant clay intraclasts; nonmarine



FAIR POINT FORMATION: coarse-grained, pebbly, clay-rich sandstone; conglomeratic at base; nonmarine

APHEBIAN



LOW GRADE METASEDIMENTARY AND METAVOLCANIC ROCKS: arkosic sandstones, felsic and mafic volcanics, turbidites, phyllite; locally ferruginous, gold bearing shear zones, with quartz-tourmaline veins (**Waugh Lake Group**); arkosic sandstone with pebble bands interbedded with subordinate phyllonitic chloritic argillite (**Burntwood Group**)



GRANITOIDS: reddish, medium- to coarse-grained, megacrystic, well foliated, feldspar-blue quartz-biotite granite (**Arch Lake Granitoid**); pink-spotted medium grey, medium-grained, megacrystic, massive granite (**Francis Granite**); red to pink, medium- to fine-grained, equigranular, massive to poorly foliated biotite granite (**Chipevyan Red Granite**); light grey to brownish grey, medium-grained, rarely megacrystic, massive to poorly foliated granodiorite (**La Butte Granodiorite**); dark greenish to brownish red, medium-grained, equigranular, massive to poorly foliated, feldspar-quartz-biotite granodiorite (**Wylie Lake Granitoids**); light grey to pink or reddish, medium- to fine-grained, equigranular, massive to foliated, alkali feldspar-quartz-plagioclase-biotite granite (possibly K feldspar-enriched **Wylie Lake Granitoid?**); grey, medium-grained, megacrystic, poorly foliated, feldspar-quartz-biotite quartz diorite (**Fishing Creek Quartz Diorite**); light to medium grey, medium-grained, equigranular, moderately foliated to massive, alkali feldspar-quartz-plagioclase-biotite granite (possibly K feldspar-enriched **Fishing Creek Quartz Diorite?**); light to medium grey, medium- to coarse-grained, megacrystic, well foliated, biotite-quartz-feldspar granite (**Collin Lake Granitoids**); dark grey, with red to pink megacrystic augen feldspars, medium-grained, foliated, blue grey quartz-biotite granite (**Thesle Lake Granite**); whitish grey, medium- to coarse-grained, locally megacrystic, massive to foliated, feldspar-quartz-biotite granodiorite (**Slave Granitoids**)



MYLONITIC ROCKS: dark grey to dark green, fine-grained, massive rock; light grey felsic varieties present locally; commonly chlorite epidote-rich; well-foliated with streaky patches of quartz and feldspar; includes protomylonites

ARCHEAN



CHARLES LAKE GRANITOIDS: subhedral feldspars in coarse-grained, massive to poorly foliated megacrystic granite; buff to grey with dark spots of hornblende and local feldspar megacrysts in fine- to medium-grained, massive to slightly foliated grey hornblende granite; equigranular, medium- to coarse-grained, massive to locally foliated leucocratic granite



HIGH-GRADE METASEDIMENTARY ROCKS: typically dark greenish grey, fine-grained quartzite; interlayered with ferruginous and garnetiferous zones; minor amphibolite; locally fine- to medium-grained metamorphic quartz-feldspathic phase; fine-grained retrograde phyllite and schist, and phyllonite



GRANITE GNEISSES: pink to reddish, fine- to medium-grained, equigranular to rarely megacrystic, well banded to foliated, granitic composition, quartz-feldspar bands interlayered with mafic-rich bands; predominantly biotite-rich but rarely hornblende; commonly migmatitic

Steep Bank River
First Bed Rock

For Map # 23

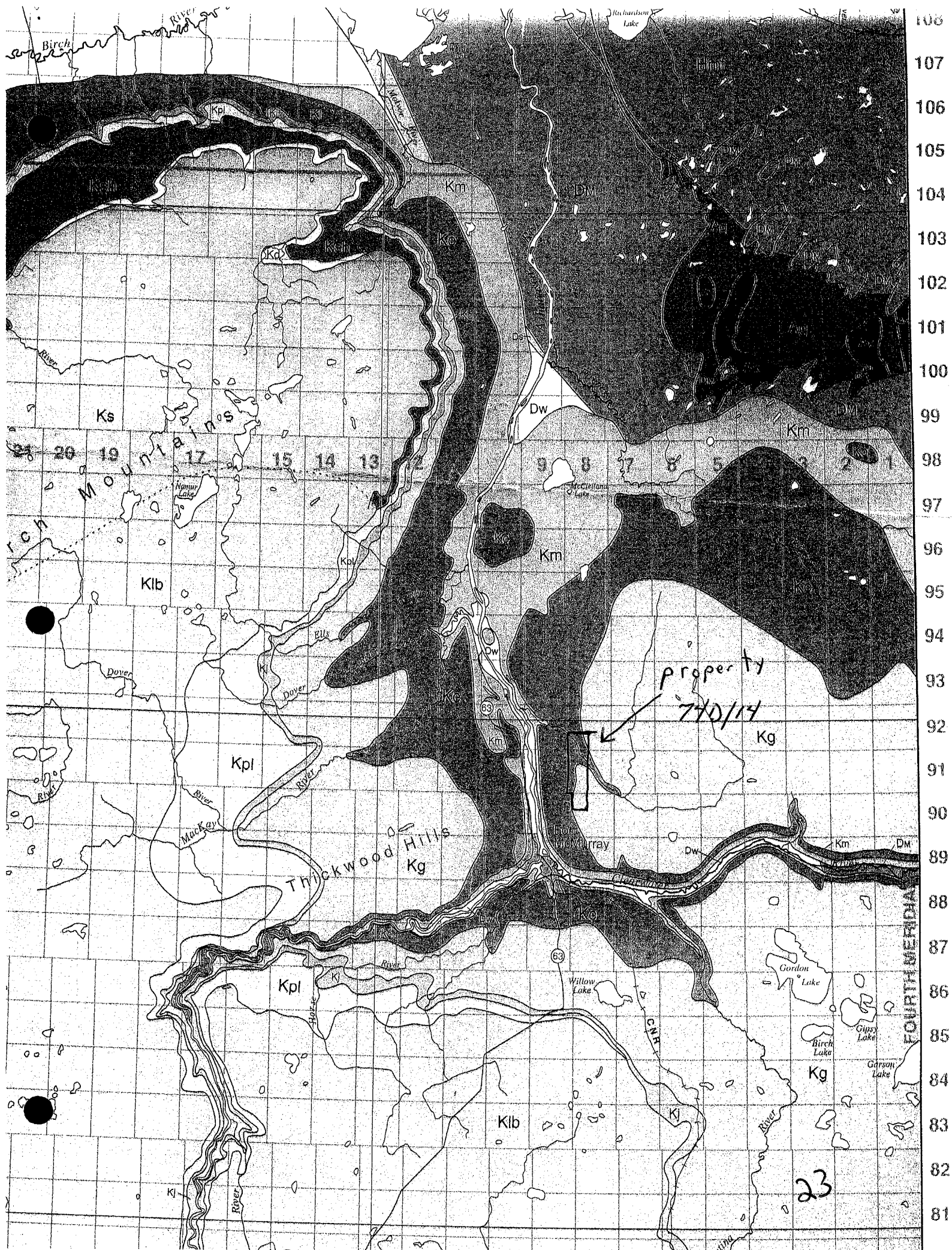


Table 2. Generalized Stratigraphy For The Bitumount Area ¹

SYSTEM	GROUP	FORMATION	MEMBER	DOMINANT LITHOLOGY
Upper Cretaceous	La Biche north Start steep bank	La Biche	CAH	Shale
		Dunvegan		Sandstone & siltstone
		Shaftesbury		Shale, bentonites, fish-scale horizon
Lower Cretaceous	Missouri	Pelican		Sands
		Joli Fou		Shale
	Mannville start south	Grand Rapids		Lithic sands
		Clearwater	✓	Shale & glauconitic sands
		McMurray		Quartzose sands, heavy oil
Jurassic?		Beaver River		Quartzose sandstone
Upper Devonian	Beaverhill Lk.	Waterways	Mildred	Argillaceous limestone
			Moberly	Limestone & shale
			Christina	Shale & limestone
			Calumet	Limestone & shale
			Firebag	Shale, minor limestone
Middle Devonian		Slave Point		Limestone, local breccia
	Upper Elk Point	Prairie Evapoite		Salt, anhydrite (gypsum), shale & dolomite
		Methy		Dolomite, minor reefs
	Lower Elk Point	McLean River		Shale, siltstone & dolomite
		Cold Lake		Salt, minor shale
		Ernestina		Shale, limestone & Anhydrite
		Lotsberg		Salt, minor shale
		LaLoche		Arkosic sand & conglomerate
Precambrian				Granitic basement

Start

¹Modified after Carrigy (1959, 1973), Norris (1963, 1973) and Hamilton (1971).

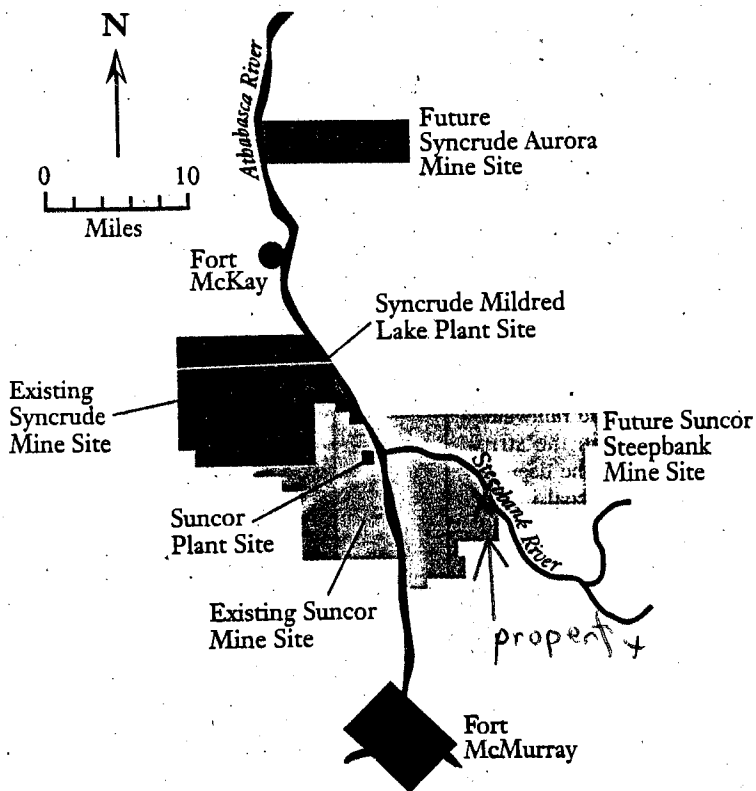
Back in 1967, when Great Canadian Oil Sands Ltd. (one of the precursors to Suncor) invested \$250 million to build the first commercial plant to extract bitumen from the oil sands and up-grade it to salable crude, the plant was designed to produce 45,000 barrels of product per day. Today, the operation cranks out 78,400 barrels a day and plans are in place to increase further to 105,000 barrels per day by the year 2000.

To get just one barrel of product, the operation mines one and a half tonnes of oil sand. So, to feed the expanded plant, the mine will have to be capable of supplying 72.6 million tonnes of oil sands per year compared with the current 48.9 million tonnes.

Key to the expansion plans is a wholesale change in the corporate culture at Suncor — essentially bringing the company out of its 1960s mindset and into the 1990s way of thinking, or, as Executive Vice President of the Oil Sands Group, Dee Parkinson prefers to state it: "creating economic value by doing things that make environmental sense."

"In the past, managers didn't under-

The Oil Sands Mines of Tomorrow



TWO SCOOPS OR THREE?

Three, actually. And about 100 seconds. That's

how long it takes, on average, to load each of our 218-tonne trucks at Mildred Lake.

It's taken a little bit longer for us to develop into one of Canada's premier mining companies.

In the past 10 years we've grown from a single coal mine in British Columbia to eight diversified operations in North America, with a ninth under development in Mexico.

We're proud of our achievements. And equally proud to be involved in Alberta's exciting oil-sand industry.

Fording
COAL LIMITED
ENERGY FOR THE FUTURE

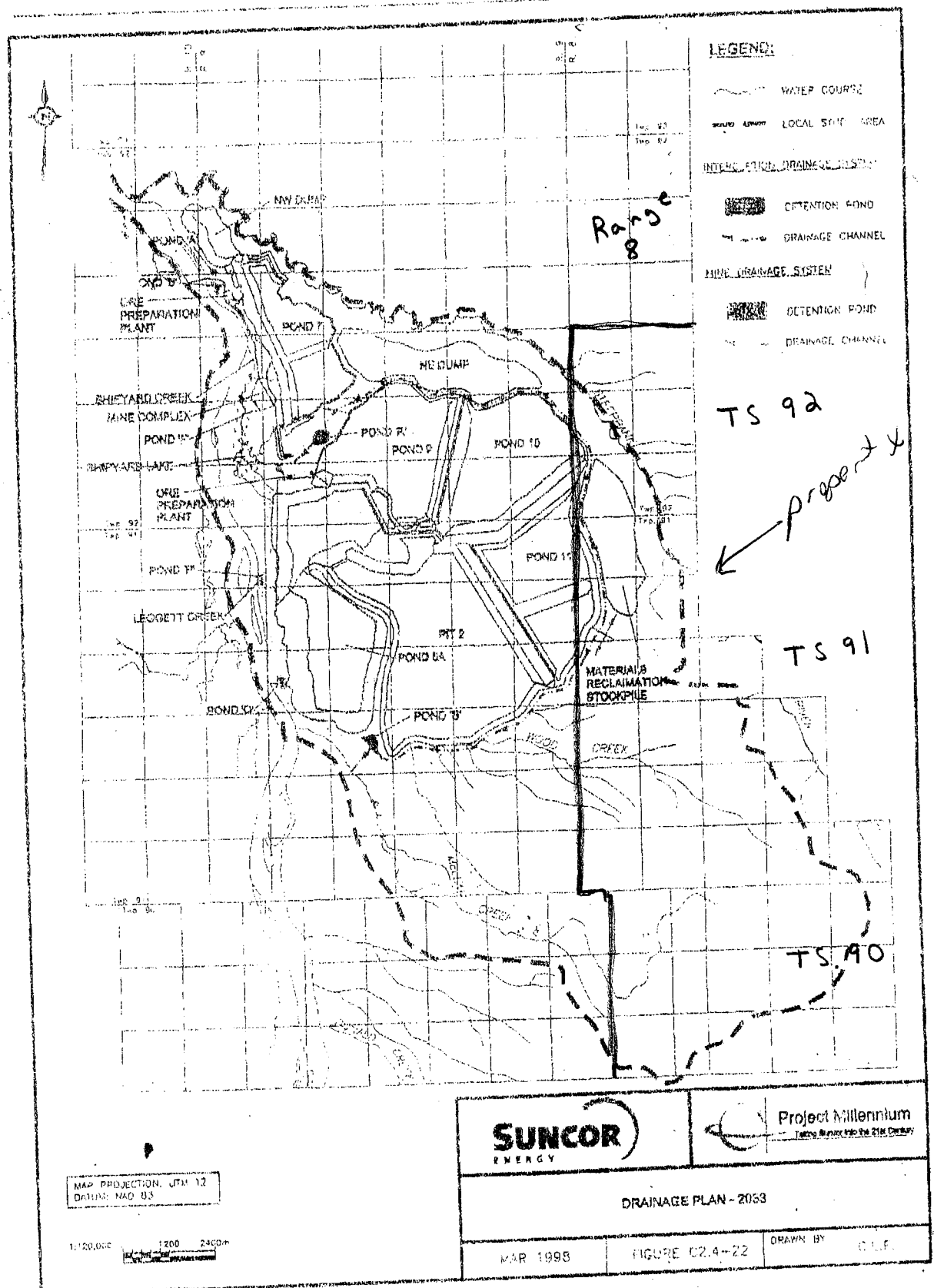


Figure C2.4-22 Drainage Plan - 2033

steep bank River

26

GOLD AND PLATINUM GROUP ELEMENTS

ROCKPECKER TIP # 218 -- If your ore tests positive for GOLD, have it tested for PLATINUM GROUP METALS. If it tests positive for platinum & palladium, have the ore assayed for OSMIUM, RHODIUM, and RUTHENIUM. Two or more of these metals are usually alloyed together as PLATINUM GROUP METALS.

ROCKPECKER TIP # 219 - ASSAYS can pick up low GOLD values ranging to .008 oz. Au/ton with good repeatability and acceptable limits. With low gold values a check assay can be ordered where INQUARTS of gold are added to the sample. (This is a spiking procedure where an ore of known gold value is added to the sample.) For example: If you have 1 gold coin and place it in a glass of water, then add 2 more gold coins, you expect to count 3 coins.

THE ROCKPECKER TIP PROBLEM -- What if you only count 2 coins ?

IT HAS BEEN FOUND THAT CERTAIN NATURAL, PLATINUM GROUP ELEMENT ORES, WHEN COMBINED WITH GOLD, BARELY SHOW THE GOLD VALUE AND SOMETIMES NONE OF THE PLATINUM GROUP ELEMENTS. In fact, the more spiking or inquarting of gold into the sample, the lower the GOLD values reported. The reason for this strange behavior is unknown. It is as if the gold is being eaten without trace. Your tip-off to look more closely, will be a fire assay which produces a gold bead that looks unusual, oftentimes indicating the probable presence of other elements. THESE MAY BE PGM'S. CHECK !

FOR THESE REASONS, GOLD TEST # 6 AND GOLD TEST # 7 ARE PRESENTED.

IF YOUR PRE-ASSAY TESTS INDICATE GOLD, PLATINUM, PALLADIUM AS PRESENT, AND THE FEE-ASSAY REPORT READS "NONE REPORTABLE", YOU MAY HAVE THIS STRANGE ORE.

If test # 6 GOLD SPOT TEST shows the presence of GOLD, you should retest for antimony, sulfides, and tellurium as combining elements in the GOLD ORE before ROASTING. Too high a roasting heat makes ores containing those elements REFRACTORY. (If you consider using the rosebud on your acetylene torch, you must be extremely careful in heating.) HEATING temperatures OVER 1000 C (1800 F) lock gold, platinum and palladium into a refractory so that chemical identity is retained in spite of high temperatures. THIS MEANS THE ORE SHOULD NEVER EXCEED "VERY DULL RED HEAT".

ROASTING ORE -- Ore is roasted to get rid of sulfides, tellurides, antinomides, and to reduce elements to the metallic state.

PROCEDURE -- The idea is to check for heavier elements in your crude ore. You'll need a few pounds of ore. Crush it, bring it to a dull red heat, stirring, until all the gases such as smoke and fumes are released. Then pulverize the sample. Pan it to concentrate the "heavies" and wash off the lighter material. Use a magnet to remove the magnetics. USE 1 SPOONFUL FOR TESTS.

GOLD,
MATERIALS NEEDED --

For Gold Spot Test

OTHER MATERIALS NEEDED
dishes, 4 cc's pure
(KI), alcohol lamp.

TEST #

TEST RESULT -- TEST

TEST #

TEST RESULT -- TEST

CONFIRM ROSE
solution, the
dish. RESULT

ducting the TEST AC
the solution turns
on the dish bottom
solution, the higher

STEEP BANK RIVER ASSAYS

SAMPLE LOCATION UTM N 6315100
E 482505

TILL SAMPLES 200 m RADIUS.



Intertek Testing Services

Bondar Clegg

Lab
Report

1

CLIENT: MR. LARRY MACGOUGAN
REPORT: V97-01599.0 (COMPLETE)

DATE RECEIVED: 10-JUL-97

PROJECT: NONE GIVEN

DATE PRINTED: 30-JUL-97

PAGE 1 OF 2

SAMPLE NUMBER	ELEMENT UNITS	AU PPB	PT PPB	PD PPB
R2 3		3	<5	<1
R2 4		4	<5	<1

Steep Bank River

Green Shale - Drill hole

High Iron 15%.

~~prop~~ - Lihlx Till slab

Normal Assay

ITS

Intertek Testing Services

Bondar Clegg

2

Geochemical
Lab
Report

CLIENT: MR. LARRY MACGOUGAN

PROJECT: NONE GIVEN

REPORT: V97-02342.0 (COMPLETE)

DATE RECEIVED: 04-SEP-97

DATE PRINTED: 22-SEP-97

PAGE 3 OF 3

SAMPLE NUMBER	ELEMENT UNITS	AU PPB	PT PPB	PD PPB
------------------	------------------	-----------	-----------	-----------

P12 1		10	<5	<1
Duplicate		42	<5	1

Steep Bank River

Rusty iron stone To Black
Till Sample

Normal Assay

Bondar-Clegg & Company Ltd.

130 Pemberton Avenue, North Vancouver, B.C., V7P 2R5, Canada

Tel: (604) 985-0681, Fax: (604) 985-1071



Intertek Testing Services

Bondar Clegg

3

Geochemical Lab Report

CLIENT: MR. LARRY MACGOUGAN

REPORT: V97-02018.0 (COMPLETE)

DATE RECEIVED: 12-AUG-97

PROJECT: NONE GIVEN

DATE PRINTED: 25-AUG-97

PAGE 1 OF 2

SAMPLE NUMBER	ELEMENT UNITS	AU PPB	PT PPB	PD PPB
84 7		16	<5	1
84 8		11	<5	<1
84 9		15	<5	3

Steep Bank River

Sand stone Till

Normal Assay

Bondar-Clegg & Company Ltd.

130 Pemberton Avenue, North Vancouver, B.C., V7P 2R5, Canada

Tel: (604) 985-0681, Fax: (604) 985-1071

Iron - Carbon

Limestone

4

Steep Bank River

Purpose: To determine Au and Ag content by cyanidation of Sample #1, (460-012).

Procedure: The sample was pulverized to 100% passing 100 mesh, and then pulped with water to 33% solids in a 2.5 L bottle. Lime and NaCN were added and the leach carried out over 48 hours on rolls. At the end of the leach period the pulp was filtered and washed thoroughly with water. The pregnant/wash solution and the residue were submitted for gold and silver analyses.

Feed: 380 g of Sample # 1 (460-012)

Solution Volume: 770 mL

Pulp Density: 33 % solids

Sol'n Composition: 2 g/L NaCN

pH Range: 10.5 - 11.2 with Ca(OH)_2

Reagent Consumption (kg/t of cyanide feed) NaCN: 0.22 CaO: 1.86

Time hours	Added, Grams				Residual		Consumed		pH
	Actual		Equivalent		Grams		Grams		
	NaCN	Ca(OH) ₂	NaCN	CaO	NaCN	CaO	NaCN	CaO	
0 - 4	1.61	0.41	1.53	0.31	1.46		0.07		11.0-9.9
4 - 22	0.08	0.28	0.08	0.21	1.50		0.04		11.1-10.5
22 - 30	0.04	0.08	0.04	0.06	1.54		0.00		11.1-10.6
30 - 48	0.00	0.17	0.00	0.13	1.56	0.02	-0.02	0.70	11.2-10.9

Total	1.73	0.95	1.65	0.72	1.56	0.02	0.08	0.70
-------	------	------	------	------	------	------	------	------

Results:

Product	Amount g, mL	Assays, mg/L, g/t		% Distribution	
		Au	Ag	Au	Ag
48 hour Preg/Wash	1359	0.025		> 81.9	
CN Residue	375.8	< 0.02	*	< 18.1	
Head	375.8	< 0.11		100.0	

The residue Au assay was reported as less than the analytical detection limit of 0.02 g/t, therefore the 48 hour gold extraction is greater than 81.9%.

Normal NaCN Leach Test

To: MR. LARRY MACGOUGAN
Box 56
Coronation, Alberta
TOL 1C0



5

Certificate of Assay
Loring Laboratories Ltd.

Sample No.	OZ./TON GOLD	OZ./TON SILVER
<u>"Assay Analysis"</u> #1B	0.010	<0.01
<p>- 30g start - iron Carbon Lime stone - Leach with Sulphurous Leach - send Leach Residue To Loring Coronation - Calculate Back To 30g - <u>Experimental Assay</u></p>		

I HEREBY CERTIFY that the above results are those assays
made by me upon the herein described samples:

Assayer

Rejects and pulps are retained for one month unless specific arrangements are made in advance.

6 Geochemical Lab Report

CLIENT: MR. LARRY MACGOUGAN
REPORT: V99-00011.0 (COMPLETE)

DATE RECEIVED: 05-JAN-89

PROJECT: NONE GIVEN

DATE PRINTED: 8-FEB-89

PAGE 1A(1/ 2)

SAMPLE NUMBER	ELEMENT UNITS	Au PPM	Pt PPM	Pd PPM	Au Wt1 GM	AU PPB	PT PPB	PD PPB	Au PPB	Pt PPB	Pd PPB	Rh PPB	Os PPB
P4 SAMPLE 1					15.10	9	7	10					
P4 SAMPLE 2					7.66	16	14	20					
P4 SAMPLE 3									4	<20	<20	<5	<10
B4 SAMPLE 4		0.189	0.048	0.058									

Normal Assay

- iron stone same sample

Steep Bank River

Interrek Testing Services - Bondar Clegg
130 Pemberton Avenue, North Vancouver, B.C., V7P 2R5, Canada
Tel: (604) 985-0681, Fax: (604) 985-1071

To: MR. LARRY MACGOUGAN
Box 56
Coronation, Alberta
TOL 1C0



Certificate of Assay
Loring Laboratories Ltd.

629 Beaverdam Road, NE Calgary Alberta
Tel: (403)274-2777 Fax: (403)275-0541

7
File No : 38866
Date : February 14, 1997
Samples :
Project :
P.O.#

Sample No.	OZ./TON GOLD	OZ./TON SILVER	OZ./TON PLATINUM
1	0.001	<0.01	<0.001
2	0.016	<0.01	<0.001
3	<0.001	<0.01	<0.001

1st and 3rd Normal assay
2nd Leach Residue Fired
Experimental Assay

I HEREBY CERTIFY that the above results are those assays
made by me upon the herein described samples :

Assayer

Rejects and pulps are retained for one month unless specific arrangements are made in advance.

To : MR. LARRY MACGOUGAN
Box 56
Coronation, Alberta
T0C 1C0



Certificate of Assay
Loring Laboratories Ltd.

629 Beaverdam Road, NE Calgary Alberta
Tel: (403)274-2777 Fax: (403)275-0541

File No : 38872
Date : February 24, 1997
Samples : Filters
Project :
P.O.#

Sample No.	PPB Au	PPM Ag	PPB Pt
<u>"Assay Analysis"</u>			
1	<5	<0.1	<10
2	<5	<0.1	<10
3	<5	<0.1	<10
4	<5	<0.1	<10
Steep Bank Grab Samples Assay <u>Normal Assays</u>			

I HEREBY CERTIFY that the above results are those assays
made by me upon the herein described samples :

Assayer

Rejects and pulps are retained for one month unless specific arrangements are made in advance.

To: MR. LARRY MACGOUGAN
Box 56
Coronation, Alberta
T0L 1C0



Certificate of Assay
Loring Laboratories Ltd.

629 Beaverdam Road, NE Calgary Alberta
Tel: (403)274-2777 Fax: (403)275-0541

9
File No : 40438
Date : September 17, 1998
Samples :
Project :
P.O.#

Sample No.	Au oz/ton	Ag oz/ton
<u>"Assay Analysis"</u>		
# 1	< 0.001	< 0.01
# 2	< 0.001	< 0.01
# 3	< 0.001	< 0.01
Steep Bank - iron stone Light color <u>Normal assay</u>		

I HEREBY CERTIFY that the above results are those assays
made by me upon the herein described samples :

Assayer

Rejects and pulps are retained for one month unless specific arrangements are made in advance.

To: MR. LARRY MACGOUGAN
Box 56
Coronation, Alberta
T0L 1C0



File No : 39435
Date : August 25, 1997
Samples :
Project :
P.O.#

Certificate of Assay Loring Laboratories Ltd.

629 Beaverdam Road, NE Calgary Alberta
Tel: (403)274-2777 Fax: (403)275-0541

Sample No.	ppb Au	ppb Pt	oz/ton Ag
<u>"Geochemical Analysis"</u>			
# 4	< 5	---	< 0.01
# 4B	< 5	< 5	< 0.01
Step Bank Normal Assay # 4 B Sample Rock as page 5 ^A Leach			

I HEREBY CERTIFY that the above results are those assays
made by me upon the herein described samples :

Assayer

Rejects and pulps are retained for one month unless specific arrangements are made in advance.



Intertek Testing Services

Bondar Clegg

11

Geochemical Lab Report

CLIENT: MR. LARRY MACGOUGAN

REPORT: V98-01591.4 (COMPLETE)

PROJECT: NONE GIVEN

DATE RECEIVED: 01-SEP-98

DATE PRINTED: 14-SEP-98

PAGE 1A(1/ 4)

SAMPLE NUMBER	ELEMENT UNITS	AU	PT	PD	Au	Ag	Ag	Cu	Pb	Zn	Mo	Ni	Co	Cd	Bi	As	Sb	Fe	FeOL	Mn	Te	Ba	Cr	V	Sn	W	La	Al	Mg	Ca	Na	K	Sr	Y	Ga	Li	Nb	Sc	Ta	Ti		
		PPB	PPB	PPB	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PCT	PCT	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PCT	PCT	PCT	PCT	PCT	PPM	PPM	PPM	PPM	PPM	PPM	PCT			
SAMPLE 4		5	<5	2																																						
SAMPLE 1		15	<5	34																																						
SAMPLE 2																																										
SAMPLE 3																																										

Till Sample

Steep Bank

- iron Stone

Normal Assay

11



Intertek Testing Services

Bondar Clegg

12

Geochemical Lab Report

CLIENT: MR. LARRY MACGOUGAN

REPORT: V98-01591.4 (COMPLETE)

PROJECT: NONE GIVEN

DATE RECEIVED: 01-SEP-98

DATE PRINTED: 14-SEP-98

PAGE 1B(2/ 4)

SAMPLE NUMBER	ELEMENT Zr UNITS PPM
------------------	-------------------------

SAMPLE 4

SAMPLE 1

SAMPLE 2

SAMPLE 3

6

Till sample
Iron
Stone
Steep Bank
Normal Assay

21

(13)

Enzyme Leach Job #: 9966 Report#: 9911 Customer: Larry Machougan Customer's Job #: ----

Trace Element Values Are in Parts Per Billion. Negative Values Equal Not Detected at That Lower Limit.

Values = 999999 are greater than working range of instrument. S.Q. = That element is determined SEMIQUANTITATIVELY.

Sample ID:	S.Q.Li	S.Q.Be	S.Q.Cl	S.Q.Sc	S.Q.Ti	V	Mn	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo	Ru
Sample #1	389	-20	4415575	36	322	1369	696	5	33	21	-10	-1	-1	20	-30	1861	94	6168	2	3	-1	66	-1

- lime stone Till
 Steep Bank
 Normal Assay

Same Sample
 page 13 - 14 - 15

13

40

(14)

Enzyme Leach J
Trace Element V
Values = 99999

Sample ID:	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au
Sample #1	-1	-1	-0.2	0.7	-0.2	3	3	-1	28	1	164	3	5	1	2	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	-0.1	-1	-1	-1	-0.1

15

Enzyme Leach J
Trace Element V
Values = 99999

Sample ID:	S.Q.	Hg	Tl	Pb	Bi	Th	U
Sample #1	-1.0	-1	1	-1	2	9	

15

42

Experimental Assay #1

All same sample:

Page 1- 2- 3

- All the same rock
- Limestone, Ironstone (Fort McKay)

MUSKEG RIVER.

UTM N 6332420

E 464110

Fire Assays
Machat

Saskatchewan
Research Council

RE: Beads and Roasted/Unroasted Ores As Per Your Letter

Bead #	Dore Wt mg	Au ppm*	Residual Au Bead**	mg Ag by ICP	mg Pb by ICP	µg Au in bead
1	1.95	0.01	No	1.90	-	<0.03
2	2.07	1.82	Yes	2.04	-	5.46
3	2.05	0.12	Yes	1.95	-	0.36
4	0.35	0.06	Yes	0.40	-	0.18
***5	5.05	0.02	Yes	3.09	1.85	0.06

* Au ppm in the original 3g ore sample by AA

**Residual Au beads left after parting were too small to weigh. We confirmed they were gold by microscopic examination. Bead #1 produced no visible residual Au bead after parting.

***Bead #5 was unusual in appearance. It was dull, flat and very rough. All other beads were typical.

In all cases except Bead #5 the wt in mg of the dore correlated with the mg of Ag determined by ICP on the parting solutions. We analyzed the Bead #5 parting solution for Pb, Pt, and Pd to determine its composition and account for the high dore weight. No Pt or Pd were detected, however, the equivalent of 1.85 mg of Pb was found. The presence of Pb accounts for 97.8% of the original dore #5.

- 3 gram Assays
- Lime stone Mud stone Briqde by Fitcher
- Scorification Assay
- 30gr Lead 2grm Flour only

Experimental Assay



Intertek Testing Services

Bondar Clegg

2

Geochemical Lab Report

CLIENT: MR. LARRY MACGOUGAN

REPORT: V97-01600.0 (COMPLETE)

DATE RECEIVED: 11-JUL-97

PROJECT: NONE GIVEN

DATE PRINTED: 18-AUG-97

PAGE 3 OF 3

SAMPLE NUMBER	ELEMENT UNITS	AU PPB	PT PPB	PD PPB	Ag PPM
------------------	------------------	-----------	-----------	-----------	-----------

1		17	8	10	<0.1
Duplicate					<0.1

no Pre Leach

R2-2

same Rock as

2248 PPB Gold

- iron stone shale

- Normal assay

Bondar-Clegg & Company Ltd.

130 Pemberton Avenue, North Vancouver, B.C., V7P 2R5, Canada

Tel: (604) 985-0681, Fax: (604) 985-1071



Intertek Testing Services
Bondar Clegg

3

Geochemical
Lab
Report

CLIENT: MR. LARRY MACGOUGAN
REPORT: V97-01600.0 (COMPLETE)

DATE RECEIVED: 11-JUL-97

PROJECT: NONE GIVEN

DATE PRINTED: 18-AUG-97

PAGE 1 OF 3

SAMPLE NUMBER	ELEMENT UNITS	AU PPB	PT PPB	PD PPB	Ag PPM
R2 1		17	8	10	<0.1
R2 2		2248	115	18	<0.1

- iron stone

1st Normal Assay

- 2nd (A) Leach 30gram ore
(B) Send Leach Residue To Bondar Clegg
Experimental Assay
Calculated Back To 30gram start

EXPERIMENTAL ASSAY #3

Same Sample:

Page 1-7; SEM of Leach Residual

Page 8; Fire Leach Residue

SAME AS EXPERIMENTAL ASSAY #1

UTAH IV 6332420

E 464110

MUSKIE RIVER.

ARC

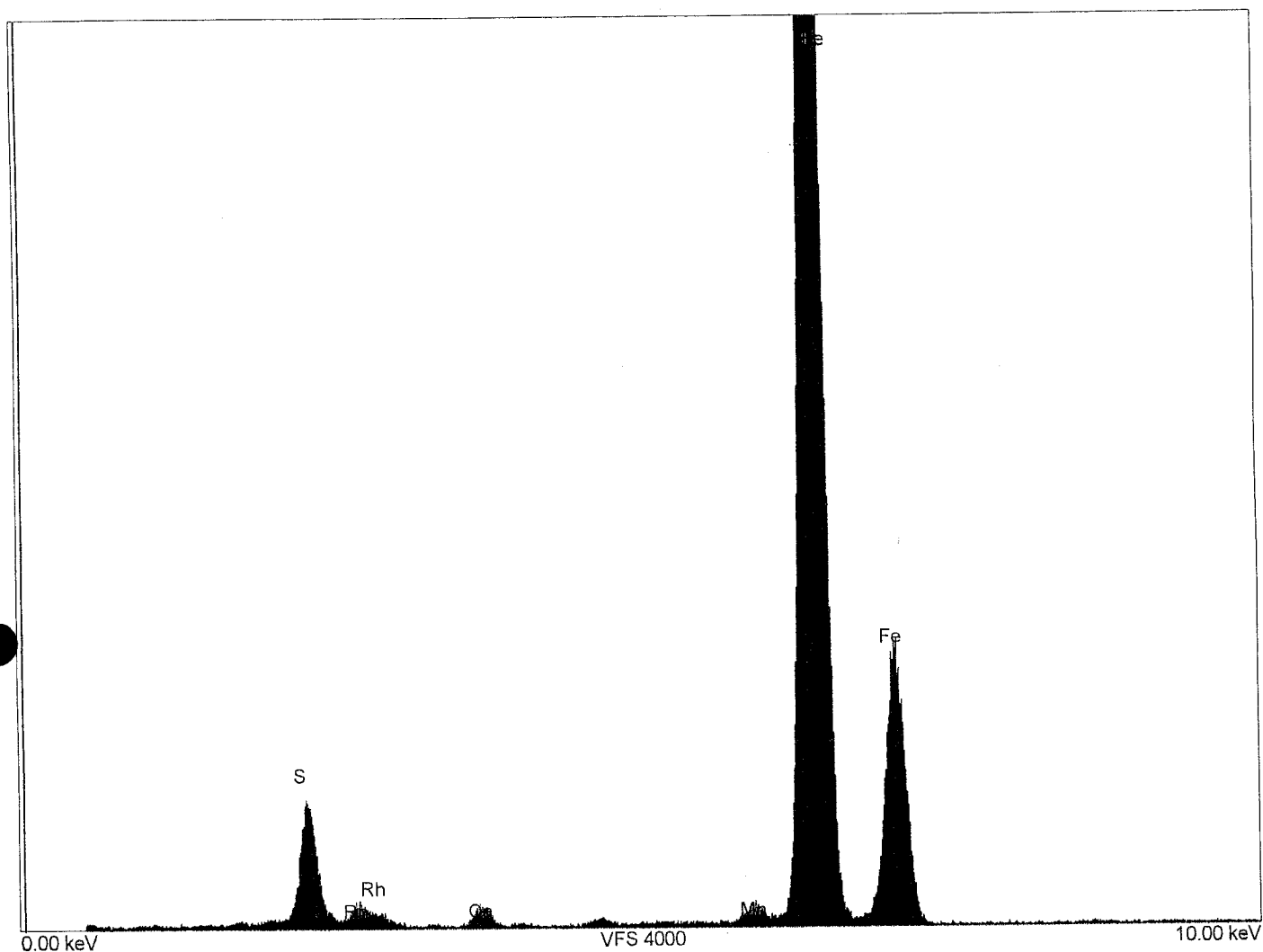
Alberta Research Council Analytical Services

Sample??

