CANADIAN PRECAMBRIAN IRON-FORMATIONS: AGES AND TRACE ELEMENT COMPOSITIONS

by

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Proterozoic mio- and eugeosynclinal rocks surround the Superior Province of Quebec and adjoining Labrador on all sides. They unconformably overlie an Archean basement complex and mark the boundary of the Superior and Churchill Provinces of the Canadian Shield on the west, north and east.

Rb-Sr whole-rock isochron studies on volcanic and sedimentary rocks from the Belcher Fold Belt in Hudson Bay, and sedimentary rocks from the Labrador Trough and the Lake Mistassini area of Quebec yield ages of 1800, 1870, and 1790 m.y., respectively. These determinations substantiate previous correlations between these areas based on stratigraphic and structural similarities. Consequently, the concept of a Circum-Ungava Geosyncline appears to be valid on geochronological grounds. Geosynclinal development appears to have been terminated by the onset of the Hudsonian orogeny at about 1800 m.y., since part of the succession dated in the Belcher Fold Belt consists on flysch-type sediments overlain by continental deposits. This probably indicates that sedimentation and uplift were occurring in the miogeosyncline in response to eugeosynclinal deformation to the east.

Trace element studies on three Algoma-type iron-formations in the Canadian Shield reveal anomalous europium enrichments. The possible sources of this are discussed and it is tentatively interpreted that the europium anomalies are the result of normal marine chemical precipitation under the anoxygenous conditions existing in the Archean atmosphere. Rare earth patterns of iron-formation samples from the Timagami and Michipicoten areas indicate that carbonate complexing caused enrichment in the heavy rare earths. The trace element abundances of these Algoma-type iron-formations are remarkably similar to those of the younger Superior-type Sokoman iron-formation and are unlike those of modern sediments associated with volcanic activity. Consequently, Algoma-type iron-formations are probably not derived from volcanic emanations, as previously thought.

Trace element data from the Sokoman iron-formation of the Labrador Trough suggest that the elements studied were adsorbed onto hydrated ferric oxide in the oxide facies and incorporated into crystallizing iron silicate and iron carbonate minerals in the silicate-carbonate facies. The rocks indicate, both texturally and geochemically, that they have undergone varying amounts of change during diagenesis. Unlike the Algoma-type iron-formations, Eu behaves normally in this younger iron-formation, but there is some evidence for anomalous Ce behavior.

Textural, trace element, geological and geochronological data on the Sokoman iron-formation indicate that it was deposited during the period when oxygen was first introduced into the atmosphere by biological activity. It is suggested that the Sokoman and Lake Superior banded cherty iron-formations are atypical and represent the products of the termination of banded iron-formation deposition. The Australian, Hamersley and South African Transvaal deposits are believed to be more normal and were produced by biological and inorganic activity under an anoxygenous atmosphere, probably rich in carbon dioxide.

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AGE DETERMINATIONS AND CORRELATIONS IN THE CIRCUM-UNGAVA GEOSYNCLINE

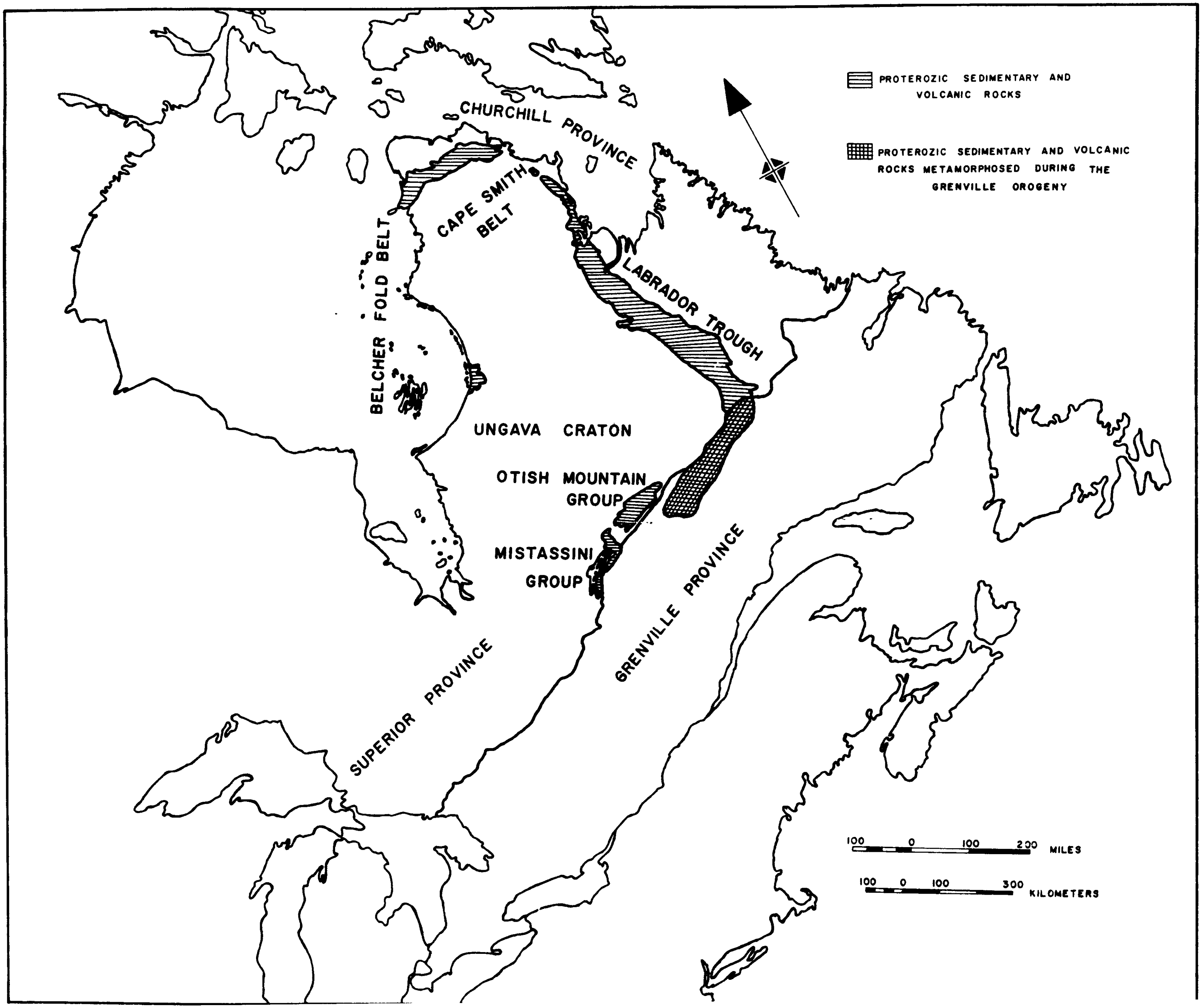
Introduction

A striking aspect of the Precambrian of Quebec and adjoining Labrador is the ring of Aphebian sedimentary and volcanic rocks surrounding the Superior Province (Fig. 1). Erosional remnants of the Circum-Ungava Geosyncline in the Belcher Fold Belt, the Cape Smith Belt and the Labrador Trough encircle the Archean gneisses of the Ungava Craton on the west, north, and east, respectively (Dimroth *et al.* 1970).

To the south the Superior Province is truncated by the Grenville Province. Recognizable Aphebian strata, however, are found for some 400 miles south-southwest along the Grenville-Superior boundary from where the Labrador Trough passes into the Grenville. Metamorphosed equivalents of the Trough strata extend 200 miles along the boundary before the last recognizable remnants disappear. Only a few miles north of their termination is the northeast boundary of the Otish Mountains Group. The Otish Mountains Group and similar appearing rocks of the Mistassini Group extend another 200 miles to the southwest before ending at the western end of Lake Mistassini.

Previous efforts toward the correlation of these geosynclinal rocks include those of Wahl (1953), Bergeron (1957*a*,*b*) and Dimroth *et al.* (1970). Wahl (1953) was the first to correlate the rocks of the Belcher Fold Belt, Labrador Trough, and Mistassini on the basis of their similar stratigraphy, lithology and geologic history. Bergeron (1957*b*) essentially agreed with Wahl's interpretation and stated that the lithological similarities and essential continuity of outcrop of the Belcher Fold Belt,

FIGURE 1.



▤ PROTEROZIC SEDIMENTARY AND VOLCANIC ROCKS
▦ PROTEROZIC SEDIMENTARY AND VOLCANIC ROCKS METAMORPHOSED DURING THE GRENVILLE OROGENY
CHURCHILL PROVINCE
CAPE SMITH BELT
BELCHER FOLD BELT
LABRADOR TROUGH
UNGAVA CRATON
OTISH MOUNTAIN GROUP
MISTASSINI GROUP
GRENVILLE PROVINCE
SUPERIOR PROVINCE
100 0 100 200 MILES
100 0 100 300 KILOMETERS

Cape Smith Belt and Labrador Trough suggested that these rocks were deposited in a continuous geosyncline (1957*a*). This geosynclinal interpretation has recently been accepted and amplified by Dimroth *et al.* (1970) who synthesized the available data and suggested that the Belcher Fold Belt, Cape Smith Belt and Labrador Trough are the preserved erosional remnants of the Circum-Ungava geosyncline.

Age determinations on these rocks had been limited for the most part to K-Ar ages on the granitic basement which these strata unconformably overlie, and on the weakly to more strongly metamorphosed geosynclinal rocks themselves. K-Ar ages determined on the Belcher Fold Belt (Hofman and Jackson 1969) have a mean age of approximately 1650 m.y. reflecting the low grade metamorphism developed during the Hudsonian deformation. These rocks are known to unconformably overlie basement gneisses in the Richmond Gulf area that give Archean ages (Wanless *et al.* 1968). Thus the rocks of the Belcher Fold Belt must have been deposited between 2500 m.y. and 1650 m.y. The work of Beall *et al.* (1963) has established a similar situation in the Labrador Trough, although rocks giving K-Ar ages up to 2060 m.y. have been found within the Trough strata. These older ages were interpreted as relicts and thus seemingly put a minimum limit of 2060 m.y. on the deposition of the Labrador Trough. Quirke *et al.* (1960) reported several K-Ar ages for rocks from the Mistassini area but these appear to have been partially reset by the Grenville and/or Hudsonian orogenies as ages of 1610 m.y. and 1290 m.y. were obtained for the basement gneisses and sedimentary rocks, respectively.

Thus, in summary, the correlations between these rocks have been based on similar lithologies, geologic histories and continuity around the Ungava craton, and age measurements only bracket their deposition within very broad limits.

The present study was undertaken to determine the absolute age of the Circum-Ungava Geosyncline and to attempt to correlate the Mistassini Group with the Circum-Ungava rocks by radiometric dating. It was also of interest to obtain a more accurate estimate of the age of the Superior Type iron-formations found within the Circum-Ungava and Mistassini strata for future global correlations with similar deposits elsewhere. These have been related to possible changes in the rate of production of oxygen by organisms and thus to the emergence of oxygen in the atmosphere (Cloud 1968). The Rb-Sr whole-rock isochron method was used to avoid the effect of minor metamorphism that had reset previous K-Ar determinations on the Belcher, Labrador Trough, and Mistassini rocks.

Analytical Procedures

The chemical preparations and analytical techniques used in this study are those currently in use at the M.I.T. Geochronology Laboratory and are given in detail by Reesman (1968). Because the rocks were generally rich in radiogenic Sr^{87} the isotopic measurements were made on 6 inch-radius, 60° sector, solid source, single filament Nier-type mass spectrometers.

Rb and Sr concentrations were determined by isotope dilution using Rb^{87} and Sr^{84} enriched spikes. Sr^{87}/Sr^{86} ratios were calculated from the spiked analyses and normalized to a Sr^{86}/Sr^{88} ratio of 0.1194.

Analytical precision has been monitored by frequent analysis of the Eimer and Amend spec-pure $SrCO_3$ standard (Lot #492327). Eighteen normalized Sr^{87}/Sr^{86} analyses average 0.7083 ± 0.0009 (2σ). Recent studies by Spooner (1969) and Gates (1971) average 0.7083 ± 0.0008 and 0.7082 ± 0.0004 for the normalized Sr^{87}/Sr^{86} ratio of the same standard on two of the instruments. Based on these results analyses on the three mass spectrometers are considered to be directly comparable and the error in the Sr^{87}/Sr^{86} ratio is estimated to be ± 0.0010. The uncertainty in the Rb^{87}/Sr^{86} ratio is assumed to be ± 3%.

The best straight line fit and the intercept of the isochrons on the Sr^{87}/Sr^{86} axis have been determined using the least-squares computer program of York (1966). Ages have been computed using the Rb^{87} decay constant of $1.39 \times 10^{-11}\ yr^{-1}$.

Age of the Upper Volcanics, Belcher Islands

The sedimentary and volcanic rocks of the Belcher Islands represent part of an embayed miogeosynclinal sequence of the Circum-Ungava Geosyncline (Dimroth *et al.* 1970). As in the Labrador Trough, basin filling was cyclical but appears to be in the reverse order. Basin instability and basic volcanism initiated individual cycles rather than terminated them. As stability gradually returned, the spilitic basalts were followed by greywackes and argillites which grade into interbedded and massive orthoquartzites and dolomites. The detailed stratigraphy is given in Table I after Jackson (1960, in Dimroth *et al.* 1970).

The second depositional cycle ends with the Kipalu Iron Formation grading upwards into tuffaceous rocks (Hofman and Jackson 1969) marking the beginning of the last sedimentary cycle. Twelve samples of these upper volcanics of the Flaherty Formation and eight samples of slate from the overlying Omarolluk Formation and one argillite from the Flaherty Formation have been analyzed (Table II). One sample from the Laddie Formation which lies considerably below these upper formations has also been analyzed. Individual isochrons of the volcanics and slates are presented in Figure 2. The volcanics and slates define isochrons of 1755 ± 69 m.y. and 1790 ± 89 m.y. and initial Sr^{87}/Sr^{86} ratios of 0.7056 ± 0.0010 and 0.7059 ± 0.0013, respectively. The composite isochron shows an age of 1798 ± 38 m.y. with initial Sr^{87}/Sr^{86} of 0.7055 ± 0.0005. In all cases sample R8043 has been excluded from the computations as it falls considerably outside the limits of experimental error. Sample R8033 has also been excluded as it is known to be stratigraphically older than the other samples.

Both the volcanics and the slates appear to be very similar and it is felt that the slates have been formed from basaltic detritus as suggested by Jackson (in Dimroth *et al.* 1970). The Sr content of the slates (180 ppm) is remarkably similar to

TABLE I

Table of Formations: Belcher Fold Belt (after Jackson, in Dimroth *et al.* 1970)

Formation	Lithology	Thickness (feet)
Loaf	(Molasse) arkose, quartzite, argillite, conglomerate	700+
Omarolluk	(Flysche) greywacke, argillite, lithic and arkosic quartzite, tuff	7000+
Flaherty	Basalt, tuff, agglomerate, feldspar porphyry	960-6400
Kipalu	Ferruginous argillites	200-380+
Mukpollo	Quartzite, feldspathic quartzite	130-475+
Rowatt	Upper: interbedded quartzite and dolomite	620-1000
	Lower: dolomite, arenaceous dolomite	150-280
Laddie	Upper: argillite, quartzite, dolomite	660±
	Lower: interbedded argillite, limestone, dolomite	425±
Costello	Interbedded limestone, dolomite, argillite, slate, argillite at base	800-1200
Mavor	Dolomite with stromatolitic zones	450-550+
Tukarak	Upper: interbedded argillite, limestone, dolomite	200-230
	Lower: argillite, dolomite, quartzite	

TABLE I (cont'd.)

Formation	Lithology	Thickness
McLeary	Upper: dolomite with stromatolitic zones Middle: dolomite with few stromatolitic zones, quartzite Lower: interbedded dolomite and quartzite	1200-1420
Fairweather	Argillite, quartzite, dolomite, tuff, arkose, basalt	1200-2000
Eskimo	Basalt, feldspar porphyry, argillite, tuff, agglomerate, granular jasper	(0?)-3000+
Kasegalic	Dolomite with stromatolitic zones, limestone, argillite	4000
?		

TABLE II

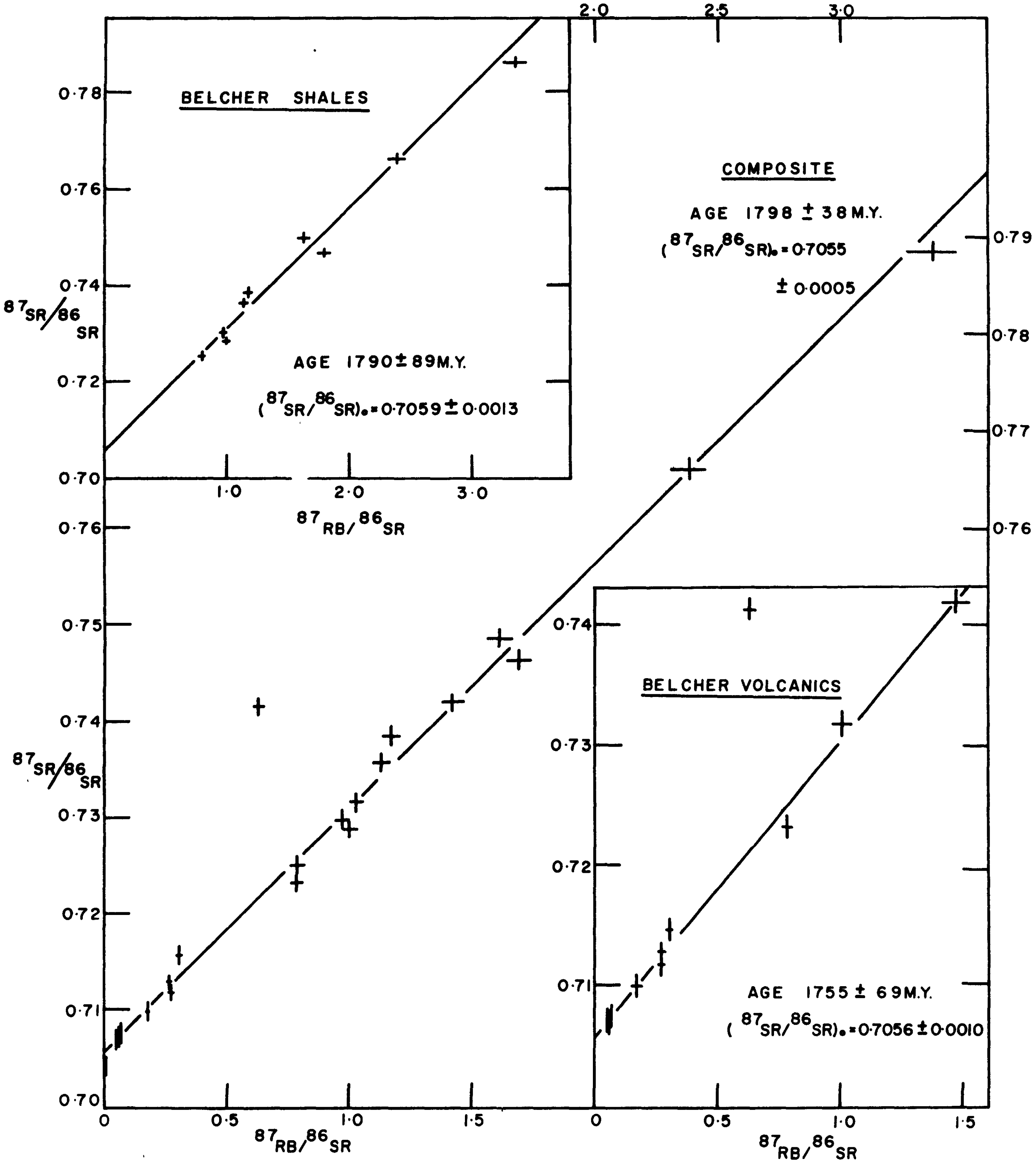
Analytical data - Belcher Islands

Sample	Formation	Rock Type	Rb (ppm)	Sr (ppm)	Rb^{87}/Sr^{86}	Sr^{87}/Sr^{86}
R8028	Omarolluk	Slate	91.1	226	1.17	0.7384
R8029	Omarolluk	Slate	129	158	2.38	0.7660
R8030	Omarolluk	Slate	66.0	244	0.785	0.7250
R8031	Omarolluk	Slate	66.4	199	0.967	0.7298
R8032	Omarolluk	Slate	62.9	166	1.13	0.7357
R8034	Omarolluk	Slate	137	116	3.37	0.7885
R8035	Omarolluk	Slate	74.8	129	1.69	0.7462
R8036	Omarolluk	Slate	70.6	128	1.61	0.7485
R8059	Flaherty	Argillite	77.1	224	0.997	0.7288
R8042	Flaherty	Volcanic	3.64	205	0.0515	0.7070
R8043	Flaherty	Volcanic	8.46	40.2	0.625	0.7415
R8044	Flaherty	Volcanic	12.3	205	0.173	0.7098
R8045	Flaherty	Volcanic	16.2	45.4	1.03	0.7317
R8046[1]	Flaherty	Volcanic	1.71	507	0.0098	0.7041
R8046[2]	Flaherty	Volcanic	0.85	37.1	0.066	0.7075

TABLE II (cont'd.)

Sample	Formation	Rock Type	Rb (ppm)	Sr (ppm)	Rb^{87}/Sr^{86}	Sr^{87}/Sr^{86}
R8047	Flaherty	Volcanic	1.82	88.2	0.060	0.7072
R8048	Flaherty	Volcanic	18.2	196	0.271	0.7117
R8049	Flaherty	Volcanic	28.6	106	0.782	0.7232
R8050	Flaherty	Volcanic	61.6	122	1.47	0.7418
R8051	Flaherty	Volcanic	29.8	283	0.305	0.7156
R8052	Flaherty	Volcanic	14.8	160	0.267	0.7128
R8033	Laddie	Argillite	153	33.5	13.8	1.0938

FIGURE 2.


BELCHER SHALES
AGE 1790 ± 89 M.Y.
(^{87}SR/^{86}SR)$_0$ = 0.7059 ± 0.0013
^{87}SR/^{86}SR
0.78
0.76
0.74
0.72
0.70
1.0
2.0
3.0
^{87}RB/^{86}SR
COMPOSITE
AGE 1798 ± 38 M.Y.
(^{87}SR/^{86}SR)$_0$ = 0.7055 ± 0.0005
2.0
2.5
3.0
0.79
0.78
0.77
0.76
0.76
0.75
0.74
0.73
0.72
0.71
0.70
0
0.5
1.0
1.5
^{87}RB/^{86}SR
BELCHER VOLCANICS
AGE 1755 ± 69 M.Y.
(^{87}SR/^{86}SR)$_0$ = 0.7056 ± 0.0010
0.74
0.73
0.72
0.71
0
0.5
1.0
1.5
^{87}RB/^{86}SR

that of the volcanics (168 ppm) and the initial Sr^{87}/Sr^{86} of both the slates and the volcanics are indistinguishable within the limits of experimental error. The higher Rb content of the slates (85 vs 16 ppm) is attributed to the fixation of Rb during the deposition of the slates.

In view of the above factors the volcanic and slate samples are considered to have formed part of the same Sr isotopic system at the time of their deposition, and the composite isochron is believed to give the best age estimate. As the individual isochrons are indistinguishable from the composite within the limits of experimental error, the upper volcanics are considered to have been deposited at 1798 ± 38 m.y. This age is consistent with the suggestion of Hofman and Jackson (1969) that the major folding of the Belcher Group may have occurred shortly after the deposition of the Loaf Formation which conformably overlies the Omarolluk. According to Jackson (in Dimroth *et al.* 1970) the Omarolluk may represent a flysch-like sequence of turbidite deposits in relatively deep and quiet waters. These grade upward into shallower water deposits and the conformably overlying Loaf Formation consists of terrestrial conglomeratic and arkosic sandstones possibly representing a terrestrial molasse sequence. These changes are presumably the result of uplift in the miogeosyncline in response to the beginning of Hudsonian deformation in the eugeosyncline.

Sample R8033 from the Laddie Formation, as well as being stratigraphically older than the other samples, appears to be derived from a different source. Its high Rb/Sr ratio and low Sr content are unlike those of the other slate samples analyzed and are very similar to those of the Labrador Trough. Its association with dolomites and quartzite is again similar to the Labrador samples and suggests a continental source rather than a basaltic one. For these reasons this sample was excluded from all computations of age in the Belcher Islands. It is of interest to note that this sample falls on the Attikamagen Slate isochron of the Labrador Trough within the limits of experimental error.

Age of the Sokoman Iron-Formation, Central Labrador Trough

Mio- and eugeosynclinal rocks of the Labrador Trough extend over 600 miles from Payne Bay, south-southeasterly, to the Grenville Front at Sawbill Lake. They unconformably overlie Archean gneisses of the Superior Province on the west and remetamorphosed Archean gneisses on the east (Beall *et al.* 1963). The detailed stratigraphy of the Labrador Trough has recently been summarized by Dimroth (1968) and Dimroth *et al.* (1970). Along most of its length it can be divided into an eastern zone of mainly mafic intrusives and extrusives and a western zone of predominantly sediments. The stratigraphic filling represents two or possibly three tectonic cycles beginning with a sandstone-precipitate sequence and terminating with the deposition of shales in the miogeosyncline and intense volcanic activity in the eugeosyncline. A marginal unconformity separates the first and second cycles and erosional unconformities are found within the sequence.

The Sokoman Iron-Formation constitutes the precipitate phase of the second sedimentary cycle and is continuous throughout most of the length of the Labrador Trough. It is the host rock for the residual hematite-goethite ore deposits of the Knob Lake area and its metamorphosed equivalents south of Sawbill Lake constitute the metataconite ores of the Grenville Province. A series of 19 slate samples from formations above and below the Sokoman Iron-Formation have been analyzed from the Knob Lake area (Table III). The generalized stratigraphy of the sample area is given in Table IV. A composite isochron of all the samples analyzed and individual isochrons of the underlying Attikamagen Slate and the overlying Menihek Slate are shown in Figure 3. The composite isochron yields an age of 1879 ± 43 m.y. and initial Sr^{87}/Sr^{86} of 0.7133 based on a least-squares fit of the data. This value for the initial ratio is not significant in the age calculation due to the high Sr^{87}/Sr^{86} ratios of the samples and, owing to the lack of precision in the extrapolation, is not meaningful in the genesis of the sediments.

The Menihek Slate samples define an age of 1855 ± 74 m.y. based on an initial Sr^{87}/Sr^{86} ratio of 0.7033 ± 0.0010 determined by least-squares fit. The Attikamagen Slate samples are too high in Sr^{87}/Sr^{86} and have insufficient spread in Rb/Sr ratios to permit a meaningful estimate of initial Sr^{87}/Sr^{86}.

Parts of the Attikamagen formation contain considerable

TABLE III

Analytical Data - Knob Lake Area

Sample	Formation	Rb (ppm)	Sr (ppm)	Rb^{87}/Sr^{86}	Sr^{87}/Sr^{86}
R7838	Menihek	156	40.8	11.4	1.0133
R7839	Menihek	141	27.7	15.3	1.0879
R7840	Menihek	126	23.0	16.3	1.1037
R7841	Menihek	163	32.2	15.7	1.1342
R7623	Menihek	101	48.7	6.07	0.8606
R7624	Menihek	141	80.1	5.11	0.8369
R7625	Menihek	143	63.0	6.66	0.8775
R7627	Attikamagen	170	59.5	8.45	0.9628
R7626	Attikamagen	217	54.8	11.8	1.0268
R7845	Attikamagen	191	54.3	10.5	0.9980
R7846	Attikamagen	219	40.5	16.4	1.1485
R7847	Attikamagen	186	64.0	8.64	0.9591
R7848	Attikamagen	244	55.6	13.1	1.0409
R7943	Attikamagen	215	60.9	8.30	0.9497
R7944	Attikamagen	156	191	2.38	0.7916

TABLE III (cont'd.)

