Canadian Mineralogist
Vol. 21, pp. 655-660 (1983)

Ir IN KEWEENAWAN BASALTS OF THE MAMAINSE POINT FORMATION, ONTARIO

N.W.D. MASSEY*, J.H. CROCKET AND A. KABIR

Department of Geology, McMaster University, Hamilton, Ontario L8S 4M1

ABSTRACT

Olivine-phyric lavas of the Mamainse Point Formation (Lake Superior, Ontario) show an average Ir content of 0.48 ppb. This is about ten times that of overlying plagioclase-phyric lavas, which average 0.041 ppb Ir. Similar though smaller differences in Cr and Ni contents of the two rock types appear to result from the incorporation of earlier-formed cumulate olivine and chromite into the olivine-phyric lavas. Ir tenors of plagioclase-phyric lavas may thus be more representative of this Proterozoic sequence; they are comparable to those found in modern ocean-floor basalts and ancient ophiolitic suites.

Keywords: geochemistry, basalt, Proterozoic, Mamainse Point Formation, Ontario, iridium, chromium, nickel, cumulates.

SOMMAIRE

Les laves à phénocristaux d'olivine de la formation de Mamainse Point (lac Supérieur, Ontario) contiennent, en moyenne, 0.48 ppb d'iridium, soit environ dix fois plus que les coulées à phénocristaux de plagioclase qui les recouvrent (0.041 ppb). Des différences moins frappantes dans la concentration de Cr et de Ni dans ces deux types de basaltes résulteraient de l'incorporation de cumulats d'olivine et de chromite dans les laves à olivine. La teneur en iridium des basaltes à plagioclase serait donc la plus représentative de cette séquence protérozoïque; ces roches sont comparables, à ce point de vue, aux basaltes des fonds océaniques modernes et des suites ophiolitiques anciennes.

(Traduit par la Rédaction)

Mots-clés: géochimie, basalte, protérozoïque, formation de Mamainse Point, Ontario, iridium, chrome, nickel, cumulats.

INTRODUCTION

The Mamainse Point – Alona Bay area lies at the eastern end of Lake Superior, about 80 km north of Sault Ste Marie (Fig. 1). The late Proterozoic Mamainse Point Formation, of Keweenawan age, rests unconformably on the Archean granite–greenstone terrane of the Superior Province. A thickness of 4000 to 5000 m of the formation is exposed; it is dominated by mafic flows, with subordinate shallow-level felsic intrusive bodies and interlayered coarse clastic sediments (Annells 1973, Thomson 1953).

The mafic flows are mainly ophitic or melaphyric in lithology, although occasional coarser gabbroic and glomeroporphyritic types are found. Sparse (5%) phenocrysts of olivine or plagioclase (or both) are developed in many flows, with olivine-phyric flows at the base of the sequence giving way to plagioclase-phyric flows higher up. Some of the olivine-phyric flows may contain up to 20% olivine phenocrysts, suggesting the incorporation of early-formed cumulate olivine in these flows.

Low-grade burial metamorphism in the zeolite and prehnite–pumpellyite facies has resulted in alteration of the original mineralogy, with only augite remaining relatively fresh. The effects of alteration are most severe in vesicular zones at the tops and bottoms of flows. Consequently, the data presented here have been determined on samples collected from flow centres.

Fortunately, a large group of elements (Al, Fe, Mg, Ti, P, Y, Zr, Nb, Ni, Cr, Co, *REE*, Th, Ta, Hf and U) appear to have been immobile or only moderately affected by geochemical readjustments accompanying burial metamorphism (Massey 1980). Stratigraphic variation in these immobile elements reveals trends with stepwise cyclicity that allow the Mamainse Point sequence to be subdivided into five successive series (Massey 1980). The Alona Bay volcanic rocks are believed to be stratigraphically equivalent to the series-I lavas of Mamainse Point; both are olivine-phyric. The others series (II–V) are plagioclase-phyric. CIPW norms and discriminant diagrams based on immobile elements allow the volcanic rocks to be classified as tholeiites.

