A STUDY OF THE LEAD ISOTOPIC COMPOSITION

OF GALENA AT MANITOUWADGE, ONTARIO

by

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ABSTRACT

Lead isotope compositions of galena from the Fox Creek Fault at Manitouwadge, Ontario form an anomalous linear array of values on a standard $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot and a $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot. The last geologically reasonable time for galena mineralization along the Fox Creek Fault is during the Keweenawan age, 1100 million years ago. Using the slope of the anomalous lead line and this time of 1100 million years as the time of final galena mineralization along the fault gives an age of 2000 million years as the maximum time of emplacement of uranium parent of the anomalous leads into the crust. The corresponding Th/U ratio for the source of the anomalous leads is 5.3.

Lead isotope compositions of galena from the main ore zone at Manitouwadge are extremely homogeneous and do not show a lineation, other than along a ^{204}Pb error line, which would indicate them as anomalous leads. It is improbable for the ore zone deposits to be as young as 2700 million years as required by Tilton and Steiger (1969).

In order to relate ore zone leads to Fox Creek Fault leads at least a three stage lead growth model is required. Possibly no genetic relation exists between ore zone and Fox Creek Fault galenas analysed to date.

Single galena crystal lead isotope variations should be studied in detail within the Fox Creek Fault

itself. Sulphur isotope studies may help to determine
the relation between ore zone and fault zone galena at
Manitouwadge.

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CHAPTER I

1.1 INTRODUCTION

Manitouwadge is about 165 miles east-northeast of Thunder Bay, Ontario and is about 60 miles north of Lake Superior. The townsite is about 40 miles by road north of Trans-Canada Highway #17 at Struthers, and is served by spur lines of both the Canadian National and Canadian Pacific Railways.

Manitouwadge has been an important metal producing area since 1957. The Geco mine, owned by Noranda Mines Ltd., is the largest deposit in the area, and in the 1957-1971 period produced 639,630 tons of zinc, 377,830 tons of copper, 29,013,600 oz. silver, and minor lead and gold from 19,544,170 tons of ore. Reserves are about 30 million tons of 4.4% Zn, 2% Cu, and 1.8 oz. Ag.

The isotopic composition of lead in galena at Manitouwadge has been discussed in scientific literature since 1957. Frequently discussions on the age of the earth have centered around the lead isotopic composition at Manitouwadge. This thesis attempts to add insight into the origin of Manitouwadge leads.

1.2 GEOLOGY

Geology of the Manitouwadge area is shown in Figure 1 and has been described by E. G. Pye (1957), E. H. M. Chown (1957), Brown et. al. (1960) and Timms and
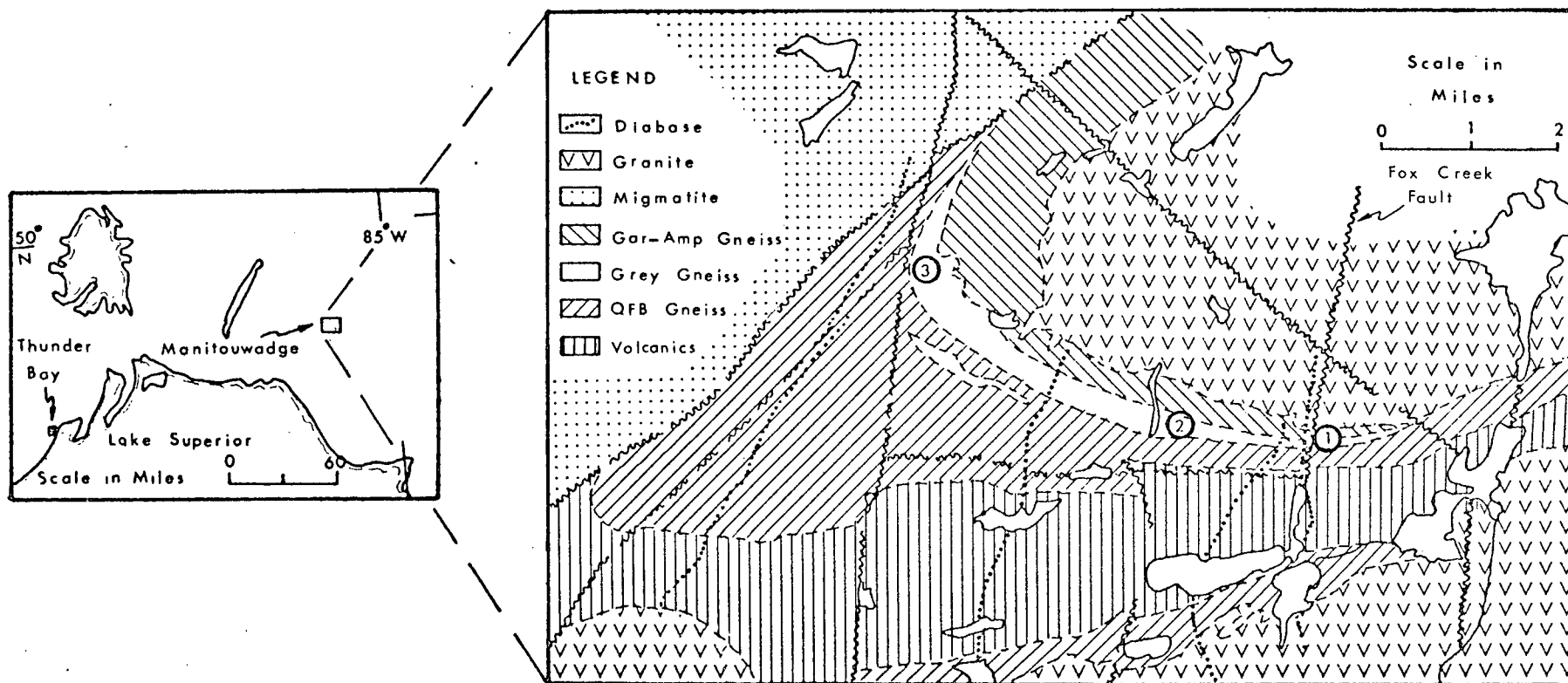
Figure 1 Geology of the Manitouwadge area modified after Pye (1957) and others. Locations of the Geco, Willroy, and Willecho mines are indicated by circled numerals 1, 2, and 3, respectively.

Marshall (1959).

Manitouwadge lies within the Superior Province of the Canadian Shield as a roof pendent of metasedimentary-metavolcanic rocks surrounded by granites, granodiorites and migmatites. The metasedimentary-metavolcanic sequence is of Keewatin age although its time relationship with other Keewatin rocks of the Shield is not known. The sequence forms a syncline with an axis trending 050° and plunging 15° to 20° to the northeast. Dips along the limbs of the syncline are steep. Relic bedding is noticeable in the metasediments and pillow structures can be found in the metavolcanics. Tops is not known due to high grade amphibolite facies metamorphism which occurred during the Kenoran Orogeny. This orogeny also obscured primary sedimentary structures and distorted the syncline. The strata are cut by pegmatite dikes and microgranodiorite dikes and sills which possibly were intruded during late phases of Kenoran Orogeny.

The eight known orebodies in the Manitouwadge area are hosted by a grey gneiss sequence thought to be sedimentary in origin. This unit is located toward the top or concave side of the plunging syncline, as depicted in Figure 1.

The major orogenic event in this area occurred 2700 million years ago as dated by Rb-Sr measurements according to Tilton and Steiger (1969). Hanson et. al.

(1971) also report Rb-Sr ages of 2700 million years for rocks from northern Minnesota, which is within the same subprovince of the Canadian Shield as Manitouwadge.

A swarm of northeast trending diabase dikes of probable Keweenawan age cut this older deformed terrain. A major Keweenawan intrusive complex is located about 50 miles south-southwest of Manitouwadge, along the structural boundary between the Superior Province and Southern Province. An enormous amount of basic volcanism and diabase intrusion occurred in the Southern Province during the Keweenawan, which has been dated by Goldich et. al. (1961) and the Geological Survey of Canada as occurring from 1200 to 900 million years ago. The intrusives were emplaced early in the evolution of the Southern Province, and are common in the surrounding Archean terrain, Halls (1966).

Ore deposits at Manitouwadge are conformable within the metasediments and have been classed as copper-zinc type not unlike other ore deposits which occur in an east-west belt across Ontario and part of Quebec. The Geco main zone and the Willroy #1 zone occur in a muscovite-quartz schist along with some bands of iron formation. Iron formation completely encloses the other Willroy and Willecho orebodies. The orebodies are classified as replacement deposits by Pye (1957), with three modes of occurrence: (1) massive ore (2) lode fissures and (3) disseminated ore. Pegmatite dikes have been replaced

in places by ore, which has been taken by many geologists
to indicate that mineralization is younger than pegmatite
intrusion. However, minor remobilization of ore could
have occurred during the waining stages of the Kenoran
Orogeny, and may be the cause of this "replacement".
Suffel et. al. (1971) suggest this latter view. Ore
appears to be located in long low-amplitude drag folds
which possibly were formed during regional folding.

