SOLID SOURCE LEAD ISOTOPE STUDIES WITH APPLICATION TO

ROCK SAMPLES FROM THE SUPERIOR GEOLOGICAL PROVINCE

by

JOHN MALCOLM OZARD

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ABSTRACT

Data of good quality is necessary to further the study of rock lead isotopic interpretations. An internal standard (double-spike) was employed to correct for fractionation accompanying the single filament analyses, and lead isotope ratios with a standard deviation of 0.15% were obtained. Lead sulphide mounted on tantalum was employed for the lead analyses. Discrimination in the analyses using tantalum filaments was consistent with the theoretical fractionation laws. This was not found to be the case for rhenium.

Lead and uranium analyses from the Vogt-Hobbs area near Lake Timagami, Ontario and from the Rice Lake-Beresford Lake Area, Manitoba revealed variations from a simple two stage model that could not be accounted for by experimental error. Interpretation of the data yields a three stage history for both of these regions, marked by major events at approximately 3400 and 2600 my ago. This earlier crustal history is supported by ore lead data from the vicinity. Both of the suites have a lower average value of (U^{238}/Pb^{204}) for the second stage, of their three stage history, than is characteristic of the source of single stage leads.

Variations from closed system behaviour for the Ontario samples is attributed to lead remobilization at the time of the Grenville event. Remobilization of the lead tends to mask the 2600 my old event.

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The Vogt-Hobbs area is characterized by more acidic igneous rocks and more radiogenic lead than the Rice Lake-Beresford Lake area. These differences are thought to represent the environment 2600 my ago or earlier.

The Manitouwadge lead analysed by Ostic resembles the lead ~ 2600 my ago in the Rice Lake-Beresford Lake rock samples. The Rice Lake-Beresford Lake rock samples are shown according to the interpretation presented, to have had a crustal history prior to 2600 my ago. This lends weight to arguments that exclude Manitouwadge from the class of single stage leads used in calculations of the age of the earth.

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CHAPTER I

INTRODUCTION

Perspective

There have been many studies of variations in lead isotope abundances in natural minerals. The resulting data have led to numerous unanswered questions pertaining to the solid earth.

The majority of precise analyses have been those of ore bodies containing at least a few percent of lead. However, any understanding of lead isotope abundance variations in the crust is incomplete until more is known about lead isotope variations in crustal rocks. A clue as to the possible significance of rock lead can be had when one realizes that the lead contained in a typical ore body could have been extracted from about 10 cubic kilometers of rock (Sinclair, 1965).

In an effort to clarify the understanding of available data on lead extracted from whole rocks, Ulrych and Reynolds (1966) presented an interpretation analogous to rubidium-strontium whole rock studies (Nicolaysen, 1961). In their model the first stage, called by them the "common lead environment", can be likened to the history of some common leads and may correspond to more than one lead-uranium system. The second stage, the "radiogenic lead environment", is the one in which the uranium-lead system presently observed is responsible for the last enrichment of the radiogenic lead component through the decay of uranium and thorium. Details of this interpretation will be elaborated in Chapter 5.

Ulrych and Reynolds examined Zartman's data from the Llano Uplift, Texas, in the light of their interpretation. Although the interpretation was applied to the best data available at the time, ages and isotope ratios determined were very imprecise. Of the scatter exhibited by the data it was not clear what proportion arose from open system behaviour of the rocks and what proportion arose from experimental errors.

More recently Ulrych has presented an alternative scheme for extracting information from rocks having a two stage history (Ulrych, 1967). This was a modification of a model by Gerling and Shukolyukov, 1957, which extracts more directly the time at which the first and second stages commenced. These two ages correspond to the age of the earth and time of formation of the second stage. Clearly the assumption of only two stages is more restrictive than the interpretation described in the earlier paragraphs, but it may be appropriate in special cases.

One objective of this thesis is to contribute new data of sufficient quality to further the understanding of such lead isotope interpretations.

A second objective of this study is to compare the behaviour of U-Pb and Rb-Sr systems in the same region. A recent study by Wanless et. al. (in press) of samples taken from the vicinity of the Grenville Front near Chibougameau, Quebec, has shown that the response of the Rb-Sr system, to metamorphism, is in marked contrast to that found for the K-Ar system. Most notable is the anomalously high K-Ar ages possible and the low apparent Rb-Sr ages for the mineral biotite. This sort of anamolous behaviour leaves the significance of K-Ar and Rb-Sr biotite ages open to question unless supporting evidence is available.

A final objective is to draw any inferences that may be possible concerning the geochronologic history of the regions studied; or knowing the geologic history to draw conclusions that may be generalities for U-Pb systems.

To draw possible inferences concerning the geochronologic history of the regions studied is definitely a secondary objective. It is realized that the samplings of this study are less than ideal for interpretative studies.

Delineation of the Present Study

Clearly, data of good accuracy is required to meet the objectives stated above. Much of the published data for rock lead isotope abundances is much too imprecise for the purpose. The first objective was to obtain data of acceptable quality.

When this study was being investigated two promising techniques were being developed. Catanzaro (1967) had successfully analysed 500 micro-gram reference samples with a standard deviation of 0.03% in Pb²⁰⁶/Pb²⁰⁴. In this triple filament technique the sample is evaporated from two rhenium side filaments and ionized on a center platinum filament at approximately 1500°C. No fractionation of the lead was detectable from ratios obtained in the first study, but fractionation of about 0.03% was later reported in the Pb²⁰⁸/Pb²⁰⁶ ratio (Catanzaro, 1968). This work has been recognized as an outstanding achievement.

The alternative technique, usually called double spiking (Compston and Oversby, 1969), requires two analyses. The first is a conventional solid source single filament analysis with attendant fractionation of up to 2%. Then a second

analysis is required to establish the magnitude of the fractionation. In simple terms, this is done by adding large quantities of 2 isotopes of known ratio and measuring the composition of the mixture. The second analysis enables one to correct for fractionation. A smaller total sample is required for this technique; the present studies were made with 100µ gm samples.

Both techniques were used in the present investigation, but the double spike technique was found to be far more satisfactory for rock lead analyses because of better sensitivity.

The mass spectrometer available for this study was a 12 inch, single focussing, 90 degree, gas source analyser, which was under construction when the research began. The first part of the project consisted of converting the instrument to solid source, assembling with the help of R.D. Russell the necessary electronic supplies, and the installation of improved pumping systems for the source and collector regions. A.Loveless designed and supervised the installation of a new thick lens source and magnet shims to achieve second order focussing, which resulted in greater sensitivity and a more simplified operation than we had before (Ozard and Russell, 1969; Loveless and Russell, in press).

Since the double spiking technique assumes the form of fractionation patterns, it was thought necessary to observe such patterns for our machines. The results of this study will be reported in chapter 3 (see also Ozard and Russell, in press).

Various techniques were used to extract the lead and uranium in forms suitable for mass spectrometric analysis. Although not new,

most of these techniques had not been used previously at this laboratory. These included the oxalate technique of Cooper and Richards (1966), the sulphide technique of Patterson (Mair, 1958), the volatilization technique of Masuda (1962) and Tatsumoto (1966), and the dissolution method of Doe (1967). Details of this work will be found in the following chapters.

In order to contribute meaningfully to interpretations of whole rock U-Pb analyses, it is desirable to study rocks for which the interpretable effects are large. The present day uranium and lead concentrations, and only these can be measured, are probably representative of the last stage of development of the lead. In the light of this consideration the oldest known rocks are likely to be the most suitable.

To meet the second objective of the research (a comparison of Rb-Sr and U-Pb systems in the same region) it would be necessary to have Rb-Sr analyses of samples taken from the same region. Although analyses of sample splits would be preferable for a detailed geological understanding, analyses of the same bodies of rock should provide a reasonable comparison on a broad scale.

An obvious choice in Canada is the Superior geological province. Two regions were selected, both of which had been the subject of extensive geochronological investigations. One of these is the Rice Lake-Beresford Lake area of south-eastern Manitoba, which is well within the Superior province. Turek and Peterman (1968) found ages of 2500 to 2700 my in this region. The second area was on the Grenville side of the Grenville front in an area studied by Grant (1964a, 1964b). The importance of understanding the complicated phenomena in the region of the front has

already been mentioned. The writer accompanied Dr. Grant to the Timagami region and collected, with him, the samples for the present study.

This is one of the first studies to achieve lead isotopic composition measurements of this precision and accuracy for whole rocks. Earlier analyses of this precision have been carried out for ores or minerals containing larger concentrations of lead or uranium. In many of the earlier studies the concentrations of lead or uranium were one or more orders of magnitude larger. For cases in which whole rocks were analysed prior to 1969 the precision or accuracy were definitely poorer.

CHAPTER II

METHOD OF URANIUM AND LEAD EXTRACTION

Introduction

The objective in extracting lead and uranium is to obtain pure samples of these elements that are representative of the whole rock. Although isotopic dilution was used to determine concentrations, quantitative recovery is required to ensure there is no significant discrimination between common and radiogenic lead.

Throughout the uranium and lead extraction procedures care must be taken to ensure that the samples are not contaminated. As isotope ratios correct at the 0.1% level were the primary objective of the analytical techniques, contamination errors should be kept below this level. To this end filtered air was supplied to keep the laboratory at a positive pressure. Reagents were purified as described in the appendix.

Rock Preparation

Samples from Ontario were collected by the writer and J. Grant. When necessary, dynamite and drilling were employed to ensure that the samples were fresh. The samples from Manitoba were collected by A. Turek. Only the largest and least weathered of these samples were used. The whole rocks, which weighed about 20 kg in total, were split into pieces of approximately 100 g and the weathered fragments were removed.

Contamination of whole rocks during crushing is much more critical than for mineral separates, as the latter are usually leached with acid to remove any lead or uranium held on the grain surfaces.

Unweathered pieces were crushed to pass approximately 40 mesh size. The first half through the crusher was used to flush out any rock dust not removed by cleaning. A 250 gm split from the second portion was further crushed by hand to pass 100 mesh. All polyethylene containers used to store the samples were soaked in 15% nitric acid for 24 hours, and the tin soldered stainless steel sieves were cleaned of particles of rock with a fine soft brush.

Volatilization of Lead

Extraction of lead by volatilization was chosen in preference to a perchloric-hydrofluoric acid attack. The pyrochemical technique is less hazardous and less liable to contaminate the samples, and partial separation of the elements is achieved by the distillation. Furthermore it is impractical to dissolve 40 g samples while it is quite practical to extract lead from this quantity by volatilization, with no additional effort.

At first, samples of U.S. Geological Survey analysed granodiorite (GSP-1) were heated in a tube resistance furnace at 1000°C to 1100°C in a hydrogen stream at atmospheric pressure. As only 80 to 90% recovery was achieved, the need for higher temperatures was indicated. The importance of sufficiently high temperatures has been noted by other researchers (Masuda, 1962; Tatsumoto, 1966; Welke, 1968) in the case of basic rocks. Tatsumoto reports at least 95% recovery at 1300°C, while Welke (1968) considers temperatures above 1150°C essential for 90% recovery. The results of this study, to be presented later, show that similar temperatures are appropriate for granodiorites.

In order to obtain higher temperatures, radio frequency induction heating was used. The apparatus is shown in Figure 2-1. The sample, in the form of 100-mesh powder, was mixed thoroughly with one fifth of its weight of purified graphite powder. For concentration determinations, lead-206 spike was added at this stage. The graphite crucible was then placed inside the envelope and the chamber evacuated. The evacuation had to be performed slowly to prevent loss of sample. After about one hour the pressure reached 10^{-3} mm of mercury and the diffusion pump was switched on. To heat the crucible, the voltage applied to the work coil was raised in 20 equal steps over a two hour period so that the final brightness temperature was 1350°C. This temperature was maintained for one hour, then the crucible was allowed to cool and, for ratio determinations, a second loading was placed inside the envelope and heated. The mirror was then dissolved in 50 ml of 1.5N hydrochloric acid. Although the mirror dissolved with a violent reaction, the acid was allowed to remain in contact with the envelope overnight.

Between lead volatilizations, the graphite was purified by heating to 1450°C for one hour. After heating, the Vycor insert was rinsed with 50% hydrofluoric acid for two minutes, then soaked in nitric acid for twelve hours, and finally rinsed with triple-distilled water.

