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BACKGROUND LEVELS OF MERCURY AND ARSENIC IN PALEOPROTEROZOIC ROCKS OF THE MESABI IRON RANGE, NORTHERN MINNESOTA

UNIVERSITY OF MINNESOTA

Minnesota Geological Survey
D.L. Southwick, *Director*

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By

G.B. Morey and R.S. Lively

University of Minnesota
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BACKGROUND LEVELS OF MERCURY AND ARSENIC IN PALEOPROTEROZOIC ROCKS OF THE MESABI IRON RANGE, MINNESOTA

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G.B. Morey and R.S. Lively

INTRODUCTION

This study was primarily designed to calculate background levels of mercury and arsenic in the Biwabik Iron Formation of the Mesabi range. A second objective was to evaluate the ability of various laboratories to provide analytical data for mercury and arsenic that is reasonably priced yet sufficiently reliable for the purpose of environmental screening.

Mercury and arsenic where present in sufficient concentrations are considered to be hazardous substances. They may be naturally occurring, of anthropogenic origin, or some combination thereof. To establish natural background levels and to reduce the possibility of anthropogenic sources, 191 samples of the Biwabik Iron Formation were collected from drill-core sites located south of the Mesabi range (Fig. 1). Ten samples of the overlying Virginia Formation were also analyzed for comparison. Four of the selected sites were jointly drilled by the Minnesota Geological Survey and the Iron Range Resources and Rehabilitation Board (IRRRB) in 1966 and 1967; principal facts for these holes are summarized in Pfleider and others (1968). The fifth site, U.S. Steel 17,700 was drilled sometime in the 1950s, and the core was donated to the Minnesota Geological Survey in the late 1960s; principal facts for it are summarized in Morey and others (1972).

SAMPLE MATERIAL

The original joint project of the Minnesota Geological Survey and the Iron Range Resources and Rehabilitation Board was undertaken in 1966 and 1967 to evaluate the possible underground mining of taconite south of the Mesabi range. As part of the study, the Biwabik Iron Formation

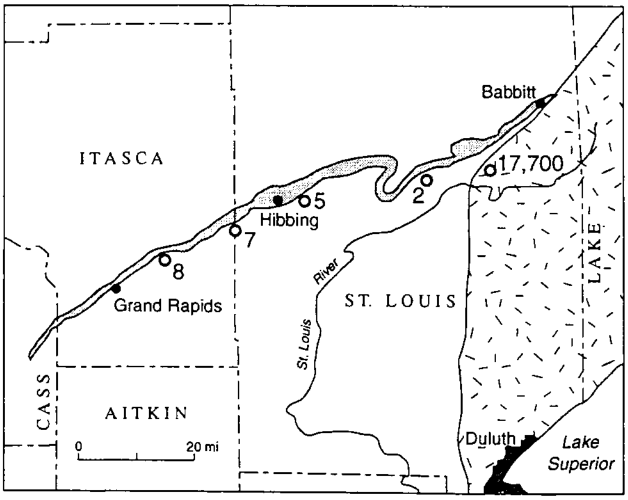

Figure 1. The Mesabi range, northern Minnesota, showing the locations of drill holes discussed in the text. Stipple represents generalized subcrop distribution of the Biwabik Iron Formation. Ticks represent subcrop distribution of the Duluth Complex.

Table 1. Thickness (in feet) of the Biwabik Iron Formation, Virginia Formation, and other geologic units penetrated by drill holes on the Mesabi range.

[Location of drill holes shown on Figure 1. Data for holes 2, 5, 7, and 8 from Pfleider and others (1968); data for hole 17,700 from Morey and others (1972). Leaders (--), no data]

HOLE	2 Biwabik	5 Buhl	7 Keewatin	8 Calumet	17,700 U.S. Steel
GEOLOGIC UNIT					
Glacial sediment	103	182	1213	214	25
Duluth Complex	--	--	--	--	198
Virginia Formation	1,486	305	577	1,131	522
Biwabik Iron Formation[1]					
Upper slaty	95	80	--	198	75
Upper slaty & Upper cherty	--	--	147	--	--
Upper cherty	202	262	--	109	175
Lower slaty	123	118	131	20	41
Lower cherty	193	233	282	337	--
Lower cherty & Basal red	--	--	--	--	111
Basal red	17	20	31	32	--
TOTAL IRON-FORMATION	630	713	591	692	402
Pokegama Quartzite	51+	52+	56+	7+	53
Basement	--	--	--	--	10
TOTAL DEPTH	2,270	1,252	1,437	2,044	1,210

[1] Stratigraphic interpretations for the Biwabik Iron Formation depend on the concept of intercalated cherty and slaty strata. *Cherty iron-formation* appears coarse grained in hand specimen; it also is thick bedded to massive, and rich in quartz and iron oxides. *Slaty iron-formation* is generally fine grained, finely laminated, and composed mostly of iron silicates and iron carbonates. From a sedimentological view, cherty strata mainly consist of reworked material, reflecting energetic bottom environments, whereas slaty strata in general represent essentially undistributed, chemically precipitated mud. Thus, the cherty rocks have textural attributes similar to so-called allochemical varieties of limestone. The slaty rocks have textural attributes akin to orthochemical varieties of limestone.

Beds or groups of beds that have cherty or slaty attributes are interlayered on all scales in the Biwabik Iron Formation. In general, the slaty members contain 40 percent or more slaty strata; the cherty members typically contain less than 30 percent slaty strata.

was classified according to stratigraphic nomenclature in use at that time by mining companies and exploration geologists. The resulting classification scheme (Table 1) was subsequently used by the Mineral Resources Research Center of the University of Minnesota to subdivide the iron-formation into intervals that generally measured five feet. The NX core (about 1-7/8 inches in diameter) was split and one half was returned to archives. That material is currently stored at the Department of Natural Resources, Division of Minerals Core Library in Hibbing, Minnesota. The remaining half was crushed to less than 150 mesh and again split into halves. One half of the crushed rock was used for crude ore analyses and standard Davis-tube tests as reported in Pfleider and others (1968). The remaining crushed material (approximately 1.95 kilograms in weight) was collected in cardboard boxes and stored first at the U.S. Bureau of Mines, Fort Snelling, Minnesota, and later at the Minnesota Geological Survey. For the current project, crushed material stored at the Minnesota Geological Survey was recovered and split four times to produce a sample weighing approximately 0.24 kilogram or 240 grams. That sample was in turn quartered to produce four duplicate samples, each weighing approximately 60 grams.