Galena samples were collected during September of
1970 by the author from the Geco, Willroy and Wilecho ore
zones. At both the Willroy and Geco zones galena appears
to have been emplaced later than other sulphides, which
it often replaces. Galena constitutes less than one
percent of the Geco ore, and occurs in the massive ore and
along fractures in wallrock inclusions in the massive ore,
along fractures in pegmatite dikes assiciated with
disseminated ore, and associated with the Fox Creek Fault.
Galena in the Fox Creek Fault is more abundant and occurs in
much larger crystals than in other parts of the mine.
Fox Creek Fault galena is usually associated with calcite
which is not common elsewhere at Geco. The Fox Creek Fault
was inaccessible at the time of the author's visit, and so
samples of galena from there were donated from the Geco
office collection by Mr. T. Bakker and Mr. R. Weeks.
Samples from the Willroy and Willecho mine were donated
by Mr. E. Autio, the chief geologist.
Suffel et. al. (1971) point out that many characteristics

of the Manitouwadge area are consistent with severe
metamorphism. They note that the ore displays metamorphic
granoblastic textures which indicates an origin prior
to metamorphism, possibly of sedimentary or submarine
volcanic origin. The conformable nature of ore supports
this hypothesis.

Since grade of metamorphism is high in this area
it seems unlikely that the genesis of these orebodies
will ever be firmly resolved. The author favors a
sedimentary origin.

CHAPTER II

2.1 ANALYTICAL PROCEDURES

The 13 galena-bearing samples analysed during this
study were individually crushed and galena was separated
by hand, as much as possible. Approximately four grams
of galena from each sample were placed in 100 milliliters
of 6 molar hydrochloric acid, and held at about 60° C for
about 6 hours. The resulting hot solution containing
lead chloride was then filtered, and cooled to precipitate
lead chloride crystals. After about 2 hours, residual
liquid was decanted, lead chloride crystals were washed
in distilled water, dried in a warm oven overnight
and stored in a clean bottle.

A 30 cm. long ion exchange column with a 100-200
mesh Dowex 1×8 chloride form exchange resin was used to
purify the lead chloride since galena in the samples was
always associated with sulphides of iron, zinc and copper.
This ion exchange purification is based on a study by
Kraus and Nelson (1955) with details given in Appendix A.
After purification, lead chloride was converted to
crystalline lead nitrate which was stored. A detailed
flow chart of the analytical procedures is given in
Appendix A.

The silica gel-phosphoric acid method as des-
cribed by Cameron et. al. (1969) was used to make the
lead analyses on a single outgassed filament of rhenium.

Essentially this method increases the ionization efficiency of lead on a hot filament and can be used for very small (nanogram) masses of lead. Details of the silica gel procedure are given in Appendix B.

A double spike was used to correct for mass dependent fractionation which occurs in the source region of the mass spectrometer. The double spike used in this study was prepared by Mrs. C. Curtis, of this laboratory, from lead nitrate standards supplied by the Oak Ridge National laboratory U.S.A. The double spike has been calibrated by Dr. J. M. Ozard, and by the author against the N.B.S. equal atom standard, SRM 982. Calibration results are shown in Appendix C.

2.2 MASS SPECTROMETRY

The mass spectrometer used in this study was a 12 inch, 90° sector, first order focusing, solid source mass spectrometer as described by Russell et. al. (1971) and Blenkinsop (1972). A digital computer is used on-line with the mass spectrometer as a standard feature at this lab to assist in data reduction. Voltages proportional to the ion current flow at the collector are measured digitally. This data is filtered giving peak heights above baseline heights which then is converted by the computer to isotopic ratios for each pair of spectra scanned and the results are recorded on a teletype.

The mass spectrometer chamber was reduced to a pressure of about 2×10^{-7} millimeters of mercury, by an oil diffusion pump, a process requiring two hours after the sample had been inserted in the source region. Liquid nitrogen was placed into a cold finger near the source, which further reduced the pressure, to about 0.5×10^{-7} millimeters of mercury.

The magnet current supply and the high voltage supply were usually turned on and allowed to warm up for ten minutes before the filament current was turned on. The filament current was increased gradually from zero to around 1.8 amperes over five minutes which brought the filament temperature to around 1000° C. as determined by an optical pyrometer. Lead beams were large enough to give good precision at about 1200° C. The ion current for the ^{204}Pb peak must be greater than 10^{-13} amperes to give sufficient precision of isotope measurement, and temperatures were adjusted to achieve at least this amount.

Measurement of precise lead isotopic ratios also requires a stable rate of ionization in the source region, because only one ion beam can be measured at a time. If the ionization is unstable over the time the four beams of lead are scanned, meaningful isotopic ratios could only be obtained by averaging many measurements. Speed and precision of measurements of isotopic composition depend greatly on stability of the rate of ionization in

the source region.

At normal operation temperatures of 1050° C.
to 1300° C silica gel is probably a liquid upon the filament.
The ionization of lead atoms may take place as the atom
evaporates from the filament or as the gaseous atom collides
with the hot filament. No general theory exists to explain
the sequence of events in the thermal ionization of an
atom from a hot filament. The analyst must decide by
trial and error the optimum values of filament temperature,
filament position, and heating sequence which yield
precise analyses.

Usually ionization would be stable enough to
begin measurement after 10 to 30 minutes of monitoring
the beam at operation temperature. A typical group of
eight scans of a stable beam of sample 791 are shown in
Figure 2a. Even highly stable ion beams have some
transients and an example can be seen at minute 62 on
a ^{204}Pb peak.

Measurements were continued for each sample until
precision was estimated to be approximately 0.05 percent.
Scan records were edited of scans with obvious transients,
such as on the ^{204}Pb peak near minute 62 in Figure 2a,
before final reduction of data to a mean, standard
deviation, and standard error of the mean for the isotope
ratios.

A particularly unstable beam, from sample 802,

Figure 2a

Sample 791

Example of a typically stable lead isotopic ionization at 1230°C.

IONIZATION INTENSITY
^{204}Pb × 10^{-13} ampere
^{206}Pb & ^{207}Pb × $3 × 10^{-13}$ ampere
^{208}Pb × $9 × 10^{-13}$ ampere