Lead blanks were from 0.1 to 0.5μ g. These measurements include contamination from chemical processing and are therefore an upper limit for the contamination during the volatilization step. The blank represents about 0.2% of the sample lead for concentration runs and 0.05% of the sample for ratio determinations. The contaminant isotope ratios



were measured and found to be approximately those of modern lead. As the sample and contaminant ratios differ by only 50% at most the maximum error introduced in a ratio determination is 0.025%.

A fusion technique is often considered necessary to extract lead for concentration determinations. Doe compared a borax fusion method with his hydrofluoric-perchloric acid attack and found identical values for the two procedures (Doe, 1967). Therefore the acid attack may be considered as satisfactory as the borax fusion for extracting the lead from a granodiorite. The acid attack is often criticized because it is thought to leave accessory minerals such as sphene and zircon undissolved. However a sphene separate was entirely dissolved at this laboratory by using an acid attack similar to that of Doe (R. Culbert, personal communication). Furthermore, the high temperatures required for the borax fusion technique may be responsible for lead loss by volatilization or by alloying with the crucible, which effects are less likely with the acid attack. (See also Tatsumoto, 1966)

Analysed granodiorite, GSP-1, was analysed under a variety of conditions at this laboratory to determine the lead concentration. The results are listed in Table 2-1. Heating a mixture of rock and graphite at 1350°C, for at least one hour, gives lead concentrations consistent with the acid attack. It is concluded that the volatilization technique, used in this study, may be employed in determining lead concentrations by isotope dilution.

Doe reports a value of 58.7 ppm, by weight, for the lead concentration of this rock. However the standard is divided into quart scoops then split for distribution (Doe, personal communication) so that such a difference for the lead concentration is quite possible.

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CONCENTRATION MEASUREMENTS FOR STANDARD GRANODIORITE GSP-1.

ANALYSIS	METHOD		TEMPERATURE	CONCENTRATIONS		
104	Tube fur	nace in	hydrogen	1000°C	45.8	
105	11		**	1100°C	52.1	
107	Inductio	n heatin	g in vacuum	1350°C	55.3	
115		**	**		55.3	•
117	11	11	n	11	55.1	•
119	Perchlor	ic-hydro	fluoric acid	· .	55.2	

Concentrations are in ppm by weight.

Extraction of Uranium

Uranium was extracted for concentration determinations. The dissolution procedure was that described by Doe et. al. (1967). The sample was dissolved in hydrofluoric-perchloric acid and the uranium concentration was determined by isotope dilution. As four times Doe's quantity of rock (and hence acid) was employed, and as the surface area for evaporation was only slighly greater, the dissolution took three days, a time considered to be long enough to guarantee complete dissolution. No evidence of undissolved minerals was found when the residue was dissolved in 1.5N hydrochloric acid at 80°C.

An ammonium hydroxide precipitation was used at a pH of 7 to precipitate insoluble metallic hydroxides. After centrifuging, the precipitate was taken up in 1.5N hydrochloric acid, and was ready for the separation of other elements. The blank for the above procedure was from 0.02 to 0.05μ g of uranium and represented less than 0.5% of the sample.

Separation and Purification of Uranium and Lead

By using Dowex 1 x 8 resin, nitric acid, hydrochloric acid, and distilled water it was possible to separate and purify lead and uranium sufficiently for mass spectrometric analysis. In the mass range in the vicinity of singly charged lead no contaminant ions were found. Thorium was usually observed in the analysis of uranium, but no attempt was made to remove it. Some analysts have spiked for thorium and run the thorium analysis after uranium.

Solid source mass spectrometer analysis of lead is very inefficient (typically one ion from 10^5 atoms) because of the high

FIGURE 2-2 FLOW CHART FOR CHEMICAL SEPARATION

VOLATILIZATION OF LEAD

PERCHLORIC-HODROFLUORIC ACID DISSOLUTION

SAMPLE ADDED TO CHLORIDE RESIN COLUMN DISSOLVED IN 1.5N HYDROCHLORIC ACID

AFTER URANIUM ELUTION LEAD IS ELUTED WITH DISTILLED WATER

REPEAT FIRST COLUMN FOR LOW CONCENTRATION SAMPLES

LEAD ENTERS SMALL CHLORIDE RESIN COLUMN DISSOLVED IN 1.5N HYDROCHLORIC ACID COLUMN IS WASHED WITH HYDROCHLORIC ACID LELUTE LEAD WITH 6N

HYDROCHLORIC ACID

PRECIPITATE LEAD WITH HYDROGEN SULPHIDE SOME URANIUM PASSES THROUGH THE COLUMN THE REMAINDER IS ELUTED WITH HYDROCHLORIC ACID

URANIUM ENTERS NITRATE RESIN COLUMN DISSOLVED IN 7N NITRIC ACID

COLUMN IS WASHED WITH 7N NITRIC ACID

> URANIUM IS ELUTED WITH DISTILLED WATER FOLLOWED BY 1.5N HYDROCHLORIC ACID

NITRATE RESIN COLUMN PROCEDURE NEPEATED WITH SMALL COLUMN

LEAD SULPHIDE

URANYL NITRATE

ionization potential of this element. In order to have measurable ion beams, therefore, tens to hundreds of micrograms of lead are required for an analysis. Because it is impractical to extract larger quantities from granitic rock containing about 10 ppm of lead, it is essential to achieve maximum ionization efficiency. The chemical separation should be designed to remove materials of low ionization potential which tend to neutralize lead ions (Mair, 1958). In particular, every effort should be made to keep the concentration of sodium and potassium as low as possible. These are the most abundant ions commonly present during the analysis of lead in the mass spectrometer.

The purification adopted for lead was based on a study by Kraus and Nelson (1955). The separation depends on the fact that lead is held on Dowex 1 x 8 (anion exchange resin chloride form) in hydrochloric acid solutions between OM and 6M. No other ion in their study showed a peak at 1.5 molar hydrochloric acid with desorption at OM and 6M molar hydrochloric acid. A brief description of the column procedure follows; the details are to be found in the appendix.

The first column procedure was obtained by personal communication from the U.S.G.S. in Denver, and serves to separate the uranium and purify the lead. The sample from the volatilization step (for lead) was dissolved in 1.5N hydrochloric acid, and was added to the prepared resin column. The resin was washed with 1.5N hydrochloric acid. Triple distilled water was used to elute the lead.

At this stage the major contaminants of the lead are probably iron, zinc, cadmium, indium, tin, and antimony. A second small column (Catanzaro and Gast, 1960) may be used to remove the major part of all

of these elements. The lead is added in 1.5N hydrochloric acid to the second prepared column. The column is washed with 1.5N acid and the lead eluted with 6N hydrochloric acid. This completes the lead purification.

Three columns were used to obtain sufficiently pure uranium for mass spectrometer analysis. The first column was used to separate the uranium from the lead when both are being extracted from the same split. The residue from the hydroxide precipitation containing the spiked uranium in 1.5N hydrochloric acid was added to the prepared resin column. Then resin was washed with 1.5N hydrochloric acid. The acid passing through the column will contain all the uranium.

Uranium from the first column remains to be purified. A column of Dowex 1 x 8 resin, nitrate form, was used to purify it. The uranium was added to the column in 7N nitric acid, then the resin was washed with more 7N nitric acid. The uranium (and the thorium) were eluted with water followed by 6N hydrochloric acid. A similar procedure using a smaller volume of resin was used to improve the purification of the uranium. The uranium was sufficiently pure to produce large stable beams from 1 gm of rock containing 1 ppm of uranium.

CHAPTER III

MASS SPECTROMETRY

Sample Ionization Technique

The solid source single filament lead sulphide loading adopted for the greater part of this study was first described by Mair (1958) and attributed to C.C. Patterson. The oxalate technique of Cooper and Richards (1966) and the triple filament method of Catanzaro (1967) were also employed. Several variants on these methods were tried, some a number of times, with little success.

When adequate quantities of lead are available the triplefilament method of Catanzaro can be employed. In this method lead hydroxide is precipitated on two rhenium side filaments. These filaments are heated by passing a current through them to evaporate the sample. The centre platinum ionizing filament is heated to 1500° C. It was possible to produce either stable ion beams of 10^{-11} amperes that lasted an hour, or higher sensitivity for a shorter period, from 500μ g samples. However only about one analysis in two was successful, and when lead extracted from rocks was analysed lower sensitivity was usually obtained. On account of the time required to extract 500μ g quantities of lead from rocks this method was considered unsuitable.

A more sensitive technique that gave absolute ratios was needed. Comparison of sensitivities reported in the literature showed that the oxalate and sulphide single filament loadings are ten times as sensitive as that reported for the triple filament technique. This was confirmed by analyses performed in this study. The paper by Compston and Oversby (1969) indicated that errors caused by fractionation accompanying single filament lead analyses can be adequately corrected by using double spiking. The gain in effective sensitivity is about a factor of five as two runs in the mass spectrometer are required for the double spiking correction.

Both of the single filament loadings give sufficient sensitivity. On account of the simpler sample pre-treatment for filament loading the sulphide was used for the rock lead analyses. Lead sulphide and ammonium nitrate solution were carefully dried on outgassed tantalum filaments. Stable total lead beams of 5 x 10^{-11} amps were routinely achieved from 75µ g loadings. This method proves very reliable if the technique described in the appendix is followed exactly. It is most important to dry the filament loading slowly to prevent the sample from flaking off the filament. Furthermore the correct pH for precipitation of the sulphide and the gradual beam building during the analysis are prerequisites for good stability and sensitivity.

Lead and Uranium Isotopic Analysis

The filament heating pattern employed for the lead isotopic analysis was based on that described by Cooper and Richards for the oxalate technique (personal communication). The filament temperature was raised uniformly to 750°C over a period of an hour and left at this temperature for two hours. In this way it is possible to volatilize the lower melting point materials preferentially, and achieve a further purification of the lead in the mass spectrometer. Residual alkali beams were comparable to those reported by Cooper and Richards $(1 \times 10^{-11} \text{ A})$, and tended to die away during the analysis. Over the

next hour the temperature was gently raised to 850°C at which temperature adequate sensitivity was achieved.

Data taking for a lead analysis consisted of peak hopping, followed by scanning. The baseline just below mass 204 was first recorded on all shunts, then a peakhop set consisting of ten sets of the sequence: baseline, 204, 206, 207, and 208 peak tops. Baselines were again taken on all shunts and the spectrum scanned twice. For all analyses of rock lead reported the digital voltmeter readings were recorded manually. On account of the high sensitivity and stability any operator bias in this operation is much less than 0.1%. This method was preferred to measuring each ratio 204/206, 207/206, 208/206 in turn, because it ensures the same fractionation conditions for all ratios.

The baseline values obtained from the scanned spectrum pair were used to correct for pressure scattering. For the pressures encountered, about 1×10^{-7} mm of mercury, the corrections to a peak were about 0.05% of its height.

Peak hopping enables one to monitor four peaks, and the baseline in little more than one minute. For such short periods a linear extrapolation may be employed between successive values of a peak top for ratio determinations. The maximum systematic error incurred from such an approximation was 0.01%. The small size of this error is a consequence of the small and approximately linear growth in peak height over short periods.

For uranium isotopic analysis a triple-filament rhenium-ribbon source was used. The heating pattern employed was developed by the United States National Bureau of Standards (1966). Fractionation is inherent in triple filament uranium analysis, but the variation of fractionation can be minimized by employing identical filament conditions. The acidity of the uranyl nitrate solution, sample size and temperature of the filament were shown to be important factors in the study performed by the National Bureau of Standards.

The data reported in this Thesis were all obtained from low temperature analyses of approximately 10µ g samples. By extrapolating the data presented by the National Bureau of Standards fractionation of about -0.4% in the U238/U235 ratio would be expected. All fractionated data presented by the N.B.S. shows an enrichment of the lighter isotope. The extremely reproducible sample behaviour during the analysis is considered to be an indication that filament conditions were successfully reproduced from one analysis to another. Consequently fractionation should provide a bias for all uranium data but no significant between-run error at the 1% level. Further details of the analytical procedure are to be found in the appendix.

Data taking was similar to that for lead analysis except that only two peak tops were monitored. Pressure scattering, although corrected for, was less than 0.1% as the poorer peak shape and small peak separation per mass unit are offset by the three mass unit separation between peaks.