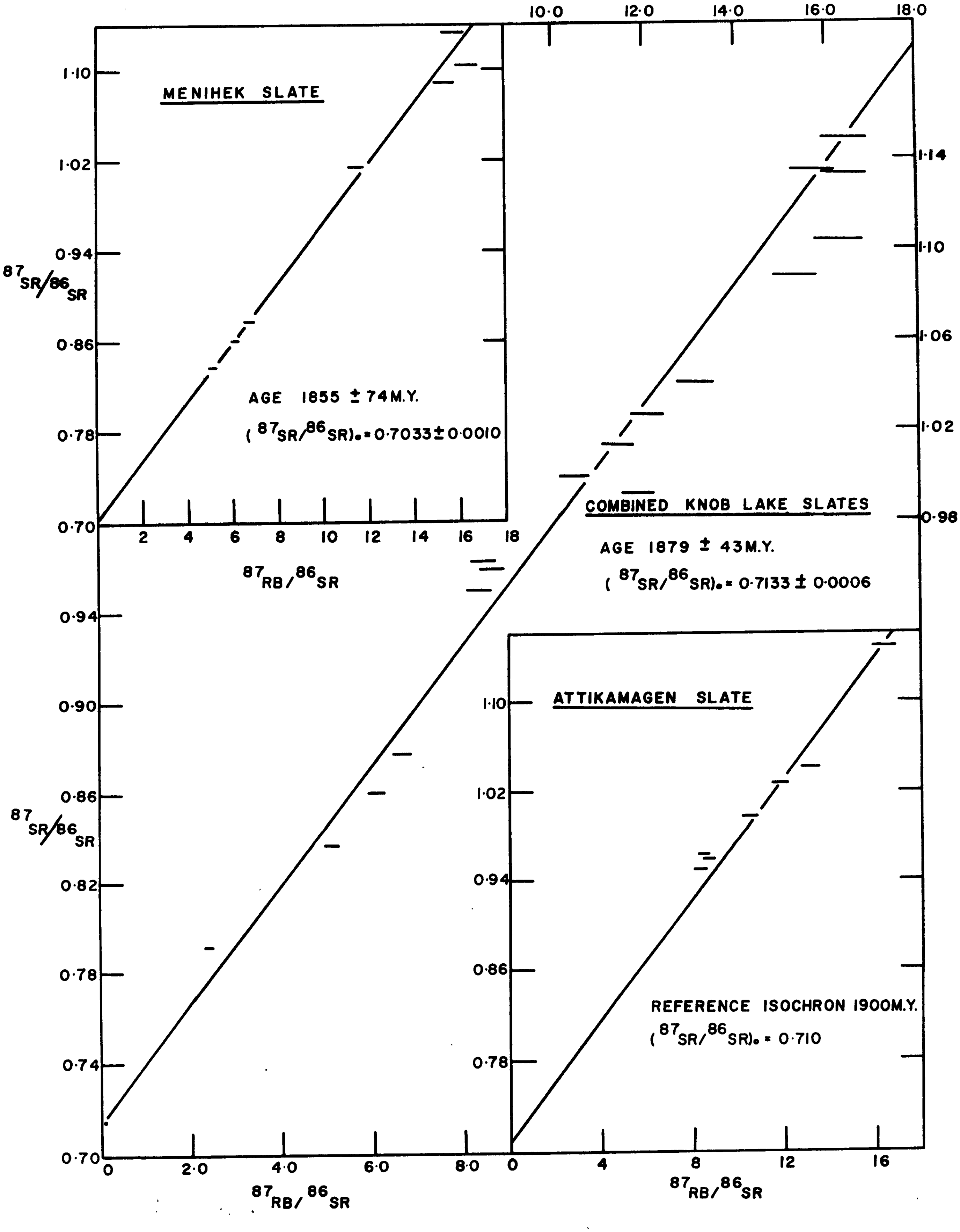
Sample	Formation	Rb (ppm)	Sr (ppm)	Rb^{87}/Sr^{86}	Sr^{87}/Sr^{86}
R7660	Ruth	86.8	22.0	11.9	0.9919
R7849	Ruth	37.8	1220	0.090	0.7147
R7851	Ruth	37.6	1150	0.094	0.7146
R7728	Ruth	86.7	15.9	16.4	1.1332

TABLE IV

Generalized stratigraphy, Knob Lake Area (after Gross 1968)

	Formation
PROTEROZOIC	Menihek Slate
	Sokoman Iron-Formation
	Ruth Slate
	Wishart Quartzite
	Fleming Chert
	Denault Dolomite
	Attikamagen Slate
	Major Unconformity
ARCHEAN	Ashuanipi

FIGURE 3.


MENIHEK SLATE
AGE 1855 ± 74M.Y.
(^{87}SR/^{86}SR)$_0$ = 0·7033 ± 0·0010
^{87}SR/^{86}SR
1·10
1·02
0·94
0·86
0·78
0·70
2
4
6
8
10
12
14
16
18
^{87}RB/^{86}SR
COMBINED KNOB LAKE SLATES
AGE 1879 ± 43M.Y.
(^{87}SR/^{86}SR)$_0$ = 0·7133 ± 0·0006
10·0
12·0
14·0
16·0
18·0
1·14
1·10
1·06
1·02
0·98
0·94
0·90
0·86
0·82
0·78
0·74
0·70
0
2·0
4·0
6·0
8·0
^{87}RB/^{86}SR
^{87}SR/^{86}SR
ATTIKAMAGEN SLATE
REFERENCE ISOCHRON 1900M.Y.
(^{87}SR/^{86}SR)$_0$ = 0·710
1·10
1·02
0·94
0·86
0·78
0
4
8
12
16
^{87}RB/^{86}SR

amounts of carbonate, especially near the gradational contact with the overlying Denault Dolomite. This carbonate appears to have been susceptible to Rb loss during recrystallization. Analyses of twelve dolomite (Table V) samples from the three areas studied bear this out. As all the dolomites were deposited at approximately the same time they should have had similar initial isotopic compositions. The calculated initial Sr^{87}/Sr^{86} of these dolomites vary from 0.7046 to 0.7192 which is inconsistent with this. It is felt that the spread in calculated initial ratios is due to Rb loss from the carbonates during recrystallization and furthermore, that slate samples containing carbonate must be held suspect for the same reason. This loss of Rb is apparent in sample R7944 which is from a gradational zone between the Attikamagen and Denault formations. It is composed of approximately equal amounts of dolomite and white mica and its high Sr^{87}/Sr^{86} ratio suggests that it did not remain a closed system.

The other Attikamagen samples contain little or no carbonate and thus should more nearly approach the closed system requirements for meaningful age determinations. A 1900 m.y. reference isochron drawn using a geologically reasonable initial ratio of 0.710 (Fig. 3) provides an acceptable fit to the data points excluding R7944. The remaining scatter is somewhat greater than that expected through experimental error alone and is presumably due to minor losses or gains of Rb. This 1900 m.y. age is consistent with both the composite and Menihek Slate isochron ages and supports an age of 1870 ± 50 m.y. for the Soko-

TABLE V

Analytical Data - Dolomites

Sample	Area	Rb (ppm)	Sr (ppm)	Rb^{87}/Sr^{86}	Sr^{87}/Sr^{86}	$(Sr^{87}/Sr^{86})_0$
R7500	Knob Lake	1.74	22.0	0.097	0.7123	0.7099
R7842	Knob Lake	2.08	81.3	0.074	0.7075	0.7056
R7843	Knob Lake	1.64	85.3	0.056	0.7081	0.7067
R7844	Knob Lake	1.87	75.4	0.072	0.7083	0.7065
R8037	Belcher	17.9	116	0.447	0.7282	0.7170
R8038	Belcher	5.1	40.7	0.361	0.7219	0.7129
R8039	Belcher	3.5	37.4	0.271	0.7192	0.7124
R8040	Belcher	25.9	33.3	2.27	0.7760	0.7192
R8009	Mistassini	2.97	60.9	0.141	0.7121	0.7086
R7958	Mistassini	1.46	42.5	0.099	0.7071	0.7046
R7655	Mistassini	2.07	56.1	0.107	0.7175	0.7148
R7656	Mistassini	1.45	54.8	0.077	0.7174	0.7155

man iron-formation.

The whole-rock Rb-Sr age of 1870 m.y. for this section of the Labrador Trough is considerably older than the common Hudsonian 1600 m.y. K-Ar ages reported by Beall *et al.* (1963) and Wanless *et al.* (1968) for the Labrador Trough strata. It probably represents the primary depositional age of these rocks despite the suggestion by Beall *et al.* that a 2060 m.y. K-Ar age they obtained puts a minimum limit on the age of the Labrador Trough strata. This old age was found for an argillite with biotite layers located within the biotite-muscovite subfacies of regional metamorphism developed during the Hudsonian orogeny. Rather than representing a minimum limit for the deposition of the Trough sediments, this rock is probably an isolated case where excess radiogenic Ar^{40} has been incorporated into crystallizing minerals. The low K content of this particular rock would make any excess Ar^{40} much more important in the calculated age than in more K-rich rocks. Consequently, the second sedimentary cycle of the Labrador Trough appears to have begun at approximately 1870 ± 50 m.y.

Age of the Mistassini Group, Lake Mistassini Area, Quebec

The Mistassini group is a succession of little-deformed Proterozoic sedimentary rocks unconformably overlying Archean basement in a 100 mile arc around Lake Mistassini.

The regional geology has been treated in detail by Bergeron (1957*a*,*b*) and Quirke *et al.* (1960) and will only be summarized here. Briefly, the crystalline basement consists of a schistose series of metasediments and volcanics intruded by granite and granite gneiss. This is overlain with profound unconformity by at least 6500' of chemical and clastic sediments of the Mistassini group which have been divided by Bergeron (1957*b*) into five formations (Table VI). Breaks in the succession such as those in the Upper Albanel formation and at the base of the Temiscamie appear to be disconformities rather than major breaks.

The strata have a regional strike between 10° and 45° to the northeast and dip to the southeast. Deformation increases to the southeast towards the fault contact with the Grenville gneisses but metamorphism appears to be of exceedingly low grade. Two periods of deformation are observed with northeast fold and fault systems produced during the Grenville deformation being superimposed upon an earlier period of east and southeast undulations.

Seven samples of the Temiscamie formation have been analyzed for Rb and Sr by isotope dilution (Table VII). They define an isochron (Fig. 4) of 1787 ± 55 m.y. and an initial Sr^{87}/Sr^{86} ratio of 0.7015 ± 0.0008. This age is considerably older than the K-Ar age of 1290 m.y. reported by Quirke *et al.* (1960) for the lower slate of this formation and indeed is older than the K-Ar and Rb-Sr biotite ages of the basement gneisses of 1610 and 1670, respectively. These biotite ages may reflect a previous Hudsonian event possibly related to the earlier period of deformation noted in these rocks, although as only one rock has been analyzed, this is purely speculative. The 1290 m.y.

TABLE VI

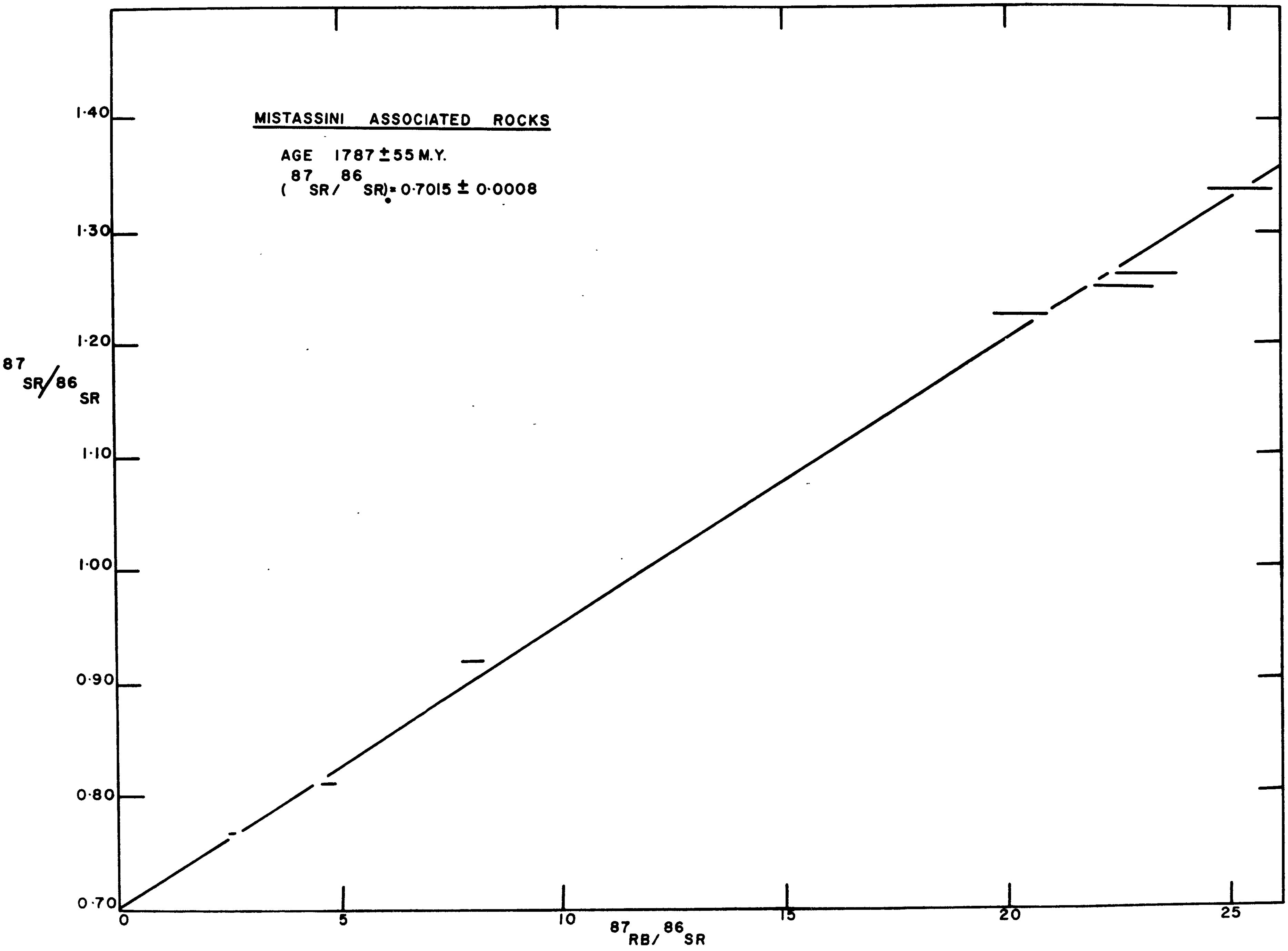
Table of formations (after Bergeron 1957*b*)

	Formation	Lithology
PROTEROZOIC	Temiscamie	Upper slate member: slate, arkose, greywacke
	Temiscamie	Iron-formation
	Temiscamie	Lower slate member
	Temiscamie	Quartzite: quartzite, conglomerate
	Upper Albanel	Dolomite
	Lower Albanel	Dolomite
	Cheno River	Arkosic conglomerate, greywacke, pebble conglomerate, sandstone, dolomite
	Papaskwasati	Well-bedded quartzose sandstone, quartz pebble conglomerate at base.
	Major Unconformity	
ARCHEAN	Basement Complex	

TABLE VII

Analytical Data - Temiscamie Formation, Mistassini

Sample	Member	Rb (ppm)	Sr (ppm)	Rb^{87}/Sr^{86}	Sr^{87}/Sr^{86}
R7957	Quartzite	29.5	10.8	8.06	0.9195
R8013	Lower Slate	250	30.5	25.2	1.3373
R8011	Upper Slate	273	36.1	23.1	1.2616
R7956	Lower Slate	199	26.8	22.6	1.2511
R7657	Lower Slate	257	38.5	20.3	1.2257
R8008	Slate	163	101	4.71	0.8106
R8012	Lower Slate	149	175	2.51	0.7660


MISTASSINI ASSOCIATED ROCKS
AGE 1787 ± 55 M.Y.
(^{87}SR/^{86}SR)$_o$ = 0·7015 ± 0·0008
^{87}SR/^{86}SR
1·40
1·30
1·20
1·10
1·00
0·90
0·80
0·70
0
5
10
15
20
25
^{87}RB/^{86}SR

sediment age is probably the result of several different processes including two periods of deformation, a weak metamorphism, and probably diffusional losses and at best puts a lower limit on the deposition of the Mistassini sediments. The Rb-Sr whole-rock age determined here confirms that these K-Ar ages are survival ages, and the low grade of metamorphism similar to that of the Labrador and Belcher rocks suggests that the age determined may closely approximate the time of deposition.

Discussion and Implications

The close agreement obtained between the ages of the Labrador Trough and the Belcher Fold Belt confirms the general correlation between these two sedimentary basins. Similarly, the correlation of the Cape Smith Belt with these two basins is put on a firmer basis by its position between two isochronous ones. Thus it appears that the concept of the Circum-Ungava Geosyncline (Dimroth *et al.* 1970) is tenable on geochronological as well as stratigraphical and structural grounds.

The 1800 ± 40 m.y. age of the upper volcanics of the Belcher Islands appears to be well established. The good agreement between the shale, volcanic, and composite isochrons and the geological evidence suggesting that the Hudsonian deformation was underway during deposition of the overlying Omarolluk Formation substantiate this age. In light of the above information, sedimentation in the Belcher segment of the Circum-Ungava Geosyncline must have terminated shortly after 1800 m.y. The Kipalu Iron-Formation which conformably underlies the upper volcanics cannot be significantly older than 1800 m.y., and hence its age is also established.

Development of the Labrador Trough appears to have been substantially the same as that of the Belcher Belt. The slightly older age obtained for the Sokoman Iron-Formation is consistent with the geological development depicted by Dimroth (in Dimroth *et al.* 1970). The Sokoman lies within the second sedimentary cycle of the Labrador Trough (see Table VIII), unlike the dated material from the Belcher Islands which is from near the top of the stratigraphic section. If the difference in age between the two belts is significant, then it is not likely that the Kipalu Iron-Formation of the Belcher Belt correlates with the Sokoman Iron-Formation of the Labrador Trough. If the Kipalu has a correlative in the Trough, then it is more likely to be the upper iron-formation of the third sedimentary cycle that is found in the northern parts of the Trough.

Detailed correlations within the two basins must remain speculative, but the determined ages suggest that the rocks of the upper cycles may be generally correlatible. Whether or not the two iron-formations of these cycles are equivalent is much more tenuous. If the source of the iron was a deeply weathered landmass, then the proximity of the two basins and their similar source areas would make their correlation more likely. However, if the source of the iron was volcanic activity in the eugeosyncline, there is no compelling reason for them to be equivalent.

The general correlation of the Mistassini Group with the

Labrador and Belcher rocks (Wahl 1953, Bergeron 1957*b*) appears to be borne out by the 1787 ± 55 m.y. age obtained on the Temiscamie Formation. This is remarkably close to the 1800 m.y. age of the Belcher upper volcanics. If the onlap of younger formations onto the Superior basement observed both in the Labrador Trough and its southern extension into the Grenville Province (Jackson, in Dimroth *et al.* 1970) holds true to the southwest, and the transgressive sequence observed in the Mistassini group indicates that it does, then the Mistassini and Otish Mountains groups may be the youngest rocks of the Southern Province of the Labrador Trough. Through greater onlap these rocks may have escaped being incorporated into the Grenville orogeny and now appear as outliers exposed on the north side of the thrust fault separating the Grenville and Superior Provinces. The low initial ratio of the Mistassini isochron is consistent with this interpretation as it requires a source region of low Sr^{87}/Sr^{86} such as would be found in a zone of basic volcanic rocks within a eugeosyncline to the south. If the above interpretation is correct, the Temiscamie Iron-Formation may correlate in a general way with the Kipalu and upper iron-formation of the Belcher and Labrador basins.

In addition to correlations within the three areas studied, the ages determined have considerable bearing on correlations and interpretations made on these and other areas of the Canadian Shield. If the Otish Mountains Group is correlative with the Mistassini Group, as is likely (Bergeron 1957*b*, Young 1970) then the interpretation of Gross (1968) that the rocks of the

Otish Mountains area may have been derived from a belt uplifted during the Grenville orogeny is invalid. Similarly, the suggestion that the Huronian Supergroup may be correlative with the Otish Mountains Group (Frarey and Roscoe 1970) would be unfounded as the Huronian sediments were deposited at approximately 2300 m.y. (Fairbairn *et al.* 1969).

Correlations between the rocks of the Circum-Ungava Geosyncline and those of the Animikie basins in the Lake Superior area although not definitely proven are put on a more substantial basis with the dates obtained here. The similarity of the age obtained by Peterman (1966) for the Mahnomen Formation (1.85 b.y.) and the ages of the Circum-Ungava rocks points to their being roughly synchronous. Although Peterman interprets the age of the Mahnomen as a metamorphic age, Faure and Kovack (1969) suggest that it is more likely to be a primary depositional age and the writer is inclined to agree. More work on the Superior rocks will hopefully resolve this problem but the general correlation between the two areas appears to be reasonable in light of present information.

The above correlations are shown in Table VIII. The Lake Superior rocks have been excluded as the great distances separating these areas would make such correlations too tenuous to be meaningful. Hopefully, further radiometric measurements on the Lake Superior sections will make more detailed comparisons justifiable. The stratigraphic relationships shown are similar to those tentatively suggested by Dimroth (1970, written communication, 1970) with the addition of the Mistassini and Otish Mountains areas. It must be emphasized that these correlations are approximate and units within compared sequences probably are not correlatible in many cases.

TABLE VIII

Tentative correlations in the Circum-Ungava Geosyncline

Table VIII

Belcher Fold Belt	Cape Smith Belt
	Angular Unconformity (K-Ar~1450 m.y.)
	Chukotat Group peridotite, gabbro, basalt, shale, quartzite. conglomerate, chert, sandstone.
Angular Unconformity (K-Ar~1650 m.y.)	Angular Unconformity (K-Ar~1600 m.y.)
Loaf Fm. (Molasse-type) Omarolluk Fm. (Flysch-type) (1800 m.y.) Flaherty Fm. basalt	Povungnituk Group gabbro, basalt, slate.
Mukpollo and Kipalu Fm. dolomite, sandstone, iron-fm	dolomite, iron-fm, quartzite.
	Angular Unconformity
Fairweather to Rowatt Fm. argillite, dolomite, quartzite. Eskimo Fm. basalt Kasegalic Fm. dolomite ?	Archean
Angular Unconformity	
Archean (K-Ar~2500 m.y.)	

Table VIII (cont'd)

Labrador Trough (between 57° and 59°N.)	Labrador Trough (between 57° and 59°N.)
Angular Unconformity (K-Ar~1610 m.y.)	Angular Unconformity (K-Ar~1610 m.y.)
basalt slate	basalt slate
Upper iron-fm. and Abner dolomite	Irene Lake iron-fm.
slate, conglomerate greywacke.	slate, basalt.
Fenimore iron-fm.	Sokoman iron-fm. (*1870 m.y.*)
quartzite	quartzite, dolomite. shale, basalt. greywacke. dolomite, sandstone. arkose
Angular Unconformity	Angular Unconformity
Archean	Archean (K-Ar~2500 m.y.)

Table VIII (cont'd)

Southern Labrador Trough (Grenville)	Otish Mountain Group
	red sandstone, red shale
schist	sandstone, conglomerate.
Wabush iron-fm.	Angular Unconformity
quartzite, marble. schist	Archean
Angular Unconformity	
Archean	

Table VIII (cont'd)

Mistassini	
Angular Unconformity (K-Ar~1600 m.y.?)	
slate	
iron-fm., slate, quartzite *(1790 m.y.)*	
dolomite conglomerate, greywacke, sandstone. quartzite, pebble conglomerate.	
Angular Unconformity	
Archean	

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Age and trace element compositions of Algoma-type iron-formations of the Canadian Shield

Introduction

Nearly all the Archean greenstone belts of metavolcanic and sedimentary rocks in the Canadian Shield contain banded cherty iron-formations as an integral part of the basin filling. These have been named Algoma-type by Gross (1965) for the widespread occurrence, variety of lithological facies and typical depositional environment exhibited in the Algoma District of Ontario.

Algoma-type iron-formations typically consist of alternating bands of ferruginous grey or jasper chert and magnetite and/or hematite. The other iron-formation facies of James (1954) are generally less well developed, although locally, as in the Michipicoten area of Ontario, massive siderite and sulphide beds can form a major part of the iron-formation. There is some evidence (Goodwin 1962; Gross 1965) that the particular facies of iron-formation may vary with the enclosing rock type, but later studies (Goodwin and Shklanka 1967; Ridler 1970; Goodwin and Ridler 1970) suggest that individual iron facies correspond to basin configuration during deposition. Thus, oxide facies give way to carbonate and finally to sulphide facies rocks with deepening water and the previously noted relationship of iron-formation facies and rock type may be due only to similar depositional environments and not to some other genetic relationship.

Structurally, the iron-formations are generally lense shaped varying from several hundred feet to inches in thickness. These lenses are usually only a few miles in length although discontinuous lenses may extend for tens of miles in some belts (Gross 1966). Recent studies on the overall basin geometry, stratigraphy and development of certain greenstone belts in Ontario (Goodwin and Shklanka 1967; Ridler 1970; Goodwin and Ridler 1970) show that the iron-formations in these belts are usually restricted to certain stratigraphic positions and form important marker horizons. Thus, although individual iron-formations may lense out, they may be stratigraphically much more persistent than previously thought.

The depositional environment of Algoma-type iron-formations is eugeosynclinal with associated rocks being typically pillowed andesites, tuffs, pyroclastics, rhyolites, greywackes, agglomerates and slates. Tuffs and other fine-grained clastic rocks are commonly found interlayered with the iron-formation and Gross (1965) reports that transitions from cherty iron-formation to cherty graphitic and pyritic slate commonly occur along strike. The iron-formations are spatially related to the volcanism and appear to generally follow the cessation of individual volcanic cycles. These cycles begin with widespread quiet effusive mafic to intermediate submarine lavas and terminate with more violent domical accumulations of acid lavas and pyroclastics.

The source of iron for these deposits is generally agreed to be of volcanic origin (Goodwin 1962, 1964; Gross 1965; Ridler 1970). Several examples of iron being supplied to sedimentary basins at the present time by fumarolic and hot spring activity associated with volcanic areas (Zelenov 1958; Butzova 1966) show that a volcanic source of the iron is conceivable. Furthermore, the generally high arsenic content of many of these rocks (Gross 1966) and the presence of base metals such as copper in disseminated minerals, support this hypothesis.

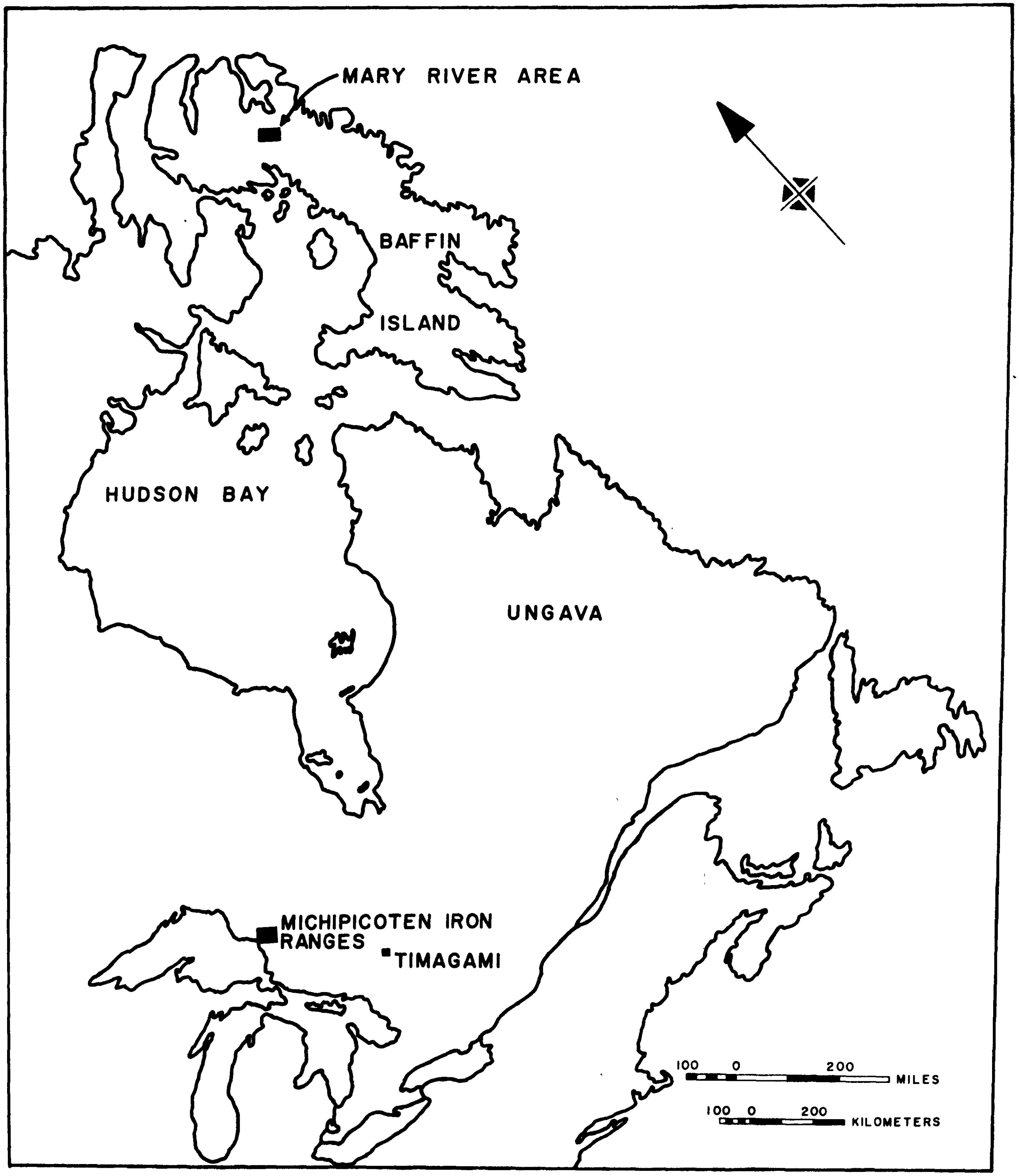
Although several of these iron-formations have been studied in detail, there have been almost no trace element analyses reported apart from two spectrographic determinations on siderite and banded chert from the Helen Mine at Michipicoten (Goodwin 1961). To get a better understanding of these important sources of iron ore, a trace element study was undertaken of three of these Algoma-type iron-formations in the Canadian Shield. In conjunction with the trace element studies, Rb-Sr whole-rock isotopic analyses were made on the two areas not previously reported. These ages are discussed along with the general geology of the three areas prior to the presentation and interpretation of the trace element data.