Figure 2b

Sample 802

Example of a particularly unstable lead isotope ionization

IONIZATION INTENSITY
× $27 × 10^{-13}$ ampere
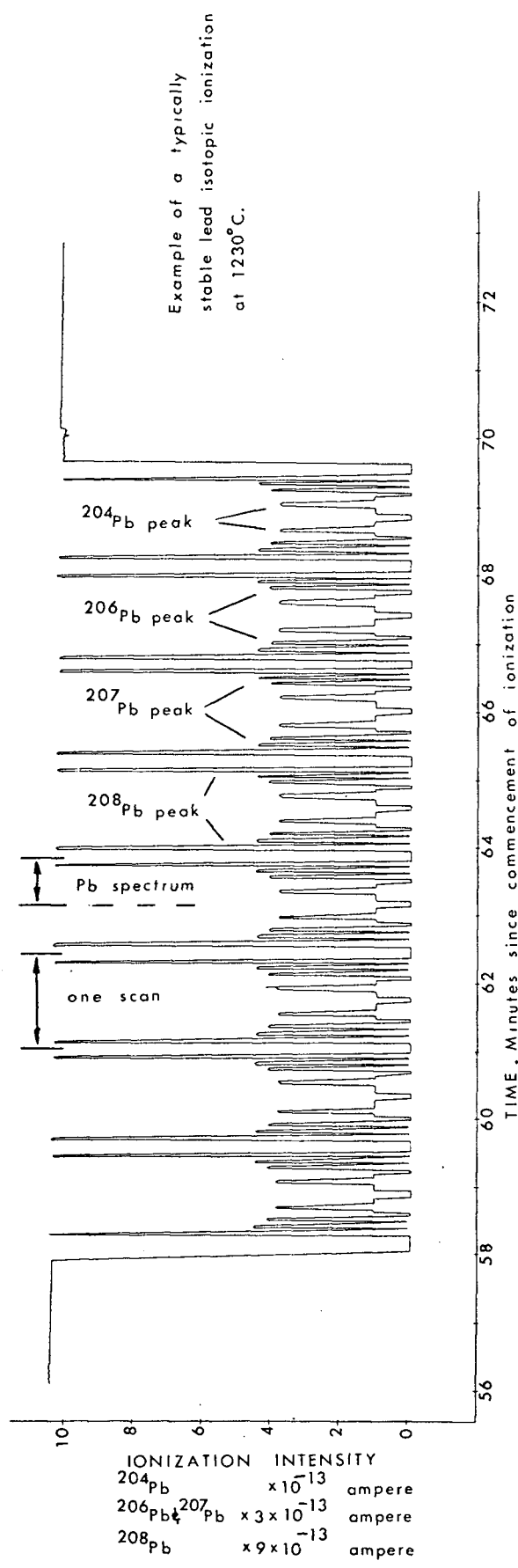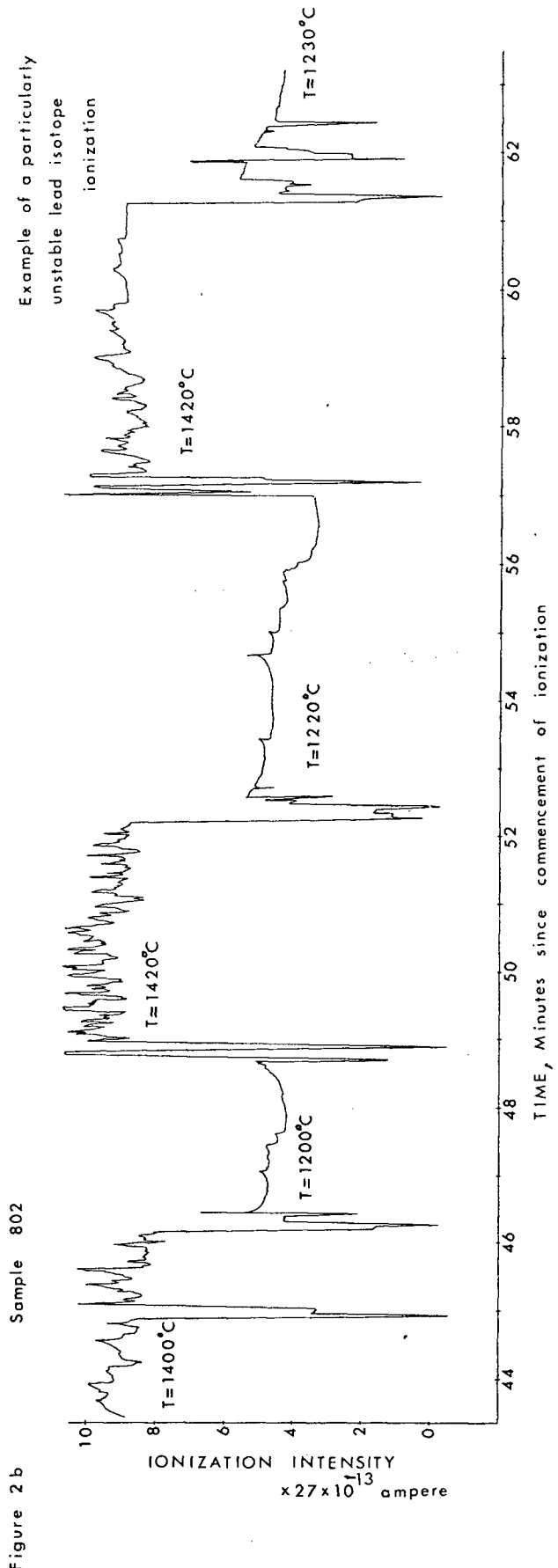
is shown in Figure 2b. After about one hour of ion-
ization at normal run temperatures the beam intensity
was still highly irregular. Figure 2b not only shows
this irregularity, it also shows a heating technique
used to stabilize beams. Often if the ion beam is
unstable, increasing the filament temperature 200°- 300°C.
for 2-3 minutes and then bringing it back down increases
the stability. This particular run was unsuccessful,
for when the beam finally stabilized, the sample was
too depleted to give a sufficient ionization beam.

CHAPTER III

3.1 ANALYTICAL RESULTS AND INTERPRETATION

The results of this study of the isotopic com-
position of galena at Manitouwadge, Ontario, are shown in
Table 1. Two samples from Manitouwadge were double spiked
to correct for mass-dependent fractionation within the
source region of the mass spectrometer. Fractionation
corrections for the silica gel-phosphoric acid procedure
used here were about 0.1 percent for the $^{206}Pb/^{204}Pb$ ratio;
this was deemed insignificant to the results of this study
and so fractionation corrections have ignored. Double
spike calibration and corrections and replicate analyses
of galena from Broken Hill, the U.B.C. standard lead,
are given in Appendix C.

Sample	$\dfrac{^{206}Pb}{^{204}Pb}$	$\dfrac{^{207}Pb}{^{204}Pb}$	$\dfrac{^{208}Pb}{^{204}Pb}$
782 Fox Creek Fault 750 level	29.815±.017*	17.481±.010*	46.72±.03*
783 Fox Creek Fault ? level	29.186±.007	17.389±.006	46.24±.019
784 Fox Creek Fault 1000 level	31.72 ±.013	17.817±.007	50.09±.016
785 Fox Creek Fault ? level	29.309±.009	17.403±.005	46.27±.016
786 Fox Creek Fault 250 level	32.10 ±.002	17.868±.012	50.49±.04
787 Geco Main Ore 1129 level	13.192±.005	14.370±.007	32.98±.023
789 Geco Main Ore 250 level	13.195±.006	14.377±.007	32.96±.017
790 Geco Main Ore 2250 level	13.206±.006	14.394±.009	33.02±.025
791 Geco Main Ore 2300 level	13.204±.004	14.384±.005	32.98±.019
800 Geco Main Ore 550 level	13.184±.003	14.340±.003	32.86±.007
802 Geco Main Ore ? level	13.223±.006	14.382±.005	33.01±.030
805 Willroy #3 zone	13.182±.004	14.349±.004	32.91±.017
807 Willecho (Lunecho) mine	13.177±.005	14.359±.007	32.94±.018

* The ± figures are standard errors of the mean.

/

Table 1

The data of Table 1 has been presently graphically
on Figure 3 and Figure 4, the $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$
plot and the $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot respectively.
A single stage growth curve for lead, after Cooper et. al.
(1969) has been added to each Figure.

In Figure 3, two distinct lead isotopic populations
may be seen, one homogeneous cluster of values below the
growth curve, which has been plotted at a more detailed
scale in the Figure, and another group which forms an
anomalous linear array to the right of the growth curve.
Samples from the Fox Creek Fault all lie along this anom-
alous lead line while ore zone samples from the Geco,
Willroy, and Willecho mines all have very closely the
same composition. A ^{204}Pb error line has been drawn
through the ore zone lead composition in Figure 3 and
any differences in the ore zone lead composition probably
may be ascribed to ^{204}Pb measurement error. A least square
fit line, after York (1969), has been fitted to the lead
compositions from the Fox Creek Fault and is shown in
Figure 3. This best fit line does not intersect within
experimental error the ore zone lead composition.

Figure 4 shows on the $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$
plot much the same relationships as that shown on the
$^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot in Figure 3. The Fox
Creek Fault leads form an anomalous linear array while
the leads of the main ore zones of the Geco, Willroy, and

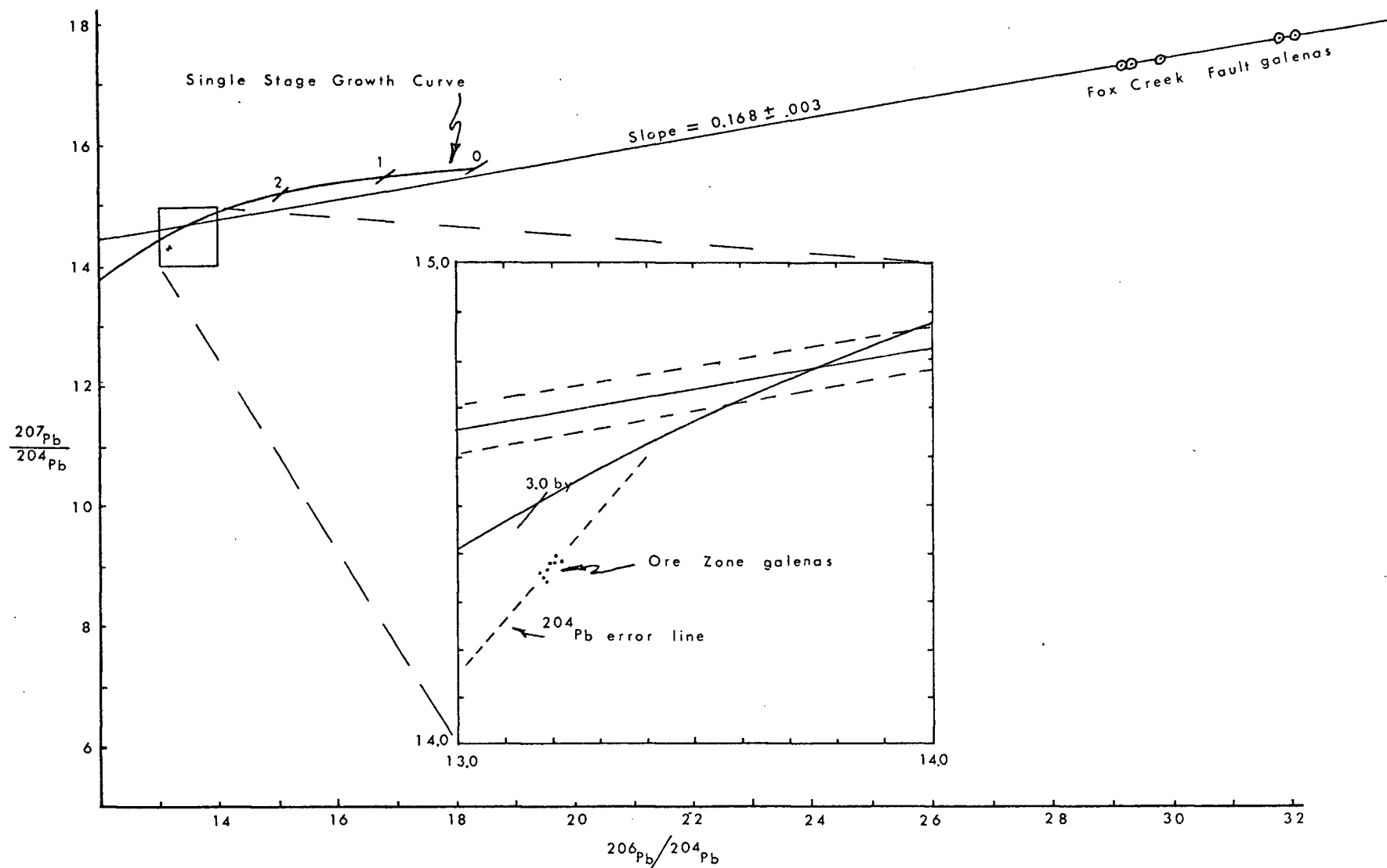Figure 3 $^{207}Pb/^{204}Pb$ - $^{206}Pb/^{204}Pb$ compositions for galena from Manitouwadge, Ontario. Growth curve after Cooper et. al. (1969) labeled in units of billions of years before present.