250 Karl Clark Road
Edmonton, Alberta T6N1E4
Tel. (403) 450-5429
Fax. (403) 450-5477

Date : 08/06/98
Time : 2:48:33PM

Spectrum: 10a Folder: MacGOUGAN



Acquisition parameters

Current 20 μ A
Voltage 38 kV
Filter 1 ---
Station 2
Range 20 keV
L.Time 50 sec
CPS 4918
D.Time 44 %
Tube Direct
Collimator 4
Throughput Low
Atmosphere Vacuum
Date 08/06/98
Time 2:44:30PM

ROI information

Not defined

Overlap information

No overlaps

Acquisition status

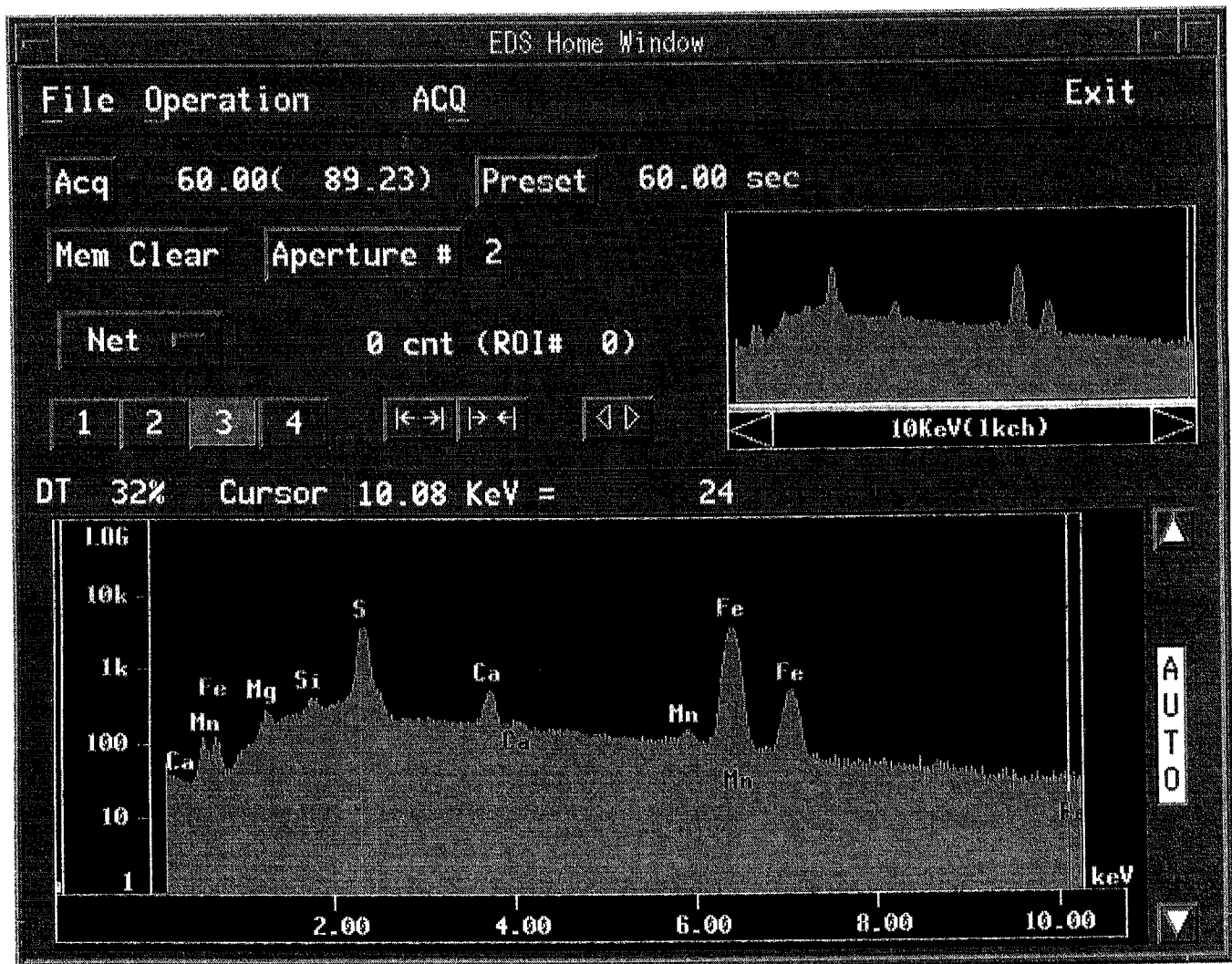
Current proc.
Current batch

Voltage 0.0 kV
Emission curr. 1.0 μ A
Filament curr. 4.6 A
Zero DAC 108
Zero Shift -1
Zero Width 101
Gain DAC 120
Temperature 27 $^{\circ}$ C
Vacuum level 1539
Nitrogen level 30 %

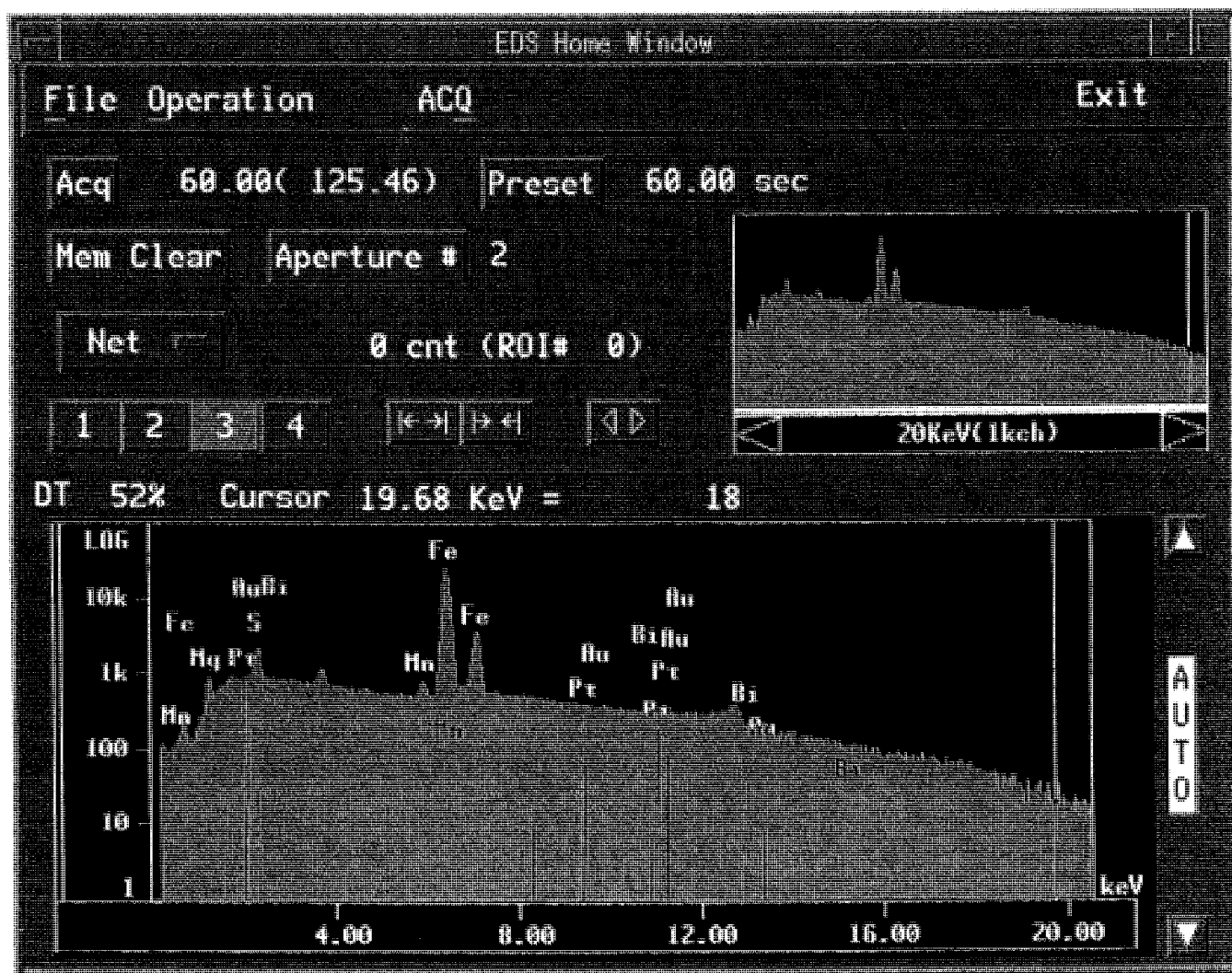
Cursor information

Position: 0.04 keV Counts: 0

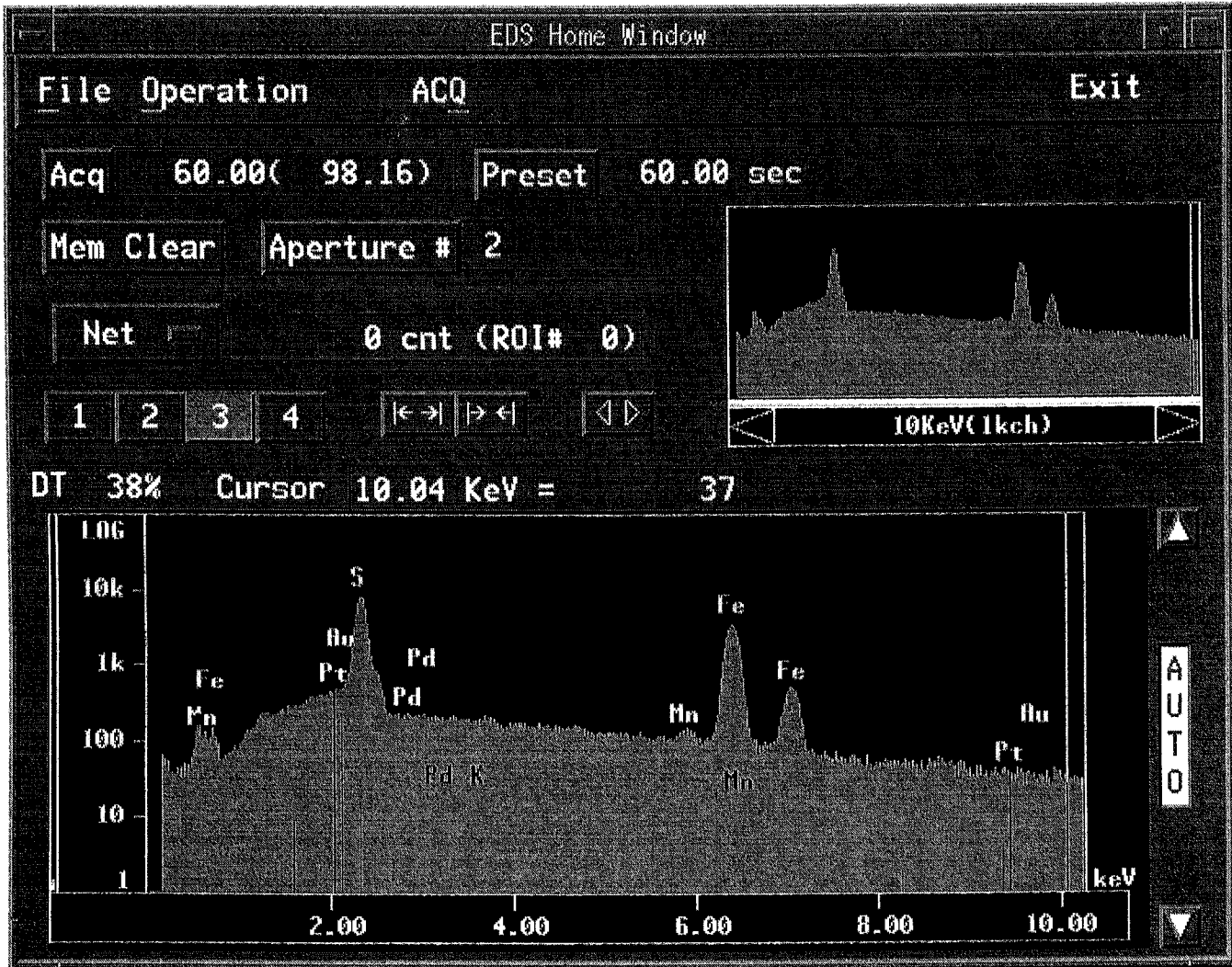
9A 2



9A 3

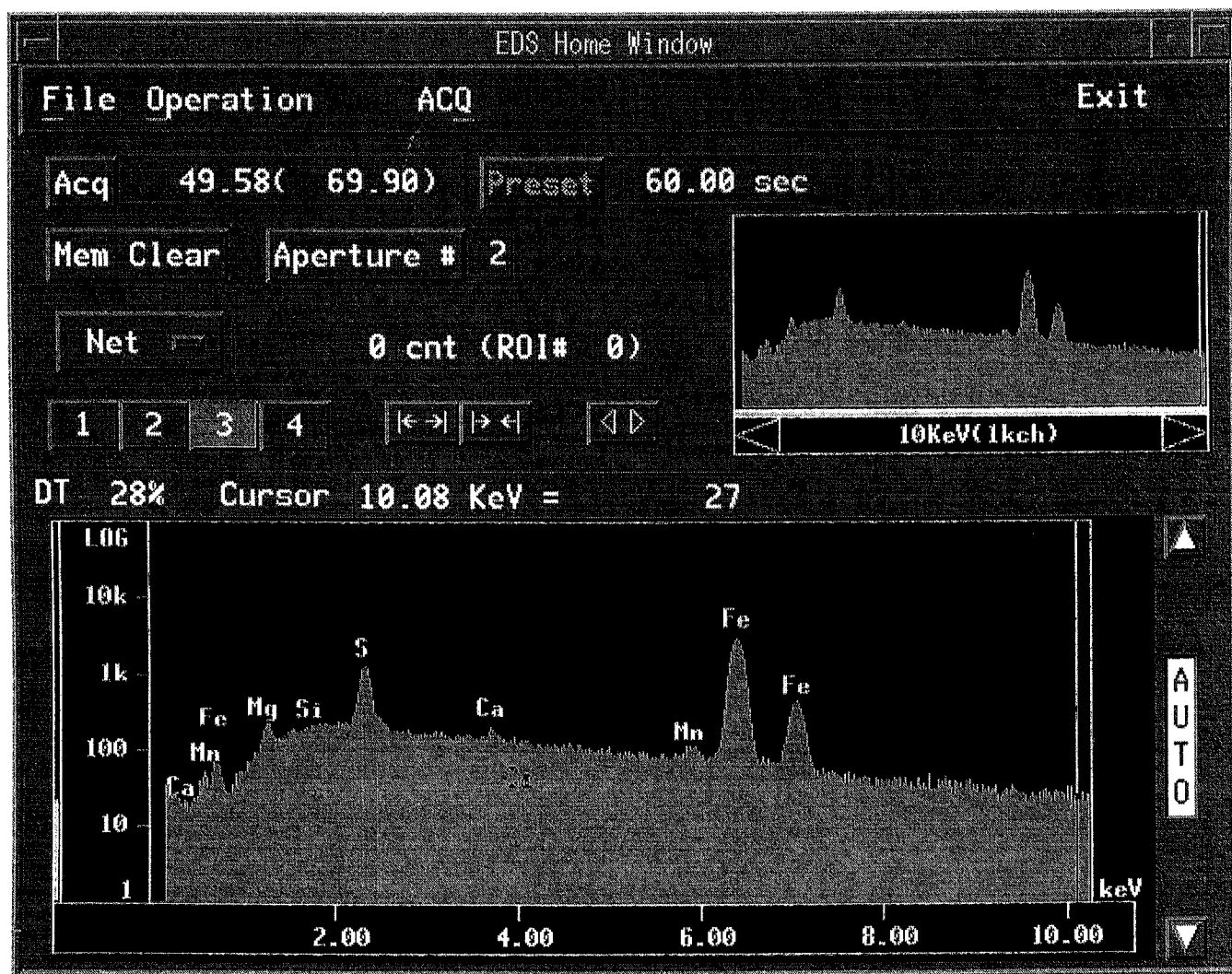


9A 4

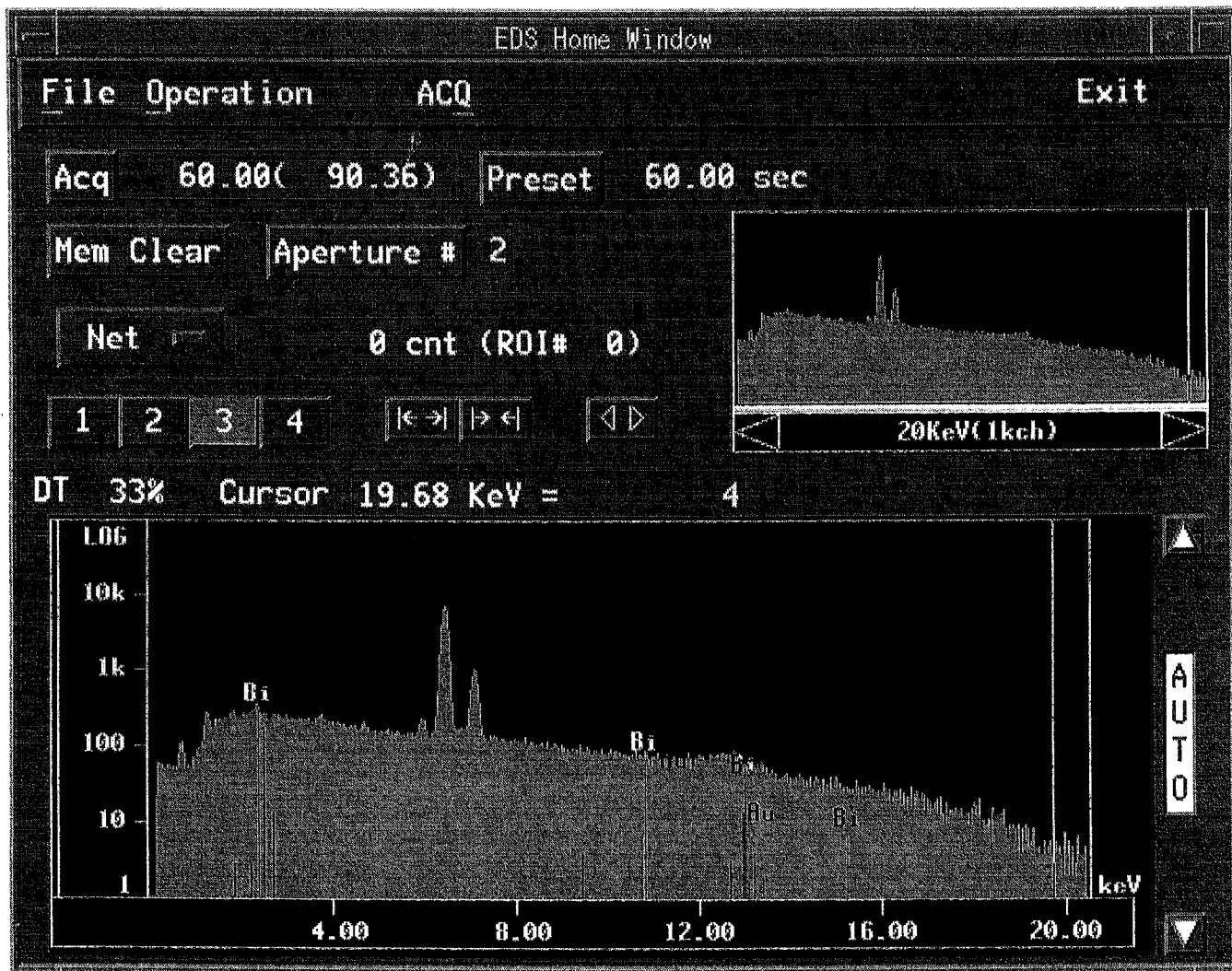


5

9A

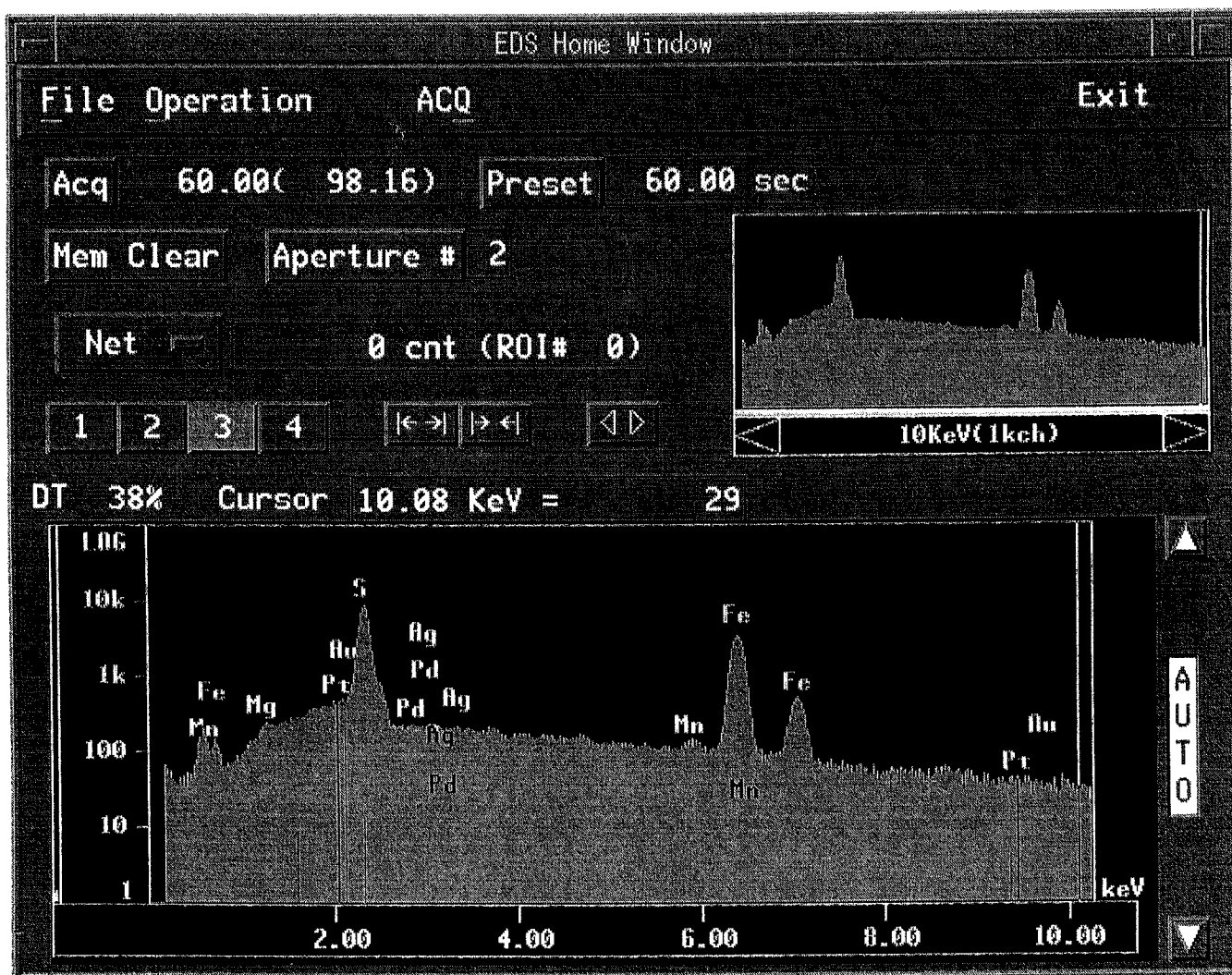


6 9A



7

9A



8 12

Saskatchewan Research Council Geoanalytical Services
125-15 Innovation Blvd., Saskatoon, SK., S7N 2X8
Phone:306-933-5426 Fax:306-933-5656

M273 MACGOUGAN JUNE 25/98 (3)

1	Au	ppb	ICP	* = NI SULFIDE FUSION
2	Pt	ppb	ICP	** = NORMAL FIRE ASSAY
3	Pd	ppb	ICP	
4	Pd	ppm	AA	

5
6
7
8
9

	Au	Pt	Pd	Pd
* 11A	<10	30	4200	<0.05
* 13A	<10	30	4150	<0.05
** LARRY 1	<1	3	<1	<0.05

pre

EXPERIMENTAL ASSAY #5

Same Samples:

Page 1-2-3;	Roasted Beads
Page 4-5-6;	Roasted Beads
Page 7-8-9;	Roasted Beads
Page 10-11-12;	Roasted Beads
Page 13;	Roasted Beads
Page 14;	Roasted Beads
Page 15-16;	Roasted Beads
Page 17-18;	Roasted Beads
Page 19-20;	Roasted Beads
Page 21-22;	Roasted Beads
Page 23;	Roasted Beads
Page 24;	Roasted Beads
Page 25;	Roasted Beads
Pages 26-28	Roasted Beads

UTM N 6315100

E 482505

Spectrum file : ILM30

#1. LIVETIME(spec.)= 200

ENERGY RES AREA
7.4 71.96 103100
TOTAL AREA= 856943

...
Peak at .36 keV omitted?
Peak at .92 keV omitted?
Peak at 5.40 keV omitted?
FIT INDEX= 3.07

ELMT	APP.CONC	ERROR(WT%)
P K : 0	4.079	.070
SiK : 1	.183	.029
S K : 3	1.250	.038
PbM : 1	-.336	.094* < 2 Sigma*Not used for quantitation
PbL : 1	1.924	.481
FeK : 1	34.251	.179
NiK : 1	4.396	.120
CuK : 1	69.330	.345

ZAF CALCULATIONS

...[3 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

Spectrum: #1

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
P K : 0	.824	4.201 +-	.072	7.953
SiK : 1	.515	.302 +-	.048	.630
S K : 3	.825	1.285 +-	.039	2.351
PbL : 1	.697	2.343 +-	.585	.663
FeK : 1	1.104	26.316 +-	.138	27.627
NiK : 1	.991	3.765 +-	.103	3.760
CuK : 1	.952	61.789 +-	.307	57.016
TOTAL		100.000		100.000

3 Bents
B. Pen

001 HCL
Si Brake down

Spectrum file : ILM30

#1

LIVETIME(spec.)= 200

ENERGY	RES	AREA
7.4	71.96	103100
TOTAL AREA=		856943

...
Peak at .36 keV omitted?
Peak at .92 keV omitted?
Peak at 5.40 keV omitted?
FIT INDEX= 3.00

ELMT	APP.CONC	ERROR(WT%)
P K : 0	4.079	.070
SiK : 1	.183	.029
S K : 3	1.250	.038
PbM : 1	-.336	.094* < 2 Sigma*Not used for quantitation
PbL : 1	1.928	.481
FeK : 1	34.251	.179
NiK : 1	4.397	.120
CuK : 1	69.328	.345
AuL : 1	.237	.319* < 2 Sigma*
PtL : 1	.008	.343* < 2 Sigma*

ZAF CALCULATIONS

...[3 iterations]

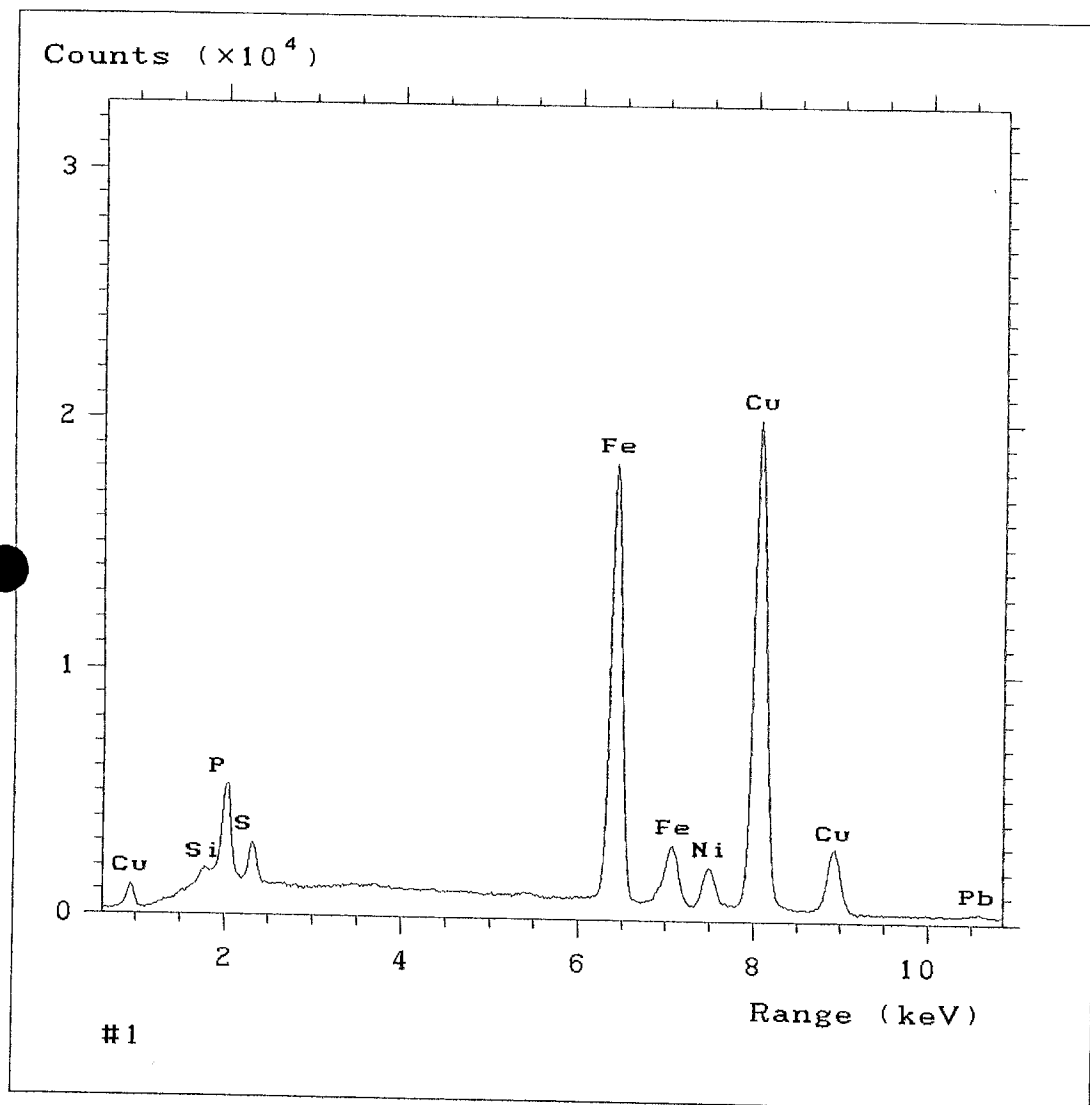
20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

Spectrum: #1

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
P K : 0	.825	4.184 +-	.072	7.945
SiK : 1	.516	.301 +-	.048	.629
S K : 3	.824	1.284 +-	.039	2.355
PbL : 1	.697	2.340 +-	.583	.664
FeK : 1	1.104	26.259 +-	.137	27.648
NiK : 1	.991	3.753 +-	.103	3.759
CuK : 1	.952	61.589 +-	.306	57.000
AuL : 1	.711	.282 +-	.379 <1 sd , below confidence limit	
PtL : 1	.709	.009 +-	.409 <1 sd , below confidence limit	
TOTAL		99.709		100.000



Spectrum file : ILM31

#2

LIVETIME(spec.)= 200

4

ENERGY	RES	AREA
7.5	71.77	97780
TOTAL AREA=		826514

...
Peak at .38 keV omitted?
Peak at 5.40 keV omitted?
FIT INDEX= 3.52

ELMT	APP.CONC	ERROR(WT%)
P K : 0	.177	.048
AlK : 1	1.034	.034
SiK : 1	6.357	.047
TiK : 1	.214	.040
FeK : 1	77.853	.251
CuK : 1	.169	.087* < 2 Sigma*

ZAF CALCULATIONS

...[3 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

Spectrum: #2

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
P K : 0	.819	.229 +-	.062	.362
AlK : 1	.446	2.455 +-	.080	4.443
SiK : 1	.576	11.692 +-	.087	20.324
TiK : 1	1.023	.222 +-	.042	.226
FeK : 1	.968	85.192 +-	.275	74.484
CuK : 1	.854	.210 +-	.108 <2 sd	.161
TOTAL		100.000		100.000

001 14A

Spectrum file : ILM31

#2

LIVETIME(spec.)= 200

ENERGY	RES	AREA
7.5	71.77	97780

TOTAL AREA= 826514

Peak at .38 keV omitted?

Peak at 5.40 keV omitted?

FIT INDEX= 1.96

ELMT	APP.CONC	ERROR(WT%)
P K : 0	.177	.048
AlK : 1	1.034	.034
SiK : 1	6.357	.047
TiK : 1	.214	.040
FeK : 1	77.853	.251
CuK : 1	.170	.087* < 2 Sigma*
PtL : 1	.004	.327* < 2 Sigma*
AuL : 1	-.296	.296* < 2 Sigma*

ZAF CALCULATIONS

...[3 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

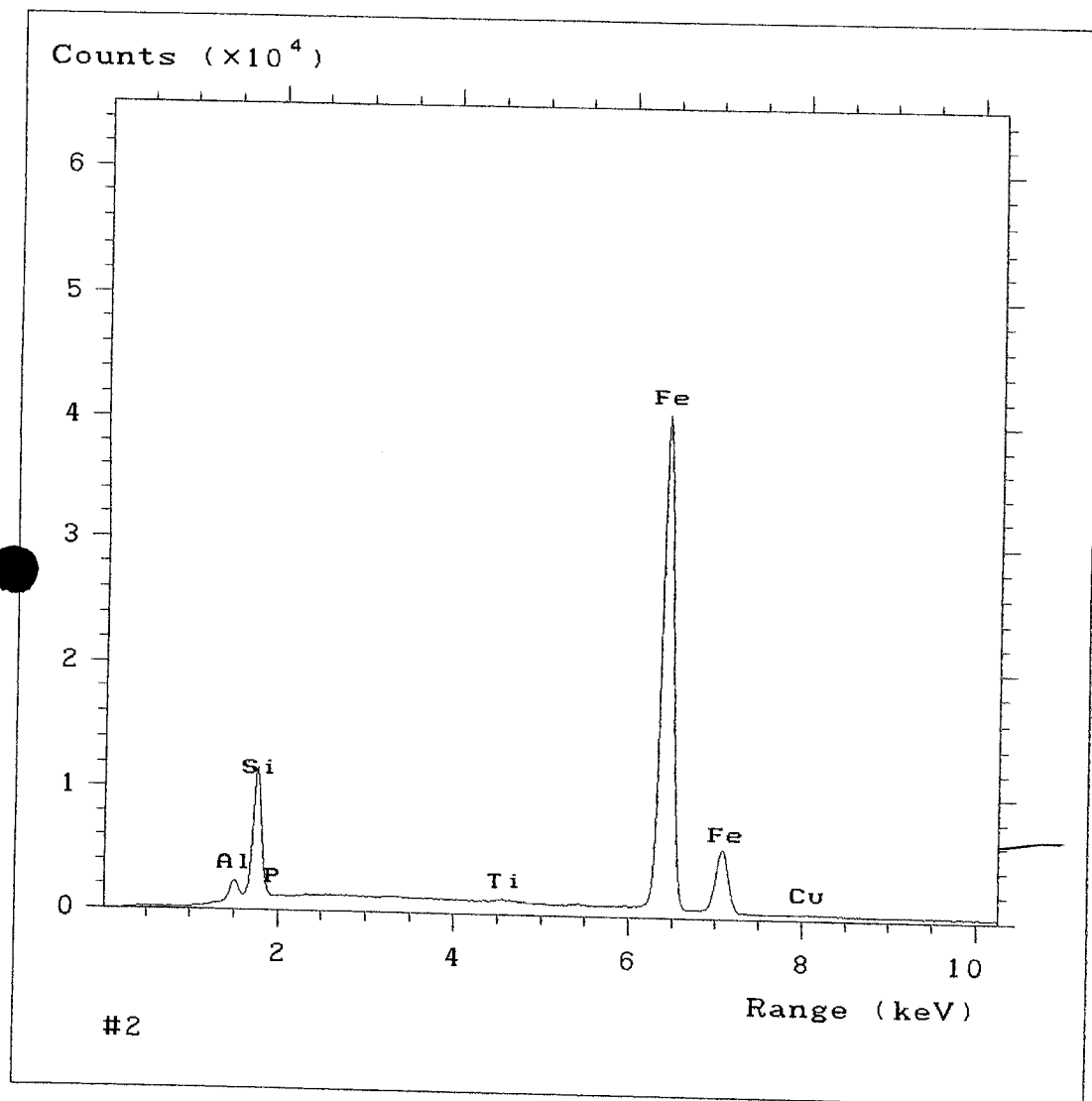
Spectrum: #2

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
P K : 0	.819	.229 +-	.062	.362
AlK : 1	.446	2.455 +-	.080	4.443
SiK : 1	.576	11.691 +-	.087	20.324
TiK : 1	1.023	.222 +-	.042	.226
FeK : 1	.968	85.186 +-	.275	74.484
CuK : 1	.854	.210 +-	.108 <2 sd	.162
PtL : 1	.685	.006 +-	.506 <1 sd	
AuL : 1	.686	-.431 +-	.431 <2 sd	
TOTAL		99.994		100.000

below confidence limit
warning -ve conc. not in totals



Spectrum file : ILM33

#4 LIVETIME(spec.)= 200

7

ENERGY	RES	AREA
7.5	72.02	124954
TOTAL AREA= 1011410		

...
Peak at .36 keV omitted?
Peak at .92 keV omitted?
FIT INDEX=11.79

ELMT	APP.CONC	ERROR(WT%)
P K : 0	7.260	.090
S K : 3	3.241	.049
FeK : 1	87.498	.266
CuK : 1	15.688	.189

ZAF CALCULATIONS

...[3 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

Spectrum: #4

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
P K : 0	.890	6.941 +-	.086	11.794
S K : 3	.856	3.222 +-	.048	5.288
FeK : 1	.998	74.647 +-	.227	70.337
CuK : 1	.879	15.191 +-	.183	12.581
TOTAL		100.000		100.000

001 - Sn R
- Carbon B

Bic Pen
2 Bic

Spectrum file : ILM33

#4

LIVETIME(spec.)= 200

8

ENERGY RES AREA
7.5 72.02 124954
TOTAL AREA= 1011410

...
Peak at .36 keV omitted?
Peak at .92 keV omitted?
FIT INDEX= 5.68

ELMT	APP.CONC	ERROR(WT%)
P K : 0	7.260	.090
S K : 3	3.241	.049
FeK : 1	87.498	.266
CuK : 1	15.687	.189
PtL : 1	-.284	.351* < 2 Sigma*
AuL : 1	-.130	.322* < 2 Sigma*

ZAF CALCULATIONS

...[3 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

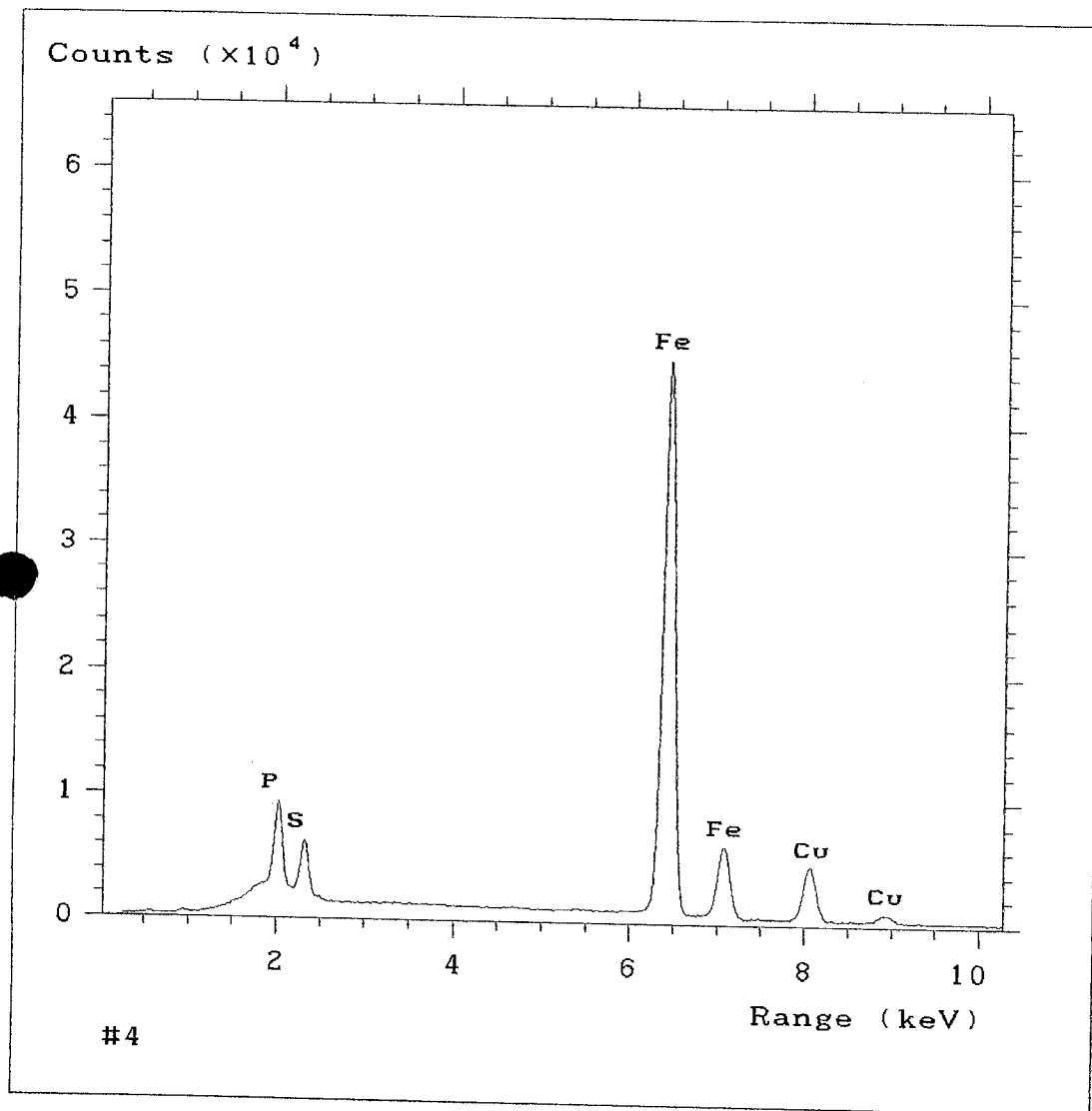
Spectrum: #4

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
P : 0	.890	6.941 +-	.086	11.794
S K : 3	.856	3.222 +-	.048	5.288
FeK : 1	.998	74.648 +-	.227	70.337
CuK : 1	.879	15.190 +-	.183	12.581
PtL : 1	.694	-.409 +-	.506 <1 sd , warning	-ve conc. not in totals
AuL : 1	.695	-.188 +-	.463 <1 sd , warning	-ve conc. not in totals
TOTAL		100.000		100.000

9



Spectrum file : ILM34

LIVETIME(spec.)= 200

10

#5
ENERGY RES AREA
7.6 72.71 131297
TOTAL AREA= 1085944

...
Peak at .36 keV omitted?
Peak at 2.32 keV omitted?
Peak at 3.64 keV omitted?
Peak at 5.42 keV omitted?
Peak at 12.78 keV omitted?
FIT INDEX= 7.79

ELMT	APP.CONC	ERROR(WT%)
SiK : 1	.359	.022
FeK : 1	130.730	.288

ZAF CALCULATIONS

...[3 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

Spectrum: #5

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
SiK : 1	.561	.486 +-	.029	.962
FeK : 1	.999	99.514 +-	.219	99.038
TOTAL		100.000		100.000

Nit -

Spectrum file : ILM34

#5 LIVETIME(spec.)= 200

ENERGY	RES	AREA
7.6	72.71	131297
TOTAL AREA= 1085944		

...
Peak at .36 keV omitted?
Peak at 2.32 keV omitted?
Peak at 3.64 keV omitted?
Peak at 5.42 keV omitted?
FIT INDEX= 2.54

ELMT	APP.CONC	ERROR(WT%)
SiK : 1	.359	.022
FeK : 1	130.731	.288
PtL : 1	.173	.316* < 2 Sigma*
AuL : 1	-.028	.297* < 2 Sigma*

ZAF CALCULATIONS

..[2 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

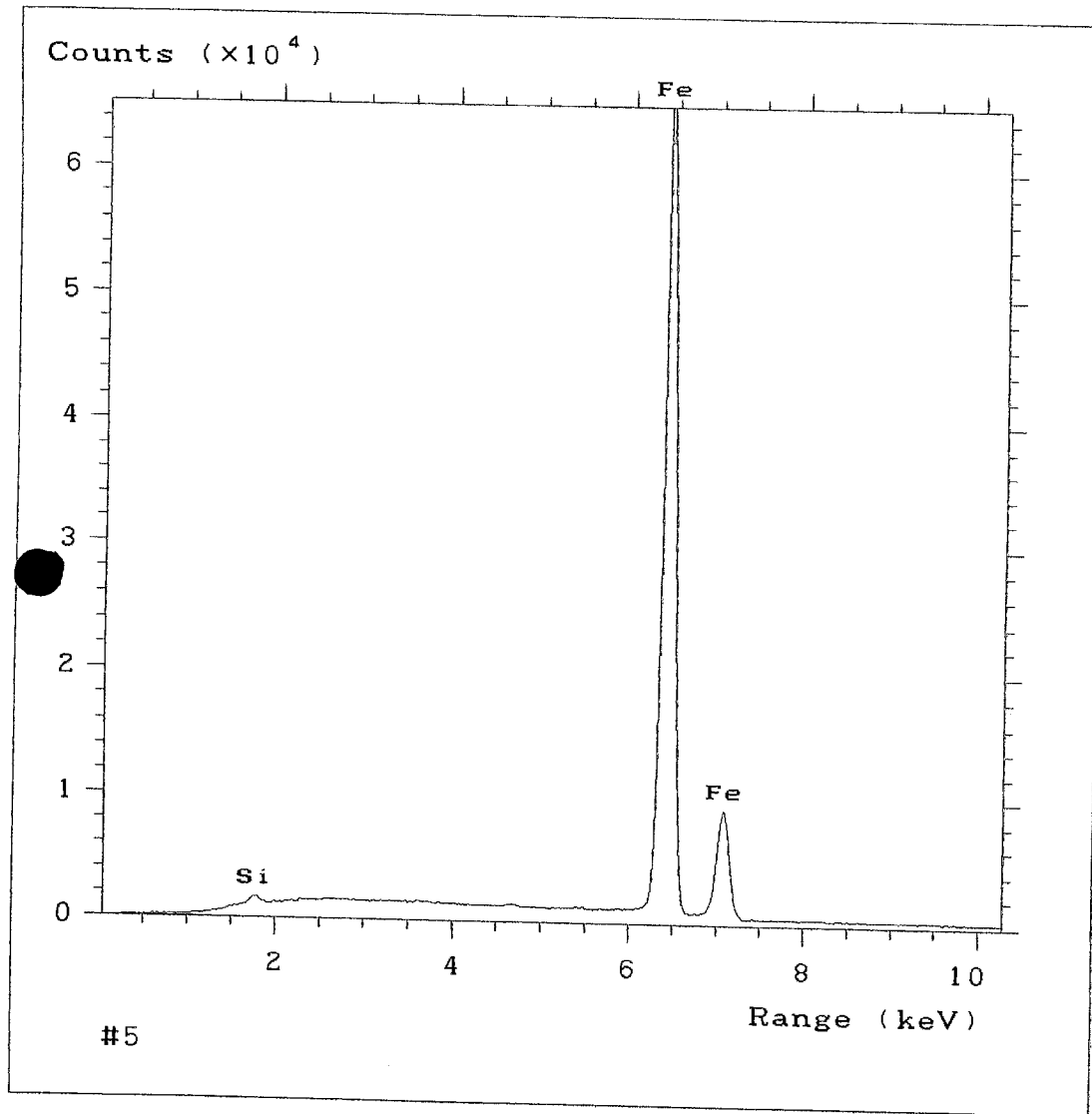
Spectrum: #5

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
SiK : 1	.562	.485 +-	.029	.962
FeK : 1	.999	99.233 +-	.219	99.038
PtL : 1	.701	.187 +-	.342 <1 sd ,	below confidence limit
AuL : 1	.702	-.040 +-	.423 <1 sd ,	warning -ve conc. not in totals
TOTAL		99.718		100.000

12



Spectrum file : ILM50

#3

LIVETIME(spec.)= 200

13

ENERGY	RES	AREA
7.5	71.67	94833
TOTAL AREA=		785814

...
Peak at .14 keV omitted?
Peak at .38 keV omitted?
Peak at 3.68 keV omitted?
FIT INDEX=16.89

ELMT	APP.CONC	ERROR(WT%)
P K : 0	11.785	.093
FeK : 1	77.518	.248
NiK : 1	.181	.070
CuK : 1	.210	.079

ZAF CALCULATIONS

..[2 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

Spectrum: #3

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM. %
K : 0	.921	13.792 +-	.109	22.399
FeK : 1	.974	85.726 +-	.275	77.203
NiK : 1	.883	.221 +-	.085 <3 sd	.189
CuK : 1	.860	.263 +-	.099 <3 sd	.208
TOTAL		100.002		100.000

001
HCL
Carbon
Blau

Spectrum file : ILM51

#4

LIVETIME(spec.)= 200

14

ENERGY	RES	AREA
7.5	71.82	102853

TOTAL AREA= 853198

Peak at .16 keV omitted?

Peak at .38 keV omitted?

FIT INDEX= 2.55

ELMT	APP.CONC	ERROR(WT%)
P K : 0	2.395	.059
AlK : 1	.094	.024
SiK : 1	.332	.028
CaK : 3	.445	.037
CrK : 1	.628	.053
MnK : 1	.193	.061
FeK : 1	95.198	.275
CuK : 1	.116	.083* < 2 Sigma*

ZAF CALCULATIONS

..[2 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

Spectrum: #4

CHEM.&MATERIALS ENG.

11 elmts analysed, NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
P K : 0	.890	2.671 +-	.066	4.671
AlK : 1	.425	.220 +-	.055	.441
SiK : 1	.567	.581 +-	.049	1.121
CaK : 3	1.188	.372 +-	.031	.503
CrK : 1	1.243	.501 +-	.042	.522
MnK : 1	.969	.198 +-	.062	.195
FeK : 1	.991	95.325 +-	.275	92.434
CuK : 1	.866	.133 +-	.095 <2 sd	.114
TOTAL		100.001		100.000

008
no +4.7

Spectrum file : ILM41

#4

LIVETIME(spec.)= 500

ENERGY	RES	AREA
7.4	71.68	243697

TOTAL AREA= 2004489

...

Peak at .38 keV omitted?