The petrogenesis of the Mamainse Point volcanic rocks was modeled from major and immobile trace-element abundances, including rare-earth elements, by Massey (1980).The preferred model for magma generation, which relies heavily on rare-earth patterns, suggests that parental magmas were generated by dynamic melting within a rising diapir of garnet lherzolite mantle. Incompatible element ratios, particularly Th/U, imply that volcanic rocks of series I, II and III were formed from one diapir, whereas rocks of series IV and V were probably generated in a second diapir labeled with a slightly different Th/U ratio. Variation trends in Al_2O_3, FeO_t, MgO, TiO_2, Ni and Cr in the five volcanic series suggest

*Present address: Precambrian Section, Ontario Geological Survey, 77 Grenville Street, Toronto, Ontario M5S 1B3.

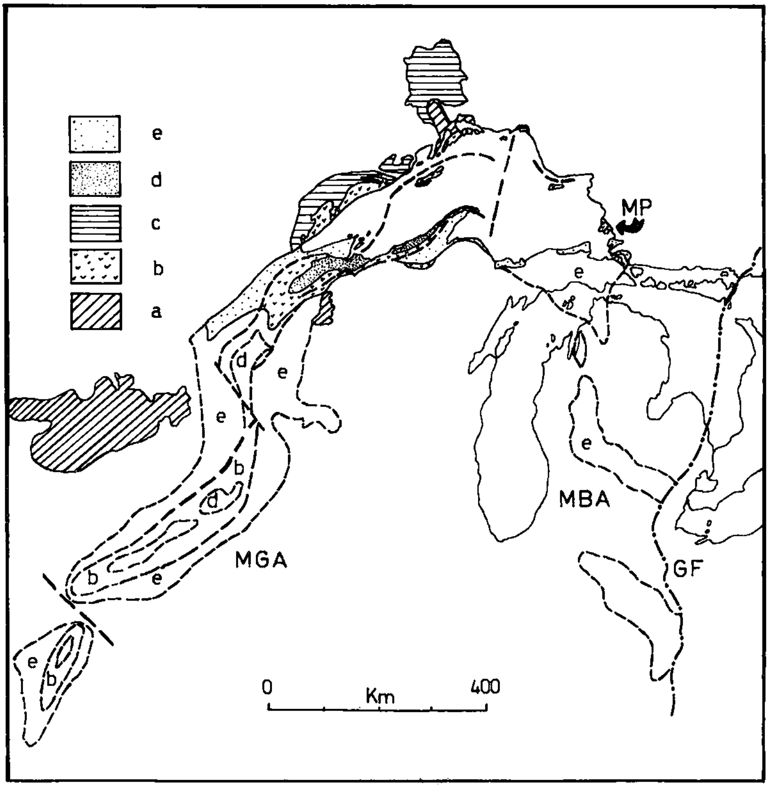

FIG. 1. Generalized geological map of the Keweenawan Rift, Lake Superior area. a: Pre- and Lower Keweenawan sediments, b: Lower and Middle Keweenawan volcanic rocks, c: intrusive rocks, d: Oronto Group and equivalents, e: Bayfield–Jacobsville Group. Strata are shown shaded where exposed, unshaded where buried beneath the Palaeozoic cover (boundaries shown with dashed line). Major faults are indicated by heavy dashed lines. MP Mamainse Point, MBA Michigan Basin gravity anomaly, MGA Midcontinent Geophysical Anomaly, GF Grenville Front.

that shallow-level fractional crystallization of olivine, plagioclase and very small amounts of chromite has occurred.

Ir Results and Discussion

Iridium was determined by radiochemical neutron-activation analysis using, with minor modification, the procedure of Crocket *et al.* (1968). Samples of 250 mg were irradiated in the McMaster reactor at a neutron flux of approximately 10^{13} neutrons/cm^2/s for 3 days. After a decay period of 3 weeks, Ir was separated radiochemically and the 74-day ^{192}Ir counted on an intrinsic germanium detector. The sensitivity limit for Ir is 0.005 ppb.

Ir Results and Discussion

Ir contents, along with Ni and Cr, are listed for individual samples in Table 1. Averages for the various series are given in Table 2, together with the averages for the olivine-phyric and plagioclase-phyric flows. The major feature of the data is the clear distinction between olivine-phyric and plagioclase-phyric lavas. Ir values differ by an order of magnitude, 0.48 ppb for olivine-phyric flows compared to 0.041 ppb for the plagioclase-phyric flows. Similar differences are also found in the Cr and Ni contents, which are higher in olivine-phyric flows by factors of 5.5 and 3, respectively. There are no significant differences in average Ir content of the Ir-poor plagioclase-phyric flows of series II–V (Table 2). Differences in average Ni and Cr content of the plagioclase-phyric flows are more distinct. Plots of Ir against Cr and against Ni are shown in Figures 2 and 3, respectively.