Figure 4 ^{208}Pb/^{204}Pb - ^{206}Pb/^{204}Pb compositions for galena from Manitouwadge, Ontario. Growth curve after Cooper et. al. (1969) labeled in units of billions of years before present.
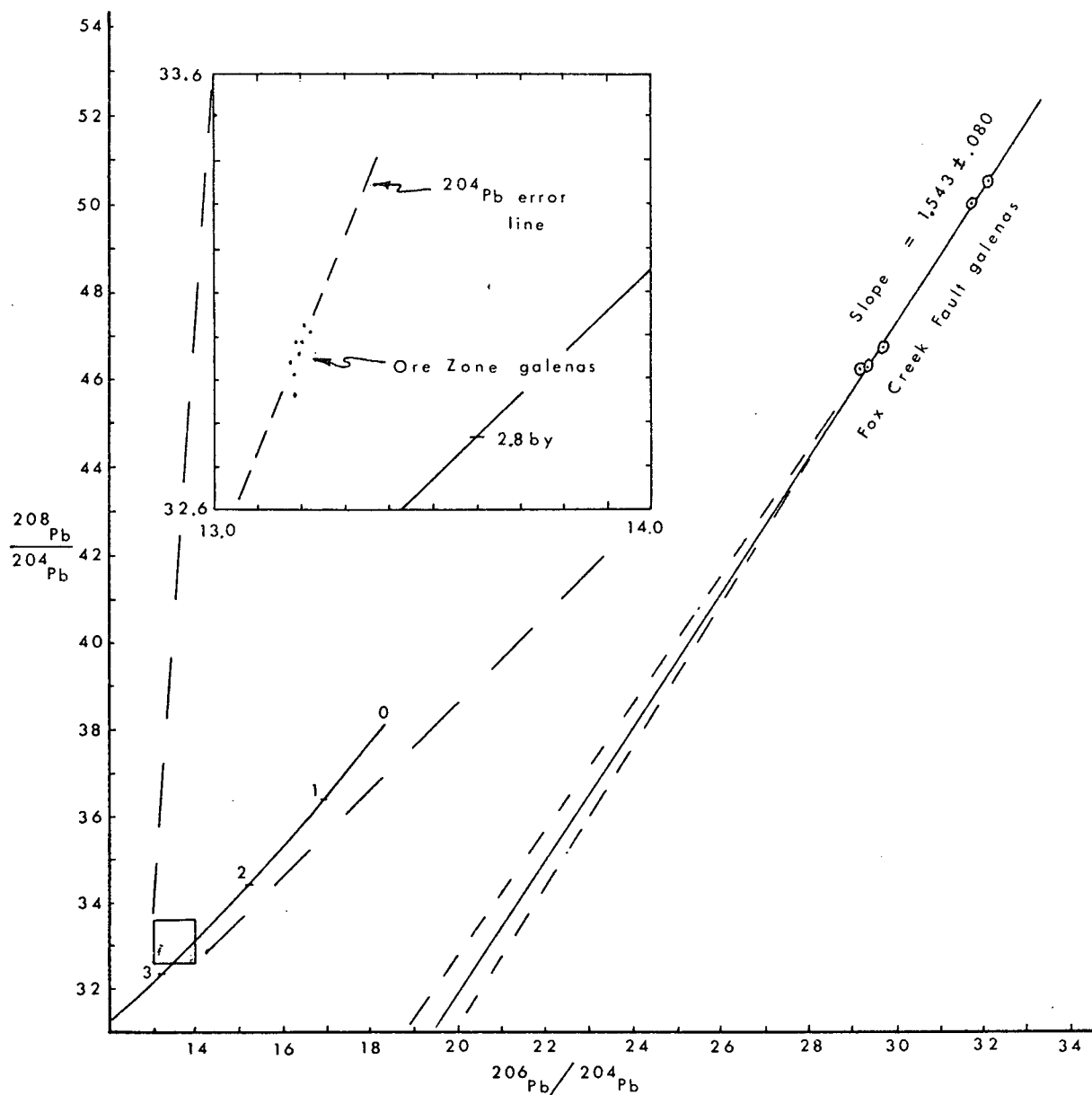
Willecho mines form a tight cluster of values above the growth curve. A section of Figure 4 containing the ore zone leads has been plotted at a more detailed scale and shows the isotopic compositions have a lineation along a ^{204}Pb error line. A least square fit line, after York (1969), through the Fox Creek Fault leads is well defined on this plot which seldom shows isotopic relations as well as the ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb plot. The anomalous line in this Figure 4 diverges even farther away from the ore zone lead composition than in Figure 3.

Problems presented by the isotopic composition of lead at Manitouwadge to previous interpreters may assist in explaining the present results.

At the University of Toronto, Russell and Farquhar (1957) made the first analyses of the lead isotopic composition of galena from Manitouwadge. They found that the lead composition of the main ore zone came from an environment of U-Th-Pb similar but not equal to that of many conformable ore deposits.

Stanton and Russell (1959) suggested that conformable ore deposits usually have a simple lead isotopic evolution model while leads from vein type environments have a more complex evolution. Galena leads at Manitouwadge however presented a problem to this hypothesis because they were homogeneous and fit Stanton's classification for conformable ore deposit and yet plotted below the simple

model growth curve determined by many younger conformable deposits.

Ostic (1963) discovered a highly anomalous lead composition within the Fox Creek Fault at Manitouwadge. This led to the suggestion by Slawson et. al. (1963) and Ostic et. al. (1967) that the Manitouwadge ore zone is part of an anomalous lead suite directly related to the anomalous leads along the Fox Creek Fault. Ostic regarded the ore zone lead composition to be contaminated slightly by anomalous leads similar to that found along the Fox Creek Fault.

A different interpretation of the lead isotopic composition at Manitouwadge was made by Tilton and Steiger (1965) and Tilton and Steiger (1969). Their argument is straight forward. They postulated that the longer lead is mobile in the earth the better are its chances to combine with leads from other U-Th-Pb systems and so become anomalous. They thought best to base calculations of the age of the earth on very ancient lead mineralizations which may have had less chance for contamination. Manitouwadge was chosen as a single example of an old mineralization and was combined in a single stage growth equation to calculate the age of the earth. Tilton and Steiger rely heavily on the observations by Pye (1957) that the ore zone mineralization must have been after emplacement of the Kenoran intrusives which date by Rb-Sr at about 2700 million years. The earths age is then

calculated as 4700 million years or about 200 million years older than previously calculated by Ostic et. al. (1963). It is interesting to note that Tilton and Steiger ignore the possible anomalous nature of the ore at Manitouwadge as postulated by Slawson et. al. (1963).

This difference of opinion between Slawson et. al. (1963) and Tilton and Steiger (1965) and (1969) is a difference in views on the origin of the main ore zone deposits. The results of this study listed in Table 1 and shown on Figure 3 and Figure 4 have a definite bearing on the origin of the ore at Manitouwadge and may help to clear up the above mentioned differences of opinion.