FIT INDEX=15.41

ELMT	APP.CONC	ERROR(WT%)
SiK : 1	15.087	.035
TiK : 1	2.288	.027
CrK : 1	.412	.027
FeK : 1	67.211	.132

ZAF CALCULATIONS

...[3 iterations]

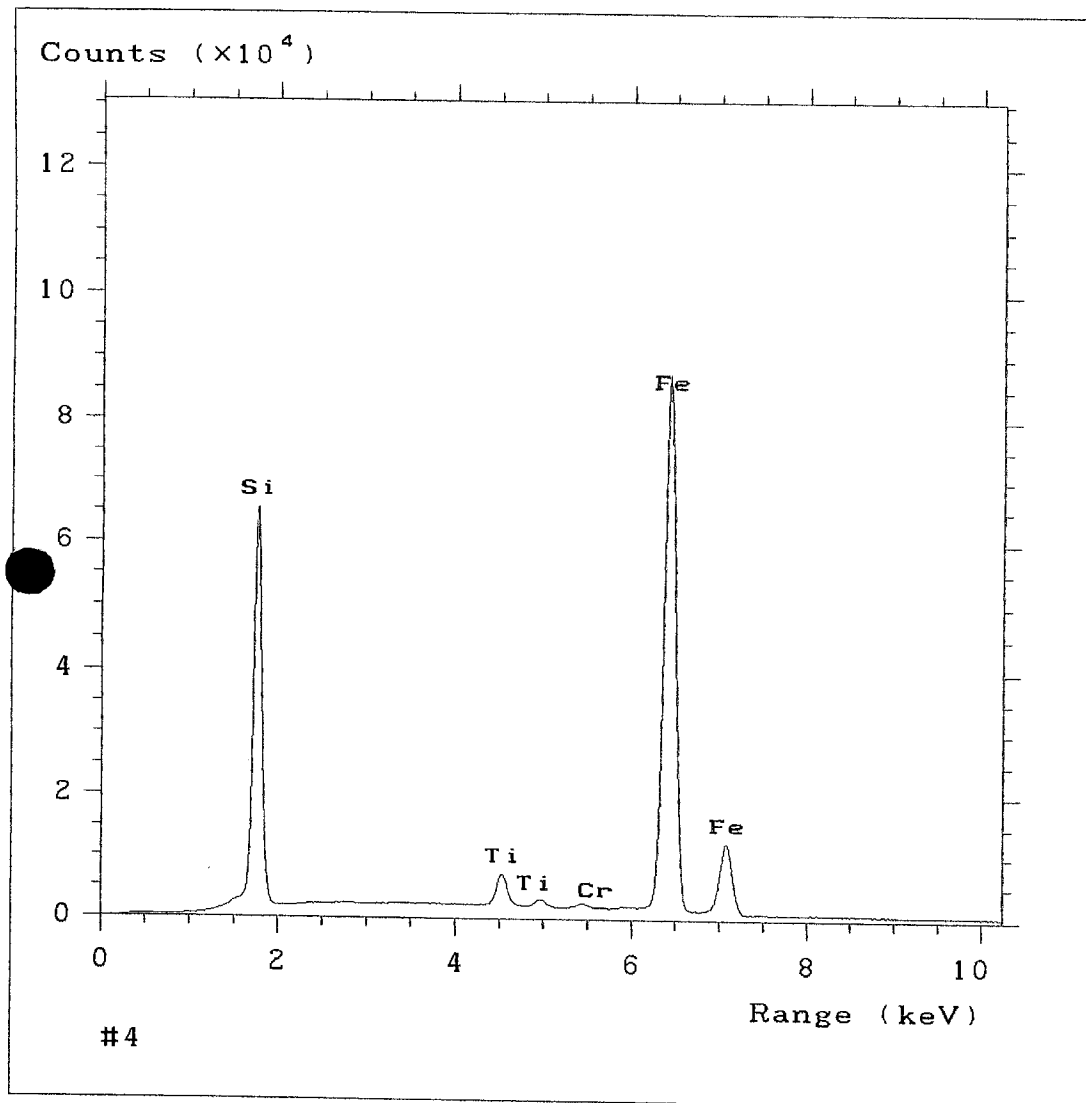
20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

Spectrum: #4

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
SiK : 1	.617	24.788 +-	.057	39.452
TiK : 1	.976	2.379 +-	.028	2.221
CrK : 1	1.085	.385 +-	.025	.331
FeK : 1	.941	72.448 +-	.143	57.995
TOTAL		100.000		100.000



Spectrum file : ILM20

Black Powder

LIVETIME(spec.)= 300

17

ENERGY RES AREA
- 7.7 72.22 163121

TOTAL AREA= 1334273

Peak at .36 keV omitted?

Peak at .56 keV omitted?

FIT INDEX=**, **

ELMT	APP.CONC	ERROR(WT%)
SrL : 0	.264	.082
S K : 3	34.591	.095
CrK : 1	.226	.033
FeK : 1	7.685	.078
NiK : 1	19.490	.139

ZAF CALCULATIONS

...[2 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

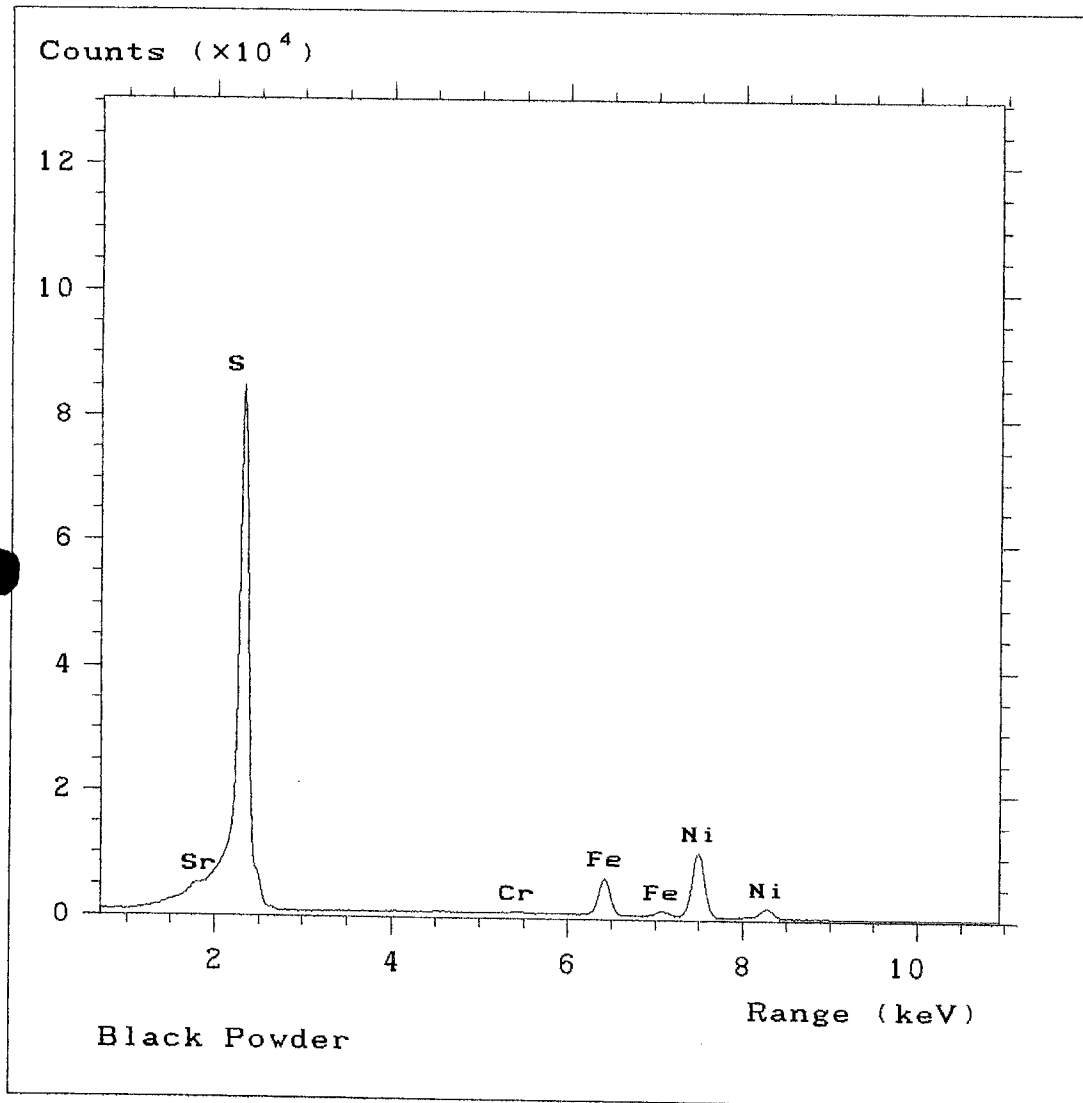
Spectrum: Black Powder

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
SrL : 0	.730	.539 +-	.167	.248
S K : 3	.949	54.306 +-	.149	68.284
CrK : 1	.898	.375 +-	.055	.291
FeK : 1	.939	12.200 +-	.124	8.806
NiK : 1	.892	32.580 +-	.233	22.371
TOTAL		100.000		100.000

Sas S Re
Ni S Cl Take away Black
Residue



Spectrum file : ILM40

#1 LIVETIME(spec.)= 500

19

ENERGY	RES	AREA
7.6	72.48	271799
TOTAL AREA= 2237506		

...
Peak at .40 keV omitted?
Peak at 12.80 keV omitted?
FIT INDEX= 3.97

ELMT	APP.CONC	ERROR(WT%)
P K : 0	.127	.027
SiK : 1	.156	.014
SnL : 1	4.882	.068
CrK : 1	.170	.032
FeK : 1	99.532	.177

ZAF CALCULATIONS

..[2 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

Spectrum: #1

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

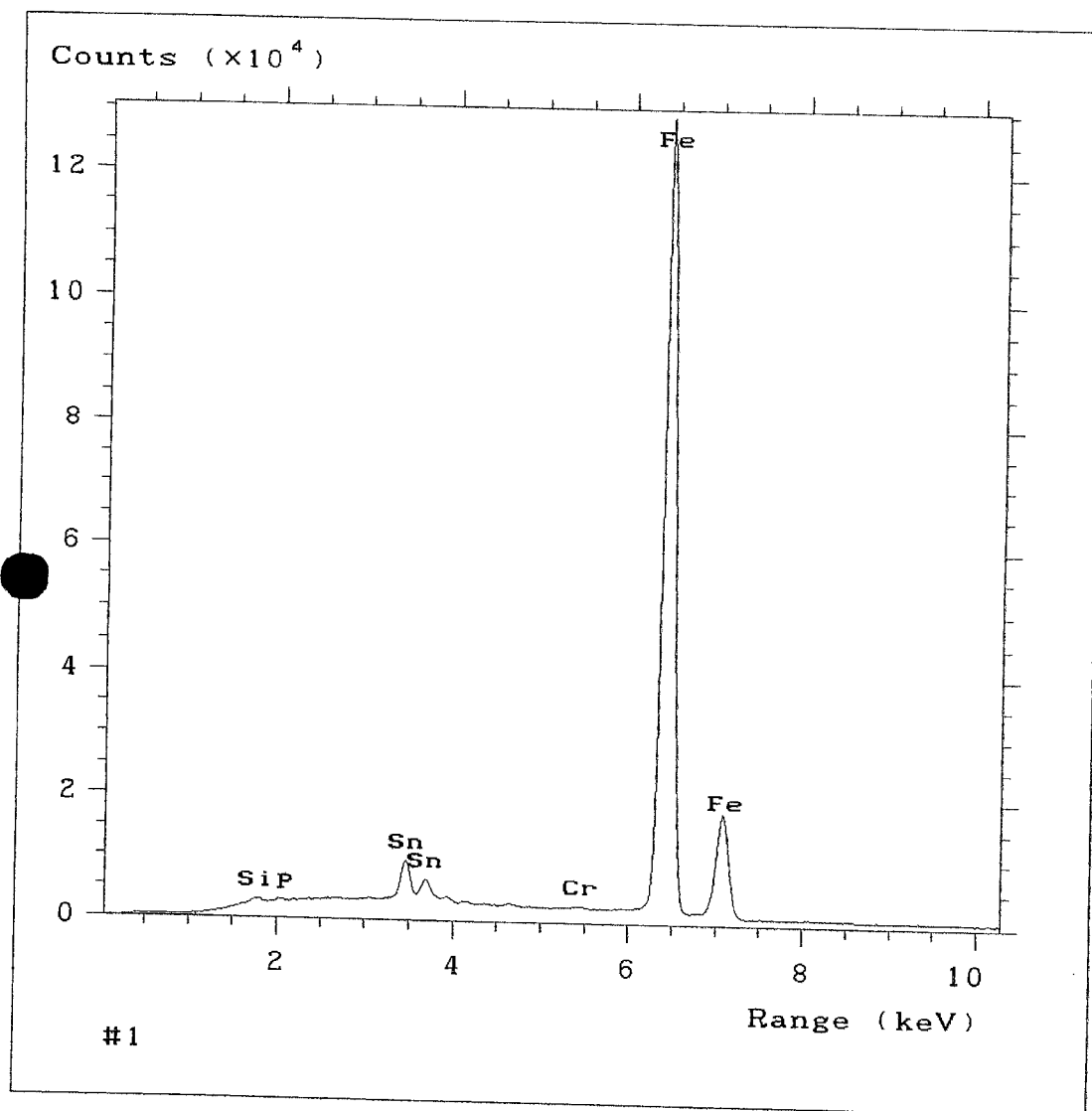
ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
P K : 0	.894	.134 +-	.028	.247
SiK : 1	.567	.259 +-	.024	.528
SnL : 1	.876	5.263 +-	.073	2.538
CrK : 1	1.200	.134 +-	.026	.147
FeK : 1	.997	94.211 +-	.168	96.540
TOTAL		100.000		100.000

001

8.2 g mol

N, f

H₂O₂ Boil



Spectrum file : ILM21

Metallic Sphere

LIVETIME(spec.) = 500

21

ENERGY	RES	AREA
7.5	71.36	229891
TOTAL AREA= 1848605		

...
Peak at .38 keV omitted?
FIT INDEX=22.90

ELMT	APP.CONC	ERROR(WT%)
NaK : 0	.177	.035
MgK : 1	.100	.018
AlK : 1	.085	.016
SiK : 1	5.307	.026
CaK : 3	.925	.023
TiK : 1	1.874	.030
V K : 0	.761	.033
FeK : 1	74.556	.155
P K : 0	.223	.025
S K : 3	.118	.015

ZAF CALCULATIONS

...[3 iterations]

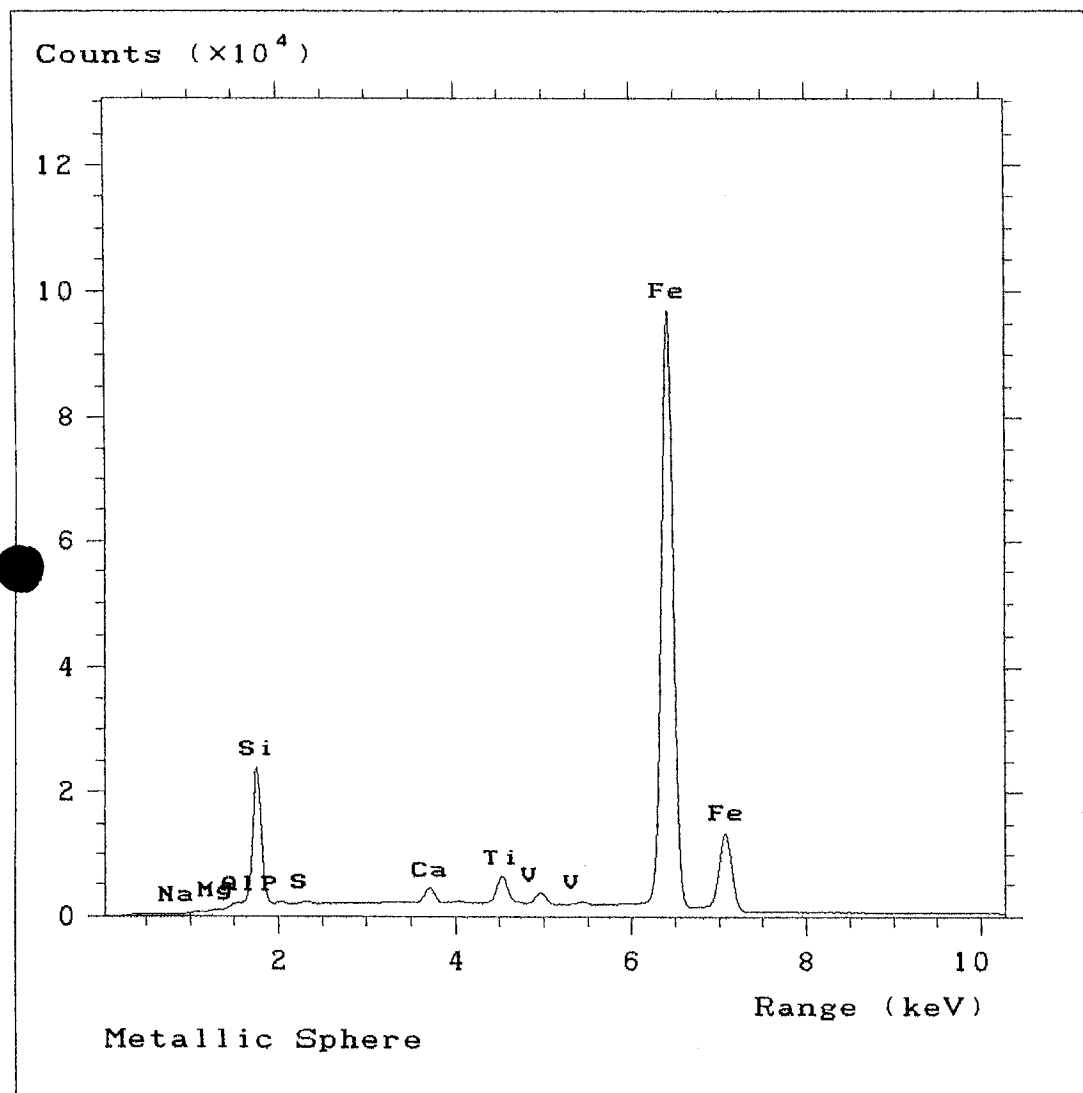
20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

Spectrum: Metallic Sphere

CHEM.&MATERIALS ENG.

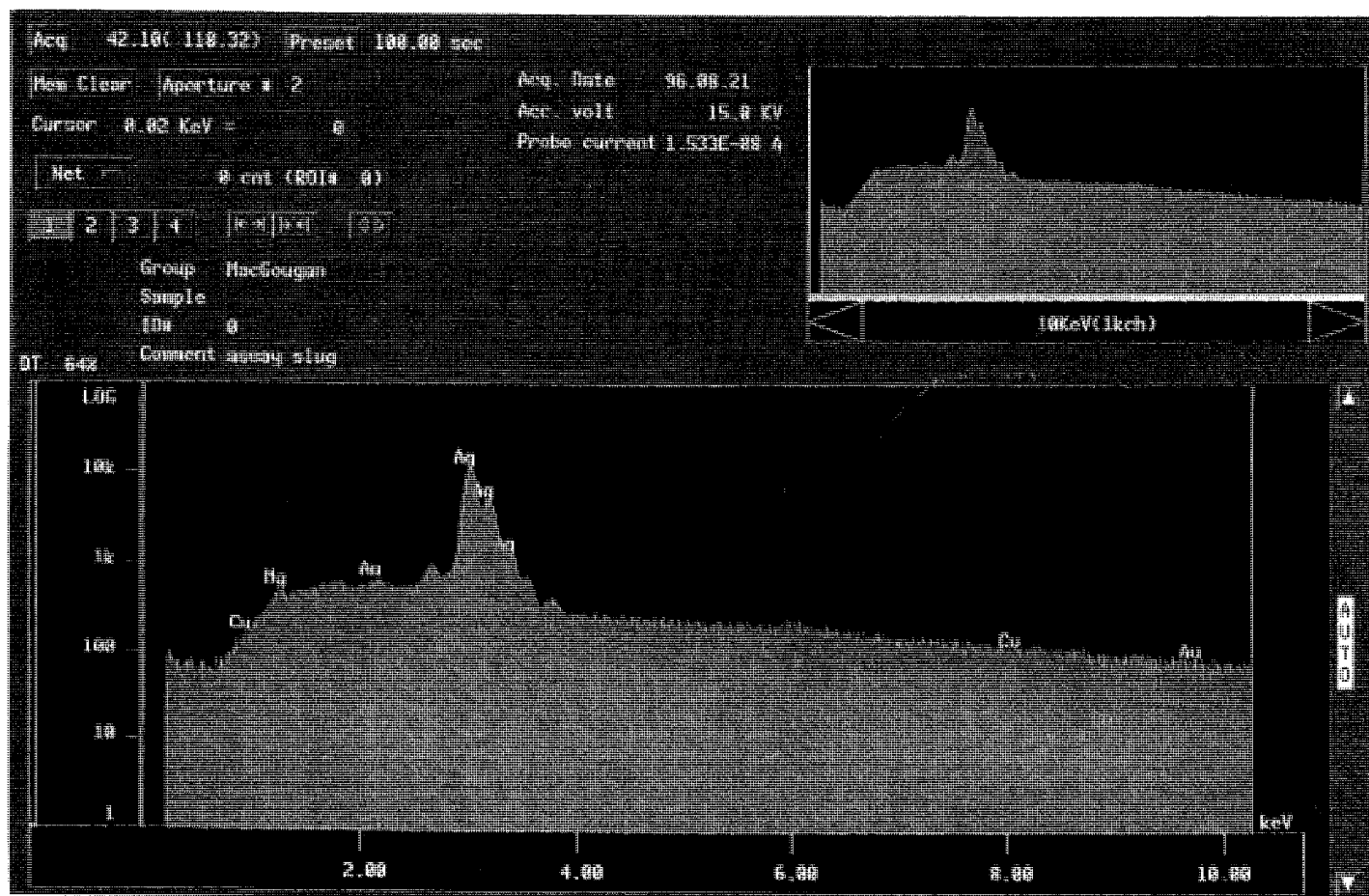
All elmts analysed,NORMALISED

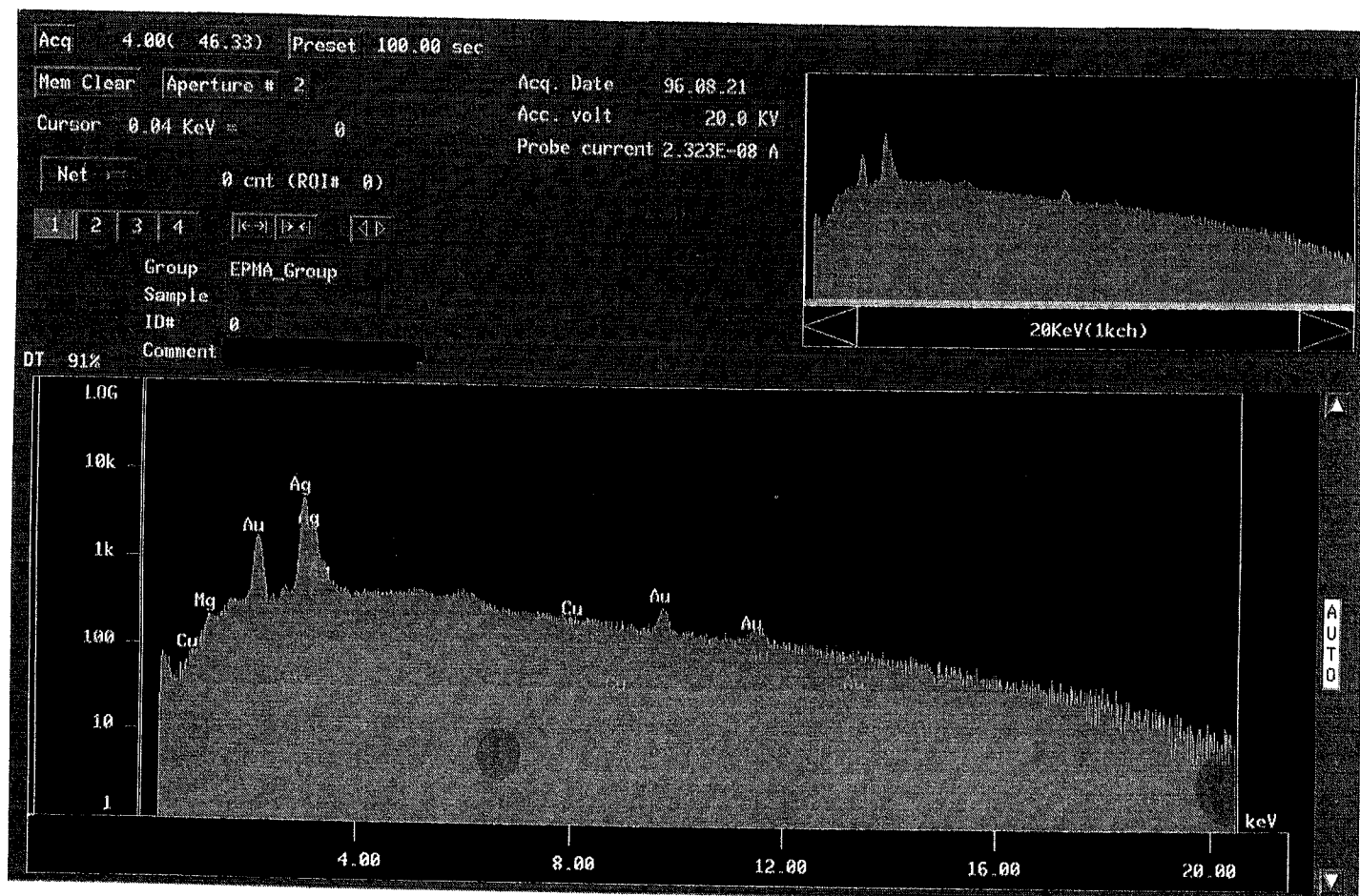
ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
NaK : 0	.378	.517 +-	.102	1.117
MgK : 1	.333	.330 +-	.061	.675
AlK : 1	.441	.211 +-	.039	.389
SiK : 1	.583	10.016 +-	.049	17.719
CaK : 3	1.155	.882 +-	.022	1.094
TiK : 1	1.023	2.016 +-	.032	2.092
V K : 0	1.065	.787 +-	.034	.768
FeK : 1	.968	84.796 +-	.176	75.444
P K : 0	.839	.292 +-	.033	.469
S K : 3	.857	.151 +-	.019	.234
TOTAL		100.000		100.000



23

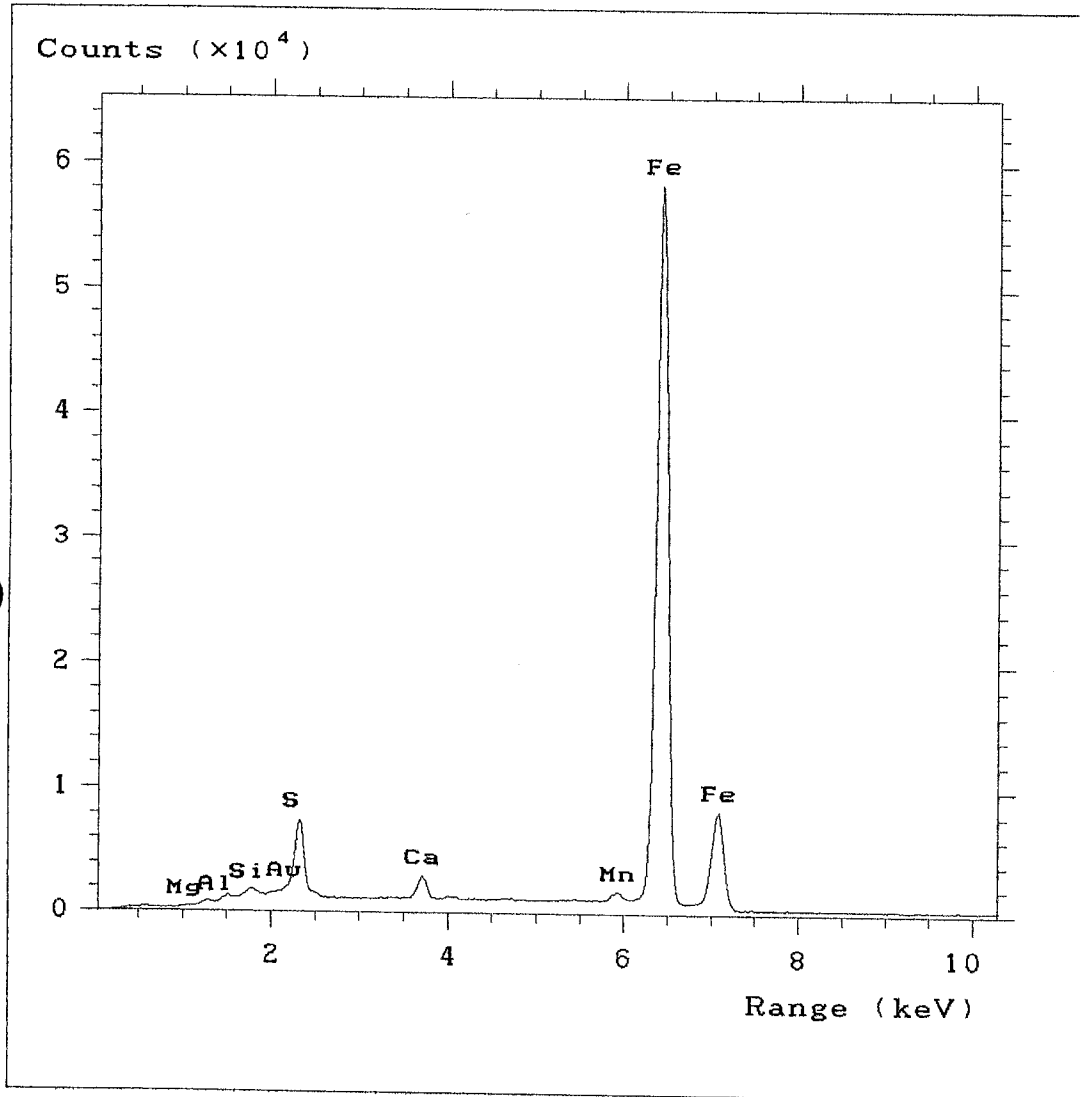
Gold Bead From Mac Hwy





25

1A



Spectrum file : ILM32

LIVETIME(spec.)= 200

0 26

#3
ENERGY RES AREA
7.5 72.58 106395
TOTAL AREA= 884630

...
Peak at .38 keV omitted?
Peak at 1.28 keV omitted?
Peak at 2.32 keV omitted?
Peak at 3.68 keV omitted?
Peak at 5.44 keV omitted?
FIT INDEX= 2.85

ELMT	APP.CONC	ERROR(WT%)
SiK : 1	.287	.020
PbL : 1	1.260	.404
FeK : 1	102.620	.256
CuK : 1	1.351	.089

ZAF CALCULATIONS

..[2 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

Spectrum: #3

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
SiK : 1	.563	.480 +-	.034	.963
PbL : 1	.690	1.718 +-	.550	.468
FeK : 1	1.002	96.349 +-	.240	97.279
CuK : 1	.874	1.453 +-	.096	1.290
TOTAL		100.000		100.000

cup
HCL
- Cupel iron

Spectrum file : ILM32

#3

LIVETIME(spec.)= 200

ENERGY RES AREA
7.5 72.58 106395
TOTAL AREA= 884630

...
Peak at .38 keV omitted?
Peak at 1.28 keV omitted?
Peak at 2.32 keV omitted?
Peak at 3.68 keV omitted?
Peak at 5.44 keV omitted?
FIT INDEX= 2.69

ELMT	APP.CONC	ERROR(WT%)
SiK : 1	.287	.020
PbL : 1	1.261	.404
FeK : 1	102.620	.256
CuK : 1	1.351	.089
PtL : 1	.092	.293* < 2 Sigma*
AuL : 1	.103	.271* < 2 Sigma*

ZAF CALCULATIONS

...[2 iterations]

20.00 kV TILT = .00 ELEV = 35.00 AZIM = .00 COSINE = 1.000

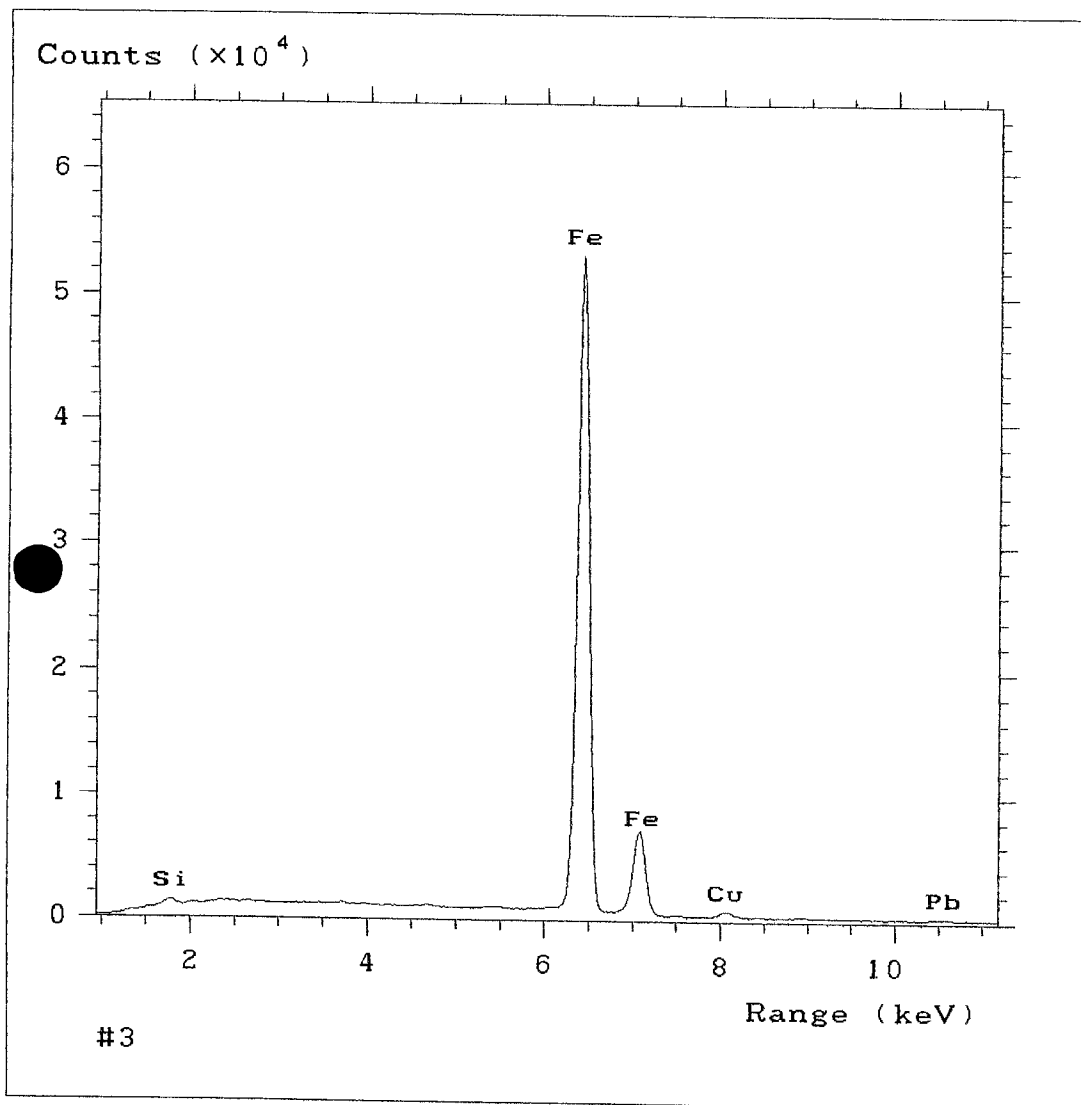
Spectrum: #3

CHEM.&MATERIALS ENG.

All elmts analysed,NORMALISED

ELMT	ZAF Ratio	%ELMT	Error	ATOM.%
SiK : 1	.564	.478 +-	.033	.962
PbL : 1	.690	1.715 +-	.549	.468
FeK : 1	1.002	96.100 +-	.240	97.281
CuK : 1	.875	1.449 +-	.096	1.289
PtL : 1	.705	.122 +-	.390 <1 sd	below confidence limit
AuL : 1	.706	.137 +-	.360 <1 sd	below confidence limit
TOTAL		99.741		100.000

928



THE TRANSPORTATION OF DEPOSITION
OF
GOLD IN NATURE

8-7: THE TRANSPORTATION AND DEPOSITION OF GOLD IN NATURE

Victor Lenher

Reprinted from *Econ. Geology* 7:744-750 (1912).

Of all the factors which play an important part in the genesis of ore deposits, the agency of solution is perhaps the most fundamental for it is by solution that the chemist is able to study and to attempt to imitate the chemistry of ore deposition as carried out in nature. Any information that will throw light on the character of possible ore-bearing solutions may be expected to aid in studying the many problems incident to the solution, transportation, and deposition of the metallic ores.

In connection with some recent chemical studies which have been made with gold, certain solutions have been worked with, the deportment of which toward various reagents as well as with certain minerals, indicates a degree of stability which appears to be of geological significance. Indeed certain gold solutions possess a stability from the purely chemical standpoint which one would not be likely to expect from our general knowledge of the ease with which gold is deposited out of most of its solutions by even the mildest reducing agents.

How gold is dissolved and transported in underground waters has not been clearly shown. The suggestive work of Stokes (*ECONOMIC GEOLOGY*, I., p. 650, 1906) on the solubility of gold in cupric chloride or in ferric chloride solutions at 200° with the redeposition of metallic gold on cooling, appears to afford a possible means of transportation of gold solutions at elevated temperatures with the subsequent deposition of the gold by lowering of the temperature. The work of Emmons on "The Agency of Manganese in the Superficial Alteration and Secondary Enrichment of Gold-Deposits in the United States" (*Trans. Amer. Inst. Min. Eng.*, 1910, 767) together with the work of McCaughey (*Jr. Amer. Chem. Soc.*, 31, 1,263, 1909), and Brokaw (*Jr. of*

Geol., Vol. 18, 321, 1910), as well as the earlier work of Pearce (*Trans. Amer. Inst. Min. Eng.*, 22, 739, 1893), Rickard (*Trans. Amer. Inst. Min. Eng.*, 26, 978, 1896), McIlhiney (*Amer. Jr. Sci.*, 1896, 293), and Don (*Trans. Amer. Inst. Min. Eng.*, 27, 599, 1897), apparently require that free chlorine is the solvent for the gold in the first instance, or if not free chlorine, a solvent whose powers are practically equivalent to that of free chlorine. When the chloride solution of gold is the transporting solution, it seems obvious that the gold is subsequently deposited as metal by a reducing agent. The agency of manganese in the solution of gold and its transportation is consistent in many gold deposits with the accompanying manganese deposits and throws considerable light on the superficial transportation of gold.

The solubility of gold in such media as the alkaline cyanides can hardly be deemed of material importance from the viewpoint of a natural transporting solution. The action of concentrated sulphuric acid or strong phosphoric acid in the presence of oxidizing agents on gold will cause solution (Lenher, *Jr. Amer. Chem. Soc.*, 26, 550, 1904) but this solvent action requires a higher concentration of acid than can be expected in nature. Similarly though hydrochloric acid under pressure (Lenher, *ECON. GEOL.*, 4, 562, 1909) and nitric acid (Dewey, *Jr. Amer. Chem. Soc.*, 32, 318, 1910) at atmospheric pressure dissolve gold, the solution occurs only in concentrated acids, and the facts are of no importance in seeking for natural solvents for gold.

From all of these acid solutions the precipitation of the gold is usually assumed to take place by ferrous sulphate, metallic sulphides such as pyrites, or, in the case of Stokes' experiments, by lowering of the temperature.

The alkaline solutions which can dissolve and carry gold have not as a rule received as serious consideration as transporting media as the better known chloride solutions. Indeed the literature on alkaline gold solutions is very meager. This is particularly true in regard to the alkaline sulphide solutions.

That gold can be brought into solution by means of the alkaline sulphides has long been known, but it is doubtful if the geolog-

ical significance.

Probably that gold is dissolved in the "Stahl in the Medicæ" so suggests alkali and

In more 382, 187: suggests medium t *Inst. Min.* of gold soluble in 33, 207, Pacific co phide. I erable a they wer double s *New So* the orig solubility

These tory and solutions appears line sulph

As is many ki tion of tions co cipitate solution dition t

ical significance of the resulting solutions has been fully appreciated.

Probably at least as early as the time of Glauber it was known that gold can be rendered soluble by fusion with liver of sulphur. Stahl in the seventeenth century ("Observations Chymico-Physica Medicæ") is the first to bring out the fact clearly, and in doing so suggests that Moses burned the golden calf with sulphur and alkali and gave the solution to the children of Israel to drink.

In more recent times, Skey (*Trans. New Zealand Institute*, 5, 382, 1872) in studying the formation of gold nuggets in drift suggests the solution of gold in the alkaline sulphides as the medium by which gold can be carried. Eggleston (*Trans. Amer. Inst. Min. Eng.*, 9, 640, 1880-1881) in studying the formation of gold nuggets and placer deposits found spongy gold to be soluble in the alkaline sulphides. Becker (*Amer. Jr. Sci.* (3), 33, 207, 1887), in his studies on the mercury deposits of the Pacific coast, has shown that gold dust dissolves in sodium sulphide. He believed that some of the gold veins bear so considerable a resemblance to the quicksilver deposits that like the latter they were formed by precipitation from solutions of the soluble double sulphides. Liversidge (*Journal of the Royal Society of New South Wales*, 27, 303, 1893), in studying the question of the origin of gold nuggets, reviews the earlier work on the solubility of gold and finds it to be soluble in sodium sulphide.

These solubility experiments have been repeated in our laboratory and the fact corroborated that metallic gold is soluble in solutions of the alkaline sulphides. More significant, however, appears the fact that from these solutions of gold in the alkaline sulphides, iron pyrites will not throw out the gold.

As is well known, the metals, the metallic sulphides, and even many kinds of organic matter will precipitate gold from the solution of gold chloride. In the case of the alkaline sulphide solutions containing gold, neither pyrites nor metallic iron will precipitate the gold, but on the other hand, gold deposits out of these solutions by exposure of the solution to the air, under which condition the sulphide oxidizes.

The sulphide solutions of gold are permanent stable solutions to the ordinary reducing agents, that is, to such reducing agents as precipitate gold from the chloride solution. These alkaline sulphide solutions deposit their gold content by contact with acid or by exposure to oxidation. Not only are the alkaline sulphide solutions of gold stable to the metallic sulphides, but experiments made in sealed tubes have demonstrated that sodium, potassium, ammonium, or calcium sulphide solutions will dissolve gold leaf in the presence of pyrites without any deposition whatever of gold on the pyrites.

It is therefore obvious that through the agency of the alkaline sulphides it is possible for gold to be transported in alkaline sulphide solution through a bed of pyrites without deposition of metallic gold, and indeed it is possible to think of such a water passing through a bed of gold-bearing pyrites actually enriching itself by solution of the gold from the pyrites. To follow such a solution farther, it can be conceived that gold can be carried through a reduced zone and later the gold can be deposited by meeting acid in the reduced zone, or in absence of acid can be carried indefinitely until it reaches a zone of oxidation when the metal would be deposited.

When sodium thiosulphate is allowed to act on gold in the presence of oxygen, the double thiosulphate of gold and sodium is formed. This double thiosulphate is also formed when auric chloride and sodium thiosulphate are brought together in solution. This salt possesses remarkable stability in that the dilute acids, hydrochloric or sulphuric, do not at once decompose it, nor does ferrous sulphate or oxalic acid, two of the most common precipitating agents for gold, reduce it to metallic gold at once. All of these reagents do in time or in stronger solutions precipitate the gold from this thiosulphate compound. The extraction of metallic gold from silver ores in the thiosulphate extraction process depends on the formation of the double thiosulphate (Stetefeldt, "The Lixiviation of Silver Ores with Hyposulphite Solutions," pp. 15, 38).

These thiosulphate solutions are reasonably stable to iron pyrites, but on standing, metallic gold slowly deposits on the pyrites.

The sulphite solution in which gold can be dissolved by the double sulphite solution, the double gold sulphite solution.

Von Haase (Chem. Ztg.) has shown that the double sulphite solution of ammoniacal solution is stable out of solution.

It has been made at various times and to metallic gold is preserved for from time to time. In metallic gold is preserved in sulphite solutions and metallic iron deposits.

Both the sodium and potassium double sulphites described by Haase are more stable than the corresponding potassium double sulphite as well as the potassium double sulphite by a few degrees. The potassium double sulphite is more stable than the potassium double sulphite and the potassium double sulphite toward reduction by a small quantity of ammonium salt. This tendency is more pronounced in ammoniacal solution. This tendency indicates the stability of the double sulphite and indicates that the double sulphite is of transportation in most natural conditions while ammoniacal solution is more stable.

The alkaline solution of gold, namely the double sulphite solution, is stable when concentrated.

The sulphite solutions of gold are another example of a means in which gold can be held in alkaline solution. Curiously enough the double sulphite of gold and ammonium is quite stable, while the double gold sulphites of the alkalis are not nearly so stable.