For the total population of 54 samples, there is a strong positive correlation between Ir, Ni and Cr.

TABLE 1. Ir, Ni AND Cr CONTENTS OF BASALTS FROM THE MAMAINSE POINT FORMATION

Series	Sample No.	Ir ppb	Ni ppm	Cr ppm	Series	Sample No.	Ir ppb	Ni ppm	Cr ppm
Series I	6	·0.356	176	721	Series IV	66	0.085	44	86
	8	1.350	835	2353		67	0.044	73	128
	10	0.244	168	733		69	0.040	45	126
	13	0.318	171	479		71	0.036	42	106
	14	0.319	173	699		72	0.059	19	98
	15	0.400	153	624		74	0.036	40	186
	19	0.804	552	1113		75	0.054	113	150
	22	0.466	210	786		76	0.061	176	116
	23	0.456	360	618		77	0.031	11	24
Series II	27	0.036	120	241		78	0.054	137	136
	28	0.053	166	190		79	<0.005	<5	18
	29	0.033	137	315		81	0.023	28	86
	36	0.023	80	153		87	0.015	41	64
	37	0.029	106	300	Series V	2	0.079	162	248
	47	0.020	61	191		4	0.047	173	273
Series III	51	0.039	127	104		82	0.015	281	274
	52	0.031	128	102		84	0.019	254	388
	54	0.038	138	98		89	0.019	271	292
	54A	0.040	83	406		92	0.066	202	245
	55	0.036	181	172		93	0.026	139	253
	57	0.065	144	164		96	0.020	88	173
	58	0.066	168	146		97	0.043	196	266
	60	0.140	165	164		100	0.048	147	224
	62	0.016	31	56		112	0.030	37	201
	63	0.025	37	156	Alona Bay	102	0.410	398	996
						103	0.574	372	1058
						105	0.291	351	1058
						113	0.409	351	1222
						115	0.327	369	1260

TABLE 2. AVERAGE Ir, Ni AND Cr CONTENTS OF BASALT SERIES, MAMAINSE POINT FORMATION

Locality	Series	Ir ppb	Ni ppm	Cr ppm
Alona Bay		0.40	366	1119
Mamainse Point	I	0.52	311	903
	II	0.032±0.012	112±38	232±65
	III	0.050±0.035	120±53	157±95
	IV	0.042±0.021	59±52	102±48
	V	0.039±0.021	177±75	258±55
Ol-phyric (Alona Bay +I)		0.48	331	980
Plag-phyric (II-V)		0.041	115	178

Note: Series are numbered from base upward.

The relevant correlation-coefficients, *r*(Ir *versus* Ni) and *r*(Ir *versus* Cr), are 0.86 and 0.92, respectively, and are significant at a 0.1% level. However, with few exceptions, these elements are not strongly correlated within the subpopulations represented by the various series. Except for the olivine-phyric, Ir-rich series-I basalts and the Ir *versus* Ni correlation in series-II rocks, no correlations significant to better than a 5% confidence level were found for either Ir *versus* Ni or Ir *versus* Cr in any of the various rock-series. The strong positive correlations found for the total population arise in part from the essentially bimodal distribution of data, in which the olivine-phyric rocks represent a high Ir–Ni–Cr subpopulation and the plagioclase-phyric rocks constitute a low Ir–Ni–Cr subpopulation.

The Ir–Ni–Cr correlations for the nine series-I rocks are 0.97 and 0.96 for Ir *versus* Ni and Ir *versus* Cr, respectively; these correlations are significant at >0.1% confidence level. These strong positive correlations, the olivine-phyric character, and the high Ir, Ni and Cr contents of these rocks suggest a strong association of all three metals with olivine. The strong partition of nickel into olivine from basic magma is well known. Massey (1980) found that precipitation of small amounts of chromite was required to account for the Cr content of the various volcanic series using the fractional crystallization