The anomalous leads from within the Fox Creek Fault form a linear array as can be seen in Figure 3 and Figure 4. The slope of the line determined by these anomalous compositions may be used to determine the latest times of mineralization along the Fault zone. The times obtained in this analysis are independent of the number of mixing stages that the lead has gone through, Kanasewich (1962) and Kanasewich (1968). If a three stage model is assumed to represent the lead along the Fox Creek Fault and the slope of the anomalous line is R then:

$$R = \frac{1}{137.8} \frac{(e^{\lambda' t_2} - e^{\lambda' t_3})}{(e^{\lambda t_2} - e^{\lambda t_3})}$$

If t_3 is allowed to be zero which would correspond

to a t_3 mineralization yesterday, it is found that for a slope of $0.168\pm.003$, on Figure 3, that t_2 must be 2580 ± 50 million years. This age which coincides with the Kenoran Orogeny, would be the maximum time for emplacement of the uranium parent of the anomalous leads into the crust. Another time limit to mineralization may be obtained if t_3 is allowed to equal t_2 in the equation above. This gives 1580 ± 40 million years for the t_2 event. This time corresponds to the minimum time for uranium emplacement into the crust and is also a maximum time for a final t_3 mineralization.

This interpretation suggests a final mineralization along the Fault somewhere in the time between the present and 1580 million years ago. A geologically reasonable time for this mineralization is 1100 million years ago during the Keweenawan age. During the Keweenawan a vast amount of volcanism occurred in the Southern Province of the Canadian Shield with a structural boundary about 50 miles south of Manitouwadge. Archean terrain surrounding the Southern Province was also riddled with dike swarms at this time. Certainly temperatures necessary to mobilize galena solutions existed then, and may have caused mineralization along the Fox Creek Fault. Possibly the Fox Creek Fault itself is a result of crustal cooling after the Keweenawan intrusive activity. A large diabase dike supposedly Keweenawan in age lies parallel to and 150 feet west of the Fox Creek Fault.

If t_3 is placed at 1100 million years, t_2 becomes 2000 ± 65 million years. The corresponding Th/U ratio for the source region of the anomalous leads is then calculated as 5.3, Kanasewich (1962).

Some event that we do not know about may have caused the Fox Creek Fault galena mineralization, in which case the above mentioned times are wrong. It is of little use to theorize with so many unknowns.

The lead isotopic composition of galena from within the main ore zone at Manitouwadge is extremely homogeneous as may be seen on Figure 3 and Figure 4. The compositions show a spread along a ^{204}Pb error line. It is not possible to distinguish a pattern to these sample compositions which come from widely separated points along the ore zone. Galena lead from the main ore zone at the Geco mine is indistinguishable from Willecho mine galena lead 7 miles away. Homogeneity in lead isotopic composition is one of the characteristics of a primary lead as observed by Stanton and Russell (1959).

Another characteristic of primary lead ores noticed by Stanton and Russell (1959) is a conformable relation to its host rock. The ore zone deposits are definitely conformable (see Figure 1) within the metasedimentary grey gneiss unit.

The ore zone leads at Manitouwadge obey, as well as can be discerned, two of the criteria of Stanton and

Russell (1959) for distinguishing a primary lead and yet these same leads plot well below the primary lead growth curve determined by many younger deposits. Primary growth curves of Ostic et. al. (1967) and Cooper et. al. (1969) have $^{238}U/^{204}Pb$ ratios of 8.94 and 8.79 respectively while the primary model $^{238}U/^{204}Pb$ ratio for Manitouwadge is well below these at 8.23. The ore zone isotopic composition at Manitouwadge if "primary" is certainly different from other primary lead systems.

It is not surprising that Tilton and Steiger (1969) should postulate Manitouwadge ore zone lead as a true primary lead and use it in a single stage lead growth equation since the ore zone leads do have a gross similarity to other primary leads. Tilton and Steigers evidence for the ore to be 2700 million years old, post Kenoran intrusion, is not strong. Recent observations by Sangster (1971) on sulphide stability during metamorphism and observations by Suffel et. al. (1971) of metamorphic textures within the Manitouwadge ore zone suggest a much older age to the ore zone than Kenoran. Therefore the calculation by Tilton and Steiger placing the age of the earth at 4700 million years is based on an age which is much too young for the ore at Manitouwadge.

Ore zone deposits at Manitouwadge are probably of sedimentary origin, abundant iron formation adjacent to the ore suggests a sedimentary environment as well. Possibly the ore deposits result from island arc, submarine

volcanic type sources which deposited the volcanic rocks
at Manitouwadge.

In Figure 3 and Figure 4 as stated previously
no difference can be seen between any of the samples taken
from along the ore zone except differences due to ^{204}Pb
error. It is apparent also from these Figures that the
anomalous Fox Creek Fault leads are not simply related
to the lead isotope composition of the main ore zone. A
two-stage mixing model would require ore zone lead com-
position to plot on the projection of the Fox Creek Fault
anomalous lead line. In order to relate these two com-
positions genetically at least a three stage lead model
must be employed. The ore zone lead composition must
have existed within the fault zone prior to anomalous
lead mineralization since the fault offsets the Geco
orebody 200 feet north on the eastern side. High linearity
of lead isotope compositions from the Fox Creek Fault
suggests a mixture of two fairly homogeneous end members
therefore, the ore zone lead would have had to be throughly
mixed with some anomalous or primary lead and the final
composition would then have to lie somewhere on the extension
of the anomalous lead line. A 4 or 5 stage history of
lead growth could be used to relate the ore zone isotopic
composition to the fault zone but too many unknowns exist
to do this.

The normalized results of samples analysed from
in and around the Manitouwadge area by Ostic (1963) Doe,

Tilton, and Hopson (1965), Hart and Tilton (1966) and Tilton

and Steiger (1969) are presented in Table 2.

Sample	$\frac{^{206}Pb}{^{204}Pb}$	$\frac{^{207}Pb}{^{204}Pb}$	$\frac{^{208}Pb}{^{204}Pb}$
Ostic (1963)*			
332 Willroy mine, galena	13.311	14.423	33.192
369 Willecho mine, galena	13.316	14.425	33.257
370 Geco mine, galena	13.319	14.427	33.233
372 Fox Creek Fault, galena	29.785	17.503	46.883
Doe, Tilton and Hopson (1965)†			
KA 46 Echo Trail, Minnesota, feldspar	13.572	14.52	33.06
KA 82 Birchdale, Minnesota, feldspar	13.44	14.48	33.14
KA 249p Cusson, Minnesota, feldspar	13.681	14.58	33.08
KA 356p Echo Trail, Minnesota, feldspar	13.44	14.53	-
KA 354 Ben Island, Ontario, feldspar	13.51	14.57	33.10
Hart and Tilton (1966)§			
Lake Superior sediment			
total sample	20.53	15.87	40.34
acid leach	22.84	16.34	42.86
water leach	22.48	16.20	42.34
Tilton and Steiger (1969)†			
MG 48 Geco mine, galena	13.26	14.43	33.39
MG 38 Willroy mine, galena	13.26	14.46	33.38
MG 19 feldspar	13.63	14.57	33.39
MG 20 feldspar	13.82	14.59	33.35
MG 41 feldspar	13.80	14.57	33.35
MG 45 feldspar	13.55	14.64	33.34

* Normalized to absolute values of Broken Hill.
  Russell (unpublished) 16.009, 15.395, 35.70.
† Normalized to absolute values of C.I.T.
  Russell (unpublished) 16.586, 15.425, 36.14.
§ Values not normalized.

Table 2

The data from Table 2 above has been combined with

the new data reported in Table 1 and has been plotted on

conventional $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$
vs. $^{206}Pb/^{204}Pb$ plots in Figure 5 and Figure 6 respectively.
In each of these two Figures, only the new analyses for
Fox Creek Fault leads reported in Table 1 were used in
fitting the least square line shown. In this respect
Figure 3 through Figure 6 are identical. A single stage
growth curve after Cooper et. al. (1969) has been added
to each plot.

In Figure 5 the lead isotopic values fall in two
distinct areas. One area is below the single stage growth
curve and has been drawn at a more detailed scale within
the figure. Lead compositions within this area are of two
kinds, galena lead and feldspar lead. Galena lead com-
positions reported by this study (see also Figure 3)
show a definite lineation along a ^{204}Pb error line.
Lead compositions for galena reported by Ostic (1963)
and Tilton and Steiger (1969) do not fall significantly
off this error line. Intralaboratory differences probably
cause the spread of values shown here. The feldspar
leads of Tilton and Steiger (1969) are from granitic rocks
and pegmatites associated with the Kenoran Orogeny from
around Manitouwadge and from other Kenoran areas of
Ontario and Minnesota. The feldspar leads show more
scatter than the ore zone leads due to the wide area from
which samples were taken, these leads also lie beneath
the growth curve.