Von Haase (*Chemiker Zeitung*, 535, 1869) has studied the double sulphite of gold and ammonium. Haase worked in ammoniacal solution and was able to crystallize the double salt out of solution. The ammoniacal solution as prepared by Haase has been made and has been found to be quite stable to iron pyrites and to metallic iron. Ammoniacal sulphite solutions have been preserved for months in stoppered flasks and when tested from time to time by withdrawing small portions and acidifying, metallic gold is instantly precipitated. These ammoniacal sulphite solutions when sealed in tubes with iron pyrites or with metallic iron deposited no gold in months.

Both the sodium and potassium gold sulphites have been described by Haase. In solution, these salts are more unstable than the corresponding ammonium compound. The sodium as well as the potassium gold sulphite solutions yield gold to pyrites by a few minutes' contact. In reality a small quantity of the potassium or sodium gold sulphite added to the ammonium gold sulphite solution increases very much the instability of the latter toward reducing agents; indeed it is only necessary to add a small quantity of the sodium or potassium compound to the ammonium salt to cause the latter to lose its gold to pyrites practically as readily as though no ammonium salt had been present. This tendency on the part of the fixed alkalis to increase the instability of the ammonium gold sulphite solutions would seem to indicate that the sulphite solutions are not so plausible a means of transportation of gold in underground waters, inasmuch as in most natural waters sodium and potassium salts are present, while ammonium salts are found only in traces. Indeed natural ammoniacal solutions free from the alkalis are quite unknown.

The alkaline solutions of gold in the lower form of valence of gold, namely the aurous state, present some interesting phenomena when considered from the viewpoint of transportation of gold.

The aurous state of gold is produced when the ordinary or auric salts are reduced in a certain definite manner. The agencies by which this lower state of oxidation of gold can be produced are limited.

Aurous chloride and bromide are produced by the action of a moderate heat on the ordinary auric chloride or bromide. Experiments made recently in this laboratory show that by proper control sulphur dioxide, one of the best laboratory reducing agents and one of the common reagents used to precipitate gold from solution, can be used to effect the reduction of gold from the auric to the aurous state.

When sulphurous acid is added to a neutral or acid solution of gold without having present some other salt, it is very difficult to stop the reduction of the auric form of gold at the aurous state, the tendency being to produce complete reduction with the precipitation of metallic gold. If, however, a large excess of any of the alkaline chlorides, calcium, magnesium or zinc chlorides, be present, the reduction of the auric form of gold to the aurous state by means of sulphurous acid can be readily controlled. When an ordinary auric chloride solution is treated with a large excess of one of the above mentioned chlorides, and the solution then treated with a solution of sulphurous acid, the amber yellow color of the auric chloride gradually fades until the solution is rendered completely colorless. This colorless stage represents the existence of the aurous form of the gold, and the gold exists in this solution in all probability as a double aurous chloride.

Solutions of gold prepared in the manner indicated are far more stable under certain conditions than the ordinary auric chloride solutions. These conditions in which marked stability has been observed are somewhat curious. When such a solution is kept out of air contact and when no free acid or at most very little free acid is present, the solutions are fairly stable; if, however, the solution is exposed to the air, gold begins slowly to deposit. As far as the experiments have gone on this line, it seems as though the precipitation of metallic gold from this par-

tially reduced s
duction to met:

The partially
far more stable
Here again is
gold is concern

Of the varie
which have bee
phide solution
of gold deposi
not lose its go
alkaline sulphi
solvents, and
solutions poss
nature would

tially reduced solution when exposed to the air is due to autoreduction to metallic gold by the oxygen of the air.

The partially reduced or aurous solution out of air contact is far more stable to pyrites than the ordinary or auric compounds. Here again is a suggestive solution so far as transportation of gold is concerned.

Of the various means of solution and transportation of gold which have been observed, it would appear that the alkaline sulphide solution may with study solve some at least of the problems of gold deposits. At all events, a solution is known which will not lose its gold to pyrites and yet will transport gold. The alkaline sulphides can easily be conceived as important natural solvents, and while other alkaline solutions such as the aurous solutions possess considerable stability, yet their formation in nature would not appear to be so likely as the sulphide solution.

In the paper entitled *Further Studies on the Deposition of Gold in Nature*, Lenher (1918, pp. 161-163, 183-184) gives data on the solubility of gold hydroxide at elevated temperatures 100°C-200+°C and discusses the behavior of gold chlorides toward calcite and magnesite under the action of heat and pressure. The introduction and observations of this paper are of considerable interest.

Introduction

The various explanations which have been offered for the deposition of gold in nature have accounted in a satisfactory manner for the formation of certain deposits. Unquestionably, the alkaline sulphides play a very important part in the transportation of gold. The alkaline sulphides can, however, transport gold only in a zone free from oxidizing agents, since the oxidizing agents as well as the acids precipitate metallic gold from its sulphide solution. From the sulphide solutions gold is not deposited by the common reducing agents, but on the contrary, its precipitation takes place either by oxidation or by acidification.

Presumably a large proportion of the gold which has been transported and deposited in the zone of oxidation has been carried in solution as the chloride or double chloride. From such a solution the gold is in a large measure deposited by reducing agents as pyrites or some other sulphide, by a ferrous mineral or by an organic reducing agent. Reduction from the chloride solution or from alkaline solutions is also accomplished in the zone of oxidation by the oxidized ores of manganese or by such oxidizing agents as will deposit gold by the phenomenon of autoreduction.

Some of the more important gold deposits, however, cannot be explained by the theories proposed. For example, the low-grade gold ores in quartz commonly consist of a vein or bed of quartz containing very finely divided gold disseminated through it. This gold may appear in particles which are sufficiently large that they can be observed with the naked eye, but for the most part the gold particles are usually so small that they are indistinguishable. Moreover, the low-grade gold ores are usually remarkably uniform so far as their gold content is concerned; that is to say, their precious metal content varies comparatively little, and, expressed in actual percentage of gold present, the variation is insignificant.

Again, the various theories offered for the transportation and deposition of gold fail to account for the general presence of silver with the gold. For example, the alkaline sulphide solutions, which are so important in the transportation of gold, do not appear to deport themselves similarly with silver. Silver sulphide is according to our experiments quite insoluble in the alkaline sulphide solutions and in the sulphaurate solutions. Hence the transportation of gold by the alkaline sulphides cannot explain the transportation of silver, nor can this method of transportation of gold in the light of our present knowledge be reconciled by the presence of silver in gold deposits. Up to the present time the presence of silver in gold is usually accounted for by the general principle that metallic silver will precipitate metallic gold from a gold solution as the two metals

stand in that commonly evolved by means of a

Experiment quite another gold is rather well known, I easily into moderate degree of stability, when it is exposed to the air. The fact that posed by sufficient oxide of gold considerable

From our experiments more resistant by the expansion

The action are plentiful dissolved in the solution when they combine then if the temperature is sure which steadily 100 at

It should be hydroxide taken in contact with hydroxide does not occur in nature to the stability its stability is gold are the nature of any of the

The action sodium chloride while the action to prevent

Inasmuch as for silver chloride native gold methods data are lacking procedure, yet magnesium carbonate, with 150° is compared

The above

stand in that order in the electrochemical series, a fact which is so commonly evidenced in photography in the "toning" of a silver print by means of a gold solution.

Experiments recently conducted in our laboratory have shown quite another side to the deposition of gold in nature. The oxide of gold is rather remarkable for its stability. The oxide of silver, as is well known, like many of the silver compounds, breaks down rather easily into metallic silver and oxygen, under the action of only a moderate degree of heat. Gold oxide, on the other hand, is remarkably stable under the action of heat up to moderately high temperatures, when it gradually dissociates into metallic gold and oxygen. The fact that the oxide of silver and the oxide of gold are decomposed by sufficient elevation of the temperature and the fact that the oxide of gold can be formed so readily in nature, probably are of considerable importance in the formation of certain gold deposits.

Observations

From our experiments it is evident that the compounds of gold are more resistant to high temperatures when the pressure is that exerted by the expansion of steam, than they are at atmospheric pressures.

The action of calcium carbonate or magnesium carbonate, which are plentiful in nature both in the form of carbonate rocks and dissolved in the natural waters, is to first precipitate auric hydroxide when they come in contact with a water containing gold chloride; then if the temperature becomes higher than 310° under the pressure which steam would exert at those temperatures, which is approximately 100 atmospheres, crystals of metallic gold are produced.

It should be borne in mind that while the precipitation of auric hydroxide takes place readily when a gold chloride solution comes in contact with the alkaline earth carbonates, auric oxide or auric hydroxide do not occur in nature. No oxidized gold compound occurs in nature, and although we have repeatedly called attention to the stability of gold oxide, it must be distinctly borne in mind that its stability is only relative, and that in general the compounds of gold are the most easily broken down into metal of the compounds of any of the metals.

The action of various salts, such as magnesium chloride and sodium chloride, is to somewhat lower the decomposition point while the action of calcium chloride appears to have a slight tendency to prevent this decomposition.

Inasmuch as the alkaline chlorides are solvents to a slight degree for silver chloride, it is possible that the existence of silver in the native gold may be accounted for in this way. While experimental data are lacking on the coprecipitation of gold and silver by this procedure, yet we have ample evidence that calcium carbonate or magnesium carbonate in all of their natural forms precipitate silver carbonate, which at the boiling point of water or in the autoclave at 150° is completely reduced to metal.

The above experiments, in which an attempt has been made to

imitate as closely as possible the conditions existing in nature, appear to be sufficiently suggestive to be offered as an explanation of at least how it is possible that certain gold deposits have been produced.

Transport of gold in hypogene (hydrothermal) solutions as chloride complexes has appealed to a number of investigators, particularly Ogryzlo (1935), Krauskopf (1951), and Helgeson and Garrels (1968). Ogryzlo (1935) examined the solubility of gold in water containing a number of components including chlorides, sodium carbonate, sodium sulfide and sodium bisulfide. The summary and conclusions from his paper *Hydrothermal Experiments with Gold*, (pp. 423-424) follow:

Summary and Conclusions

1. 20 per cent. hydrochloric acid vapor in a dynamic system has no action on gold between 250° and 600°C.
2. When chlorine and steam are passed over gold, AuCl_3 is formed. The volatilization of AuCl_3 in the presence of chlorine and steam begins below 125°C, increases rapidly to a maximum at 200°C, and then decreases rapidly to almost nothing at 400°C. The decrease in the amount of volatilization above 200°C is due to the fact that around this temperature the dissociation pressure of the AuCl_3 increases much more rapidly than the vapor pressure. It is possible that the presence of water vapor may have an effect on the temperature at which maximum volatilization takes place. Pressure would tend to prevent dissociation and would, therefore, affect the temperature of maximum volatilization.
3. Gold dissolves in weak hydrochloric acid at high temperatures and pressures. The amount dissolved increases with the concentration of the acid and the temperature and pressure. Pressure is an important factor in causing solution. Larger quantities of gold are dissolved in the presence of air than in the presence of carbon dioxide or nitrogen.
4. The writer did not find that aqueous solutions of alkali chlorides have an appreciable solvent action on gold in the presence of air or nitrogen and under high temperature and pressure conditions, although Lenher reports that they have.
5. Sodium carbonate was not found to have solvent action on gold at high temperatures and pressures. This is not in agreement with Doelter's work.
6. Stokes found that gold dissolves in hydrochloric acid solutions of ferric chloride at high temperatures and pressures and in the absence of oxygen. This was confirmed by the writer.
7. The writer found that Na_2S solutions dissolved only traces of gold at high temperatures and pressures, and none at room temperature. These results do not agree with those of Becker, Egleston, and Lenher.
8. On the other hand, considerable quantities of gold are dissolved by solutions of NaHS at high temperatures and pressures. Some gold is also dissolved by NaHS at room temperature.

In this investigation possible the evidence shows that alkaline aqueous acid solutions, from chloride contact with nature. In hot tried as a double acidification of

In a closed system tion products with tion of the chlorine under high temperature not carried in pressure condition with the equilibrium phase as AuCl_3 which volatilizes factor is uncertain

Krauskopf (1951) and free energy data results reported in the *Gold*, (pp. 869-870) f

1. Solubilities of reasonably well
2. In acid solution provided that re an acid solution fairly strong oxidizing pressures the hydroxy ing agent; at low Cu^{++} must be present agent be present bly means that g at low temperatures agents like H_2S a tion of gold in gene movement
3. The solubilities which do not co
4. Gold may be dilute solutions, as the very stable
5. Gold may be of mechanisms, cated than a fall

10

91

In this investigation an attempt was made to imitate as closely as possible the conditions existing in nature. The experimental evidence shows that gold may be transported either in acid or slightly alkaline aqueous solutions and also in the vapor phase as AuCl_3 . In acid solutions, gold is probably carried as a chloride. Precipitation from chloride solutions would result when the solutions come in contact with one of the many reducing agents which occur in nature. In hot alkali hydrosulphide solutions, gold is probably carried as a double sulphide of the alkali metal and gold. Oxidation or acidification of the solution would cause precipitation.

In a closed system, the partial pressures of AuCl_3 and its dissociation products would tend to prevent both volatilization and dissociation of the chloride after an equilibrium has been reached. Therefore, under high temperature and pressure conditions AuCl_3 is probably not carried in the vapor state. However, under somewhat reduced pressure conditions when the solutions and gases are in communication with the earth's surface, gold may be transported in the vapor phase as AuCl_3 . It is difficult to place limits on the temperature at which volatilization would take place in Nature, as the pressure factor is uncertain.

Krauskopf (1951) calculated the solubilities of gold from electrode potential and free energy data and found results that agreed well with the experimental results reported in the literature. The summary from his paper *The Solubility of Gold*, (pp. 869-870) follows.

Summary

1. Solubilities of gold calculated from thermodynamic data agree reasonably well with experimental results.
2. In acid solutions gold may be transported as the ion AuCl_4^- , provided that reducing agents are absent. The metal is dissolved by an acid solution provided that the solution contains Cl^- and that a fairly strong oxidizing agent is present. At high temperatures and pressures the hydrogen ion of the acid is a sufficiently strong oxidizing agent; at low temperatures a substance like MnO_2 , O_2 , Fe^{+++} , or Cu^{++} must be present in addition. The requirement that an oxidizing agent be present, or at least that a reducing agent be absent, probably means that gold would not be transported in acid vein solutions at low temperatures, since such solutions would contain reducing agents like H_2S and Fe^{++} . On the other hand, solution and transportation of gold in acid solution is probably the mechanism of supergene movement of gold.
3. The solubility of gold in naturally-occurring alkaline solutions which do not contain sulfide is negligible.
4. Gold may be transported in alkaline sulfide solutions, even in dilute solutions near the neutral point. The gold is probably present as the very stable ion AuS^- .
5. Gold may be precipitated from solution by any one of a number of mechanisms, but there is no need to call on one more complicated than a fall in temperature or pressure or both.

6. If a solution of gold at high temperature and pressure is cooled, part of the metal may be forced out of solution but may appear as a sol rather than as a precipitate. In this form it may remain in suspension down to low temperatures.
7. Because gold may be transported in solutions of various compositions, the presence of gold in a vein deposit gives little information as to the character of the vein fluids.
8. In sea water gold is probably present as both AuO_2^- and AuCl_4^- . A limit to the amount dissolved may be set by the formation of these ions from metallic gold with the aid of dissolved oxygen.

Helgeson and Garrels (1968) also applied thermodynamic calculations to the solubility, hydrothermal transport, and deposition of gold. They concluded that sufficient gold can be carried in solution as aurous chloride complexes to account for hydrothermal gold ore deposits precipitated above 175°C . The concluding section of their paper *Hydrothermal Transport and Deposition of Gold* follows.

Concluding Remarks

The solubility of gold has been the subject of repeated alchemical, experimental, theoretical, economic, industrial, and geologic investigation for thousands of years. Despite all of this attention, the origin of hydrothermal gold deposits is still poorly understood. Most theories of hydrothermal gold deposition fail to account for the geologic characteristics of gold ore deposits. Much of the pertinent experimental work has been semi-quantitative at best, and the fugacity of oxygen and pH are rarely controlled and/or monitored in such experiments. As a result, high-temperature gold solubilities predicted from thermodynamic data cannot be checked adequately against experimental results reported in the literature. As least for the present, the credibility of thermodynamic predictions of gold solubilities at high temperatures rests with the extent to which such predictions agree with the geologic occurrence of gold. In this respect, and from a thermodynamic and chemical standpoint, the geochemical model of gold deposition presented above appears to be realistic.

It has been demonstrated that gold can be dispersed in significant concentrations in aqueous solutions as a stable colloid, [Fron del, C., 1938. Stability of colloidal gold under hydrothermal conditions, *Econ. Geology* 33:1-20.] as alkali thioaurate or gold sulfide complexes in alkali sulfide solutions [Krauskopf, K. B., 1951. The solubility of gold, *Econ. Geology* 46:858-870; Smith, F. G., 1943. The alkali sulphide theory of gold deposition, *Econ. Geology* 38:561-590.] and as AuCl_4^- in highly oxidizing acid solutions [Cloke, P. L., and W. C. Kelly, 1964. Solubility of gold under inorganic supergene conditions, *Econ. Geology* 59:259-270; Kelly, W. C., and P. L. Cloke, 1961. The solubility of gold in near-surface environments, *Mich. Acad. Sci., Arts, and Letters Papers* 46:19-30; Krauskopf, K. B., 1951. The solubility of gold, *Econ. Geology* 46:858-870.]. The results of this study suggest that none of these is a requirement for the hydrother-

mal transport
tions indicate
in the aurous
0.02 ppm gold
ore deposits.

The order
formation of
few simple c:
1,000 feet hig
ture profile fi
 10^9ft^3 of solu
gold along c
(predicted fr
ure 10], 4.25
precipitated
ounce of go
body. Even a
would take r
flow velocity

Hydrother
transfer that
deposits at h
mathematic
tions to a gi
geochemical
positions an
of gangue, c
ore deposits

12

mal transport and deposition of gold. Thermodynamic considerations indicate that gold is carried in hydrothermal solutions primarily in the aurous state and geologic observations suggest that less than 0.02 ppm gold in solution is sufficient to account for major gold ore deposits.

The order of magnitude of the mass transfer involved in the formation of major gold deposits can be determined by making a few simple calculations. For example, to precipitate a quartz vein 1,000 feet high, 1,000 feet long, and one foot wide over a temperature profile from 300° to 200°C requires 2.3×10^8 short tons or $7.6 \times 10^9 \text{ ft}^3$ of solution. Assuming the solution is saturated with respect to gold along curve *a* (based on geologic consideration) or curve *g* (predicted from thermodynamic calculations) in Figure 9 [and Figure 10], 4.25 short tons of gold and 13,000 tons of pyrite would be precipitated from solution along with the quartz. At \$35.00 per troy ounce of gold, the quartz vein would constitute a \$4,400,000 ore body. Even assuming a conservative flow rate of $10,000 \text{ ft}^3 \text{ day}^{-1}$, it would take no more than 2,000 years to form this ore body, and the flow velocity in the vein would only be $0.2 \text{ cm minute}^{-1}$.

Hydrothermal ore deposition is an irreversible process of mass transfer that can be evaluated quantitatively for most types of ore deposits at high temperatures from a thermodynamic, chemical and mathematical standpoint. Geologic application of such calculations to a given ore deposit is hindered primarily by the lack of key geochemical data. These data are, specifically, fluid inclusion compositions and temperatures of filling, compositions and mass ratios of gangue, ore, and alteration minerals, and mineral associations in ore deposits and altered wall rocks adjoining veins (p. 634).

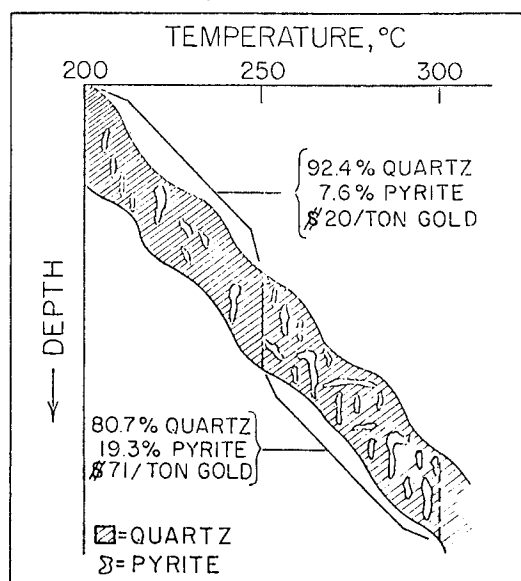
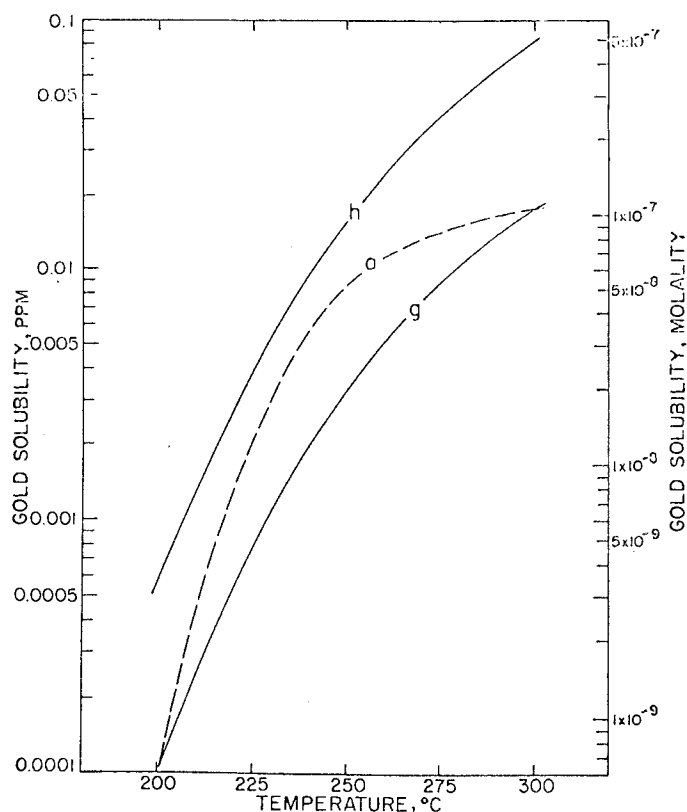
Figure 9. (Top). Computed solubility of gold at elevated temperatures. Curve *a* corresponds to curve *a* in Figure 2, which is based on geologic considerations. Curves *g* and *h* represent solubilities computed from thermodynamic data and mass transfer calculations for cooling hydrothermal solutions with different initial compositions at 300°C (see text). All three curves are for a solution in equilibrium with quartz, pyrite, and gold.

Figure 10. (Bottom). Schematic illustration of the gold-quartz vein precipitated along curve *g* in Figure 9. The relative proportions of quartz and pyrite are indicated by the hatched and clear areas, respectively. The gold values given above are based on a gold price of \$35.00 per troy ounce and the vein width corresponds to the stopping width of ore.

(See over for figures.)

13

94



Boyle (1969) from a number of experiments present in gold of the wall rock percentages of general present from highly ac presently prec of gold under Rytuba and I experimentall gold in the B $[\text{AuS}]^-$ compl these near-ne

One cannot both past and Excepting co thermal gold probable, how sulfide or sul

Alkali sulfi in hydrotherm wall rock alte soluble in alk and that gold excess at low trated alkali complex ion present in th solubility of a pyrite-pyrr kbar. Maxim concluded th predominate and $[\text{Au}(\text{HS})_2]^-$ first two cor suggesting t transport of

The sulfi tions betwe stable to me spring wat: alteration s sulfide comple nism for go

Smith (19 series of ex tellurium in gold is solu other comr

14

Boyle (1969) has criticized this proposed acid-chloride transport mechanism from a number of angles, pointing to the general low content of chloride now present in gold veins and their wall rock alteration zones, the alkaline character of the wall rock alteration associated with gold deposition, the low transfer percentages of alumina in alteration zones associated with gold deposits, the general presence in gold deposits of carbonates that are difficult to precipitate from highly acid solutions, and the general alkaline nature of hot spring waters presently precipitating gold. Others have also criticized the chloride transport of gold under hydrothermal conditions, among whom may be mentioned Rytuba and Dickson (1977) and Weissberg (1970), the latter having shown experimentally and by examination of thermal waters presently precipitating gold in the Broadlands, Ohaki and Waiotapu areas, New Zealand, that the $[\text{AuS}]^-$ complex is more than adequate to account for the transport of gold in these near-neutral low-salinity hydrothermal solutions.

One cannot doubt that gold is solubilized as a chloride complex, as proven by both past and more recent data (Vilor and Shkarupa, 1971; Henley, 1973). Excepting conditions where minerals such as alunite are precipitated in hydrothermal gold deposits, an indication of relatively high acidity, it appears more probable, however, that gold is transported under hydrothermal conditions as a sulfide or sulfide-arsenide-antimonide complex.

Alkali sulfide, bisulfide, sulfide-arsenide-antimonide, and telluride complexing in hydrothermal solutions seems most probable considering the mineralogy and wall rock alteration effects in gold deposits. It has long been known that gold is soluble in alkali hydrogen sulfide (e.g., NaHS) solutions at low temperatures, and that gold sulfide is soluble in solutions of alkali sulfide and polysulfide in excess at low temperatures. At high temperatures gold is also soluble in concentrated alkali sulfide solutions. There is some agreement that the principal complex ion in such solutions is $[\text{AuS}]^-$, although some $[\text{AuS}_2]^-$ may also be present in the systems. In a recent paper Seward (1973), determined the solubility of gold in aqueous sulfide solutions from pH 4 to 9.5 in the presence of a pyrite-pyrrhotite redox buffer at temperatures from 160°C to 300°C and 1 kbar. Maximum solubilities were obtained in the neutral region of pH. It was concluded that three gold complexes contributed to the solubility: $[\text{Au}_2(\text{HS})_2\text{S}]^{2-}$ predominated in alkaline solution, $[\text{Au}(\text{HS})_2]^-$ in the near neutral pH region, and $[\text{Au}(\text{HS})]^0$ with less certainty in the acid pH region. The stabilities of the first two complexes are much greater than chloroaurate (I) species, a feature suggesting that the chloride complexes play only a subsidiary part in the transport of gold in neutral and alkaline hydrothermal solutions.

The sulfide and polysulfide complexes of gold are stable in aqueous solutions between a pH of 6 and at least 10. The $[\text{AuS}]^-$ complex is also relatively stable to metallic sulfides and a number of other reductants. Because many hot spring waters are alkaline, and other effects such as certain types of wall rock alteration suggest alkaline solutions, transport of gold as soluble alkaline sulfide complexes has appealed to a number of investigators as a transport mechanism for gold during the formation of hypogene deposits.

Smith (1943, p. 582-589) reviewed the literature and carried out an extensive series of experiments involving the solution and transport of gold, silver, and tellurium in alkali sulfide solutions. He was able to show experimentally that gold is soluble in, and can be crystallized from, such solutions, and that two other common gold minerals, electrum (Au, Ag) and calaverite (AuTe_2), can be

15

96

similarly synthesized. The discussion and conclusion on the transport and deposition of gold, silver, and tellurium in his classic paper *The Alkali Sulphide Theory of Gold Deposition* deserve special attention because of their probable importance in the formation of hypogene gold ores (Paper 8-8).

8-8: THE OF G

F. G. S.

Copyright ©
from pages

The solubility sulphide has been concentration. They are considerably of sodium sulphide metallic sulphide of sodium thiom rather than their postulated that geological conditions concentration should

The factors in the formation of ore-bearing solutions may be discussed. Ore-bearing solutions are considered to be of two types of ore deposition: regions of near-surface sulphide has been hot springs in solution probably greater action of the ore. There are three. One, not so common, sulphate ion by noticed at Keweenaw S. Burbank, et al. *Prof. Paper 144*, solutions circulate was simultaneous probably due to oxidation making and doubtless the wallrock to sulphate of the wallrock. Pyrite is usually altered rock. The aluminum mine

(Text continues on page 173.)

8-10: THE TRANSPORTATION OF GOLD BY ORGANIC UNDERGROUND SOLUTIONS

Fred W. Freise

Copyright © 1931 by the Economic Geology Publishing Company; reprinted from *Econ. Geology* 26:421-431 (1931).

ALL mining companies or individual miners who have worked alluvial gold deposits in Brazil realize that gold placers thoroughly exhausted may after a period of years once more be panned and yield a profitable amount of newly accumulated gold. The native gold digger maintains that every gold placer within ten years is again valuable enough to be worked over once more and that the *pinta que paga*, i.e. the "paying spark" reappears the sooner if the exhausted gold field has been hidden from the sun by vegetation or other means.

The author worked gold placers at the eastern boundary of the State of Minas Geraes in the districts of Palma and Muriahé in 1908 and 1909 and for the second time in 1926; the first time monazitic sands were the principal object of the mining work, but the gold contents of the gravel (8.5 grams per ton) were recovered, since they almost defrayed the pay roll. But when, in 1926, the same places were opened again, an average of 4.85 grams of gold per ton was realized near the bottom rock, the metal being quite different from the original gold, both in color, purity, coarseness, and affinity to mercury. The nature of the territory and the sequence of the strata precludes the hypothesis of mechanical transfer from a higher point; the occurrence suggested that this gold had been brought to its place by chemical transportation.¹

In the eastern part of the State of Rio, the author opened up some gold placers in 1912; the gold content of the gravel was 11.6 grams per ton, and the average yield was 10.85 grams. When, in 1926, the old diggings, quite overgrown with "caapœira"

¹ Details concerning the above-mentioned gold and monazitic deposits were published by the writer in *Zeit. f. d. Berg-, Huetten- u. Salinenwesen i. Preuss. Staate*, vol. LVII., pp. 47-64, 1910.

(second g
above the
greenish v
ferently fi
gold.

Finally,
undergrou
had occasi
an importa
These taili
in certain
much as 3
more the
recovery v
hardly be
attributed

These c
of the age
its origin
properties
called, we
means of
observed
toughness
gold were
see wheth
one, the g
inches, co
action of
weighed
exposed to
for many
intervals
these tests

(second growth), were reopened, the lowest layers immediately above the granitic bed rock yielded 4.66 grams per ton, of a greenish variety of gold which chemically behaved quite differently from the commonly known allotropic modifications of gold.

Finally, an opportunity to see gold transported chemically by underground solutions was given to the writer in 1927, when he had occasion to examine the large tailing heaps accumulated by an important gold mining company in the center of Minas Geraes. These tailings generally showed 0.48 grams of gold per ton, but in certain parts overgrown by shrubberies there was found as much as 3.69 grams per ton. Since for the last twenty years or more the average ore treated assayed 9.5 to 10.2 grams and the recovery was 9.0 to 9.5, this high content in the tailings can hardly be ascribed to losses in milling and treatment, but must be attributed to accumulation after the tailings had been dumped.

These observations suggested an investigation into the nature of the agents that might have caused the transport of gold from its original point to lower levels. The physical and chemical properties of the original gold and the "new gold," as it may be called, were investigated. The specific gravity was determined by means of the specific-gravity bottle; the color and the surface were observed under the microscope; differences in hardness or in toughness could not be investigated since the particles of the new gold were too small. To examine the affinity to mercury, *i.e.* to see whether the new gold is a "free milling" or a "refractory" one, the gold samples were passed over copper plates of 4 to 6 inches, coated with a thin film of mercury. To determine the action of cyanide solutions on the two varieties of metal, carefully weighed portions of gold of the same degree of fineness were exposed to solutions of cyanide of potassium of various strengths for many days. The gold in solution was determined at equal intervals for both kinds of gold under treatment. The results of these tests are shown in Table I.

TABLE I.
PHYSICAL AND CHEMICAL PROPERTIES OF THE DIFFERENT KINDS OF GOLD
OBSERVED.

Kind of Gold.	Spec. Grav- ity.	Color.	Surface.	% Metal Caught on Mercury.	% Gold Dissolved in KCN-solu- tion of . . . %					
					.5		1.0		2.5	
					When in Contact during . . . Hours					
					24	144	24	144	24	144
Common placer gold, 98.3% Au, 1.7% Cu	19.562	Yellow.	Scarred	66.45	16.2	33.5	22.4	55.7	43.7	88.8
"New" gold, 100% Au.	19.222	Greenish	Plain	18.38	3.5	11.8	10.1	48.2	21.4	44.5
"Black" gold, after crust was taken off. 100% Au.	19.217	Greenish	Plain	16.66	2.9	11.5	9.9	40.4	19.7	43.9

It will be noted that the new gold is very refractory against mercury but is relatively more soluble in cyanide solutions.

It is remarkable that the physical and chemical properties of the new gold are, even in minute details, identical with those of the so-called "black gold" (*ouro preto*) found in Brazil at many places near the ancient State capital of Minas Geraes, which drew its name from the numerous deposits of "black gold" in its vicinity. These were worked out by the first discoverers in the districts of Itabirito, Diamantina, Sabará, Santa Barbara, São Gonçalo do Sapucahy, Carangola, all in Minas. Black gold is also commonly found in the districts of Rio Verde, Formosa, Santa Luzia in the State of Goyaz, and in the district of Santa Rita do Araguaia in Matto Grosso. The native prospector generally inadvertently throws it away with the heavy residuals in the pan, such as titanite, black garnet, magnetite, rutile, wolframite, and tourmaline; only by chance is it detected in the pan when the surface of the gold is given thorough attention. Black gold, as it is found at these places, is gold covered with a dark brown to dull black coating of 2 to 25 μ in thickness; where larger grains of metal are found, they prove to be composed of several smaller individuals each of which preserves its own coating. A washing with a 5 per cent. solution of K_2CO_3 at a temperature of 35°–45° is sufficient in most cases to make the coating disappear;

where the required, v acid. The moved by to the met dark varie Fe_2O_3 and In so far whether tl brown one (humate o

The abc the "black acids form sponible levels. To first with coal found ward with of humific

The bro ash, 36.28 matter, an substances by Simek² stance whi vacuum at 4.98 per c ash, of w P_2O_5 . Se this raw p solutions i

In orde pensions tl ties of go exposed to

² See Bren

where the coating is thicker, a cautious heating to 300° – 330° is required, which is followed by a washing with dilute sulphuric acid. The sulphate of iron which is then formed has to be removed by washing before cyanide or other agents can be applied to the metal, which then shows its customary yellow color. The dark varieties of "black gold" show 0.22 to 0.35 per cent. of Fe_2O_3 and the browner ones, 2.85 to 3.5 per cent., in the coating. In so far as the writer's investigations go, it cannot be said whether there is only one kind of coating or several kinds; the brown one which was investigated can be considered as $\text{C}_2\text{O}_7\text{H}_{12}\text{Fe}$ (humate of iron).

The above considerations as to the character of the coating of the "black gold" flakes suggest that waters charged with organic acids formed by the decomposition of vegetable matter were responsible for the transportation of gold from higher to lower levels. To check this idea, several series of tests were made, first with an artificial product prepared from bituminous brown coal found in the vicinity of Carangola, Minas Geraes, and afterward with "black water" generated in virgin forests from centers of humification of decayed vegetation.

The brown coal contained 21.33 per cent. water, 15.62 per cent. ash, 36.28 per cent. fixed carbon, and 26.77 per cent. of volatile matter, and held in its combustible matter about 68 per cent. of substances soluble in alkali. According to the process indicated by Simek² this raw product was used to isolate a dark brown substance which, after a long period of drying, first in air, then in vacuum at 55°C ., showed upon analysis 67.21 per cent. carbon, 4.98 per cent. hydrogen, 1.23 per cent. nitrogen, and 7 per cent. ash, of which the most important constituents were Fe_2O_3 and P_2O_5 . Separation by solubility of the different components of this raw product was not tried; for the experiments described, solutions in water were used.

In order to determine the minimum concentration of such suspensions that would act upon free gold, carefully weighed quantities of gold in the form of plates of uniform granulation were exposed to solutions of known concentration contained in glass

² See *Brennstoff Chemik*, vol. 9, 1, 12, p. 381, 1928.

TABLE II. REACTIONS OF HUMIC ACIDS ON GOLD UNDER DIFFERENT CONDITIONS.

Strength of Solution.	Kind of Water.	Gold Experimented on.		Conditions.	Duration of Experiment, Hours.	Dissolved.	
		Shape.	Fineness.			Mg.	%
.10	Rain water, airless	Plate, .01"	850/1000	No Motion	24	8.354	.05
		Dust, .01"	850/1000	"	48	15.228	.91
.50	Rain water, airless	Plate, .01"	1000/1000	Constant Motion	48	23.075	1.14
		Dust, .005"	1000/1000	"	72	25.553	2.35
2.50	Rain water, aerated	Dust, .005-.1 mm.	900/1000	No Motion	24	2.134	.005
		Same material as before	1000/1000	"	48	2.664	.0062
4.00	Rain water, airless	Dust, .005-.1 mm.	900/1000	No Motion	24	Traces	0
		Same material as before	900/1000	"	48	Traces	0
10.00	Rain water	Dust, .002-.08 mm.	600/1000-975/1000	Slow Motion + air	24	32.551	3.68
		Gold precipitated by FeSO_4	900/1000	"	48	65.001	7.21
5.00	Dist. water	Plate, .01"	900/1000	No Motion	24	97.101	11.08
		Same material and same conditions of experiment	900/1000	"	72	27.101	3.11
10.00	Dist. water with 1 % of K_2CO_3	Plate, .01"	900/1000	No Motion	96	111.402	12.50
		Same material and same conditions of experiment	900/1000	"	192	168.249	19.28
10.00	Dist. water with 1 % of K_2CO_3 , 1 % of NaHCO_3	Plate, .01"	900/1000	No Motion	300	175.455	20.21
		Same material and same conditions of experiment	900/1000	"	24	23.450	1.56
10.00	Aq. dist. with .5 % KNO_3 , .5 % NaCl	Plate, .01"	900/1000	No Motion	48	42.761	2.84
		Same material and same conditions of test	900/1000	"	72	70.111	4.66
10.00	Water with .5 % Na_2SO_4 , .5 % CaHCO_3	Plate, .01"	900/1000	No Motion	240	166.300	11.00
		Same material and same conditions of test	900/1000	"	48	Traces	0
10.00	Dist. water with 1 % of K_2CO_3 , 1 % of NaHCO_3	Plate, .01"	900/1000	No Motion	96	Little more	Traces
		Same material and same conditions of test	900/1000	"	24	Traces	0
10.00	Dist. water with 1 % of K_2CO_3 , 1 % of NaHCO_3	Plate, .01"	900/1000	No Motion	30	Reaction stopped	Reaction stopped
		Same material and same conditions of test	900/1000	"	30	Reaction without effect	Reaction without effect
10.00	Dist. water with 1 % of K_2CO_3 , 1 % of NaHCO_3	Plate, .01"	900/1000	No Motion	After 12 h. without any effect	After 12 h. without any effect	After 12 h. without any effect
		Same material and same conditions of test	900/1000	"	After a few hours no effect whatever	After a few hours no effect whatever	After a few hours no effect whatever

bottles that were
stances distilled
access to the a
was conducted
was carried on
the same conc
shown in Table

The data of

1. Gold is at
character, provi
cluded. Oxyge
may readily be
brown to ches
suspensions are
per cent. solutic

2. Distilled v
ganic acid solut
rain water is c
different minera
acids; e.g. the
destroy the hur
sulphates, and r
the stability of
determined wh
varies with diff
ducted at field

3. The finen
fluence the solu
copper, and pal
cerned. Differ
of the acids on r
In the latter ca
used; metal pre
rapidly attacked
of these differe
different precipi

bottles that were kept in slow, continuous motion. In some instances distilled water free from air was used; in others, free access to the air was allowed. Another series of experiments was conducted under free admission of carbonic acid, and a third was carried on with water mineralized with one or more salts in the same concentration as in subsoil water. The results are shown in Table II.

The data of Table II. allow of the following conclusions:

1. Gold is attacked by humic acids, even those of a very dilute character, provided sufficient time is allowed and oxygen is excluded. Oxygen rapidly destroys the organic combination, as may readily be seen by the clarifying of the water from dark brown to chestnut and reddish yellow to gold yellow; clear brown suspensions are absolutely innocuous to gold metal, even in 20 per cent. solutions.

2. Distilled water and water freed from air maintain the organic acid solutions in their full activity for a considerable time; rain water is only slightly inferior. With natural waters, the different minerals contained in them act differently on the organic acids; e.g. the carbonates and bicarbonates are the first salts to destroy the humic acids in the water, then follow sulphates, bi-sulphates, and nitrates; chlorides seem to have but little effect on the stability of the organic acids. The writer has not as yet determined whether the susceptibility of the metal to solution varies with different temperatures; all experiments have been conducted at field temperatures.

3. The fineness of the original metal does not appear to influence the solubility in the humic acids, at least so far as silver, copper, and palladium, as constituents of the gold ore, are concerned. Differences can be noted, however, between the reactions of the acids on natural gold and on gold produced by precipitation. In the latter case, solubilities vary according to the precipitant used; metal precipitated by ferrous sulphate, for example, is less rapidly attacked than gold precipitated by oxalic acid. The causes of these differences have not yet been investigated; probably the different precipitates are different allotropic varieties of gold.

Following these investigations more elaborate experiments were made, utilizing moor water or black water from the Serra dos Aymorés, the divide between the States of Minas Geraes and Espirito Santo and one of the thickest virgin forest districts of the whole country.³

Observation shows that these waters, which are dark yellow to brown or black in color, absolutely clear and transparent, low in oxygen or free from it, and of a strong acid reaction, quickly attack all the easily soluble components of the rocks such as the combinations of K_2O , Na_2O , CaO , and MgO . A relative concentration of the iron and manganese hydroxides and oxides is followed by the destruction of these constituents; the alumina and phosphoric anhydride combinations, if not destroyed and transported, are at least affected. Finally there remains merely silicic acid free from any metallic accessories except oxides of tin, tungsten, titanium, and zirconium. Gold, silver, and palladium disappear among the first constituents destroyed.

There can be no doubt that the black waters transport metallic combinations in the form of definite chemical compounds and not by adsorption; formulas can be established for the majority of metals, *i.e.* iron, copper, and manganese, for their combination with humic acids, and this is true of gold also.

After the black water has dissolved the metals, contact with the open air is sufficient to oxidize the metals and to cause them to form a scum on the water surface, in the case of iron, copper, and manganese (and probably of some other common metals also). In the case of gold, however, other conditions are necessary to bring about its reappearance. Simple contact with the atmosphere is not sufficient to separate it, since oxygen does not act

³ Under normal conditions, an acre of ground produces in this region about 3,500 cubic feet of timber, 8 to 11 per cent. of which decays annually (about 7.5 to 10.5 tons); 80 per cent. of this raw material disappears by quick fermentation which leaves only 5 per cent. or even less, equal to one eighth inch, as humus on the ground, while 20 per cent. suffers transformation under water, giving origin to the so-called black waters (*rios negros* or *rios pretos*) commonly noted on geographical maps of the tropics. Although these black waters are not so extensive in this part of Brazil as in the Amazon districts, or in Sumatra or Borneo, they carry annually thousands and thousands of tons of rock material in suspended colloidal form to the ocean or to deeper levels alongside the Rio Doce.

intensely enough precipitation of circulation meet sulphate waters

While investigation of the side valleys of the Rio Doce on the left bank of the Serra dos Aymorés, the elements the process that go on in the purpose a wood long, was built a flume was filled with washed sand of clay, or with pebbles. The filling was in jets. The upper sand and clay, but in this section of gold dust of at once if panned a constant stream that carried from black water was a flume was covered water allowed to be measured at the point it passed through a permitted sample of the sand or other

With each filling

⁴ The conglomerate (head) in Minas Geraes by gold that originates. It is highly probable that the State of Minas are black waters which

intensely enough on the gold humate; it is indispensable for the precipitation of gold that the gold humate in its underground circulation meet strongly mineralized waters such as carbonate or sulphate waters.⁴

While investigating a small placer gold deposit in one of the side valleys of the Rio Pancas, one of the affluents of the Rio Doce on the left which comes down from the center of the Serra dos Aymorés, the writer verified in an extensive series of experiments the processes of gold solution, transport, and redeposition that go on in nature in the manner described above. For this purpose a wooden flume six feet wide, four feet deep, and 50 feet long, was built with an inclination of one inch in three feet; this flume was filled for nine-tenths of its length with thoroughly washed sand of determined fineness, or with mixtures of sand and clay, or with pure kaolin, according to the details shown in Table III. The filling was evenly packed each time by means of water jets. The upper tenth of the flume was finally filled with sand, sand and clay, or pure kaolin, as in the longer part of the flume, but in this section there was admixed a carefully weighed amount of gold dust of known fineness and grain that could be recognized at once if panned out. Into this end of the flume was delivered a constant stream of black water derived from a nearby rivulet that carried from 6 to 10 per cent. of raw humus. Before the black water was introduced into the head of the flume, the whole flume was covered with water-tight boards. The amount of water allowed to sink into and pass through the flume filling was measured at the lower end by means of a tank fed by a pipe that passed through the bottom boards of the flume. This tank also permitted samples to be taken of the water that sank through the sand or other filling.