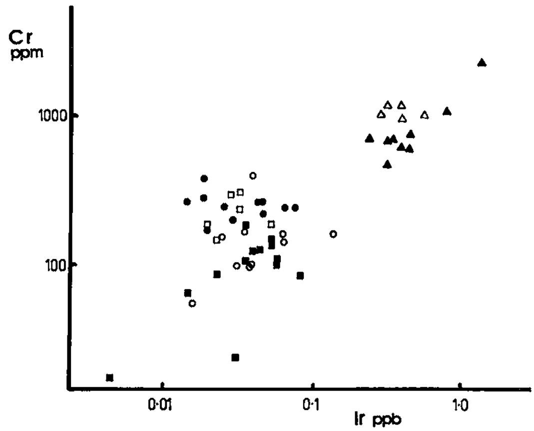

FIG. 2. Cr *versus* Ir for Mamainse Point basalts. Samples are divided into series (see Table 1): open triangles Alona Bay volcanic suite, closed triangles series I, open squares series II, open circles series III, closed squares series IV, closed circles series V.

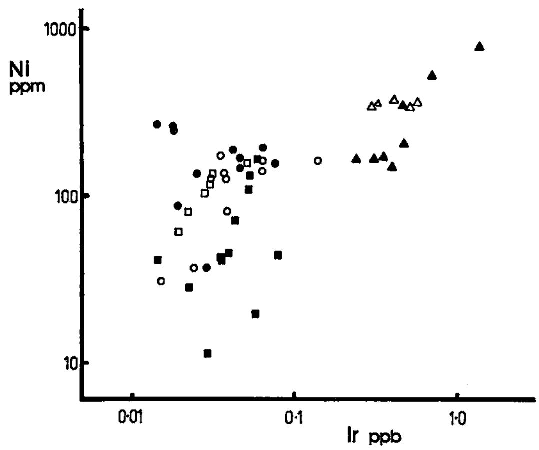

FIG. 3. Ni *versus* Ir for Mamainse Point basalts. Symbols as in Fig. 2.

modeling-techniques of Allègre *et al.* (1977). It is suggested that all these observations are reasonably accounted for by proposing that the olivine grains of series-I rocks carry minute inclusions of chromite, which in turn concentrate Ir. The concentration of Ir by chromite has been demonstrated in several studies of mineral separates from sulfur-poor mafic and ultramafic rocks (Gijbels *et al.* 1974, 1976, Oshin & Crocket 1982).

Concentration of Ir with olivine in mafic-ultramafic rocks has been suggested in other studies. Keays & Davison (1976) found an enrichment of Ir in sulfur-poor dunitic komatiites from Western Australia. Keays (1982) argued that Ir is concentrated with olivine in dunitic komatiites and that the concentration mechanism is probably an early precipitation of an iridium–osmium alloy along with olivine. It was also noted that Ir enrichment in sulfur-poor olivine-rich rocks is characteristic of those rocks that crystallize in a plutonic environment, being usually absent in extrusive komatiites. Whereas the Mamainse Point volcanic rocks are tholeiitic and generally much poorer in Ir than komatiitic rocks, the tendency for olivine of plutonic rocks to show Ir enrichment is compatible with the suggestion presented here for the Mamainse Point olivine-phyric volcanic rocks. As olivine, along with plagioclase and chromite, are inferred to be on the liquidus at extrusion, it is probable that a significant fraction of these minerals precipitated as cumulates in high-level magma chambers and that the Ir enrichment took place in this environment. Whereas the precise mechanism by which the Ir–olivine association becomes established is uncertain, a strong case can be made for chromite as the Ir concentrator on a basis of high Cr content and high positive Cr–Ir correlation in olivine-phyric rocks, and model calculations that require the precipitation of small amounts of chromite, possibly as small inclusions within olivine.

Another possible explanation of the high Ir content of the olivine-phyric rocks is that they carry magmatic sulfides. Whereas the Ir–Ni correlation might arise by concentration of the metals in sulfide, the Ir–Cr correlation is not explained by a sulfide control, and this mechanism is discounted as a likely means of concentrating Ir in the olivine-phyric volcanic rocks. Phenocrysts are the distinctive characteristic of these lavas and can explain the high Ir, Ni and Cr if the olivine is interpreted as being concentrated in earlier-formed cumulates that have been variably incorporated into the lavas. This mechanism would be expected to have profound effects on the compatible elements, such as Ir, but little effect on mildly compatible or incompatible elements. To fully explain the Ir and Cr data, however, some chromite must also be incorporated, possibly as small inclusions within the olivine grains.