The second area of Figure 5 lies along a linear array

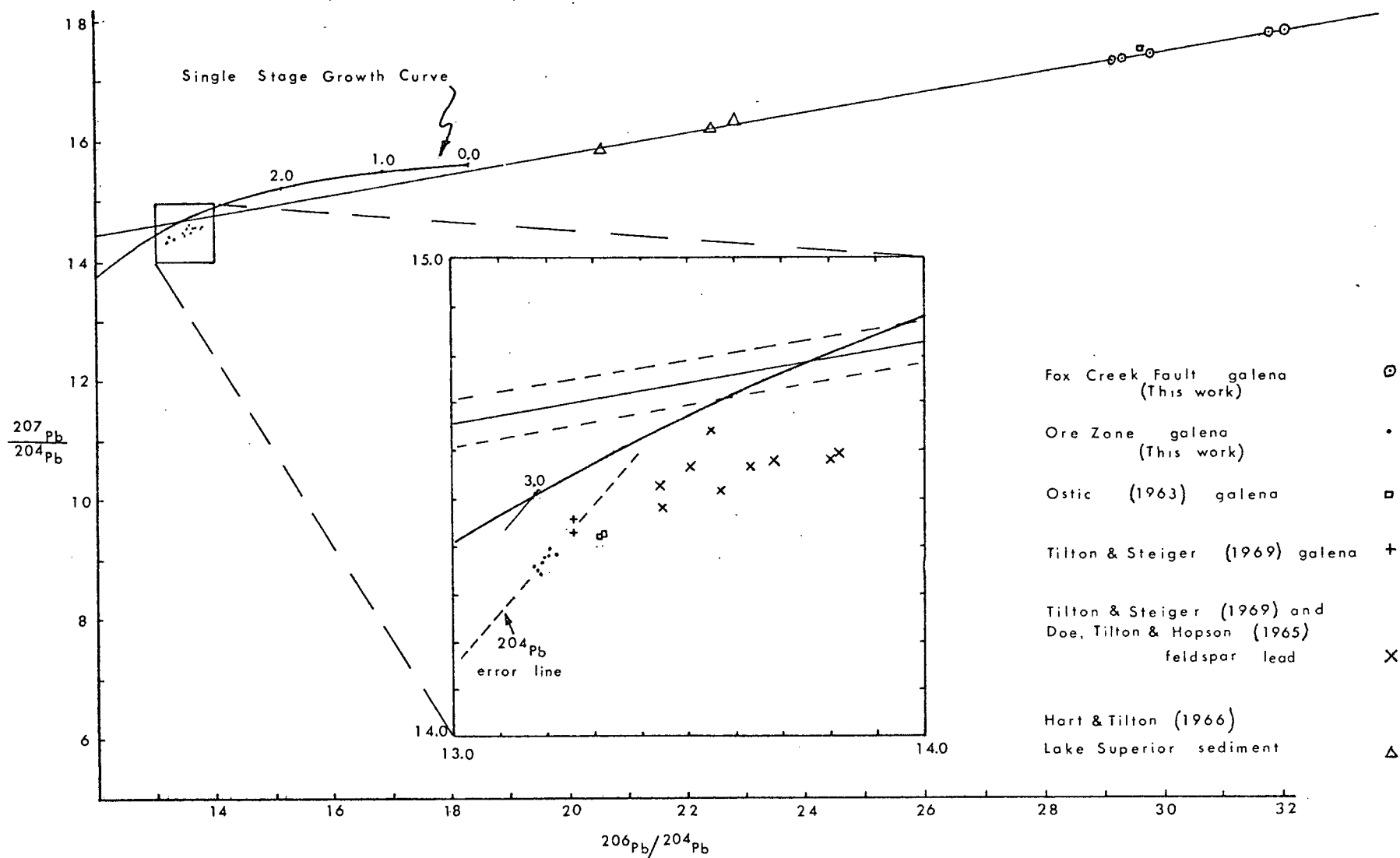**Figure 5** $^{207}Pb/^{204}Pb - ^{206}Pb/^{204}Pb$ compositions of rocks and ores at Manitouwadge, Ontario and its environs. This figure shows all pertinent data to date.

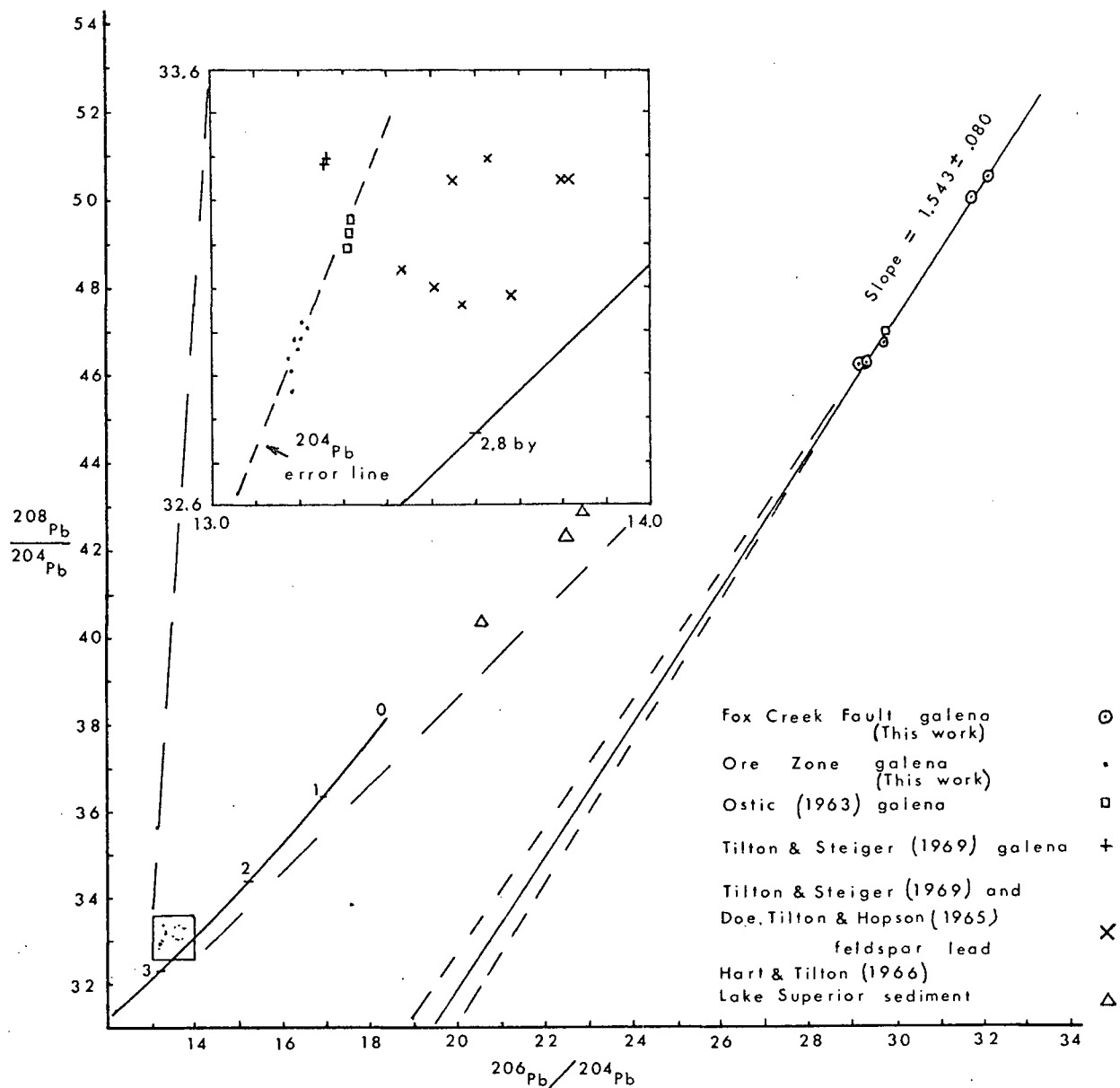**Figure 6** $^{208}Pb/^{204}Pb$ - $^{206}Pb/^{204}Pb$ compositions of rocks and ores at Manitouwadge, Ontario and its environs. This figure shows all pertinent data to date.

of points to the right of the growth curve. The anomalous
lead composition found by Ostic (1963) from the Fox Creek
Fault lies close to the line defined in this study.
Possibly intralaboratory differences if known, would bring
this composition down to coincide with the line. Lake
Superior sediment values of Hart and Tilton (1966) fall
extremely close to the line determined by the Fox Creek
Fault galenas. These values of Hart and Tilton (1966)
have not been normalized to any absolute standard.

Figure 6 is the $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot
for the combined results to date on Manitouwadge and
shows much the same relation as in Figure 5. Three areas
of lead isotope compositions may be found in this figure,
one adjacent to the growth curve and two others which form
distinct linear arrays. The area adjacent to the growth
curve shows the galena values of Ostic (1963), Tilton
and Steiger (1969) and the new data of this report scat-
tered along a ^{204}Pb error line. Feldspar leads in this
figure show similar variation to the feldspar leads plotted
on the $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot of Figure 5.
Fox Creek Fault lead analysed by Ostic (1963) falls on the
line determined by the new analyses although it was not used
to determine the line shown here. In this figure the
values of Hart and Tilton (1966) from Lake Superior sedi-
ment form their own linear array well away from the anom-
alous lead line of the Fox Creek Fault samples. The line
determined by these sedimentary lead compositions passes

close to the general lead composition of Archean rocks
and ores at Manitouwadge.