With each filling, one experiment lasted sixty days; at ten-day

⁴ The conglomerates known by the name of *tapanhoancanga* or *canga* (nigger head) in Minas Geraes, famous for their gold and diamonds, are partly cemented by gold that originally circulated in solutions formed in the manner here described. It is highly probable that the deposits of lignite known and partly explored in the State of Minas are the remainders of those virgin forests that gave origin to the black waters which transported the gold solutions mentioned here.

Phanerozoic Analogues for Carbonaceous Matter in Witwatersrand Ore Deposits

J. PARNELL

Department of Geology, Queen's University, Belfast BT7 1NN, United Kingdom

Abstract

Thoriferous bitumen nodules in quartz-pebble conglomerates and pebbly sandstones of Phanerozoic age in the British Isles are analogues for the uraniferous bitumen nodules (flyspeck) in the Archean Witwatersrand gold-uranium deposits. They are comparable in morphology, relationship to bedding planes, replacive behavior toward quartz, mineralogy, fragmentation, and displacement of inclusions. In each case the quartz-rich sedimentary host rocks represent regionally important transgressive deposits.

The contrast in dominant radioelement (thorium or uranium) probably reflects differences in mobility of the elements as a function of variable Eh conditions. The Phanerozoic thoriferous nodules occur only in pale (low Eh) beds which lack uranium deposits, but in the Archean Witwatersrand deposits fractionation of uranium and thorium may not have been as marked.

In the Phanerozoic examples there is good evidence for migration of hydrocarbons through the host rocks and the bitumen nodules can confidently be attributed a hydrocarbon origin. By analogy, this supports proponents of a hydrocarbon origin for the Witwatersrand carbon, rather than a microbial origin.

THE GENESIS of mineralization in the Witwatersrand gold fields of South Africa has long been a matter for debate. In particular, two basic aspects of the mineralization have been subject to fundamentally different interpretations. The metaliferous phases in the Archean quartz-pebble conglomerates of the Witwatersrand have been attributed to either detrital authigenic origins (Simpson and Bowles, 1977; Smits, 1984; Phillips and Myers, 1989; Reimer and Mossman, 1990; Robb and Meyer, 1991); and carbonaceous matter with which gold and other metals are closely associated has been widely interpreted as representing cyanobacterial or other microbial kerogen (Snyman, 1965; Hallbauer, 1975, 1986; Zumberge et al., 1978; Dyer et al., 1988; Ebert et al., 1990; Smits, 1992), but alternatively as the residue of migrating hydrocarbons (Schidlowski, 1981; Robb and Meyer, 1991). The understanding of the origin of the carbon is very important, as it constrains both the timing and mechanism of metal uptake by the carbon, and the prediction of carbon distribution in support of gold exploration. The resolution of the origin of the carbon in these Early Proterozoic rocks is hindered by the highly indurated state of the rocks and the advanced degree of maturation of the carbon. An apparent absence of younger analogues has also limited our understanding of the mineralization. Here I report a comparable style of mineralization involving carbonaceous matter in quartz-pebble conglomerates and pebbly sandstones of Paleozoic age in the British Isles. In this case the nature of the carbon is better understood, and by analogy may aid the understanding of the Witwatersrand carbon.

The Witwatersrand quartz-pebble conglomerates contain seams of carbon and widespread nodules of carbon (flyspeck) which are highly enriched in uranium and also other elements including gold. Conglomerates-pebbly sandstones in two regions of the British Isles have been studied in detail for their content of similar nodules of carbon which are highly enriched in thorium. The nodule-bearing sequences are in the Carboniferous North West Irish basin (Parnell and Monson, 1990) and in the Welsh borderland in rocks of Silurian age (Parnell et al., 1991). Nodule-bearing quartz-pebble con-

glomerates are particularly prominent in the Llandovery Folly Sandstone of Powys, Wales.

Carbonaceous Matter in Precambrian Deposits

Precambrian quartz-pebble conglomerates mineralised by gold and/or uranium include the deposits of the Witwatersrand basin; the Blind River-Elliott Lake district, Ontario; the Jacobina district, Bahia, and the Gandarela syncline, Minas Gerais, Brazil; and the Francevillian basin, Gabon. The Canadian, Brazilian and Gabon deposits are in Lower Proterozoic sediments, and the Witwatersrand deposits are Archean hosted (Robb et al., 1990). The nature of this type of mineralization is reviewed by Pretorius (1981). A fundamental aspect of the Witwatersrand deposits is the occurrence of seams and nodules of carbonaceous matter, mineralised by gold and uranium and therefore used as an exploration guide. The Canadian deposits similarly contain both seams and discrete globules, and also fracture fillings (Willingham et al., 1985; Mossman, 1987). In Brazil, the Moeda Formation of the Gandarela syncline also includes carbon seams and granules (Renger and Minter, 1986), and some uranium in the Jacobina deposits is located within carbon granules (Horscroft, 1986). The Francevillian basin includes uranium concentrations so rich that they gave rise to several natural fission reactors at Oklo, some of which show a very close relationship to carbonaceous matter, including fracture fillings, vug fillings and intergranular reservoir bitumens (Gauthier-Lafaye and Weber, 1989; Cortial et al., 1990). Clearly, carbonaceous matter is a consistent component of this type of ore deposit, and it is important to understand its origin. Samples from Brazil and Gabon as well as from the Witwatersrand are used in this comparison with Phanerozoic carbonaceous matter.

Phanerozoic Analogues

Nodule-bearing sequences

Detailed accounts of the distribution of thoriferous bitumen nodules in the Welsh borderland and northwest Irish basin are given by Parnell and Eakin (1989) and Parnell and

Monson (1990), respectively. The following is a summary of pertinent aspects.

Welsh borderland: Bitumen nodules occur widely distributed in the Llandovery Folly Sandstone near the town of Presteigne, in pebbly sandstones and microconglomerates. The nodules are up to 1 mm in diameter and are replacive, particularly toward quartz grains and pebbles. The nodules contain numerous inclusions of thorite and thorianite. Ten kilometers to the northeast, similar-sized nodules occur in the Wenlockian Letton grits, and also in the Longmyndian (Upper Proterozoic) Brampton grits which also consist of conglomerates and pebbly sandstones (locations figured in Parnell et al., 1991). The Letton grits nodules contain inclusions of monazite; the Brampton grits nodules contain lesser amounts of carbon and consist predominantly of titanium and iron oxides. The latter nodules are concentrated in seams and show some coalescence. The nodules in Silurian rocks are generally isolated, but preferably may occur concentrated along certain layers. The nodule-bearing sequences all lie upon a Late Proterozoic basement. The Silurian rocks are characterized by shallow-marine faunas.

Northwest Irish basin: Submillimeter bitumen nodules occur in siliciclastic units of lower Carboniferous age over a region of 1,500 km² in North West Ireland. The sandstones are predominantly fluviodeltaic, with some marginal marine influence. The Carboniferous onlaps a crystalline basement surface of Caledonian granite and metasedimentary rocks. Nodules occur in sandstones and, near to the basement surface, in conglomerates and pebbly sandstones. The nodules are most abundant in the coarser marginal rocks nearest to an outcrop of radioelement-rich granite. The nodules are replacive and contain inclusions of thorite and a mixed thorium phosphate-silicate phase (Monson, 1993). It has been possible to place hydrocarbon migration within the diagenetic sequence for the sandstones (Fig. 1).

Comparison with Witwatersrand sequences

The carbonaceous matter in the Phanerozoic rocks shows many similarities with that in the Witwatersrand conglomerates and similar Archean-Proterozoic rocks elsewhere. The comparison includes nodular form, relationship to bedding planes, multiple carbon phases, aggressive behavior toward quartz, mineralogy of inclusions, and fragmentation and displacement of inclusions, as well as a similarity in petrography and paleoenvironment of the host rocks. The analogy is itemized as follows:

1. The major host to the mineralized carbonaceous matter is a quartz-pebble conglomerate-pebbly sandstone in each case. The Witwatersrand and Huronian conglomerates are well described (Roscoe, 1981) and represent major transgressive deposits. In the Welsh borderland, the thoriferous bitumen nodules occur particularly in conglomerates of the Folly Sandstone, deposited during a regionally important Llandovery transgression upon Precambrian rocks (Ziegler et al., 1968). In the North West Irish basin, nodules occur mostly in sandstones, but are best developed in a pebbly facies deposited where Carboniferous sedimentation transgressed the margin of a plutonic-metamorphic topographic high.

2. The carbon in the Witwatersrand occurs in two promi-

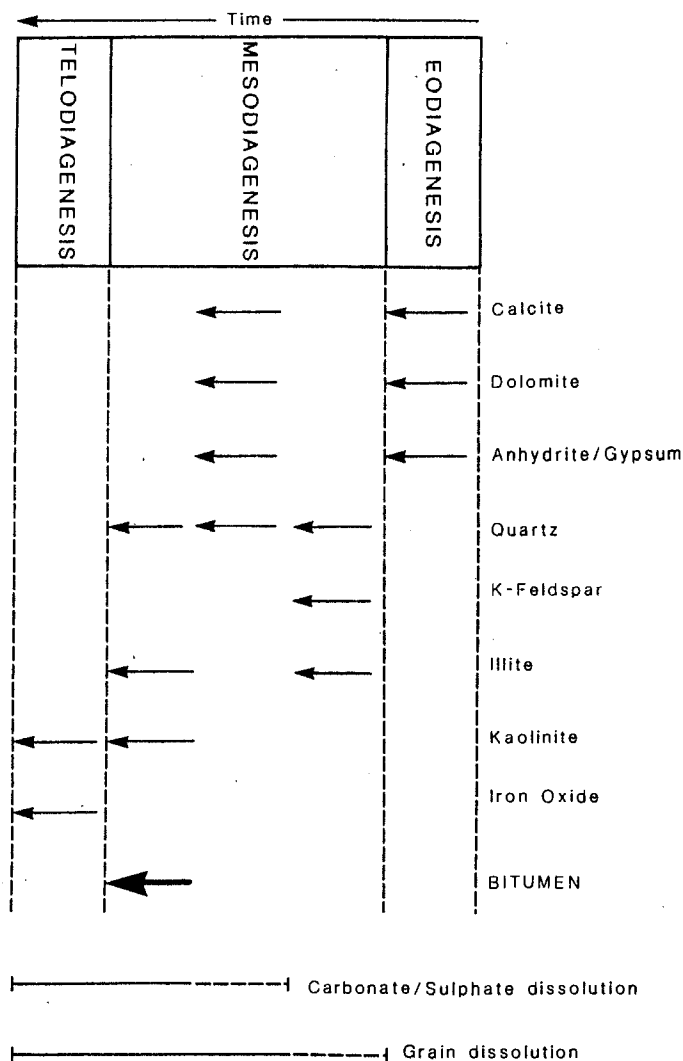


FIG. 1. Diagenetic sequence for host sandstones to thoriferous bitumen nodules, northwest Irish basin, showing that bitumen is paragenetically late. Maximum temperature of mesodiagenesis reached 140°C.

nant forms: seams of carbon up to a few centimeters thick which (1) pass between, or (2) are moulded around, quartz pebbles (Schidlowski, 1981). The relationship between these forms is described below. In addition to the seam morphology, flyspeck nodules may be concentrated along certain layers. The thoriferous carbon nodules in the Welsh borderland and northwest Ireland are very similar to the flyspeck nodules, all up to 1 mm diam (Parnell et al., 1990). They are similarly concentrated on certain bedding planes (Fig. 2A), which probably reflects an anisotropy in permeability and access to mineralizing fluids. Where the nodules are most abundant, they are seen to be partially coalesced together along layers parallel to the bedding (Fig. 2B).

3. There is evidence for the introduction of carbon in more than one phase. Petrographic studies of the Witwatersrand rocks show that there are uraniferous and nonuraniferous carbon phases, which may be in contact with each other (Landa et al., 1990; Smits, 1992). There are similarly uraniferous and nonuraniferous carbon phases in close proximity in the

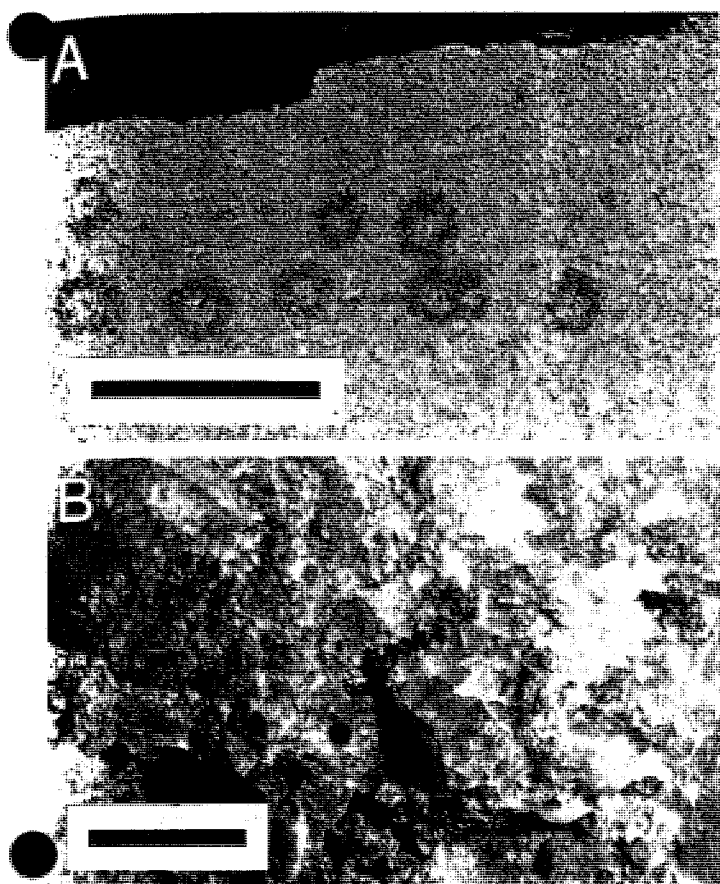


FIG. 2. Bedding plane siting of thoriferous bitumen nodules. A. Cross section of sandstone bed, northwest Irish basin, showing two horizons of nodules (encircled). B. Plan view of sandstone bed, Welsh borderland Silurian, showing partial coalescence of nodules. Scales: A = 2 cm, B = 1 mm.

Huronian Supergroup (Mossman, 1987). In the Welsh borderland, the thoriferous bitumen nodules in Llandovery sandstones are closely associated with nonthoriferous fracture-bound bitumens in the sandstones and superjacent Wenlockian limestones. The nodules themselves can show a network of nonthoriferous veinlets which appear to postdate the thoriferous phase (Fig. 3A), a feature which is similar to the sequence in the Witwatersrand.

A texture seen in some cases consists of a distinctive composition of bitumen around uraninite-thorite crystals, evinced in backscattered images (Fig. 4 compares this texture in the Proterozoic of Oklo and the Silurian of the Welsh borderland). The crystal coatings probably have compositions distinct from the background bitumen due to the effects of radiation.

4. The carbon in both cases has replaced the outer parts of quartz pebbles and other clasts. Carbonaceous nodules exhibit scalloped margins penetrating into the quartz pebbles; this is almost ubiquitous in Witwatersrand samples and samples from the Welsh borderland, and common in the Irish samples. Nodules are also found wholly isolated within quartz pebbles in each case: it is assumed that carbon entered the pebbles through microfractures in the quartz and then grew replacively. Many nodules occur at pebble contacts, where they penetrate two or more pebbles, precluding the possibil-

ity of mechanical transport with the pebbles. Some clasts have attracted many adhering nodules, partially coalesced to form a semicontinuous coating: examples are seen in both Phanerozoic (see fig. 1c of Parnell et al., 1990) and Proterozoic cases.

5. The detailed petrography of the nodules is similar. In addition to their replacive behavior toward siliciclastic grains, they exhibit patterns of mineral inclusions which appear to represent disintegration and displacement (Fig. 5). Examples exist showing a zonation in inclusion mineral composition, and the effects of irradiation from the radioactive minerals are evident in the immediately adjacent rock. I have drawn attention elsewhere to the radioactive blasting halos which occur around thoriferous bitumen nodules and to their marked similarity to those previously documented from the Witwatersrand (Parnell et al., 1990). Nodules embedded in

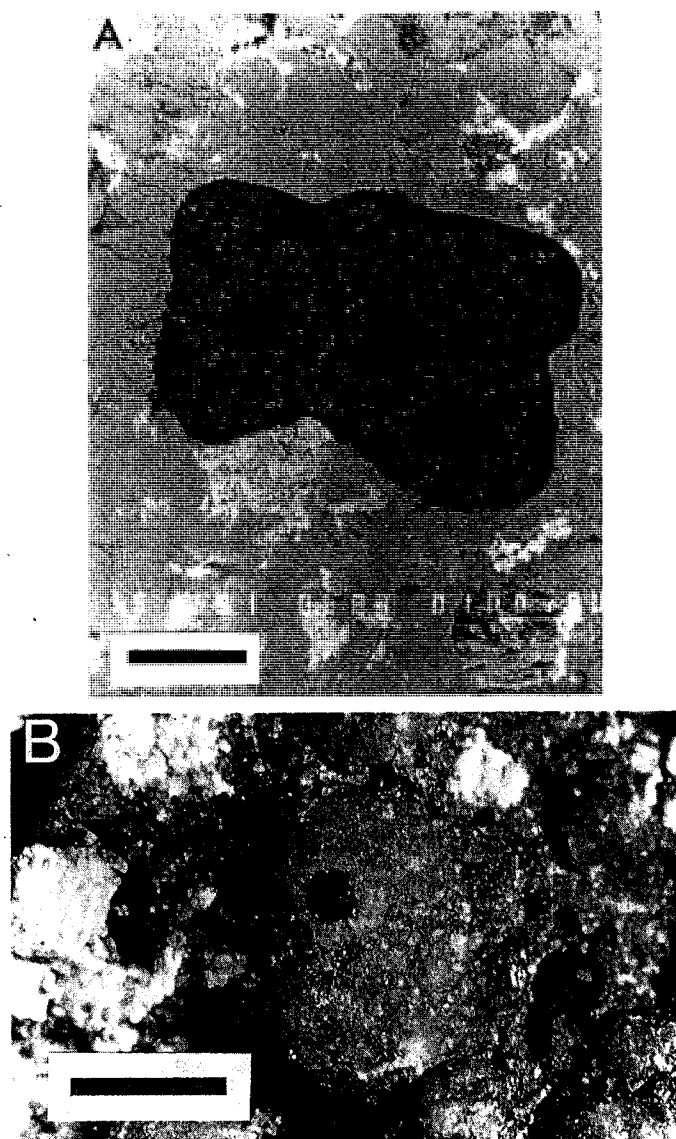


FIG. 3. Thoriferous bitumen nodules, Welsh borderland Silurian. A. Backscattered electron micrograph showing inclusions of thorite-thorianite (bright spots) and veining by nonthoriferous (inclusion-free) bitumen. B. Nodule surrounded by radiation halo, visible in ordinary light. Scales: A = 100 μ m, B = 2 mm.

quartz pebbles in the Welsh borderland have halos in the quartz which may even be visible to the naked eye (Fig. 3B). The halos reflect a metamict state in the crystal structure of the quartz, as a consequence of radiation damage.

6. The mineralogy of metalliferous inclusions within the nodular carbon is closely comparable. The flyspeck nodules in the Witwatersrand contain predominantly uraninite, with some coffinite and also some uranium in the form of uraniferous titanates (brannerite and similar) (Schidlowski, 1981; Smits, 1984). Nodules of similar size to flyspeck in the Brazilian Moeda Formation contain a much more significant titanium component: most of the titanium occurs as uranium titanates and some nodules are exclusively titanate minerals without carbon (Fig. 6A). The thoriferous nodules contain inclusions of thorite, thorianite, or monazite. In the Welsh borderland, some nodules in the late Precambrian consist predominantly of titanium oxides, and like the titanate nod-

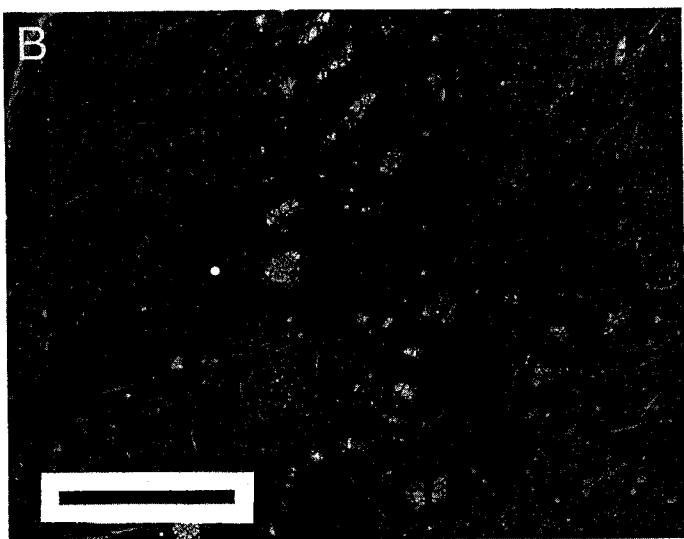
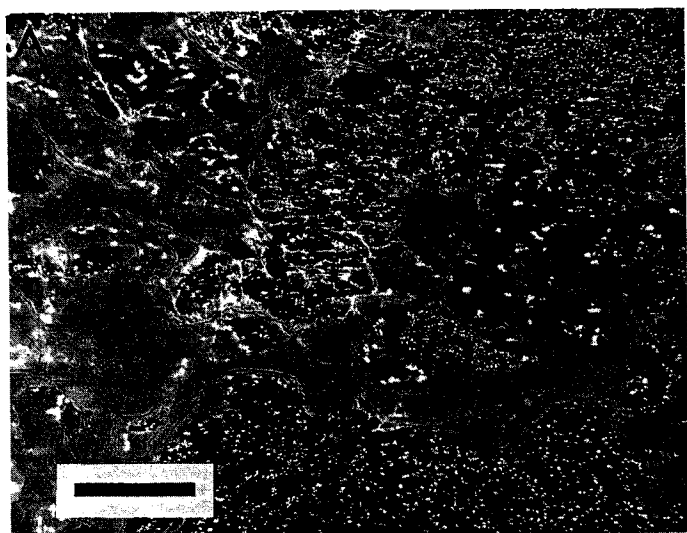


FIG. 4. Backscattered electron micrographs showing bitumen immediately around uraninite-thorite inclusions, distinct from background bitumen, probably due to effects of radiation immediately around inclusions. A. Uraninite-bearing bitumen, Oklo, Gabon. B. Thorite-bearing bitumen, Welsh borderland Silurian. Scales: A and B = 100 μm .

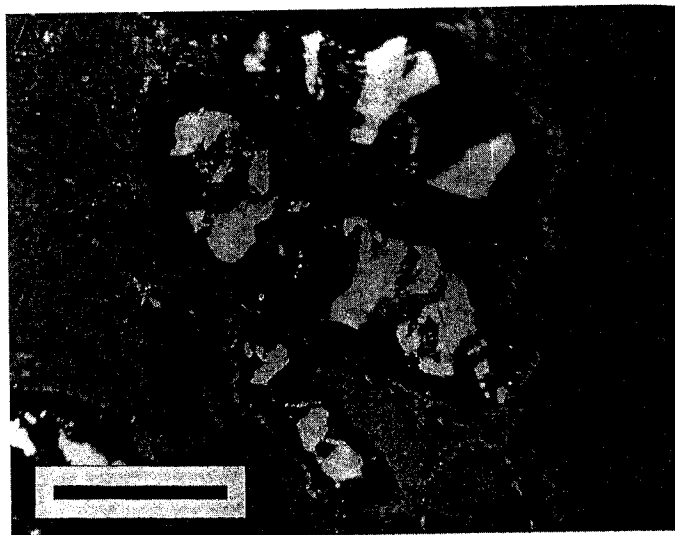


FIG. 5. Backscattered electron micrographs showing inclusions within bitumen exhibiting fragmentation and displacement of inclusion segments. A. Uraninite-bearing bitumen, Witwatersrand. B. Thorite-bearing bitumen, northwest Irish basin. Scales: A = 100 μm , B = 40 μm .

ules of the Moeda Formation, may even be completely mineralized without carbon (Fig. 6B).

Discussion

Origin of Phanerozoic carbon nodules

An origin for the Phanerozoic carbon nodules from migrating hydrocarbons seems incontestable. The occurrences of thoriferous bitumen nodules discussed here from the British Isles, and several occurrences in other countries, all occur in basins which are hydrocarbon-prospective today or have been in the geologic past (Parnell et al., 1990). In each case, the nodules occur in the vicinity of ordinary (pore-filling or fracture-bound) oil residues. In the Welsh borderland, the nodule-bearing sandstones are above a probable Precambrian-lower Paleozoic source rock, which also contains bitumen in crosscutting fractures (Parnell et al., 1991). Quartz crystals in veins cutting through the Llandovery nodule-bearing rocks and the overlying Wenlockian exposed to the south contain

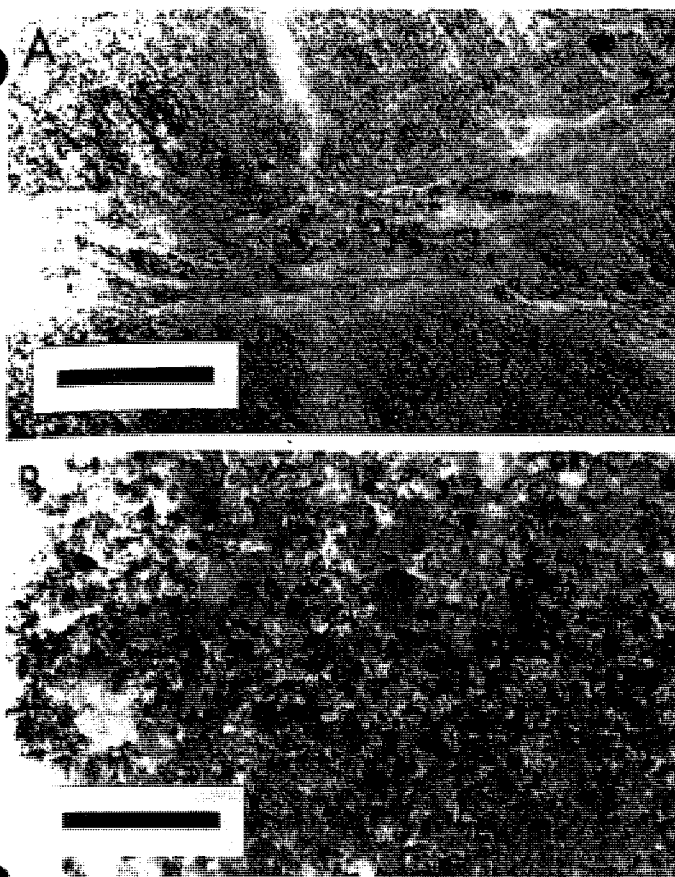


FIG. 6. Titanium-rich nodules. A. Seam of uranium titanate nodules (arrowed) in Moeda Formation, Brazil. B. Titanium oxide nodules in sandstone, Welsh borderland Precambrian. Scales: A = 4 mm, B = 2 mm.

abundant fluid inclusions which readily fluoresce in ultraviolet light due to their high content of fluid hydrocarbons (Fig. 7). In northwest Ireland the nodules occur in sandstones above and below a shale-bituminous limestone source rock, and there are, in addition, bitumens located nearby in hydrothermal fractures and in reservoir channel sandstones (Parnell

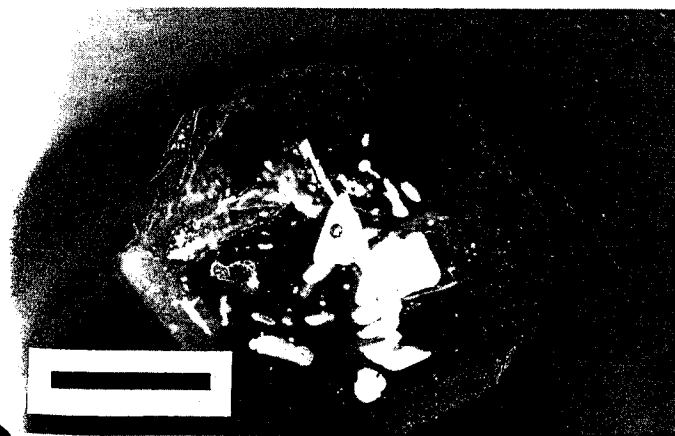


FIG. 7. Quartz crystal from crosscutting fracture in Welsh borderland Silurian, showing fluid inclusions fluorescing under ultra-violet light due to hydrocarbon content. Scale: 1 mm.



FIG. 8. Gradation from carbon (bitumen) seam to discrete bitumen nodules in Witwatersrand sample. Scale: 2 mm.

and Monson, 1990). An example of the same phenomenon in Australia was shown by organic geochemical evidence to be probably related to oil elsewhere in the sequence (Rasmussen et al., 1989).

Morphology of carbon

In the Phanerozoic analogues described, carbon is in nodular form, with rare examples of coalescence and a preferred occurrence along bedding planes. In the Witwatersrand rocks, flyspeck nodules are common, as are seams of carbon. On detailed examination, the seams are seen to consist of closely packed nodules (Fig. 8). Where the nodules show a preferred orientation, they are elongate normal to bedding rather than bedding-parallel (Fig. 9A, B). This implies that the seam morphology is only due to coalescence of nodules, not growth of a carbon structure in a horizontal plane. Thus the concentration of Witwatersrand carbon along bedding planes is similar to that in Phanerozoic rocks but with a greater degree of coalescence. The elongation of the Witwatersrand nodules normal to bedding is due to the high lateral density of nodules (as seen in a plan view of a seam; Fig. 9A), which meant that expansion could only occur out of the bedding plane, to give the columnar morphology described by some workers (e.g., Hallbauer, 1975). Fragmentation of uraninite inclusions is a widely observed phenomenon in uraniferous organic matter (e.g., Parnell, 1988a; Eakin and Gize, 1992), explicable by the effects of irradiation. The phenomena associated with irradiation of organic matter are well discussed elsewhere (e.g., Curiale et al., 1983; Willingham et al., 1985; Rasmussen et al., 1993). In essence, alpha radiation (and to some extent beta and gamma radiation) induces condensation and polymerization reactions within fluid hydrocarbons, i.e., migrating oil and gas, which causes precipitation of viscous-solid hydrocarbon coatings around radioelement-bearing grains. Subsequent intense flux of alpha particles into the coating has a significant effect upon the polymeric hydrocarbon, causing progressive hardening (Charlesby, 1987). The polymer experiences a swelling effect as further fluid hydrocarbons enter the crosslinked structure. Volume increases of an order of magnitude are recorded in experimental studies (Bauman and Glantz, 1957). This enormous expansion ex-

Artificial Transmutation - The process of bombarding a nucleus with alpha particles, protons, or neutrons to give an unstable nucleus, which can then emit a proton or neutron in order to

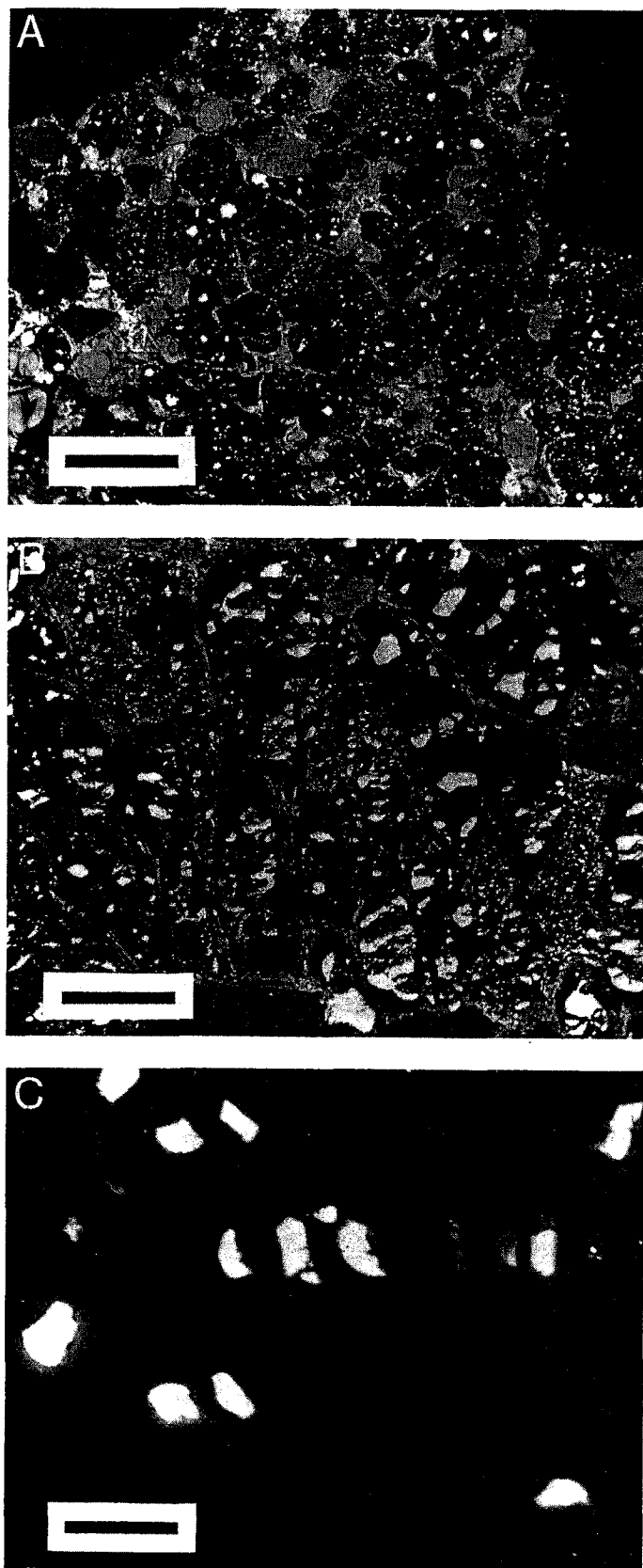


FIG. 9. Bitumen nodule morphology. A. Plan view of Witwatersrand seam showing it to consist of closely packed nodules. B. Cross section of Witwatersrand seam showing it consists of closely-packed nodules elongate normal to bedding, with fragments of uraninite inclusions displaced apart

plains the observed displacement of the fragments of uraninite in the Witwatersrand nodules and the thorite-thorianite in the Phanerozoic nodules. The high degree of expansion of uraninite in one orientation (i.e., bedding-normal) in the Witwatersrand bitumen is also seen in Phanerozoic uraniferous bitumens (Fig. 9C shows an example from the Isle of Man; compare with Fig. 9B). A further effect of radiation is radiolysis of pore water to produce large amounts of free radicals, which may be responsible for the replacement of detrital grains.

Contrast in uranium and thorium enrichment

There are many known examples of solid bitumens which are highly enriched in radioelements and contain inclusions of radioelement minerals (Parnell, 1988a); however, in any one occurrence the mineral inclusions are either predominantly uraniferous or predominantly thoriferous. Bitumens are not comineralized by both uranium and thorium and fractionation of the two elements has clearly occurred at some stage. Fractionation is most likely to reflect differences in the mobility of the two elements as a function of prevailing pH-Eh conditions rather than a difference in metal-organic interaction. In Phanerozoic and late Proterozoic siliciclastic sequences, uraniferous bitumens tend to occur in red beds whereas thoriferous bitumens occur in white-gray beds, a feature which reflects the preferential mobility of uranium and thorium in high and low Eh conditions, respectively. In the north of Ireland, the white-gray Carboniferous sandstones in the west are thorium mineralized, whereas Permian and Triassic red sandstones and siltstones in the east are uranium mineralized (Parnell et al., 1990). However, the pale-colored Witwatersrand conglomerates are uranium mineralized rather than thorium mineralized. There is still debate about the content of oxygen in the atmosphere at the time of Witwatersrand sedimentation, but it is almost certain that the oxygen content was not at its present level and consequently red beds were not widely developed. As a result the potential for uranium to be oxidized and transported as the hexavalent ion, and consequently fractionated into red beds, was very limited, and it is not surprising that uranium occurs in paler (low Eh) beds. The Witwatersrand uraninite contains thorium (up to several percent), and unpublished observations by the author suggest that there is a limited content of thorium in the Witwatersrand carbon, within a titanate-silicate phase which is paragenetically later than the uraninite, indicating that fractionation was thus not as complete as in younger successions.

Origin of uranium-thorium minerals

As noted above, the uraninite and other metalliferous phases in the Witwatersrand have been interpreted as both detrital and authigenic in origin (Simpson and Bowles, 1977; Smits, 1984). It is not the purpose of this account to debate further the detailed evidence relating to this aspect of the Witwatersrand mineralization, but it is notable that there is similar ambiguity over the origin of the thoriferous phases in

in this orientation. C. Analogous displacement of uraninite inclusion fragments in a consistent orientation in bitumen, Laxey mine, Isle of Man. Scales: A = 400 μ m, B = 100 μ m, C = 40 μ m.

Younger rocks. Thoriferous mineral cores to bitumen nodules were discovered independently by Parnell (1988b) and Raschussen et al. (1989), who attributed an authigenic and detrital origin to their respective examples. The expansion-fragmentation process could cause such disruption to single detrital grains so that they appear to consist of an array of small authigenic crystals. There are numerous descriptions of how reactive minerals in coals and shales, particularly uraniferous zircons, do act as nuclei for bituminous coatings (e.g., Stach, 1958; McKirdy and Kantsler, 1980). However, nodules in the Welsh borderland have been reported in crosscutting mineral veinlets and in the moldic porosity of fossils (Parnell and Eakin, 1989), indicating that at least some of the mineral inclusions have an authigenic origin. I and my colleagues have assumed that most of the thoriferous bitumen nodules which we have examined are diagenetically enriched in thorium (Parnell and Eakin, 1989; Parnell and Monson, 1990; Parnell et al., 1990; Monson and Parnell, 1993). This interpretation is similar to the model of uranium enrichment of hydrocarbons for the Witwatersrand deposits described by Phillips and Myers (1989), although most workers believe that a major portion of the uraninite is detrital (Robb and Meyer, 1991).

Relationships with granite

The uranium and thorium in the carbonaceous matter is probably of a predominantly plutonic provenance. The hinterland of the Witwatersrand basin includes several Archean granites (Robb et al., 1993), and the northwest Irish basin is adjacent to the Caledonian Barnesmore Granite (Parnell and Monson, 1990). The granites are updip from the sedimentary basins, and consequently, hydrocarbon-bearing fluids may have migrated through the upper (weathered, fractured) parts of the granites. In the Archean granites, Robb et al. (1993) have reported carbonaceous nodules nucleated about uraninite crystals in the granites themselves, a direct indication of hydrocarbon migration through the rocks. Carbonaceous matter has not been observed in the Barnesmore Granite, but weathered specimens of the granite contain numerous small crystals of the same thorium phosphosilicate (thorite var.) which occurs in the bitumen nodules found in the adjacent sediments (Monson and Parnell, 1993) and in Carboniferous sandstones in several other parts of the British Isles. The thorite crystals in the granite appear too small and delicate to have been the source, through erosion, of the thorite in the sediment-hosted bitumen nodules. It is also doubtful if so much thorite would occur as the primary thorium phase in the granite, which is more likely to be monazite or the thorium oxide mineral thorianite. Furthermore, the Barnesmore Granite is probably a fractionated I-type granite (I.G. Meighan, pers. commun.), which is unlikely to have contributed large amounts of detrital monazite or thorite. Rather, the thorite in the granite was probably precipitated from the same ground waters which interacted with migrating hydrocarbons to precipitate the thorite-bearing bitumen nodules. This implies that thorium precipitation was not completely dependent upon organic matter but may have been localized by it in the sandstones. The weathered granite is porous; the granite had been unroofed by Carboniferous times (Parnell and Monson, 1990) and probably experienced the deep oxidative weathering which affected northwest Europe in Permian

times, so this porosity may date to the Paleozoic and have facilitated ground-water penetration. It should be noted, however, that we are relatively ignorant of the conditions under which thorium silicate could be precipitated, particularly at low temperatures.

Consequences for Witwatersrand mineralization

If the Phanerozoic thoriferous bitumen nodules can be regarded as an analogue for the Witwatersrand uraniferous carbon nodules, their genesis can help us to constrain the origin of the Witwatersrand carbon.

The unequivocal origin of the Phanerozoic carbon as a residue of migrating hydrocarbons strongly supports the school of thought that the Witwatersrand carbon is a migrated rather than an indigenous form. The concept that the Witwatersrand carbon may be derived from a microbial precursor is partly based upon so-called "filamentous" or "columnar" structures normal to the carbon seam orientations. These elongate structures in fact represent preferred displacement of fragmented uraninite inclusions within carbon nodules (see above), in an orientation normal to bedding (Fig. 9B). Fragmentation and displacement of thorite-thorianite can also be observed within thoriferous bitumen nodules, but displacement in a preferred orientation has not been noted.

The replacive thoriferous bitumen nodules appear to have grown late in the diagenetic sequences of the host sandstones. If the same timing can be applied to the Witwatersrand nodules (whose paragenetic context is difficult to assess directly due to the effects of metamorphism), this imposes some constraint on the timing of other mineralization within the Witwatersrand conglomerates. Petrographic evidence suggests that part of the gold mineralization is remobilized (Phillips et al., 1987), postdates the formation of carbon nodules, and therefore would have postdated the main diagenetic processes which were experienced by the conglomerates.

Conclusions

The thoriferous bitumen nodules found in Phanerozoic conglomerates and sandstones are a good analogue for the carbonaceous nodules which occur in Witwatersrand gold-uranium deposits. The analogy includes: (1) hosting in a quartz-pebble conglomerate-pebbly sandstone representing deposits of regional transgressions, (2) concentration of nodules along certain layers, (3) evidence for more than one phase of carbon, (4) disintegration and displacement of mineral inclusions within carbon, and (5) comparable mineralogy including oxides, silicates and titaniferous phases.

The source of the carbon in the Phanerozoic bitumen nodules was migrating hydrocarbons. The strong analogy with the Witwatersrand nodules suggests that the carbon in the Witwatersrand deposits was, similarly, migrating hydrocarbons. This is consistent with the views of some workers who claim a hydrocarbon origin on geochemical evidence (Schidlowski, 1981; Robb and Meyer, 1991), as opposed to a microbial origin favored by many other workers on petrographic evidence.

Acknowledgments

I am grateful to B. Nagy for providing samples from the Witwatersrand, and to the staff of the Queen's University

electron microscopy unit for technical support. The manuscript benefited from reviews by *Economic Geology* referees. This paper is a contribution to IGCP project 357.