ANALYTICAL PROCEDURES

One hundred and ninety-one samples of the Biwabik Iron Formation and ten samples of the Virginia Formation were submitted to Xral Laboratories, Don Mills, Ontario, for analysis of mercury and arsenic. The rock samples were pulverized to 75 microns and digested in a mixed acid environment, from which mercury was recovered and analyzed by cold vapor absorption spectrometry. Arsenic was determined by atomic absorption spectrometry following digestion of the pulp by aqua regia and conversion to a hydride. Fourteen samples of iron-formation and one of the Virginia Formation were included as blind duplicates for comparative purposes. As part of internal quality-control procedures, Xral Laboratories also repeated analyses of nineteen samples. For the second part of the project, ten duplicate samples of iron-formation were submitted to Chemex Laboratories, Activation Laboratories, Ltd., and Frontier Geosciences, Inc., for analysis of mercury only. Lastly, ten of the original 191 samples were reanalyzed by Xral Laboratories for total organic carbon to test the hypothesis that a correlation could exist between mercury concentrations and carbonaceous material.

Chemex and Activation laboratories used analytical methods and equipment similar to those used by Xral. Detection limits for these laboratories were 5–10 ppb (parts per billion). Frontier Geoscience used digestion methods similar to the other labs but utilized cold vapor atomic fluorescence spectrometry to analyze mercury, rather than cold vapor atomic absorption spectrometry. Frontier estimated a detection limit of 0.5 ppb for mercury. All laboratories reported using quality-assurance and quality-control procedures involving replicate analyses and internal mercury standards. None of the internal standards, however, replicated the iron-formation matrix.

RESULTS

The results of the various analytical procedures are summarized in Tables 2–3. There is a good correlation among original, duplicate, and replicate analyses for mercury (Fig. 2) and arsenic (Fig. 3) as provided by Xral Laboratories. There also is a good correlation among the mercury data provided by Xral Laboratories, Activation Laboratories, and Chemex Laboratories (Fig. 2). However, for unknown reasons the results obtained from Frontier Geosciences are systematically low when compared to the other laboratories.

DISCUSSION

The data in Table 2 show a considerable spread in mercury values for the Biwabik Iron Formation—17 ppb to 1310 ppb. All the reported values are more than the lower detection limits of 0.5–10 ppb mercury.

Mercury values in the cherty rocks differ little from east (hole 2) to west (hole 7) along the Mesabi range (Fig. 4). Furthermore, little if any difference exists between cherty rocks, in which magnetite is the dominant iron oxide (the so-called Ore-zone rocks that contain magnetic iron equal to or more than 20 wt. percent), and cherty rocks, in which hematite is the dominant iron oxide (the so-called Basal-red rocks that contain magnetic iron equaling no more than 2 or 3 wt. percent) (Table 2).

The slaty rocks across the Mesabi range have mercury concentrations that are broadly similar to concentrations in the cherty rocks, although the slaty rocks tend to show a wider spread of values (Fig. 4). For example, nine slaty samples have more than 200 ppb mercury, whereas only five samples of cherty rock exceed that value. The Lower slaty rocks in hole 2 contain somewhat more mercury than do those in hole 7. Similarly, the Intermediate slate in hole 2 contains considerably more mercury than does the Intermediate slate in hole 5, and the Upper slaty rocks in hole 2 contain somewhat more mercury than do the Upper slaty rocks in hole 5. Collectively, these data suggest that mercury is more abundant in the slaty rocks at the east end of the range. Nonetheless, no significant stratigraphic or geographic constraints appear to limit the distribution of mercury in the Biwabik Iron Formation.

Although only ten samples of the Virginia Formation were analyzed, the data in Table 2 show some interesting results. Unmetamorphosed samples have mercury values in the range of 190–508 ppb. In contrast, samples of the Virginia Formation that are metamorphosed to the cordierite grade

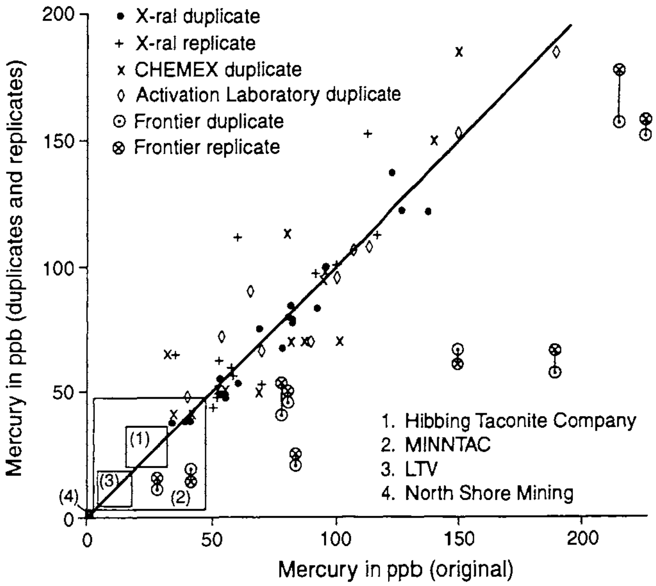

Figure 2. Correlation of duplicate and replicate analyses for mercury in the Biwabik Iron Formation as reported by various analytical companies. Squares represent ranges of values for various mining operations as reported by Coleraine Research Laboratories (1997). Vertical line between some points indicate replicate Frontier analyses.

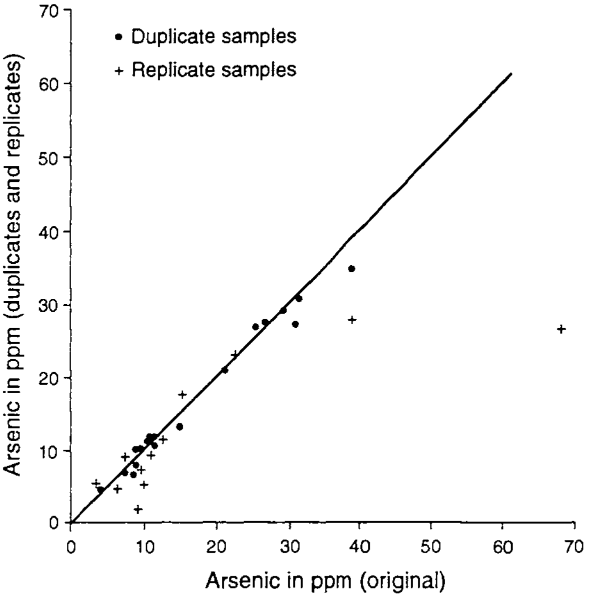

Figure 3. Correlation of Xral duplicate and replicate analyses for arsenic in the Biwabik Iron Formation, Mesabi range.

in U.S. Steel hole 17,700 contain only 29–38 ppb. The data suggest that metamorphic processes can effectively remove mercury from fine-grained shaly rocks.