Fox Creek Fault lead samples may not be at all
related to the samples of the ore zone. The Geco ore is
primarily copper-zinc, and grades less than one percent lead.
It is probable therefore that very little of the ore zone
lead exists in the Fox Creek Fault zone. The fault at the
Geco mine consists of a breccia zone up to 80 feet wide and
is extremely wet underground. Pye (1957) states that post
fault pyrite, marcasite, and galena mineralization pos-
sibly related to hot solutions caused by Keweenawan dike
intrusion has occurred within the fault zone. The author
has noticed that large galena crystals seem to exist in the
fault zone invariably associated with calcite, while
ore zone galena crystals are normally smaller, more dis-
seminated and associated with silicates or massive
sulphides. No variation of isotopic composition with depth
in the fault seems to exist.

The author prefers a zero correlation model between
the ore zone leads and the Fox Creek Fault leads analysed
to date. The three or more stage mixing model required to
relate the ore zone leads to the fault zone leads appears
complex. A complete isotopic homogenization of lead
within the fault zone, prior to a final anomalous mineral-
ization as required by a multistage model appears less
likely than a simple mineralization completely unrelated
to the ore zone lead isotopic composition.

The results of Russell and Farquhar (1957) are of interest here although their analyses are from an older technological era and cannot be directly compared with any of the newer data presented here. Russell and Farquhar analysed galena from certain faults cutting Keweenawan age rocks around Thunder Bay, Ontario, and found they were anomalous. The anomalous lead isotopic composition of galena from these faults formed a linear array very much the same as the Fox Creek Fault anomalous leads except the slope is steeper (.186) on a $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot. These anomalous leads were not simply related to Keewatin type leads analysed by Russell and Farquhar from Steeprock Lake, Ontario, Sioux Lookout, Ontario and from Manitouwadge. This result is similar to the new results reported here from within Manitouwadge's Geco mine itself. This similarity strengthens the argument that the leads along the Fox Creek Fault are related to Keweenawan igneous activity.

The relation of the Fox Creek Fault galenas to Keweenawan intrusives is supported further by the lead isotopic composition of a Lake Superior sediment analysed by Tilton and Hart (1966). This sediment lead, although not normalized to absolute, plots extremely close to the anomalous line determined by the Fox Creek Fault leads. Lake Superior is to a large extent underlain and surrounded by Keweenawan intrusive and volcanic rocks, Halls (1966).

Estimates by White (1966) place the total volcanic thickness in parts of Lake Superior at greater than 30,000 feet. The sediment within Lake Superior must be influenced by the huge amounts of Keweenawan rocks around the lakes drainage basin, the similarity of this sediment lead to the lead along the Fox Creek Fault then may hint that fault leads are of Keweenawan origin.

It would be interesting to intensively sample the galenas of the fault zone to see if and where the ore zone galenas might be contaminated with these anomalous leads. A lead isotopic composition for the Keweenawan volcanics would be of great use, and in particular an isotopic analysis of lead from the large diabase dike 150 feet west of the Fox Creek Fault would also be interesting. A re-analysis of the Keweenawan galenas studied by Russell and Farquhar (1957) would also assist interpretation. Isotopic variations can possibly be found within single crystals of galena from within the Fox Creek Fault. It would be interesting to know whether lead emplaced by mineralizing solutions along the fault have become more or less radiogenic with time; single crystal studies should answer this. Sulphur isotope studies may possibly show a difference in source between ore and fault zone galenas.

Recent arguments by Richards (1971) and Le Couteur (1973) favour a source for primary lead of conformable ores within the crust itself. This requires a change of

view on the words "primary lead", which in their hypothesis is a well-mixed lead from upper crustal sources. The simple explanation of a primary lead originating from a homogeneous U-Th-Pb environment in the mantle to being emplaced into the crust does not appear correct any more. They also suggest that connate brines within a sedimentary basin may act as the agent for both removal and precipitation of ore metals and that this brine solution can allow for the great mobility of lead necessary to produce a homogeneous isotopic composition. Perhaps the ore zone lead at Manitouwadge is actually a primary lead formed in a similar method to those advanced by Richards (1971) and Le Couteur (1973).

Previous interpretations of lead isotopes at Manitouwadge have neglected to state that Manitouwadge is primarily a copper-zinc deposit with relatively minor amounts of lead. This small amount of lead makes the deposit vulnerable to the additions of small amounts of anomalous, multistage lead, early in the sediments' history. This small smount of lead may also hint that the original crust from which these sedimentary metals were derived was at an early stage in its metallogenic evolution, with few lead minerals.

3.2 SUMMARY

The lead isotopic composition of galena from Manitouwadge, Ontario forms two distinct populations. Galena leads from the main ore zone have a remarkably uniform lead isotope composition while galenas from within the Fox Creek Fault form an anomalous linear array of lead isotope compositions.

Lead isotopic compositions of galena from the Fox Creek Fault form an anomalous lead line on a standard $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot and a $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot. Time limits obtained from the slope of the anomalous line place 2580 ± 50 million years as the maximum age of emplacement for the uranium parent of the anomalous leads into the crust. The minimum time for uranium emplacement is 1580 ± 40 million years which is also a maximum time for final lead mineralization along the Fox Creek Fault. The last geologically reasonable time for galena mineralization along the Fault is during the Keweenawan age, 1100 million years ago. Using this time for final galena mineralization requires an age of 2000 million years for the time of uranium emplacement into the crust. The corresponding Th/U ratio for the source of the anomalous component of leads along the Fox Creek Fault is 5.3. Possibly the Fox Creek Fault is itself a result of Keweenawan igneous intrusive activity.

The lead isotopic composition of lead in galena sampled from the main ore zone does not show any linear trend, other along a ^{204}Pb error line, that might support an argument to classify them as anomalous leads. The lead isotopic composition from the main ore zone plots below the single stage lead growth curve of Cooper et. al. (1969) determined by many younger primary lead deposits. It is not yet resolved whether the ore zone leads are actually primary or anomalous.

The ore deposits are probably much older than the 2700 million year age postulated by Pye (1957) and Tilton and Steiger (1969). Metamorphic textures in the ores as observed by Suffel et. al. (1971) support this idea. Ore only occurs within metasedimentary rocks which does not appear to support a Kenoran Orogenic age of the ore as required by Tilton and Steiger (1969). Possibly the ores are the result of submarine volcanism and were deposited as a sediment in an ancient ocean. Possibly a crustal averaging process similar to those described by Richards (1971) and Le Couteur (1973) formed the ores at Manitouwadge.

The ore zone lead isotope composition is not related in a simple fashion to the lead isotope composition along the Fox Creek Fault. At least a three stage mixing model is required to relate ore zone leads to Fault zone leads. It is very possible that Fox Creek Fault leads sampled to date are not at all related to ore zone leads

since less than one percent of the ore is lead at the
Geco mine.

Detailed studies of lead isotopes in the Fox
Creek Fault would be interesting. It should be possible
to find ore zone leads contaminated by anomalous leads
in or near the Fault. Single crystal lead isotopic
variations can possibly be measured from Fox Creek Fault
galenas. It would be interesting to know whether
mineralizing solutions along the Fault have become more
or less radiogenic with time. Lead isotope determinations
of the large diabase dike 150 feet west of the Fox Creek
Fault have not been done and are suspected by the author
to be very similar to the Fox Creek Fault leads. Sulphur
isotope studies may be able to distinguish between ore
and fault zone leads.

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APPENDIXES

A. Ion exchange column preparation

This is a procedure suggested by Dr. Ulrych at this lab, which is modified from a procedure given in Catanzaro and Gast (1960). Figure A-1 shows this procedure.

The materials necessary for this procedure are dowex (1×8, 100-200 mesh) resin in chloride form, an ion column, 1.5 molar reagent grade hydrochloric acid, and pure distilled water.