REFERENCES

- Bauman, R., and Glantz, J., 1957, The effect of copolymer composition on radiation cross-linking: *Journal of Polymer Science*, v. 26, p. 397-399.
- Charlesby, A., 1987, Radiation chemistry of polymers, in Farhatziz, and Rodgers, M.A.J., eds., *Radiation chemistry—principles and applications*: New York, VCH Publishers, p. 451-475.
- Cortial, F., Gauthier-Lafaye, F., Lacrampe-Couloume, G., Oberlin, A., and Weber, F., 1990, Characterization of organic matter associated with uranium deposits in the Francevillian Formation of Gabon (Lower Proterozoic): *Organic Geochemistry*, v. 15, p. 73-85.
- Curiale, J.A., Bloch, S., Rafalska-Bloch, S., and Harrison, W.E., 1983, Petroleum-related origin for uraniferous organic-rich nodules of southwestern Oklahoma: *American Association of Petroleum Geologists Bulletin*, v. 67, p. 588-608.
- Dyer, B.D., Krumbein, W.E., and Mossman, D.J., 1988, Nature and origin of stratiform kerogen seams in Lower Proterozoic Witwatersrand-type paleoplacers—the case for biogenicity: *Geomicrobiology Journal*, v. 6, p. 33-47.
- Eakin, P.A., and Gize, A.P., 1992, Reflected-light microscopy of uraniferous bitumens: *Mineralogical Magazine*, v. 56, p. 85-99.
- Ebert, L.B., Robbins, E.I., Rose, K.D., Kastrup, R.V., Scanlon, J.C., Gebhard, L.A., and Garcia, A.R., 1990, Chemistry and palynology of carbon seams and associated rocks from the Witwatersrand goldfields, South Africa: *Ore Geology Reviews*, v. 5, p. 423-444.
- Gauthier-Lafaye, F., and Weber, F., 1989, The Francevillian (Lower Proterozoic) uranium ore deposits of Gabon: *ECONOMIC GEOLOGY*, v. 84, p. 2267-2285.
- Hallbauer, D.K., 1975, The plant origin of the Witwatersrand "carbon": *Minerals Science and Engineering*, v. 7, p. 111-131.
- 1986, The mineralogy and geochemistry of Witwatersrand pyrite, gold, uranium and carbonaceous matter, in Anhaeusser, C.R., and Maske, S., eds., *Mineral deposits of southern Africa*: Johannesburg, Geological Society of South Africa, v. 1, p. 731-752.
- Horscroft, F.D., 1986, The occurrence of gold in quartz-pebble conglomerate at Jacobina, Bahia, Brazil: *Geocongress '86 Symposium*, Johannesburg, Extended Abstract Volume, p. 259-262.
- Landais, P., Dubessy, J., Robb, L.J., and Nouel, C., 1990, Preliminary chemical analyses and Raman spectroscopy on selected samples of Witwatersrand kerogen: *University of the Witwatersrand Economic Geology Research Unit Information Circular* 222, 8 p.
- McKirdy, D.M., and Kantsler, A.J., 1980, Oil geochemistry and potential source rocks of the Officer basin, South Australia: *APEA Journal*, v. 20, p. 68-86.
- Monson, B., 1993, Mineralogy of thoriferous bitumen nodules, northwest Irish basin, in Parnell, J., Kucha, H., and Landais, P., eds., *Bitumens in ore deposits*: Heidelberg, Springer-Verlag, p. 350-361.
- Monson, B., and Parnell, J., 1993, Thoriferous bitumen nodules and hydrocarbon exploration in Carboniferous sandstones, British Isles: Preliminary results, in Parnell, J., Ruffell, A.H., and Moles, N.R., eds., *Geofluids '93, Contributions to an International Conference on Fluid Evolution, Migration and Interaction in Rocks*: Bath, Geological Society Publishing House, p. 439-442.
- Mossman, D.J., 1987, Stratiform gold occurrences of the Witwatersrand type in the Huronian Supergroup, Ontario, Canada: *South African Journal of Geology*, v. 90, p. 168-178.
- Parnell, J., 1988a, Mineralogy of uraniferous hydrocarbons in Carboniferous-hosted mineral deposits, Great Britain: *Uranium*, v. 4, p. 197-218.
- 1988b, Metal enrichments in bitumen: A review: *Mineralium Deposita*, v. 23, p. 191-199.
- Parnell, J., and Eakin, P., 1989, Thorium-bitumen mineralization in Silurian sandstones, Welsh borderland: *Mineralogical Magazine*, v. 53, p. 111-116.
- Parnell, J., and Monson, B., 1990, Sandstone-hosted thorium-bitumen mineralization in the northwest Irish basin: *Sedimentology*, v. 37, p. 1011-1022.
- Parnell, J., Monson, B., and Tosswill, R.J., 1990, Petrography of thoriferous hydrocarbon nodules in sandstones, and their significance for petroleum exploration: *Geological Society of London Journal*, v. 147, p. 837-842.
- Parnell, J., Robinson, N., and Brassell, S., 1991, Discrimination of bitumen sources in Precambrian and lower Palaeozoic rocks, southern U.K., by gas chromatography-mass spectrometry: *Chemical Geology*, v. 90, p. 1-14.
- Phillips, G.N., and Myers, R.E., 1989, The Witwatersrand gold fields: Part II. An origin for Witwatersrand gold during metamorphism and associated alteration: *ECONOMIC GEOLOGY MONOGRAPH* 6, p. 598-608.
- Phillips, G.N., Myers, R.E., and Palmer, J.A., 1987, Problems with the placer model for Witwatersrand gold: *Geology*, v. 15, p. 1027-1030.
- Pretorius, D.A., 1981, Gold and uranium in quartz-pebble conglomerate: *ECONOMIC GEOLOGY 75TH ANNIVERSARY VOLUME*, p. 117-138.
- Rasmussen, B., Glover, J.E., and Alexander, R., 1989, Hydrocarbon rims on monazite in Permian-Triassic arenites, northern Perth basin, Western Australia: Pointers to the former presence of oil: *Geology*, v. 17, p. 115-118.
- Rasmussen, B., Glover, J.E., and Foster, C.B., 1993, Polymerization of hydrocarbons by radioactive minerals in sedimentary rocks: Diagenetic and economic significance, in Parnell, J., Kucha, H., and Landais, P., eds., *Bitumens in Ore Deposits*: Heidelberg, Springer-Verlag, p. 490-509.
- Reimer, T.O., and Mossman, D.J., 1990, The Witwatersrand controversy revisited: *ECONOMIC GEOLOGY*, v. 85, p. 337-343.
- Renger, F.E., and Minter, W.E.L., 1986, Proterozoic placers of the Moeda Formation within the Gandarela syncline, Minas Gerais, Brazil: *Geocongress 86 Symposium*, Johannesburg, Extended Abstract Volume, p. 335-339.
- Robb, L.J., and Meyer, F.M., 1991, A contribution to recent debate concerning epigenetic versus syngenetic mineralization processes in the Witwatersrand basin: *ECONOMIC GEOLOGY*, v. 86, p. 396-401.
- Robb, L.J., Davis, D.W., and Kamo, S.L., 1990, U-Pb ages on single detrital zircon grains from the Witwatersrand basin, South Africa: Constraints on the ages of sedimentation and on the evolution of granites adjacent to the basin: *Journal of Geology*, v. 98, p. 311-328.
- Robb, L.J., Landais, P., Meyer, F.M., and Davis, D.W., 1993, Nodular kerogen in granites: Implications for the origin of carbonaceous matter in the Witwatersrand basin, South Africa, in Parnell, J., Ruffell, A.H., and Moles, N.R., eds., *Geofluids '93, Contributions to an International Conference on Fluid Evolution, Migration and Interaction in Rocks*: Bath, Geological Society Publishing House, p. 446-449.
- Roscoe, S.M., 1981, Temporal and other factors affecting deposition of uraniferous conglomerates. U.S. Geological Survey Professional Paper 1161, p. W1-W17.
- Schidlowski, M., 1981, Uraniferous constituents of the Witwatersrand conglomerates: Ore-microscopic observations and implications for Witwatersrand metallogeny: U.S. Geological Survey Professional Paper 1161, p. N1-N29.
- Simpson, P.R., and Bowles, J.F.W., 1977, Uranium mineralization of the Witwatersrand and Dominion Reef system: *Royal Society of London Philosophical Transactions*, v. A286, p. 527-548.
- Smits, G., 1984, Some aspects of the uranium minerals in Witwatersrand sediments of the Early Proterozoic: *Precambrian Research*, v. 25, p. 37-59.
- 1992, Mineralogical evidence for geochemical environment at the earth's surface during deposition of Witwatersrand reefs: *Institution of Mining and Metallurgy Transactions*, sec. B, v. 101, p. 99-107.
- Snyman, C.P., 1965, Possible biogenetic structures in Witwatersrand thucholite: *Geological Society of South Africa Transactions*, v. 68, p. 225-233.
- Stach, E., 1958, Radioaktive inkohlung: *Brennstoff-Chemie*, v. 39, p. 329-331.
- Willingham, T.O., Nagy, B., Nagy, L.A., Krinsley, D.H., and Mossman, D.J., 1985, Uranium-bearing stratiform organic matter in paleoplacers of the lower Huronian Supergroup, Elliot Lake-Blind River region, Canada: *Canadian Journal of Earth Sciences*, v. 22, p. 1930-1944.
- Ziegler, A.M., Cocks, L.R.M., and McKerrow, W.S., 1968, The Llandovery transgression of the Welsh borderland: *Palaeontology*, v. 9, p. 346-350.
- Zumbege, J.E., Siglio, A.C., and Nagy, B., 1978, Molecular and elemental analyses of the carbonaceous matter in the gold and uranium-bearing Vaal reef carbon seams, Witwatersrand sequence: *Minerals Science and Engineering*, v. 10, p. 223-246.

Occurrence and distribution of invisible gold in a Carlin-type gold deposit in China

SHUI HE MAO

Institute of Comprehensive Utilization of Mineral Resources, Emei, Sichuan 614200, People's Republic of China

ABSTRACT

From the results of EPMA on various minerals from the ore and from SEM observations and chemical dissolution experiments on pyrite in a Carlin-type gold deposit (Banqi gold deposit, Guizhou, China), the following conclusions are drawn:

Pyrite is the most important Au-bearing mineral. Most of the pyrite grains occur as anhedral granules consisting of earlier formed, euhedral crystal cores containing little or no Au and As and later formed rims that are rich in Au and As. The average tenor of Au is 257.6 ppm in pyrite, about 600 ppm in rims of anhedral grains, and less than 82 ppm in cores.

There is a positive correlation between the concentrations of Au and As, so the distribution of Au is similar to that of As in SEM images and EPMA data.

EPMA data show highly variable Au concentrations at different spots in a Au-rich rim within a pyrite grain. Moreover, in chemical dissolution tests on pyrite, most of the Au is not in the supernatant HNO_3 solution but remains in the undissolved residues and is available for leaching into $\text{KI} + \text{I}_2$ Au-leaching solution. All these facts illustrate that Au in pyrite occurs as ultramicroscopic native gold inclusions, not as isomorphous substitution.

It is shown that more than 60% of the Au given by chemical assay of clay minerals occurs in submicrometer-size pyrite inclusions in which Au is remarkably enriched.

The Au contents in other minerals, such as arsenopyrite, quartz, calcite, or barite, are all below the detection limit of EPMA. Considering the results of chemical assays of these mineral separates, it is concluded that these minerals are not significantly Au bearing.

Knowledge of the mode of occurrence and distribution characteristics of invisible Au in Carlin-type deposits is beneficial to metallurgical process design for Au recovery. In this case, sufficient oxidation and leaching of the pyrite surface layer will produce satisfactory recovery at reduced cost in time, energy, and reagents.

INTRODUCTION

There is a type of Au-bearing ore in which the Au tenor is quite high—sometimes reaching tens of ppm—but the Au in the ore is not visible by reflected and transmitted light microscopy at high magnification. Generally, this Au is called invisible Au, ultramicroscopic Au, or submicrometer Au.

Because ultramicroscopic Au is invisible, it is extremely difficult to study its occurrence and distribution by conventional determinative means. Spending a great deal of time, the mineralogist can assay hand-picked mineral separates to obtain the average content of Au in each mineral. However, such analyses of mineral separates convey no information as to whether the Au is homogeneously distributed within and among the mineral crystals, is in solid solution, or is present as submicroscopic inclusions.

Assumptions and inferences have been made about the manner of occurrence of invisible Au (Boyle, 1979; Zhang et al., 1987; Cabri et al., 1989; Bakken et al., 1989; Cook and Chrysosoulis 1990). However, there is some controversy about whether the Au is present in chemical com-

bination in sulfide minerals such as pyrite and arsenopyrite (i.e., structurally incorporated Au) or whether the Au occurs as submicroscopic inclusions. But none of the studies provides direct and convincing evidence to confirm the inferences. Using an electron-probe microanalyzer (EPMA) and a scanning electron microscope (SEM), the author has investigated the distribution characteristics and concentration of invisible Au at different spots in Au-bearing minerals of various grain sizes, crystal forms, and paragenetic stages. Furthermore, the distribution of invisible Au is displayed by the distribution of As, which is positively correlated with Au in pyrite. Therefore, the present research work has provided a scientific basis for selecting an economical and effective treatment and extraction process for the ore from Banqi gold deposit, Guizhou, a Carlin-type gold deposit in China.

SAMPLE PREPARATION

The unoxidized (primary) ore sample consists of drill cuttings from many parts in the Banqi deposit, which is an epithermal disseminated gold deposit in China. The tectonic position of the Banqi gold deposit is in the syn-

taxis zone
graben
eralization
in part
Triassic
control
arch di
and the
consist
that are
and sul
The
selected
tions th
microsc
tigation
ground
to -20
Fe, Al,
used to
the oth
moving
separat
produc
chemic
The
total m
sample
estimat
accurat

Optical

Mine
examin
sections
Modal
pyrite v
and zo
optical

EPMA

The
mineral
equippe
(EDS) s
strumen
with be
eter abo
dards: A
senopy
routine
sured b
ing spe
metho
tromete
the cov
od is n

taxis zone of the Youjing late Palaeozoic era-Triassic rift graben and late Precambrian Yangzi platform. The mineralization district emerges in Devonian-Triassic strata; in particular, the mineralized horizons are in the lower Triassic Ziyun formation. The ore bodies are multiply controlled by the vertical main fault of the anticline and arch districts, the fracture zones between the horizons, and the rock characteristics. The most rock is tectonite consisting of clastic rocks of terrigenous sedimentation that are enriched in clayey, silty, and organic materials and sulfides.

The total ore sample weighs 2438 g. Ore blocks were selected for preparing the polished sections and thin sections that were used for mineralogical studies by optical microscopy and for SEM observation and EPMA investigations. The rest of the sample was crushed and then ground to -100 mesh; then a portion was further ground to -200 mesh for Au assay and chemical analyses of S, Fe, Al, and K. Most of the sample of -100 mesh was used to prepare two pyrite concentrates (one >0.074 mm, the other <0.074 mm) by sieving and panning, then removing impurities such as barite by use of a dielectric separator and by hand selecting under a microscope. This produced pure pyrite mineral separates for Au assay and chemical dissolution experiments.

The clay mineral separate with grain size <10 μm and total mass 860 mg was prepared using the pulverized ore sample and a precipitation method. The grain size was estimated according to the precipitation speed and not accurately measured.

EXPERIMENTAL METHODS

Optical microscopy

Mineralogical composition of the ore was obtained by examining quite a number of polished sections and thin sections with reflected and transmitted light microscopy. Modal analysis and the statistics of size distribution of pyrite were determined by point counting. Crystal forms and zoning characteristics of pyrite were investigated by optical microscopy.

EPMA and SEM analyses

The analyses of pyrite, As-bearing pyrite, and other minerals were performed on a JEOL 733 electron probe equipped with a TN 5500 energy-dispersive spectrometer (EDS) system and TN 5600 automation system. The instrument was operated at 25 kV (accelerating voltage) with beam current (cup reading) 20 nA and beam diameter about 1 μm , using the following X-ray lines and standards: $\text{AuL}\alpha$ (metal), $\text{FeK}\alpha$ and $\text{SK}\alpha$ (pyrite), $\text{AsL}\alpha$ (arsenopyrite). Fe, S, and As can be measured by EDS with routine procedure; the trace element Au can only be measured by wavelength-dispersive spectrometry (WDS) using special procedures and precautions. The common method for measuring background is to move the spectrometer to both sides of the peak position and measure the count rates, but in detecting trace elements this method is not suitable. In the present work, a pure pyrite crys-

tal free of Au was employed as a standard for measuring background. The background count rate was measured at the $\text{AuL}\alpha$ peak position on the blank pyrite standard. One wavelength-dispersive spectrometer with a LiF crystal was dedicated to determine the Au concentration, so that during the entire procedure the spectrometer was not moved from the $\text{AuL}\alpha$ position. To reduce the detection limit and the counting statistics error, the counting time for detecting the trace Au was set at 100 s. Under the above conditions, the precision for detecting trace Au in pyrite was improved. The same method for background measurement was used to measure the Au concentrations in arsenopyrite, quartz, calcite, barite, etc. The TASK program provided by Tracor Northern is capable of doing EDS and WDS measurements simultaneously and then performing the quantitative corrections for atomic number, absorption, and fluorescence effects with the ZAF program included in TASK. If $\text{AuM}\alpha$ were chosen as the analyzed line and PET as the diffraction crystal, there would be the advantage of lower background count rate and therefore better sensitivity. Unfortunately, there is some overlap between $\text{AuM}\alpha$ (5.840 Å) and the third order line of $\text{FeK}\alpha$ (5.812 Å). Therefore, $\text{AuL}\alpha$ is preferable as the analyzed line.

There are several expressions for calculating the detection limit (C_{DL}) by EPMA (Toya and Kato, 1983; Cox, 1983; Ziebold, 1967). In routine work, expression 1 is employed to calculate C_{DL} for a given element:

$$C_{\text{DL}} = \frac{3\sqrt{I_{\text{B}}t}}{(I_{\text{P}} - I_{\text{B}})t} = \frac{3\sqrt{I_{\text{B}}}}{(I_{\text{P}} - I_{\text{B}})\sqrt{t}} \quad (1)$$

where I_{P} is the peak count rate, I_{B} is the background count rate both in counts per second (cps), and t is the counting time. Under the operating conditions mentioned above, I_{P} for Au is approximately 8900 cps, I_{B} is approximately 73 cps, t is 100 s, and the calculated value of C_{DL} by expression 1 is 0.029%. Considering uncertainties such as instrumental instability or sample polish imperfections, the practical C_{DL} value for detecting trace Au in pyrite is estimated to be 0.05%. Therefore, a Au concentration less than 0.05% in any analyzed spot is considered to be zero. If the invisible Au in pyrite is distributed homogeneously, it is almost impossible to be detected by EPMA under the operating conditions employed in this study. However, when the Au is relatively enriched in some areas within pyrite, it becomes possible to investigate the variation and enrichment characteristics of the invisible Au and the relationship between Au and other elements.

Chemical dissolution experiments

Chemical dissolution experiments on pyrite were carried out according to the flow chart shown in Figure 1 using a pyrite sample with the grain size <0.074 mm and total mass 400 mg. Au in solutions and in residue were concentrated by fire assay, then analyzed by atomic absorption spectrometry (AAS). Fe was analyzed by wet chemistry. In the experiments, pyrite is dissolved in HNO_3

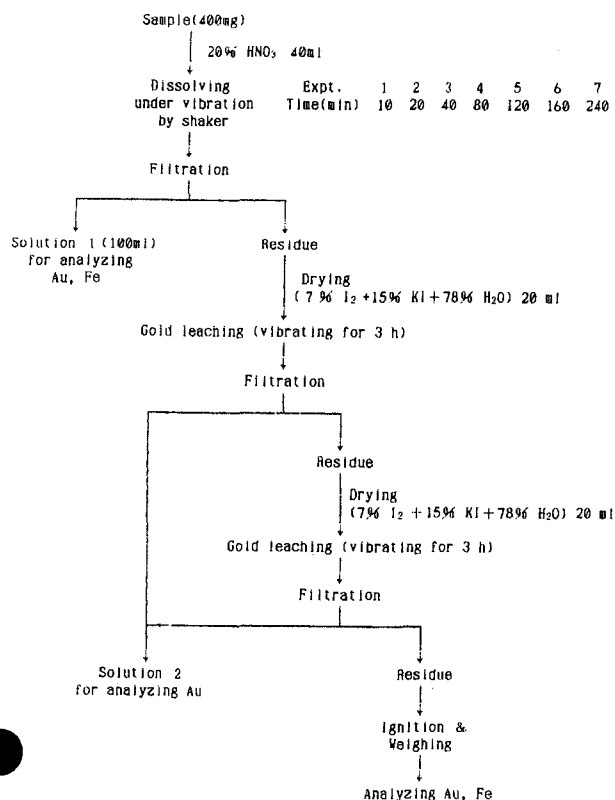


Fig. 1. Flow chart of dissolution experiment on pyrite.

but particulate Au remains insoluble. The addition of a KI + I₂ solution can leach Au from the residue.

RESULTS

Mineralogical and chemical composition of the ore

Fire assay analysis yielded 31.02 ppm Au, and chemical analyses yielded 2.40% S, 3.41% Fe, 2.59% Al, and 1.63% K in bulk ore. The mineralogical study by optical microscopy showed that the sulfides in the ore sample are pyrite, arsenopyrite, marcasite, stibnite, pyrrhotite, chalcopyrite, realgar, orpiment, and pentlandite. The other common minerals present are quartz, illite, kaolinite, calcite, dolomite, apatite, and barite. Modal analysis and point-counting statistics gave 4.7% pyrite (including small

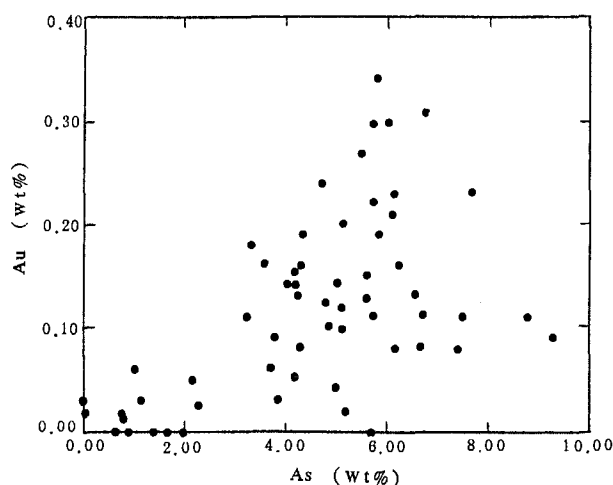


Fig. 2. Correlation between Au and As concentrations in tiny pyrite grains (<10 μm).

quantity of some other sulfides), 68.7% quartz and some carbonates, 26.6% clay minerals.

The pyrite occurs as euhedral crystals and as anhedral granules. The size distribution of pyrite is as follows: pyrite <0.074 mm, 87.40%; pyrite >0.074 mm, 12.60%. More than 95% of the pyrite grains larger than 10 μm occur as anhedral granules; only 5% of these are euhedral and subhedral crystals. The concentrations of Au in different size fractions of pyrite in the ore differ considerably. According to the fire assay results, the Au concentration in pyrite <0.074 mm averages 275.0 ppm, whereas that in pyrite >0.074 mm is 137.1 ppm. Therefore, the pyrite averages 257.6 ppm Au.

Occurrence and distribution of Au in pyrite determined by EPMA and SEM in pyrite grains <10 μm

One hundred and twenty small pyrite grains (<10 μm) from multiple samples were selected for Au analysis by EPMA. In 28 grains the Au concentrations are below the detection limit (0.05%) and As concentrations are in the range 0–5.64% (average 2.05%). In the other 92 grains the Au concentrations are higher than the detection limit, ranging from 0.05% to 0.34% (average 0.15%); As concentrations range from 1.60% to 9.29% (average 5.22%) (Table 1). Figure 2 shows the positive correlation between Au and As concentrations.

TABLE 1. Concentrations of Au and As in minerals analyzed by EPMA

	Spots with Au conc. (>0.05%)						Spots with Au conc. (<0.05%)		
	Ana. sp.	sp.	Au (%)		As (%)		sp.	As (%)	
			Range	Ave.	Range	Ave.		Range	Ave.
py. (<10 μm)	120	92	0.05–0.34	0.15	1.60–9.29	5.22	28	0–5.65	2.05
Int. of py.*	73	10	0.05–0.11	0.08	0–9.13	2.67	63	0–3.77	0.81
Rims of anh. py.*	57	44	0.05–0.46	0.18	0.85–7.37	5.61	13	0–4.51	0.76
Rims of euh. py.*	18	0					18	0–0.49	0.12

Note: Ana. = Analyzed, anh. = anhedral, Ave. = Average, conc. = concentration, euh. = euhedral, Int. = Interiors, Py. = Pyrite, Sp. = Spots.

* Pyrite grains >10 μm.

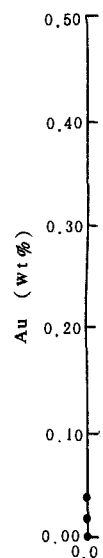


Fig. 3. Rims of pyrite grains.

Interior

Randomly selected pyrite grains (10 μm to 1 mm) were analyzed for Au and As. The concentrations of Au in different size fractions of pyrite in the ore differ considerably. According to the fire assay results, the Au concentration in pyrite <0.074 mm averages 275.0 ppm, whereas that in pyrite >0.074 mm is 137.1 ppm. Therefore, the pyrite averages 257.6 ppm Au.

In rims

The concentrations of Au in the rims of pyrite grains are higher than those in the interiors. The average concentration of Au in the rims is 0.11% (range 0.05–0.34%).

Fifty randomly selected pyrite grains (10 μm to 1 mm) were analyzed for Au and As. The concentrations of Au in different size fractions of pyrite in the ore differ considerably. According to the fire assay results, the Au concentration in pyrite <0.074 mm averages 275.0 ppm, whereas that in pyrite >0.074 mm is 137.1 ppm. Therefore, the pyrite averages 257.6 ppm Au.

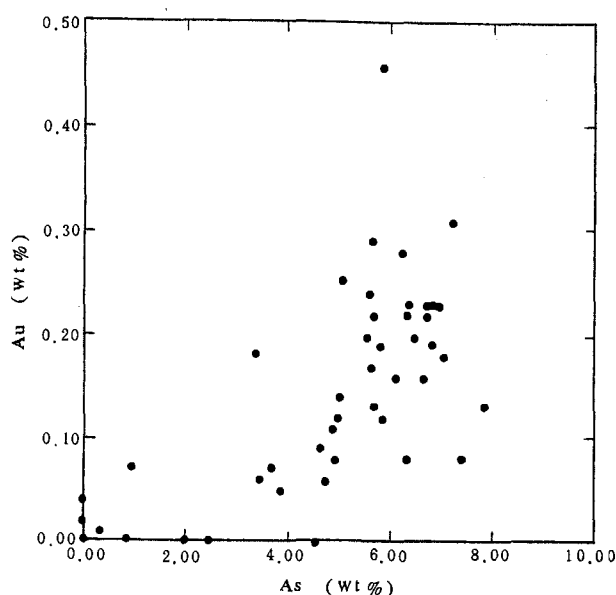


Fig. 3. Correlation between the Au and As concentrations in rims of anhedral pyrite grains $> 10 \mu\text{m}$.

Interior of the pyrite grains $> 10 \mu\text{m}$

Randomly chosen pyrite grains within the range of $10 \mu\text{m}$ to about $100 \mu\text{m}$, with different crystal forms in a number of polished sections, were analyzed. Several spots were analyzed in each grain, yielding 73 spots in total. Among them, 63 spots had Au concentrations $< 0.05\%$ and As concentrations ranging between zero and 3.77% (average 0.81%). Only in ten spots are the Au concentrations higher than the detection limit, ranging from 0.05% to 0.11% (average 0.08%); in the ten, As concentrations range between zero and 9.13% (average 2.67%) (see Table 1).

In rims of pyrite grains $> 10 \mu\text{m}$

The concentrations of Au and As in the rims of euhedral pyrite grains are quite distinct from rims of anhedral pyrite grains. Data on Au and As concentrations in 18 spots located near the edges of several euhedral pyrite grains are shown in Table 1. Au concentrations are everywhere below the detection limit, and As concentrations range between zero and 0.49% (average 0.12%).

Fifty-seven spots were analyzed in a number of anhedral pyrite grains. In 13 spots, the Au concentrations are below the detection limit, and the As concentrations range from zero to 4.51% (average 0.76%). In the other 44 spots, the Au concentrations are higher than the detection limit, ranging from 0.05% to 0.46% (average 0.18%), and the As concentrations range from 0.85% to 7.37% (average 5.61%) (Table 1). Figure 3 shows the positive correlation between the concentrations of Au and As. The particular relation between the concentrations of Au and As indicates that the distribution of trace Au can be displayed qualitatively using the X-ray images of As in pyrite grains.

X-ray images in Figures 4 and 5 that were produced

by electron beam scanning clearly show that As is conspicuously enriched in the rims of pyrite grains, and little or no As is contained in the interior of pyrite grains. Therefore, according to the positive correlation between the concentrations of Au and As, it is believed that Au must be enriched in the rims of pyrite grains. The secondary electron images (SEI) in Figures 4 and 5 show that there are boundary lines between the rims and interiors of pyrite grains. This indicates that anhedral pyrite grains in this gold deposit consist of earlier formed, euhedral crystal cores containing little Au and As and later formed rims containing remarkably rich Au and As, i.e., with a distinct zoning texture.

Au concentrations in arsenopyrite and other minerals determined by EPMA

Arsenopyrite. Au concentrations have been determined in 22 spots that are located at rims and interiors of arsenopyrite grains of different shapes and sizes, selected in several polished sections. Except one spot with a Au concentration equal to 0.15% , the Au concentrations are below the detection limit. In addition, the arsenopyrite is very sparsely disseminated in the ore.

Quartz. Within tens of quartz grains with different sizes, 59 spots were selected in different areas for Au analysis. In five spots the Au concentrations are just above the detection limit: 0.06 , 0.05 , 0.09 , 0.07 , 0.08% ; the Au concentrations in the other 54 spots are below detection limit. Additionally, chemical assay shows that the average Au concentration in quartz is 0.08 ppm (Song and Diao, 1989).

Calcite. In 40 analyzed spots, only two have Au concentrations just above detection limit, 0.06% and 0.05% . The Au concentrations in the other 38 spots are below the detection limit. The chemical assay indicates that the Au concentration in carbonates averages 0.08 ppm (Song and Diao, 1989).

Barite. One spot had a Au concentration just at the detection limit (0.05%); Au concentrations are otherwise below the detection limit.

On the basis of the above results, it can be concluded that arsenopyrite, quartz, calcite, and barite are not significant Au-bearing minerals.

Clay minerals. The clay minerals are illite and kaolinite. Among 70 randomly selected spots in clay minerals, Au concentrations detected by EPMA are well above the detection limit in some spots. However, the EDS spectra of the corresponding spots show small peaks of S, As, and Fe, indicating that there may exist some very fine, As-bearing pyrite inclusions in the clay mixture. This inference is confirmed by the electron-beam scanning images for clay minerals. To determine whether the Au detected in some spots of clay by EPMA is contained in the clay mineral itself or in the micropyreite inclusions, the clay mineral separate with grain size $< 10 \mu\text{m}$ was prepared for chemical analysis of the concentrations of Au and S, and then the content of pyrite was calculated from

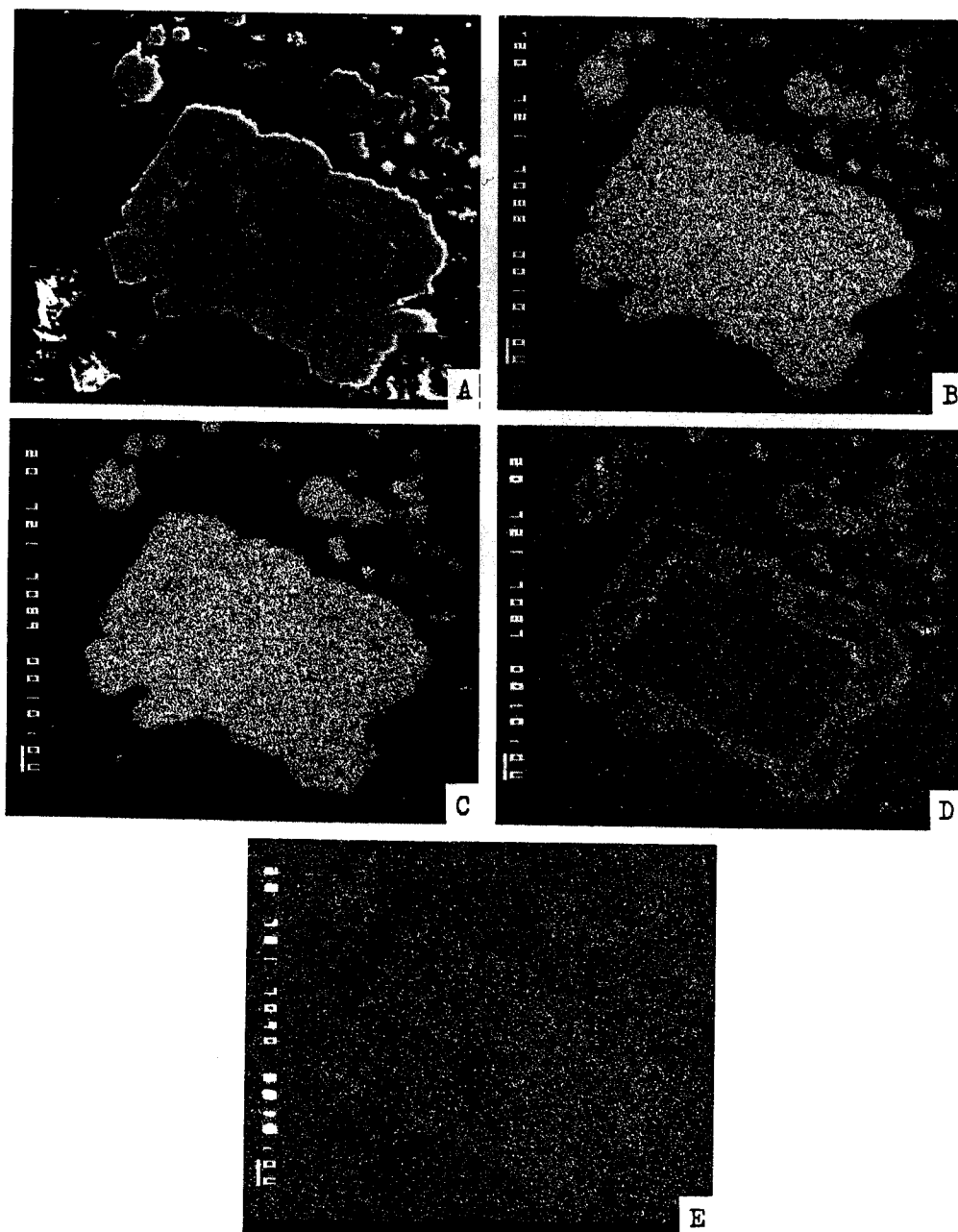


Fig. 4. Electron-beam scanning images on an anhedral pyrite grain. (A) SEI, (B) FeK α , (C) SK α , (D) AsL α , (E) AuL α .

the S concentration. Au assay of 860 mg of clay mineral separate of grain size $< 10 \mu\text{m}$ yielded 33.24 ppm Au and 1.75 wt% S, which can be recalculated as 3.27% pyrite as microscopic inclusions identified by SEM. The average Au concentration in clay minerals is far below the detection limit of EPMA, so it is believed that the Au detected in some spots of clay minerals is actually or mostly contained in micrometer-size pyrite inclusions that are remarkably enriched with Au. Another question of interest is what percentage of the Au content given by clay assays

occurs in micropyrroite inclusions vs. in the clay mineral structures. It is reasonable to consider that the Au concentration in micropyrroite inclusions is probably at least equal to that in rims of the anhedral pyrite grains, i.e., 600 ppm or more (see below). Combining this with assay data of the clay mineral separate, we can make a rough calculation: the Au quantity contained in a 1-g clay sample is 33.24 μg , the quantity of pyrite inclusions is 0.0327 g, and these contain about 19.6 μg of Au at the 600 ppm level. Therefore, it is reasonably certain that about 60%

or more
microp

Results

To c
SEM re
have b
results
ble 2, tl
and the
due are

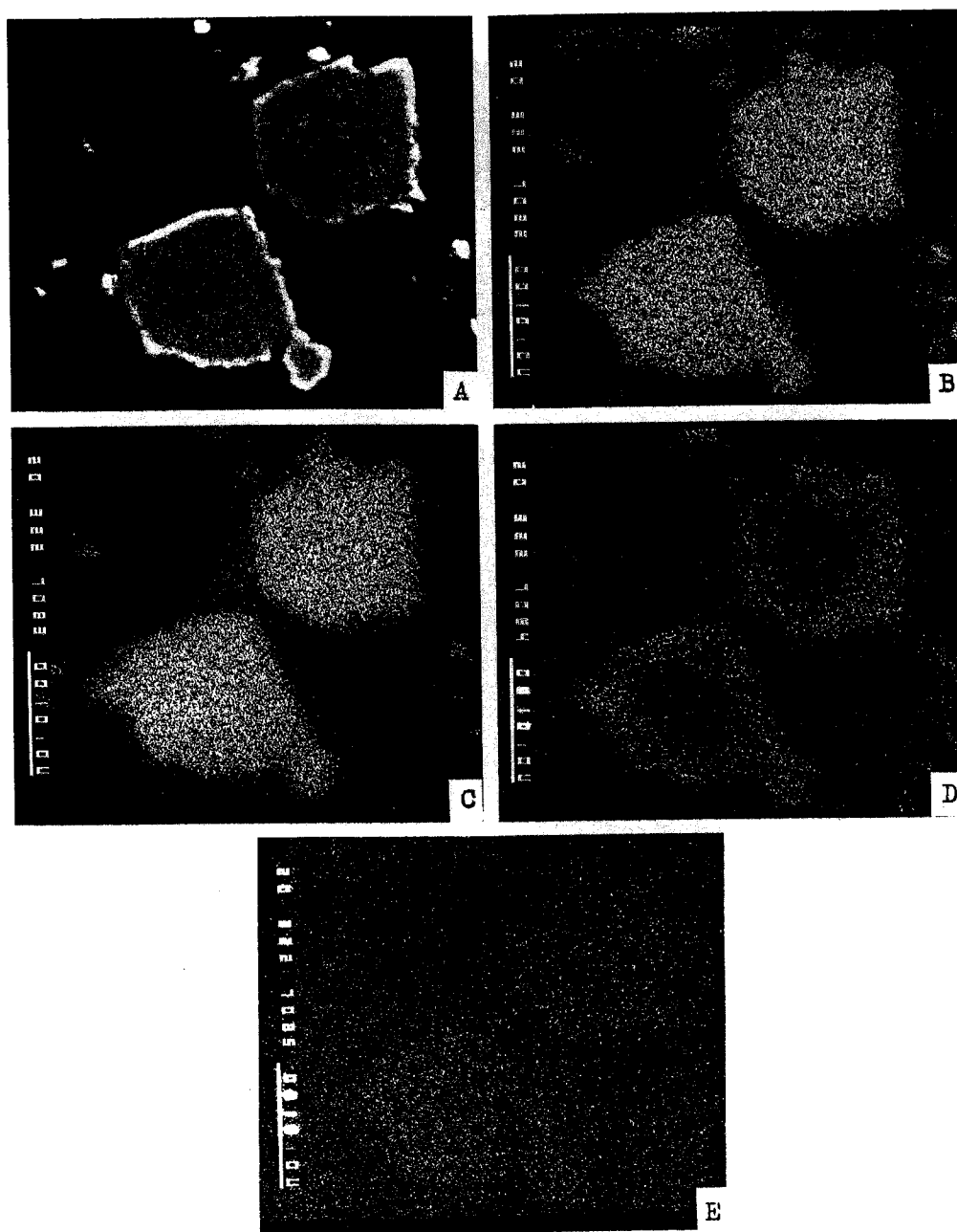


Fig. 5. Electron-beam scanning images on an anhedral pyrite grain. (A) SEI, (B) FeK α , (C) SK α , (D) AsL α , (E) AuL α .

or more of the Au in clay mineral assays occurs in the micropyrte inclusions.

Results of chemical dissolution experiments

To confirm the conjecture drawn from the EPMA and SEM results, chemical dissolution experiments on pyrite have been carried out, and a series of very meaningful results were obtained (Table 2). Using the data from Table 2, the correlations between the leaching time by HNO₃ and the Au concentrations both in solutions and in residue are shown in Figure 6. The correlations between the

leaching time by HNO₃ and the Au concentrations both in dissolved pyrite and in undissolved pyrite remaining in the residue are shown in Figure 7.

In experiments lasting 10, 20, and 40 min, the Au concentrations in HNO₃ solution increase approximately linearly with time, so the solution is undersaturated with Au. There appears to be a large excess of NO₃⁻ ion relative to dissolved S species, so complete oxidation of dissolved S seems likely. In this case, the Au solubility would not be affected by formation of complexes with polysulfide, thiosulfate, sulfite, or other incompletely oxidized S an-

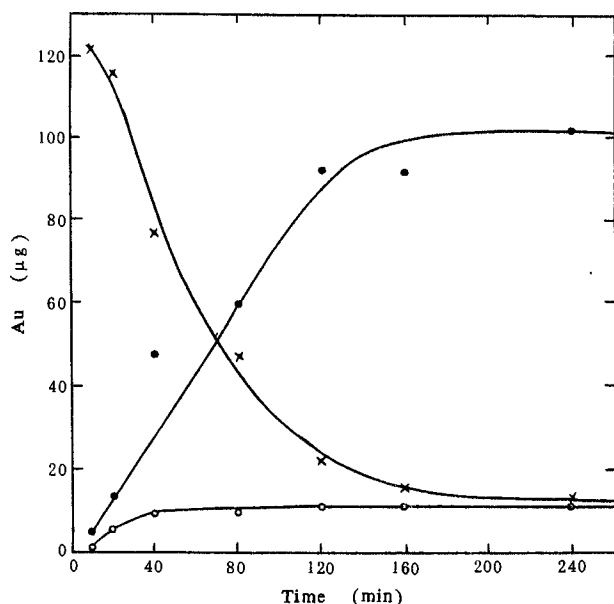


Fig. 6. Correlation between dissolution time (min) by HNO_3 and the Au contents (μg) in solutions and in residue. Open circles are in HNO_3 solution, solid circles in $\text{KI} + \text{I}_2$ solution, crosses in residue.

ions that might enhance the solubility of crystalline Au as more pyrite dissolves in longer experiments (Webster, 1986). Therefore, the first three experiments did not precipitate Au that was liberated from pyrite during the dissolution of pyrite. On the other hand, the Au that was liberated from the dissolved pyrite and was not present in the HNO_3 solution was dissolved subsequently upon the addition of $\text{I}_2 + \text{KI}$. This must represent Au that occurred in pyrite as discrete metal particles, not as crystalline Au. Therefore, it is reasonable to conclude that most of the Au contained in pyrite occurs as ultramicro-crometer particulate native gold inclusions.

The Au concentration in the $\text{KI} + \text{I}_2$ solution increases dramatically with dissolution time up to 120 min, then increases very slowly (Fig. 6). After 160 min, the Au concentration reaches a plateau even though more pyrite is continuously dissolved by HNO_3 , and the Fe concentra-

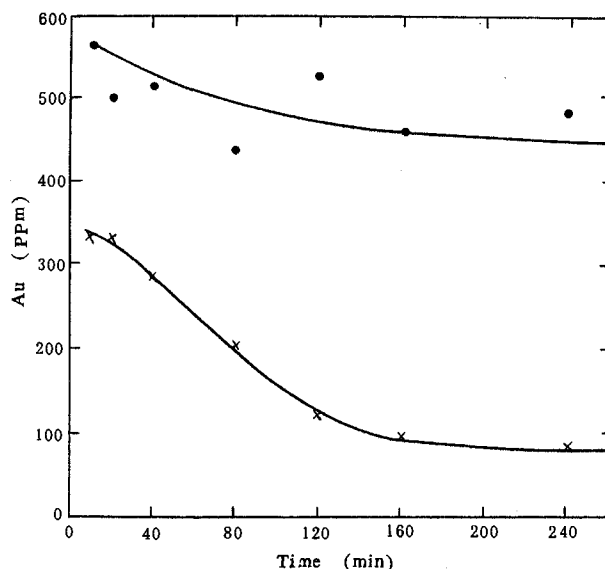


Fig. 7. Correlation between dissolution time (min) by HNO_3 and the Au concentrations (ppm) both in dissolved pyrite and in undissolved pyrite remaining in residue. Solid circles are in dissolved pyrite, crosses in undissolved pyrite.

tion in HNO_3 solution increases up to 240 min. This suggests that in the period between 160 and 240 min the Au concentrated in pyrite rims has been dissolved out.

The concentration of Au in the residue decreases sharply over the interval between 10 and 120 min, and then it gradually slows down. After 160 min, little variation of Au concentration is detected in the residue. This result is in good agreement with the above description, i.e., the upper curve in Figure 6 and lower curve in Figure 7 are mirror images.

It is likely that when the dissolution time is less than 120 min, the dissolution is of pyrite rims in which Au is enriched. However, there is a wide range of size distribution for pyrite grains and of thickness for pyrite rims. It is likely that the rims of pyrite grains with smaller size and thinner rims have already been dissolved out in less than 120 min. Therefore, it is reasonable to assume that the Au concentration in pyrite dissolved by HNO_3 in 10

TABLE 2. Results of chemical dissolution experiments on pyrite

No.	Disso. time (min)	Au cont. (μg)				Fe conc. in HNO_3 Sol. 1 (mg/mL)	Py. quan. in HNO_3 Sol. 1 (mg)	Resi. quan. (mg)	Fe cont. in resi. (%)	Py. quan. in resi. (mg)	Au conc. in dissd. Py. by HNO_3 (ppm)	Au conc. in undis. Py. (ppm)
		HNO_3 Sol. 1 (100 mL)	$\text{KI} + \text{I}_2$ Sol. 2	Resi.	Total							
1	10	0.95	5.17	121.26	127.38	0.05	10.74	329.5	51.02	361.12	569.8	335.8
2	20	5.79	13.72	115.74	135.25	0.18	38.67	319.0	50.65	347.15	504.5	333.4
3	40	9.36	48.38	77.22	134.96	0.52	111.71	265.0	47.26	268.96	516.9	287.1
4	80	9.83	60.50	47.11	117.44	0.74	158.97	227.8	47.44	232.22	442.4	202.9
5	120	11.04	92.76	24.01	127.31	0.91	195.49	200.3	45.34	195.06	531.0	123.1
6	160	11.28	92.28	15.86	119.42	1.04	223.42	180.5	44.84	173.79	463.5	91.3
7	240	12.34	102.00	12.70	127.04	1.09	234.16	167.5	43.08	155.10	488.3	81.9

Note: Disso. = Dissolving, Sol. = solution, cont. = content, Resi. = Residue, conc. = concentration, Py = Pyrite, quan. = quantity, undis. = undissolved, dissd. = dissolved.

min w
additi
of the
ment c
to cont
of an h
It is
of pyr
proxim
after d

Of th
most i
the py
of an e
tle Au
Au an
crystal
ppm.

hedra
rior of

Usu
invisit
(see Fi
invisit
amine
tive co

In c
liberat
solutic
dissolv
by the
dicat
Au-ric
is con
pyrite
not as

The
senop
the de
the re
clear t

Mo
assay
rite in

The
that f
U.S.A
rence
the po
tions,
als, a
indica
mon
Romt
1989;
In]

min was that in pyrite rims, i.e., 569.8 ppm (Table 2). In addition, microscopic observation shows that about 5% of the pyrite grains prepared for the dissolution experiment occur as euhedral crystals, which have been proved to contain little or no Au, so the Au concentration in rims of anhedral pyrite grains should be near 600 ppm.