General Geology and Rb-Sr whole-rock ages

Algoma-type iron-formation, Timagami, Ontario

Algoma-type iron-formation of the Lake Timagami area of Ontario (see Fig. 5) is part of an inlier of metavolcanics and sediments within younger Archean granitic rocks. This greenstone belt may be part of the "Abitibi Belt" of the Superior Province of the Canadian Shield (Goodwin 1968) and is unconformably overlain by Proterozoic sediments of the Cobalt

FIGURE 5.


MARY RIVER AREA
BAFFIN
ISLAND
HUDSON BAY
UNGAVA
MICHIPICOTEN IRON RANGES
TIMAGAMI
100 0 200 MILES
100 0 200 KILOMETERS

Group. The detailed geology of the Lake Timagami area is given by Moorehouse (1942) and Simony (1964) and the generalized stratigraphy of the area is shown in Table IX.

Iron-formation is found in two discontinuous bands trending approximately east-west. Both are probably part of the same stratigraphic horizon as there is considerable evidence for a synclinal structure (Moorehouse 1942). None of the bands extend for more than six miles along strike and they appear to be typical of Algoma-type iron-formation as described by Gross (1965). Varying in thickness from several feet to more than 500 feet, they form tabular, steeply dipping bodies conformable with the rest of the sedimentary and volcanic strata. They are generally associated with tuffs, agglomerates and slates indicative of deposition during a relatively quiet interval in a period of dominantly intense vulcanism.

Compositionally, the iron-formation is strongly banded and consists of alternating layers of grey, cherty quartz, jasper, magnetite, sugary white quartzite and occasional tuff. Carbonate and silicate facies are present to a minor extent, and pyrite is found both in the iron-formation and in the adjacent metasediments and volcanics. The separate bands range from microscopic size up to two or three inches in width, and are often branching or lenticular. Larger scale layering, however, does appear to be quite persistent along strike.

Metamorphic grade in this area reaches the epidote-amphibolite facies of regional metamorphism except near igneous intrusions where localized thermal aureoles occur. The rocks

TABLE IX

Table of formations, Timagami, Ontario (after Moorehouse 1942, and Simony 1964)

PROTEROZOIC	LATE MAFIC INTRUSIVE ROCKS
	Olivine diabase dikes
	Intrusive Contact
	"Nipissing" quartz diabase, granophyre
	Intrusive Contact
	COBALT GROUP
	Lorrain Formation: feldspathic quartzite, arkose
	Gowganda Formation: argillite, slate, greywacke, breccia, conglomerate, quartzite
	Great Unconformity
ARCHEAN	LAMPROPHYRE: Amphibolite, carbonate, diorite and greenstone dikes
	Intrusive Contact
	GRANITE INTRUSIVES: Quartz porphyry, feldspar porphry, felsite dikes and intrusives. Granite, granodiorite, including porphritic types, albite granite, granite and aplite dikes.
	INTERMEDIATE INTRUSIVES: Diorite, quartz diorite, and sheared equivalents, peridotite, and metadiabase intrusives.
	Intrusive Contact

TABLE IX (cont'd.)

ARCHEAN	BASIC VOLCANICS:	Basic and intermediate lava flows, pillow lavas, amygdular lavas, pyroclastics, tuffs, dioritic and recrystallized rocks, chlorite, carbonate, and hornblende schist.
	ACID VOLCANICS:	Rhyolite, quartz and feldspar porphry, acid tuffs, agglomerates, carbonate and sericite schist.
	BANDED IRON-FORMATION	

are undoubtedly of Archean age as they are overlain with profound unconformity by the Huronian Cobalt Group dated at approximately 2300 m.y. (Fairbairn *et al.* 1969).

In an attempt to make a more accurate estimate of the age of the iron-formation, ten whole-rock Rb-Sr analyses were made on the volcanics associated with the iron-formation and on one greywacke. The results are shown in Fig. 6 and Table X. They define a poor isochron and yield an age of 2221 ± 120 m.y. and initial Sr^{87}/Sr^{86} of 0.7083 ± 0.0017 by the computerized least-squares method of York (1966). This age is conspicuously low for Archean rocks but is consistent with the ages obtained by Fairbairn *et al.* (1966) on the volcanics at Kirkland Lake immediately to the north of this area. Those Keewatin and Timiskaming volcanics give whole-rock ages of 2376 ± 40 m.y. and 2368 ± 48 m.y., respectively. They are intruded by the Round Lake pluton which has been dated by the Rb-Sr whole-rock isochron method at 2530 m.y. by Fairbairn *et al.* (1966) and at 2390 m.y. by Purdy and York (1968). A K-Ar age of 2570 m.y. and a Rb-Sr age of 2550 m.y. for a biotite (Aldrich and Wetherill 1960) and another biotite K-Ar age of 2605 m.y. (Lowdon *et al.* 1963) from this pluton appear to establish an age greater than 2500 m.y. The low whole-rock Rb-Sr age determined by Purdy and York (1968) may be due to analytical difficulties because of the small spread in Rb/Sr ratios, or the samples may have been affected by the process which lowered the ages of the volcanics in the area.

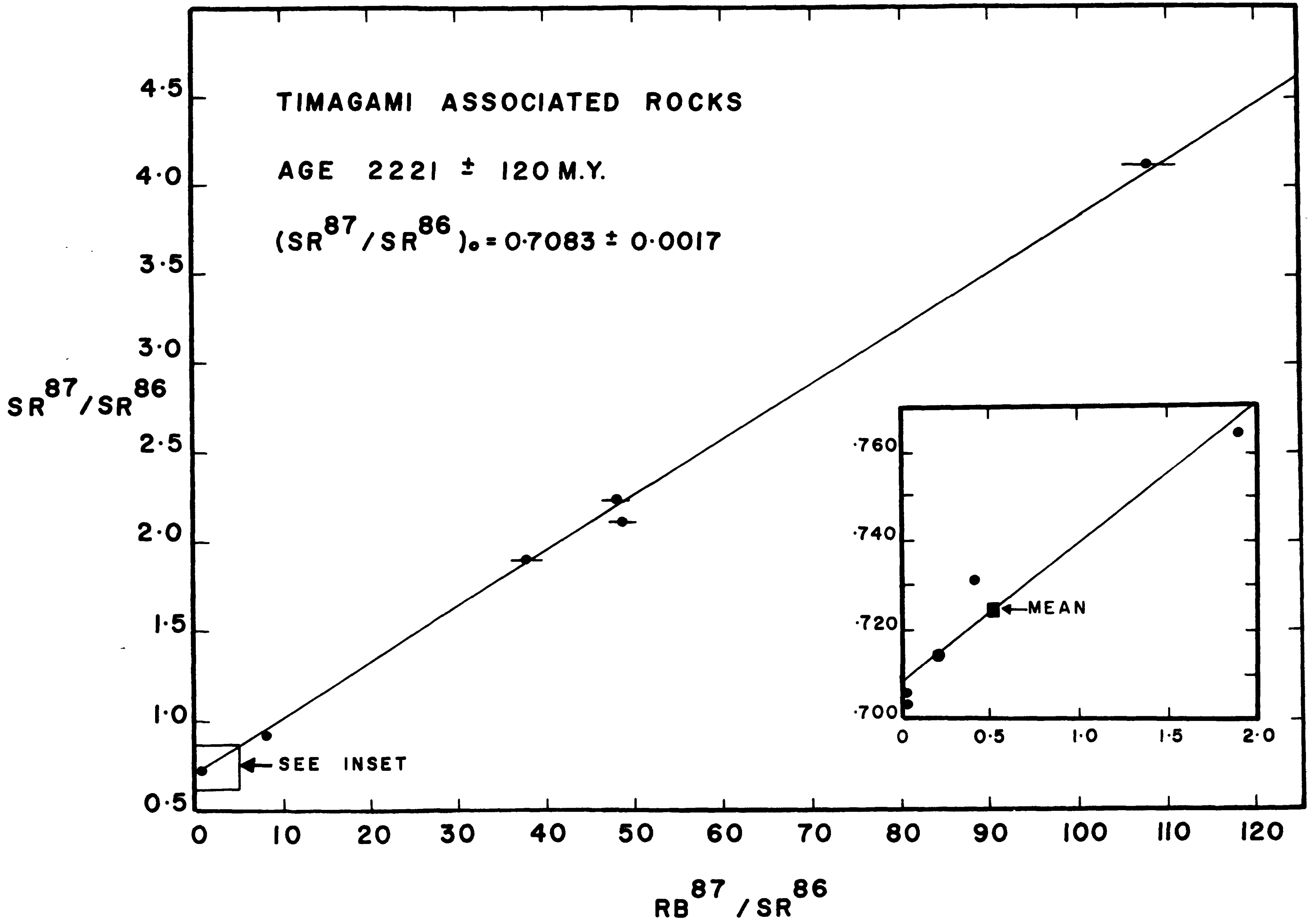
Thus it appears that a number of volcanic rocks in this part

TABLE X

Rb-Sr isotopic data, Timagami, Ontario

Sample	Rb (ppm)	Sr (ppm)	Rb^{87}/Sr^{86}	Sr^{87}/Sr^{86}
R7721	1.27	241	0.0153	0.7046
R7719	60.2	91.2	1.91	0.7646
R7723	82.0	585	0.406	0.7317
R7707	7.93	114	0.202	0.7147
R7718	181	68.6	7.82	0.9462
R7714	137	9.67	47.6	2.2303
R7722	253	17.2	48.5	2.1160
R7708	214	18.3	37.7	1.9005
R7724	1.90	74.0	0.074	0.7066
R7713	226	8.10	108	4.1108

FIGURE 6.


TIMAGAMI ASSOCIATED ROCKS
AGE 2221 ± 120 M.Y.
$(Sr^{87}/Sr^{86})_o = 0.7083 \pm 0.0017$
Sr^{87}/Sr^{86}
Rb^{87}/Sr^{86}
4·5
4·0
3·5
3·0
2·5
2·0
1·5
1·0
0·5
0
10
20
30
40
50
60
70
80
90
100
110
120
SEE INSET
·760
·740
·720
·700
0
0·5
1·0
1·5
2·0
MEAN

of the Superior Province have been affected by isotopic redistribution at some time after the Kenoran orogeny (~ 2490 m.y., Stockwell 1968) In the Timagami area this may be related to the intense carbonatization, shearing, and sericitization of the volcanics under the village of Timagami reported by Bennet (1969). Consequently, the primary depositional age of the iron-formation in the Timagami area is known only to be greater than 2490 m.y.

Michipicoten iron-formations, Ontario

Banded iron-formations, clastic sediments and thick piles of volcanics of the Andesite-Rhyolite Association constitute a greenstone belt surrounded by younger regional granites in the Michipicoten area of Ontario (Fig. 5). The general geology of the area has most recently been described by Goodwin (1962) and will only be outlined here. Briefly, the volcanics show marked lithological and structural variations over short distances. Volcanic activity appears to have been cyclical with three separate phases, beginning with widespread quiet effusive outpourings of intermediate to basic flows followed by rapid, violent discharge of felsic pyroclastics forming broad domical accumulations. The last stage appears to have been prolonged hot-spring and fumarolic activity with considerable alteration and leaching of the breccia domes. The sedimentary rocks appear to be conformable to the enclosing volcanics and Goodwin (1961) interprets them as being formed as a result of contemporaneous erosion of subaerially exposed volcanics.

The banded iron-formations are associated with the late stage fumarolic and hot-spring activity and form two mutually gradational facies. Iron-formation enclosed in sedimentary rocks form lensy discontinuous bands, typically of interlayered chert, siliceous magnetite and jasper, similar to most Algoma-type iron-formations elsewhere in the Canadian Shield. Iron-formation associated with volcanic rocks, however, is composed of much thicker members of more homogeneous mineralogy. Uppermost is a banded chert up to 800 feet thick which is the thickest and most persistant member of the iron-formation. According to Goodwin (1961) this is underlain by a lensy, discontinuous pyrite member followed by a thicker unit composed mainly of siderite, which reaches a thickness of 350 feet at the Helen Mine. This siderite-pyrite-chert type of iron-formation typically overlies andesite-rhyolite pyroclastic and breccia deposits which have been intensely altered to depths of several hundred feet and is overlain by the effusive mafic and intermediate lavas of the succeeding volcanic cycle.

This greenstone belt has recently been dated by Brooks *et al.* (1970) who obtained Rb-Sr whole-rock isochron ages of 2700 ± 80 m.y. and 2550 ± 100 m.y. on the Lower and Upper Volcanic Series, respectively. These results may represent the primary age of these rocks as low and high grade metamorphic rocks all fall on the same isochrons and the differing ages obtained for the two series indicate that the dates obtained are not the result of regional metamorphism. Since the Helen Iron Range overlies the Lower Volcanic Series it is thus reasonably well dated at about 2700 m.y.

Mary River area, Baffin Island

High-grade iron deposits near the north end of Baffin Island were discovered in the Mary River area in 1962 (see Fig. 5). The general geology of the area and deposits have been outlined by Jackson (1966) and Gross (1966). The deposits are found within Algoma-type iron-formation which forms lenticular masses within a metavolcanic and sedimentary sequence. This sequence of acid and basic metavolcanics, metasediments and iron-formation has been infolded and faulted within younger granitic terrane, forming numerous small belts isolated by erosion. They have been intruded by at least two different granites, the youngest of which was accompanied by widespread granitization and potash metasomatism (Jackson 1966) and by basic dikes and serpentinized ultrabasic rocks.

The iron-formation is of rather unusual nature. According to Gross (1966) thin layered quartz magnetite and quartz hematite facies are most common, but silicate facies rocks occur in certain areas. The most distinctive and unique feature of these rocks has been the development of nearly pure beds of magnetite and occasional hematite within the iron-formation. They range in thickness from a few inches to tens of feet and are interlayered with more typical thin magnetite-quartz beds. The iron deposits themselves are of exceptional ore quality as they typically have less than one percent impurities and occur as zones of massive magnetite or hematite. They have been formed by leaching and oxidizing of the original iron-formation combined with supergene enrichment, followed by burial and high-grade metamorphism. Gross believes, however, that leaching and enrichment alone could not produce such pure iron oxide and that much of the protore must have been originally rich in iron. Consequently, only small amounts of impurities would have to be removed from the original beds to form the present ore.

The metamorphic grade appears to be quite high in the sediments and volcanics. According to Jackson (1966) many of the rocks have been regionally metamorphosed to the almandite amphibolite facies and thermal metamorphism was locally important. The last period of widespread metamorphism appears to have occurred during the Hudsonian orogeny as shown by the K-Ar ages (Table XI) reported by Wanless *et al.* (1966, 1970). For this reason these rocks have been included in the Churchill Province of the Canadian Shield by Stockwell (1968).

Gross (1966) believes that these rocks are Archean in age and 16 Rb-Sr whole-rock isotopic analyses were undertaken on the metavolcanics and sediments to determine whether this could be substantiated. The analyses are given in Table XII and shown on a Rb-Sr isochron plot (Fig. 7).

The analyzed samples do not define a reasonable isochron due to the complex history of the area. Reference isochrons drawn with a geologically reasonably initial Sr^{87}/Sr^{86} ratio of 0.710 indicate that the rocks are at least as old as 1950 m.y. and sample R7813 suggests that they may be at least 2650 m.y. The large amount of scatter of the data points is consistent with a primary Archean age for these rocks modified by varying

TABLE XI

K-Ar ages Mary River area, Baffin Island (after Wanless *et al.* 1966, 1970)

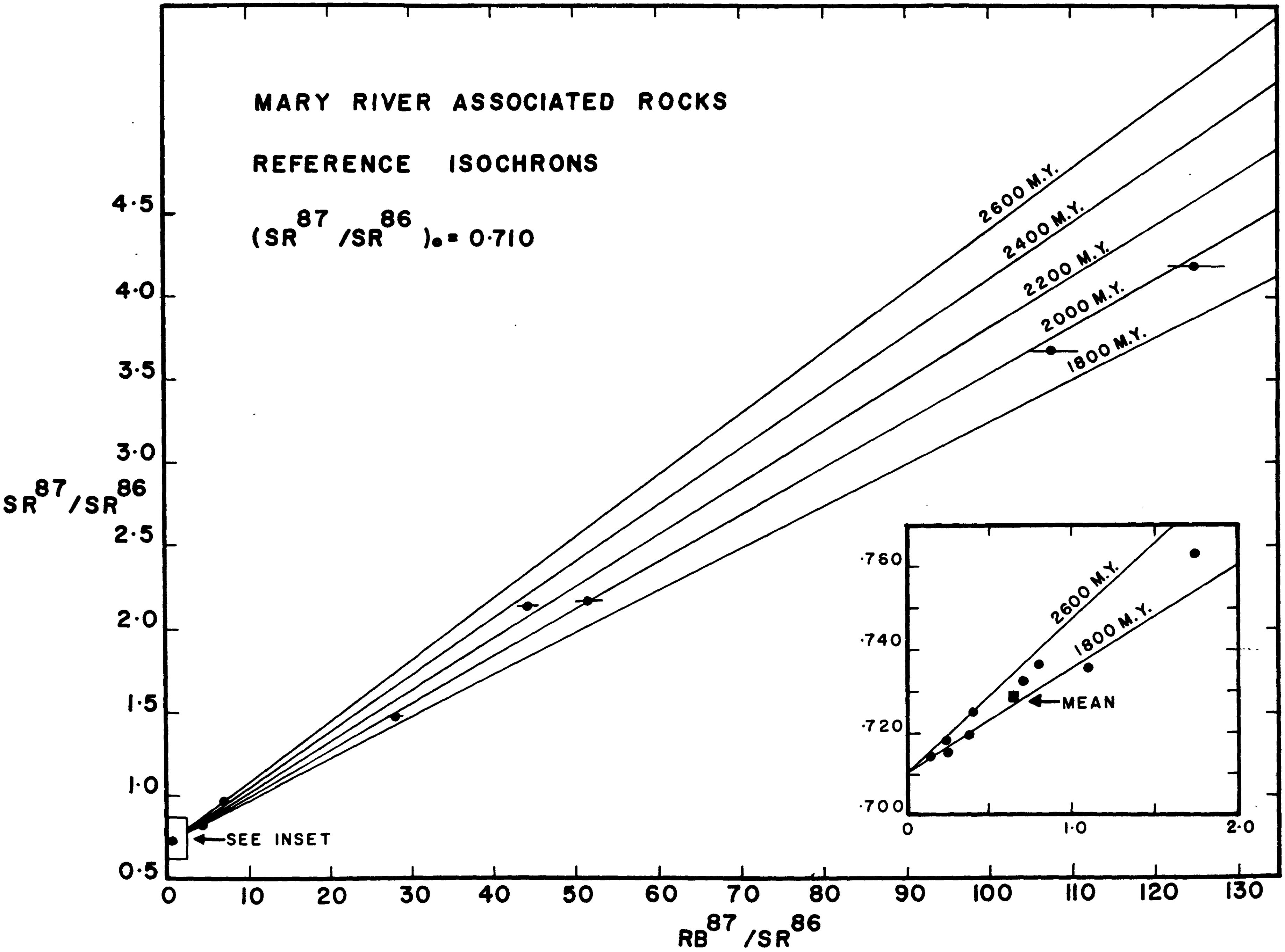
Rock description	Mineral	Age (m.y.)
	Muscovite	1750 ± 50
Mica schist	Biotite (mainly chlorite)	1610 ± 210
Meta-pyroclastic (?) rock	Biotite	1865 ± 60
Gneissic granite	Muscovite	1655 ± 50
Quartz monzonite pegmatite (cuts iron-formation)	Muscovite	1675 ± 50
Amphibolite sill	Hornblende	1525 ± 55
Meta-orthoquartzite	Muscovite	1670 ± 55
Biotite schist	Biotite	1685 ± 50

TABLE XII

Rb-Sr isotopic data, Mary River area, Baffin Island

Sample	Rb (ppm)	Sr (ppm)	Rb^{87}/Sr^{86}	Sr^{87}/Sr^{86}
R7807	87.9	147	1.74	0.7626
R7813	140	59.9	6.93	0.9703
R7802	13.5	35.5	1.10	0.7358
R7815	147	102	4.23	0.8353
R7814	8.86	104	0.247	0.7813
R7804	96.8	401	0.700	0.7327
R7808	150	9.62	51.7	2.1700
R7809	245	8.49	108	3.671
R7811	237	13.6	43.7	2.1379
R7801	693	78.4	27.9	1.4808
R7805	19.3	149	0.375	0.7196
R7806	5.36	100	0.155	0.7144
R7810	135	491	0.801	0.7366
R7812	1871	58.3	125	4.1902
R7816	34.2	254	0.391	0.7253
R7817	33.4	388	0.249	0.7156

FIGURE 7.


MARY RIVER ASSOCIATED ROCKS
REFERENCE ISOCHRONS
(SR87/SR86)₀ = 0·710
2600 M.Y.
2400 M.Y.
2200 M.Y.
2000 M.Y.
1800 M.Y.
SR87/SR86
4·5
4·0
3·5
3·0
2·5
2·0
1·5
1·0
0·5
RB87/SR86
0
10
20
30
40
50
60
70
80
90
100
110
120
130
SEE INSET
·760
·740
·720
·700
0
1·0
2·0
2600 M.Y.
1800 M.Y.
MEAN

amounts of isotopic redistribution during the intense deformation and metamorphism of the Hudsonian orogeny. Thus it appears that the basement at least in this part of Baffin Island is of Archean age, and consequently, the outline of the Archean continent at the time of the Kenoran orogeny must be extended at least as far as the northern tip of Baffin Island.

Trace element results and discussion

Analyses for Co, Cr, Sc, Th, As, La, Ce, Nd, Eu, Sm, Ho, Yb, and Lu, have been obtained on ten samples of iron-formation from the three areas by instrumental neutron activation analysis (I.N.A.A.). The technique used is similar to the one reported by Gordon *et al.* (1968) with several refinements which are discussed in Appendix 1. The estimated (1σ) analytical errors are 10% for Co, Cr, La, Ce, Nd, Sm, Eu, Yb, and Lu, and 20% for Th, Sc, and Ho. The precision and accuracy of the analyses for all elements except Th are believed to be the same as the estimated analytical error. For Th, a high blank value, and extremely low abundance allows only a maximum limit to be placed on its abundance in these rocks. A detailed discussion of the errors and analyses is given in Appendix 1.

The trace element data are presented in Tables XIII and XIV and the rare earth data are shown graphically in Figs. 8-10. The rare earth data has first been normalized to the average of 9 chondrites reported by Haskin *et al.* (1968) and then renormalized to the average chondrite normalized pattern (Lu=1) of two Archean basalts from Africa reported by Frey *et al.*

FIGURE 8.

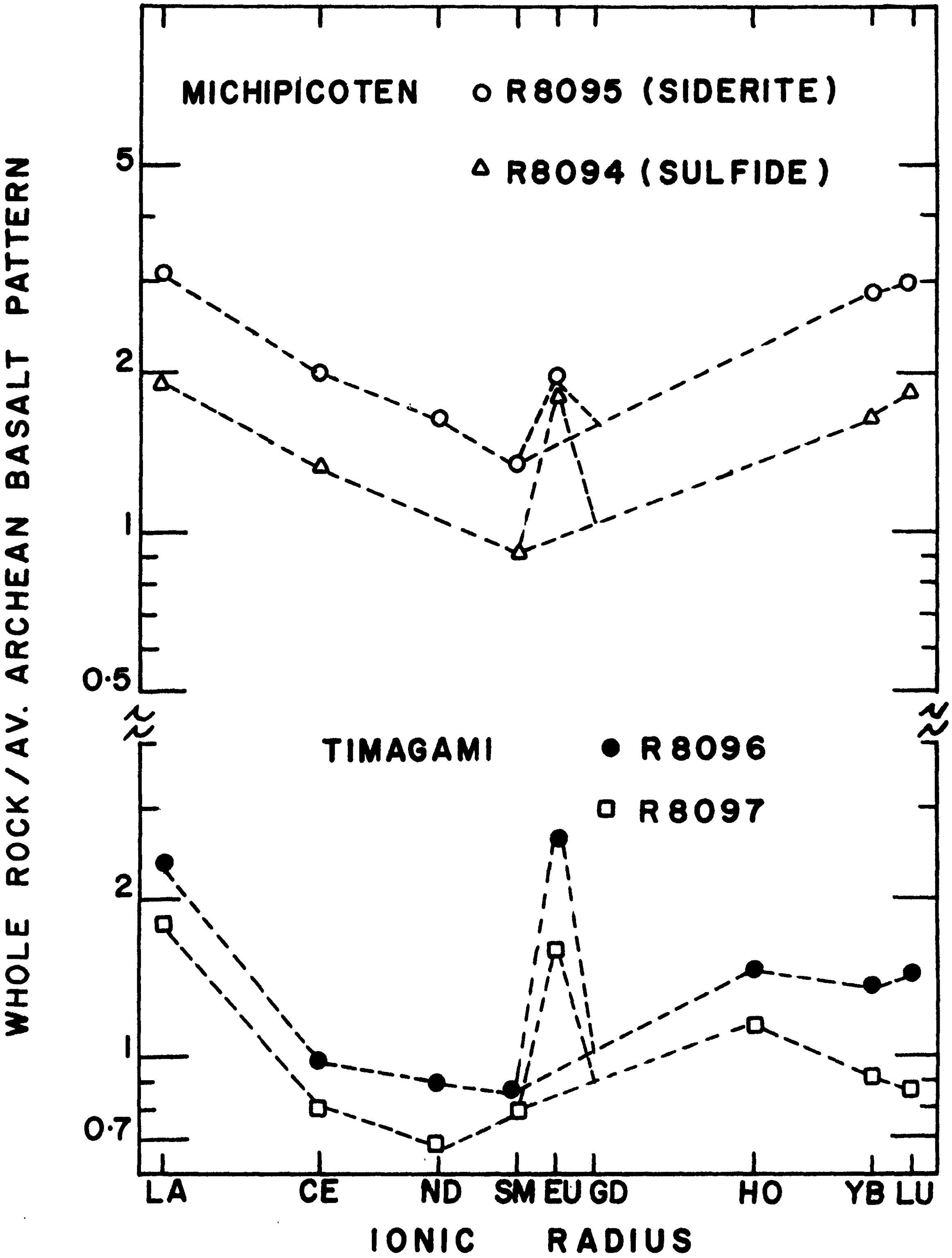

MICHIPICOTEN
○ R8095 (SIDERITE)
△ R8094 (SULFIDE)
TIMAGAMI
● R8096
□ R8097
5
2
1
0·5
2
1
0·7
LA
CE
ND
SM
EU
GD
HO
YB
LU
IONIC RADIUS
WHOLE ROCK / AV. ARCHEAN BASALT PATTERN