Instrumentation

Analyses were carried out with a 90° sector, 12 inch radius, single stage solid source mass spectrometer. The instrument was designed principally by R.D. Russell, and incorporates a focussing thick lens ion source (Loveless and Russell, 1969) and second order focussing shims. When focussed for singly ionized lead atoms, it has a resolution of about 400 at mass 200. The electronic supplies are almost entirely solid state.

For precise analyses, adequate beam intensity is essential. This was partly achieved by using an ion source that transmits ions efficiently and partly by using a solid source, for which fairly efficient ionization techniques exist. By analysing lead samples in the thin lens previously used by us and with the new thick lens source, it is estimated that a factor of about three was gained in transmission efficiency. This design permitted precise analyses of 100µ g quantities of lead on a routine basis.

The measuring system, filament and high voltage supplies were designed by Russell and constructed before the rock lead analyses were performed. The solid state measuring system proved extremely reliable; it incorporated peak selection in conjunction with the magnet current supply. A third aspect of the measuring system is the provision of peak height, shunt and scan direction information for recording on magnetic tape. An intercessor was built by Loveless to sequence the output of the digital voltmeter and measuring system for input to the seven track tape recorder. However the greater part of the rock lead analyses were recorded manually as the computer reduction was set up

for scanned rather than peak-switched data.

The measuring system incorporates a ladder attenuator which determines the shunt ratios. To calibrate the ladder attenuator a precision decade divider (Electro-scientific Instruments, Model 622 A. maximum deviation from linearity one part in 10^6 and input resistance 10^5 ohms) and null detector were employed in a bridge. The calibrated shunt values were found to be within 0.1% of the nominal values as specified by the manufacturer (also Electro-scientific Instruments).

As a more thorough calibration of the measuring system a voltage source was inserted in the feedback lead. This voltage was supplied by the decade divider just described. The voltage, applied in the feedback lead, to produce a constant output above the baseline for different attenuations, provides a calibration of the measuring system including the digital voltmeter. The values for each shunt ratio for the two different methods agreed to better than 0.1%, and were used in all calculations.

A stable ion beam enables one to make precise ratio determinations more easily. As the ion beam strength is an exponential function of temperature, the current used to heat the filament must be well regulated. A portion of the filament current was fed through the filament of a temperature limited diode. The anode current was used for providing feedback, and with this arrangement fluctuations of the ion beam caused by filament current variation were less than 0.1% over a period of one minute.

Before converting the mass spectrometer to a solid ionization source the writer had investigated the possibility of improving the

efficiency of the gas ionization source. A gas source was designed on the basis of a mathematical theorem presented by Naidu (1966). This theorem specifies the electrostatic field to guide charged particles along a prescribed set of paraxial paths. The gas source was designed to produce damped oscillatory trajectories. The new gas source was found to have an overall efficiency the same as the modified Nier source that had been used previously (Ozard and Russell, 1969). Computations by Loveless verified that the failure to improve efficiency was a direct consequence of the initial conditions assigned by Naidu.

Loveless then designed a solid source with the aid of a computer program to calculate ion trajectories. This new solid source has fewer electrodes than the conventional solid source but still employed damped oscillatory trajectories to focus the ions. As the ion source produces ions with a larger angular divergence, the magnet of the mass spectrometer was fitted with shims to provide second order focussing. The collector also had to be modified to accept ions with a larger angular convergence.

CHAPTER IV

DISCRIMINATION IN LEAD ISOTOPE ABUNDANCE MEASUREMENT

Introduction

The triple filament technique developed by Catanzaro (1967) was shown by him to give isotopic ratios agreeing closely with the known values for synthetic mixtures of separated lead isotopes. A double spike has been used by Compston and Oversby (1969) and by Cooper, Reynolds and Richards (1969) to obtain unfractionated values for lead isotope ratios. Double spiking depends on calibration against the NBS equal-atom standard for an absolute reference, and hence on Catanzaro's results.

For routine isotopic analysis of lead from rocks, double spiking is much more attractive, mainly because of greater sensitivity. However, reduction of double spiked data assumes that all discrimination effects are due to mass dependent fractionation processes, and hence assumes particular numerical values for the relative fractionation of each isotope ratio. Therefore it is appropriate to investigate the discrimination properties of the mass spectrometer used in this study.

Fractionation of lead isotopes through physical-chemical processes has been of long standing interest. The vapour pressure and affinity of isotopes of lead was related to the physical properties as early as 1919 by Lindemann. The difficulties of fractionating lead

The first half of this chapter was presented in Zurich at the Conference on Geochronology of Phanerozoic Orogenic Belts, and has been submitted for publication.
isotopes are recounted by Richards et. al. (1926). Duchylard et. al. (1953) also searched for fractionation, in multistage Grignard reactions which are involved in the preparation of lead tetramethyl for mass spectrometer analysis. Senftle and Bracken (1954) calculated isotopic fractionation data for lead diffusion processes in nature.

Clearly it is desirable to know as much as possible about instrumental discrimination in order to try to better control and correct for it. Quantitative corrections have generally been based on a fractionation process, often considered to derive from physicalchemical mass dependent processes (for example, Doe, 1967; Dodson, 1963). In the following sections data is presented which appears to be sufficiently precise to show that this assumption, though a good approximation, may actually be inadequate for precise double spiking corrections where the fractionation is large.

Theory of Fractionation

Since the effect of greatest importance is the behaviour of the mass spectrometer as a whole, rather than a specific process such as fractionation on the filament, it is useful to consider the theory in its most general form. Dodson (1963) suggests a derivation that is independent of the analytical form of the fractionation law, and assumes only that it is a smooth function of mass. To predict the expected fractionation the following derivation has been used which, though equivalent to Dodson's, is more compact and refers specifically to lead.

Define the isotope ratios

$$x = Pb^{206}/Pb^{204}$$
; $y = Pb^{207}/Pb^{204}$; $z = Pb^{208}/Pb^{204}$

where the chemical symbols represent the intensity of the measured ion beam at each mass number.

Now for a small change in ion beam intensity

$$\frac{\delta x}{x} = \frac{\delta P b^{206}}{P b^{206}} - \frac{\delta P b^{204}}{P b^{204}}$$
, and

similarly for $\frac{\delta y}{y}$ and $\frac{\delta z}{z}$.

$$\frac{\delta y}{\delta x} = \frac{y}{x} \left\{ \frac{\delta P b^{207} / P b^{207} - \delta P b^{204} / P b^{204}}{\delta P b^{206} / P b^{206} - \delta P b^{204} / P b^{204}} \right\}.$$
 (4-1)

Let us assume that the ratios $\delta Pb^{207}/Pb^{207}$, etc., are functions only of mass number in the sense that the ratios vary smoothly with mass for a given chemical element, regardless of the mechanism of the fractionation.

Then $\delta Pb^M / Pb^M = f(M)$, M = mass number,

and

$$\frac{\delta y}{\delta x} = \frac{y}{x} \left\{ \frac{f(207) - f(204)}{f(206) - f(204)} \right\}$$
(4-2)

Similarly

 $\frac{\delta z}{\delta x} = \frac{z}{x} \quad \left\{ \frac{f(208) - f(204)}{f(206) - f(204)} \right\}$

(4-3)

If f(M) is a smooth function of M, then we may expand about f(204), using a Taylor's series. Thus

$$f(207) = f(204) + 3f'(204) + \frac{9}{2}f''(204) \dots,$$

and $f(207) - f(204) \approx 3f'(204).$
Similarly $f(206) - f(204) \approx 2f'(204),$

 $f(208) - f(204) \simeq 4f'(204)$.

Substituting relationship (4) into (2) and (3) gives

$$\delta y / \delta x = 1.5 y / x$$
 (4-5)

(4-4)

$$\delta z / \delta x = 2.0 z / x \qquad (4-6)$$

The error made by dropping the terms in $f^{(M)}$ is very small in common cases. Where $f(M) \propto 1/\sqrt{M}$, for example, ratio $\delta y/\delta x$ should be 1.49 y/x and for $\delta z/\delta x$, should be 1.97 z/x.

This analysis is general enough to include discrimination resulting from vapour pressure, ionization potential and diffusion constant differences, from multiplier discrimination, ionization processes generally and from other purely mass or momentum dependent phenomena. It does not include non linearities of collector or measuring system (which are purely amplitude dependent), geometrical masking of parts of the ion beam (which does not vary <u>smoothly</u> with mass) and pressure scattering (which varies with mass and amplitude).

Lead Oxalate Analyses

In this part of the study the single filament technique employed followed that of Cooper and Richards (1966). The sample

TABLE 4-1

<u>Рь²⁰⁶</u> Рь ²⁰⁴	<u>Pb</u> ²⁰⁷ Pb ²⁰⁴	<u>Р</u> ь ²⁰⁸ Ръ ²⁰⁴
· · · ·	· · · · · · · · · · · · · · · · · · ·	
19.046 ± 0.02	16.000 ± 0.02	39.164 ± 0.04
19.124 ± 0.02	16.094 ± 0.02	39.471 ± 0.04
19.106 ± 0.01	16.071 ± 0.01	39.4 21 ± 0.02
19.205 ± 0.01	16.176 ± 0.01	39.7 21 ± 0.02
18.700 ± 0.04*	15.590 ± 0.07	38.140 ± 0.17
18.690 ± 0.04*	15.580 ± 0.07	38.150 ± 0.15
18.710 ± 0.05*	15.660 ± 0.04	38.190 ± 0.24

New analyses of a single sample with the standard deviation of the mean reported. An asterisk indicates triple-filament analyses.

FIG. 3-1 FRACTIONATED LEAD OXALATE DATA 16.3 <u>Pb</u>207 REPLICATE ANALYSES OF REAGENT LEAD Pb²⁰⁴ ERROR BARS ONE STANDARD DEVIATION 16.2 16.1 SINGLE FILAMENT 16.0 15.9 SLOPE = 1.11 ± 0.03 15.8 15.7 TRIPLE FILAMENT 15.6 15.5∟ 18.4 19.4 18.6 18,8 19.0 19.2 Pb²⁰⁶/Pb²⁰⁴

29a



29ъ



material was reagent lead nitrate, subsequently washed free from alkalis with ethyl alcohol. The lead was converted to lead oxalate in ammonium nitrate solution, and then dried on an outgassed filament of rhenium.

The triple filament technique as described by Catanzaro (1967) was also used. The sample, in the form of lead hydroxide was loaded on rhenium side filaments. Ionization was effected by a platinum center filament at 1450°C "brightness temperature".

The single filament spectra were scanned magnetically, and the output recorded on digital magnetic tape. The computation of the isotope ratios was done entirely by computer using an adaptation of the procedure of Weichert et. al. (1967). In terms of the inter-analysis variations obtained, the ion beam measurement introduced insignificant noise. The triple filament measurements were obtained using the peak-switching technique, described earlier. Minor variations in technique seemed not to affect the ratios obtained.

The analyses are shown in Table 4-1 and plotted in Figures 3-1 and 3-2. The straight lines in the figures are the least squares slopes, calculated after York (1966).

For comparison with theory it is convenient to integrate equations (5) and (6) to give

log y = 1.5 log x + c(4-7) log z = 2.0 log x + c'(4-8)

Least square lines were fitted to the logarithms of the isotopic ratios. From the theory, the slopes on logarithmic plots should be 1.5 and 2.0, respectively. Table 4-2 shows the observed slopes for the data. For the y/x graph the experimental result falls below the theoretical result by six standard deviations and for the z/xgraph, by nine standard deviations. Therefore the mass spectrometer gives fractionation slopes differing from the theory at a confidence level well above 99.5%.

Discussion

Because it is very probable that a fractionating process would be a smooth function of mass, i.e., one for which second order terms are negligible, it is hard to believe that the theory derived can be inadequate. To check further on this point quantitative checks for specific fractionation processes were made.

The characteristics of the fractionation, themselves, suggest a complex process. Specifically:

(1) While it is comparatively easy to obtain constant isotope abundances during the analysis of a single filament loading
(Doe, 1967), it is much more difficult to reproduce analyses loaded separately.

(2) The fractionation process depletes the lighter isotope in preference to the heavier, which suggests that the fractionating step precedes the ionization.

(3) The magnitude of the fractionation, up to 2%, is much larger than would be expected for a single-stage process for such a heavy element as lead.