Arsenic values in the Biwabik Iron Formation range from 0.5 ppm to 925 ppm (parts per million) (Table 3), and they are in relatively good agreement with duplicates and replicates (Fig. 3). Values are broadly similar across the Mesabi range (Fig. 5). Furthermore, there is no significant difference in concentrations reported from slaty strata and various kinds of cherty strata in hole 2 and hole 5. However, the Upper cherty and Lower slaty beds in hole 7 contain on average 2 to 2.5 times more arsenic than the Lower cherty beds.

Table 2. Mercury (in parts per billion) in the Biwabik Iron Formation and Virginia Formation, Mesabi range.

[Drill holes shown on Figure 1. Analytical procedures described in text. Leaders (--), no data; IRRRB, Iron Range Resources and Rehabilitation Board]

Depth in feet	Xral Laboratories					Frontier Geosciences
	Original	Xral internal replicate	MGS blind duplicate	Activation Laboratory	Chemex Laboratory	Replicate in parentheses
IRRRB Biwabik Hole 2 (SW1/4SE1/4, sec. 22, T. 58 N., R. 16 W.)						
BIWABIK IRON FORMATION						
Upper slaty						
1614–1617.9	210	--	--	--	--	--
1617.9–1620	163	--	--	--	--	--
1620–1624.5	340	--	--	--	--	--
1624.5–1627.8	172	--	--	--	--	--
1627.8–1633.4	226	--	--	--	--	152 (156.9)
1633.4–1635.7	236	--	--	--	--	--
1635.7–1645	1310	--	--	--	--	--
1645–1650	174	--	--	--	--	--
1650–1651.9	114	--	131	--	--	--
1651.9–1655.7	124	--	--	---	--	--
1655.7–1665	69	--	--	--	--	--
1665–1670	93	84	--	--	--	--
1670–1675	70	--	--	--	--	--
1675–1683.8	71	--	--	--	--	--
Lower slaty						
1886.2–1895	90	--	--	--	--	--
1895–1900	73	--	--	--	--	--
1900–1905	138	--	--	--	--	--
1905–1914.1	137	--	--	--	--	--
1914.1–1921.8	203	--	--	--	--	--
1921.8–1930	122	--	81	--	--	--
1930–1935	111	--	--	--	--	--
1935–1940	128	123	--	--	--	--
1940–1945	133	--	--	--	--	--
1945–1950	238	--	--	--	--	--
1950–1955	94	--	--	--	--	--
1955–1961.3	84	--	--	--	--	--
1961.3–1970	183	--	--	--	--	--
1970–1975	89	--	--	--	--	--
1975–1980	131	--	--	--	--	--
1980–1985	74	--	--	--	--	--
1985–1990	94	--	--	--	--	--
1990–1995	111	--	--	--	--	--
1995–2003.5	107	--	--	--	--	--
Intermediate slate						
2008.5–2008.8	405	459	--	--	--	342 (338)
Lower cherty						
2008.8–2013	216	--	--	--	--	158 (177)
2013–2018.1	79	68	42	--	--	--
2018.1–2026	98	--	--	--	--	--
2026–2034.4	56	--	--	--	--	--
2034.4–2040	87	--	--	--	--	--
2040–2045.8	53	--	63	--	--	--
2045.8–2053	83	--	--	--	--	--
2053–2058	29	--	--	--	--	--
2058–2064	41	38	--	--	--	--
2064–2070	108	--	--	--	--	--
2070–2075	34	--	--	--	--	--
2075–2080	53	--	42	--	--	--
2080–2085	60	--	--	--	--	--
Ore zone						
2130–2135	81	87	--	72	70	--
2135–2140	58	--	--	--	--	--
2140–2145	56	--	--	--	--	--
2145–2150	61	--	--	--	--	--
2150–2155	35	--	65	91	40	--
2155–2160	63	--	--	--	--	--
2160–2165.6	53	--	--	--	--	--
2165.6–2170	37	--	--	--	--	--
2170–2175	98	--	--	--	--	--
2175–2180	59	--	57	--	--	--
2180–2185	53	55	--	72	50	--
2185–2190	55	--	--	--	--	--
2190–2197	55	--	--	--	--	--
Basal red						
2197–2202	82	82	--	--	--	20.5 (22.8)
2202–2210	52	--	48	--	--	--
2210–2218	47	--	--	--	--	--
IRRRB Buhl Hole 5 (SE1/4NW1/4 sec. 36, T. 58 N., R. 20 W.)						
BIWABIK IRON FORMATION						
Upper slaty						
524.1–530	122	--	--	--	--	--
530–535.8	79	--	--	--	--	45.3 (47.2)

Continued on following page

Table 2 *continued.* Mercury (in parts per billion). . . .

Depth in feet	Xral Laboratories			Activation Laboratory	Chemex Laboratory	Frontier Geo-sciences
	Original	Xral internal replicate	MGS blind duplicate			Replicate in paren-theses
Upper slaty *continued*						
535.8–540	53	--	--	--	--	--
540–545	62	--	--	--	--	--
545–550	29	--	--	--	--	--
550–555	27	--	--	--	--	13.1 (15.1)
555–560	77	--	83	--	--	--
560–567	35	--	--	--	--	--
567–575.6	48	--	--	--	--	--
Lower cherty *and* **Ore zone**						
1080–1085	96	--	--	--	--	--
1085–1090	70	--	54	--	--	--
1090–1095	83	--	--	--	--	--
1095–1100	100	--	--	--	--	--
1100–1105	59	--	--	--	--	--
1105–1110	41	--	--	49	40	19.0 (17.9)
1110–1115	101	--	100	97	100	--
1115–1124	94	101	--	--	--	--
1124–1130	185	--	--	189	140	58.4 (65.7)
1130–1135	150	--	--	153	140	68.4 (62.3)

IRRRB Keewatin Hole 7

(NE1/4SE1/4 sec. 36, T. 57 N., R. 22 W.)