FIGURE 9.
Mary River Area

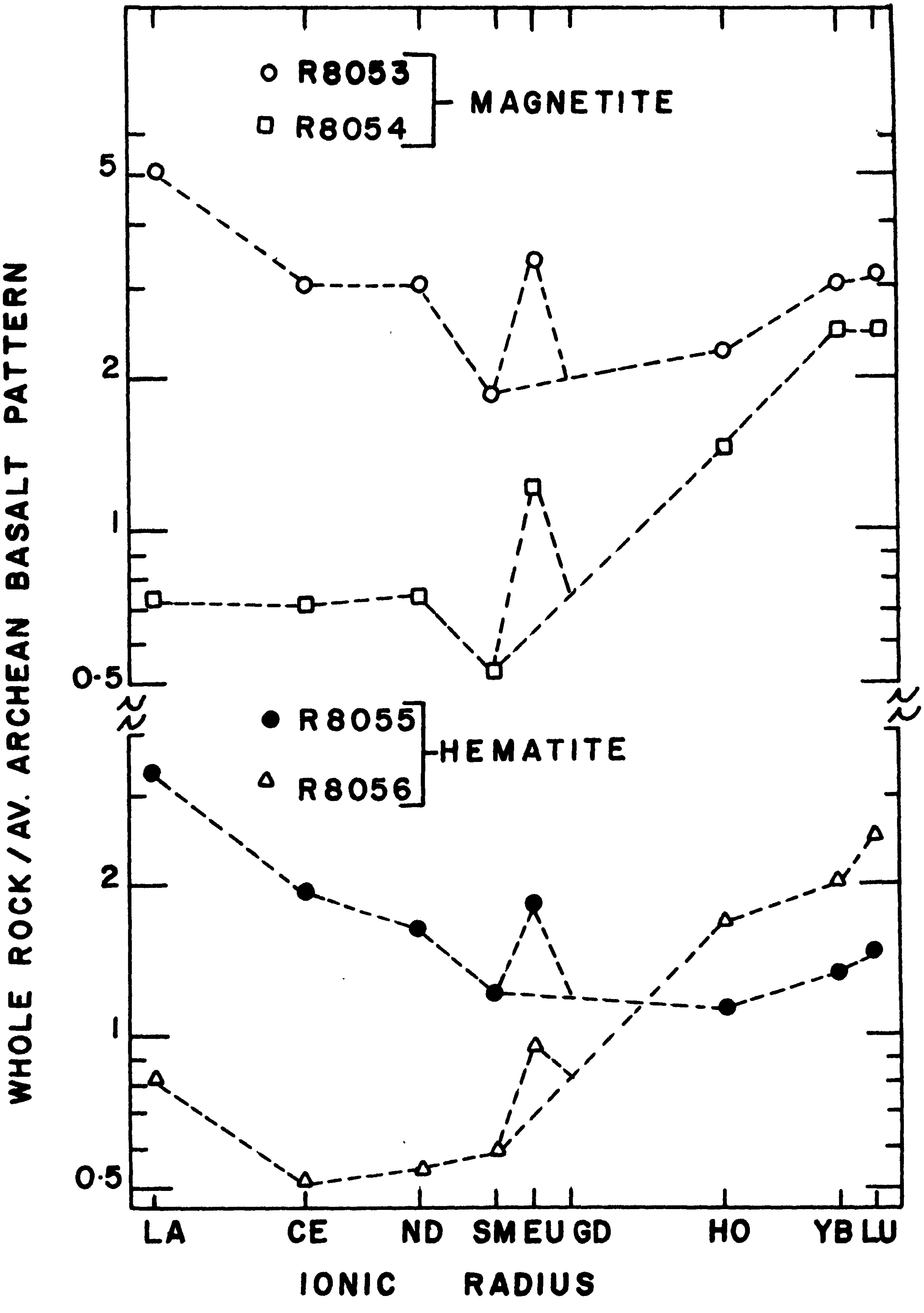


FIGURE 10.
Mary River Area

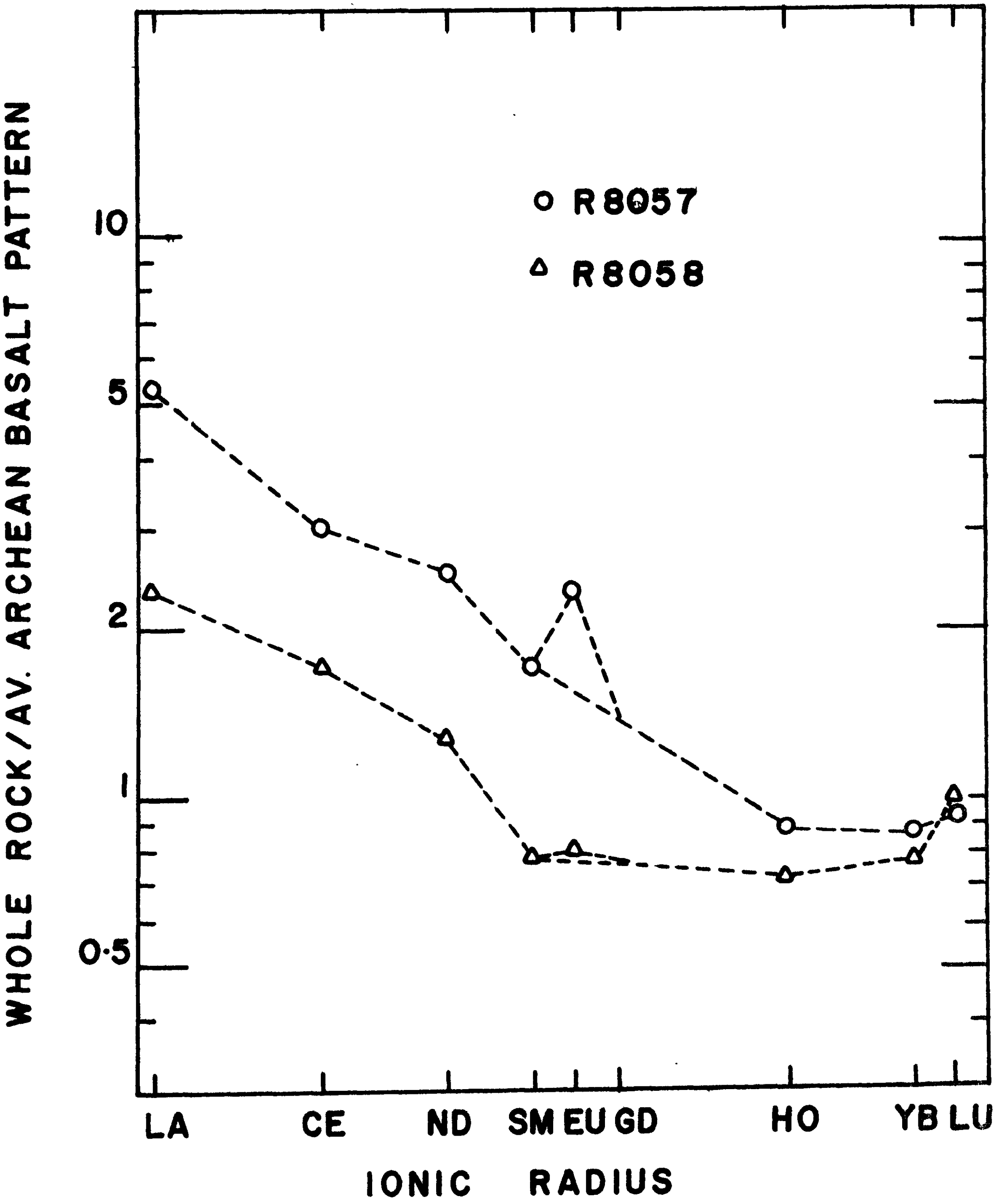


FIGURE 11.

Archean basalts

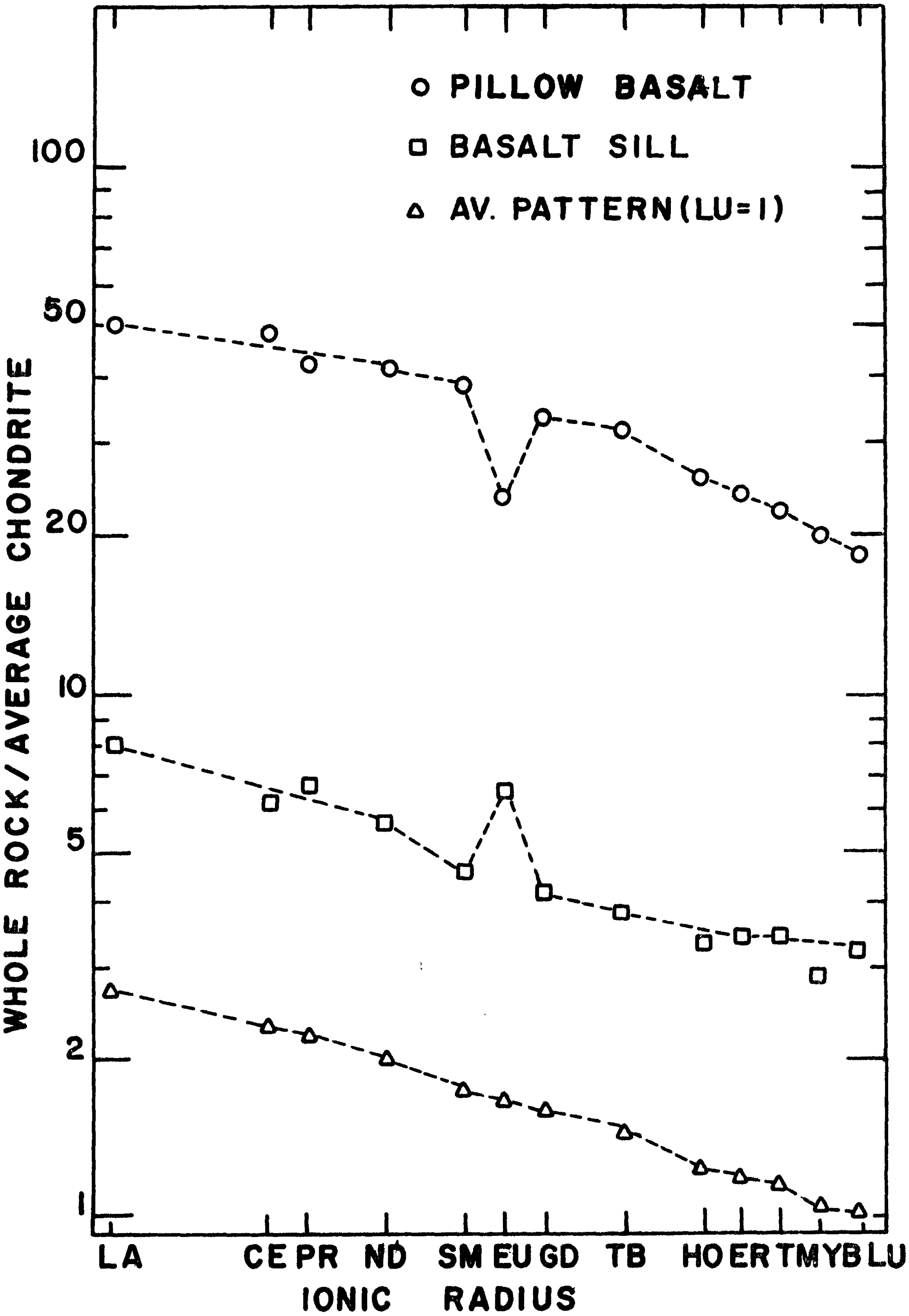


TABLE XIII

Trace element abundances in Algoma-type iron-formations, Timagami and Michipicoten, Ontario (ppm)

	R8094[1]	R8095[2]	R8096[3]	R8097[4]
La	1.49	2.44	1.82	1.37
Ce	2.71	4.06	2.01	1.64
Nd	-	2.01	1.09	0.821
Sm	0.293	0.433	0.274	0.256
Eu	0.261	0.220	0.303	0.183
Ho	-	-	0.124	0.0973
Yb	0.356	0.615	0.289	0.194
Lu	0.0621	0.102	0.0486	0.0296
Co	39.8	1.35	1.01	1.85
Cr	15.86	15.2	1.39	0.564
Sc	1.40	1.82	0.120	0.085
Th	<0.20	<0.21	<0.042	<0.050

[1] Sulfide facies Michipicoten

[2] Siderite facies Michipicoten

[3] Banded jasper-magnetite Timagami

[4] Banded jasper-magnetite Timagami

TABLE XIV

Trace element abundances (ppm) in Algoma-type iron-formations, Mary River area, Baffin Island

	R8053*	R8054*	R8055†	R8056†	R8057**	R8058††
La	3.93	0.561	2.55	0.612	4.12	1.76
Ce	6.17	1.46	3.92	1.05	6.11	3.47
Nd	3.66	0.918	1.97	0.699	3.12	1.55
Sm	0.599	0.169	0.389	0.192	0.549	0.256
Eu	0.389	0.138	0.213	0.110	0.269	0.0913
Ho	0.191	0.124	0.0988	0.145	0.0753	0.0615
Yb	0.662	0.531	0.286	0.446	0.184	0.169
Lu	0.106	0.0846	0.0580	0.0868	0.0322	0.034
Co	37.2	36.1	0.708	0.403	2.10	3.87
Cr	1.37	3.41	1.62	2.25	1.62	10.3
Sc	0.693	0.979	0.360	0.323	0.599	0.926
Th	<0.476	<0.309	<0.105	<0.124	<0.049	<0.963

*	Massive magnetite
†	Massive hematite
**	Banded magnetite-hematite iron-formation
††	High-grade banded magnetite iron-formation

(1968). Since no other analyses are available from Archean basalts, no estimate of the variability in rare earth patterns is known for these rocks. The results are plotted with the ionic radii of Whittaker and Muntus (1970) as abscissa and the relative abundance of the individually normalized rare earths as ordinate.

The chondrite normalized patterns of the two Archean basalts are shown in Fig. 11. Also shown, is the average of the two patterns obtained by normalizing the individual patterns to Lu=1. These rocks are less light rare earth enriched relative to chondrites than the basalt composite reported by Frey *et al.* (1968) by a factor of about 3 and display Eu anomalies. Whether relatively less fractionated rare earth patterns are characteristic of Archean basalts cannot be determined from the meager data presently available. However this may be the case at least for greenstone belts in the Canadian Shield as they are deficient in K_2O compared to more recent basalts (Goodwin 1968; Baragar 1966) and light rare earth enrichment appears to be greater for more alkaline basalts (Frey *et al.* 1968). Although both African basalts show europium anomalies the pillow basalt has a negative anomaly and the basic sill a positive one. Consequently the average pattern of the two has essentially no anomaly and when normalizing the iron-formation data to this average basalt pattern, no europium anomalies will be artificially created.

The two most striking aspects of the iron-formation analyses and rare earth patterns are the very low absolute trace element abundances and the presence of positive europium anomalies for nine of the ten rocks analyzed (Fig. 8-10). In addition, most of the rare earth patterns show a minimum in the region Nd to Gd thus indicating that these rocks are relatively enriched in the heavy rare earths compared to the Archean basalts. If the analyses were normalized to more normal (ie. more light enriched) rocks, this enrichemnt in the heavy rare earths would be even more pronounced. Lastly, the rare earth patterns from each area have their own distinguishing characteristics. Each analysis from Michipicoten and Timagami is almost identical to the other analysis from the same area and the analyses from the Mary River area, are notable for their diversity.

The low absolute abundances of both the rare earth elements and the rest of the trace elements except for arsenic is consistent with the previous studies on Precambrian cherty iron-formations. Landergren (1948) has noted the remarkable deficiency of the Swedish Precambrian banded iron ores in the other ferride elements; titanium, vanadium, chromium, cobalt and nickel. Consequently it appears that iron has not acted as a scavanger for minor elements (Goldberg 1954) during the deposition of Algoma-type iron-formations. The minor elements which are usually enriched in these rocks; arsenic and sometimes copper and sulphur (Gross 1966), may be derived from volcanic emanations. Goodwin (1961) reports that the footwall volcanics and iron-formation of the Helen Iron Range in the Michipicoten area are enriched in the relatively volatile constituents boron and arsenic which he equates with a presumed hot-spring, fumarolic environment.

Europium

The most important and striking aspect of the rare earth patterns of Algoma-type iron-formations is the positive Eu anomalies they exhibit. All three of the areas studied show this enrichment in Eu and only one sample of the ten analyzed does not show a definite positive anomaly. In addition, all the iron-formation facies studied exhibit this. Thus it does not appear to be restricted to a certain depositional environment or specific Eh-pH conditions.

The usual explanation for Eu anomalies in igneous rocks is the preferential incorporation of Eu in feldspars (Towell *et al.* 1965; Haskin *et al.* 1966) as Eu^{+2} due to crystal chemical effects (Haskin and Frey 1966; Schnetzler and Philpotts 1967). The results presented here are difficult to explain by this mechanism if the rare earths incorporated in the iron-formation are coming directly from volcanic processes. The widespread association of these rocks with the termination of volcanic cycles indicates that these iron deposits would probably be the end products of igneous differentiation. Previous studies (Haskin *et al.* 1966; Balashov and Nesterenko 1966) indicate a broad trend of decreasing Eu with increasing differentiation. With this in mind it is difficult to conceive of a process in which Eu could be preferentially enriched in late stage volcanic emanations. There are a number of possible mechanisms which might produce the observed Eu enrichments in these sediments and these will now be considered.

Since Eu has behaved differently from the rest of the rare earths, it must have been in the +2 oxidation state at some time in its geological history. There are three possible periods when this could have occured: a. during formation of the igneous rocks b. during weathering, leaching etc. when Eu was released from crystalline phases or c. during precipitation of the iron-rich minerals from seawater. These periods will be considered separately for ease of discussion.

As mentioned, Eu anomalies in igneous rocks are usually attributed to preferential incorporation of Eu into feldspar. If the source of iron for these sediments is due to the release of iron-rich exhalations after differentiation in a magma chamber (Gross 1965) it is difficult to reconcile this with the production of a late stage Eu concentration. This could only be accomplished if a significant portion of the Eu in the magma was present in the +2 oxidation state or was able to be converted to the +2 state by some mechanism.

An extremely low oxygen fugacity would be required to reduce a significant amount of the Eu in a basaltic magma to the +2 oxidation state. This might be possible if metallic iron was present in the upper part of the mantle due to a frozen rind effect, preventing infall into the core of some iron during the early differentiation of the earth. If this was the case, basaltic magmas could be generated in regions containing metallic iron as part of the oxygen buffer, until escaping volatiles from the interior of the earth had oxidized all the iron in the outer rind. This would mean that oxygen fugacities in the generated basaltic liquids would be much lower than in more recent basalts in which Eu behaves normally. The larger ionic size, smaller charge and other crystal chemical effects might lead to the concentration of Eu^{+2} in late stage magmatic fluids. These differentiates could conceivably be enriched in iron because of low oxygen partial pressure during magmatic differentiation, thus accounting for both the source of iron and the Eu enrichment of these deposits.

However, if this were the case, anomalous behavior of Eu should also be observed for meteoritic material, most of which contains metallic iron or presumably has been associated with metallic iron sometime during its history. This is not observed for most meteorites and indeed they are noted for their regularities in distribution of the rare earths (Haskin *et al.* 1966). Even the Ca-rich achondrites which may have undergone extensive reworking and recycling at high temperatures have normal Eu abundances. Two Ca-poor achondrites do show depletions in Eu, however, combined with fractionation of the rest of the rare earths (Haskin *et al.* 1966). This suggests that Eu may under certain circumstances, be lost from these systems under strong reducing conditions . Consequently although meteoritic rare earth abundances do not support the above contention they do not rule it invalid.

Another possible cause of anomalous behavior during igneous processes, may lie in the higher vapor pressure of Eu metal and EuO in equilibrium with solid Eu_2O_3 compared to the adjacent rare earth Sm and its compounds (Panish 1961). The higher volatility of Eu might allow it to be preferentially incorporated in a vapour phase and hence to be enriched in late stage volatile-rich magmatic differentiates.

An alternative to the release of Eu rich fluids during igneous processes may be the preferential breakdown of minerals containing anomalous Eu abundances during weathering or fumarolic and hot-spring activity. Goodwin (1961) presents convincing evidence for hot-spring and fumarolic activity in the Michipicoten area leading to the deposition of these iron-formations. He showed that wall rock alteration consisted of removal of SiO_2, Na_2O, K_2O and minor CaO which are feldspar components and the addition of CO_2, FeO, MnO, and minor MgO. It is possible that feldspars with positive Eu anomalies were preferentially leached from these rocks and hence the leaching solutions became relatively enriched in Eu compared to the other rare earths. When the "volcanic emanations" entered the marine environment, Goodwin envisions siliceous bicarbonate solutions losing CO_2 to the atmosphere, resulting in the precipitation of carbonate beds in the vinicity of the source areas. Considerable silica and lesser amounts of the ore constituents would be more widely dispersed before precipitation, and these presumably would form the banded jasper-magmatite ore typical of Algoma-type deposits.

If the positive Eu anomalies are produced from preferential leaching of some Eu enriched phase such as feldspar or for that matter from igneous differentiation processes, the greatest Eu enrichments might occur in the massive siderite beds at Michipicoten. Siderite would be the first mineral to be precipitated if the above process of Goodwin is valid. Presumably the rare earths incorporated in the siderite would closely resemble the rare earth abundances of the "volcanic emanations", as the emanating solutions would have little chance to mix with the marine waters before precipitation of siderite. This is not the case as seen in Fig. 8 where the sulfide facies exhibits a larger anomaly than the siderite facies. Although no analyses of banded jasper-magnetite facies is available from the Michipicoten area, those from the Timagami area (Fig. 8) also have much greater Eu anomalies than the siderite. Indeed the oxide facies rocks may have greater Eu enrichment than the sulfide facies.

This arguement is not conclusive however, because of the short resident times in the marine waters (Goldberg *et al.* 1963). With short residence times, it is possible that essentially all of the rare earths in a marine basin could be derived from volcanic activity during certain time periods. Consequently the anomalous Eu might still be due to initial volcanic or hot-spring enrichment even in the more sedimentary differentiated oxide facies rocks.

Although the above discussion outlines a number of possible explanations for Eu enrichment in these iron-formations directly or indirectly stemming from volcanic processes, none of them are especially convincing. Consequently a sedimentary source of these Eu anomalies can not be ruled out. Why Eu should behave differently in a normal sedimentary environment is not immediately apparent. Possibly the lack of free oxygen in the period prior to 2500 m.y. (Cloud 1968; Holland 1962) caused Eu contained in feldspars and other minerals to be released during weathering in the same oxidation state as it was found in the minerals. If this were the case, the Eu enrichments in these chemical sediments might be due to preferential precipitation of Eu^{+2} because it was less soluable than the other rare earths.

Alternatively more Eu may have been released during the weathering cycle than the other rare earths due to leaching or altering of feldspars. Condie (1967) reports that Archean greywakes in Wyoming are low in Ca due to the replacement of Ca in feldspars by Na, and the release of Ca into solution. This reaction might also release Eu into solution enriching seawater in Eu relative to the other rare earths and chemical precipitates from the marine waters would thus show enrichment in Eu.

The merits of all the above explanations for Eu anomalies in Algoma-type iron-formations can best be evaluated by taking into account the results of Wildeman and Haskin (1971). Their data shows an apparent trend towards increasing relative Eu concentration in sediments with age. Thus Eu may have been relatively more abundant during the early sedimentological history of the earth's surface. Consequently, special mechanisms required to produce excess Eu just for these iron-formations, do not seem to be as probable as a general one, which can account for the overall increased Eu content of the Archean sediments. It is informative to note in this regard that the most Eu enriched sediment sample is the Soudan slate from Minnesota which is interbedded with Algoma-type iron-formation and itself contains a considerable amount of iron oxide.

The reason for the increasing Eu concentration with age of these sediments is almost as difficult to explain as the high Eu contents of the iron-formations. However, it is reasonable to assume that a general enrichment in Eu of sediments was caused by processes that acted over large areas and that were not restricted to isolated, exceptioal, volcanic activity. Consequently Eu enrichment must have been a feature of early crustal development or, Eu behaved differently during surface processes. The fact that the Eu anomalies associated with the iron-formations, appear to be anomalously great even compared to the Eu enriched Archean sediments tentatively suggests that the processes probably were associated with sedimentation. Consequently chemical sediments which incorporated essentially no detrital rare earths would have the greatest Eu anomalies.

It is immediately obvious that much more work is needed, to at least eliminate some of the possibilities for these high Eu abundances in Archean sediments. Analyses of Archean volcanic rocks and their derived sediments would be most helpful in this regard. Ideally a small greenstone belt containing banded iron-formation should be studied in detail.

Rare earth patterns and abundances

The rare earth patterns exhibited by these Algoma-type iron-formations are remarkably similar for both individual analyses from the Timagami and Michipicoten areas, although the patterns of each area differ somewhat from each other. The siderite and sulfide facies patterns from Michipicoten are almost identical to one another excepting the extent of the Eu anomaly, strongly suggesting that the rare earth elements were precipitating from the same source, with little modification. The siderite sample however, is considerably more enriched (~1.6 times) in absolute abundance. The same situation is present for the Timagami samples. The two patterns are again very similar, essentially varying only in the extent of the Eu anomaly. The six rare earth patterns from the Mary River area present a different situation. They are distinguished by their diversity rather than their similarities. This is not altogether unexpected as Gross (1966*b*) accounts for the extremely high-grade of these deposits by leaching and supergene enrichment of iron. This certainly would have affected the trace element contents of these ores. In addition these rocks have been highly metamorphosed during the Hudsonian orogeny and probably were also disturbed by the Kenoran episode.

The Michipicoten patterns are distinguished by depletion in the intermediate rare earths, relative to the South African basalts with a minimum in the region near Sm. The Timagami patterns are but slightly modified from the Michipicoten ones. La appears to be abnormally enriched and the depletion in the heavy rare earths is less pronounced, but otherwise both the patterns and absolute abundances of the rare earths are remarkably similar.

The depletion in the intermediate rare earths from these areas, may be due to a combination of two effects. The source of the light rare earth enrichment may be the rare earths supplied to the sedimentary basin. As mentioned, the Archean basalt pattern used to normalize the iron-formation data is depleted in the light rare earths by a factor of about 3, relative to the basalt composite of Frey *et al.* (1968). If the source of rare earths was more like the basalt composite, then the iron-formations would not be enriched in the light rare earths compared to the source and would just exhibit a heavy rare earth enrichment. This enrichment in the heavy rare earths could be explained by the greater stability of the heavy rare earth carbonate complexes (Beus 1958; Kosterin 1959). The light rare earths would be precipitated along with the clastic fraction in near shore environments, while the heavy rare earths would be transported farther, and hence, become relatively enriched in the basin as in modern ocean waters (Høgdaul *et al.* 1968). The iron-formations precipitated from solution would reflect this enrichment in heavy rare earths like the carbonates reported by Balashov *et al.* (1964).

The rocks from the Mary River deposits are notable for their diversity, rather than their similarities, in rare earth patterns (Fig. 9 and 10). Unlike the two other areas, banded magnetite-hematite iron-formation sample (R8057), is relatively enriched in the light rare earths. This is in agreement with the light rare earth enrichment of hematite and magnetite reported by Balashov and Goryainov (1966) for metamorphosed iron-formation. If the small variation observed, for samples from the other areas is indicative of homogeneity in rare earth patterns for individual areas, then this pattern may represent the original rare earth composition of these deposits before enrichment processes altered them. Relative to R8057 all the other samples are depleted in the light rare earths. This may indicate that the light rare earths were preferentially removed in the ore-forming process. In addition, if the absolute abundances of the rare earths in these rocks were originally similar to that of R8057, then considerable amounts of heavy rare earths were added to the high-grade magnetite and hematite samples.

Another interesting aspect of the enriched samples is the variability in the rare earth patterns within similar material. Both the hematite (R8055, R8056) and the magnetite (R8053, R8054) samples, which are greater than 99% pure, exhibit large differences in fractionation of the rare earths. This must be due to variation in the ore-forming process, although the actual cause is not immediately apparent.

Other trace elements

The abundances of Co, Cr, Sc, and Th do not show any consistent patterns, but instead appear to reflect the different areas. For instance, Sc is highest for Michipicoten (1.4-1.8ppm) lowest for Timagami (0.09-0.12ppm) and intermediate for Mary River (0.32-0.98ppm). Within the individual areas, abundances for all elements except Co are relatively constant. Co is enriched in the sulfide facies at Michipicoten as expected, because of its siderophile nature. In the Mary River samples it is anomalously high in the magnetite samples (by a factor of 10), possibly indicating epigenetic processes as Gusel'nokov and Volkov (1966) have shown that Co is enriched in the iron ores of the Mikhaylovka area where epigenetic mineralization occurs.

The abundances of these trace elements, along with the rare earths are in the same range as those found for the younger Superior-type iron-formations of the Labrador Trough. This may be indicative of their derivation from normal weathering processes, since marine precipitates from hydrothermal exhalations (Bostrom and Peterson 1966) are strongly enriched in Cr. There is no evidence for this in these rocks.

Conclusions

Algoma-type iron-formations of the Canadian Shield are characterized by positive Eu anomalies. These are tentatively interpreted as being products of normal weathering under special conditions exhisting during the Archean when oxygen was absent from the atmosphere. Much more work, however, is required before this can be substantiated.

Rare earth patterns indicate that carbonate complexing was probably important in the marine geochemistry of the rare earths during this period as it is to-day, but there is no evidence that it was more important than now. Since the abundances of all the trace elements are remarkably similar to those of the younger Sokoman iron-formation and are unlike those of modern sediments, associated with volcanic activity, it does not appear that these trace elements were derived from volcanic exhalations.

Consequently a volcanic source of iron is not supported by the data obtained in this study.

This brief survey of Algoma-type iron-formations has indicated that much more trace element work is necessary before their origin is understood. The effort should prove rewarding, however, both in obtaining a better understanding of these deposits and in gathering evidence pertaining to the evolution of the atmosphere and hydrosphere.