It is apparent that the Au concentration in the interior of pyrite (euhedral core of anhedral pyrite grain) is approximately equal to or less than that in the pyrite residue after dissolving for 240 min, i.e., 82 ppm.

DISCUSSION AND CONCLUSIONS

Of the various minerals in the ore, pyrite is clearly the most important Au-bearing mineral. More than 95% of the pyrite grains occur as anhedral granules that consist of an earlier formed, euhedral crystal core containing little Au and As and later formed rims notably enriched in Au and As. There is little or no Au in euhedral pyrite crystals. The average Au concentration in pyrite is 257.6 ppm. The average Au concentration in the rims of anhedral pyrite grains is about 600 ppm, whereas the interior of the grains contains less than 82 ppm.

Usually there is no way of observing and displaying the invisible Au in pyrite grains because of its trace content (see Figs. 4E and 5E). The distribution characteristic of invisible Au in pyrite can however be displayed and examined by imaging arsenic by SEM because of the positive correlation between the concentrations of Au and As.

In chemical dissolution experiments on pyrite, the Au liberated from dissolved pyrite does not enter into HNO₃ solution but resides in the residue together with the undissolved pyrite. The Au in the residue can be dissolved by the Au-leaching solution. In addition, EPMA data indicate that Au concentrations at different points in the Au-rich rims of pyrite grains are remarkably different. It is confirmed from these facts that the invisible Au in pyrite occurs as ultramicroscopic native gold inclusions, not as isomorphous substitution.

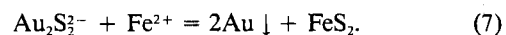
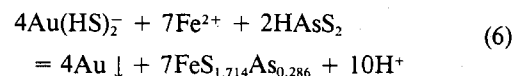
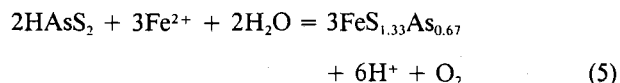
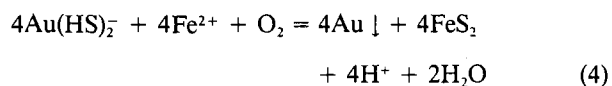
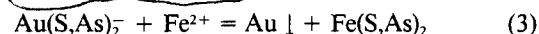
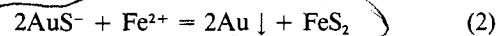
The Au concentrations in other minerals, such as arsenopyrite, quartz, calcite, or barite, are nearly all below the detection limit of EPMA (0.05%). In association with the results of chemical assays of mineral separates, it is clear that these minerals are not substantially auriferous.

More than 60% of the Au content given by chemical assay of clay minerals occurs in submicrometer-scale pyrite inclusions in which Au is remarkably enriched.

The ore in the Banqi gold deposit is very similar to that from the Carlin and Cortez gold mines, Nevada, U.S.A., in the following aspects: the manner of occurrence and distribution characteristics of the invisible Au, the positive correlation between Au and As concentrations, the microstructure of the main Au-bearing minerals, and the mineralogical composition of the ore. This indicates that the Carlin-type gold deposits have common and special features (Wells and Mullens, 1973; Romberger, 1986; Cathelineau et al., 1989; Bakken et al., 1989; Cook and Chrysosoulis, 1990).

In hydrothermal ore-forming solutions, the Au(HS)₂⁻

and Au₂S₃⁻ species are the most stable known inorganic complexes of Au⁺ (Seward, 1989). Other species may also exist, such as AuS⁻ (Chen, 1987; Qin, 1987). In hydrothermal solutions containing appreciable As, a certain proportion of S may be complexed with As, and complexes consisting of Au, S, and As, such as Au(S,As)₂⁻, may form. With changes in oxidizing and reducing conditions, temperature, pressure, or pH in the mineralizing environment, the Au complex may decompose leading to Au deposition. When Fe²⁺ and As are present in solution, the decomposition of Au complexes may take place as follows:



Therefore, in various kinds of gold deposits, pyrite is commonly the most important Au-bearing mineral; Au concentration in pyrite is correlated very closely with As concentration; Au usually occurs as micrometer or ultramicroscopic (submicrometer) native gold inclusions.

Knowledge of the special mode of occurrence and distribution characteristics of invisible Au in such ores is useful to metallurgical process design of oxidizing-roasting, chloridizing, and cyanide leaching. In this case, sufficient oxidization and leaching of the pyrite surface layer will produce satisfactory Au recovery.

ACKNOWLEDGMENTS

This work was supported by the Chinese Academy of Geological Sciences. I wish to thank my colleagues, G. Li, L. Bian, W. Lu, Z. Gong, S. Diao, and M. Liu, for giving valuable assistance and suggestions.

REFERENCES CITED

- Bakken, B.M., Hochella, M.F., Marshall, A.F., and Turner, A.M. (1989) High-resolution microscopy of gold in unoxidized ore from the Carlin mine, Nevada. *Economic Geology*, 84, 171-179.
- Boyle, R.W. (1979) The geochemistry of gold and its deposits. *Geological Survey of Canada Bulletin*, 280.
- Cabri, L.J., Chrysosoulis, S.L., de Villiers, J.P.R., Laflamme, J.H.G., and Buseck, P.R. (1989) The nature of "invisible" gold in arsenopyrite. *Canadian Mineralogist*, 27, 353-362.
- Cathelineau, M., Boiron, M.C., Holliger, P., Marion, P., and Denis, M. (1989) Gold in arsenopyrite: Crystal chemistry, location and state, physical and chemical conditions of deposition. *Economic Geology*, Monograph 6, 328-341.
- Chen, S. (1987) Geochemistry and mineralization of gold. *Journal of Chengdu College of Geology*, 16, 8-17 (in Chinese).

78-F. Behaviour during Processes Connected with Magmatism (Pegmatites, Gas Transport, Ore Deposition)

I. Introduction

The major ore deposits of the platinum metals are associated with dunitic ultrabasic rocks and gabbroic rocks containing Cu—Ni sulfides, typically pyrrhotite, pentlandite and chalcopyrite. The association of platinum metals with sulfides, tellurides, selenides, arsenides and antimonides is well established. Survey studies of platinum metal abundances, mainly in sulfide minerals, are reported by I. and W. NODDACK (1931), GOLDSCHMIDT and PETERS (1932) and HAWLEY and RIMSAITE (1953). These data are condensed and summarized in Table 78-F-1.

The analytical uncertainties noted in Sections D and E are applicable to sulfide analysis, although the higher platinum metal concentrations probably permit better accuracy because sensitivity is not such a critical factor. The main features of platinum metal geochemistry in sulfide and related minerals and ore deposits indicated by these data include the following:

a) The extensive data of I. and W. NODDACK (1931) show that Pd and Pt are the principal platinum group metals in sulfides and that Pd is more abundant than Pt. However, exceptions do occur and are noted in 3) below.

b) Selenides and tellurides contain much higher platinum metal contents than sulfides. The occurrence of both high selenium-tellurium and platinum metal values in some Cu—Ni sulfide ore deposits, and the occurrence of platinum metal tellurides such as moncheite and kotulskite (GENKIN *et al.*, 1963) indicate a strong geochemical association of these metals with the platinum group.

c) Nickeliferous sulfides, as indicated by the survey of HAWLEY and RIMSAITE (1953) are generally higher in platinum metals than non-nickeliferous sulfides. In both types of deposits chalcopyrite, rather than pyrrhotite, is the major host for Pd and probably also Pt. In Cu—Ni sulfide deposits associated with gabbroic or ultrabasic rocks such as Insizwa, South Africa or Rankin Inlet, Canada, pyrrhotite is enriched in Ru, Os, Ir and possibly Rh, relative to chalcopyrite. As chalcopyrite is usually later than the bulk of the pyrrhotite in such deposits, it seems likely that Pt and Pd are more concentrated than Ru, Ir or Os in the late residual fluids of sulfur-rich magmas.

The distribution of platinum metals in a number of ore deposits including the Sudbury district, Canada (HAWLEY, 1962; HAWLEY and RIMSAITE, 1953), the Noril'sk deposit, U.S.S.R. (GINZBURG and ROGOVER, 1961), the Inaglinsk massif, South Yakutia, U.S.S.R. (RAZIN *et al.*, 1965) and the Bushveld Complex (WAGNER, 1929; SCHNEIDERHÖHN and MORITZ, 1931; HAGEN, 1954) has been investigated and is discussed below.

II. Sudbury Complex, Canada

At Sudbury platinum metals are associated with pyrrhotite-pentlandite-chalcopryite mineralization occurring as discrete minerals including sperrylite, michenerite and froodite and probably also in solid solution or as extremely fine disseminations in the major sulfides, particularly chalcopryite, and in arsenides. The available data are given in Table 78-F-2 and 78-F-3, and were obtained largely by HAWLEY and RIMSAITE (1953) who used a fire assay-emission spectrographic method.

As indicated by the pyrrhotite and chalcopryite data for the Falconbridge Mine, an extremely heterogeneous distribution of platinum metals may occasionally be found. This is probably due to sporadic inclusion of platinum minerals. Only tentative conclusions concerning relationships between major minerals and platinum metals can therefore be drawn from these data. Two generalizations, suggested particularly by the weight percentage data, are noted:

a) In pyrrhotite platinum is generally higher than palladium although the Falconbridge pyrrhotites do not appear to show this trend.

b) In general chalcopryite and pentlandite are enriched in palladium relative to platinum.

One analysis indicated a marked enrichment of Pd in arsenides. HAWLEY (1962) regards the chalcopryite mineralization as later than the bulk of the pyrrhotite and notes a consistent increase in palladium with the normal paragenetic order of these minerals. Ten year mine production figures suggest approximately equal Pt and Pd contents.

III. Noril'sk, U.S.S.R.

The distribution of Pt, Pd and Rh in the Noril'sk deposit was investigated by GINZBURG and ROGOVER (1961) using a spectrochemical method. Pyrrhotite, chalcopryite and pyrrhotite-chalcopryite concentrates were separated from the main ore-bearing rocks and from veins and encrustations. The results, summarized in Table 78-F-4 suggest that:

a) In disseminated sulfides from the main ore-bearing rocks (figures in parentheses in Table 78-F-4) Pd and Pt are concentrated in chalcopryite whereas Rh is enriched in pyrrhotite.

b) There is an enrichment of Pd over Pt, with the Pd/Pt ratio for all data in Table 78-F-4 averaging 6.1. In the disseminated ores the enrichment of Pd relative to Pt is higher in chalcopryite than in pyrrhotite.

c) In massive sulfides from veins and incrustations a Rh enrichment in pyrrhotite occurs as in the disseminated ores. The Pd/Pt ratio is more variable but the highest ratio, 9, is found in chalcopryite as in the disseminated ore. However, total platinum metals are higher in pyrrhotite rather than chalcopryite.

IV. Inaglinsk Massif, South Yakutia, U.S.S.R.

Platinum metals in the Inaglinsk Massif were studied by RAZIN *et al.* (1965). The Inaglinsk Massif is a complex pipe-like intrusive with a dunite core and a peripheral zone of alkali syenite rocks. The contact between these rocks, called apodunite, varies from peridotite at the inner contact with dunite through pyroxenite and alkalic gabbro to melanocratic alkali syenite on the outer contact.

Table 78-F-1. *Platinum metal concentrations in sulfide, selenide-telluride and arsenide minerals, ppm*

Sample description	Method and author ^a	Ru	Rh	Pd	Os	Ir	Pt
Sulfides: Mainly pyrrhotite, pyrite, chalcopyrite	(W/X) ^{5b}	0.01—0.04 ^c 0.014 (24)	0.02—2 0.2 (23)	0.2—9 3.7 (39)	0.9—2 0.4 (26)	0.2—1.0 0.5 (26)	0.2—5 0.95 (84)
Selenide-Tellurides	(W/X) ⁵	—	2—12 7.0 (2)	5—90 46 (4)	0.05—0.1 0.075 (2)	0.6—15 5.5 (4)	10—50 27.5 (4)
Molybdenite	(FA/S) ³	—	0.05—0.2 0.08 (4)	0.02—0.5 0.09 (8)	—	0.3	0.02—1 0.17 (9)
Molybdenite: Telemark, Norway	(W/X) ⁵	0.006 (60)	—	—	0.01 (60)		0.06 (60)
Co and Ni sulfides and arsenides: Mainly cobaltite, niccolite, gersdorffite, linnaeite	(FA/S) ³	—	—	0.1—0.5 0.3 (3)	—	—	0.1—0.5 0.2 (13)
Non-nickeliferous sulfide ore deposits, mainly from eastern Canada							
Chalcopyrite	(FA/S) ⁴		0.003—0.13 0.06 (6)	0.004—1.8 0.45 (13)			0.09—0.41 0.15 (4)
Pyrrhotite			0.03—0.06 0.045 (2)	0.004—0.056 0.02 (6)			
Pyrite			0.003	0.012			

Nickeliferous sulfide ore deposits

Pyrrhotite, Rankin Inlet, Northwest Territory, Canada	(FA/S) ⁴	1.6—2.1 1.9 (2)	0.3—0.6 0.5 (3)	3.8—5.2 4.5 (3)	10	1.0—1.0 1.0 (2)	1.3—2.7 2.1 (3)
Pyrrhotite, Lynn Lake, Manitoba, Canada			0.018	1.36			0.18
Pyrrhotite, Duluth Gabbro, Minnesota, U.S.A.			0.07	1.47			0.11
Pyrrhotite-Pentlandite, Insizwa, South Africa		0.41	0.38	0.38	0.34	0.51	0.48
Chalcopyrite-Cubanite, Insizwa, South Africa		0.09	0.06	13.8			2.1
Chalcopyrite, Mosalani Mines, Bihar India	(FA/S) ²						0.025—0.070 0.050 (4)
Almalyk ore region, Central Asia, U.S.S.R.							
Pyrite	(FA/S) ¹			0.014			
Chalcopyrite				0.21			0.02
Sphalerite				0.003			
Galena				0.032			
Molybdenite					2		

^a 1. BADALOV, S., and S. TEREKHOVICH (1966). 2. DAS SARMA, B., *et al.* (1966). 3. GOLDSCHMIDT, V., and CL. PETERS (1932). 4. HAWLEY, J., and Y. RIMSAITE (1953). 5. NODDACK, I., and W. NODDACK (1931).

^b Table I, Section 6 from Reference No. 4 excluding minerals from meteorites. Averages are weighed according to the number of samples of each mineral analysed.

^c The data include the range (top), average (middle) and number of samples (in parentheses) if more than one.

Table 78-F-2. *Platinum metals in minerals from the Sudbury complex, Canada, ppm*

Sample description		Referenc ^a Ru and method	Rh	Pd	Os	Ir	Pt	
Means from South range deposits	Pyrrhotite	(FA/S) ¹	0.04 to 0.35	0.28	0.60	0.37	0.2 to 0.33	0.52
	Chalcopyrite			0.27	1.17			1.30
Falcon- bridge mine	Pyrrhotite	(FA/S) ¹			34.2 0.13			15.6 0.17
	Chalcopyrite				34.28 1.61			1.54 3.77
	Pentlandite				17.50 12.65			29.8 34.2
	Pyrite				0.31			0.37
	Arsenides				246.8			trace
	Nickel- offsets	Pentlandite and Pyrrhotite	(FA/S) ¹	0.10		2.00		
Creighton	Pyrrhotite	(N) ⁴			0.10			0.48
	Chalcopyrite				0.013			0.72
	Pentlandite				6.3			0.2
Strathcona mine	Pyrrhotite, mafic norite	(N) ² and (N) ³	0.019		0.082	0.009	0.010	
	Pyrrhotite, xenolithic norite		0.054		0.025	0.023	0.053	
	Pyrrhotite, footwall		0.004		0.212	0.003	0.002	
	Chalcopyrite, footwall		0.014		0.962	0.003	0.001	

^a HAWLEY, J., and Y. RIMSAITE (1953). 2. HSIEH, S. (1967). 3. KEAYS, R. (1968). 4. MORRIS, D., *et al.* (1963).

Platinum metals are found mainly in dunite as discrete minerals, minerals including native platinum (Pt, Fe), iridic platinum (Pt, Fe, Ir), nevyanskite (Ir, Os), sperrylite (PtAs₂) and cooprite (PtS), and in association with silicate and oxide minerals. The deposit is similar to the Urals type of platinum mineralization according to RAZIN *et al.*

Individual platinum metals were determined in whole rock samples by a quantitative spectrographic method following chemical enrichment. The data are presented in Table 78-F-5. High total platinum metal values occur in the dunite core carrying segregated chrome spinels. These rocks are particularly distinctive, since both Ir and Rh are higher than Pd. No other rocks noted in this survey had such high relative Rh and Ir values. The Pd/Pt ratios are low and vary from 0.13 to 0.20 in all the dunitic rocks.

Table 78-F-3. *Platinum metal ratios in common Sudbury ore minerals, percent.* (After HAWLEY, 1962)

Mineral and description	Number of samples	Rh	Pd	Pt	Total platinum metals in ppm
Pyrite	3	2.5	41.4	56.4	1.90
Pyrrhotite	37	7.8	32.7	61.6	1.36
Pentlandite	3	7.5	59.5	33.0	5.42
Chalcopyrite	7	0.9	81.4	17.7	7.69
Minerals from an offset deposit					
Pyrite		7.5	42.2	50.3	
Pyrrhotite		7.0	48.7	44.3	1.87
Pentlandite		10.3	64.6	25.1	10.52
Chalcopyrite		0.22	71.5	28.3	8.06
Mill average (6 months)		2.0	65.0	33.0	5.33
10 year production, Sudbury ores ^a		13	41	46	

^a The Rh figure includes Ru + Ir.Table 78-F-4. *Pt, Pd and Rh data for sulfides from the Noril'sk deposit, U.S.S.R.* (After GINZBURG and ROGOVER, 1961)

Sample Descriptions	Number of samples	Rh wt.-% and ppm/1% Ni (in parentheses)	Pd	Pt	Total platinum metals in ppm
Mineral concentrates from the main ore-bearing rocks ^a					
Chalcopyrite	27	1, (0.4)	86, (32)	13, (5)	
Chalcopyrite-pyrrhotite	29	4, (0.7)	83, (14)	13, (2)	
pyrrhotite	19	21, (1)	66, (4)	13, (0.9)	
Sulfides from veins and incrustations ^b					
Pyrrhotite, veins		37%	53%	11%	19
Pyrrhotite, incrustations		15%	73%	13%	20.6
Chalcopyrite, veins		—	83%	17%	4.5
Chalcopyrite, incrustations		0.8%	90%	10%	5.1

^a Summarized from Table 1, p. 918. For each mineral weighed averages were calculated from the original data, expressed in grams/ton/1% nickel, and converted to a weight percent basis.^b Summarized from Tables 4 and 5, p. 921 and 922.

Pure mineral separates were analysed for total platinum metals. The minerals were decomposed by heating with NH_4F or $\text{HCl} + \text{H}_2\text{SO}_4$ and the soluble platinum metals determined gravimetrically after purification from base metals. Chrome spinels were analysed colorimetrically after HCl decomposition. Platinum minerals occurring in intimate intergrowths with silicates did not dissolve, and were discarded after separation from host minerals. The total platinum values obtained are regarded as representing platinum metals in solid solution or adsorbed in silicates. The validity of this interpretation depends on whether the platinum minerals were

Table 78-F-5. *Platinum metal content in rocks of the Inaglinsk Massif, U.S.S.R., ppb.*
(After RAZIN *et al.*, 1965)

Sampling point	Rock	No. of analyses	Pt	Pd	Ir	Rh	Os	Ru	Total average platinum metals
Core of massif	Dunite with accessory chrome-spinels	5	300 to 4,000 ^a 500	40 to 600 100	2—40 17	1.7 to 80 50	7—60 8	2—30 5	680
Core of massif	Dunite with segregation chrome-spinels	6	300 to 600 400	20 to 60 50	200 to 900 400	20 to 700 270	5—9 7.5	3—6 4.5	1,132
Inner contact of the apodunite zone	Apodunite olivine-pyroxene rocks (analogues of pyroxenite)	4	30—90 80	9—20 12	0.4 to 40 15	0.4 to 5 2.5	2—8 4	0.9—4 2.2	96
Outer contact of the apodunite	Apodunite pyroxene biotite-K feldspar rock (analogue of mica shonkinite)	1	8	2	5	3	0.3	0.5	19
Periphery of massif	Pulaskites	1	2	3	2	5	traces (<0.2)	0.2	12

^a Range above and average below.

completely insoluble in the various reagents used to attack the silicates. Proof that no dissolution of platinum minerals occurred is lacking and, as noted by WRIGHT and FLEISCHER (1967), the extreme fine grain size of these minerals would favour solubility. The data are presented in Table 78-F-6 and indicate the following:

a) chrome-spinel is the principal concentrator of platinum metals. Olivine is the second major host, but, on the average, contains about 30 times less platinum than chrome-spinel;

b) in the dunites the weakly serpentinized rocks contain higher platinum metal contents than the medium serpentinized rocks. The authors suggest that while olivine accumulates large amounts of platinum metals during magmatic crystallization there is some loss during epigenetic alteration;

c) pyroxene, mica, magnetite and apatite contain very small amounts of platinum metals.

The association of platinum metals with chrome-spinel was further investigated by analysis of morphologically similar chrome-spinel with approximately the same degree of epigenetic alteration taken from the center and periphery of the dunite core.

The average value for total platinum metals in nine samples from the core of the intrusive is 30 ppm whereas two samples from the periphery average 96 ppm. The authors consider that the lower temperature chrome-spinels at the periphery are more active concentrators of the platinum metals than the higher temperature spinels from the center of the intrusive.

Table 78-F-6. *Total platinum metals in minerals of the Inaglinsk massif, U.S.S.R., ppm.*
(After RAZIN *et al.*, 1965)^a

Rock ^c type	Description and sample number	Whole rock	Oli- vine	Chryso- tile	Chome- spinel	% total Pt metals present as Pt minerals
Dunite with accessory chrome- spinel	Fresh, slightly serpen- tinized; I-135	—	0.8	not detected	20	—
	Fresh, slightly serpen- tinized; I-130	4.7	2	0.15	10	—
	Fresh, medium serpen- tinized; I-105	1.0	0.4	0.3	20	64.8
	Intensively weathered, medium serpentinized, I-101	—	0.5	0.7	50	—
Apo- dunite	Mica-pyroxene-olivine rock ^b , fresh, slightly serpentinized, I-111	0.11	0.06	0.28	20	53.7

B

^a Data summarized from Tables 4 and 7, p. 123 and 126 respectively, RAZIN *et al.*

^b Diopside and phlogopite from the apodunite, sample I-111, contained 0.002 and 0.004 ppm total platinum metals respectively.

^c Platinum metals were detected in trace amounts only in magnetite and apatite in these rocks.

V. Bushveld Complex, South Africa

In the Bushveld, platinum metals are found in high concentration in the Merensky Reef (WAGNER, 1929; COUSINS, 1964) and the Mooihoek, Driekop and Onverwacht dunite pipes. Some data of geochemical significance on the Bushveld occurrences have been presented by SCHNEIDERHÖHN and MORITZ (1931) and HAGEN (1954).

The Merensky Reef, a pegmatitic pyroxenite normally bounded on top and bottom by thin chromite seams is characterized by high platinum metal values within or adjacent to the top and bottom chromite bands, although the chromite crystals themselves do not contain platinum (COUSINS, 1964). Platinum minerals found include ferroplatinum, braggite and cooperite with smaller amounts of laurite, stibiopalladinite and sperrylite. SCHNEIDERHÖHN and MORITZ (1931) analysed sulfide and silicate minerals from the Merensky Reef for platinum metals by microdrilling of polished sections, followed by direct analysis by emission spectrography. High values for silicate minerals suggest that some of their results (Table 78-F-7) may generally be high.

Pt and Pd are the most abundant sulfides with Pt in excess of Pd and the other metals present in approximately equal but much smaller amounts. The relative proportion of Merensky Reef platinum metals, computed from Cousins data (1964) are:

Pt = 63%, Pd = 28%, Ru = 5%, Rh = 2.7%, Ir = 0.7% and Os = 0.6%. In the samples examined by SCHNEIDERHÖHN and MORITZ no discrete platinum minerals were observed and they concluded that the platinum metals were in solid solution in sulfides. They also noted that the highest platinum metal contents were in the earliest sulfides, pyrite and pyrrhotite. The well-established occurrence of discrete platinum metal minerals in the Merensky Reef (WAGNER, 1929; RAMDOHR, p. 759, 1960) indicates, however, that only part of the total platinum metal content can be in solid solution in sulfides.

Table 78-F-7. *Platinum metal content of minerals from the Merensky Reef, Bushveld Complex, South Africa, ppm.* (After SCHNEIDERHÖHN and MORITZ, 1931)

Location	Mineral ^a	Ru	Rh	Pd	Ir	Pt
Klipfontein- ^b	Pyrite	0.5—1	1	5—10	0.5—1	10—50
Krondaal,	Pyrrhotite					
Rustenburg	Pentlandite	0.5	0.5—1	5	0.5—1	5—10
District	Bronzite	—	0.1—0.5	0.5—1	0.1—0.5	1—5
Schildpadnest, ^c	Pyrite	0.1—1	0.1—1	10—100	0.1—1	10—100
Rustenburg	Pyrrhotite					
District	Pentlandite	0.1—1	0.1—1	1—10	0.1—1	1—10

^a Platinum metal concentrations in chalcopyrite from both localities were below the detection limit.

^b Olivine, diallage and plagioclase were also analysed in the Klipfontein sample. In olivine 1 and 0.5 ppm Pt and Pd respectively were found and in diallage 1—5 ppm Pt was obtained.

^c In the Schildpadnest sample chromite, olivine, diallage and serpentine + millerite were analysed. No platinum metals were detected.

SCHNEIDERHÖHN and MORITZ also determined platinum metals in minerals from the Mooihoek and Driekop dunite pipes and a few determinations for the Mooihoek and Onverwacht pipes were reported by HAGEN (1954). The highest platinum metal concentrations are found in the iron-rich hortonolite cores of the Mooihoek and Onverwacht pipes whereas in the Driekop pipe, which lacks concentric structure and marked fractionation of iron, the distribution of high platinum metal values is more irregular. The platinum metals occur as discrete minerals including mainly ferroplatinum, sperrylite and, at Driekop, geversite, according to STUMPFL (1961). In addition small quantities of braggite, cooprite, laurite, stibiopalladinite, osmiridium and osmite are associated with the major platinum group minerals. Using an electron microanalyser STUMPFL (1961) identified eight additional new platinoid-rich minerals, principally compounds of antimony, arsenic and bismuth, in mine concentrates from Driekop.

Data for whole-rock samples from dunite pipes are given in Table 78-F-8. An increase in platinum metal content in the hortonolite facies of the Mooihoek and Onverwacht pipes is apparent. In the Driekop mine where the degree of iron enrichment is small, little difference is found in the olivine and hyalosiderite facies. WAGNER regards the hortonolite cores of the pipes as later than the forsterite mantle because of both the lower temperature indicated by the iron-rich composition and the presence of mineralizers suggested by the association of phlogophite, hornblende and fluorapatite with the hortonolitic rocks. The platinum metals are therefore

Table 78-F-8. *Platinum metal content of dunite pipes from the Bushveld Complex, South Africa, ppm*

Pipe	Rock type and description	Author ^a Ru and method	Rh	Pd	Ir	Pt	
Mooihoek	Medium grained hortonolite dunite	S ²	0.5	0.5—1	1—5	0.5	5—10
	Coarse grained hortonolite dunite in the vicinity of pegmatitic veins	S ²	0.5—1	1—5	5—10	1	10—50
	Chromite band in hortonolite dunite	S ²	0.5—1	1—5	5	1	0—50
	Hortonolite, inner core, No. 8	Fa/S ¹		0.29	0.65		12.3
	Hortonolite, inner core, No. 106	FA/S ¹			0.02		0.3
	Olivine, outer rim, No. 31 ^b	FA/S ¹			0.07		0.07
Driekop	Olivine dunite, surface	S ²		0.1—0.5	1		1—5
	Hyalosiderite dunite, surface	S ²		0.5	1—5		1—5
	Hyalosiderite dunite, 400 foot level	S ²		0.5	1—5		1—5
	Weathered dunite, surface	S ²		0.5—1	1—5	0.5	5—10
Onverwacht	Olivine, outer rim, No. 16	FA/S ¹			0.004		0.02
	Hortonolite, inner core, No. 17	FA/S ¹			0.013		3.2

^a 1. HAGEN, J. (1954). 2. SCHNEIDERHÖHN, H., and H. MORITZ (1931).

^b VINCENT and SMALES (1956) obtained 0.123 Pd for this sample

considered to be fractionated and concentrated in late or residual fluids which gave rise to the hortonolite cores.

As in the Merensky Reef, Pt and Pd are the most abundant metals with Pt in excess of Pd. Rh is the third most abundant metal and Os and Ru minerals are known to be present.

SCHNEIDERHÖHN and MORITZ also found platinum metal contents up to 5 ppm Pt in silicate minerals such as hornblende, mica and diallage from the Mooihoek and Driekop pipes. Such high platinum values were regarded as resulting from the presence of inclusions of platinum minerals. The large difference between Hagen's Pd values for two hortonolite samples from the inner core of the Mooihoek pipe suggest non-uniform distribution of this metal.

VI. Discussion

A summary of some of the properties of the platinum metal distributions and mineral associations for the ores discussed above is presented in Table 78-F-9. The platinum metals of highest concentration in these ores are Pt and Pd followed by

Table 78-F-9. *Summary of platinum metal distribution in the Sudbury, Noril'sk, Inaglinsk and Bushveld deposits*

Deposit	Pd/Pt	Sulfide, silicate or oxide minerals with highest platinum metal content		
		Rh	Pd	Pt
Sudbury	1	Pyrrhotite Pentlandite	Chalcopyrite Pentlandite	Chalcopyrite Pentlandite
Noril'sk	6	Pyrrhotite	Chalcopyrite	Chalcopyrite
Inaglinsk (whole rock samples)	0.25	Total platinum metals highest in chrome-spinels		
Bushveld Merensky Reef	0.4		Pyrite Pyrrhotite	Pyrite Pyrrhotite
Bushveld Dunite Pipes	0.2	Pt and Pd highest in hortonolitic facies		

Rh with Ru, Os and Ir occurring at considerably lower concentration levels. In Cu-Ni sulfide deposits associated with gabbroic rocks Pd equals or exceeds the Pt content on the average, whereas in deposits associated with dunitic rocks Pt is the more abundant of the two metals. The Merensky Reef ores, which are associated with significant quantities of Cu-Ni sulfides and in this sense are comparable with Sudbury and Noril'sk, are an exception. However, they do show some analogy with the dunitic deposits in that platinum metals are concentrated in the chromite layers immediately above and below the pyroxenitic facies of the Reef.

In the Cu-Ni sulfide ores of Sudbury and Noril'sk Pt and Pd are dominantly associated with chalcopyrite and pentlandite whereas Rh is distinctly higher in pyrrhotite, particularly at Noril'sk. The Merensky Reef, however, is different in that pyrite and pyrrhotite rather than chalcopyrite are richest in Pt and Pd according to SCHNEIDERHÖHN and MORITZ's data. Although distinctive platinum metal — sulfide mineral associations are apparent, it is by no means clear whether the platinum metals are in solid solution or are mechanically admixed as discrete minerals with the sulfides. STUMPFL (1962) has discussed the genesis of platinum ore deposits pointing out that discrete platinum metal minerals have been recognized in all these deposits. He concluded (p. 622) that while the "possibility that traces of Pt-metals enter the lattice of sulfides" cannot be disregarded, "the bulk of the Pt-metals in the above deposits is fixed in independent Pt-minerals".

While the presence of platinum minerals in Cu-Ni sulfide ores is well established — it is unlikely that the strong association of Pt and Pd with copper but Rh with iron sulfides is accidental. Two possible reasons for the existence of these relationships follow.

a) Because of favourable crystallochemical factors Pt and Pd form dilute solid solutions with chalcopyrite, cubanite and pentlandite. If solubility is favoured at high temperatures exsolution may occur on cooling with the formation of cooprte or braggite. Rh, again because of crystallo-chemical factors, may be capable of substitution only in the pyrrhotite lattice.

b) Pt and Pd may form complex ions, possibly with S, As or Sb and with square coplanar stoichiometry (by analogy with known low temperature S complexes of Pd)

which inhibit solid solution of these metals but increase solubility in S-rich melts. These Pt metals therefore tend to occur in highest concentration in residual or late magmatic solutions as discrete minerals, and in association with the youngest major sulfide in the paragenetic sequence, usually chalcopyrite. If Rh does not form a species of high solubility in a sulfur-rich melt, it may be adsorbed, coprecipitated or otherwise enter into solid solution with the earliest major sulfide in the paragenesis, pyrrhotite.

Accurate data on the platinum metal concentrations in individual sulfide minerals from Cu—Ni sulfide ores are required to test the validity of these hypotheses.

The occurrence of platinum metals in dunitic rocks is characterized by two important features including enrichment in spinels, particularly in massive or segregation type chromite, and in the youngest dunitic rocks. High platinum metal values are found in the chromite layers marking the upper and lower boundaries of the Merensky Reef (COUSINS, 1964), and in chrome-spinel of the Inaglinsk Massif. The occurrence of high platinum metal values in the youngest facies of dunitic rocks is particularly apparent in the Mooihock and Onverwacht pipes where a core of hortonolitic olivine is present. Also at Inaglinsk the dunitic core, which presumably crystallized later than the dunite on the periphery, is highest in platinum metals. A suggested explanation is that low solubility of platinum metals in silicate lattices has led to concentration in residual magmatic fluids or melts where they have finally crystallized as native metals, sulfides, arsenides or antimonides depending on the availability of these elements. RAZIN *et al.* (1965) maintain that in the Inaglinsk Massif, silicates do carry platinum metals. However, the interpretation of their data is open to some doubt as previously noted. The reason for the association of platinum metals with chrome spinels is unclear. RAZIN *et al.* appeal to substantial solid solution or adsorption of platinum metals, whereas COUSINS (1964) and WAGNER (1929) maintain that Merensky Reef and other Bushveld chromite is free of platinum metals although supporting analytical data are not presented.

METALLOIDENY OF
HEAVY OILS,
NATURAL BITUMENS,
AND OIL SHALES

By RICHARD L. HARRIS, JR.

Copyright 1924

METALLOGENY OF HEAVY OILS, NATURAL BITUMENS, AND OIL SHALES

Copyright 1994 by AOSTRA. All rights reserved. Printed in Canada. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior permission of the publisher.

ISBN 0-7732-1316-3

PUBLISHED BY

ALBERTA OIL SANDS TECHNOLOGY AND RESEARCH AUTHORITY
500 HIGHFIELD PLACE
10010-106 STREET
EDMONTON, ALBERTA, CANADA
T5J 3L8

5.1 ACCUMULATION AND COMPOSITION OF THE SHALES

In the Phanerozoic section, a fairly distinct periodicity has been found in the accumulation of the sapropelic carbonaceous rock facies termed oil shales, black shales, domanikites, and the like. Many of these are enriched in Mo, U, Re, V, Se, Cd, Bi, Tl, Ag, Au, As, Sb, and other rare and disseminated elements. Against a relatively high overall geochemical background in carbonaceous rocks, groups of formations are distinguished which are characterized by a certain combination of rare elements. The content of the elements is several orders of magnitude higher than their clarkes and may reach the levels of economic ore concentrations. On the basis of current ideas concerning the concentrating function of organic matter, sapropelic carbonaceous formations as a source of metals should reflect the conditions of accumulation and fossilization of the organic matter and the environment of deposition. The difference in the environments in which black shales of different genetic types are formed is manifested not only in the distribution and concentration of rare and disseminated elements, but also in the mineral composition of the rocks, which enables us to correlate their composition and metal potential. A proposed compositional classification (Goldberg, Mitskevich, and Lebedeva, 1991) was based on a combination of methods, including X-ray, silicate and carbonate-chemical, and petrographic, with the chemical methods of principal importance. The chemical analyses were recalculated to the complete mineral composition, bringing out the main components of these rocks: free authigenic silica; carbonates; and clastic components, which consist mainly of clay minerals. On the basis of processing about 500 analyses of black shales from various basins with respect to these components, five types of rocks were distinguished. The first three types — siliceous, clayey-siliceous, and siliceous-carbonate — can be classified as sediments of the domanik type on the basis of the details of their formation, distribution, and composition. These rocks always contain an elevated, often high, amount of free authigenic silica which most investigators believe to be planktonogenic. Domanikites are the sediments of uncompensated ("starved"), relatively deep-sea basins, accumulated at an extremely low rate (up to 6 m/Ma) with an oxygen deficit in the bottom water and extensive hydrogen sulfide contamination. The decisive factors in the accumulation of organic matter in these sediments are the low sedimentation rates, with very slight inorganic dilution, and a high degree of fossilization of organic matter, mainly due to the formation of organo-montmorillonite compounds. At the same time, these factors promoted long-term processes of absorption of the metals by active organic matter from the sea water during early diagenesis, which led to the formation of strong geochemical anomalies. It is well known that functional groups with coordination saturation of oxygen and nitrogen atoms rise to the surface of organic matter and take part in binding metals in compounds of the chelate type.

Another variety of carbonaceous deposit is oil shale proper, which is composed of clastic and clay-carbonate rocks practically devoid of authigenic silica. Most of the richest oil shale deposits, containing up to 20–50 percent organic matter, are related to these. The main factor controlling the accumulation of large masses of organic matter apparently was the abruptly increased primary bio-productivity (the P factor of Yudovich and Ketris, 1988).

Because oil shales, as a rule, were formed in shallow marine or continental basins, the accumulation and preservation of organic matter is guaranteed only if the sedimentation rate is high, leading to rapid burial of the sediment. In addition, a considerable amount of organic matter (including humic) was introduced with the clastic material, as is indicated, particularly, by the presence of highly carbonaceous rocks in the purely clastic sections of intermontane basins. It is noteworthy that, in contrast to domanikites, the predominant clay minerals of oil shales proper are hydromicas and

kaolinite, which do not form organomineralic compounds and do not preserve organic matter. The separation of organic matter from the inorganic components of oil shales determines their distinctive qualitative parameters: the output of shale resin and the heating capacity. In addition, the specifics of the formation of oil shales did not foster the concentration of these elements in oil shales. These factors include a high sedimentation rate, a brief period of diagenesis and rapid separation of the sediment from the bottom water layer, and, frequently, accumulation in closed freshwater bodies which were impoverished in rare elements in the aqueous environment.

Table 5.1 summarizes the most important indices for distinguishing the environment of formation as well as the mineralogic, lithologic, and geochemical characteristics of domonikites and oil shales proper.

5.2 ORE SPECIALIZATION OF THE SHALES

The classification of domonikite and oil shale facies that has been worked out on the basis of composition and genetic criteria is tied in with the distribution of included rare and disseminated elements.

The material on which these formulations were based includes numerous data on the trace element composition of black shales published in our own and in the foreign literature, as well as results of analytical investigations of shales made by neutron activation, X-ray fluorescence, and emission spectral analyses. The various basins studied include, among others, the Baltic, West Siberian, Olenek, Timan-Pechora, Volga, and Central Asian.

In dealing with the problems of classification, most attention has been paid to study of the patterns of distribution of rare elements in carbonaceous facies of various types as the basis for the prediction of their metal potential. On the basis of calculations made for the concentrations of a number of elements in black shales, we were able to ascertain the nature of the association of organophilic elements and, on that basis, to classify the principal Phanerozoic carbonaceous facies of the world. These metallogenic facies were determined on the basis of a series of elements that had stable maximum values of concentration coefficients (C_c) for the type of facies in question: the ratio of the elemental content of a rock enriched in organic matter (≥ 5 wt%) to its clark for clays. In addition, the next series of elements which considerably exceeds the clark level was taken into account in the classification. In some black shale facies, secondary mineralization has been superposed on the primary geochemical background of the facies. This is related to the introduction and deposition of metals at geochemical barriers, as a rule in mineral form. In addition, in zones of old upwelling, strong geochemical anomalies appear, mainly in P, U, and V, which blur the main series of rare and disseminated elements accompanying the planktonogenic sapropelic organic matter of black shales.

Table 5.2 gives the main metallogenic types of domonikite and oil shale that have been distinguished, and the concentration coefficients of elements defining these types. The combination of elements accompanying sapropelic organic matter in domonikites on the one hand, and in oil shales on the other, remains fairly constant. In the various associations, mainly domonikite, only redistribution of the elements in the concentration order is observed, with the formation of typical metallogenic associations of a relatively small number of elements (Mo, Re, U, Se, V, Zn, Cd, Bi, Ag, Tl, and others).

TABLE 5.1
Comparative characteristics of oil shales and domanikites

Indicators	Oil shales	Domanikites
Regime of deposition/rate of deposition (m/Ma)	Compensated, relatively high, up to 50–100	Uncompensated low, up to 1–6
Facies setting	Shallow sea, lagoons, lakes	Relatively deep sea (up to 500–1000 m); extensive hydrogen sulfide contamination of water above bottom
Tectonic setting	Intraplatform synclises, shallow depressions on platform structures, intermontane basins	Platforms, chiefly regions of pericratonic subsidence; geosynclinal regions
Area of occurrence (km ²)	Isolated basins, tens to hundreds, rarely thousands	Continuous over areas of tens to hundreds of thousands to a few million
Host rocks	Sandstones, siltstones, conglomerates, effusives, clayey rocks, rarely carbonates; coal is found	Clayey and clay-carbonate rocks, limestones
Type of rocks enriched in organic matter	Clayey and carbonate-clayey oil shales, usually silty	Siliceous, clayey-siliceous, clayey and siliceous-carbonate domanikites
Rock-forming minerals	Hydromicas, kaolinite, montmorillonite, calcite, dolomite, pyrite; considerable silt admixture	Montmorillonite, calcite, dolomite, opal, chalcedony, pyrite; slight admixture of silt
Thickness of sequence containing rocks rich in organic matter (m)	Hundreds, sometimes a few thousand	A few tens
Number of intercalations (beds) rich in organic matter	Tens	Isolated; one or two economically ore-bearing
Amount of organic matter at end of diagenesis (%)	15–50	5–20, rarely up to 35
Type of organic matter	Humite-sapropelite, sapropelite	Mainly sapropelite
Heating capacity (Kcal/kg)	1000–4500 (usually 2000–2500)	800–2500 (usually about 1000)
Yield of shale tars (%)	3.5–32.5 (usually 10–15)	1.5–8 (usually 3–4)
Content of elements	About clarke; above clarke: Mo, Re, sometimes P, U, Se, Cd, Au, Ag, As, Cu	Everywhere 1–4 orders above clarke: Re, Mo, Se, Cd, Bi, Ag, Au, As, Tl, Sb, U, V, Zn; often P, Ni; sometimes Cu, Pb, Co, Cr

Among domonikites of clayey-siliceous (siliceous-clayey) composition, two main metallogenic types are distinguished: Mo-U-V (Re, Bi) and Mo-Se-Zn (Table 5.2).

Classic examples of the first metallogenic type are the Cambrian Alum Shale and Ordovician Dictyonema shales, underlying the territory from northern Norway to southern Sweden. The accumulation of the Alum shales corresponded to the stage of maximum transgression with minimal sedimentation rates (1 to 2 m per Ma). In the stratigraphic section of the Alum shales, which is from 1219 m (Nyarke) to 50 m thick (Skane), three members with different contents of organic matter, sulfur, and metals are distinguished. A general tendency is observed toward an increase in concentration of C_{org} , S, U, Mo, and Ni upward in the section. Numerous inclusions of concentrated organic matter (up to 80 percent), the so-called "kolms," containing up to 10 percent FeS_2 and 2000–5000 g/t U, are confined to the Peltura zone of the upper Renstad member (Andersson *et al.*, 1985); the background concentrations are 15–30 percent C_{org} , 135–337 g/t U, and 240–340 g/t Mo. In the Tremadocian Dictyonema shales, a very high concentration of V is observed, despite a decrease in the organic matter content to 68 percent.