A fractionating law of the form $M^{-n/2}$ predicts slopes lower than 3/2. The expected characteristics of the residue from a Rayleigh distillation can produce a range of slopes including the observed values. However, the magnitude of the fractionation could not be reconciled with the observed slopes. Studies of solid-solid diffusion and thermal diffusion ended in similar results, although the latter examinations were quite superficial.

In view of the difficulties in understanding the results, it is appropriate to look for an explanation in terms of experimental errors in the measurements. The lead-204 peak is the smallest and therefore the most susceptible to error. Lead-204 measurement uncertainties are of the order of 0.1% and therefore can only make a minor contribution to the change in slope. By itself, lead-204 error would give slopes on logarithmic plots of unity, rather than 1.5 and 2. If the two effects combine to give the observed lines, they would have to be correlated, which seems unlikely.

For pressure scattering, in the simplest case where scattering is symmetrical and a fixed proportion of each peak appears under its immediate neighbours, the slope of the Pb^{208}/Pb^{206} vs Pb^{207}/Pb^{206} (logarithmic) graph should be about $-\frac{1}{4}$. (It is more difficult to predict the slope for the other ratios, because of the greater separation of lead-204 from the rest of the spectrum, and

because of its different abundance.)

For the Pb^{208}/Pb^{206} vs Pb^{207}/Pb^{206} graph, the slope predicted by the theory given is 2.0 for the logarithmic plot. The data presented in this paper gives slopes of 1.42 ± 0.2. The discrepancy cannot therefore be attributed to Pb^{204} measurement error, and is unlikely to be due to pressure scattering.

There remains to question whether this effect is particular to our mass spectrometers, or whether it is a more general phenomenon. Some measurements by J. Blenkinsop shown in Figure 32 (unpublished data) can be used as a check of the validity of the theory for strontium analyses with the same instruments. The predicted slope on log-log plots is 0.50, while the measured slope is 0.49. То provide some additional basis for comparison, we have also used data by Ulrych (unpublished), Doe (set 1, Doe et. al. 1967) and Cooper and Richards (1966). The results of the calculations are found in Table 4-2. It is difficult to reach conclusions about the individual sets, but the weighted mean of all data (1/weight α square of standard deviation) does not change the conclusion. However, it is difficult to evaluate the significance of this result, because it is biased strongly towards data that was conveniently accessible and probably not representative. For example, Doe et. al. (1967) report that newer data (for which numerical isotope ratios were not tabulated) do seem to fit the fractionation model.

It must be concluded from the available data that isotopic fractionation is the dominant source of error in single filament

		•
	$\frac{Pb^{207}}{Pb^{204}}$ vs. $\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{208}}{Pb^{204}} vs. \frac{Pb^{206}}{Pb^{204}}$
Calculated slope for fractionation (log-log plot)	1.5	2.0
This paper	1.29 ± 0.04	1.59 ± 0.11
This paper*	1.32 ± 0.03	1.53 ± 0.05
Ulrych*	1.30 ± 0.04	1.84 ± 0.09
Doe (Set 1)	1.27 ± 0.20	1.73 ±0.27
Cooper and Richards	1.66 ± 0.18	2.14 ± 0.16
Weighted mean of last four values	1.318 ± 0.03	1.642 ± 0.11

	. <u>TA</u>	BLE	4-2 a	
Logarithmic	Slopes	for	Fractionated	Data

These include triple filament as well as single-filament data.

Slopes obtained from a least squares fit on a log-log plot with the standard deviation of the mean reported. All data sets include single filament analyses, an asterisk indicates triple filament analyses also employed. Ulrych's data is taken from a personal communication. For source of remaining data see DOE et. al. (1967) and COOPER and RICHARDS (1966). lead isotope measurement by solid source mass spectrometry. In addition, some analyses show discrimination patterns that differ significantly from the elementary theory. Clearly it is advisable for laboratories using the double spiking technique to question the discrimination patterns of their instruments.

Theory of Double Spiking

A sample is said to be double-spiked when there are added to it two enriched isotopes in a fixed (known) proportion. Two analyses are required to obtain fractionation free data by double spiking. First the lead sample is analysed and data with fractionation of unknown magnitude is obtained. Then an analysis of the sample mixed with the double spike is performed to determine the magnitude of the fractionation; the data obtained in this analysis also includes fractionation. The fractionated data may then be corrected on the basis of an appropriate fractionation law, provided the absolute ratios of the spike are known.

The ratio of the added isotopes in the doubly-spiked sample will be dominated by the known ratio in the double spike that has been added. Any difference between the known and measured ratio of the enriched isotopes in the mixture may be attributed to fractionation. This measure of fractionation may be used to correct the ratio of the two unspiked isotopes in the mixture. These two isotopes in the mixture are dominated by the sample, so that one of the ratios of the sample is now known. Since the magnitude of the fractionation is known all isotope ratios of the unspiked analysis may be corrected for fractionation.

In principle, the spiked mixture has one isotope ratio determined by the double-spike and another independent ratio, by the sample. In practice, all isotopes are influenced by spike and sample compositions. Since, at the beginning of the correction calculation, the true isotopic composition of the sample is unknown, an iterative procedure is used. Convergence is very rapid.

Which isotopes to add is determined by the least abundant isotopes in the sample. Increasing the abundance of the least abundant isotope enables one to measure precise isotopic ratios more easily. Lead-204 and lead-207 are the least abundant isotopes in most lead samples encountered. The choice of lead-207 is to be preferred to lead-206 as any pressure scattering effect on the ratio of the remaining pair of isotopes is likely to produce a smaller error.

Clearly, the ideal double spike contributes only two isotopes so that the remaining isotopes are representative of the sample. However contributions to unspiked isotopes of ten to twenty percent can be easily allowed for without introducing errors in the final sample composition, provided the composition of the spike is exactly known.

The equation on which the fractionation correction was based will now be derived. The symbol Pb^{206} will represent the measured ion beam intensity corrected for errors that assume the

form of the fractionation law, and free of any other error at the 0.1% level. The suffixes m, s, and sp will indicate mix, sample and spike respectively. Ion beam intensities corrected for fractionation, which will be called 'true', are related by the expression:

$$\left(\frac{Pb^{i}}{Pb^{207}}\right)_{m} = \frac{(Pb^{i})sp + (Pb^{i})s}{(Pb^{207})sp + (Pb^{207})s}$$

which may be modified to read:

$$\left(\frac{Pb^{i}}{Pb^{207}}\right)_{m} = \frac{\left(\frac{Pb^{i}}{Pb^{207}}\right)_{s} Q + \left(\frac{Pb^{i}}{Pb^{207}}\right)_{sp}}{1 + 0}$$
(7)

where Q =
$$\frac{(Pb^{207})s}{(Pb^{207})sp}$$

If i = 204 this expression gives the ratio $\left(\frac{Pb^{204}}{Pb^{207}}\right)_{m}$ in terms of the known value of this ratio in the spike, and the true value of $\left(\frac{Pb^{204}}{Pb^{207}}\right)_{s}$, for which an approximate value is known. Q may be estimated by substituting i = 206 or 208 in (7). The value of $\left(\frac{Pb^{204}}{Pb^{207}}\right)_{m}$ is then calculated from these quantities. In this way fractionation in the mixture data is reduced to one fifth of the fractionation in the sample data. (The factor of one fifth is a function of Q and the numerical value is specific to the composition and relative quantities of spike and sample used in this study.) The difference between the observed and calculated values of $\left(\frac{Pb^{204}}{Pb^{207}}\right)_m$ are used as estimates of the fractionation in the mixture. Then by using the relationship for fractionation, e.g. equations (5) and (6), the mixture analysis may be corrected for fractionation.

The sample composition may be expressed in terms of the mixture and spike compositions. The most useful relationship is:

$$\left(\frac{Pb^{208}}{Pb^{206}}\right)_{s} = \frac{Pb_{m}^{208} - Pb_{sp}^{208}}{Pb_{m}^{206} - Pb_{sp}^{206}}$$

which can be written

$$\left(\frac{Pb^{208}}{Pb^{206}}\right)_{s} = \left(\frac{Pb^{208}}{Pb^{206}}\right)_{m} + \left(\frac{1}{R}\right) \left(\frac{Pb^{208}}{Pb^{206}}\right)_{m} - \left(\frac{1}{R}\right) \left(\frac{Pb^{208}}{Pb^{206}}\right)_{sp}$$

where R = $Q\left(\frac{Pb^{206}}{Pb^{204}}\right)_{s} \left(\frac{Pb^{204}}{Pb^{206}}\right)_{sp} \left(\frac{Pb^{208}}{Pb^{206}}\right)_{m}$ obtained from (7) had fractionation of about one fifth of the sample analysis. Since the second and third terms are small, are approximately known, and almost cancel, the value of $\left(\frac{Pb^{208}}{Pb^{206}}\right)_{s}$ calculated has the same percentage of fractionation as $\left(\frac{Pb^{208}}{Pb^{206}}\right)_{s}$. Fractionation effects are thus reduced by a factor of five Pb^{208} m in one iteration.

In the computer reduction seven iterations were employed although convergence was usually achieved after three. From the equations it is easily shown that the uncorrected fractionation after a single iteration is directly proportional to the value of Q. This is a property of the sample and spike compositions in this particular

study.

Two enriched isotopes of lead were purchased for the double spiking, the one 89% lead-204 the other 92% lead-207. These were weighed out and dissolved to make stock solutions of 30 and 300 ppm of lead by weight. A mixture of these two, the 7/4 spike, was prepared with a Pb^{207}/Pb^{204} ratio of ten. As attempts by Compston and Oversby (1969) and Cooper, Reynolds and Richards (1969) to determine the composition gravimetrically failed, this method was not employed.

Calibration was performed by analysing the spike alone and a mixture containing the 7/4 spike and NBS equal atom standard. The analyses were repeated to improve reliability. The value of the standard reported by Catanzaro (1968), and the fractionated values of mixture and spike analyses were employed in the iterative procedure described above. The data before correction is presented in Table 4-3. Corrected values and values obtained by the triple filament technique are presented in Table 4-4. The results obtained by double spiking differ from the mean of the triple-filament values by about 0.1%. This agreement is considered quite satisfactory for the purposes of this study. Table 4-5 shows the values of doublespiked and sample composition after each iteration.

For the values listed in Table 4-4 the theoretical fractionation slopes were employed. When the observed slopes, presented earlier in this chapter, were used in the fractionation correction the agreement was definitely poorer. The calibration therefore

TABLE	4-2	Ъ
-		

Logarithmic Fractionation Slopes for Rhenium and Tantalum

	$\frac{Pb^{207}}{Pb^{204}}$ vs $\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{208}}{Pb^{204}}$ vs $\frac{Pb^{206}}{Pb^{204}}$
Calculated slope for	c	
fractionation (log-	log	
plot)	1.5	2.0
Doe, Tantalum	$1.47 \pm 0.10^*$	2.10 ± 0.20
Doe, Rhenium	1.35 ± 0.09	2.39 ± 0.30

one standard deviation of the mean quoted

favours the theoretical slope, i.e. the tantalum analyses of the two standards are fractionated according to the theoretical slope. The theoretical value was used throughout the study.

Doe recently reduced his unpublished single filament data. The logarithmic slopes (personal communications) are given in Table 4-2b. The results provided independent evidence which indicates that rhenium filaments produce discrimination that does not fit well the theoretical fractionation slope. Tantalum filaments do however produce slopes corresponding to the fractionation law. The use of the theoretical slope for tantalum is thus justified by independent evidence.

TABLE 4-3

FRACIIONATED DATA FUR SPIKE CALIBR	SRATION
------------------------------------	---------

	<u>Рь²⁰⁶</u> Рь ²⁰⁴	Pb ²⁰⁷ Pb ²⁰⁴	<u>рь²⁰⁸</u> Рь ²⁰⁴	
	•			
7/4 Spike	0.2866	10.095	0.6343	
11	0.2854	10.076	0.6348	
7/4 Spike and Equal Atom	3.1490	10.624	3.4780	
u	3.1950	10.626	3.5260	
7/4 Spike and		•		
Broken Hill #1	1.6885	10.585	3.7840	
Equal Atom	36.959	17.305	37.242	
Broken Hill #1	16.038	15.478	35.998	
H	16.040	15.452	35.865	•

All data obtained by single filament sulphide technique, one standard deviation of mean less than 0.1%.