BIWABIK IRON FORMATION

Depth in feet	Xral Laboratories			Activation Laboratory	Chemex Laboratory	Frontier Geo-sciences
	Original	Xral internal replicate	MGS blind duplicate			Replicate in paren-theses
Upper cherty						
[1]792.2–800A	635	--	--	--	--	--
[1]792.2–800B	674	--	--	--	--	--
800–805	174	--	--	--	--	--
805–810	153	--	--	--	--	--
810–815	116	--	--	--	--	--
815–820	143	--	--	--	--	--
820–825	132	131	--	--	--	--
[1]825–834A	111	--	--	--	--	--
[1]825–834B	147	--	--	--	--	--
834–840	131	--	--	--	--	--
840–845	134	--	--	--	--	--
845–850	113	--	--	--	--	--
850–855	64	--	--	--	--	--
855–860	70	--	--	--	--	--
860–865	84	--	--	--	--	--
865–870	71	--	--	--	--	--
870–875	67	--	--	--	--	--
875–880	116	--	--	--	--	--
880–885	55	48	--	--	--	--
885–890	71	--	--	--	--	--
Upper cherty ***continued***						
890–895	53	--	--	--	--	--
895–900	48	--	--	--	--	--
900–905	50	--	--	--	--	--
905–910	106	--	--	--	--	--
910–917.1	117	--	--	--	--	--
917.1–920	72	--	--	--	--	--
920–925	78	--	--	--	--	--
925–930	67	--	--	--	--	--
930–936.1	36	--	--	--	--	--
936.1–937.8	309	--	--	--	--	--
Lower slaty						
937.8–945	50	--	44	--	--	--
945–950	52	--	--	--	--	--
950–955	69	--	--	67	50	--
955–960	44	--	--	--	--	--
960–965	51	--	--	--	--	--
965–970	78	--	--	--	--	--
970–975	82	85	--	--	--	--
975–980	[Sample missing]					
980–985	82	--	--	--	--	--
985–990	95	--	--	--	--	--
990–995	53	48	--	--	--	--
995–1000	64	--	--	--	--	--
1000–1005	60	--	--	--	--	--
1005–1010	63	--	--	--	--	--
1010–1015	58	--	--	--	--	--
1015–1020	73	--	--	--	--	--
1020–1025	51	--	--	--	--	--
1025–1030	68	--	--	--	--	--
1030–1038.2	44	--	--	--	--	--
1038.2–1045	62	--	--	--	--	--
1045–1050	66	--	--	--	--	--
1050–1056.3	80	--	--	--	--	--
1056.3–1061.1	[Sample missing]					
Intermediate slate						
1061.1–1067.9	241	255	260	--	--	--
Lower cherty						
1067.9–1069	203	--	--	--	--	--
1069–1075	209	--	--	--	--	--
1075–1080	139	--	--	--	--	--
1080–1085	83	--	--	--	--	--
1085–1090	46	--	--	--	--	--
1090–1095	153	--	--	--	--	--
1095–1100	68	--	--	--	--	--
1100–1105	93	--	--	--	--	--
1105–1112.7	63	--	--	--	--	--
1112.7–1120	102	--	--	--	--	--

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[1] The sample for this interval was stored in two boxes; material from each box (A and B) was analyzed separately.

Continued on following page

Table 2 *continued.* Mercury (in parts per billion). . . .

Depth in feet	Xral Laboratories					Frontier Geosciences
	Original	Xral internal replicate	MGS blind duplicate	Activation Laboratory	Chemex Laboratory	Duplicate in parentheses
Lower cherty *continued*						
1120–1125	69	76	--	--	--	--
[1]1125–1134A	113	--	--	--	--	--
[1]1125–1134B	61	--	--	--	--	--
1134–1140	43	--	18	--	--	--
1140–1145	64	--	--	--	--	--
1145–1150	23	--	--	--	--	--
1150–1155	56	--	--	--	--	--
1155–1160	65	--	--	--	--	--
Lower cherty *and* **Ore zone**						
1160–1165	42	--	--	--	--	--
1165–1170	68	--	--	--	--	--
1170–1175	113	--	--	109	80	42.4 (51.7)
1175–1180	52	--	--	--	--	--
1180–1185	67	--	--	--	--	--
1185–1190	94	--	--	--	--	--
1190–1195	57	--	--	--	--	--
1195–1200	106	--	--	107	70	--
1200–1205	86	--	--	--	--	--
1205–1210	76	--	--	--	--	--
1210–1215	73	--	--	--	--	--
1215–1220	60	54	--	--	--	--
Lower cherty						
1220–1225	54	--	--	--	--	--
1225–1230	46	--	--	--	--	--
1230–1237.4	63	--	--	--	--	--
1237.4–1245	39	40	--	--	--	--
1245–1250	43	--	--	--	--	--
1250–1255	68	--	--	--	--	--
1255–1260	44	--	--	--	--	--
1260–1265	54	--	--	--	--	--
1265–1270	51	--	--	--	--	--
1270–1275	64	--	--	--	--	--
1275–1280	46	--	--	--	--	--
1280–1285	75	--	--	--	--	--
[1]1285–1294A	91	--	--	--	--	--
[1]1285–1294B	98	--	--	--	--	--
[1]1294–1302A	122	--	--	--	--	--
[1]1294–1302B	139	123	--	--	--	--
[1]1302–1310A	57	--	--	--	--	--
[1]1302–1310B	78	--	--	--	--	--
1310–1315	35	--	--	--	--	--
1315–1320	69	--	--	--	--	--
1320–1325	68	--	--	--	--	--
1325–1330	73	--	--	--	--	--

Depth in feet	Xral Laboratories					Frontier Geosciences
	Original	Xral internal replicate	MGS blind duplicate	Activation Laboratory	Chemex Laboratory	Duplicate in parentheses
Lower cherty *continued*						
1330–1335	53	--	--	--	--	--
1335–1340	69	--	--	--	--	--
1340–1345	17	--	--	--	--	--
1345–1350.2	38	--	--	--	--	--
Basal red						
1350.2–1355	27	--	--	--	--	--
1355–1360	34	36	--	--	--	--
1360–1365	44	--	--	--	--	--
1365–1373.9	91	--	--	--	--	--
1373.9–1381.5	450	--	--	--	--	--

IRRRB Buhl Hole 5

(SE1/4NW1/4 sec. 36, T. 58 N., R. 20 W.)