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Trace element composition of the Sokoman iron-formation, Labrador Trough

Introduction

The Sokoman Formation of the Labrador Trough and its correlatives form one of the major sedimentary iron belts of the world. It is exposed almost continuously for about 600 miles along the Quebec-Labrador border from the Grenville Front in the south to Hudson Straight in the north, in a narrow belt of Proterozoic sedimentary and volcanic rocks. The Labrador Trough itself, constitutes only part of a much more extensive ring of similar Proterozoic rocks containing Superior-type iron-formation which make up the erosional remnants of the Circum-Ungava geosyncline surrounding the eastern part of the Superior Province of the Canadian Shield.

Economically, the iron-formation of the Labrador Trough constitutes one of the most important sources of iron ore in the world and the very large ore reserves of the area insure that it will remain so for many years to come. Iron ore is being presently mined in the Knob Lake area in the south-central region of the Labrador Trough from high-grade residual, enriched hematite-goethite bodies. In addition, large reserves of low-grade metataconite iron-formation suitable for producing high quality iron-ore concentrates have recently been developed in the southern extension of the Labrador Trough within the Grenville Province. This southern extension contains the greatest reserves of potential iron ore in North America and will become increasingly more important as the higher grade deposits in the Knob Lake area become exhausted. Low-grade metataconite iron-formation is also known to occur in the northern parts of the Labrador Trough and may become an important source of iron ore in the future.

General Geology

The Labrador Trough, the longest and best preserved segment of the Circum-Ungava geosyncline, is composed of two lithotectonic zones along most of its length. The western zone constitutes the miogeosyncline and is made up mainly of continental shelf-type deposits, while the eastern eugeosynclinal zone is underlain mostly by mafic intrusive and extrusive rocks. Both zones have been deposited upon Archean gneisses with profound unconformity. The trough is bounded on the west by Archean gneisses of the Superior Province, and on the east by re-metamorphosed Archean gneisses (Dimroth *et al.* 1970; Beall *et al.* 1963) of the Churchill Province.

The evolution of the Labrador Trough has recently been outlined by Dimroth (1970) and Dimroth *et al.* (1970). Briefly, an east-west continental fault graben formed initially in the south-center of the trough accompanied by coarse clastic, red bed deposits. These continental deposits grade upwards into a marine orthogeosynclinal sequence made up of three cycles beginning with orthoquartzites and precipitate sediments (iron-formation or dolomite) and culminating in the deposition of shales and greywackes in the miogeosyncline and in intense submarine volcanism in the eugeosyncline. A repeatedly uplifted geanticlinal area was located in the center of the geosyncline and clastic detritus appears to have been derived from both the cratonic area to the west, and from tectonically uplifted lands to the east of the geosyncline. Dimroth (1970) envisions the sedimentary cycles occurring as follows:

(1) Slow deposition of sandstones and chemical sediments under slow basin subsidence with relatively slow uplift of the craton to the west and more rapid uplift of the eastern hinterland.

(2) Sudden acceleration of basin subsidence accompanied by faulting and uplift of a central geanticline. Shales and greywackes rapidly deposited from eroded deposits of step one.

(3) Continued rapid subsidence of the basin and faulting, particularly in the eastern part, and deposition of a very thick pile of mafic volcanic material.

This cycle appears to have occurred three times in the development of the Labrador Trough although the three cycles are not represented in all areas. Basin development appears to have migrated from south to north as the first sedimentary cycle appears to be absent from the northern segment of the trough above latitude 57°N. Similarly, the third cycle is absent or poorly developed in the south and central parts, but is well developed in the north. Iron-formations are present both at the beginning of the second and third sedimentary cycles, although the Sokoman Formation (which constitutes the precipitate phase of the second cycle) is the thickest and most persistent of the two.

Sokoman Formation

The Sokoman Formation forms part of a succession of quartzite-slate-iron-formation-slate which persists throughout the Labrador Trough and forms the most important marker unit in the trough. However, in places, the order of succession may vary or other formations may appear. The iron-formation, according to Gross (1968) is rarely less than 100 feet thick on the western margin of the trough and generally thickens considerably to the center of the belt before thinning and apparently pinching out to the east. The thickness of the iron-formation is quite variable along the strike with variation apparently being due to an original undulatory erosion surface on which the sediments of the Labrador Trough, named the Kaniapiskau Supergroup, were deposited. One of the thicker areas of accumulation was in the Knob Lake area which has been extensively studied because of its high-grade residual deposits of hematite-goethite. The iron-formation is more than 550 feet thick in this area and the stratigraphic succession described by Gross (1968)(see Table IV) gives some insight into the sequence of geologic events surrounding the deposition of the iron-formation.

The lowest unit is the Attikamagen slate consisting of thinly bedded, fine-grained argillaceous material, varying from greyish green to dark grey, black or reddish grey. The Attikamagen grades up into the Denault dolomite or the Wishart quartzite, in areas where the dolomite is absent, with textures of the coarser beds closely resembling those of tuffaceous greywackes. The Denault dolomite is composed of granular mixtures of dolomite and ankerite in fairly massive beds, some of which are fragmental. Lenses and nodules of chert occur along bedding planes and stromatolitic structures are present in some of the beds. The Denault grades into either the Wishart quartzite or the Fleming chert, which is a chert breccia of unusual nature. It is interpreted by Gross as being formed by the precipitation of silica in quiet water with periodic storms brecciating the flat horizontal layers. The Fleming chert also is gradational into the Wishart quartzite, a generally well-rounded arkosic quartzite, forming massive beds and one of the most persistent units in the Kaniapiskau Supergroup. Overlying the Wishart is the Ruth slate which marks the beginning of abundant iron deposition in the Labrador Trough.

The Ruth Formation is a thinly banded, fissile, black, grey-green, or maroon ferruginous slate from 10 to 120 feet thick containing lenses of black chert and varying amounts of iron oxides. It also contains abundant finely disseminated carbon which Harrison (1952) attributes to organic origin. Much of the slate contains more than 20% iron and, where in gradational contact with the overlying Sokoman iron-formation, consists of alternating beds of black clastic material and cherty beds of silicate-carbonate iron-formation containing carbon and hydrated iron oxides.

The Sokoman Formation consists of a lower silicate-carbonate member overlain by oxide facies rocks, which in turn are overlain by a dominantly chert facies with lower iron content. A detailed stratigraphic section and description of the Sokoman is given in Table XV. Table XVI gives chemical analyses of typical iron-formation from near the French Mine in the Knob Lake area. These analyses show extremely well the chemical characteristics of the Sokoman iron-formation and Superior-type iron-formations in general. The extreme purity of these rocks is immediately obvious as in all cases iron and silica constitute over 95% of the total analyses excluding the water content. Al_2O_3 is uniformly low and less than 1%. Ca is also very low, along with the alkalies Na and K. Mn and Mg are concentrated in the silicate-carbonate facies and phosphorous is uniformly low in all facies.

The Menihek slate conformably overlies the Sokoman Formation and with its deposition the chemical sedimentation of silica and iron essentially ceased. The Menihek is a thinly banded, fissile, grey to black argillaceous slate with abundant fine dusty carbon disseminated throughout the rock or concentrated in wavy bands along bedding planes. It interfingers to the east with the Menihek basalts, marking the top of the second despoitional cycle and in the Knob Lake area is the youngest stratigraphic formation exposed.

TABLE XV

Stratigraphy of Sokoman Iron-Formation, Knob Lake Area (after Gross, 1968)

		Member	Composition	Thickness (feet)
UPPER IRON-FORMATION (U.I.F.)	Lean Cherts	Lean Chert (L.U.I.F.)	Low iron in streaky carbonates, silicates and goethite	60 to 80
		Red (R.U.I.F.)	Iron-oxide granules in red jasper and grey cherts, mostly low in iron	0 to 50
		Yellow (Y.U.I.F.)	Blotchy carbonate and minnesotaite with minor Fe oxide. Much light porcelaneous chert	20 to 60
		Grey (G.U.I.F.)	Iron oxides in granules, spotty carbonate. Low in iron	10 to 50
		Upper Red Cherty (U.R.C.)	Similar to L.R.C., decrease in Fe towards top, carbonate in spot and disseminated towards top. Iron distribution in hematite-magnetite-rich granules. Manganese in rhodocrosite increases towards top. 30-45% Fe.	80 to 150

TABLE XV (cont'd.)

Member	Composition	Thickness (feet)
Brown Cherty (B.C.)	Less uniform, mainly hematite-magnetite with spotty siderite in grey to greenish chert. Slaty beds composed of minnesotaite and carbonate in grey-green chert matrix. 30% Fe, or less; ferrous iron more abundant. Fe silicates and carbonate more abundant especially along bedding surfaces.	50 to 80 (less in some areas)
Pink Cherty & Grey Cherty (P. and G.C.)	Uniform generally as to L.R.C. in mineralogy. 30% iron, or less in many parts.	80 to 160 combined
Lower Red Cherty (L.R.C.)	Jasper chert matrix with chert and hematite-magnetite-martite granules and oolites. Minor minnesotaite, stilpnomelane, ferruginous carbonate, hydrous iron oxide. 30-70% iron oxide, 30-40% Fe. Apparent decrease in iron content upward.	30 to 60

TABLE XV (cont'd.)

	Member	Composition	Thickness (feet)
SILICATE-CARBONATE IRON-FORMATION	Silicate-Carbonate Iron-Formation (S.C.I.F.)	Chert matrix with minnesotaite, siderite, magnetite, minor amounts of stilpnomelane, carbon. Occasional thin dark clastic beds. Usually less than 30% Fe. Most chert beds in upper parts.	20 to 100

TABLE XVI

Chemical analyses (%) of iron-formation facies, French Mine, Knob Lake area (from Gross, 1968)

	S.C.I.F.	L.R.C.	P.C.	G.C.	B.C.	U.R.C.	G.U.I.F.
SiO_2	49.41	41.42	48.16	51.24	43.77	49.01	56.49
Al_2O_3	0.68	0.79	0.53	0.42	0.42	0.37	0.37
Fe_2O_3	16.34	54.49	46.96	41.97	49.85	44.50	38.10
FeO	24.19	1.35	1.50	3.25	2.27	3.65	1.99
CaO	0.02	0.00	0.01	0.00	0.00	0.00	0.00
MgO	2.95	0.37	0.31	0.62	0.37	0.19	0.00
Na_2O	0.03	0.08	0.03	0.02	0.02	0.03	0.03
K_2O	0.07	0.01	0.01	0.01	0.01	0.01	0.01
H_2O^+	5.20	0.98	2.04	2.10	2.54	1.94	2.42
H_2O^-	0.38	0.06	0.04	0.05	0.05	0.02	0.03
TiO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P_2O_5	0.08	0.04	0.04	0.03	0.04	0.05	0.04
MnO	0.65	0.02	0.02	0.02	0.03	0.03	0.03
CO_2	0.22	0.02	0.02	0.06	0.02	0.04	0.04
S	0.05	0.05	0.03	0.00	0.00	0.00	0.00

TABLE XVI (cont'd.)

	S.C.I.F.	L.R.C.	P.C.	G.C.	B.C.	U.R.C.	G.U.I.F.
C	0.15	0.12	0.10	0.08	0.13	0.04	0.03
TOTAL	100.42	99.80	99.80	99.87	99.52	99.88	99.57

Petrography of the Sokoman Iron-Formation

The reports of Dimroth (1968) and Dimroth and Chauvel (1971) describing the sedimentary textures, petrography and diagenesis of the various iron-formation facies exposed in the central segment of the Labrador Trough provide much insight into the depositional history and post-depositional processes which have affected these rocks. Because of the importance of these studies in the interpretation of the results to be presented, the pertinent features of these two papers will be reviewed in some detail. Since the later paper by Dimroth and Chauvel essentially developes and expands the ideas of the first paper, the following summary of these papers is based on the paper of Dimroth and Chauvel.

The basis for the following approach was the observation by Dimroth (1968) that the textures exhibited by the iron-formation are similar to those of the limestones, and hence the principles of limestone petrology were applied to the study of iron-formations. Thus, iron-formation textures can be thought of as composed of textural elements (Table XVII) with the various rock types observed being formed by a combination of these textural elements (Fig. 12).

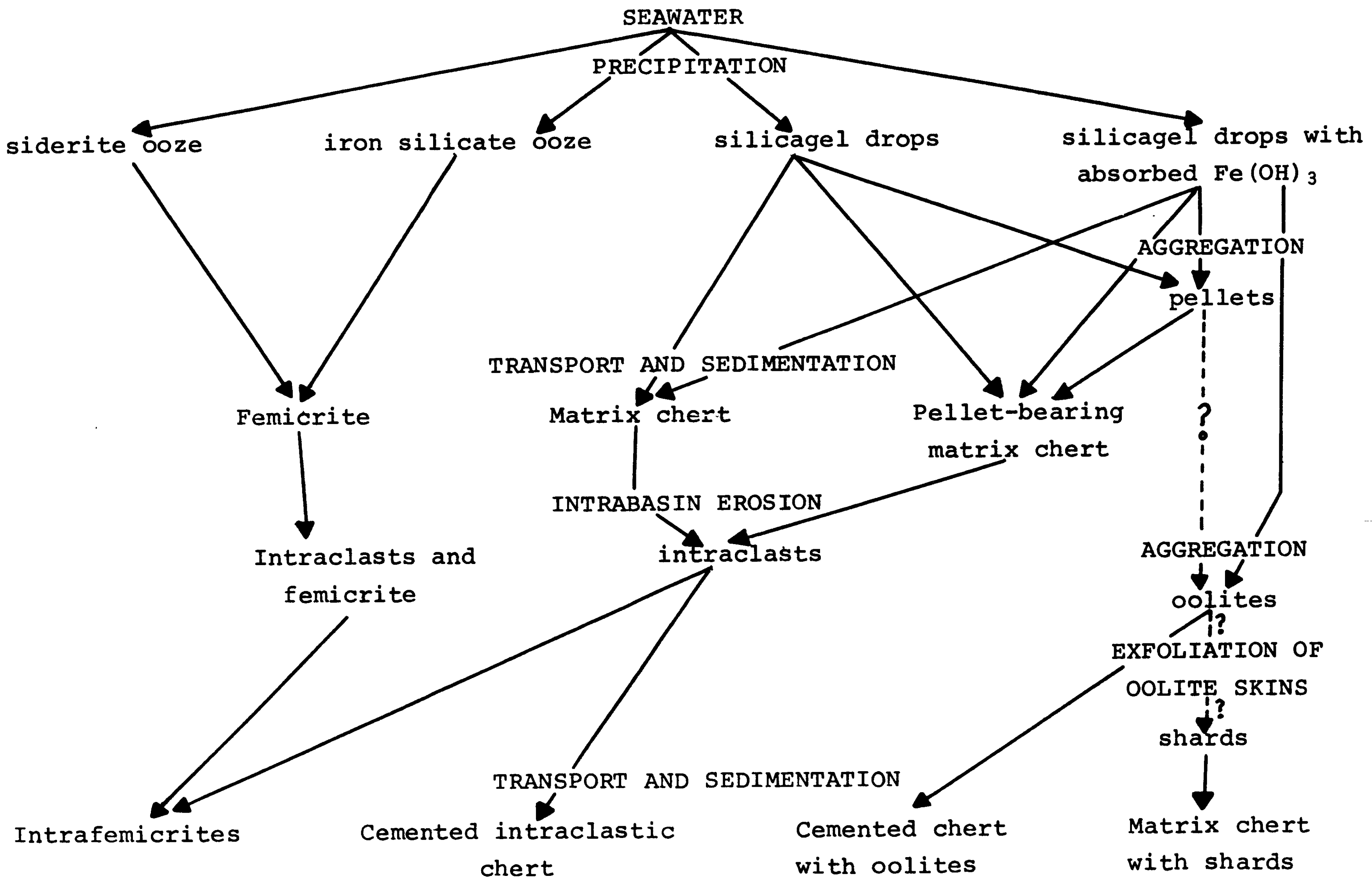
The textural elements are composed of orthochems, the matrix and cement, and allochems which are discrete particles. The orthochems are composed of: 1. iron silicate and iron carbonate making up the femicrite; 2. matrix chert, and 3. cement chert. The femicrite occurs both as laminated or ribboned beds and as matrix for intraclasts. From its depositional

TABLE XVII

Textural elements of limestones and ironstones
(from Dimroth, 1968)

Limestones	Ironstones
ORTHOCHEMS	
microcrystalline calcite matrix (micrite)	microcrystalline iron silicate and siderite matrix (femicrite)
	microcrystalline matrix chert
calcareous cement (spar)	microcrystalline cement chert
ALLOCHEMS	
pellets	pellets
intraclasts	intraclasts
oolites	oolites
fossils	shards

Fig. 12. Formation of rock types (from Dimroth, 1968)



features and lack of agglutination, it apparently was deposited in the form of finely crystalline siderite and iron silicate muds. The matrix chert is believed to have been deposited as fine droplets of silica gel with absorbed Fe^{+3} oxide hydrate in oxidizing environments, but separated from iron deposition in reducing environments. As with the femicrite, matrix chert forms laminated or ribboned beds and supporting matrix between allochem grains. The cement chert, like the matrix chert in silicate-carbonate facies rocks, is relatively devoid of hematite dust. It fills spaces between allochems and commonly extends into dessication cracks in them. Rarely, various ferriferous carbonates occur as cement filling.

The allochems are made up of pellets, intraclasts, oolites, pisolites and shards. The pellets are unsharply bounded, ovoid particles of silica, approximately 0.2 mm in diameter. They may be flocculation units formed by the aggregation of silica gel drops in water, or may have originated within the sediment by diffusion before compaction as they are flattened parallel to the bedding. The intraclasts are simply fragments of unconsolidated sediments, varying from 0.1 mm to 10 cm in largest dimension, that have been transported and redeposited. They show varying mechanical properties at the time of deposition and commonly were quite firm, although not always. In addition, they commonly show shrinkage cracks proving their derivation from a hydrated material. The oolites and pisolites (large oolites up to 5 cm in diameter) are composed of a nucleus, commonly an intraclast containing hematite dust, and a concentric laminated skin. This type of nuclei contains numerous irregular shrinkage cracks and is generally separated from the skin by a thick concentric shrinkage crack indicating the nuclei shrank more than the skin. They were generally firm when deposited, although some were definitely quite soft. The authors believe that the oolites were probably formed by accretion of silica gel mixed with hydrated ferric oxide at the surface of any object, serving as a nucleus, kept in suspension in a high energy aqueous environment.

With the above information one can make general remarks about the paleogeography of the depositional environment with the reservation that many of the rock types can form in various environments. Generally though, Dimroth and Chauvel suggest that

(1) laminated matrix chert and femicrites were probably deposited by slow traction currents in which particles of different size and composition were sorted to varying degrees.

(2) ribboned matrix chert and femicrite (unsharp zonation on cm size scale) were probably dropped from suspensions in a quiet environment without much sorting.

(3) cross-bedded intraclastic and oolitic rocks showing good sorting were deposited by strong traction currents.

(4) intraclastic rocks containing large intraclasts loosely set in a matrix must have been deposited from suspension; where intraclasts and matrix are of the same composition, they probably represent storm layers.

As expected from the above discussion, various cycles of sedimentation are observed with the first cycle being the deposition of orthochemical rocks. Following this, second cycle rocks containing allochems could be deposited followed by more cycles with complex intraclasts composed of fragments of rocks from previous cycles.

Combining the textural evidence bearing on the paleogeography, the types of particles deposited, experimental and field observations, Dimroth and Chauvel have come to several important conclusions bearing on the precipitation and deposition of these Superior-type iron-formations:

(1) these cherty, iron-rich rocks were formed by the precipitation of four primary types of particles from seawater: siderite, an iron silicate, silica gel, and silica gel with adsorbed iron oxide hydrate.

(2) iron oxide hydrate was precipitated under oxidizing conditions, siderite under reducing conditions, and the iron silicate under conditions with Eh below the "hematite-siderite fence" (Krumbein and Garrels, 1952).

(3) under oxidizing conditions, iron and silica were precipitated as mixed gels, with compositional variations reflecting changes in seawater chemistry.

(4) under reducing conditions, iron and silica were precipitated separately, and laminations are due to hydrodynamic separation of different particles and not chemical fluctuations of seawater in response to seasonal or other changes.

(5) laminations in oxide facies are discontinuous, and hence reflect local fluctuations of chemistry and not systematic variations.

(6) depth of deposition is highly variable for both hematite and silicate-carbonate facies, reflecting only that particles of both reduced and oxidized states of iron could be transported into oxidizing and reducing environments, respectively, without changes in oxidation state.

(7) although silicate-carbonate facies rocks were always deposited in deeper water than contemporaneous hematite facies rocks, James' inference (1954) that siderite is always deposited in a low-energy environment is not always correct. The classical picture of siderite facies grading into silicate facies, and finally into oxide facies presented by James (1954) has been observed, but more commonly, carbonate and hematite facies interfinger in an environment of relatively high hydrodynamic energy.

(8) The causes of chemical variation in iron-formations is quite complex, with water depth not the only variable. Others probably include water circulation, organic activity, seasonal fluctuations and basin configuration.

In addition to providing information on the genesis of the iron-formation, Dimroth and Chauvel's study has shown that these cherty iron-rich rocks are extremely unstable systems, suffering extensive diagenetic alterations. Early diagenetic changes include the desiccation and shrinkage of gels, compaction and cementation. Solution voids formed and were filled with cherty quartz, magnetite, iron silicate and lastly by iron dolomite from the outside in. Intense iron migration took place in hematite iron-formation, and to a lesser extent in the silicate-carbonate rocks. Iron enrichment took place in veins paralleling the bedding, whereas other laminae or spots are leached. Much of the specular hematite and magnetite resulted from this iron migration. Most of the iron migration occurred before and during cementation and compaction as iron appears to have been more mobile in the more hydrated cores of the oolites than in the less hydrated skins. Diagenetic affects are most intense where siderite and hematite facies rocks are interbedded. The siderite- and hematite-bearing rocks are almost invariably recrystallized extensively with a zone devoid of hematite and generally poor in iron compounds between the rock types.

In the vicinity of the high grade hematite-goethite deposits of the Knob Lake area, considerable alteration due to supergene processes has also affected these rocks. This has consisted of oxidation, leaching of silica and iron enrichment.

The dehydration, iron migration, recrystallization and other processes Dimroth and Chauvel have outlined will certainly have affected some, if not all, of the trace elements contained in these rocks. Despite this drawback, trace element distributions within the various iron-formation facies may shed considerable light both on the mode of deposition of these rocks and on the diagenetic alterations they have undergone. Even though these banded cherty iron-formations have been studied by numerous authors, there is an almost total lack of trace element data on them. Except for the work of Landergren (1948) on the Swedish Precambrian, only scattered analyses are available and even these are of dubious value.

In light of the complex post-depositional history of these chemical sediments, trace element studies on these rocks require careful interpretation. However, the importance of these rocks, not only as the source of iron ore, but also in the interpretation of the evolution of the earth's surface, makes such studies worthwhile. Consequently, analyses of the iron-formation itself and the sediments with which it is associated were undertaken.

Experimental Results and Discussion

Eighteen samples of iron-formation from the central part of the Labrador Trough were analyzed for La, Ce, Nd, Sm, Eu, Ho, Yb, Lu, Co, Cr, Th and Sc by the technique outlined previously and given in detail in Appendix 1. In addition, five samples of the sediments associated with the iron-formation in the Knob Lake area were analyzed for the same elements by a refined application (Buma 1970) of the method presented by Gordon *et al.* (1968). The results of these analyses are given in Tables XVIII and XIX.

The results obtained for the sediments associated with the Sokoman iron-formation are in general agreement with other analyses of similar rock types. The absolute rare earth abundances of both the shale composites and individual shales are all within 50% of those of the average North American Shale composite reported by Haskin *et al.* (1968) and well within the observed variation in shales (Haskin *et al.* 1966). The Labrador Trough shales, however, do appear to be more enriched in

TABLE XVIII

Trace element analyses: Sokoman iron-formation, central Labrador Trough

		La	Ce	Nd	Sm	Eu	Ho
*	R7513	0.503	0.688	0.377	0.0757	0.0277	0.0295
	R7511	1.108	2.791	0.790	0.174	0.0573	0.0751
	R7949	0.402	1.22	0.504	0.129	0.0382	0.0721
	R8066	4.48	7.49	3.98	0.582	0.208	0.220
†	R7950	1.12	1.40	0.793	0.174	0.0601	-
	R7951	0.964	2.23	1.12	0.273	0.0635	-
	R7953	1.82	4.64	2.03	0.484	0.179	0.0891
	R7955	1.35	2.07	1.106	0.218	0.0735	0.0474
	R8017[1]	2.47	3.71	2.08	0.400	0.168	-
	R8017[2]	7.08	10.7	5.87	0.783	0.269	0.171
	R8018	43.4	55.5	27.7	3.32	0.979	0.442
	R8015	4.21	6.86	3.60	0.708	0.242	0.170
**	R7622	1.49	1.88	1.17	0.220	0.0619	0.0606
	R7592	0.617	1.05	-	0.0913	0.0186	-
	R8022	0.0901	1.40	0.785	0.149	0.0817	-
	R8019	2.73	5.13	2.55	0.501	0.135	1.79
	R8020	2.55	3.70	2.07	0.324	0.105	1.22
	R8023	0.171	0.410	0.221	0.0503	0.0164	0.0209

* "altered" oxide facies

† "normal" oxide facies

** silicate-carbonate facies

TABLE XVIII (cont'd.)

		Yb	Lu	Co	Cr	Th	Sc
*	R7513	0.0902	0.0139	4.76	17.0	<0.013	0.308
	R7511	0.257	0.0531	5.52	49.2	<0.146	0.877
	R7949	0.239	0.0313	1.70	48.1	<0.143	0.048
	R8066	0.970	0.131	5.77	1.87	<0.453	0.333
†	R7950	0.177	0.0252	0.629	23.7	<0.041	0.046
	R7951	0.071	0.0084	0.932	19.1	<0.107	0.616
	R7953	0.173	0.0224	3.59	57.5	<0.158	0.231
	R7955	0.0815	0.0134	1.82	29.0	<0.135	0.058
	R8017[1]	0.318	0.0441	8.55	2.59	<0.063	0.120
	R8017[2]	0.502	0.0678	16.8	1.03	<0.215	0.171
	R8018	1.04	0.154	9.29	1.26	<0.264	0.449
	R8015	0.374	0.0439	1.52	2.88	<0.206	0.320
**	R7622	0.133	0.0289	2.82	1.46	<0.037	0.056
	R7952	0.028	0.0048	2.45	12.2	<0.017	0.28
	R8022	0.107	0.0165	6.26	2.04	<0.044	0.050
	R8019	0.403	0.0564	3.77	1.43	<0.071	0.053
	R8020	0.336	0.0492	6.24	16.0	<0.064	0.050
	R8023	0.0567	0.0083	2.95	1.43	<0.023	0.046

* "altered" oxide facies

† "normal" oxide facies

** silicate-carbonate facies

TABLE XIX

Trace element analyses: Associated sediments, central Labrador Trough

	La	Ce	Nd	Sm	Eu	Tb
Attikamagen Composite	47.2	73.8	28.6	5.49	0.995	0.582
R7847 (Attikamagen)	34.7	60.7	-	5.08	0.881	0.590
Menihek Composite	41.3	69.9	30.5	6.09	0.881	0.663
R7838 (Menihek)	55.4	111.4	-	9.31	1.46	1.033
R7843 (Dolomite)	0.946	2.025	-	0.267	0.0371	-
Average North American Shale*	32*	73*	33*	5.7*	1.24*	0.85*

* Haskin *et al.* (1968)

TABLE XIX (cont'd.)