TA	BLE	4-4
-		

SPIKE, EQUAL ATOM AND BROKEN HILL #1 COMPOSITION

· ·	<u>Pb</u> ²⁰⁶	Pb ²⁰⁷	Pb ²⁰⁸	
·	Pb ²⁰⁴	Pb ²⁰⁴	Pb ²⁰⁴	
*7/4 Spike	0.2841	10.013	0.6296	
*Equal Atom	36.702	17.125	36.725	
*Broken Hill #1	15.995	15.386	35.662	
**Broken Hill #1	16 002	15 38/	35 609	•
"	16.002	15.364	35.009	
11	16.015	15.403	35.750	
**Equal Atom	· · ·	•		
Triple Filament	36.738	17.160	36.745	
		•		

Compositions from Table 4-2 corrected for fractionation

Triple filament analyses this study, one standard deviation of mean less than 0.1%.

Catanzaro's triple filament value used in 7/4 spike calibration calculation.

BROKEN HILL #1			BROKEN HI	BROKEN HILL #1 AND 7/4 SPIKE		
$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{207}}{Pb^{204}}$	$\frac{Pb^{208}}{Db^{204}}$	$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{207}}{Db^{204}}$	$\frac{Pb^{208}}{Pb^{204}}$	
г у 	ru	r U	r U		г <i>о</i>	
16.040	15.452	35.865	1.688	10.585	3.784	
15.999	15.393	35.682	1.679	10.494	3.741	
15.995	15.387	35.664	1.678	10.490	3.739	
15.995	15.386	35.662	1.678	10.490	3.739	
15.995	15.386	35.662	1.678	10.490	3.739	

TABLE 4-5

VALUES AFTER EACH ITERATION FOR FRACTIONATION CORRECTION

Each line of data represents one complete iteration. Three further iterations produce no further change.

CHAPTER V

SAMPLE LOCATIONS AND DESCRIPTIONS

Vogt-Hobbs Area, Ontario

This area is astride the Grenville Front near Lake Timagami. Rocks from this vicinity are particularly suitable for a study of the behaviour of uranium-lead systems because of the possibility of observing the effect of the increasing metamorphism towards the south. The Grenville Front is defined here principally by the transition from a metamorphic grade of the greenschist facies in the north to the amphibolite facies in the south. Grant was able to trace rock units across this boundary and locate equivalents on the basis of lithology. It is the leucogranite to the north and some of its equivalents to the south that were sampled.

For this first study, rocks expected to contain large quantities of uranium and lead are to be preferred. Examination of the literature shows that acid rocks generally contain more lead and uranium than more basic rocks. A more specific investigation by Doe (1967) indicates that lead content depends on feldspar type and abundance. Potassium feldspars are found to contain from 20 to 60 ppm typically, while coexisting sodium-calcium feldspars contain about one third the concentrations. For this reason the more accessible acidic rocks were collected. A regional and a simplified geologic map (Figure 5-1) show the general location of the region and serve to identify the sample locations. The samples were all collected from outcrops close to the logging road shown in Grant's more detailed map (Grant, 1964). As he personally supervised the collection of the Ontario samples studied in this Thesis, it was possible to sample the same sites as were used for his Rb-Sr study. Portions of the following sample descriptions are taken from Grant, 1964.

Gl was taken from the south side of a leucrocratic albite stock two miles in diameter called the Vogt granite. This pink, medium-grained, albite granite contains less than 5% green biotite. The potassium feldspar, microcline microperthite, may form phenocrysts. Accessory minerals include muscovite, chlorite, epidote, sphene, apatite, zircon and opaque minerals. This is the only sample from north of the Grenville Front.

A similar granite forms a belt about four miles long and a half mile wide centered on the south end of Sinton Lake and astride the Grenville Front. Sample G2 is representative of the pink leucocratic albite granite phase of this body while G3 represents the quartz monzonite to granodiorite phase. CSCH was taken from a vein of pegmatite rich in potassium feldspar, and included small traces of the surrounding quartz-biotite-plagioclase schist. The sample from the vein was collected because of its potentially high lead content. The surrounding rock is described as migmatite and occupies much of this region. The remaining sample G5 was also thought to be derived from the same original granite, shows cataclasis and is also a quartz monzonite.



FIGURE 5-1 REGIONAL AND SIMPLIFIED GEOLOGIC MAPS VOGT HOBBS AREA

Rice Lake-Beresford Lake Area, Manitoba

This area has been of particular interest to geologists since 1911 on account of the gold discovery at that time. A map showing the location and general geology of the area is presented in Figure 5-2 (based on Stockwell and taken from Turek, 1968). The region consists of a potassic granite in the north and a gneissic belt in the south. The Rice Lake group lies between these two and has been intruded by basic dykes and sills which have in turn been intruded by quartz diorite plutons.

Samples analysed from this area were from the northern potassic granite and the sample locations are marked on Figure 5-2. Each of the hand specimens was stained with sodium cobaltinitrate to determine the potassium feldspar content. The rocks were then classified according to their quartz and potassium feldspar content.

Samples 29 and 47 may be approximately classified as quartz diorite while 78, 207 and 214 are granodiorites. All of the Manitoba samples are distinctly more gneissic in structure than the Ontario samples, and show considerable inhomogeniety. There are also indications of replacement of potassium feldspars or potassium feldspars replacing other feldspars. On the average the Manitoba samples contain approximately 10 to 15% potassium feldspar; this is slightly less than one half of the potassium feldspar content of the Ontario samples.



FIGURE 5-2 REGIONAL AND SIMPLIFIED GEOLOGIC

MAP TAKEN FROM TUREK 1968

	Pb ²⁰⁶	Pb ²⁰⁷	Pb ²⁰⁸
	Pb ²⁰⁴	Pb ²⁰⁴	Pb ²⁰⁴
	.		······
29	18.766	15.656	36.211
47	15.266	14.934	34.863
78	16.169	15.158	35.412
207	16.697	15.225	38.806
214	16.933	15.402	37.464
G1	23.399	16.564	40.831
G2	27.411	17.137	39.863
G3	19.834	15.938	39.413
CSCH	21.655	16.343	36.826
G5	14.832	15.128	35.192

TABLE 5-1

UNCORRECTED SINGLE FILAMENT ROCK LEAD ANALYSES

New analyses of rock lead samples, standard deviation of mean less than 0.1%. The analyses were carried out with the single filament sulphide technique. This is the data before the double spiking corrections.

	Pb ²⁰⁶	Pb ²⁰⁷	Pb ²⁰⁸	
	Pb ²⁰⁴	Pb ²⁰⁴	Pb ²⁰⁴	
29	3.0700	10.907	5.983	
47	1.6880	10.522	3.846	
78	1.9146	10.604	4.192	
207	2.3002	10.711	5.324	. ·
214	1.9847	10.652	4.390	
G1	1.9810	10.586	3.597	
G2	2.9840	10.773	4.542	
G3	2.2996	10.675	4,624	
CSCH	3.5970	11.048	6.247	
G5	1.6469	10.542	3.863	

TABLE 5-2

UNCORRECTED DOUBLE SPIKED SAMPLE ANALYSES

New analyses of rock lead samples mixed with double-spike, standard deviation of the mean less than 0.1%. Analyses carried out by single filament sulphide technique and not corrected for fractionation.

TAB	LE	5-3

ANALYSES OF ROCK LEAD SAMPLES CORRECTED FOR FRACTIONATION

	Pb ²⁰⁶	Pb ²⁰⁷	Pb ²⁰⁸	
	Pb ²⁰⁴	РЪ ²⁰⁴	Pb ²⁰⁴	
	· · · · · · · · · · · · · · · · · · ·		· · · · · · · · · · · · · · · · · · ·	
29	18.651	15.512	35.768	
47	15.247	14.906	34.776	
78	16.040	14.977	34.848	
207	16.634	15.140	38.516	•
214	16.793	15.211	36.844	
G1	23.343	16.504	40.635	
G2	27.345	17.075	39.670	
G3	19.723	15.804	38.972	
CSCH	21.579	16.257	36.569	
G5	14.746	14.996	34.783	

The above data were obtained by correcting the data of Table 4-1 for fractionation with data from Table 4-2. All Manitoba samples have entirely numerical labels.

New Rock Lead Data

All isotopic composition analyses for rock lead data were obtained by using the single filament sulphide technique. The raw sample and double-spiked sample analyses are reported in Tables 5-1 and 5-2. The rock lead compositions were corrected for fractionation by assuming a fractionation law of the form;

 $\frac{dy}{dx}$ = 1.5 $\frac{y}{x}$ and $\frac{dz}{dx}$ = 2.0 $\frac{z}{x}$

The standard deviation of the mean, for the raw data, was less than 0.1% in all cases and typically 0.05%. Errors in the three sample ratios, the three double spiked ratios and the three spike ratios, all contribute towards the errors in the fractionationcorrected data. A numerical experiment was performed to determine the effect of errors in the sample, spike and mixture ratios. Perturbations of + 0.1% were applied to each of the nine ratios in turn, the other eight ratios being free of this perturbation. All nine ratios were chosen to incorporate fractionation of 0.13% per mass unit. A second study was also performed in which the perturbation was + 1.0% and the fractionation 1% per mass unit. The percentage change in a sample ratio divided by the percentage perturbation is called the error magnification for that ratio. The error magnifications were found to be the same for the two cases studied and are given in Table 5-4.

TABLE 5-4

ERROR PROPAGATION FOR BROKEN HILL #1

ERROR MAGNIFICATIONS FOR [†] PERTURBATION	<u>Рь²⁰⁶</u> Рь ²⁰⁴	_{РЬ} ²⁰⁷ РЬ ²⁰⁴	<u>рь²⁰⁸ Рь²⁰⁴</u>
*SAMPLE RATIO RAISED:			
206/204	+ 2.1	+ 1.7	+ 2.2
207/204	+ 0.1	+ 1.2	+ 0.3
208/204	- 1.1	- 1.7	- 1.2
DOUBLE-SPIKED RATIO RAISED:		• .	
206/204	- 1.3	- 2.0	- 2.7
207/204	- 0.9	- 1.5	- 1.9
208/204	+ 1.3	+ 2.0	+ 2.6
SPIKE RATIO RAISED:		:	
206/204	+ 0.2	+ 0.3	+ 0.3
207/204	+ 0.8	+ 1.3	+ 1.5
208/204	0.2	- 0.3	- 0.4
· · · · · · · · · · · · · · · · · · ·			

[†] The error magnifications are tabulated under the reduced sample ratios to which they refer.

All ratios incorporated fractionation and only one ratio was raised at a time. The fact that the error magnification was not found to be a function of the magnitude of the fractionation, indicates that large fractionation corrections can probably be made as precisely as small corrections. However in this study the use of tantalum filaments was preferred because of the small magnitude of the fractionation and the reduced likelihood of large errors from corrections for fractionation.

The source of the errors in the reduced data can be divided into two parts. The error introduced by the spike ratios determines the absolute calibration of the final data and is a constant value for all of the analyses. This error arises when the spike is calibrated. The agreement between the double spiked measurements and the triple filament values of the standards (see Table 4-2) indicates that error from this source is probably less than 0.1%.

The second portion of the error varies from analysis to analysis and determines the reproducibility. A numerical estimate of the standard deviation for the reduced data may be obtained by considering any reduced isotope ratio, R_i , to be a function of the six measured isotope ratios R_1 , R_2 , ... R_6 , employed in the fractionation correction:

 $R_{i} = f(R_{1}, \ldots, R_{6}).$

The standard deviation, σ , of such a compound quantity is a function of the standard deviations, σ_1 , ... σ_6 of the six ratios:

$$\sigma^{2} = \left(\frac{\partial f}{\partial R_{1}}\right)^{2} \sigma_{1}^{2} + \dots + \left(\frac{\partial f}{\partial R_{6}}\right)^{2} \sigma_{6}^{2}$$
(5-1)

If the quantities $\left(\frac{\partial f}{\partial R_{i}}\right)$ are approximated by the error magnifications listed in Table 5-4 then for a standard deviation σ_{i} of 0.05% for each ratio the standard deviation, σ , for the reduced data will be 0.22%.