Depth in feet	Original	Xral internal replicate	MGS blind duplicate	Activation Laboratory	Chemex Laboratory	Frontier Geosciences
VIRGINIA FORMATION						
202–203	386	--	--	--	--	[2]203
223–224	508	--	--	--	--	--

IRRRB Keewatin Hole 7

(NE1/4SE1/4 sec. 36, T. 57 N., R. 22 W.)

Depth in feet	Original	Xral internal replicate	MGS blind duplicate	Activation Laboratory	Chemex Laboratory	Frontier Geosciences
VIRGINIA FORMATION						
695–696	394	--	--	--	--	--
955–956	146	--	156	--	--	--

IRRRB Calumet Hole 8

(SE1/4NE1/4 sec. 36, T. 55 N., R. 24 W.)

Depth in feet	Original	Xral internal replicate	MGS blind duplicate	Activation Laboratory	Chemex Laboratory	Frontier Geosciences
VIRGINIA FORMATION						
267–268	190	--	--	--	--	--
815–816	338	--	--	--	--	--
970–971	168	--	--	--	--	--

U.S. Steel Hole 17,700

(NE1/4NW1/4NW1/4 sec. 34, T. 59 N., R. 14 W.)

Depth in feet	Original	Xral internal replicate	MGS blind duplicate	Activation Laboratory	Chemex Laboratory	Frontier Geosciences
VIRGINIA FORMATION						
350–351	29	--	--	--	--	--
542–543	38	--	--	--	--	--
595–596	35	--	--	--	--	--

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[1] The sample for this interval was stored in two boxes; material from each box (A and B) was analyzed separately.

[2] Only one sample for this interval was analyzed by Frontier Geosciences..

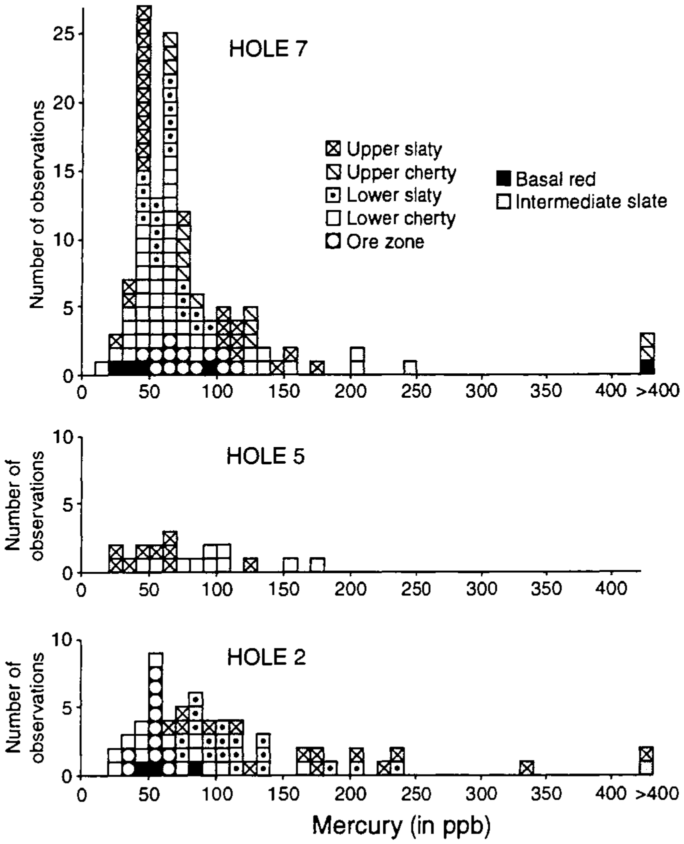

Figure 4. Mercury values by drill hole and stratigraphic unit in the Biwabik Iron Formation of the Mesabi range.

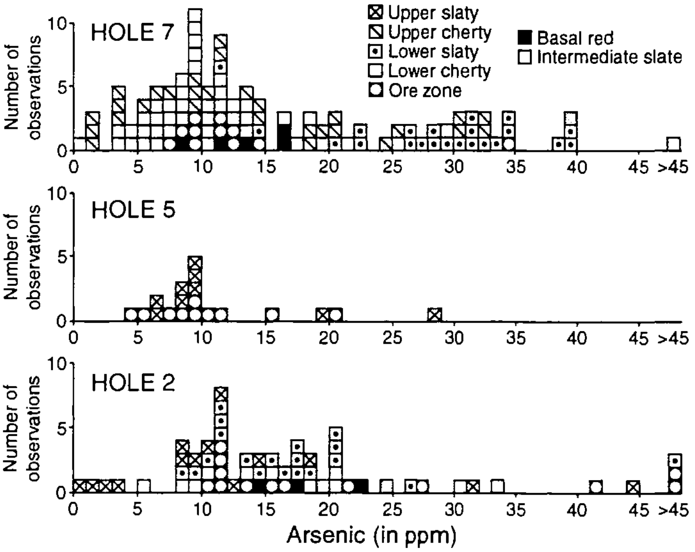

Figure 5. Arsenic values by drill hole and stratigraphic unit in the Biwabik Iron Formation of the Mesabi range.

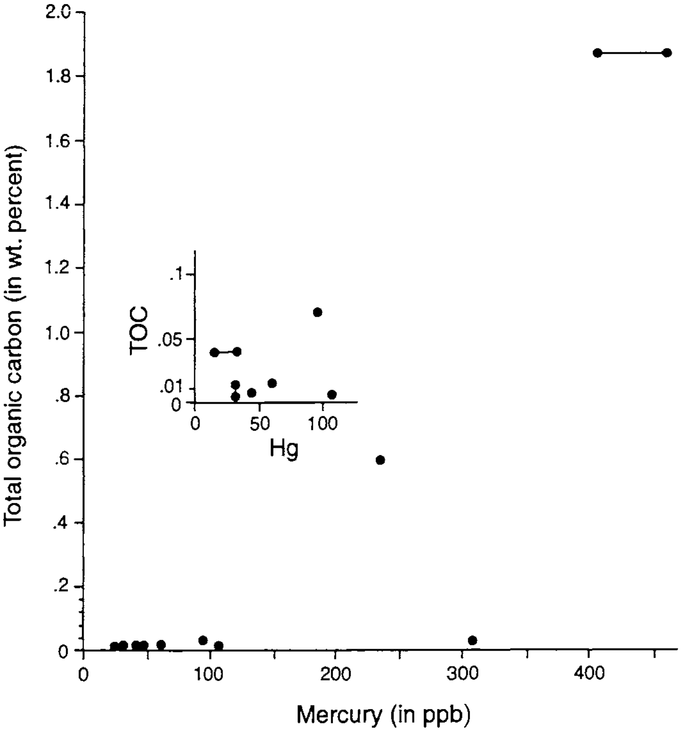

Figure 6. Content of mercury vs. total organic carbon in selected samples of the Biwabik Iron Formation, Mesabi range. Horizontal lines link replicate samples. TOC, total organic carbon; Hg, mercury.