	Yb	Lu	Co	Cr	Th	Sc
Attikamagen Composite	1.19	0.254	14.8	97.41	21.2	15.2
R7847 (Attikamagen)	1.27	0.294	-	-	-	-
Menihek Composite	2.42	0.410	6.64	57.2	12.2	9.90
R7838 (Menihek)	2.64	0.462	-	-	-	-
R7843 (Dolomite)	0.0623	0.0133	-	-	-	-
Average North American Shale*	3.1*	0.48*	19†	90†	12†	13†

* Haskin *et al.* (1968)

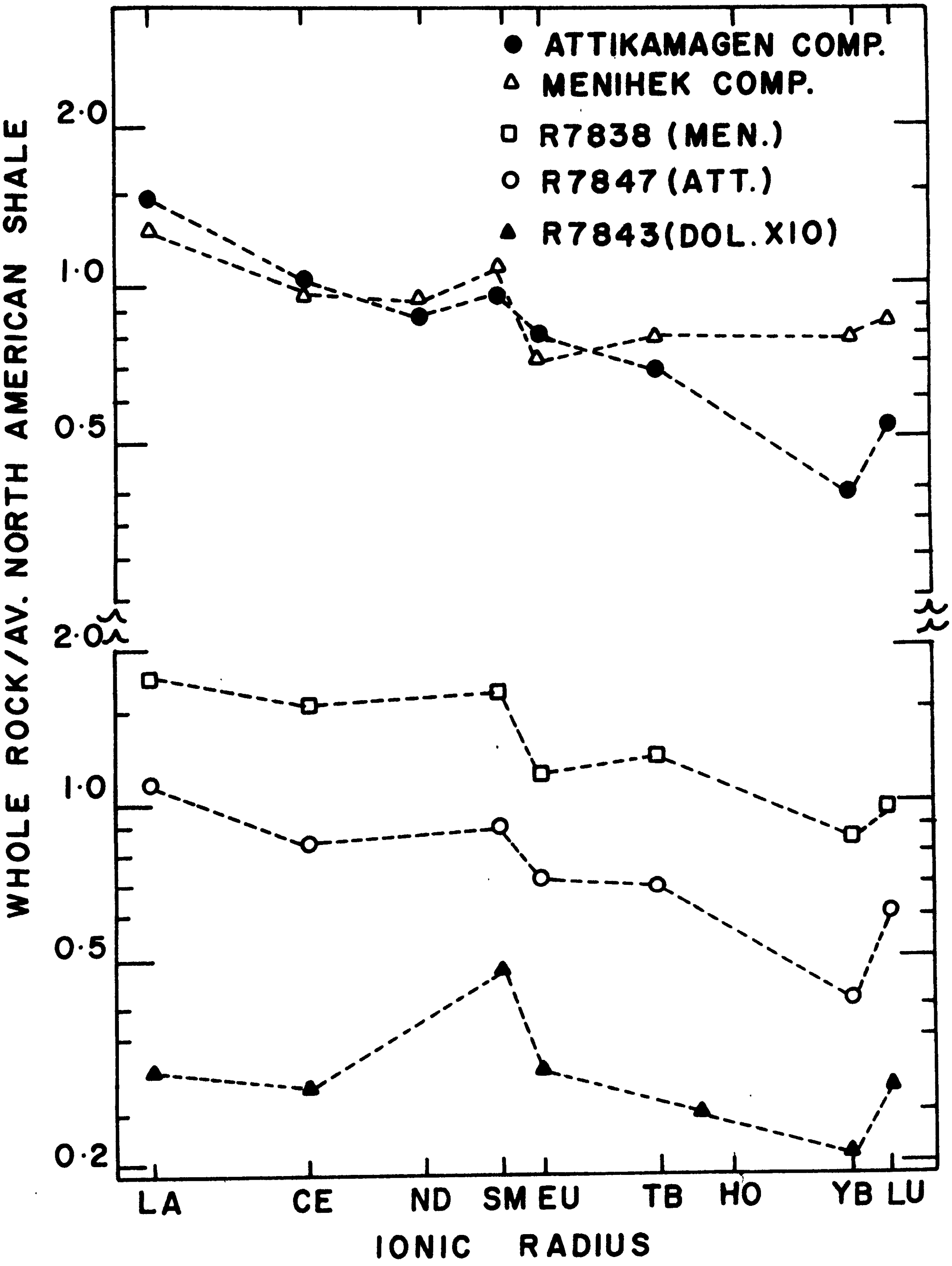
† Turekian and Wedepohl (1961)

the light rare earths than the composite of North American Shales, as seen in Fig. 13, where the sediment analyses of this study have been normalized to the North American Shale composite. In addition, all the sediments appear to have a slightly larger negative Eu anomaly than the average North American Shale. The rare earth pattern of the dolomite is very similar to that of the Labrador shales, having the same relative negative Eu anomaly and relative light rare earth enrichment. The similarity between the shale rare earth patterns and that of the dolomite, and the low absolute abundance of the rare earths in the dolomite suggest that most of the rare earths in the dolomite are probably incorporated in minor amounts of clay minerals. The smaller degree of light rare earth enrichment of the dolomite may indicate that the carbonate itself has incorporated relatively more heavy rare earths than is typical of the clastic sediments, as shown by Balashov *et al.* (1964).

The other trace elements analyzed for in the shale composite are quite similar to the average contents of these elements in shales as given by Turekian and Wedepohl (1961) and are shown in Table XIX. Thus, although the Attikamagen slates appear to be generally richer in these other trace elements than the Menihek slates, neither appear to be anomalous with respect to other similar rocks.

The trace element contents of the iron-formation samples, however, are drastically different from those of the associated sediments. The absolute rare earth abundances of these chemical precipitates are, with one exception, much lower than those

FIGURE 13.



● ATTIKAMAGEN COMP.
△ MENIHEK COMP.
□ R7838 (MEN.)
○ R7847 (ATT.)
▲ R7843 (DOL. X10)
WHOLE ROCK/AV. NORTH AMERICAN SHALE
2·0
1·0
0·5
2·0
1·0
0·5
0·2
LA
CE
ND
SM
EU
TB
HO
YB
LU
IONIC RADIUS

of the shales. Likewise, the rare earth patterns are fundamentally different. The other trace elements in the iron-formation samples bear no relation to those of the clastic sediments. All of these features reflect the origin of these rocks, as chemical precipitates from the marine environment and hence they bear little relation to the clastic debris that was deposited in the Labrador Trough before and after their deposition.

The rare earth patterns of the iron-formation samples are presented as Figs. 14-18, with the ionic radii of Wittaker and Muntus (1970) as abscissa and normalized to the average rare earth contents of the two composite shales. This average composite should give the best available estimate of the rare earths associated with the clastic material supplied to the sedimentary basin before and after the deposition of the iron-formation. To eliminate any seemingly anomalous behavior of Eu for the iron-formation samples due to the negative Eu anomaly of the average shale composite, a normal interpolated value for Eu in the average composite was used.

The iron-formation samples all exhibit heavy rare earth enrichment relative to the composite shale, with the exception of sample R8018. In addition, only one iron-formation sample (R7952) exhibits a definite negative Eu anomaly. These results are in general agreement with the findings of Balashov *et al.* (1964) for carbonates of the Russian Platform and analyses of present day seawater reported by Høgdaul *et al.* (1968). Modern seawater is enriched in the heavy rare earths relative to mo-

FIGURE 14. Silicate-Carbonate facies

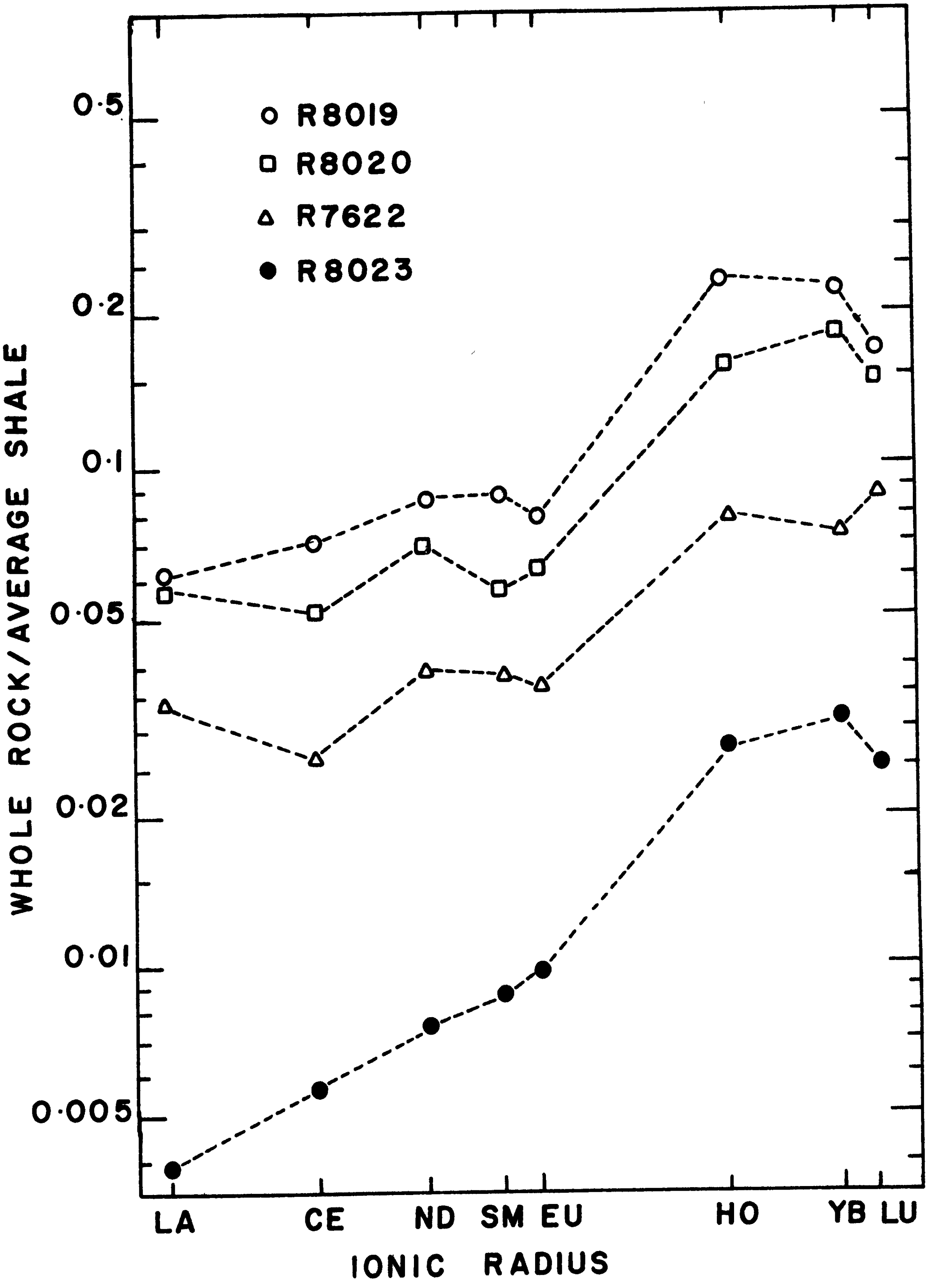


FIGURE 15.

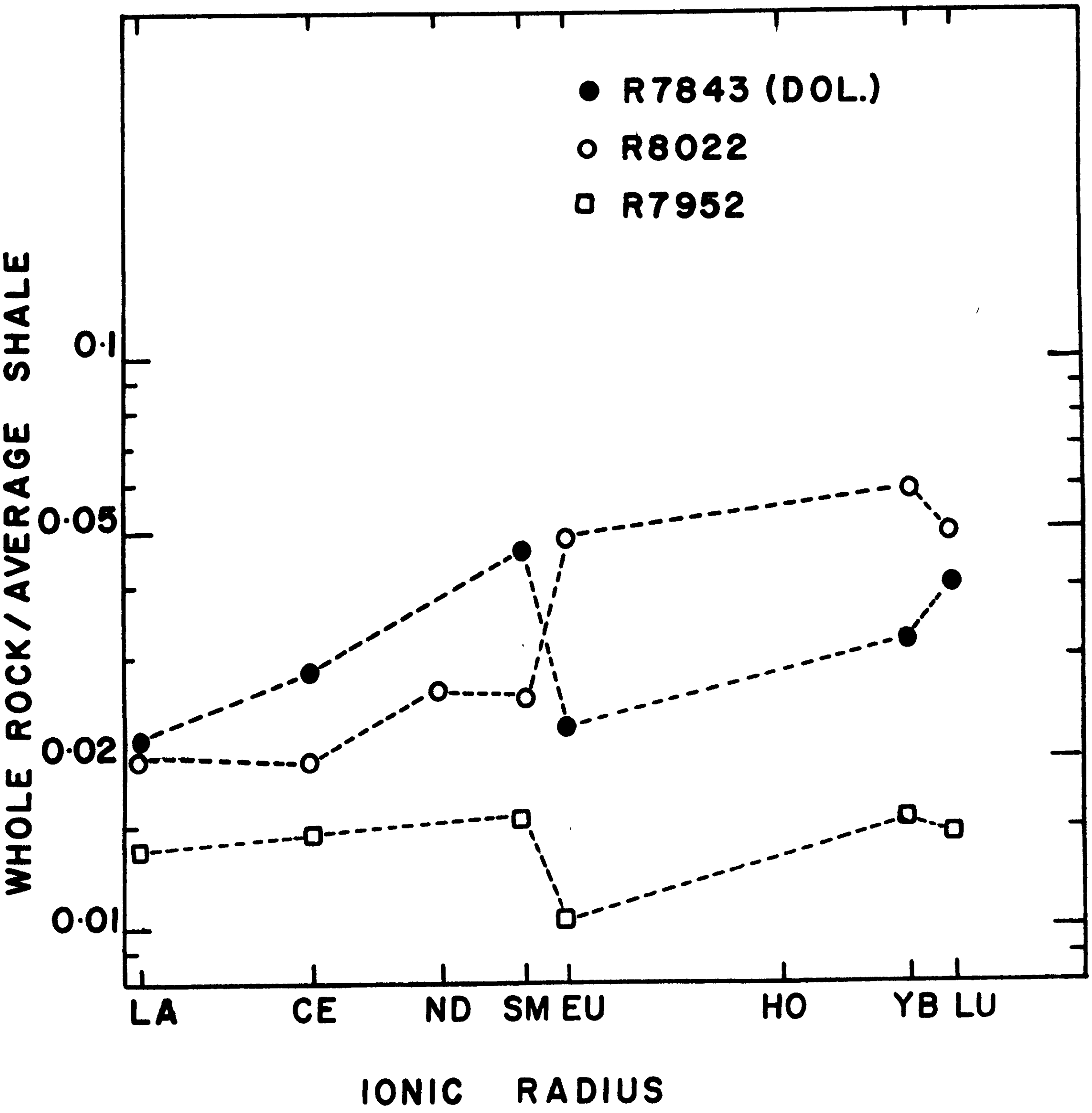

● R7843 (DOL.)
○ R8022
□ R7952
WHOLE ROCK/AVERAGE SHALE
0·1
0·05
0·02
0·01
LA
CE
ND
SM
EU
HO
YB
LU
IONIC RADIUS

FIGURE 16. "Normal" oxide facies

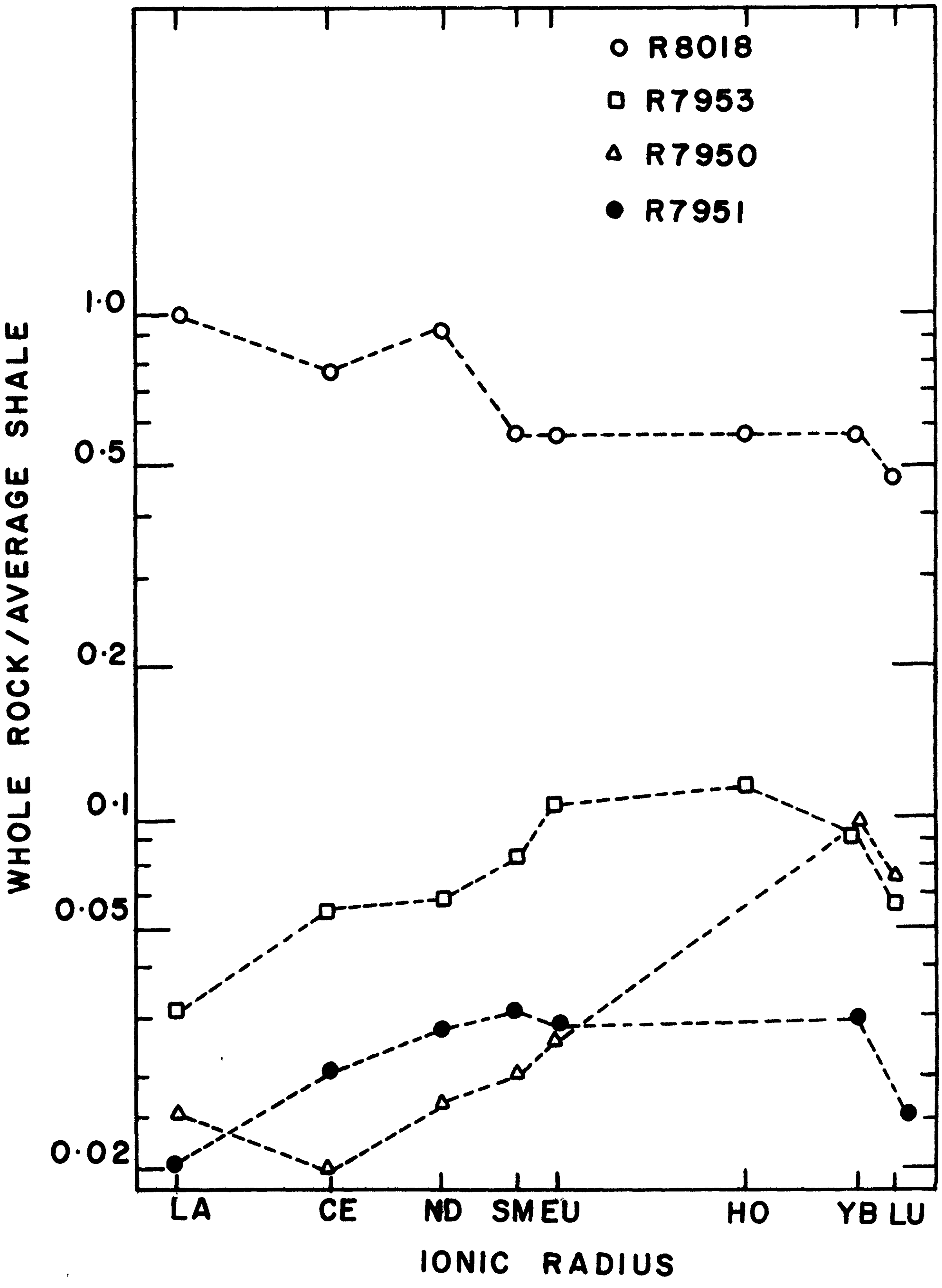


FIGURE 17. "Normal" oxide facies

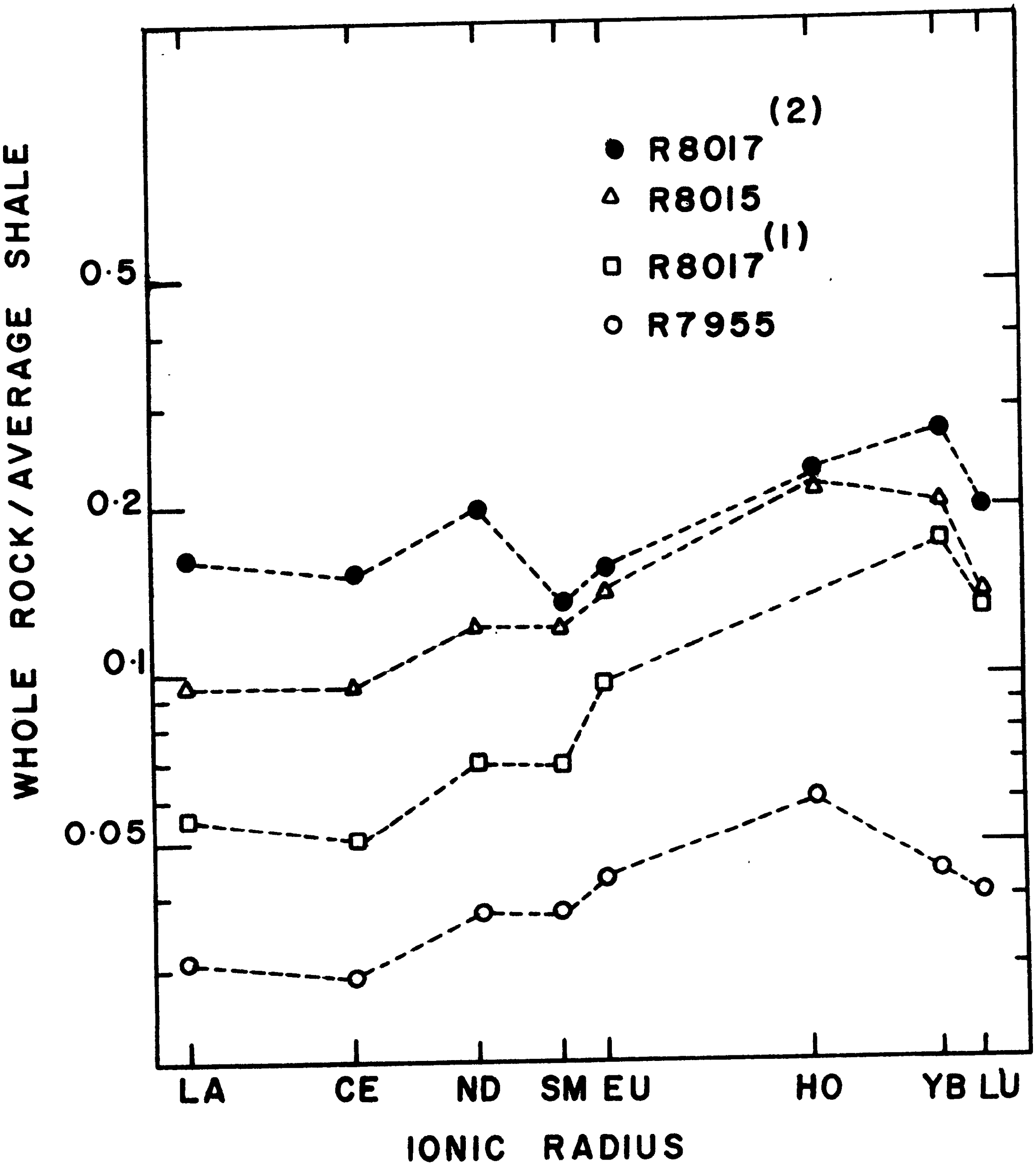
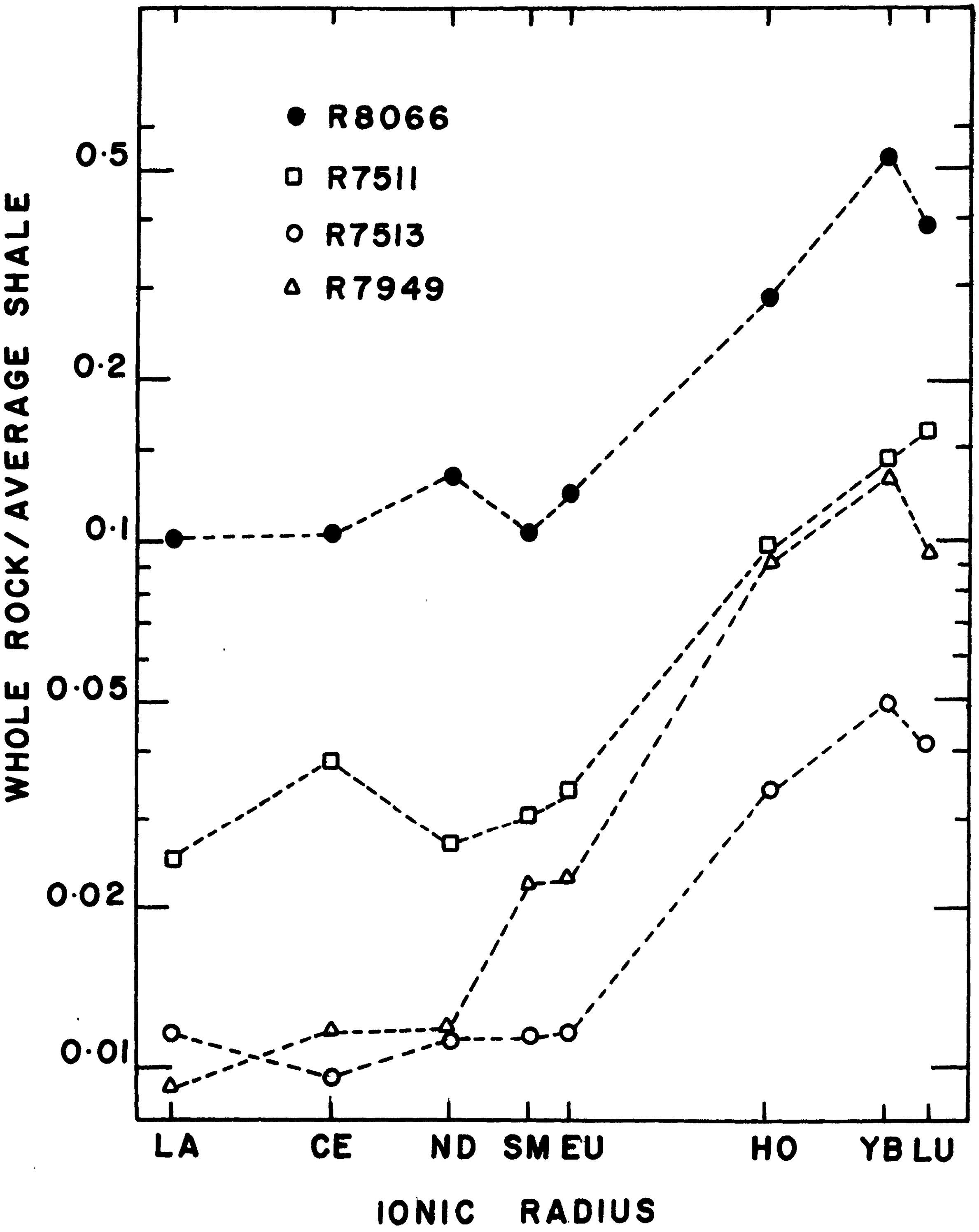


FIGURE 18. "Altered" oxide facies



dern sediments and the carbonates studied by Balashov *et al.* are also relatively enriched in the heavy rare earths compared to contemporaneous clastic sediments. This enrichment in heavy rare earths appears to be typical of modern seawater, and precipitates from seawater, such as the carbonates reported by Balashov *et al.* These iron-formation samples show the same enrichment. The lack of a negative Eu anomaly in the iron-formation samples similarly points to the derivation of these rocks directly from seawater.

With these general observations in mind there are also differences in rare earth patterns between the various facies of iron-formation. The iron silicate-carbonate facies rocks (Figs. 14 and 15) generally show little relative fractionation of the light rare earths (La - Eu) compared to the shales, but considerable and constant enrichment in the heavy rare earths (Ho, Yb, Lu). The oxide facies rocks can be divided into two groups, one of which shows considerable variation in rare earth patterns (Figs. 16 and 17) and another which shows very strong enrichment in the heavy rare earths (Fig. 18). Finally, sample R7952 shows a strong similarity to the rare earth composition of the composite shale (Fig. 15).

The silicate-carbonate facies rocks (R7622, R8019, R8020, R8022, R8023) are essentially composed of siderite, minnesotaite, chert and magnetite in varying proportions. From thin section observations (see Appendix 1) the absolute abundance of the rare earths in these rocks appears to be roughly inversely proportional to the chert (quartz) content indicating that silica is acting essentially as a dilutent. A similar observation was made by Balashov and Goryainov (1966) for the ferruginous metaquartzites of the Imandra region of the Kola Peninsula. The rare earth patterns, however, are essentially identical and presumably reflect the rare earth composition of the precipitated femicrite. The relative enrichment in the heavy rare earths for the silicate-carbonate facies rocks is consistent with Balashov and Goryainov's findings that the heavy rare earths were preferentially incorporated in the dark silicates. Since the Labrador Trough rocks are relatively unmetamorphosed, it appears that this feature is probably due to preferential uptake of the heavy rare earths by the siderite and original iron silicate when they were precipitated in crystalline form from the seawater. This may be due to the smaller ionic radii of the heavy rare earths which would facilitate their substitution for Fe^{+2} (ionic radius 0.74 Å) in the crystallizing minerals.

Sample R7952 is distinguished from the other iron-formation rare earth patterns by its strong resemblance to the average shale composite. The normalized pattern is indistinguishable from the shale pattern within the limits of the experimental error, both in the general fractionation of the rare earths and in the presence of a negative Eu anomaly. This sample contains fibrous riebeckite along what appears to be shear surfaces. Dimroth and Chauvel (1971) indicate that this is typical of the occurrence of riebeckite in the Labrador Trough and that riebeckite is definitely of metamorphic origin. The high sodium content of riebeckite ($Na_2Fe_3^{+2}Fe_2^{+3}Si_8O_{22}[OH]_2$) is not consistent with the trace amounts of alkalies, especially sodium, present in normal iron-formation from the Labrador Trough (see Table XVI). Sodium must therefore have been initially present in this rock, incorporated in clay minerals or have been introduced during metamorphism and shearing. This suggests that the rare earths in this sample have a similar origin, thus accounting for the similarity between the rare earth patterns of sample R7952 and the average shale composite. Consequently, this sample probably does not represent a true chemical precipitate and will be excluded from further consideration.

The oxide facies rocks show much more variation, both in rare earth fractionation and in absolute abundance, than the silicate-carbonate facies rocks. A group of four rocks (R7511, R7513, R7949, R8066; see Fig. 18) which have been extensively recrystallized and appear to have undergone considerable migration of iron, show strong enrichment in the heavy rare earths (4-14 times the relative La abundance). Relict textures indicate that these rocks were originally identical to other oxide facies rocks which have suffered less iron migration and/or alteration. In light of this, it appears that the rare earth composition of these rocks has been altered and the heavy rare earths concentrated in these "altered" oxide facies rocks.
The increasing stability of the rare earth carbonate complex ($(Re[CO_3]_3)^{-3}$ (Beus 1958; Kosterin 1959) with increasing rare earth atomic number can conceivably account for this enrichment in the heavy rare earths.