TABLE 3. AVERAGE Ir CONTENTS (ppb) OF SULFUR-POOR MAFIC ROCKS

	n	Ir, ppb	References
Ocean-floor basalt (mainly Mid-Atlantic Ridge)	39	<0.057	a,d,f,h,i,j
Oceanic intraplate and off-ridge island basalts (mainly tholeiites)	27	0.36	a,b,e,f
Continental plateau basalts (mainly tholeiites from Parana, Karroo, Deccan and Columbia River)	54	0.092	b,c
Diabase dykes, North and South Carolina	9	0.27	f
Great Lake dolerite, Tasmania	20	0.082	g
Ophiolitic Mg-rich basalt	8	0.056	k
Ophiolitic Fe-rich basalt	10	0.019	k

References: a Baedecker et al. (1971), b Crocket unpubl. data, c Crocket & Skippen (1966), d Crocket & Teruta (1977), e Crocket et al. (1973), f Gottfried & Greenland (1972), g Greenland (1971), h Hertogen et al. (1980), i Keays & Scott (1976), j Laul et al. (1972), k Oshin (1981).
n: number of samples

COMPARISON WITH OTHER AREAS

Although only a relatively small data-base is available, comparison of Ir contents in the Mamainse Point Formation volcanic rocks with those of basalts from other areas is useful. Table 3 includes basalts, mainly tholeiites, from several settings: ocean-floor basalts, oceanic and continental intraplate basalts. Although there is some variation within each group (due to different degrees of fractionation, for example) that is not apparent in the tabulation, there is a significant difference in average Ir contents in basalts from different geological settings. In particular, ocean-floor and ophiolitic basalts show low Ir contents (0.056 ppb), whereas intraplate basalts are much richer in Ir (0.36 ppb). The continental plateau basalts are also higher than ocean-floor basalts and compare more closely with the oceanic within-plate basalts.

A cursory comparison might suggest that the olivine-phyric volcanic rocks of the Mamainse Point Formation are comparable to the oceanic intraplate and continental plateau basalts, whereas the plagioclase-phyric rocks are comparable with the ocean-floor basalts. However, if the higher Ir contents of the olivine-phyric lavas result from inclusion of earlier-formed cumulate olivine and chromite, their useful comparison with other rock suites may be precluded. It is suggested that the low Ir content of the plagioclase-phyric rocks is more representative of the parental magma. Data on immobile incompatible elements for the Mamainse Point Formation tholeiites has already led to the suggestion that they compare very closely with ocean-floor basalts (Massey 1980). Ir data seem compatible with this conclusion.

This comparison is interesting because the Mamainse Point Formation, like other Keweenawan sequences, is subaerial and believed to have accumulated in an elongate rift (King & Zietz 1971, Chase & Gilmer 1973). The Ir data presented here, along with geophysical (Halls 1978) and other geochemical data (Massey 1980), lead to the interpretation of the Keweenawan Rift as an immature proto-oceanic rift.

ACKNOWLEDGEMENTS

The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. Scholarship support to the senior author from the Natural Sciences and Engineering Research Council of Canada and the Ontario Graduate Scholarship Program is appreciated. The thoughtful comments of the two referees contributed significantly to the improvement of the final manuscript.

REFERENCES

ALLÈGRE, C.J., TREUIL, M., MINSTER, J.-F., MINSTER B. & ALBARÈDE, F. (1977): Systematic use of trace elements in igneous processes. I. Fractional crystallization processes in volcanic suites. *Contr. Mineral. Petrology* **60**, 57-75.

ANNELLS, R.N. (1973): Proterozoic flood basalts of eastern Lake Superior: the Keweenawan volcanic rocks of the Mamainse Point area, Ontario. *Geol. Surv. Can. Pap.* **72-10.**

BAEDECKER, P.A., SCHAUDY, R., ELZIE, J.L., KIMBERLIN, J. & WATSON, J.T. (1971): Trace element studies of rocks and soils from Oceanus Procellarum and Mare Tranquillitatis. *Proc. 2nd Lunar Sci. Conf.* **2**, 1037-1061.

CHASE, C.G. & GILMER, T.H. (1973): Precambrian plate tectonics: the Midcontinent gravity high. *Earth Planet. Sci. Lett.* **21**, 70-78.