Clearly this is an oversimplication as the quantities $\left(\frac{\partial f}{\partial R_{i}}\right)$ were identified with the value of this quantity when all but one ratio is correct. It is instructive to consider a special case to show how errors in the six ratios may actually interact. The most common form of error in lead isotope ratio determinations results from measurement errors for the lead-204 peak. If such an error occurs then all ratios to lead-204 experience the same percentage change. If the mixture analysis incorporates lead-204 error, then a partial cancellation of errors could be anticipated (see Table 5-4). This effect was verified by numerical tests. A similar situation arises for the sample analysis. Thus if error of measurement of the lead-204 peak is the only source of error in the sample and double-spiked analysis then equation 5-1 is effectively reduced to two terms. In this case, the estimated standard deviation for the final data, from an initial standard deviation for the raw ratios of 0.05%, is 0.1%. Numerical reductions, incorporating lead-204 error, gave errors in the reduced sample ratios in agreement with the predicted errors.

There are two checks of the reproducibility of the data. The first of these results from the measurement of the Pb^{208}/Pb^{206} in the mixture, which should relate simply to the same ratio in the sample. During the fractionation correction the difference between

the Pb²⁰⁸/Pb²⁰⁶ ratio in the corrected mixture ratios and the uncorrected sample ratios is used indirectly as a measure of If the Pb^{208}/Pb^{206} ratio were not reproducible then fractionation. there would result a much larger range and average magnitude of fractionation. The average fractionation of 0.215% per mass unit is in close agreement with fractionations of 0.13% and 0.15% per mass unit obtained by Doe (1967) and Zartman (1969) for lead sulphide loadings on tantalum (the standards analysed by these two workers have been analysed on triple filament by Catanzaro, 1969). The magnitude of the average fractionation in this study is higher than the reported fractionation for the standards. However it was found during this study that the analyses of rock leads generally showed greater fractionation than the analyses of standards. This is probably a function of the purity of the samples.

The second reproducibility check arose because concentrations were measured separately by using radiogenic lead, rather than combining the concentration determination with the double spiking correction. Two concentrations were determined, one is based on the sample Pb^{208}/Pb^{206} ratio and the other on the sample Pb^{207}/Pb^{206} ratio. The concentrations calculated from the two ratios agreed to within the precision of the measurements. This implies that the sample Pb^{208}/Pb^{207} ratios were reproducible to about 0.2% or better.

The fact that the double spiked analysis was not used to determine lead concentrations also left one unused equation in the fractionation correction. This equation was used to obtain a second

estimate of the proportion of double spike and sample in the mixture. The two estimates were averaged in the reduction and were equal at the end of the reduction. Clearly this increases the reliability of the correction.

Compston and Oversby (1969) claim that fractionation may be corrected by double-spiking to give a sample composition whose 95% confidence limits are \pm 0.1%. In that study, one sample analysis was corrected for fractionation by using replicate double spiked analyses. Their uncertainty therefore only reflects errors arising from the double spiked analysis, whereas sample analyses tend to have a larger standard deviation. Consequently the expected 95% confidence limits of the reduced data for pairs of sample and double-spiked analyses, each contributing errors, would be about double this value, or \pm 0.2%.

In conclusion the technique used in this thesis is believed to be as precise as that of Compston and Oversby (1969), but studies of propagation of errors yield a more pessimistic view of the precision available from data of this quality.* For interpretations of this data a reproducibility of \pm 0.3% (95% confidence level) will be assumed. In addition the uncertainty of the composition of the double spike adds a possible bias of \pm 0.1% which is not significant for the interpretations.

Note that Compston and Oversby's Pb^{206}/Pb^{204} ratios and Pb^{208}/Pb^{204} ratios each differ from the triple filament values by 0.2%.

Uranium and Lead Concentration Determinations

Lead concentrations were calculated from the ratios obtained from samples spiked with radiogenic lead; uranium-235 was added to determine uranium concentrations. The details of the calculation procedure are given in the Appendix. Optimum spiking curves are also found there. It is quite easy to perform precise mass spectrometric analyses for the lead concentration determinations, as only the abundant isotopes, lead-206, lead-207 and lead-208, need be measured. Because sensitivity is not a serious problem it was possible to do these analyses by triple filament.

Before discussing the precision of the concentration measurements a comment will be made on the precision required. The quantities of greatest importance that are derived from the concentrations are the ratios U^{235}/Pb^{204} and U^{238}/Pb^{204} . The ratio U^{238}/Pb^{204} varies from 0.4 to 20 whereas the lead isotope ratio Pb^{207}/Pb^{204} varies from 15 to 17. Consequently if the relative errors in the concentrations are ten times the relative errors in the isotope ratios, then the relative errors in the variable portions of these quantities are about the same. In view of the precision and accuracy of the ratio determinations, concentrations measurements correct to 1% were attempted.

Reproducibility of lead concentrations can be estimated from Table 2-1. The total variation is less than 0.5% for the conditions employed in this study. Concentrations of lead and uranium for the two suites analysed in this study are listed in Table 5-5.
TABLE 5-5

URANIUM AND	LEAD	CONCENTRATIONS
-------------	------	----------------

	LEAD	URANIUM	
29	10.49	1.992	
47	7.79	0.469	
78	17.19	1.456	
	•	1.457	
207	10.74	1.050	
214	15.12	1.456	
		1.460	
Gl	29.95	11.78	
G2	37.12	2.118	
G3	21.337	5.626	
СЅСН	23.89	6.467	
G5	38.88	0.225	
GSP-1		2.207	
	· .	2.206	

Lead and uranium concentrations are total lead and total uranium in parts per million by weight. One standard deviation is 0.25% for a concentration determination. Uranium concentration determinations show equally good reproducibility as can be seen for the three duplicate analyses. The uranium concentration determined for GSP-1 is about 8% less than the preferred value given by Doe et. al. (1967). However as his values vary from 2.2 to 3.2 ppm an 8% discrepancy is of doubtful significance. Clearly the present reproducibility is significantly better than Doe et. al. (1967).

Uranium isotopic ratio determinations are subject to fractionation errors even when carried out by a triple filament method. Unlike lead, this fractionation is reported to lead to an enrichment in the lighter isotope (NBS Technical Note, 1966). A correction was made in the concentration calculation corresponding to an enrichment of 0.4% in the lighter isotope. Although this correction is only an estimate on the basis of reported fractionation this correction should reduce the magnitude of any such error to negligible size. Regulations did not permit the purchase of the large quantities of uranium supplied for standards suitable for measuring fractionation. For the purposes of computation the 95% confidence limits for a concentration determination are ± 0.5%. This includes the error magnification and spike calibration.

CHAPTER VI

INTERPRETATION OF ROCK LEAD DATA

In order to complete the first objective of this research the data will be interpreted in the light of the lead-lead and lead-uranium models of Russell and Farquhar (1960), Ulrych and Reynolds (1966), Ulrych (1967) and Russell et. al. (1968). It is then possible, by using other published data, to compare the results for the uranium-lead and rubidium-strontium systems for the two localities investigated. Finally, it is possible to look at the interaction of geologic events and uranium-lead systems.

Lead-Lead Interpretations

The rock samples analysed are equivalent to common leads mineralized at the present. For common leads it is found most instructive to plot Pb^{207}/Pb^{204} vs Pb^{206}/Pb^{204} as is done for the Manitoba and Ontario data in Figures 6-1 and 6-2. Russell and Farquhar (1956, 1960) have shown that, for samples whose radiogenic component was produced between t_1 and t_2 , and which contain the same common lead component, a linear relationship results on the Pb^{207}/Pb^{204} vs Pb^{206}/Pb^{204} plot. The slope, R, on such a plot is given by:

$$R = \frac{1}{\alpha} \left\{ \frac{\exp (\lambda't_1) - \exp (\lambda't_2)}{\exp (\lambda t_1) - \exp (\lambda t_2)} \right\}$$
(6-1)

(All new symbols in this chapter are defined in Table 6-1.)

FIG. 6-I ISOTOPIC ABUNDANCES RICE LAKE -BERESFORD LAKE AREA



FIG. 6-2 ISOTOPIC ABUNDANCES VOGT-HOBBS AREA



For leads mineralized at the present, $t_2 = 0$. The points shown were fitted with least squares straight lines as described by York (1966). Even though rather pessimistic figures for the 95% confidence limits of the data points are shown in Figures 6-1 and 6-2, the Ontario data still appear to differ significantly from a straight line. Although the number of points is very small, a numerical estimate of the goodness of fit can be made. Assuming 95% confidence limits of 0.3% for the data, the chi-square test indicates that there is a 25% probability of exceeding the value of chi-squared for the Manitoba suite and a probability of 1% of exceeding the value of chi-squared for the Ontario suite. This signifies that the Manitoba suite approximates the Russell-Farquhar model. The Ontario data cannot reasonably be considered to be even a poor statistical sample from a population that fits the Russell-Farquhar model. It will be shown later, however, that the data does admit interpretation.

For the Manitoba potassic granites the inferred age, based on the observed slope, is 2750 ± 150 my, where the error limits are one standard deviation (as elsewhere in this thesis unless otherwise stated). The standard deviation quoted is based on York's estimate and represents the fit of the data points to the line, and not the standard deviation of the slope based on the precision of the data points (Williamson, 1968). As York's estimate is larger than Williamson's this is a more pessimistic (though in fact more realistic) estimate of the standard deviation of the age. This procedure is used throughout the remainder of this chapter.

$\begin{array}{r} \text{At present} \\ \textbf{t} = \textbf{0} \end{array}$	At time t	At time t _o
a	x	a _o
b	У	ь _о
C	Z	с _о
μ	$\mu e^{\lambda t}$	$\mu e^{\lambda t}$ o
μ/α	μ/α ^{eλ't}	μe ^{λ't} o
К	Ke ^{λ'} t	Ke ^{λ"t} o
Value in 1	$0^{-9}(years)^{-1}$	Parent Atom
0.15	37**	U ²³⁸
0.97	22	u ²³⁵
0.04	99	Th ²³²
	a b c μ μ/α K Value in 1 0.15 0.97	a x b y c z μ $\mu e^{\lambda t}$ μ/α $\mu/\alpha^{e\lambda't}$ K K $e^{\lambda't}$ Value in 10 ⁻⁹ (years) ⁻¹ 0.1537** 0.9722

TABLE 6-1

Symbols and Constants Used in Age Determination

The slope for the Ontario suite gives an age of 2,580 \pm 80 my. The smaller standard deviation in the slope of the line is not an indication that the Ontario data fits the assumptions of the model better than the Manitoba data; as has already been mentioned the converse is true. The smaller standard deviation in the Ontario data is a consequence of a larger range of isotope ratios in the Ontario suite.

More can be said about the lead-lead plot when an initial composition for the common lead is available for these suites. This matter will be discussed further when the common lead component has been obtained from the uranium-lead interpretations.

Uranium-Lead Interpretations

Ulrych and Reynolds (1966) have shown that whole rock uranium-lead data may be interpreted in a manner analogous to rubidium-strontium whole rock interpretations. For rocks starting from a common initial Pb^{206}/Pb^{204} ratio, and for which the rock has remained closed to the transfer of lead and uranium, the present Pb^{206}/Pb^{204} ratio is given by the expression:

$$\left(\frac{Pb^{206}}{Pb^{204}} \right)_{p} = \left(\frac{Pb^{206}}{Pb^{204}} \right)_{it} + \left(\frac{U^{238}}{Pb^{204}} \right)_{p} (e^{\lambda + -1}), \quad (6-2)$$

with a similar expression for Pb^{207}/Pb^{204} . If a suite of rocks satisfies the assumptions then a linear relationship results with a slope, R, which depends only on t; t can be obtained from:

 $t = \frac{1}{\lambda} \ln (1 + R).$ (6-3)

When the Manitoba data, Figures 6-3 and 6-4, are interpreted in this manner the ages from the lead-207 - uranium-235-lead-206 - uranium-238 plots are 2,626 \pm 200 my and 2,238 \pm 205 my respectively. As the standard deviation of the age based on the fit of the points to the line is greater than the standard deviation based on the precision of the data, the model is only considered to be an approximation to the history of the samples.

Similar plots of the Ontario data show that the data as a whole cannot be approximated by the single stage model. The slopes, ignoring G2, correspond to ages of 2,230 \pm 350 my and 1,874 \pm 400 my respectively for the lead-207 and lead-206 plots.

If these samples are treated as uranium minerals then a Pb^{207}/Pb^{206} age may also be determined. This age is not independent of the two lead uranium ages just determined. However to make such an age determination it is necessary to correct for common lead. This has already been done in the Russell-Farquhar model by assuming the common lead-component to be identical for all samples.