Arsenic values are 2–17.1 ppm in unmetamorphosed samples from the Virginia Formation (Table 3), whereas metamorphosed samples are 3.7–16.3 ppm. The limited data suggest that the metamorphic processes had little effect on the distribution of arsenic.

It is noteworthy that seven of the ten analyzed samples of iron-formation contain 0.1 wt. percent or more total organic carbon (Table 4). One sample, the Intermediate slate from hole 2, contained 1.84 wt. percent total organic carbon and 405-459 ppb mercury. A second sample of cherty shale from hole 7 contained 309 ppb mercury, but less than 0.01 wt. percent total organic carbon. No correlation is apparent between mercury and total organic carbon in the Biwabik Iron Formation (Fig. 6).

CALCULATION OF BACKGROUND LEVELS

Although it is unknown why the results provided by Frontier Geosciences are systematically lower than the results provided by other analytical laboratories, the general coherence of the latter results suggest that the Xral data can be used to calculate provisional background levels for mercury and arsenic in the Biwabik and Virginia formations.

A background level is defined by the United States Environmental Protection Agency as "the concentration of a hazardous substance that provides a defensible reference point that can be used to evaluate whether or not the release of that hazardous substance from a site has occurred" (USEPA, 1995). The background level should reflect the concentration of the hazardous substance in the medium of concern for the environmental setting on or near the site (USEPA, 1995). Ideally, background sampling is conducted to distinguish site-related contamination from naturally occurring or other non-site-related levels of chemicals. Background samples should be collected at or near potentially hazardous waste sites from uncontaminated material that has the same basic characteristics as the medium of concern at the sites.

A variety of published statistical methods are available to calculate background levels in geologic materials (for example, Gilbert, 1987). According to Kesar and Asti (1999), such background calculations may be equated to the upper one-sided, 95-percent confidence limit of the mean concentration of each element. Using the Xral data, each element was tested for normality by D'Agostino's test for $n > 50$ (Gilbert, 1987). The results indicate that a lognormal model is the best distribution for both mercury and arsenic (Figs. 7 and 8). The data were transformed to natural logarithms, and the upper confidence limit (*UCL*) of the arithmetic mean of the transformed data was calculated by equation 1. The results have been converted to parts per billion or parts per million values for use in the following discussion.

$$95\%UCL = e(\bar{x} + 0.5s^2 + \frac{sH}{\sqrt{n-1}}) \qquad (1)$$

Where

$95\%UCL$ = upper confidence limit,
$\bar{x}$ = mean of the transformed data,
s = standard deviation of the transformed data,
H = H statistic (Gilbert, 1987), and
n = number of samples

MERCURY

Mercury values are 17–1310 ppb in the Biwabik Iron Formation. The Xral Biwabik data collectively display lognormal characteristics, have a calculated mean of 79.2 ppb, and a 95-percent upper confidence limit of 102 ppb. For comparative purposes, the mean and 95-percent upper confidence limits for so-called Ore-zone material in holes 2, 5, and 7 were calculated separately. The results differ only slightly from hole to hole (hole 2, $\bar{x}$ = 56.82 ppb and UCL = 68 ppb; hole 5, $\bar{x}$ = 90.2 ppb and UCL = 133 ppb; hole 7, $\bar{x}$ =70.9 ppb and UCL = 102 ppb) and from the collective Ore-zone values of $\bar{x}$ = 69.8 ppb and UCL = 86.6 ppb. Mean values for mercury in the Virginia Formation are 147 ppb with a 95-percent upper confidence limit of 825 ppb.

ARSENIC

Arsenic values are 0.5–92.5 ppm in the Biwabik Iron Formation. The data collectively have lognormal characteristics, a calculated mean of 12.9 ppm, and a 95-percent upper confidence limit of 18.5 ppm. These values are well within the range of arsenic values ($\bar{x}$ = 15 ppm; range <3–40 ppm) previously reported by Morey (1992). Mean values for arsenic in the Virginia Formation include an average of 9.4 ppm and a 95-percent upper confidence limit of 13.2 ppm.

CONCLUSIONS

An earlier study of Ore-zone iron-formation at several production facilities along the Mesabi range identified mercury levels in the general range of 0.75–45 ppb (Coleraine Minerals Research Laboratory, 1997). The values were provided by Frontier Geosciences, and they are considerably lower than concentrations from the Biwabik Iron Formation that were determined by the Xral, Chemex, and Activation laboratories for this study. However, the Coleraine results are closer to the lower mercury values reported by Frontier as part of this study. The results may be related to variations in how mercury is chemically extracted from samples, to differences in instruments used for the analysis, or to the mercury standards used by the laboratories. In regard to the question of extraction, Frontier Geosciences reanalyzed 10 samples using a different digestion procedure; the results obtained differed only slightly from their original data.

Problems associated with analytical procedures and equipment are generally resolved by using reference or calibration standards that involve an appropriate matrix and concentration. Unfortunately, no iron-formation standard is available. Mercury levels in the Biwabik Iron Formation must remain ambiguous until this issue is resolved. If the State of Minnesota wishes to move forward in environmental issues related to mercury, it should underwrite research involving analysis of mercury

Table 3. Arsenic (in parts per million) in the Biwabik Iron Formation and Virginia Formation, Mesabi range.

[Analysis by Xral Laboratories. Drill-hole locations shown on Figure 1. Analytical procedures described in text. Leaders (--), no data; IRRRB, Iron Range Resources and Rehabilitation Board; MGS, Minnesota Geological Survey.]