CROCKET, J.H., KEAYS, R.R. & HSIEH, S. (1968): Determination of some precious metals by neutron activation analysis. *J. Radioanal. Chem.* **1**, 487-507.

______, MACDOUGALL, J.D. & HARRISS, R.C. (1973): Gold, palladium and iridium in marine sediments. *Geochim. Cosmochim. Acta* **37**, 2547-2556.

______ & SKIPPEN, G.B. (1966): Radioactivation determination of palladium in basaltic and ultrabasic rocks. *Geochim. Cosmochim. Acta* **30**, 129-141.

______ & TERUTA, Y. (1977): Palladium, iridium and gold contents of mafic and ultramafic rocks drilled from the Mid-Atlantic Ridge, Leg 37, Deep Sea Drilling Project. *Can. J. Earth Sci.* **14**, 777-784.

GIJBELS, R., HENDERSON, P. & ZELS, J. (1976): Geochemistry of some trace elements in mineral separates from Rhum, Inner Hebrides, with special emphasis on iridium. *Econ. Geol.* **71**, 1364-1370.

______, MILLARD, H., DESBOROUGH. G. & BARTEL, A. (1974): Osmium, ruthenium, iridium and uranium in silicates and chromite from the eastern Bushveld Complex, South Africa. *Geochim. Cosmochim. Acta* **38**, 319-337.

GOTTFRIED, D. & GREENLAND, L.P. (1972): Variation of iridium and gold in oceanic and continental basalts. *Int. Geol. Cong. (24th)* **10**, 135-144.

GREENLAND, L.P. (1971): Variation of iridium in a differentiated tholeiitic dolerite. *Geochim. Cosmochim. Acta* **35**, 319-322.

HALLS, H.C. (1978): The Late Precambrian Central North American Rift System - a survey of recent geological and geophysical investigations. *In* Tectonics and Geophysics of Continental Rifts (I.B. Ramberg & E.-R. Neumann, eds.). D. Reidel, Dordrecht, The Netherlands.

HERTOGEN, J., JANSSENS, M.-J. & PALME, H. (1980): Trace elements in ocean ridge basalt glasses: implications for fractionation during mantle evolution and petrogenesis. *Geochim. Cosmochim. Acta* **44**, 2125-2143.

KEAYS, R.R. (1982): Palladium and iridium in komatiites and associated rocks: application to petrogenetic problems. *In* Komatiites (N.T. Arndt & E.G. Nisbet, eds.). G. Allen and Unwin, London.

______ & DAVISON, R.M. (1976): Palladium, iridium and gold in the ores and host rocks of nickel sulfide deposits in Western Australia. *Econ. Geol.* **71**, 1214-1228.

______ & SCOTT, R.B. (1976): Precious metals in ocean ridge basalts: implications for basalts as source rocks for gold mineralization. *Econ. Geol.* **71**, 705-720.

KING, E.R. & ZIETZ, I. (1971): Aeromagnetic study of the Midcontinent Gravity High of central United States. *Geol. Soc. Amer. Bull.* **82**, 2187-2208.

LAUL, J.C., KEAYS, R.R., GANAPATHY, R., ANDERS, E. & MORGAN, J.W. (1972): Chemical fractionations in meteorites. V. Volatile and siderophile elements in achondrites and ocean ridge basalts. *Geochim. Cosmochim. Acta* **36**, 329-345.

MASSEY, N.W.D. (1980): *The Geochemistry of some Keweenawan Metabasites from Mamainse Point, Ontario.* Ph.D. thesis, McMaster Univ., Hamilton, Ontario.

OSHIN, I.O. (1981): *The Abundances and Geochemistry of some Noble Metals in Thetford Mines Ophiolites, P.Q.* Ph.D. thesis, McMaster Univ., Hamilton, Ontario.

——— & CROCKET, J.H. (1982): Noble metals in Thetford Mines ophiolites, Quebec, Canada. I. Distribution of gold, iridium, platinum, and palladium in the ultramafic and gabbroic rocks. *Econ. Geol.* **77**, 1556-1570.

THOMSON, J.E. (1953): Geology of the Mamainse Point copper area. *Ont. Dept. Mines Ann. Rep.* **62**(4).

Received May 14, 1982, revised manuscript accepted March 3, 1983.