Dimroth and Chauvel (1970) envision iron migration in the oxide facies rocks as a process involving the reduction of Fe^{+3} by organic matter in relatively impermeable beds according to the following reaction

$$4Fe(OH)_3 + C + 8H^+ \rightarrow Fe^{++} + CO_2 + 10H_2O \qquad (1)$$

Iron would migrate in the ferrous state into more permeable beds where it would be oxidized according to reaction (2) or (3):

$$4Fe^{++} + 8(OH)^- + O_2 \rightarrow 2Fe_2O_3 + 4H_2O \qquad (2)$$

$$6Fe^{++} + 12(OH)^- + O_2 \rightarrow 2Fe_3O_4 + 6H_2O \qquad (3)$$

This migration of iron, and presumably other mobile elements including the rare earths, would take place in carbonate-rich solutions. Complexing of the rare earths in the form of $(Re[CO_3]_3)^{-3}$ would result in the migration of relatively more heavy rare earths which would be scavenged by the redeposited hydrated iron oxides. This is only one possible explanation for the relative enrichment in the heavy rare earths observed for these "altered" oxide facies rocks, but it does appear that the enrichment is connected to extensive iron migration.

The eight other oxide facies rocks analyzed typically show smaller degrees of heavy rare earth enrichment than the "altered" oxide facies and indeed sample R8018 shows a relative depletion in the heavy rare earths compared to the shales. This is consistent with the relative light rare earth enrichment observed for the oxide minerals (hematite and magnetite) of the Lake Imandra iron deposits (Balashov and Goryainov 1966) and indicates that the original hydrated iron oxide preferentially incorporated the light rare earths.

The wider variation in rare earth patterns observed for these rocks may be due to a number of causes. Some of the rare earths presumably were absorbed onto the ferric oxide hydrate in the precipitating silica gel. In addition, small amounts of calcium phosphate, now represented by apatite in some of the sediments, were being precipitated along with the silica. Even trace amounts of apatite will contain a significant proportion of the rare earths in these sediments. Fleischer and Altschuler (1969) report that purified apatite from six sedimentary marine phosphorites have rare earth contents which vary from 100-1000 ppm. Although this is low compared to other genetic types of apatite, it is still very great in relation to iron-formation concentrations. Consequently, if apatite is present in even trace amounts in these chemical sediments it will seriously affect both the absolute abundance and pattern of the rare earths. Thus adsorbtion onto ferric oxide, incorporation into apatite, and other unknown factors will affect the rare earth patterns of these rocks during deposition.

After deposition, the unstable nature of these iron-rich sediments presumably would produce further fractionation. Migration of the rare earths and other absorbed trace elements undoubtedly would occur under the different chemical conditions of diagenesis. The rare earths might be fixed in apatite if sufficient calcium phosphate were initially present in the sediment and hence might retain their original distribution. During recrystallization of the iron minerals and expulsion of hydrated water at least some of the rare earths might have been redistributed. Indeed, the heavy rare earth enrichment of the "altered" oxide facies rocks indicate that some redistribution must have taken place. These processes, and presumably others, would modify the original rare earth patterns of these sediments and could easily produce the observed variation.

An interesting aspect of the rare earths in these sediments is the behavior of Ce. In the modern marine environment Ce^{+3} is oxidized to Ce^{+4} and consequently Ce is depleted in seawater (Høgdaul *et al.*1968; Goldberg *et al.* 1963) presumably due to its incorporation in maganese concretions (Ehrlich 1968; Goldberg *et al.* 1963). In addition, because of the depletion of Ce in seawater apatites precipitated from seawater show negative Ce anomalies (Fleischer and Altschuler 1969; Ehrlich 1968). The iron-formation samples studied do not show any definite trends with regard to Ce, although anomalous behavior is indicated for several samples. R7511, a banded jasper-hematite sample, shows a definite enrichment in Ce compared to adjacent rare earths. R7622, a silicate-carbonate facies rock exhibits a depletion in Ce and several other samples are suggestive of similar but smaller depletions. Although this evidence is far from conclusive, Ce may have behaved anomalously in the deposition of these rocks. Wildeman and Haskin (1971) have found a Ce anomaly in a jasper sample from the Biwabik iron-formation in the Lake Superior area, so apparently conditions were sufficiently oxidizing to produce Ce^{+4} in the marine environment in the period between 1800 and 1900 m.y.

The absolute abundance of the rare earths and other trace elements in the iron-formation samples also reflects the different sedimentary facies. The iron silicate-carbonate facies rocks tend to show much less fluctuation in absolute abundance of the trace elements. The rare earth abundances are inversely related to the amount of chert that was initially present, and thus appear to be controlled by the initial carbonate and silicate content of the precipitate. This may be further proof of Dimroth and Chauvel's (1971) contention that the siderite and silicate were deposited as crystalline material. If this is the case, crystal-liquid partitioning would be relatively constant for the individual elements and their abundance would only vary within narrow limits as observed. Thus for the silicate-carbonate facies rocks Co varies between about 3 and 6 ppm, while for the oxide facies rocks it varies from 0.6 to 17 ppm. Similarly, Sc and Th are very low and constant in abundance for the silicate-carbonate rocks, while although still low in the oxide facies they exhibit much more variation. Cr varies more widely than the other elements but again the variation is less for the silicate-carbonate rocks. Consequently, the abundances of trace elements in the silicate-carbonate facies appears to be more rigidly controlled than in the oxide facies, suggesting that crystal-liquid partitioning may be the mechanism by which trace elements are incorporated in the silicate-carbonate rocks.

The higher, more erratic abundances of trace elements in the oxide facies rocks suggest that the trace elements are not being incorporated into stable crystalline structures. The higher abundances of the trace elements in the oxide facies rocks is probably due to the adsorption of these elements onto the precipitating ferric oxide hydrate. Iron oxides are known to scavenge heavy metals from water (Krauskopf 1956; Goldberg 1954; Jenne 1968) by absorption and presumably would have acted similarly during the formation of the ferric oxide hydrate in these ancient sediments. Indeed the low concentration of these trace elements in the oxide facies rocks needs explaining. Krauskopf (1956) and Jenne (1968) have shown that adsorption becomes less as pH decreases and this may be a possible reason for the low abundance. Several authors (Cloud 1968; Perel'man 1965) have suggested that the CO_2 content of the atmosphere was higher in the middle Proterozoic than at present, and hence the pH of seawater may have been lower at that time. Whether this is true or not, almost all writers agree that the pH was below the calcite fence (pH = 7.8) where iron was being deposited and hence this water was more acidic than the present marine environment. This may have resulted in a smaller degree of adsorption or, alternatively, the great amounts of ferric oxide available for absorption at any one time in the basin may have been so great that the waters were severely depleted of most trace elements. It is interesting to note in this regard that the iron-rich sediments from the Red Sea are also very low in rare earths (Schilling and Stevens 1968). Their low abundance may be due to the above causes or to another which may also apply to the iron-formation samples. If the iron oxides were being deposited rapidly and hence were being buried rapidly they would have little time to absorb other elements and hence would have low trace element contents.

The erratic behavior of the trace elements in the oxide facies rocks may be due to depositional or post-depositional effects. If the waters were depleted in trace elements due to the scavenging effects of the hydrated iron oxides, then large variations in absolute abundance would be expected as local supplies of the trace elements varied. Alternatively, if as mentioned above, the adsorption varied with depositional rate, wide fluctuations in absolute abundance would occur as the rate of deposition of the oxide varied. Variations in the rate of deposition of calcium phosphate and other trace phases would also have a great affect on the absolute abundance of these trace elements. The silicate-carbonate facies rocks would be less affected by any of the above factors as they would be deposited in deeper, more homogeneous waters.

Perhaps more important than any primary depositional variations would be the complex diagenetic changes that have affected these rocks and presumably the trace elements in them. During the dehydration and iron migration that has taken place in these rocks, much redistribution of the minor elements may have taken place. Those rocks that have had the most recrystallization would be expected to have undergone the most change, This is shown in a number of the samples analyzed. As mentioned previously, the "altered" oxide facies rocks show considerable enrichment in the heavy rare earths. Similarly, sample R8018 shows extreme enrichment in the light rare earths and in absolute abundance of the rare earths. It contains carbonate veins and extensive areas of replacement of the original hematite and quartz by carbonate and minnesotaite. This anomalous behavior must be due to this secondary carbonate and hence to post-depositional migration of the rare earths.

In conclusion, the trace element abundances support the contention that the iron carbonate and iron silicate were deposited as finely crystalline material, whereas the iron oxide was deposited in a hydrated state. Trace element abundances in the silicate-carbonate facies appear to have been governed by crystal-liquid partitioning. The hydrated iron oxides, however, probably absorbed the trace elements and as a consequence were more susceptible to post-depositional migration of these elements. There is no evidence for the anomalous behavior of Eu in these rocks unlike the older Algoma-type iron-formations studied, and hence these rocks are more like modern chemical sediments in this aspect. Ce, however, may have behaved anomalously, although the data are not definitive on this.

Origin of the Sokoman iron-formation

The origin of the Sokoman iron-formation is intertwined with the global problem of the origin of banded iron-formations in general. The number of hypotheses that have been advanced for the origin of these deposits is almost as great as the number of authors who have written on the subject. As Gross (1965) points out, however, this is partly due to the lack of differentiation between the different types of iron-formation being discussed. The discussion to follow is concerned only with those iron-formations classified as Superior-type (Gross 1965), typified by the well studied Proterozoic beds of the Lake Superior region and the Sokoman iron-formation of the Labrador Trough.

Superior-type iron-formations are typically thinly-banded cherty rocks containing negligible clastic material. The lithological facies of James (1954) are well developed and usually distinctly defined, including oxide, carbonate, silicate and more rarely sulfide-rich beds. Gross (1965) suggests that they also typically show abundant evidence of deposition in shallow water and granular to oolitic textures. Trendall (1968) however points out that this is not true of the banded cherty iron-formations of western Australia and of the Transvaal system of South Africa. Consequently, such features may be just indications of local variations and may not be an essential feature of these chemical deposits. Superior-type beds are generally associated with shelf or miogeosynclinal sediments, such as quartzite, dolomite, argillite and chert, as well as various volcanic rocks including tuffs and lavas, in long narrow belts brodering Archean cratonics areas on one side and eugeosynclinal basins on the other. The iron-formations themselves are hundreds of feet thick and typically extend for hundreds of miles along strike.

The origin of these rocks is basically a two-fold problem. The first is the source of the iron and silica required to supply the vast quantities of these elements to the sedimentary basins. The second is the mechanism by which the iron and silica are precipitated to the exclusion of essentially all the other elements.

At present iron is highly insoluble in surface waters due to the presence of dissolved oxygen. Berner (1970) reports the calculated concentration of dissolved iron in equilibrium with $Fe(OH)_3$ to be 3×10^{-6} ppm for seawater (pH = 8) and 3×10^{-5} for river water (pH = 7). Measured values of "dissolved" iron are considerably higher than this due to the methods of measurement, since most of the measured "dissolved" iron is actually in the colloidal state. Berner (1970, p. 26-H-5) has outlined the following factors affecting the solubility of iron:

(1) Valence state of iron in the solid

(2) pH

(3) The relative oxidation state of the aqueous system

(4) The nature of the solid iron phases present which are in turn a function of the concentration of H_2S, CO_2, etc

(5) The degree of hydration and crystal form of hydrated ferric oxides

(6) The complexing of ferric anions

(7) The formation of organic chelates

Analyzing these factors to determine which one may conceivably have changed between the present and the time of deposition of the Superior-type iron-formations (1800 - 2200 m.y.) we see that factors 1, 5 and 6 probably have not changed markedly.

Factor 7 has undoubtedly changed greatly. If the assertion that oxygen was absent from the atmosphere prior to about 1800 - 2000 m.y. (Cloud 1968) is correct then no life could have existed on land due to the penetration of organically destructive ultraviolet radiation to the earth's surface. Consequently, the formation of organic chelates which transport considerable amounts of iron in solution under present weathering conditions must have been quantitatively unimportant during the deposition of these deposits. This leaves factors 2, 3 and 4 which may have increased the amount and mobility of iron in solution in middle Proterozoic time. The lack of atmospheric oxygen certainly would drastically affect the solubility of iron since iron present in the weathering material would not be oxidized to the highly insoluble ferric state. Consequently, much more iron would be carried in true solution as the ferrous ion. The imporatnce of variation of pH with geologic time is more difficult to ascertain. The most probable cause for variation of pH with time would be a higher partial pressure of CO_2 in the primitive atmosphere. Although the evidence is not definitive on this, the presence of siderite and ankerite rather than dolomite and calcite in rocks older than about 2200 m.y. suggests that the pH of marine waters may have been somewhat lower than at present. If P_{CO_2} was significantly higher, chemical weathering would have been much more intense resulting in great quantities of iron being transported to the marine basins as ferrous bicarbonate. Factor 4 is dependent on the nature and concentration of dissolved species; hence, if CO_2 and pH varied, the solid phases in equilibrium with marine waters would also vary. From the above discussion it appears that the lack of free oxygen and the presence of a higher partial pressure of CO_2 would have been the most probable factors to have changed and drastically affected the solubility of iron in the early history of the earth.

The problem of the silica required to produce the iron silicates and chert which form such an important part of these deposits is not as difficult to explain. At present silica is considerably undersaturated in seawater, presumably due to the action of silica-secreting organisms which remove it from the solution. Degens (1965) suggests that the absence of silica-secreting organisms in the Precambrian may have allowed the silica concentration to build up to such an extent that amorphous silica was precipitated, This seems adequate to explain the great amounts of silica deposited, as considerable quantities of dissolved silica are released during the weathering of rocks and from volcanic activity.

The assertion by Cloud (1968) that the atmosphere prior to about 1800-2000 m.y. was anoxygenous is based on several lines of evidence. Detrital uraninite is found in early Proterozoic (2.0 - 2.5 b.y.) sediments in several localities. Holland (1962) has shown that uraninite is unstable in the presence of oxygen in amounts greater than about 10^{-22} atm., so the partial pressure of oxygen must have been less than this during the deposition of these sediments. The absence of red beds in this period also indicates a lack of oxygen since, as Cloud points out, molecular oxygen would be partially converted to atomic oxygen and ozone as it invaded the atmosphere by impinging ultraviolet radiation. These two species, being highly reactive, would give rise to a high rate of oxidation of surface materials with the resulting sudden appearance of red beds in the geologic column. Cloud reports that the oldest red beds are about 1800-2000 m.y. old, so again the evidence suggests that the atmosphere was anoxygenous prior to about 2000 m.y.

Since oxygen was probably not present in the atmosphere before this time, the presence of large quantities of ferric iron in the banded iron-formations of this period must be explained. Cloud's (1968) model for the development of the hydrosphere and atmosphere does this and will now be outlined insofar as it pertains to the present discussion.

The development of the modern atmosphere with its high content of oxygen requires that oxygen be developed in large quantities since the middle of the Proterozoic. This excess oxygen must have been produced by biologic activity and hence Cloud's model is concerned with the development of life in the ancient seas. The first successful life form must have been an autotroph - one that could manufacture its own food, and was probably a photoautotroph - one that manufactures food by photosynthesis. However, it is unlikely that the first photoautotroph could live in the presence of free oxygen. Consequently, such organisms must have been dependent on an associated oxygen acceptor. This oxygen acceptor may have been the ferrous ion and the ferric and ferro-ferric oxides present in the banded iron-formations would be precipitated when the dissolved ferrous ions were oxidized to insoluble ferric ions by the biologically produced oxygen.

The banded nature of these deposits would result from a fluctuating balance between the oxygen-producing biota and the supply of ferrous ion in solution, With time, however, efficient oxygen mediating enzymes must have evolved which enabled the organisms to coexist with their produced oxygen. When this happened the balance maintained between the photoautotrophs and the supply of ferrous ion would no longer control the life cycle of these organisms. The green-plant photosynthesizers could then spread out into the marine envirnment, limited only by light penetration requirements and protection against high-energy ultraviolet radiation. This would result in a great increase in the supply of oxygen in the hydrosphere and precipitation of essentially all of the dissolved ferrous ion in a last great episode of banded iron-formation. In addition, oxygen would now enter the atmosphere producing oxidation in the weathering cycle and red bed deposits. Once oxygen became available in the atmosphere, iron would be converted to the insoluble ferric state during weathering and therefore could no longer be transported in solution in significant quantities. For this reason the introduction of oxygen into the atmosphere would end the deposition of this type of banded iron-formation.

If this hypothesis is correct then the major problem of transporting the vast quantities of iron needed to form these deposits is greatly simplified. Iron would not be transported in the insoluble ferric state but rather as the more soluble ferrous ion and hence would be much more mobile in the marine basin. The iron would be more easily distributed throughout the Precambrian seas enabling ferric iron deposition to take place in relatively thin uniform layers along the edges of developing geosynclines in the depth zone of the photoautotroph limited only by ultraviolet radiation at the top and the necessary penetration of visible light at the bottom.

The source of the iron, however, is still left unexplained by Cloud's hypothesis. Much of the literature on iron-formations concerns this source and basically two opinions are held on the subject. One group believes that the iron was derived from chemical weathering of the adjacent land areas, while the other calls on direct or indirect contribution of iron from volcanic sources. It is probable that both views are correct and either source may predominate for individual deposits. Goodwin (1962) presents convincing evidence for the volcanic contribution of iron to the deposits at Michipicoten, Ontario. Similarly, iron is being contributed by volcanic sources to the marine environment at the present time (Zelenov 1958; Butuzova 1966; Von der Borch and Rex 1970). The addition of iron must certainly have occurred in a like manner in the period prior to 2000 m.y., but this does not mean that weathering of surface materials was unimportant in supplying the iron for these deposits. Indeed, with an anoxygenous atmosphere rich in CO_2, chemical weathering of surface rocks would be very great.

The long period of structural stability extending from about 2500 m.y. would allow time for extensive peneplanation with resulting increased release of dissolved constituents to the marine basins. This would include great quantities of ferrous bicarbonate and ferrous ion which would build up in concentration in seawater until precipitated out by the oxygen supplied by photosynthesis or until some mineral species became saturated with respect to the dissolved iron and other constituents in the Precambrian seas. Since weathering would occur continuously over hundreds of millions of years, and over vast areas of land, it may well have been the dominant source of iron.

If this is the mechanism by which the banded iron-formations were produced, then the Algoma- and Superior-type iron-formations were probably deposited in the same manner. Trendall's (1968) observation that the Hammersley and Transvaal deposits lack the granules and oolites described by Gross (1965) as typical of Superior-type iron-formations suggests that the distinction between the two types may be artificial. It is suggested that the differing characteristics are probably due to different tectonic settings of the two types. The contention that the source of iron for the Algoma-type was volcanic may be correct. The rapid rate of erosion in the greenstone belts would make weathering much less effective in the release of iron into solution. However, if the CO_2 content of the atmosphere was higher, it is not inconceivable that large amounts of iron could be released from the mafic minerals of the basaltic source areas into solution as ferrous bicarbonate.

Whatever the source of the iron the presence of ferric iron in these deposits indicates that organically-derived oxygen must have been available at this time and presumably a mechanism such as Cloud's acted to precipitate ferric iron. The greater proportion of magnetite in these deposits may indicate that the supply of iron was too great to be fully oxidized, or that magnetite was the stable phase under the existing Eh-pH conditions and ionic concentrations.

In the case of the Superior-type despoits, the tectonic setting is entirely different. They were formed in large sedimentary basins overlying eroded Archean basement complexes. The associated sediments such as dolomites, shales and quartzites indicate that weathering in the source areas was much more intense than for the Archean greenstone belts. In addition, the lack of even minor amounts of clastic debris in most of the iron-formations shows that great structural stability must have been maintained in the adjacent land areas or that they were deposited in parts of the sedimentary basins which were isolated from clastic material for some reason, probably structural. With this sort of geologic setting iron could be added to the basin either by volcanic or weathering processes. The lack of free oxygen would enable the concentration of iron to build up in the marine environment until saturation or organic activity caused it to be precipitated along with silica for which a similar situation would occur. The preponderance of hematite over magnetite in these deposits as compared to the older Algoma-type may indicate that the photosynthetic organisms were more efficient and/or more abundant, the supply of iron was more in line with the ability of the organisms to utilize it or that the chemical state of the hydrosphere had changed somewhat.

The presence of positive europium anomalies in the Algoma-type iron-formations, when more fully understood, should clear up some of the ambiguities between the two types. They may indicate that the marine waters were more reducing during the Archean thus causing Eu to be reduced to the +2 state and magnetite to be the stable ferric iron phase rather than hematite. Whatever the implication of Eu it must reflect a fundamental difference between the environments of deposition.

Although Cloud's hypothesis explains the source, transportation and deposition of the Precambrian banded iron-formations better than any other hypothesis, there are some aspects which need further explanation and investigation. Perhaps most important is to understand the significance of the sedimentary facies of iron-formation (James 1954) in light of this theory. James suggests that the different facies are the result of changes in Eh and pH with increasing depth and in particular the change from an oxygen rich environment in shallow near-shore waters, to oxygen depletion in deeper more distant waters. If as appears likely, oxygen was not present in the atmosphere, then James' facies concept will have to be modified. Cloud's explanation that the iron-formation facies can be visualized as incidental products of the biological activity is not very satisfactory.

Dimroth and Chauvel's study on the textures of the silicate-carbonate facies rocks of the Sokoman iron-formation and the trace element data presented in this study indicate that the iron silicate and the siderite were probably deposited as discrete crystalline particles. This suggests that the seawater must have been saturated with respect to these species and hence James' facies concept may indeed apply to those facies with reduced iron. These rocks were presumably precipitated inorganically and hence would respond to fluctuating conditions in the sedimentary environment. The seeming depth dependence of the oxide and silicate-carbonate facies rocks probably indicates a depth dependence of the organisms producing the oxygen. The lack of erosional evidence such as crossbedding, scour and fill structures and intraclastic conglomerates in the Australian and South African iron-formations indicate that they were deposited in considerably deeper water than the North American ones. It is suggested that the Australian and South African deposits were the more normal, and oxide facies rocks were deposited in the depth range of the photosynthesizers and below that depth, ferrous minerals were deposited according to the prevailing conditions of the aqueous environment.

The North American Superior-type iron-formations probably represent the deposits produced at the time when oxygen was first introduced to the atmosphere. They are clearly different in certain aspects from the Australian and South African ones, and Trendall (1968) has posed the question of whether they are really a separate type. Trendall's comparison of these deposits brings out several features such as lateral thickness variations, sedimentary structures, iron-formation lithologies and the conspicuousness of varves which differ between the Lake Superior deposits and those of the other two areas.

The Sokoman iron-formation definitely was deposited after the first introduction of oxygen to the atmosphere, since the early continental deposits of the Labrador Trough contain evidence of oxidation of detrital biotite and individual detrital grains are coated by hematite crusts (Dimroth 1968). The radiometric age of the Sokoman iron-formation (1870 m.y.) is considerably less than the age of the Hammersley (about 2000 m.y.; Compston and Arriens 1968) and the Transvaal (2000-2200 m.y.; Trendall 1968) deposits. Thus the interval between the deposition of the Hammersley iron-formations and the development of the Labrador Trough (1900-2000 m.y.) presumably saw the introduction of oxygen to the atmosphere for the first time.

When oxygen became available in the atmosphere it would also become dissolved in the near shore marine environment. As that occurred, the situation envisioned by James of a near shore oxygenated environment would be produced, resulting in the distribution of iron-formation facies according to the existing aqueous geochemical conditions. At this time inorganic oxidation of ferrous iron would occur preferentially in the high energy, turbulent, near-shore environment, where oxygen could be most easily dissolved in the marine waters. This would explain the abundant evidence of shallow water deposition in the Sokoman and Lake Superior iron-formations. Prior to the development of an oxygenated atmosphere, however, oxide facies rocks would be deposited only in the depth range of the photoautotrophs would would put a minimum depth limit of about 10 meters (due to ultraviolet radiation penetration) on the deposition of ferric iron. This 10 meter buffer of water would insulate the deposition of the older iron-formations such as the Hammersley and Transvaal from much of the shallow water turbulence. Consequently, the observed conspicuousness of varves, lateral continuity, and smaller thickness variations of the older Superior-type deposits could occur. The source of the iron for the younger Superior-type iron-formations of North America may well have been the marine reservoir of ferrous iron which had built up over the time under the anoxygenous atmosphere prior to about 1900 m.y., possibly supplmented by volcanic contributions. The deep marine waters presumably would take considerable time to come to equilibrium with the small initial oxygen content of the atmosphere, and hence iron could be transported in the deep waters under the same anoxygenous conditions as previously.

If this interpretation is correct, the development and resulting changes in the banded iron-formations of middle and early Proterozoic and Archean times resulted from the continuing evolution of the primitive atmosphere. Further study is necessary to determine whether this extension of Cloud's theory is tenable, and it is particularly important that reliable age determinations be obtained on those Superior-type iron-formations containing shallow water sedimentary features. If these all turn out to be young (less than 2000 m.y.) then not only will the introduction of oxygen to the atmosphere in the period 1900-2000 m.y. have been more firmly established but these deposits may serve as a basis for reliable worldwide correlations of Proterozoic sequences. For example, the striking similarities between the Sokoman and Lake Superior deposits would indicate that they are roughly synchronous and that the age results obtained by Peterman (1966) on the slates from the Lake Superior area represent the primary age of these deposits and not a metamorphic overprinting, as he suggests.

Along with age determinations, more detailed petrographic studies of these banded iron-formations are needed to compliment the work of Dimroth and Chauvel. Only in this way can the depositional history of these deposits be worked out. In conjunction with this, careful chemical studies are necessary to determine whether distinct chemical differences exist between the younger and older Superior-type iron-formations. From the analyses reported by Trendall (1968) for the three areas he studied, the older deposits (Hammersley and Transvaal) contain considerably more Na and K than the younger deposit (Lake Superior). The silicate mineralogy of these deposits suggest that this is not just due to random fluctuations, as Trendall states that the presence of riebeckite ($Na_2Fe_3^{+2}Fe_2^{+3}Si_8O_{10}[OH]_2$) is characteristic of the Hammersley and Transvaal iron-formations, while minnesotaite ($Fe_3Si_4O_{10}[OH]_2$) is characteristic of the Lake Superior deposits (and the Sokoman iron-formation). This change from a relatively alkali rich to an alkali poor iron silicate is undoubtedly a response to changing physico-chemical conditions in the hydrosphere and may enable a better understanding of hydrospheric evolution once the reasons for this change can be determined.

In conclusion, the development of banded iron-formations in the period before 1800 m.y. was in response to evolving hydrospheric and atmospheric conditions. The extreme sensitivity of the aqueous geochemistry of iron to changing conditions suggests that study of these deposits will not only produce a better understanding of the origin of these economically important sources of iron ore, but will also produce a great deal of evidence pertaining to the evolution of the primitive atmosphere and hydrosphere.