Another method of correcting for the common lead is employed in the modified concordia plot. The samples are assumed to have a two stage history of which the first stage is represented by the common lead present and the second stage by radiogenic additions from uranium now found in the rock. It is assumed in the model that the Pb^{207}/Pb^{206} ratio of the common lead incorporated in each rock is the same for all samples. Ulrych (1967) (see also Russell et. al. 1967) have shown that if the quantities:









$$\frac{Pb^{206*}}{U^{238}} = \left(\frac{Pb^{206}}{Pb^{204}} - a_{0}\right) \left(\frac{Pb^{204}}{U^{238}}\right)_{0}$$
$$\frac{Pb^{207*}}{U^{235}} = \left(\frac{Pb^{207}}{Pb^{204}} - b_{0}\right) \left(\frac{Pb^{204}}{U^{235}}\right)_{0},$$

are plotted as absissa and ordinate respectively, a linear relation results, if the assumptions of the model are justified for the suite of rocks. The Ontario and Manitoba data was plotted in this manner and least squares straight lines fitted (Figures 6-7 and 6-8). The time value for the upper intercept, of the linear relation with the concordia, is interpreted as the age of the earth and the lower intercept time value as the time of commencement of the last stage. The scatter of the data about these lines indicates that the lead uranium system does not satisfy the two stage model very well. The inferred commencement of the last stage for Manitoba and Ontario suites are 2430 ± 576 my ago and 1640 ± 65 my ago respectively.

A summary of the inferred ages is given in Table 6-2. The data from Manitoba shows the pattern lead-lead age > uranium 235lead 207 age > uranium 238-lead 206 age. This fits the pattern observed for loss of radiogenic lead. The lead-lead age is known to be least affected. (Lead Isotopes in Geology, 1960).

The Manitoba data did show a larger scatter on the Pb^{206}/Pb^{204} versus Pb^{207}/Pb^{204} plot than would be expected for the precision of the data. This could be the consequence of differing compositions

73.

TABLE 6-2

Interpretative Ages

MODEL	ONTARIO	MANITOBA		
Russell-Farquhar	2580 ± 80 my	2750 ± 150 my		
Modified Concordia	1640 ± 65 my	2430 ± 576 my		
Uranium-Lead				
U ²³⁵ -Pb ²⁰⁷	2230 ± 350 my	2630 ± 200 my		
U ²³⁸ -Pb ²⁰⁶	$1874 \pm 400 \text{ my}$	$2240 \pm 200 \text{ my}$		

Time limits correspond to one standard deviation for fit of data.





for the common components incorporated at the beginning of the last stage. Differing initial components for the last stage are best explained as the result of a three stage history. If this is in fact the case, then the modified concordia plot is probably not suitable for representing these samples.

The Manitoba data is then consistent with a three stage history. It remains to clarify that history. In order to discover more about the second stage it is desirable to obtain better estimates of the initial composition for the last stage. The intercepts on the uranium-235 - lead-207 and uranium-238-lead-206 plots are included on Figure 6-9. These however are poor estimates because the lead-uranium slopes have been reduced by lead remobilization. If instead intercepts are calculated on the basis of the lead-lead age and the centroid of the data on the uraniumlead plot lower intercepts result. These are also shown in Figure 6-9.

The nearest ore lead data is also plotted on 6-9 from Manitouwadge (Ostic et. al., 1967). Clearly the Manitouwadge data, including the Geco vein, fit the anomalous lead line very well. (The analyses of Ostic were corrected for sample-line fractionation). The preferred model for these samples is depicted in Figure 6-10. The time of formation of the second stage is greater than 3000 my and a best estimate based on an anomalous lead line passing through ordinary lead 2500 my old and the Manitouwadge like composition is 3500 my. The value of 2500 my is the youngest event known to have



affected the northern granite (Turek et. al., 1968). If the common lead incorporated in the Manitoba suite is to be produced as recently as possible, then the formation of the crust in this region and the production of the common lead component may have taken place at 3000 my. This is the minimum age for this event. These interpretations imply that the Manitouwadge ore leads were derived from material with a crustal history. This interpretation is in contrast to the arguments of Tilton and Steiger (1965) who employ Manitouwadge and related leads, to calculate an age for the earth of 4700 my. In their argument, they assume that Manitouwadge is a 2700 my old primary lead that has not been contaminated by crustal material.

The slope of the anomalous lead line, including the Rice Lake-Beresford Lake samples, the Manitouwadge sample and the Geco vein sample, is not significantly different from the value without the ore lead sample. If the last stage in the history of the ore lead samples is genetically as well as isotopically related to the rock lead samples, then the Geco sample was emplaced quite recently in the Fox Creek fault. It is possible that the Geco lead has been extracted recently from the rock lead adjacent to the fault. This is a closer approximation to the first argument put forward by Ostic (1963). The older age determined for the composite anomalous lead line, t_1 , is then 2760 ± 40 my, for $t_2 = 0$. There is abundant evidence for an event at this time in this area (e.g. Turek and Peterman, 1968; Goldich et. al., 1962).

TAB	LE	6-	3

Observed and Calculated μ Values For Two Stage Model

· · ·	μ ₂ μ ₁	Value from U ²³⁸ -Pb ²⁰⁶	μ_1 Value from U^{235} -Pb ²⁰⁷
MANITOBA			
29	11.51	6.94	7.647
47	3.39	7.399	7.574
78	4.83	7.615	7.507
207	5.95	6.245	7.669
214	5.75	8.205	7.813
۲		· .	
ONTARIO			
G1	27.386	7.923	7.990
G2	4.149	21.653	9.786
G3	18.366	6.591	7.421
CSCH	17.437	9.334	8.153
G5	0.3675	6.820	6.891
		· · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·

 μ_1 and μ_2 are the values of U^{238}/Pb^{204} for the first and second stages respectively extrapolated to the present.

Sec. 1

Emplacement of the Geco lead at an earlier time would imply that the Geco lead, though isotopically related, is not genetically related to the rock leads. This situation, which seems improbable isotopically, does not alter the argument put forward for the Rice Lake-Beresford Lake region.

The initial lead isotope composition of the Ontario suite, for the last stage, was also calculated on the basis of the uranium-235-lead-207 and uranium-238-lead-206 plots, in the manner used for Manitoba. It is questionable whether this procedure is valid for the Ontario suite because of inadequate sampling for rocks that have experienced lead remobilization. From the Figure (6-9), and in view of the low uranium content, G5 may be considered a close approximation to the common lead incorporated at the beginning of the last stage.

The fact that the initial lead isotope ratios fall below the growth curve can best be explained by a crustal history for the common lead component prior to the commencement of the last stage. The greater part of this initial lead was probably derived prior to 2300 my ago although the Grenville event may have caused small recent additions. Kanesewich and Farquhar (1965) have produced evidence from lead isotopic analyses of ores emplaced in nearby rocks of the Cobalt-Noranda area, that shows that a crust existed there prior to 3200 my ago. The ore deposits they examined formed a chord between 2300 \pm 150 my ago and 3250 \pm 150 my ago. Kanesewich and Farquhar were of the opinion that the ore leads entered the

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PREFERRED INTERPRETATION MANITOBA SAMPLES

PRESENT

GRENVILLE EVENT?

GECO E MPLACED? LEAD REMOBILIZED?

PRESENT LEAD-URANIUM SYSTEM ISOLATED

FIRST CRUSTAL MATERIAL FORMED IN THIS REGION - 900-1100 my?

~ 2700 my

 $- \sim 3400 \text{ my}$

SUPERIOR EVENT

AGE OF EARTH EARTH AND METEORITES

SAME ISOTOPIC COMPOSITION

4500 4 50

 $-4580 \pm 50 \text{ my}$

- 0 my

older country rock through fissures. This older country rock in the southernmost region, in the vicinity of Cobalt, is known as the Bruce and Cobalt series. Grant (1964) identifies the metamorphic rocks north of the Grenville Front and in the area studied as belonging to the Bruce and Cobalt series. An unconformity separates the overlying Bruce and Cobalt series from the older underlying granite north of the front, studied here. It may be concluded that the common lead incorporated in the Timagami samples was derived from crustal material existing prior to 2300 my ago.

Individual samples analysed in this study were probably partially derived from rocks with a quite similar common lead component 3500 to 3200 my ago, and have been subjected to an event at 2300 my ago which effected homogenization of the lead isotopic compositions that had developed up to this time. It is not possible to distinguish a spread in initial lead isotopic composition through incomplete homogenization at 2300 my ago from the effect of a partial redistribution of the common lead component in these rocks at the time of the Grenville event. That such a spread exists is confirmed by the deviations on the lead-lead plot for the Ontario data. Evidence supporting lead remobilization is discussed later in this chapter.

FIGURE 6-11

PREFERRED INTERPRETATION ONTARIO SAMPLES

PRESENT

0 my

GRENVILLE EVENT

LEAD REMOBILIZED - 900-1100 my Rb-Sr

SI	JP	ER	TOR	ĽΕ	VEI	NT	

PRESENT LEAD-URANIUM SYSTEM ISOLATED - ~ 2600 my 2

2350 Rb-Sr 2580 Pb-Pb 2700 U-Pb Zircons

FIRST CRUSTAL MATERIAL FORMED IN THIS REGION

~ 3300 my

AGE OF THE EARTH

EARTH AND METEORITES SAME LEAD ISOTOPIC COMPOSITION

4580 ± 50 my

Comparison of Uranium-Lead and Rubidium-Strontium Systems.

Turek and Peterman (1968) have carried out a very thorough rubidium-strontium study of the Rice Lake-Beresford Lake area. Their investigation included an age determination for the northern potassic granite studied in this thesis. They obtained 2550 ± 40 my (λ = 1.39 x 10⁻¹¹ yr⁻¹) for this body and an initial ratio for S_r^{87}/Sr^{86} of 0.7031 ± 0.0021. The initial ratio is consistent with a previous history in a system of moderate Rb^{87}/Sr^{86} ratio. That the potassic granite is reworked material is supported by its strongly gneissic structure and the presence of numerous xenoliths. An investigation by D. Culbert and J. Blenkinsop has shown that a large body of crustal material may exist for several hundred million years in a low rubidium to strontium environment. Their analyses were carried out on the Coast Range Batholith, British Columbia. (Culbert and Blenkinsop, to be published). The rubidium-strontium results for the Timagami region are consistent with the model presented earlier, and have indeed been used to construct the model.

J.A. Grant investigated whole rock and mineral rubidiumstrontium systems for the Grenville Front near Lake Timagami, Ontario. He determined an average primary age, from the whole rocks, of 2350 \pm 150 my with initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ of 0.703. The isochron plot showed some deviations from linearity, possibly as a result of open system behaviour. Biotite-whole rock joins yielded secondary ages of 920 my for G5, 1270 my for G2, and 1360 my for G1. Apatite-

whole rock joins generally gave greater values than the biotitewhole rock joins. These mineral ages are thought to be indicative of the Grenville event and approach the accepted Grenville age as one progresses south, i.e. in the direction of increasing metamorphism.

Clearly the lead-lead determination of 2580 ± 80 my is consistent with Grant's age from the rubidium-strontium system. It has been shown clearly that some event, probably the Grenville metamorphism, has disturbed the uranium-lead whole rock system. This was manifested by the deviations for the rubidium-strontium whole rock system from a straight line isochron plot. Furthermore the initial ratio obtained from the strontium data does not preclude an early period in an environment of low to moderate Rb^{87}/Sn^{86} ratio. It is also possible that this ratio is set by strontium additions at the same time as the uranium-lead system is formed for the last stage.

Lead Mobilization in the Timagami Samples

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Steiger and Wasserburg (1969) have analysed zircons from sample G5. Their data supports a primary age of 2689 ± 12 my. The zircons are discordant, in general, and it is thought that lead loss may have been effected by the Grenville metamorphism. That lead was lost by some of the zircons, is well established. It was probably this lead which migrated during the Grenville metamorphism and is responsible for the lead migration inferred

from the age determinations discussed earlier in this chapter. It is proposed here that the lead is redistributed on a scale dependent on the disturbing force and conditions prevailing.

If some of the radiogenic lead from the southernmost rocks has migrated north during the metamorphism, then some of the samples should have a higher lead/uranium ratio than is consistent with their age; G2 is just such a sample.