Depth in feet	Original	Xral internal replicate	MGS blind duplicate
IRRRB Biwabik Hole 2			
(SW1/4SE1/4 sec. 22, T. 58 N., R. 16 W.)			
BIWABIK IRON FORMATION			
Upper slaty			
1614-1617.9	12.3	--	--
1617.9–1620	10.9	--	--
1620–1624.5	14.9	--	--
1624.5–1627.8	31.9	--	--
1627.8-1633.4	44	--	--
1633.4–1635.7	18.9	--	--
1635.7–1645	10	--	--
1645–1650	12	--	--
1650–1651.9	0.7	--	1.9
1651.9–1655.7	1.7	--	--
1655.7–1665	2.2	--	--
1665–1670	3.9	4.5	--
1670–1675	8.2	--	--
1675–1683.8	8.1	--	--
Lower slaty			
1886.2–1895	17	--	--
1895–1900	18.4	--	--
1900–1905	20.4	--	--
1905–1914.1	14.5	--	--
1914.1–1921.8	26.1	--	--
1921.8–1930	12.3	--	11.4
1930–1935	8.6	--	--
1935–1940	11.1	11.8	--
1940–1945	92.5	--	--
1945–1950	17	--	--
1950–1955	9.4	--	--
1955–1961.3	10.2	--	--
1961.3–1970	20	--	--
1970–1975	13	--	--
1975–1980	16.7	--	--
1980–1985	11.9	--	--
1985–1990	17.9	--	--
1990–1995	20.9	--	--
1995–2003.5	15.6	--	--
Intermediate slate			
2003.5–2008.8	24.8	27.3	--
Lower cherty			
2008.8–2013	19.4	--	--
2013–2018.1	8.3	7.5	7.8
2018.1–2026	21.3	--	--
2026–2034.4	33.2	--	--
2034.4–2040	21.2	--	--
2040–2045.8	30.9	--	35.1
2045.8–2053	16.1	--	--
2053–2058	5.8	--	--
2058–2064	9.6	10	--
2064–2070	18.6	--	--
2070–2075	10.5	--	--
2075–2080	12.7	--	14.6
Lower cherty *continued*			
2080–2085	13.2	--	--
Ore zone			
2130–2135	21.2	22.2	--
2135–2140	11.6	--	--
2140–2145	10.3	--	--
2145–2150	11	--	--
2150–2155	11.9	--	12.6
2155–2160	41.2	--	--
2160–2165.6	11.7	--	--
2165.6–2170	15.9	--	--
2170–2175	54.9	--	--
2175–2180	68.2	--	26.6
2180–2185	27.5	30.2	--
2185–2190	16.8	--	--
2190–2197	13.2	--	--
Basal red			
2197–2202	14.8	13.3	--
2202–2210	22.2	--	31.7
2210–2218	17.1	--	--
IRRRB Buhl Hole 5			
(SE1/4NW1/4 sec. 36, T. 58 N., R. 20 W.)			
BIWABIK IRON FORMATION			
Upper slaty			
524.1–530	6.1	--	--
530—535.8	8.9	--	--
535.8–540	6.4	--	--
540–545	8.6	--	--
545–550	9.1	--	--
550–555	9.4	--	--
555–560	9.4	--	13
560–567	19.9	--	--
567–575.6	28.4	--	--
Lower cherty *and* Ore zone			
1080–1085	4.9	--	--
1085–1090	6.1	--	4.6
1090–1095	15.8	--	--
1095–1100	7.8	--	--
1100–1105	8.3	--	--
1105–1110	9.6	--	--
1110–1115	11.2	--	9.1
1115–1124	10	9	--
1124–1130	21.5	--	--
1130–1135	9.7	--	--
IRRRB Keewatin Hole 7			
(NE1/4SE1/4 sec. 36, T. 57 N., R. 22 W.)			
BIWABIK IRON FORMATION			
Upper cherty			
[1]792.2–800A	7.4	--	--
[1]792.2–800B	8.9	--	--
Upper cherty *continued*			
800–805	6.5	--	--
805–810	3	--	--
810–815	3	--	--
815–820	1.8	--	--
820–825	3.8	4.2	--
[1]825–834A	9.1	--	--
[1]825–834B	1.8	--	--
834–840	20.2	--	--
840–845	11.2	--	--
845–850	9	--	--
850–855	20.5	--	--
855–860	18.8	--	--
860–865	14.1	--	--
865–870	9.2	--	--
870–875	24.1	--	--
875–880	25.4	--	--
880–885	11.5	11.7	--
885–890	44.3	--	--
890–895	5.7	--	--
895–900	11.4	--	--
900–905	15	--	--
905–910	32.8	--	--
910–917.1	32.8	--	--
917.1–920	13.9	--	--
920–925	30.2	--	--
925–930	19.9	--	--
930–936.1	18	--	--
936.1–937.8	30.8	--	--
Lower slaty			
937.8–945	22.5	--	23.5
945–950	22.5	--	--
950–955	27.6	--	--
955–960	33.6	--	--
960–965	28.8	--	--
965–970	28.5	--	--
970–975	30.8	28.8	--
975–980	[sample missing]		
980–985	26.7	--	--
985–990	39.6	--	--
990–995	26.6	27.4	--
995–1000	32.4	--	--
1000–1005	34.6	--	--
1005–1010	31.0	--	--
1010–1015	39.9	--	--
1015–1020	34.2	--	--
1020–1025	31.4	--	--
1025–1030	29.8	--	--
1030–1038.2	31.7	--	--
1038.2–1045	20.3	--	--
1045–1050	14.7	--	--
1050–1056.3	12.8	--	--
1056.3–1061.1	[sample missing]		

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[1] The sample for this interval was stored in two boxes; material from each box (A and B) was analyzed separately.

Table 3 *continued.* Arsenic (in parts per million). . . .