The fine particles were removed from about 100 grams of the resin by mixing it with 100 milliliters of 1.5 molar hydrochloric acid and pouring off the fine slower settling particles. This was repeated about three times to remove most of the fine resin particles.
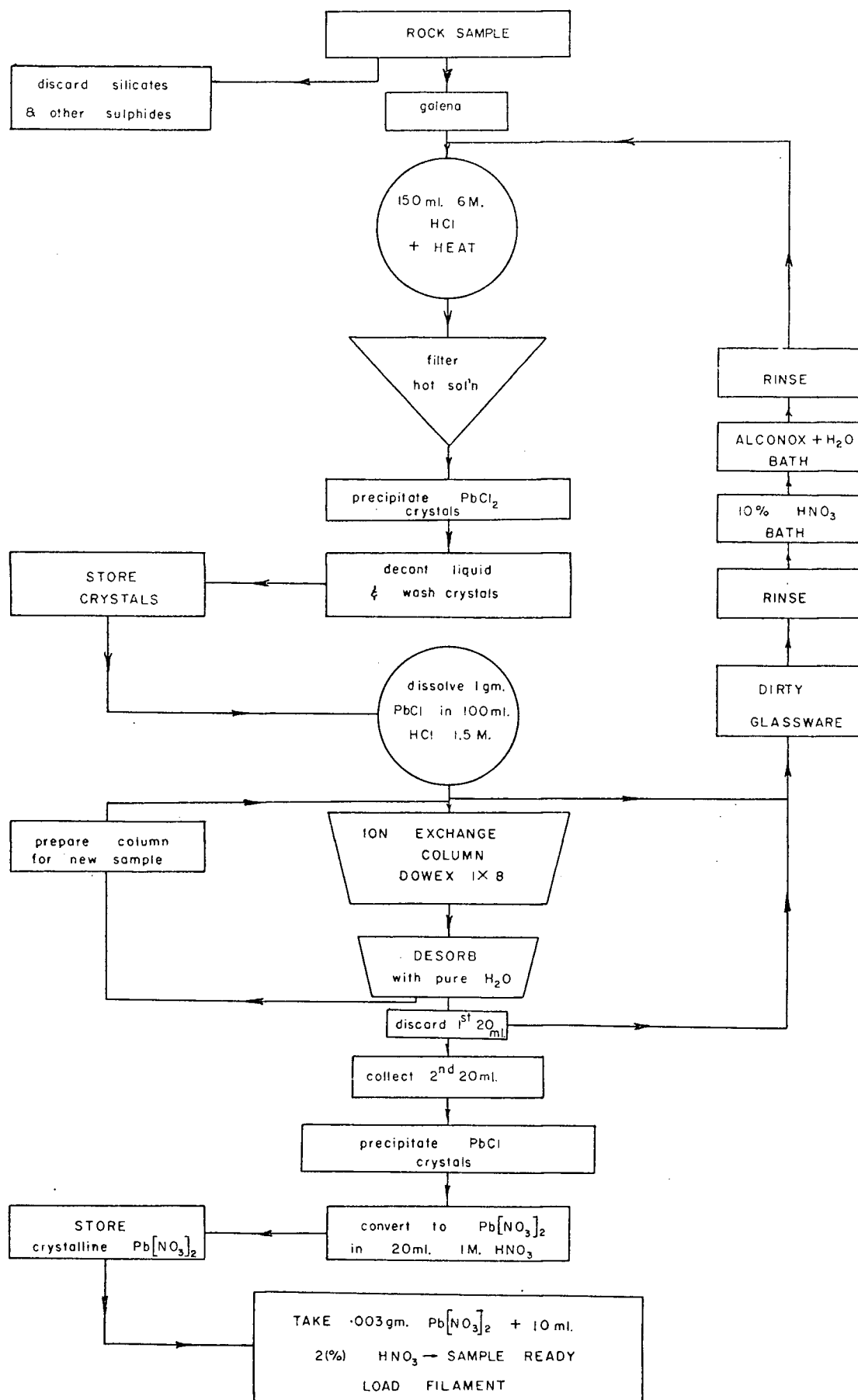
A slurry of resin and 1.5 molar hydrochloric acid was then poured into a clean glass ion column and allowed to settle to form a 28 to 29 centimeter length of resin in the column. The excess resin was carefully poured out of the column.

About 200 milliliters of distilled water was then allowed to pass through the column followed by about 100 milliliters of 1.5 molar hydrochloric acid. This prepares the resin before introduction of lead chloride into the column.

Lead chloride was dissolved to saturation in 100

FIGURE A-1   SAMPLE   PREPARATION   FLOW   CHART

milliliters of 1.5 molar hydrochloric acid, and was poured into the column. Lead ions would be split within the resin from chlorine and would adhere to the resin. After this adsorption phase the lead ions may be desorbed completely from the resin in either 0 molar or 8 molar hydrochloric acid. For this study 0 molar hydrochloric acid (distilled water) was used for desorption.

The first 10 to 15 milliliters of solution from the ion column during desorption with distilled water does not contain an appreciable concentration of lead. The results of a short test for lead is given in Table A-1.

Approx. Time (minutes)	Volume (ml.)	pH	Potassium Iodide Test
10	10	3.5	negative
20	20	3.5	positive
30	30	4.5	slight positive
40	40	5.0	negative

Table A-1

The second 20 milliliters of solution usually contains a high concentration of lead as determined by the potassium iodide test. Only this concentrated lead solution was collected.

The column after lead desorption is then eluted with 200 milliliters of pure distilled water followed by 100 milliliters of 1.5 molar hydrochloric acid and the column is ready for another sample. Care must be taken to wash the

sides of the column reservoir in the distilled water phase
to avoid contamination between samples.

A test was made for contamination between samples
by passing a radiogenic Fox Creek sample through the ion
column immediately prior to Broken Hill. The values for
Broken Hill were not affected as shown in Table A-2.

Column #1

Date	Sample	$\dfrac{^{206}Pb}{^{204}Pb}$	$\dfrac{^{207}Pb}{^{204}Pb}$	$\dfrac{^{208}Pb}{^{204}Pb}$
Feb. 28, 1972	786 Fox Creek Fault	32.10	17.893	50.52
Mar. 1, 1972	001 Broken Hill	16.004	15.358	35.52
	001 Broken Hill (Russell)	16.009	15.395	35.70
	001 Ave. of 6	15.991	15.367	35.58

Table A-2

B. Silica gel - Lead nitrate loads

The materials necessary for a silica gel lead nitrate load are listed below:

- outgassed rhenium filament
- lead nitrate solution ∿ 300 p.p.m. in 2% HNO₃
- clean pipettes
- silica gel solution
- phosphoric acid (reagent grade), 0.375 N.
- filament block
- a.c. current generator (1 watt peak power)·
- a.c. voltmeter and ammeter

The following procedure worked well it was found, but variants on this procedure may work as well.

The silica gel solution-suspension was agitated briskly and then left to stand quietly for one to two minutes. A large drop was then removed with a clean pipette and placed on the filament. The filament was then heated slowly by passing an alternating current through it of less than 1.0 ampere keeping a voltage of about 0.2 volts. Best results occur at this point if the silica gel is not allowed to lose all its water; heating was stopped when a translucent gel was visible on the filament.

One medium size drop of lead nitrate was then placed on the filament followed by a small drop of phosphoric acid, 0.375 N. The excess liquid was evaporated from the filament with further heating at 1.0 amp, 0.2 volts until the translucent gel mass appeared on the filament. If a fair amount of silica gel was present on the filament then further heating could proceed. Often a small "capping" drop of gel was placed on top at this stage to ensure

enough gel. The filament was next brought rapidly to a glowing red heat (about 1.8 amperes and 0.6 volts) for about 20 seconds and then allowed to cool. The mixture of gel, lead nitrate and phosphoric acid should turn white with initial heating and may give off white smoke for a time.

The sample is now ready to be placed into the source assembly of the mass spectrometer.

C. Precision and Double Spiking

Replicate analyses of galena lead from Broken Hill, the U.B.C. standard, are given in Table C-1 and shows good precision. Differences between these values and absolute values for Broken Hill as reported by Cooper et. al. (1969) or Russell (unpublished data) are not significant to material presented in this thesis.

Run	$\dfrac{^{206}Pb}{^{204}Pb}$	$\dfrac{^{207}Pb}{^{204}Pb}$	$\dfrac{^{208}Pb}{^{204}Pb}$
1	15.998	15.379	35.65
2	15.978	15.363	35.58
3	15.991	15.368	35.63
4	15.977	15.360	35.58
5	16.000	15.376	35.55
6	16.004	15.358	35.52
Mean	15.991	15.367	35.58
Standard Error	.005	.004	.019
Cooper et. al. 1969	16.003	15.390	35.66
Russell (unpublished)	16.009	15.395	35.70

Table C-1

Calibration of the U.B.C. ^{207}Pb - ^{204}Pb double spike was done against the N.B.S. equal atom standard S.R.M. 982 and is shown in Table C-2 below. The small fractionation corrections shown in Table C-2 are normal for silica gel-phosphoric acid procedures.

	$\dfrac{^{206}Pb}{^{204}Pb}$	$\dfrac{^{207}Pb}{^{204}Pb}$	$\dfrac{^{208}Pb}{^{204}Pb}$
Measured Ratio	.2765	9.512	.6049
Spike Corrected Ratio	.2766	9.520	.6065
Measured Ratio	.2782	9.505	.6061
Spike Corrected Ratio	.2785	9.521	.6075
Average Corrected Ratio	.2775	9.520	.6070

Table C-2

The results from double spiking two Manitouwadge samples are shown in Table C-3. Spike corrections seen here are not significant to the isotope differences studied in this thesis and so have been ignored.

Sample	$\dfrac{^{206}Pb}{^{204}Pb}$	$\dfrac{^{207}Pb}{^{204}Pb}$	$\dfrac{^{208}Pb}{^{204}Pb}$
789			
Measured Ratio	13.195	14.377	32.96
Spike Corrected Ratio	13.205	14.393	33.01
% difference	.08	0.11	0.15
786			
Measured Ratio	32.10	17.868	50.49
Spike Corrected Ratio	32.14	17.906	50.63
% difference	0.12	0.16	0.28

Table C-3