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Appendix 1

Neutron Activation Analysis

A. General:

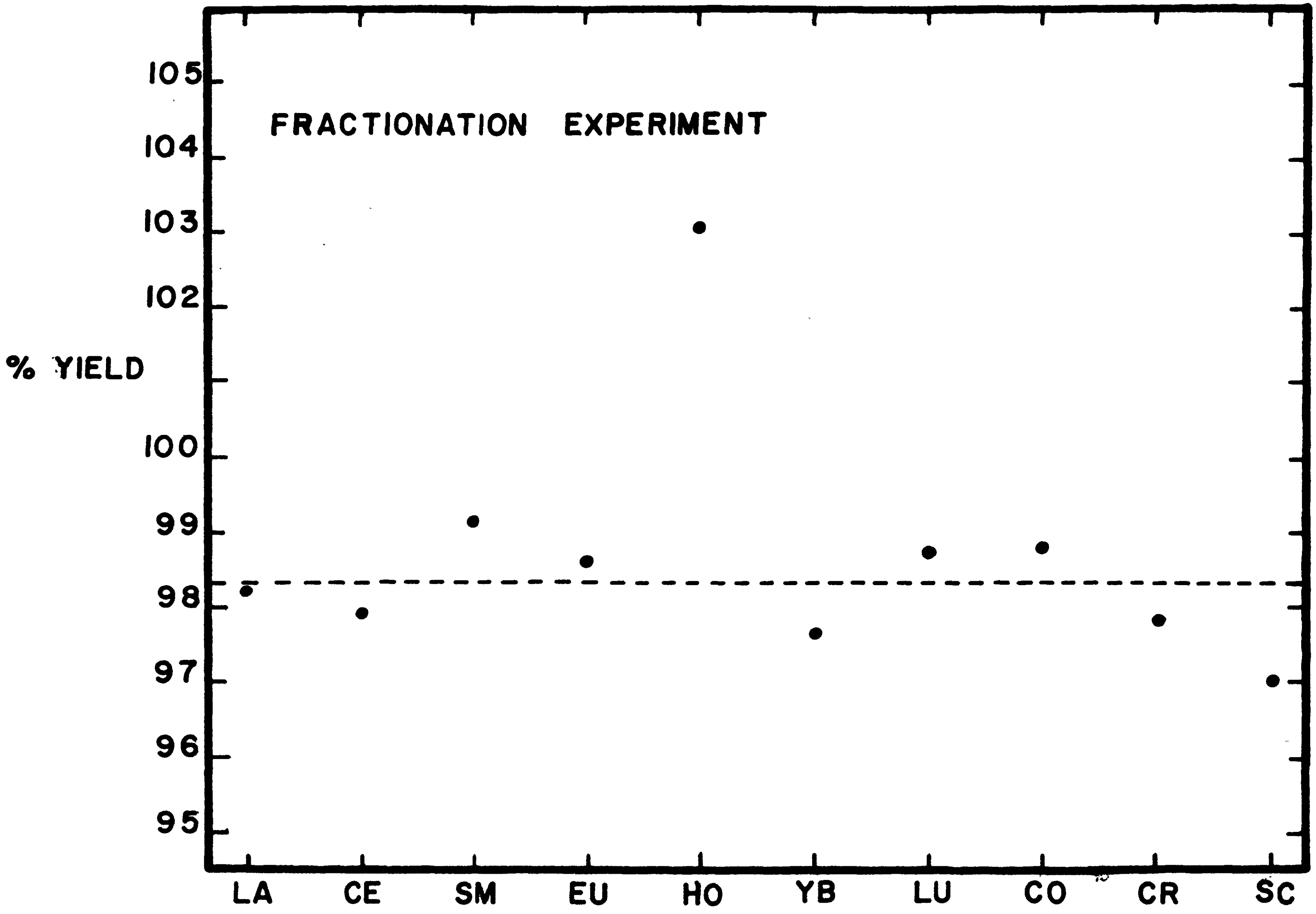
The technique of instrumental neutron activation analysis (I.N.N.A.) for whole rock samples of rocks is discussed by Gordon *et al.* (1968). This technique is being increasingly used to obtain accurate analyses of many trace and major elements in a variety of rock types. Because of the extremely low abundance of trace elements in Precambrian cherty iron-formations the extreme sensitivity of I.N.N.A. for a number of important trace elements made this technique admirably suited for the study of these rocks. Before this method could be utilized the iron had to be removed from the samples so that activity from iron isotopes would not dominate the γ-ray spectrum causing high background levels and thereby reducing sensitivity. A technique for removing iron from iron-rich samples had previously been developed for analysis of Rb and Sr by mass spectrometry (Posadas and Fryer, 1969). This was modified to suit the needs of this study and the procedure is outlined below.

B. Preparation of Samples for Irradiation:

Approximately 50 gm samples were broken up and powdered in an acid cleaned iron mortar with care taken to assure that no weathered crust was included. Then about 0.5 gm powdered samples were dissolved with a mixture of ultrapure gas-produced hydrofluoric acid and doubly vycor distilled 6.6 N hydrochloric acid in covered tephlon beakers. After perfect solution was acheived the samples were evaporated to dryness eliminating the hydrofluoric acid and silica. The residue was then redissolved in about 100 ml. of 6.6 N HCL and transferred to a clean 250 ml. polypropylene separatory funnel. Samples were agitated for about two minutes with approximately 60 ml. of the organic solvent 2-heptanone (amyl-methyl ketone), the organic and acid phases were allowed to separate and then the acid layer was drawn off into the original tephlon beaker leaving essentially all of the iron in the organic phase. The acid solution was evaporated to dryness and the chloride residue converted to nitrates by two successive dissolutions and evaporations with twice vycor distilled 6 N nitric acid. The nitrate residue was then transferred to a 2 dram polyethylene vial with a minimum volume of HNO_3 and evaporated to dryness ready for irradiation.

Since partition of some of the trace elements along with iron into the organic phase in the iron extraction procedure was a distinct possibility, an experiment was designed to monitor this. A concentrated flux monitor solution of most of the trace elements was prepared, and a portion of this was pipetted into a vial ready for irradiation. An equal portion was pipetted into a tephlon beaker to which was added 0.5 gm of sample R7622 and this mixture was taken through the same procedure as was followed in preparing the regular samples for irradiation. After irradiation the spiked sample and the flux monitor were counted together. The results are shown in Fig. 19. The rare earth elements along with Co and Cr do not appear to be fractionated and suggest that the yield of the chemical procedure is better than 98%. The poor agreement of Ho with the other rare earths

FIGURE 19.


FRACTIONATION EXPERIMENT
% YIELD
105
104
103
102
100
99
98
97
96
95
LA
CE
SM
EU
HO
YB
LU
CO
CR
SC

is entirely due to analytical uncertainty as the estimated error in this analysis is about 20%. The yield of Sc is slightly lower than that for the other other elements and this may be real as an analysis of the whole-rock powder of sample R7511 and the same powder that had been through the chemical procedure also showed a slight depletion. The partition of Sc into the organic phase is minor, however, and the Sc values obtained in this study should still give a qualitative estimate of the behavior of Sc. Consequently this experiment shows that, at least for abundances 100 times greater than those being analyzed for, there is no observable fractionation of the rare earth elements, Co, or Cr in the chemical procedure and Sc is only slightly so. Furthermore the chemical yield of the procedure is essentially 100% so the abundance estimates obtained should be accurate.

C. Estimation of Errors:

A previous study by Buma (1970) using essentially the same experimental setup as used in this study gave estimated analytical errors of ≤ 10% for La, Ce, Sm, Eu, Yb, Th, and Sc with precision and accuracy of the same magnitude based on duplicate analyses of the U.S.G.S. standard G-2. The results reported in this study are believed to be of the same quality as those reported by Buma for La, Ce, Nd, Sm, Eu, Yb, Lu, Co, and Cr. Analyses of Ho and Sc are believed to be accurate to within 20% but those of Th are only reliable estimates of maximum possible concentrations because of low abundance and high reagent contamination during the chemical procedure.

The source of analytical errors includes counting geometry, counting statistics, graphical integration, and sample geometry. For this reason only estimates of errors are meaningful and errors based on counting statistics alone would not be justified. The analytical error for all elements except Th and Ho are believed to be less than 10% (1σ). For Th and Ho poor counting statistics due to low peak to background ratios, produce higher analytical errors on the order of 20%.

Although there is no standard against which the technique used in this study could be checked, several lines of evidence support the above error estimates. Counting errors are known to be small when high peak to background ratios are achieved as shown by the consistent yield values obtained in the fractionation experiment. Furthermore, close agreement is obtained when two or more photopeaks of the same element are compared in the same count or the same photopeak, is compared from different counting periods. An estimate of the precision of the analyses can be obtained from the duplicate analyses of sample R7511 shown in Table XX. The two analyses agree well, with the percent deviations from the average of the two analyses falling within the estimated error, in all cases. These results also show that the conclusions obtained from the fractionation experiment reported earlier are applicable to the levels of trace elements being analyzed for in the iron-formations.

As mentioned, no standard rock is presently available with bulk chemistry and trace element levels resembling those of the iron-formation samples. An analyzed sample of pyroxenite (R7444) reported by Reid (1970), however, did have rare earth abundances similar to those of this study and a portion of this was analyzed in order to get an estimate of the precision of the analyses. Unfortunately R7444 had such a high content of Cr, that results for only two elements could be obtained because of the extremely high background levels. The results obtained are given below in TableXXI and show that at least for the elements obtained, the agreement between the two studies is excellent and well within the estimated precisions of the two.

Table XX

Duplicate analyses of Sample R7511 (ppm)

Element	R7511 (Fe extraction)	R7511 (whole rock)	% Deviation from average
La	1.02	1.11	4.5
Sm	0.162	0.174	3.6
Eu	0.0573	0.0603	2.6
Ho	0.0645	0.0751	7.6
Co	5.52	5.67	1.3
Cr	49.2	56.0	6.5
Sc	0.877	1.19	15.0

Table XXI

Analyses of Sample R7444 (ppm)

Element	This study	Reid (1970)	% Deviation from average
La	1.56	1.56	0.0
Sm	0.72	0.76	2.7

D. Reagent Blank:

Since the agreement between the duplicate analyses of R7511 before and after the chemical procedure was good, it was felt that reagent contamination must be low. To check this, a reagent blank was run on the chemical procedure. The results of this are shown below in Table XXII, calculated for a 0.5 gm sample.

Table XXII

Reagent Blank

Element	La	Sm	Eu	Co	Cr	Sc	Th
ppm	0.028	0.0045	0.0014	0.005	0.32	0.015	0.094

For an average iron-formation sample, the contribution of the blank to the analyses of the rare earths is approximately 2%, for Co <1%, for Cr approximately 3%, for Sc 1-10%, and for Th 10-100%. Thus, for all elements except Th, reagent contamination is minimal and will not seriously affect the results of the analyses. However, for Th, reagent contamination proably accounts for a considerable percentage of the reported values. For this reason the results are considered to be only reliable estimates of maximum possible Th concentrations.

E. Details of Analyses:

Three samples and one standard were irradiated together for 4 hours at a flux of 2.2 x 10^{13} neutrons/cm^2 sec. and then allowed to cool for a minimum of 18 hours. The standards were prepared by pipetting a 1 ml. portion of stock solution containing all the elements analyzed for, into a 2 dram polyethelene vial and evaporating to dryness before irradiation. This assured that both sample and standard geometries would be identical. The concentrations of the individual elements in the irradiation standards are given in Table XXIII. Details pertaining to the analyses are given in Table XXIII and discussed below for the individual elements.

Lanthanum: Results for La were obtained on both the 1596 kev. and the 329 kev. peaks. Both peaks gave comparable results and the reported abundance is usually the average of the two results.

Cerium: Interferences mentioned by Buma (1970), were minimized in this study as the small, high resolution detector was used for Ce analyses. This completely resolved any interference from the Fe^{59} peak at 142.5 kev. and as Buma mentions, contributions from Yb^{175} at 144.8 kev. are minimal.

Neodymium: Analyses were obtained for Nd by utilizing the Nd^{147} peak at 91.1 kev. The small detector resolved this from any neighboring peaks and analyses are limited only by low

Table XXIII

Details of analyses

Decay Time (days)	Detector	Counting Time (Hr.)	Element	Concentration Standard (ppm)	Nuclide	Peak Energy (Kev)
10	13 cc.	10	La	0.616	La^{140}	329, 1596
10	LEPS	10	Ce	1.86	Ce^{141}	145
10	LEPS	10	Nd	1.28	Nd^{147}	91
1-5	LEPS	4	Sm	0.348	Sm^{153}	103
10	LEPS (13 cc.)	10	Eu	0.136	Eu^{152}	122 (1408)
1	LEPS	4	Ho	0.168	Ho^{166}	81
10	LEPS	10	Yb	0.429	Yb^{169}	63
10	13 cc.	10	Lu	0.0541	Lu^{177}	208
10	13 cc.	10	Co	1.82	Co^{60}	1332
10	13 cc.	10	Cr	20.7	Cr^{51}	320
10	13 cc.	10	Sc	0.104	Sc^{46}	1120
10	13 cc.	10	Th	0.863	Pa^{233}	312

peak intensity.

Samarium: The 103 kev. Sm^{153} peak was counted in the period, 1-5 days, with the high resolution, small detector. The rough background problem mentioned by Buma, was overcome by the 4 hr. count necessary for the holmium analyses. In some of the Algoma-type iron-formation samples, however, two unidentified peaks, approximately 1 kev. on either side of the 103 kev. Sm peak, were encountered. These were essentially resolved from the Sm peak, but if the larger detector had been used, Sm abundances would have been too great, by about 5-10%. Consequently in future, if large detectors are used, careful inspection of the Sm peak for possible broadening on both the high and low energy sides should be made. These interferences were not noticed for any of the Sokoman iron-formation samples, but for reliable results it is suggested that the small detector be used for all samarium analyses.

Europium: Europium values were obtained early in the study on the 1408 kev. peak used by Buma. There are no interferences with this peak, but the low abundance of Eu in these rocks caused considerable intensity problems. The strong 122 kev. peak was used after Co^{57} contamination was eliminated and the only interference with this peak is the 123 kev. peak of Eu^{154}, consequently the results for Eu are excellent.

Holmium: Holmium analyses are possible only because of the extremely low abundance of Na in these rocks. Consequently the samples can be counted as soon as the activity from 2.6 hr. Mn^{56} has decayed away. Optimum counting time was found to be about 1 1/2 days. No observable interferences were noted, but possible contributions to the 81 kev. Ho^{166} peak by the 81 kev. peak of Ba^{133} may have caused the Ho analyses to be slightly high. Ba abundances in these rocks are extremely low, however, so any such contributions must be minor.

Ytterbium: Ytterbium abundances were obtained from the strong 63 kev. peak of Yb^{169}. Although the spectrum is complicated near this peak, it was resolved from any neighboring peaks and the results are good.

Lutetium: The 208 kev. spectral line was used, but placement of the baseline for peak integration was difficult for some analyses, as there appear to be a number of small peaks on the high energy side. However, the line is strong and analyses should still be accurate to within 10%.

Cobalt: The 1332 kev. Co^{60} peak has no interferences and excellent results were obtained for this element.

Chromium: Chromium abundances were determined from the Cr^{51} 320 kev. line and no interferences were noted.

Scandium: Gordon *et al.* (1968), discusses the problems associated with Sc analyses. The 1120 kev. line was used because of reduced background and extremely low Ta abundances.

Thorium: The main problem with thorium in this study was the extremely low abundance. As in Buma's study, only the center of the peak was analyzed to reduce possible interferences from Cr^{51} and Yb^{169} .

F. Comments on Sediment Analyses:

The abundances of the rare earths in the shale samples and composites were considerably greater than in the iron-formations, and as whole-rock samples were used the method of Buma (1970) was utilized for these analyses. All the elements were obtained in the manner mentioned above. In addition, terbium was obtained by integrating the two Tb^{160} peaks at 966 and 963 kev. and removing the contribution of the 964 kev. peak of Eu^{152} . The errors in these analyses are felt to be less than for the iron-formation samples due to the higher absolute abundances of the elements.

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Appendix 2

Sample Descriptions and Locations

A. Sedimentary and Volcanic Samples: The sedimentary and volcanic rocks analyzed in this study are listed and described in Tables XXIV to XXVIII under the individual areas.

B Iron-Formation Samples: The iron-formation samples used in the trace element analyses of the Algoma-type and Sokoman iron-formations are described in detail below, under the individual areas studied.

Michipicoten iron-formation:

1. R8094 (G. S. C. #68GF10) - Sulfide facies, Lucy Mine: A complex intergrowth of equal proportions of pyrite and buff colored siderite from the sulfide rich zone at the stratigraphic top of the Lucy ore zone.
2. R8095 (G. S. C. #68GF10) - Siderite facies, Lucy Mine: Buff colored siderite from the same zone as R8094, containing about 2% pyrite.

Timagami iron-formation:

1. R8096 - Oxide facies: Bright red jasper and magnetite in alternating 1/4 to 1/2 inch layers, from the North Pit, Sherman Mine.
2. R8097 - Oxide facies: Similar to R8096 but jasper is duller, from the West Pit, Sherman Mine.

Mary River iron-formation:

1. R8053 (G. S. C. #64GF-37) - Massive magnetite: Massive,

fractured magnetite from north end No. 1 deposit.

2. R8054 (G. S. C.#65GF-115) - Massive magnetite: Massive magnetite with few fractures, located at southwest contact of iron-formation and massive magnetite, from No. 1 deposit.

3. R8055 (G. S. C. #65GF-41) - Massive hematite: High-grade hematite from zone to northwest of Muriel Lake.

4. R8056 (G. S. C. #65GF-59) - Massive hematite: Hard, dense, fine grained hematite from No. 2 deposit.

5. R8057 (G. S. C. #65GFM-84) - Banded iron-formation: Banded magnetite-hematite iron-formation, composed of mosaic quartz and coarse grained magnetite from No. 4 deposit.

6. R8058 (G. S. C. #65GF-110) - Magnetite iron-formation: High-grade banded magnetite iron-formation, from east of No. 3A deposit.

Sokoman iron-formation:

1. R7511 - Upper red cherty, Schefferville: Jasper and hematite bands up to 1 inch thick, but discontinuous and in part fragmental. - In thin section the rock is strongly recrystallized with the jasper bands (chalcedony, quartz and hematite) having lost iron to the hematite bands (hematite [60-70%], with quartz and stilpnomelane and traces of chlorite). The rock was originally intraclastic or oolitic.

2. R7513 - Cherty or grey upper iron-formation, Marion Lake area, Schefferville: Siliceous iron-formation with minor amounts of jasper and iron oxides. - In thin section the rock is mainly composed of very finely recrystallized silica and approximately 15% iron oxides concentrated in the centers of what

used to be oolites. Chlorite and stilnomelane are present in trace amounts.

3. R7622 - Intraclastic silicate-carbonate iron-formation: Slightly leached, poorly banded grey-green chert iron-formation. - In thin section, the rock is composed of 50% quartz, 10% siderite, 20% magnetite and 20% minnesotaite with the iron silicate minerals often being stained brown from oxidation and leaching.

4. R7949 - Upper red cherty, Elizabeth Lake: Medium grained granular hematite iron-formation. - In thin section, the sample is composed of strongly recrystallized intraclasts (originally soft) and oolites, with large intraclasts containing pellets, small intraclasts and questionable fragments of oolites. Texturally the sample is similar to R8066, although it contains less hematite. (~40% hematite, 60% quartz).

5. R7950 - Lower red cherty, west of Retty Mine, Schefferville: Laminated jaspilite showing minor migration of iron between adjacent layers. - In thin section, the sample is composed of pellet bearing matrix chert with some early diagenetic faults filled with cement.

6. R7951 - Lower red cherty, N. W. corner, Attikamagen Lake: Laminated jaspilite from the same horizon as R7950 but reduced. -In thin section, the sample is composed of laminated pelletoidal matrix chert that has been partially reduced to siderite, magnetite and minnesotaite.

7. R7952 - Riebeckite iron-formation, Lac le Fer: Fibrous riebeckite forming along shear surfaces. - In thin section, the rock is strongly recrystallized and composed of quartz (65%),

magnetite (20%), and riebeckite (15%). Riebeckite and magnetite are often concentrated in bands and textures indicate that the rock may have originally been an oolitic iron-formation.

8. R7953 - Lower Red Cherty, Attikamagen Lake: Massive pisolitic iron-formation with pisolites up to 1/2 inch in length and showing shrikage cracks are imbedded in matrix chert. Pisolites were very soft when buried. - In thin section iron is concentrated in the centers of pisolites but otherwise there is little evidence of iron migration.

9. R7955 - Lower Red Cherty, Concession Lake: Finely granular intraclastic iron-formation. - In thin section the rock is composed of fine grained (0.5-1 mm) well sorted intraclasts, which were soft at the time of deposition, embedded in little matrix. The sample shows moderate recrystallization but little evidence of extensive iron migration. Mineralogically, it is composed of 80% quartz 15% hematite and about 5% stilpnomelane.

10. R8015 - Lower Red Cherty, Concession Lake: Dense oolitic iron-formation with occasional intraclasts. - In thin section the rock is composed of very well sorted oolites which formed around intraclasts as nuclei and are cemented by chert. Stilpnomelane occurs as a late diagenic mineral.

11. R8017 - Lower Red Cherty, Concession Lake: Ribboned matrix chert ($R8017^1$) alternates with beds of finely oolitic iron-formation ($R8017^2$).

12. R8018 - Lower Red Cherty, Concession Lake: Beds contain a few large intraclasts in an oolitic groundmass. - In thin section, carbonate forms in veins and in large replacement areas along with minor amounts of minnesotaite.

13. R8019 - Middle silicate-carbonate iron-formation (Brown Cherty), Concession Lake: Ribboned carbonate chert. - In thin section the rock is composed of alternating layers of finely and more coarsely crystalline siderite and minnesotaite bearing matrix chert. Texturally the rock exhibits a recrystallized fabric of quartz, siderite, and minnesotaite.

14. R8020 - Middle silicate-carbonate iron-formation (Brown Cherty), Concession Lake: Laminated minnesotaite iron-formation. - In thin section the rock is composed of a finely laminated matrix of minnesotaite and siderite with laminations being caused by variations in the carbonate/silicate ratio and the presence of opaque (carbon ?) partings. The rock is essentially composed of equal proportions of minnesotaite and siderite with less than 10% quartz.

15. R8022 - Middle silicate-carbonate iron-formation (Brown Cherty), Concession Lake: Coarse intraclasts set in a femicrite matrix. - In thin section the rock is composed of 65% minnesotaite, 25% siderite, and 10% quartz. Styolites occur between intraclasts and in the matrix.

16. R8023 - Upper silicate-carbonate iron-formation, Concession Lake: Recrystallized chert with traces of intraclastic textures cotaining 80% quartz, 13% minnesotaite, 6% magnetite, and 1% siderite. Some signs of later oxidation are present as the siderite appears to be altering to magnetite and hematite.

17. R8066 - Lower Red Cherty, Timmins #4 deposit, Schefferville: - Granular quartz and hematite, quite friable and definitely enriched in iron. - In thin section the rock is composed of

quartz (50%), and hematite (50%) with only traces of the original oolitic textures left.

TABLE XXIV

Sample Descriptions and Locations - Belcher Islands

Sample*	Formation	Lat. (N.)	Long. (W.)	Lithology
R8028 (Sc-57-58)	Omarolluk	56°19'	78°07'	argillite
R8029 (Sc-58-58)	Omarolluk	56°30'	78°09'	argillite
R8030 (Sc-60-58)	Omarolluk	56°31'	78°07'	siltstone-subgreywacke
R8031 (Sc-62-58)	Omarolluk	56°33'	78°10'	siltstone-subgreywacke
R8032 (Sc-64-58)	Omarolluk	56°42'	78°24'	argillite-subgreywacke
R8033 (Sc-122-58)	Laddie	55°06'	78°33'	argillite
R8034 (J-132-B-58)	Omarolluk	56°41'	78°51'	argillite
R8035 (J-143-A-58)	Omarolluk	57°05'	78°46'	subgreywacke-subarkose
R8036 (J-157-A-58)	Omarolluk	57°20'	78°30'	subgreywacke-subarkose
R8059 (J-128-1-58)	Flaherty	56°26'	78°52'	argillite
R8042 (J-25F-58)	Flaherty	56°17'	78°52'	massive basalt?-diabase?
R8043 (J115A-59)	McLeary ? Haig ?	56°06'	70°24'	argillite ?? diabase ?
R8044 (J-262-2-59)	Flaherty	56°13'	79°55'	pillowed basalt
R8045 (J-291-E-59)	Flaherty	56°34'	79°33'	tuff
R8046[1] (J-256-1-59)	Flaherty	56°15'	79°50'	tuff

TABLE XXIV (cont'd.)

Sample*	Formation	Lat. (N.)	Long. (W.)	Lithology
R8046[2] (J-250D-59)	Flaherty	56°08'	79°43'	pillowed basalt
R8047 (J-241-2-59)	Flaherty	56°02'	79°51'	pillowed basalt
R8048 (J-241-1-59)	Flaherty	56°02'	79°51'	pillowed basalt
R8049 (J-231-0-59)	Haig	56°00'	79°58'	diabase
R8050 (M-15-1-59)	Haig or Flaherty	56°27'	78°58'	diabase ?- basalt ?
R8051 (M-15A-59)	Flaherty	56°27'	78°58'	pillowed basalt
R8052 (Sc-24-58)	Flaherty	56°09'	78°57'	tuff
R8037 (J-16-2-59)	Costello	56°20'	79°00'	siliceous dolomite
R8038 (J-44E-58)	McLeary	56°05'	78°55'	siliceous dolomite
R8039 (J-93-94-D-58)	McLeary	56°11'	78°43'	argillaceous dolomite
R8040 (J-56A-58)	McLeary	56°22'	79°15'	dolomite-near a diabase

*numbers in brackets indicate Geological Survey of Canada sample numbers

Table XXV

Rb-Sr sample descriptions and locations - Labrador Trough

Sample	Formation	Area	Description
R7623	Menihek	Schefferville	black graphitic shale
R7624	Menihek	Schefferville	dark grey shale
R7625	Menihek	Schefferville	black graphitic shale
R7838	Menihek	Schefferville	black graphitc shale
R7839	Menihek	Schefferville	green-grey shale
R7840	Menihek	Schefferville	grey shale
R7841	Menihek	Schefferville	black graphitic shale
R7626	Attikamagen	Schefferville	grey-green shale
R7627	Attikamagen	Schefferville	grey shale
R7845	Attikamagen	Schefferville	green shale
R7846	Attikamagen	Schefferville	grey-green shale
R7847	Attikamagen	Schefferville	grey-green shale
R7848	Attikamagen	Schefferville	green shale
R7943	Attikamagen	Lac le Fer	grey dolomitic shale
R7944	Attikamagen	Lac le Fer	grey dolomitic shale
R7660	Ruth	Schefferville	black shale

Table XXV (cont'd.)

Sample	Formation	Area	Description
R7728	Ruth	Hematite Lake	banded jasper-green argillite
R7849	Ruth	Schefferville	red hematite rich shale
R7851	Ruth	Schefferville	red hematite rich shale
R7500	Denault	Schefferville	siliceous grey dolomite
R7842	Denault	Schefferville	fine grained grey dolomite
R7843	Denault	Schefferville	fine grained grey dolomite
R7844	Denault	Schefferville	fine grained grey dolomite

Table XXVI

Rb-Sr sample descriptions- Mistassini Area

Sample	Formation	Description
R7657 (59GF124)*	Temiscamie	black argillaceous slate
R7956	Temiscamie	black argillite
R7957	Temiscamie	fine grained quartzite
R8008	Temiscamie	graphitic slate
R8011	Temiscamie	black argillite
R8012	Temiscamie	dark grey argillite
R8013	Temiscamie	black argillite
R7655 (59GF120)*	Upper Albanel	fine grained dark grey dolomite
R7656 (59GF121)*	Upper Albanel	fragmental and reworked dolomite
R7958	Upper Albanel	sandy dolomite
R8009	Upper Albanel	dolomitic argillite

* Geological Survey of Canada sample number

Table XXVII

Rb-Sr sample descriptions - Timagami, Ontario

Sample	Description
R7707 (58GF-1046)*	fine grained greenstone
R7708 (58Gf-105C)*	greywacke
R7713 (62GFW-20)*	intermediate to acid flow or fine grained tuff
R7714 (62GFW-81)*	highly pyritic, medium grained tuff or greywacke
R7718 (62GFW-126)*	pale grey acid tuff
R7719 (62GFW-133)*	grey-green massive acid to intermediate volcanic flow
R7721 (62GFW-149)*	pyritic andesite
R7722 (62GFW-151)*	interbedded rhyolitic or dacitic tuff
R7723 (62GFW-156)*	massive rhyolite lava or tuff
R7724 (62GFW-161)*	massive green andesite

* Geological Survey of Canada sample number

Table XXVIII

Rb-Sr sample description - Mary River, Baffin Island

Sample	Description
R7801 (65GFM-59)*	agglomerate-acid to intermedaite volcanic bombs in a biotite-feldspar matrix
R7802 (65GF-1)*	metavolcanic fragmental rock
R7804 (65GF-36)*	metagreywacke
R7805 (65Gf-38)*	pillow lava - biotite-chlorite schist
R7806 (65GF-69)*	ultrabasic metavolcanic
R7807 (65Gf-102)*	metagreywacke - biotite-chlorite-quartz schist
R7808 (65GF-88)*	orgneiss - biotite-chlorite-quartz schist
R7809 (65GF-124)*	andalusite porphyroblast in muscovite schist
R7810 (65GFM-20)*	fine grained, light green, biotite-chlorite-feldspar metavolcanic
R7811 (65GFM-40)*	biotite-quartz metatuff (parent of augen gneiss?)
R7812 (65GFM-44)*	dark grey, chlorite-biotite-hornblende metavolcanic
R7813 (65GFM-48)*	light grey, biotite-quartz gneiss
R7814 (65GFM-70α)*	fine grained, dark green metagabbro
R7815 (65GFM199)*	metagabbro with spots developing

Table XXVIII (cont'd.)

Sample	Description
R7816 (65GFM225)*	metavolcanic
R7817 (65GFM226)*	metavolcanic

* Geological Survey of Canada sample number

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BIOGRAPHICAL SKETCH

The author was born on November 4, 1945 in Sudbury, Ontario Canada where he attended the Sudbury Public School System until graduation from secondary school.

He received an Honours B.Sc. degree in geology from McMaster University, Hamilton, Ontario, Canada in May 1968. While at McMaster the author received the J.P. Bickell and J.L.W. Gill Scholarships in geology. During the summers of 1964 through 1968 the author was engaged in the geological exploration programs of the International Nickel Company of Canada and the Rio Algom Company in various parts of Canada.

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The author was married to Elizabeth Anne Ferguson, May 4, 1968. The couple are expecting a child in December of 1971.