Depth in feet	Original	Xral internal replicate	MGS blind duplicate
Intermediate slate			
1061.1–1067.9	39	35.2	27.9
Lower cherty			
1067.9–1069	19.5	--	--
1069–1075	16.5	--	--
1075–1080	8.3	--	--
1080–1085	3.8	--	--
1085–1090	4.9	--	--
1090–1095	3.1	--	--
1095–1100	1.5	--	--
1100–1105	0.5	--	--
1105–1112.7	11.2	--	--
1112.7–1120	6.2	--	--
1120–1125	6.8	7.5	--
[1]1125–1134A	5	--	--
[1]1125–1134B	10.5	--	--
1134–1140	10.4	--	6.4
1140–1145	9	--	--
1145–1150	5.2	--	--
1150–1155	7.1	--	--
1155–1160	5.1	--	--
Lower cherty *and* Ore Zone			
1160–1165	7.9	--	--
1165–1170	11.8	--	--
1170–1175	34	--	--
1175–1180	12.4	--	--
1180–1185	10.5	--	--
1185–1190	8.9	--	--
1190–1195	9	--	--
1195–1200	12.8	--	--
1200–1205	9.9	--	--
1205–1210	14.4	--	--
1210–1215	9.4	--	--
1215–1220	11.7	10.8	--
Lower cherty			
1220–1225	11.2	--	--
1225–1230	12.3	--	--
1230–1237.4	11.4	--	--
1237.4–1245	10.5	11.6	--
1245–1250	9.5	--	--
1250–1255	17.8	--	--
1255–1260	6.5	--	--
1260–1265	9.7	--	--
1265–1270	12.2	--	--
1270–1275	8.5	--	--
1275–1280	6.7	--	--
1280–1285	14.2	--	--
[1]1285–1294A	14.4	--	--
[1]1285–1294B	18.5	--	--
[1]1294-1302A	25.9	--	--
[1]1294-1302B	29.3	29.3	--
[1]1302-1310A	9.7	--	--
[1]1302-1310B	7.6	--	--
1310–1315	9.5	--	--
1315–1320	4.6	--	--
1320–1325	9.4	--	--
1325–1330	7.3	--	--
1330–1335	21.9	--	--
1335–1340	13.7	--	--
1340–1345	10.9	--	--
1345–1350.2	8.9	--	--
Basal red			
1350.2–1355	14.8	--	--
1355–1360	8.5	7.9	--
1360–1365	16.5	--	--
1365–1373.9	11.7	--	--
1373.9–1381.5	13.9	--	--

IRRRB Buhl Hole 5

(SE1/4NW1/4 sec. 36, T. 58 N., R. 20 W.)

Depth in feet	Original	Xral internal replicate	MGS blind duplicate
VIRGINIA FORMATION			
202–203	17.1	--	--
223–224	16.5	--	--

IRRRB Keewatin Hole 7

(NE1/4SE1/4 sec. 36, T. 57 N., R. 22 W.)

Depth in feet	Original	Xral internal replicate	MGS blind duplicate
VIRGINIA FORMATION			
695–696	9.9	--	--
955–956	2	--	2

IRRRB Calumet Hole 8

(SE1/4NE1/4 sec. 36, T. 55 N., R. 24 W.)

Depth in feet	Original	Xral internal replicate	MGS blind duplicate
VIRGINIA FORMATION			
267–268	9.9	--	--
815–816	12.1	--	--
970–971	10.4	--	--

U.S. Steel Hole 17,700

(NE1/4NW1/4NW1/4 sec. 34, T. 59 N., R. 14 W.)

Depth in feet	Original	Xral internal replicate	MGS blind duplicate
VIRGINIA FORMATION			
350–351	16.3	--	--
542–543	3.7	--	--
595–596	13	--	--

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[1] The sample for this interval was stored in two boxes; material from each box (A and B) was analyzed separately.

Table 4. Total organic carbon, mercury, and arsenic for selected samples from the Biwabik Iron Formation, Mesabi range.

[Values for total organic carbon from Xral Laboratories; values for mercury and arsenic are from Tables 2 and 3, respectively. IRRRB, Iron Range Resources and Rehabilitation Board; wt. percent, weight percent; ppb, parts per billion; ppm, parts per million]

Sample	**Depth** (feet)	**Total Organic Carbon** (wt. percent)	**Mercury** (ppb)	**Arsenic** (ppm)
IRRRB Biwabik Hole 2				
Upper slaty	1635.7-1645	0.01	1310	10
Lower slaty	1945-1950	0.6	238	17
Intermediate slate	2003.5-2008.8	1.84	405 ([1]459)	14.8 ([1]27.3)
Lower cherty	2053-2058	<0.01 ([1]0.01)	29	5.8
	2064-2070	<0.01	108	18.6
Ore zone	2170-2175	0.07	98	54.9
IRRRB Buhl Hole 5				
Upper slaty	550-555	0.04	27 ([2]13.1)	9.4
Lower cherty and Ore zone	1100-1105	0.01	59	8.3
IRRRB Keewatin Hole 7				
Upper cherty	936.1-937.8	<0.01	309	30.8
Lower cherty and Ore zone	1160-1165	<0.01	42	7.9

[1] Xral Laboratories internal replicate.
[2] Frontier Geosciences duplicate.

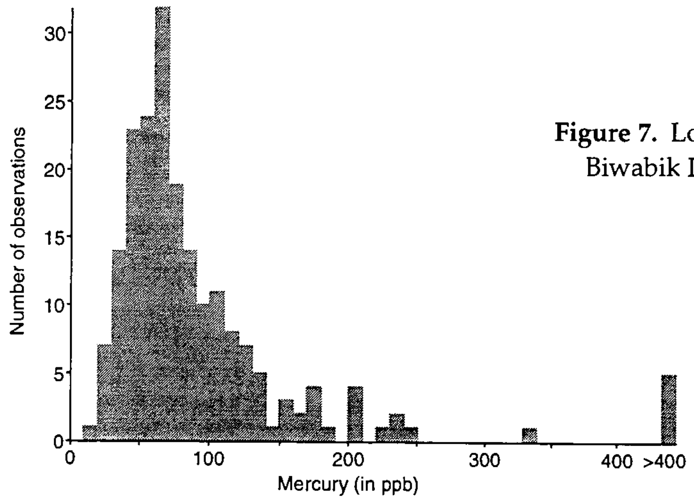

Figure 7. Lognormal distribution of mercury in the Biwabik Iron Formation, Mesabi range.

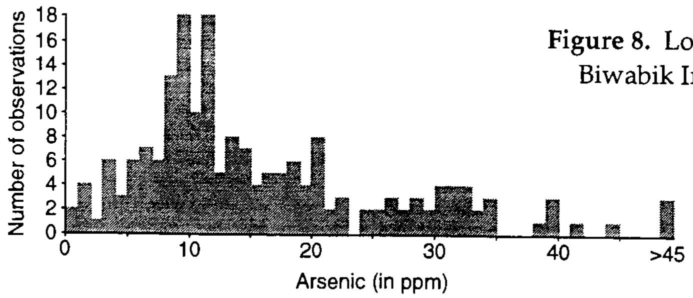

Figure 8. Lognormal distribution of arsenic in the Biwabik Iron Formation, Mesabi range.

at low concentrations and, specifically, the creation of several iron-formation standards that have known mineral compositions and a range of absolute concentrations of mercury.

ACKNOWLEDGMENTS

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