There is some support for such a suggestion. Firstly, it is well known that the majority of the uranium in a rock is found in accessory minerals and interstitially. The concentrations of uranium in the zircons, and the percentage of zircon in G5 (Steiger and Wasserburg, 1969), indicates that a significant fraction (~ 30%) of the uranium for G5 is found in the recovered zircons. A substantial fraction of the radiogenic lead produced in these zircons is lost. Interstitial lead will be remobilized much more readily. Lead in some accessory minerals, such as sphenes, will be more resistant to alteration; there is no evidence that such minerals exist in important quantities. The potassium feldspars in the area have incorporated excess radiogenic lead into their structure subsequent to their formation. On balance the assumption of remobilization of lead in this area is amply justified.

It is the scale rather than the existence of migration of radiogenic lead that may be questioned. Evidence for the migration of lead over significant distances has been presented before (Slawson, et. al., 1962). It is possible that the lead in this thesis

87 (a)

study area may have migrated over a distance of several miles.

Open system behaviour of a uranium-lead system may result from remobilization of lead and/or uranium. Without evidence in addition to the lead isotopic ratios and the lead and uranium concentrations it is not possible to say which of the lead and uranium have been mobile.

Mobility of the uranium in the Ontario suite, at the present, would provide a simple explanation for the open system behaviour as exhibited by the uranium-lead plot. However it is more likely that the daughter of a radioactive decay is subject to mobility, i.e. the lead, because it will reside in a crystal latice with which it is not compatible. It is for this reason and the reasons given in the preceding paragraphs that remobilization of lead was preferred to remobilization of uranium. **Conclusions**

The first objective of the thesis was to provide data of sufficient quality to further the understanding of lead isotope interpretations. A standard deviation of 0.15% was obtained for the lead isotope ratios and 0.25% for the lead and uranium concentrations. To achieve this precision double-spiking was employed to correct for fractionation that accompanies single filament lead isotope analyses. A study of the discrimination exhibited by the mass spectrometer was made. It was found that theoretical fractionation laws could not completely explain the discrimination pattern found for rhenium filaments. It was also found, when double-spiking was employed to correct for fractionation on tantalum filaments, that the theoretical fractionation laws give better agreement than the discrimination pattern observed for rhenium. Independent data obtained by Doc, on rhenium and tantalum filaments, has confirmed that the discrimination pattern for rhenium filaments does not fit the theoretical fractionation law while the fractionation law is quite adequate for the tantalum filaments.

The double spiking technique was employed by P. Reynolds to obtain interpretable patterns of lead isotopes. His analyses of rocks from the vicinity of Broken Hill, Australia, were the first truly interpretable analyses of lead isotopes from whole rocks.

In this thesis the lead isotope ratios for samples from the Vogt-Hobbs area near Lake Timagami revealed variations from a simple two stage model that could not be accounted for by experimental error. Comparison of the uranium-lead ages with lead-lead ages, for two suites studied, revealed open system behaviour in the last stage, which was shown to be a consequence of lead migration. The experimental uncertainties in these uranium-lead and lead-lead ages were sufficiently small that the two could be clearly distinguished. The migration of lead was found to be more pronounced for the Timagami samples than for the Rice Lake-Beresford Lake samples, which is to be expected from the known and severe metamorphic event in the Timagami region. Open system behaviour has been suggested by P. Reynolds in another precise study of rock leads (Seminar held at U.B.C., 1969).

The history of the Manitoba samples, as determined primarily from the rock lead analyses and supported by other dating schemes, may be summarized as follows. The lead now observed experienced a minimum of three stages during the past 4580 my. The first stage, from 4580 my ago to approximately 3500 my ago, was spent in a primary system, with respect to uranium and lead, having a present U^{238}/Pb^{204} ratio of 8.8 to 8.9. The first stage of the sample's history is the most remote and therefore the least accurately established. Between 3500 my and 2600 my ago a second major event accompanied by metamorphism and intrusion produced the

common lead component incorporated in the potassic granites. This 2600 my old event probably lasted several hundred million years. Since that time the granites have remained relatively undisturbed. There is some evidence in adjacent regions (Ostic, 1963) that suggests that some lead remobilization may have been associated with the Grenville event 900 my ago, however further investigation is required before the possible effect of this event can be checked in the Rice Lake-Beresford Lake area.

The Vogt-Hobbs area near Timagami in Ontario experienced a very similar history to the Rice Lake-Beresford Lake area in Manitoba. In fact it may be said with some justification that these two regions, for events that have been investigated, show only a different severity of the same events. The lead now observed was incorporated into rocks in that vicinity more than 3250 my ago. After another 1000 my this crustal material underwent a major event, approximately 2500 my ago, which may have spanned several hundred million years. The last major event in Grenville times produced the rocks as they exist today. It is very probable that the granitic rocks were not much changed from their form and composition at the time of the 2500 my event. These rocks are indeed far more acidic than the Manitoba suite and probably represent a different environment 2500 my ago or earlier. The severity of the Grenville event was such as to partially redistribute the lead, and also the rubidium and strontium, so that the 2500 my old event is somewhat masked.

The study of the two suites indicates that the associated crustal systems have a lower average present U^{238}/Pb^{204} ratio than the source of single stage ore deposits (Ostic et. al., 1967; Stacey et. al., 1969; Cooper et. al., 1969). This has been suggested as a widespread phenomena by Reynolds (1967).

The history presented for the Manitoba samples suggests that Manitouwadge is not representative of a single stage lead. This would contradict the assumption on which Tilton and Steiger (1965) calculated an age of 4750 my for the earth. The two independent ages for the earth calculated on the basis of the suites studied here were 4700 and 4540 my. These are based on essentially the same, inadequate assumptions, and are believed to be similarly in error. It is considered that the age recently calculated for the earth by Cooper et. al. (1969) is the best estimate available.

Although this study has added much new information to the understanding of lead isotopes in rocks, there is still considerable scope for further work. This study, like those preceding it, shows that there is much information to be obtained from studying lead isotope ratios, but that the benefit can be obtained only by doing many analyses of the highest quality. Over 100 isotopic analyses were required to obtain the data presented in this thesis.

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APPENDIX

Chemical Procedures

Air-borne Contamination: To reduce air-borne contamination a positive pressure of filtered air was maintained in the laboratory and whenever possible samples being processed were covered.

Apparatus: Pyrex glassware and Teflon receptacles were allowed to stand for twelve hours in hot detergent solution then rinsed. The apparatus was then stored in warm 15% nitric acid for at least twelve hours and remained there till required. All receptacles were rinsed three times with distilled, deionized water before use.

Distilled Water: Distilled water from a Barnstead still was deionized and redistilled in a borosilicate still. The lead content was 0.0001 ppm by weight. (Lead concentrations were determined by isotope dilution in all cases.)

Hydrochloric Acid: Reagent grade diluted to 20% concentration by weight, and distilled twice. Lead content was approximately 0.0001 ppm by weight.

Nitric Acid: Distilled twice at 70% concentration by weight. Lead content 0.0002 ppm by weight.

Ammonium Hydroxide: Where possible ammonia gas was used. Ammonium hydroxide of specific gravity 0.9 was prepared by bubbling ammonia gas into ice cold water.

Perchloric Acid: Perchloric acid was available commercially, double vacuum distilled in vycor and shipped in vycor. The lead content was measured to be less than 0.05 ppm.

Hydrofluoric Acid: Baker analysed reagent was used, the lead content was less than 0.05 ppm lead.

Column Preparation:

- Stir 50 gm of Dowex 1 x 8 resin with 100 ml of 1.5N hydrochloric acid and decant to remove fines; repeat twice.
- Pour slurry into columns to make one column 28 cm long by 1.1 cm inside diameter and one 10 cm long by 0.8 cm inside diameter.
- Settle columns with a long glass rod and adjust flow rate to 0.8 and 0.5 ml per minute respectively.
- 4. Wash columns with five column volumes of distilled water.
- 5. Convert to chloride form by passing through three column volumes of 1.5N hydrochloric acid.
- For nitrate-form columns use three column volumes of 7N nitric acid.

Lead Purification:

- Centrifuge lead concentrate dissolved in 1.5N hydrochloric acid; discard residue and add sample to column.
- 2. Wash column with 60 ml of 1.5N hydrochloric acid.
- Elute lead with 60 ml of distilled water. Discard first 10 ml from column and save remainder.

- Evaporate eluate to dryness and redissolve in 15 ml of 1.5N
 hydrochloric acid.
- Repeat steps one to four using one quarter the volumes of reagents and the small column.

Nitrate Resin Column for Uranium

- Add uranium dissolved in 80 ml 7N nitric acid to the large, nitrate-form column.
- 2. Wash column with three 20 ml portions of 7N nitric acid.
- 3. To elute the uranium use 10 ml portions of water. Discard all eluate till the orange colour is a few centimeters from the bottom of the column. Add additional water till the resin is quite orange, collecting the eluate. Add 6N hydrochloric acid until the resin is yellow again, continue to collect the eluate.
- Repeat the procedure with a small column using one quarter the volume of reagents.

Uranium Filament Heating Pattern

- 1. Raise the filament temperature to a brightness temperature of 2060°C. After five minutes locate and focus the rhenium-187 signal at which time the ion current will be 0.6 x 10^{-11} a. The rhenium-187 ion current remains at this value at this temperature.
- 2. Set the sample filament current at 1.5 a and re-focus the rhenium-187 signal. Turn up the side filament current until the uranium signal is 0.1 x 10^{-11} a.

- After 10 minutes total time from the start, all filaments are turned off.
- 4. When the pressure in the analyser tube is below 2 x 10⁻⁷ raise the center filament to 2060°C and maintain at this value throughout the analysis. Then set the side filament current at 1.5 a and re-focus on rhenium-187.
- 5. After another five minutes adjust the sample filament current to give a uranium signal of 0.6 x 10^{-11} a.
- 6. Leave five minutes, then raise the uranium signal to 1.2 x 10^{-11} a.
- 7. Finally, after a further five minutes, increase the uranium signal to 1.8 x 10^{-11} a. When the ion current is sufficiently stable commence taking data.

Concentration Determinations

Lead-206 (SRM 983) was employed for stable isotope dilution determinations of lead concentrations. The concentration of lead-206 in the spike solution was calibrated against "Specpure" lead solutions by mass spectrometric analysis of pipetted mixtures of these solutions. For these analyses the triple filament method of Catanzaro was employed. Pipettes used were calibrated by weighing the volumes delivered and applying evaporation corrections. Concentrations obtained gravimetrically agreed with the mass spectrometric determinations to within 0.2%. For uranium concentration determinations uranium enriched to 99.4% uranium-235 was used. Solutions were calibrated against "Specpure" uranium.

As the theory of isotope dilution is quite similar for both concentration determinations, only one case need be discussed. The explanation is facilitated by using a specific case so the discussion is based on the Pb^{206}/Pb^{208} ratio. Let $P = \frac{Pb^{206}}{Pb^{208}}$, C_n^i represent the fraction of the ith isotope, in atoms per atom, in the sample, and C_{sp}^i the concentration of the ith isotope in the spike.

Then in a mixture of spike and sample:

$$P = \left\{ \frac{C_n^{206}N + C_{sp}^{206}S}{C_n^{208}N + C_{sp}^{208}S} \right\}$$

Where N and S represent the number of moles of total lead contributed to the mixture by the sample and the spike respectively.

This may be written:

$$N = S \qquad \left\{ \begin{array}{l} \frac{PC_{sp}^{208} - C_{sp}^{206}}{C_{n}^{206} - PC_{n}^{208}} \end{array} \right\}$$

By differentiating and rearranging an expression for the fractional error in N resulting from the error in P may be obtained.

$$\frac{\partial N}{N} \frac{\partial P}{P} = P \left\{ \frac{C_{sp}^{208}}{PC_{sp}^{208} - C_{sp}^{206}} - \frac{C_{n}^{208}}{PC_{n}^{208} - C_{n}^{206}} \right\}$$

This ratio of relative errors was calculated for $C_{sp}^{206} = 0.92$, $C_{sp}^{208} = 0.013$, $C_n^{206} = 0.24$, and $C_n^{208} = 0.54$. Figure A-1 shows the optimum spiking curve. By using values of P between one and twenty, the error magnification through this effect was kept below 1.5.

FIG. A-I OPTIMUM SPIKING FOR LEAD CONCENTRATION