On the basis of concentration coefficients, the disseminated and rare elements in shales form the following series (the first figure is the minimum C_c value, the second, the maximum): Mo (35–230), U (4.5–105), V (3.4–28), As (2.5–24), Cd (7.3–23), Ag (3–14), (Sb 3–10), Zn (1.6–3.3), and Cu (1.3–3.3); in individual samples, Bi (130) and Pb (46) have been found. A fairly clear relationship of the shales richest in rare and disseminated elements, especially U and Mo, to the zones with minimum thickness of the shale-bearing member is found. It is to these zones that the shale deposits of Sweden, containing large reserves of U, Mo, and other elements, are confined (the Nyarke, Billingen-Falbigden, Renstad, and Ostergotland). For instance, the uranium reserves in the Billingen-Falbigden deposit are estimated at 1.7 million tons and those of the Nyarke deposit, 0.28 million tons (Andersson *et al.*, 1985). The source of the uranium in the shales is believed to be the weathered mantles overlying basement granites of the Baltic shield, as well as associated deposits of the uranium-albite association (Yudovich and Ketris, 1988). In addition, the strict stratification of the uranium mineralization throughout the section and its areal persistence may indicate biogenic accumulation of uranium, if its concentration in the paleo-basin is relatively high.

The kerogen mudstones of the Tremadocian Tyurisalul formation in northern Estonia may be an analog of the Dictyonema shales of Scandinavia. According to Pukkkonen (1989), the order of decreasing average values of rare and disseminated element concentration coefficients in shales is as follows: Re (143), Bi (111), Mo (69), U (15), Tl (10), Ag (10), Au (10), Cd (9.5), V (7), Sb (7), As (5), Se (5), and Cu (2.5). In some sections a high concentration of Zn (up to 7100 g/t) is observed. With the decreasing thickness of the shale layer from west to east and toward the south, from 7 to 1 m, there is an increase in the concentration of Re, V, Mo, U, P, S, Ag, As, and Ni and a decrease in the content of C_{org} , Nb, Al, and others. For instance, from the central part of northern Estonia to the Toolse deposit, the V content increases from 760 to 1040 g/t, Mo from 133 to 406 g/t, and Re from 0.05 to 0.17 g/t (Maremäe, 1989).

Black shales such as the Chattanooga (Hathaway member), which extends parallel to the Appalachians from New York to northern Texas, belong to the first metallogenic type. The Chattanooga shales were deposited in a vast (more than 650,000 km²), relatively deep, stagnant epicontinental basin with extremely slow sedimentation rates. Conant and Swanson (1961) pointed out the similarity of the Chattanooga shales to the Alum shales of Scandinavia, with respect to their conditions of formation and composition. Analysis of data on the trace-element composition also

ikites

d low, up to

p sea (up to
; extensive
ie contamina-
ove bottom

ly regions of
subsidence;
gions

r areas of tens
housands to a

ay-carbonate
s

ey-siliceous,
ceous-carbo-
s

ite, calcite,
chalcedony,
admixture of

r two econo-
ing

o 35

ite

ually about

-4)

orders above
Se, Cd, Bi,
l, Sb, U, V,
; sometimes

TABLE 5.2
Metallogenic types of domanikite and oil shale associations

Basin	Country	Age of horizon, formation	Type of association	Predominant rock composition	Organic matter, range/average (%)	Metallogenic associations (in order of decreasing C_o)		Elements forming their own minerals	Examples of deposits (metal content, g/t)	Reference
						Main	Secondary			
Type I. Mo-U-V (Re, Bi)										
Bahic	Sweden	O_1 , Dictyonema	Domanikite	Siliceous-clayey	6-15/-	(Bi), Mo, U, V	As, Au, Ag, Zn, Cu	Fe	Ostergotland (Mo-135; U-140-190; V-2000)	Anderson and others (1985); Anderson and Bjerle (1988)
		E_2-E_3 "alum shales"	Domanikite	Siliceous-clayey	5-30/12	(Bi), Mo, U, V	As, Ag, Au, Cd, Zn, Cu	P, Fe	Nyarke (Mo-270; U-135-245; V-1000); Billingen-Falbigden (Mo-270-340; U-155-337; V-780)	
	Estonia	O_1 , Pakerort, Tyurisalu	Domanikite	Siliceous-clayey	5-14/11	Re, Bi Mo, U, V	Au, Ag, Cd, Sb, As, Se	P, Pb, Zn, Fe	Toolse (V-1040; Mo-406; Re-0.17)	Pukkonen (1989); Märentie (1989); author's data
Chattanooga	USA	D_3-C_1	Domanikite	Siliceous-clayey	5-25/22	Mo, U, V	Ag, Zn, Cu, Th	P, Fe (Mo-100;	Chattanooga (Mo-100; U-80-120; V-500; Mo-200; V-1500)	Conant and Swanson (1961); Landis (1962); Vine (1964)
Type I. Mo-U-V (Re, Bi)										
Illinois	USA	C_2-C_3	Domanikite	Siliceous-carbonate	4-24/-	P, U, V, Mo, Se, Zn	Cu, Ni, Pb, Cd	P, Pb, Mo Zn, Fe	Logan Quarry (P_2O_5 -1%; U-240; V-1430; Se-300); Mecca Quarry (U-160; V-5850; Mo-1160; Se-250)	Davidson and Lakin (1961); Coveney and Martin (1983)

Mecca Quarry
(U-160; V-5850;
Mo-1160; Se-250)

Table 5.2 cont'd ...

Basin	Country	Age of horizon, formation	Type of association	Predominant rock composition	Organic matter, range/average (%)	Metallogenic associations (in order of decreasing C _p)		Elements forming their own minerals	Examples of deposits (metal content, g/t)	Reference
						Main	Secondary			
Type II. Mo-Se-Zn										
West Siberian	Russia	J ₃ v-K ₁ v, Bazhenovo	Domanikite	Siliceous-clayey	6-15/10	Mo, Se, Zn, U, As, Sb	Au, Ag, V, Ni, Cu	Fe	-	Gayshin and Bobrov (1982); Gurari and others (1988); author's data
Type III. U										
California (Ventura Los Angeles)	USA	N ₁ , Monterey, Siquoc	Domanikite	Siliceous & clayey siliceous	4-14/5.4	U	Mo, Cr, Be, Y V, Cu, Ni	P	Tembler Range (U-240)	Durham (1987)
Type IV. P-U-V (Mo, Se, Zn)										
Phosphoria (old upwelling zone)	USA	P ₁ , Phosphoria (Meade Peak horizon) "vanadium zone"	Domanikite	Siliceous-carbonate	7-10/5	P, V, U, Mo, Se, Zn	Ni, Cu, Cd, Pb	P, Zn, Pb, Fe	(P ₂ O ₅ -30.5%; U-120; V-500-4000; Se-680; Mo-500; Zn-3500)	Love (1961); Sheldon (1959);
Type V. Mo-V (Cd, Bi, Ag)										
Olenek	Russia	E ₁ -E ₂ Kuonarka	Domanikite	Siliceous-carbonate	6-33/14	Mo, V, Ag Bi, Cd	Zn, Au, Se As, Sb, Ni	P, Fe	-	Bakhturov, Yevnashenko and Perekladov (1988); Gavahin & others (1984); author's data
Eromanga	Australia	K ₁ , Tooleback	Domanikite	Siliceous-carbonate	4-26/13	Mo, Bi, Cd Se, V	Zn, U, Ni As, Ag, Sb	Fe	Julia Creek (Mo-270; V-2000; Cd-25; Se-30; Au-5; U-30)	Glikson and others (1985); Patterson & others (1985); Riley and Saxby (1982)

Table 5.2 cont'd ...

Basin	Country	Age of horizon, formation	Type of association	Predominant rock composition	Organic matter, range/average (%)	Metallogenic associations (in order of decreasing C_o)		Elements forming their own minerals	Examples of deposits (metal content, g/t)	Reference
						Main	Secondary			
Type VI. Ag-Mo-Zn (Cd, Bi, Tl)										
Atlantic Ocean		K	Domanikite	Siliceous-carbonate	~(6)	Bi, Cd, Tl, Ag Mo, Zn, V	Cu, Cr, Ni, Co	Fe	-	Brumsack (1980); Brumsack and Lew (1982)
Type VII. Re-Mo-Se (Cu, Zn, Pb, Ag)										
Edinburgh	Great Britain	P ₂ Merle Slate	Domanikite	Siliceous	4-11/-	Re, Mo	Ag, V, Ni, Cu, Co	Fe	Merle Slate (Re-0.1-30; Mo-20-800)	
Central European	Germany	P ₂ Kupferschiefer "Copper schists"	Domanikite	Siliceous	7-15/-	Cu, Zn, Pb Ag, Re, Se, Mo	Au, As, V, Ni Co, Cd, Ge, U	Cu, Pb, Zn (Cd), Ag, Fe	Mansfeld (Cu-2.5%; Zn-0.7%; Pb-0.44%; Re-0.7%; Se-300; Mo-65-920); Sangerhausen (Cu-2.95%; Zn-1.25%; Pb-0.64%; Ag-106; Re-21; Mo-201)	Wedpohl (1967); Lur'ye (1983)
	Germany	P ₂ Kupferschiefer	Domanikite	Siliceous	7-15/-	Cu, Zn, Pb Ag, Re, Se, Mo	Au, As, V, Ni Co, Cd, Ge, U	Cu, Pb, Zn (Cd), Ag, Fe	Richelsdorf (Cu-1-3%; Zn-0.6-1.0%; Pb-0.5-0.7%)	
	Poland	P ₂ Kupferschiefer	Domanikite	Siliceous	10-13/-	Cu, Zn, Pb Ag, Se, Re, Mo, Au, Pt, Pd	Au, V, Ni Bi, Ir, Os	Cu, Pb, Zn Ag, Fe	Lubin-Sieroszowice (Cu-4.5%); Zechstein (Se-300; Mo-80-310)	Kucha (1985)
Syr Darya Upper Amur	Tadzhikistan, Uzbekistan	P ₂ Suzak	Domanikite	Siliceous-carbonate	12-31/-	Re, Mo, Se, Cd	Tl, Bi, V, Ag Ni, Sb, Cu, Zn	Fe, P	Bayun (Mo-1500; Mo-1500; V-1262; Se-78; Re-5.6; Tl-6.3; P-5250); Urtabulak (Mo-1500; Re-6.2)	Kler and others (1987); Poplavko and others (1977);

8

141

Upper Amur	Uzbekistan	Suzak		carbonate			Ni, Sb, Cu, Zn		Dayan (Mo-1500; V-1262; So-78; Re-5.6; Ti-6.3; P-5250); Urtabulak (Mo-1500; Re-6.2)	Kler and others (1987); Poplavko others (1977);
------------	------------	-------	--	-----------	--	--	----------------	--	---	---

OIL SHALES

RARE ELEMENTS IN OIL (BLACK) SHALES

Table 5.2 cont'd ...

Basin	Country	Age of horizon, formation	Type of association	Predominant rock composition	Organic matter, range/average (%)	Metallogenic associations (in order of decreasing C _p)		Elements forming their own minerals	Examples of deposits (metal content, g/t)	Reference
						Main	Secondary			
Type VIII. Re-Mo										
Volga and Timan-Pechora	Russia	J _{3v1}	Oil shale	Clayey-carbonate	7-15/- 15-40/-	Re, Mo	Se, Cd, Bi, Au Ag, As, V, Ni, Sb, Zn, Ti	Fe	Kashpir; Ayyuva, etc.	Kler and others (1987); author's data
					Type IX. Mo					
West European	G. Britain Spain, France Germany Switzerland and others	J ₁ , "Posidonia shales"	Oil shale	Clayey-carbonate	10-30/-	Mo	V, Ni, Co, Cu, Cr	Fe, (Li), Sr	Stowell Peak (Mo-60); Corset (Mo-15-260); Wurttemberg (Mo-80); Moss Terri (Mo-40)	Bitterli (1960); Kunz and Baus (1975); Tourtelot (1970)
Piceance Creek Green River, Uinta, Washiki	USA	P ₂ , Green River	Oil shale	Clayey-carbonate	8-50/14	Mo,P, U	As, Zn, Cu V, Au	Na, Ba, Sr Fe, P, U	Wilkins Peak (Mo-200); (Mo-30); P ₂ O ₅ -2.2-18% U-0.005-15%	Yudovich & Ketris (1988); Meddaugh & Salotti (1983); Saelher <i>et al.</i> (1984); Saelher, Rummels, & Meglen (1984)

indicates that the content of rare and disseminated elements in these facies is of much the same type (Landis, 1962; Vine, 1964). According to data on the concentration coefficients, the principal elements in the Hathaway shales form the following series (minimum and maximum C_c): Mo (50–115), U (25.0–37.5), V (4.0–11.5), Ag (2–20), and Zn (2–11). In Tennessee alone, the in-place uranium reserves in the shales are estimated to be 4.2–5.1 million tons.

The unique conditions under which the metals accumulated in the black shales are observed in the Illinois basin, where maximum concentrations of Mo, U, V, Se, and Zn are confined to shales that were deposited on the eastern littoral zone of the basin, near the old shoreline, at the boundary between reducing and oxidizing environments (Davidson and Lakin, 1961). This single region of concentration at a geochemical barrier occupies an area of several thousand square kilometers in Indiana and Illinois, in which rare and disseminated elements form the following series with respect to C_c values (minimum and maximum C_c): Mo (360–580), Se (400–500), Zn (37–111), U (50–75), V (11–45), and so on. Coveney and Charon (1983) found that Mo in the shales is bound mainly in organic matter, V in hydromicas, and U in organic matter and phosphates, whereas Zn, Cd, Cu, Pb, and, in part, Mo are in mineral form and consist of sphalerite, chalcopyrite, covellite, molybdenite, and other sulfides.

The second metallogenic type is typical of the siliceous-shaly Volgian-Valanginian domonikites (Bazhenovo formation) of the West Siberian Basin, with stable anomalous concentrations of Mo, Se, Zn, As, Sb, and other rare and disseminated elements (Table 5.2). The bituminous mudstones (20–35 m thick) accumulated in a vast (0.8–1.0 million km²), relatively deep, uncompensated marine basin under conditions of widespread hydrogen sulfide contamination of the bottom water (Gurari, Vayts, Moskvina *et al.*, 1988). The average organic matter content in the rocks of the Bazhenovo formation is eight percent, reaching 12–15 percent in the central part of the basin. According to Gavshin and Bobrov (1982), the elements that accumulated in the organic matter are, in descending order of average values of concentration coefficients: Mo (61), U (10.5), As (7.3), Sb (6.9), Zn (5.9), V (4.6), Ni (4.1), Au (4.0), Ag (3.9), Cu (3.3), and Ba (2.8). An increase in concentration of organophilic elements from the periphery to the center of the basin is observed, with maximum values in the Salym, Surgut, and Krasnolinsk areas. According to the results of our activation analyses, the average rare and disseminated element concentration coefficients in the bituminous mudstones of the Salym area have the following values: Se (170), Mo (104), Au (25), Zn (17.5), As (16), Ag (14), V (8), Sb (5), Ni (4), and Co (2).

The main reason for the relative enrichment in rare earths of the rocks of the Bazhenovo Formation probably was the very slight mineral dilution due to the extremely low sedimentation rates. This conclusion is deduced particularly from the observed relationship between the rare and disseminated element concentrations and the ratio between the contents of organic matter and clay minerals in the rocks. From the clayey-siliceous rocks of the Bol'shoy Salym area to the siliceous-clayey rocks in the eastern part of the Shirotnoye Priob'ye ["Latitudinal Ob'"] area, to the clayey domonikites of the Nadym and Tazovsk areas, as the ratio of organic matter to clay mineral content changes from 0.5–0.4 to 0.4–0.2 and then to less than 0.1, the content of Mo, for instance, drops from 160–100 g/t to 75–50 g/t and 15–3 g/t, respectively. That same trend is traceable for other organophilic elements (U and Zn). In addition, the concentration of elements bound to the clastic components of the rock (Zn, Sr, Cr, and others) increases substantially from the central part to the perimeter of the basin.

h the same type
incipal elements
to (115), U
-place uranium

are observed in
ed to shales that
t the boundary
ingle region of
e kilometers in
with respect to
, U (50-75), V
ound mainly in
Zn, Cd, Cu, Pb,
polybdenite, and

an domanikites
ions of Mo, Se,
dstones (20-35
d marine basin
(Gurari, Vayts,
vo formation is
o Gavshin and
nding order of
i (5) V (4.6),
of organophilic
s in the Salym,
he average rare
the Salym area
(8), Sb (5), Ni

he Bazhenov
mentation rates.
n the rare and
matter and clay
to the siliceous-
to the clayey
mineral content
ce, drops from
able for other
l to the clastic
tral part to the

In the third metallogenic type, essentially siliceous, diatomaceous formations enriched in uranium are distinguished, related to the bathyal regions of the ocean basins. In particular, the black shale-diatomites in the Miocene-Pliocene Monterey and Sisquoc Formations in southern California are of this type. According to Durham (1987), the U concentration in the shales ranges from 2.5 to 1985.0 g/t. Most of the U is in organic matter and biogenic opal; the U contained in phosphate, which forms numerous inclusions in the "nodular shales," is not more than 510 percent of the total U in the rock. The extremely low concentrations of elements other than Mo in the shales are noteworthy. The order of decreasing values of their concentration coefficients is as follows (minimum and maximum C_c): Mo (5-60), Cr (0.2-1.5), Be (0.6-1.1), U (0.2-1.0), Cu (0.3-0.8), Ni (0.1-0.7), Ga (0.3-0.5), and Co (0.1-0.4). The uranium content is not accompanied by a relatively high content of Mo or other elements. Similar uraniferous diatomite deposits have also been found on the continental slope of southwest Africa.

A geochemical phenomenon among domanikites of siliceous-carbonate composition is the Permian Phosphoria Formation (type IV) (Table 5.2), unique in concentration of P, U, and V; it occurs over a vast area of the western United States. In the lower part of the Formation, in the Mead Peak horizon, there are phosphate layers containing up to 30.5 percent P_2O_5 and 0.012 to 0.024 percent U_3O_8 (Sheldon, 1959). The accumulation of phosphorus is attributed by many investigators to an ancient upwelling zone. In Wyoming, there is a highly carbonaceous carbonate-phosphate shale member ("vanadiferous zone"), with a content of 2 percent P_2O_5 , 0.56 percent V_2O_5 and 0.001-0.060 percent U. The reserves of vanadium pentoxide in this member are estimated to be 18-25 million tons (Love, 1961). Besides P and V, a broad combination of rare and disseminated elements has been found in the Phosphoria formation, among which the following predominate, on the basis of C_c : Se (660), Mo (250), Zn (87), U (37), Ni (7), and Cu (7). It is significant that redistribution of the metals throughout the formation is observed, with the formation of ore concentrations in limestone intercalations. For instance, in the Mead Peak Phosphatic deposit, individual carbonate intercalations contain up to 0.4 percent V and 0.068 percent Se.

Siliceous-carbonate domanikites with geochemical anomalies of Mo, V, Cd, Bi, Ag, and other rare and disseminated elements belong to the fifth metallogenic type (Lower to Middle Cambrian Kuonamka Formation of the Siberian platform and the Lower Cretaceous Tulebak Formation of the Australian platform). The similarity of the geologic environments in which these facies accumulated is striking: (1) area of occurrence, 700,000-750,000 km², with a thickness of 40-75 m; (2) occurrence of the shales in the form of isolated intercalations and members up to a few meters thick in rocks poor in organic matter; and (3) zoned distribution of deposits with different concentrations of organic matter, with a maximum content of as much as 10-34 percent in the interior of the paleobasins.

In the oil shales of the Kuonamka formation, Bakhturov, Yevtushenko, and Pereladov (1988) report that the following elements have the highest concentration coefficients (minimum and maximum C_c): Mo (19-180), Cd (13-163), Bi (30-110), V (1.5-13.0), and Ag (5-9). However, the concentrations of the elements are unevenly distributed vertically and horizontally in the basin. On the whole, the highest concentrations of V, Mo, Ag, Cd, Se, Sb, and other organophilic elements are confined to the lower shale member and to zones of the Kuonamka sedimentary basin, where the rates of deposition were minimal. Our calculations show that in these zones, the sedimentation rates during Lena and Amga time were 0.6-1.7 m/Ma, and for the lower shale member, probably even lower. According to the data of our detailed sampling, one or two ore-bearing layers of oil shale, 0.5-2.6 m thick and with average concentrations of 3000 to 5100 g/t of vanadium and 200 to 340 g/t of

molybdenum, are distinguished in the lower member, with maximum contents of 6500 g/t of V and 660 g/t of Mo. Study of the composition of the ore-bearing shales showed that they have a high content of the clay fraction (more than 77.5 vol% minus authigenic minerals), a C_{org} content of 12.5 to 34.5, and a lack of correlation between the concentrations of C_{org} and V, Se, and, in part, Mo. This last is probably governed by the fact that in early diagenesis, chemically active organic matter can bind only part of the elements sorbed from sea water, the rest being sorbed by clay minerals.

By analogy with the Olenek Basin, it can be assumed that in many basins of black shale sedimentation, the ore potential of the entire volume of oil shales is controlled by just one or two horizons, which accumulated under conditions of slower and more prolonged deposition.

In the sapropelic shales of the Tulebak formation, the concentration coefficients of organophilic elements, calculated from the data of Glikson *et al.* (1985) and Riley and Saxby (1982), have the following values: Mo (29.5–150.0), Bi (100), Cd (83), Se (50), V (6.5–25.0), Zn (7.5–10.0), U (3.5), and Ni (1.1–4.0). In individual samples, relatively high contents of Ag, Sb, and As are observed.

In the Julia Creek deposit, with oil shale reserves of 4 billion tons (220 million tons of shale resins), the content of V is 1600–2700 g/t, Ni, 140–320 g/t, and Mo, up to 270 g/t. Deep-sea drilling data are very important for interpreting the origin of black shales and determining the sources of their enrichment in metals. In recent years, much work has appeared on the composition and metal potential of oceanic black shales. As an example, we can cite data from Brumsack (1980) and Brumsack and Lew (1982) on the distribution and concentration of rare and disseminated elements in the Cretaceous black shales of the Atlantic Ocean, which correspond to siliceous-carbonate domanikites with regard to their conditions of sedimentation and composition. Calculations have shown that, first, the usual level of bio-productivity of ocean waters is sufficient for high concentrations of C_{org} to arise in black shales if sedimentation is slow, and second, the order of enrichment of black shales in Pb, Co, Cr, Ni, Cu, V, Zn, Mo, and Ag relative to clays is, except for Ag, the order of increasing concentrations of elements in normal sea water, which is the main source of heavy metals. The presence of high concentrations of Cd, Tl, and Bi in black shales also is noteworthy.

The seventh metallogenic type (Table 5.2) includes siliceous-carbonate domanikites with relatively high and anomalous primary concentrations of Re, Mo, Se, Cd, Tl, Cd, and other chalcophilic rare and disseminated elements. The so-called copper schists (Kupferschiefer) of the Central European Zechstein basin and the Lower Eocene Suzak shales of the Scythian-Turanian platform (Syr Dar'ya and Upper Amu Dar'ya Basins) are of this type. The distinguishing feature of these facies is the fact that the shales occur in them mainly in the form of single thin layers (0.25–2.20 m thick in Western Europe and 0.05–2.0 m thick in Central Asia) that persist over areas tens or hundreds of thousands of km². Analysis of published data (Wedepohl, 1967; Kucha, 1985; Ivanov and Poplavko, 1982) on the Kupferschiefer shows that, aside from the Cu-Zn-Pb-Ag mineralization, they contain the following set of rare and disseminated elements, listed in order of decreasing C_c values: Re (100–37,500), Se (170–500), Mo (10–460), As (13–450), Cd (15–330), Au (up to 2–50), V (2.5–35.0), and Ni (1–10). In the basal layer of the black shales, there are exceptionally high concentrations of Au and platinum-group elements (Pt, Pd, Os, and Ir). In Kucha's (1985) opinion, the concentration of gold and platinoids was the result of self-oxidation and desulfatization of organic matter. The platinum-group elements, which acted as catalysts for the oxidation process, were concentrated at a redox barrier. The radioactivity of the shales, especially that related to thucholites, intensified the process.

There are differing points of view concerning the source of the nonferrous metals in the Kupferschiefer. Wedepohl (1967) proposes a terrigenous source for the Cu, Zn, and Pb. Lur'ye (1983)

12

145

relates the formation of the mineralization to discharge of ground water from the red molasse of the "dead red [lezhnya]" into the sedimentary basin and concentration of the copper and associated metals at the shale geochemical barrier.

In the Suzak shales of the basins of Central Asia, the following elements have the highest concentration coefficients (minimum and maximum C_c): Re (880–4470), Mo (730–1450), Se (810–1000), Cd (435–790), Bi (22–100), V (15–56), Ti (20–35), Ag (11–21), and Ni (6.5–20.0) (Kler, Volkova, Gurvich *et al.*, 1987; Poplavko, Ivanov *et al.*, 1977). In the face of considerable fluctuations in the element contents for the individual areas, the order of their concentration over the whole area of occurrence of the Suzak shales remains fairly constant. In individual sections, different relationships between the organic matter content and the elements (Mo, Se, V, As, and others) are found for different concentration levels of the elements. For instance, anomalously high Mo concentrations (from 500 to 2500 g/t) fall within a relatively narrow range of variation of organic matter content (from 40 to 60 vol%), which indicates the patterns of accumulation of metals in the ore-bearing horizons established for the shales of the Olenek basin. The Suzak shales were formed in a relatively deep sea basin during the initial phase of a transgression, when rapid subsidence was not compensated by sedimentation.

Compared to domanikites, oil shale facies are acutely impoverished both in their combination of rare and disseminated elements and in the concentration of the individual elements. In clayey-carbonate oil shales (Upper Jurassic shales of the Volga and Timan-Pechora Basins, Eocene Green River Formation), mainly the rare elements Mo or Mo plus Re are found in above-clark concentrations (Table 5.2). In some oil shale formations, locally elevated concentrations of Se, As, Au, Ag, V, and other rare elements have been found, bound in both the organic and inorganic fractions.

In the Posidonia oil shales, developed over most of the European countries (Great Britain, France, West Germany, *etc.*), the average Mo concentration is 40–80 g/t, and the concentration coefficients of other rare and disseminated elements are low: V (0.5–3.0), Ni (0.4–2.7), Co (0.6–2.0), and Cu (0.2–1.6) (Bitterli, 1960; Kunz and Bauss, 1975; Tourtelot, 1970). In the Volga oil shales, according to the data of neutron activation analysis, the order of decreasing C_c values of the elements is as follows: Mo (11–34), Se (12–15), Au (4–7), Ag (46), As (0.2–2.4), V (0.6–2.1), Ni (0.4–1.5), Sc (0.6–1.5), Sb (0.2–1.5), Co (0.5–0.6), Ce (0.5–0.6), Cr (0.3–0.5), La (0.3–0.5), and Rb (0.2–0.5). According to Kler, Volkova, Gurvich *et al.* (1987), the shales contain from 0.5 to 2 g/t Re.

In the Green River shales, with unique reserves, a low concentration of rare and disseminated elements is observed despite the high organic matter content (up to 50 percent), except for individual intercalations containing U (0.005–0.15 percent) in association with phosphates (2.2–18.2 percent P_2O_5). The presence in some oil shale deposits, for example, the Wilkins Peak Member of the Green River Formation of Colorado, of relatively high contents of Mo (30–200 g/t), as well as of Se, As, and Au is related the heavy mineral fractions of the shales, which are enriched in pyrite (Meddaugh and Salotti, 1983; Saether, Runnells, and Meglen, 1984). The impoverishment of the Green River shales in rare and disseminated elements is governed by the conditions under which they were formed, that is, in a continental (lacustrine) sedimentary environment with high rates of accumulation of the oil shales (up to 50–100 m/Ma).

To a considerable extent, also in connection with the specifics of its generation and composition, the Middle Ordovician carbonate-kukersite facies of the Baltic area has extremely low concentrations

of rare and disseminated elements. As a result of our investigations, the trace elements in the shales are in the following order of concentration: Mo (0.9), Ce (0.6), U (0.5), Sb (0.5), Sc (0.5), As (0.3), Ni (0.25), V (0.2), Co (0.2), Th (0.2), Hf (0.2), and Rb (0.1). According to published data (Kler, Volkova, Gurvich *et al.*, 1987), Re (0.05 g/t) and Mo (up to 12 g/t) have also been reported.

In clayey oil shales (late Devonian-early Permian of the Kenderlyk Basin; Eocene of the Boltys depression; Permo-Carboniferous torbanite and tasmanite of New South Wales and Tasmania; Oligocene shales of the Fu-Shun Coal Basin; and others), the combination of rare elements and their concentration levels is governed largely by the composition of the surrounding rocks, which are the source of the clastic material. But on the whole, the content of ore elements in this type of oil shale is at the clark level, except for some formations enriched in Mo, Be, Sc, and other rare and disseminated elements.

The above data on the distribution of rare and disseminated elements in black shales of various composition make it possible to draw the following conclusions:

1. The accumulation of rare and disseminated elements in association with organic matter and their levels of concentration are governed by the setting in which Phanerozoic black shales were formed, mainly the depositional environment and sedimentation rate. The conclusion is confirmed that the concentration of organophilic elements arose during slow absorption of an accumulation of elements from organic matter in the layer of sea water above the bottom, rather than as a result of biological activity. On the whole, the tracing of the same type of metallogenic associations at different stratigraphic levels from Cambrian to Neogene indicates that the trace-element composition of sea water was fairly constant throughout the Phanerozoic. The highest rare and disseminated element concentrations are typical of domanikite formations, which were deposited in deep-sea basins in zones that were not compensated by accumulating sediments and, correspondingly, exhibit a reduced thickness of the shale-bearing members.
2. The horizons of ore-bearing shales with economic concentrations of Mo, V, U, Ag, Re, and other rare elements were formed only in stages of extremely slow sedimentation (probably less than 1 m/Ma), with prolonged exposure of the sediments on the basin floor. Here, not only complete bonding of rare elements by chemically active organic matter occurred, but also the accumulation of the excess elements in the inorganic part of the rock, in particular, in hydromicas, phosphates and similar components, to the actual production of mineral forms. Such conditions could have been created, in particular, at the time of the initial phase of a transgression, when rapid subsidence was not compensated by sedimentation.
3. In siliceous-clayey domanikites, a close relationship is observed between organic matter and clay minerals, which even in diagenesis form single organo-montmorillonite compounds, which sorb most metals. This determines the high average concentrations of Mo (up to 135–400 g/t), U (140–340 g/t), V (up to 1500–2000 g/t), Se (up to 300 g/t), and other rare and disseminated elements and their relatively even areal distribution, with strict stratification of the mineralization throughout the stratigraphic section.
4. Because of the low content of clay material in siliceous carbonate domanikites, most of the organic matter in the domanikites remains crystallochemically unbound to the rock, which makes it possible for ore material to be redistributed and form ore concentrations in the oil shale host rocks. Moreover, the distribution of rare and disseminated elements in these siliceous-carbonate domanikites is less uniform over the area of a basin than in siliceous-clayey domanikites, and

14

147

ments in the shales
c (0.5), As (0.3), Ni
lata, Volokva,

cene of the Boltysh
les and Tasmania;
elements and their
cks, which are the
type of oil shale is
nd other rare and

c shales of various

ic matter and their
black shales were
he conclusion is
absorption of an
the bottom, rather
e of metallogenic
tes that the trace-
zoic. The highest
ions, which were
ig sediments and,

Ag, and other
bably less than 1
t only complete
he accumulation
icas, phosphates
ions could have
on, when rapid

anic matter and
npounds, which
135-400 g/t), U
nd disseminated
e mineralization

es, most of the
c, which makes
oil shale host
eous-carbonate
manikites, and

locally high concentrations of Mo (up to 800-2600 g/t), Re (up to 5-30 g/t), V (up to 4500-6200 g/t), Se (up to 200-400 g/t), and other elements may be formed at sorption barriers, which are chiefly clayey.

5. In siliceous domanikites, with a low content of organic matter partly bound in organosilica compounds, the sorption properties of the rocks are slight, which governs the relatively low concentration of metals.
6. Domanikite facies should be considered a potential source of gold and elements of the platinum group, the concentration of which can occur at the boundary between oxidizing and reducing environments (Kucha, 1985; Shalamov, Popova, and Savitskaya, 1991).
7. In oil shale facies, the concentration of rare and disseminated elements associated with organic matter is much higher than the clarke level. This is a result of the high rates of shale accumulation, the brief period of diagenesis, and the rapid separation of the sediment from the bottom water layer. In addition, many oil shales accumulated in continental basins, and therefore lacked sea water, the main source of rare and disseminated elements.

92-8-W4

WMD 16/4 UAG-S
No 19224 152.83

7962

97-125

97/09/26

1:40,000

LN 91 W

© 1998 Alberta
AS4889-21

FS100 1/120 f/4.0 1/3 FF2.6 ED 0 STN

dt034.7

26.6V -58m5 ER00 CAM5213

AIR PHOTO SERVICES (403) 427-3520

Printed By: GLOBAL REMOTE SENSING INC.
Edmonton, Alberta

South

Map 1#

150

92-8-W4

FS100 L 140 F4.1 1/3 F2.5 F1.5 500 0.25000 26.2V -59mW FROM 14M5213

WILD 15/LUA9-S
No 1222, 152.83

97-125

97/09/26

1: 40, 000

LN 92 E

©1998 **Alberta**
AS4889-73

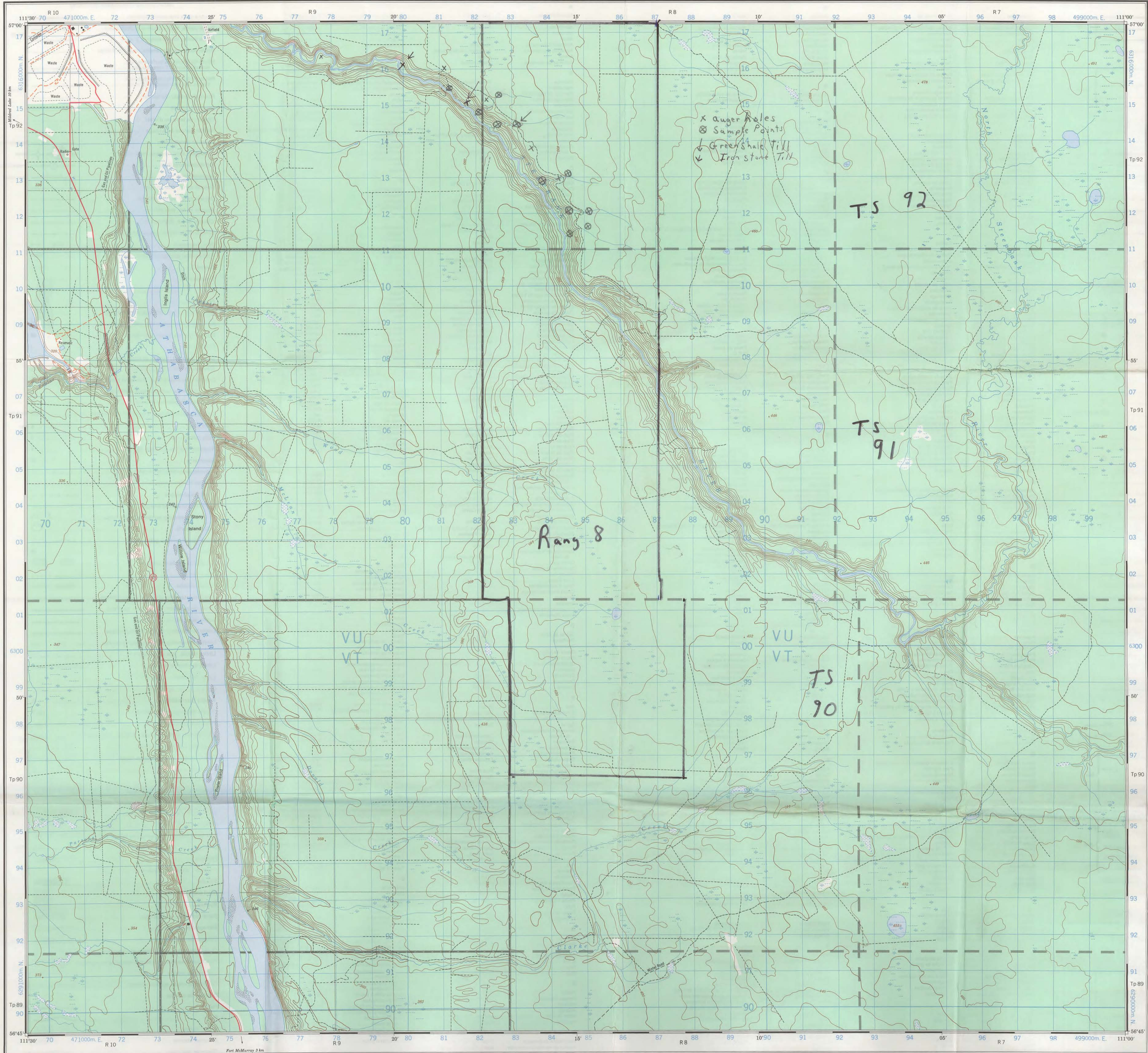
AIR PHOTO SERVICES (403) 427-3520

Printed By: GLOBAL REMOTE SENSING INC.
Edmonton, Alberta

North

Map 2[#]

151



Produced by the SURVEYS and MAPPING BRANCH, DEPARTMENT OF ENERGY, MINES AND RESOURCES, from information provided by the SURVEYS and MAPPING BRANCH, ALBERTA TRANSPORTATION. Aerial photographs 1974 and 1976. Culture check 1977. Information current as of 1976.

Copies may be obtained from the Canada Map Office, Department of Energy, Mines and Resources, Ottawa, or your nearest map dealer.

© 1979 Her Majesty the Queen in Right of Canada. Department of Energy, Mines and Resources.

Roads:
 hard surface, all weather pavé, toute saison
 hard surface, all weather pavé, toute saison
 loose or stabilized surface, all weather gravier, aggloméré, toute saison
 loose surface, dry weather de gravier, temps sec
 unclassified streets rues hors classe
 cart track de terre
 trail cut line or portage sentier, percée ou portage

FOR COMPLETE REFERENCE SEE REVERSE SIDE POUR UNE LISTE COMPLETE DES SIGNES, VOIR AU VERSO

WOOD CREEK
 IMPROVEMENT DISTRICT 18
 ALBERTA
 WEST OF FOURTH MERIDIAN - OUEST DU QUATRIÈME MÉRIDIDIEN
 Scale 1:50,000 Échelle

Metres 1 0 1000 2000 3000 4000 Mètres
 Yards 1000 0 1000 2000 3000 4000 Verges

Information concerning location and precise elevation of bench marks can be obtained by writing to the Geodetic Survey, Surveys and Mapping Branch, Ottawa.

CONVERSION SCALE FOR ELEVATIONS
 Metres 30 20 10 0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
 Feet 100 50 0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000

Contour Interval 10 Metres
 Elevation in Metres above Mean Sea Level
 North American Datum 1927
 Transverse Mercator Projection

On peut obtenir des renseignements sur le lieu et l'altitude exacte des repères de nivellement en écrivant aux Levés géodésiques, Direction des levés et de la cartographie, Ottawa.

ÉCHELLE DE CONVERSION DES ÉLEVATIONS
 Mètres 30 20 10 0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
 Pieds 100 50 0 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000

Épaisseur des courbes 10 mètres
 Élévation en mètres au-dessus du niveau de la mer
 Système de référence géodésique nord-américain, 1927
 Projection transverse de Mercator

Établi par la DIRECTION DES LEVÉS ET DE LA CARTOGRAPHIE, MINISTÈRE DE L'ÉNERGIE, DES MINES ET DES RESSOURCES, à partir des renseignements fournis par la DIRECTION DES LEVÉS ET DE LA CARTOGRAPHIE, TRANSPORT ALBERTA. Photographies aériennes prises en 1974 et 1976. Vérification des couvertures en 1977. Renseignements à jour en 1976.

Ces cartes sont en vente au Bureau des Cartes du Canada, ministère de l'Énergie, des Mines et des Ressources, Ottawa, ou chez le vendeur le plus près.

© 1979 Sa Majesté la Reine du Chef du Canada.
 Ministère de l'Énergie, des Mines et des Ressources.

Military users, refer to this map as: **MAP 74 D/14 CARTE**
 Références de cette carte pour usage militaire: **EDITION 3 MCE EDITION**

GLOSSARY GLOSSAIRE

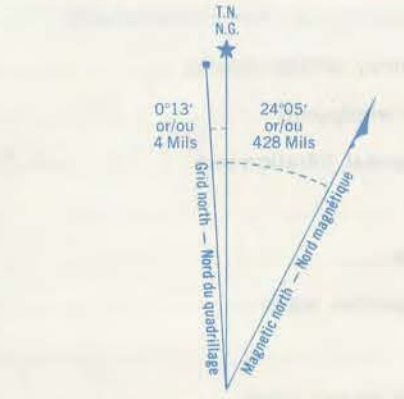
Airfield Terrain d'aviation
 Arena Arène
 City Limits Limites de ville
 Customs Douane
 Ditch Fossé
 Dump Déversoir
 Filtration Plant Usine de filtration
 Gas Gaz
 Golf Course Terrain de golf
 Junk Yard Ferraille
 Mile Mil
 Lookout Belvédère
 Mine Waste Débris de mine
 Oil Wells Puits de pétrole
 Park Parc
 Rank Patrouille
 Senior Citizens Home House de laje d'or
 Ski Area Station de ski
 String Bag Poubelle à filaments
 Swampy Lake Lac marécageux
 Tank Réservoir
 Water Eau
 Winter Road Chemin d'hiver

For a complete glossary see reverse side
 Pour un glossaire complet, voir au verso

ABBREVIATIONS ABRÉVIATIONS

Aband Abandonné, ée
 C Cemetery Cimetière
 Co County Comté
 E Elevator Élévateur
 Fr Ferry Traversier
 IR Indian Reserve Réserve indienne
 H Hospital Hôpital
 L Lot Lot
 Micro Micro Micro ondes
 Mun Municipality Municipalité
 P Post Office Bureau de poste
 PH Power House Centrale électrique
 RCMP Royal Canadian Mounted Police Gendarmes Royaux Canadienne

Res Reservoir Réservoir
 Trans Sta Transformer Station Poste de transformateur
 TFL Tree Farm Licence Licence de sylviculture



ONE THOUSAND METRE
 UNIVERSAL TRANSVERSE MERCATOR GRID
 ZONE 12
 QUADRILLAGE DE MÎLE MÈTRES
 TRANSVERSE UNIVERSAL DE MERCATOR

GRID ZONE DESIGNATION DÉSIGNATION DE LA ZONE DU QUADRILLAGE	100,000 M. SQUARE IDENTIFICATION IDENTIFICATION DU CARRÉ DE 100,000 M.
12 V	VU VT

EXAMPLE OF METHOD USED
 TO GIVE A REFERENCE TO NEAREST 100 METRES
 EXEMPLE DE LA MÉTHODE EMPLOYÉE
 POUR FURNIR DES REPÈRES À 100 MÈTRES PRÈS

REFERENCE POINT CHURCH - EGLISE (see above)
 POINT DE REPÈRE (voir ci-dessus)

EASTING: Read number on grid line immediately to left of point.
 LONGITUDE EST: Note le chiffre de la ligne du quadrillage immédiatement à gauche du repère.
 Estimate tenths of a square from this line northeast to point.
 Estimer le nombre de dixièmes du carré entre cette ligne et le repère en direction nord-est.

NORTHING: Read number on grid line immediately below point.
 LATITUDE NORD: Note le chiffre de la ligne du quadrillage immédiatement en dessous du repère.
 Estimate tenths of a square from this line southeast to point.
 Estimer le nombre de dixièmes du carré entre cette ligne et le repère en direction sud-est.

GRID REFERENCE: 975984
 Repère selon grille (référence 100,000 mètres autour 63 mètres)
 La précision relative est de 1:100,000 mètres (autour 63 mètres)

Coordinate Conversion NAD 27 to NAD 83 (WGS 84)
 Mean values for this map

Geographic: Latitude - add 0.4°
 Longitude - add 3.3°
 Grid: Northing - add 22m
 Easting - subtract 55m

Conversion des coordonnées NAD 27 à NAD 83 (WGS 84)
 Valeurs moyennes pour cette carte

Coordonnées géographiques: Latitude - additionner 0.4°
 Longitude - additionner 3.3°
 Grille: Northing (N) - additionner 22m
 Easting (E) - soustraire 55m

TABLEAU D'ASSEMBLAGE DU SYSTÈME NATIONAL DE RÉFÉRENCE CARTOGRAPHIQUE

74 D/13	74 D/14	74 D/15
74 D/12	74 D/11	74 D/10

INDEX TO ADJOINING MAPS OF THE NATIONAL TOPOGRAPHIC SYSTEM

MAP TOWN
 10815 - 100 AVE.
 EDMONTON, AB T5J 4X4
 Tel. 429-2800

WOOD CREEK
 74 D/14
 EDITION 3

Stony Bah River 149

CONVENTIONAL SIGNS

(Black unless otherwise stated)

GLOSSARY

M

GLOSSAIRE

SIGNES CONVENTIONNELS

(Noir à moins d'indication contraire)