

The University of British Columbia

FACULTY OF GRADUATE STUDIES

PROGRAMME OF THE

FINAL ORAL EXAMINATION

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

of

PETER HERBERT REYNOLDS

B.Sc., The University of Toronto, 1963

IN ROOM 301, HENNINGS BUILDING (PHYSICS)

MONDAY, OCTOBER 30, 1967, AT 2:00 P.M.

COMMITTEE IN CHARGE

Chairman: R.W. Wellwood

R.D. Russell A.J. Sinclair

J.A. Jacobs R. Nodwell

M.W. Ovenden W.F. Slawson

External Examiner: D. York

Department of Physics

University of Toronto

Research Supervisor: R.D. Russell

A LEAD ISOTOPE STUDY OF ORES AND ADJACENT ROCKS

ABSTRACT

The purpose of this thesis is to investigate the isotopic relationships between lead in orebodies and lead in adjacent igneous rocks. Past studies of rocks and ores have been largely uncorrelated, and, in addition, much of the published data is unreliable because of large experimental uncertainties and inadequate interlaboratory calibrations. These data have, however, suggested that most rock-leads originated in a system with a distinctly lower U/Pb ratio than the one associated with certain ore-leads.

Samples were obtained for the present study from four selected areas. Both rock-leads and ore-leads were analyzed from Balmat, N.Y. and from Nelson, B.C. Rock-leads from Broken Hill, Australia and from West-Central New Mexico were also studied. The isotopic abundances of ore-leads from these latter two areas have already been determined in this laboratory. Identical experimental techniques were used throughout for both rocks and ores, and a precision of better than 0.10 per cent (one standard deviation) in the measurement of isotope ratios with respect to lead-204 was achieved.

A systematic difference in isotopic composition was observed between certain of the above leads. In particular, rock-leads from Balmat and from the Nelson batholith, ore-leads from deposits associated with this batholith, and ore-leads from New Mexico (analyzed by J. Blenkinsop) were apparently derived from a primary system characterized by a present-day value of the U^{238}/Pb^{204} ratio (the μ -value) equal to 8.7 to 8.85. The significance of the isotopic composition of rock-lead from New Mexico was not revealed by the one sample studied. On the other hand, ore-

lead from one of the stratiform deposits at Balmat was apparently derived from a primary system with a μ -value of 9.0. This value agrees with the one obtained in this laboratory by R.G. Ostic for stratiform deposits selected by R.L. Stanton in accordance with geological criteria. It is also consistent with A.J. Sinclair's interpretation of the isotopic abundances of lead from the Sullivan mine and from deposits located in the Kootenay arc north and south of the Nelson batholith. In addition, both rock-leads and ore-leads from Broken Hill appear to reflect the existence of this higher μ system.

The present study has therefore provided, for the first time, definitive evidence relative to the existence of two distinct distributions of primary μ -values. Several geophysical models are discussed in an attempt to reconcile this difference, and explain in general terms the evolution of lead isotope ratios in the earth.

Also, for the first time, analyses of Nelson rocks and ores have provided clear evidence of a genetic relationship between ore deposits and granitic rocks. At the same time, lead isotope abundance patterns in plutonic rocks of batholithic dimensions were investigated.

GRADUATE STUDIES

Field of Study: Geophysics	
Advanced Geophysics	J.A. Jacobs
Radioactive and Isotopic Processes in Geophysics	R.D. Russell
Modern Aspects of Geophysics	R.D. Russell
Applied Geophysics	G.P. Erickson
Principles of Earth Science	M.A. Chinnery
Seismology	W.F. Slawson
	R.D. Russell
Related Studies:	
Fluid Dynamics	R.W. Stewart
Waves	J.C. Savage
Electromagnetic Theory	G.B. Walker

PUBLICATIONS

- Ostic, R.G., Russell, R.D. and P.H. Reynolds. A new calculation for the age of the earth from abundances of lead isotopes. *Nature*, 199, 1150 (1963)
- Russell, R.D. and P.H. Reynolds. The primary lead growth curve and the age of the earth. (Abstract) *Trans. Amer. Geophys. Union*, 45, 111 (1964)
- Russell, R.D. and P.H. Reynolds. The age of the earth Problems in Geochemistry, Acad. Sci., U.S.S.R., Vinogradov Jubilee Volume, 37 (1965)
- Ulrych, T.J. and P.H. Reynolds. Whole-rock and mineral leads from the Llano Uplift, Texas. *J. Geophys. Res.*, 71, 3089 (1966)
- Russell, R.D., Slawson, W.F., Ulrych, T.J. and P.H. Reynolds. Further applications of concordia plots to rock lead isotope abundances. Submitted for publication.

A LEAD ISOTOPE STUDY
OF ORES AND ADJACENT ROCKS

by

PETER HERBERT REYNOLDS

B.Sc., The University of Toronto, 1963

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in the Department

of

GEOPHYSICS

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

September, 1967

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and Study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of

Geophysics

The University of British Columbia
Vancouver 8, Canada

Date

Nov. 8, 1967

ABSTRACT

The purpose of this thesis is to investigate the isotopic relationships between lead in orebodies and lead in adjacent igneous rocks. Past studies of rocks and ores have been largely uncorrelated, and, in addition, much of the published data is unreliable because of large experimental uncertainties and inadequate interlaboratory calibrations. These data have, however, suggested that most rock-leads originated in a system with a distinctly lower U/Pb ratio than the one associated with certain ore-leads.

Samples were obtained for the present study from four selected areas. Both rock-leads and ore-leads were analyzed from Balmat, N.Y. and from Nelson, B.C. Rock-leads from Broken Hill, Australia and from West-Central New Mexico were also studied. The isotopic abundances of ore-leads from these latter two areas have already been determined in this laboratory. Identical experimental techniques were used throughout for both rocks and ores, and a precision of better than 0.10 per cent (one standard deviation) in the measurement of isotope ratios with respect to lead-204 was achieved.

A systematic difference in isotopic composition was observed between certain of the above leads. In particular, rock-leads from Balmat and from the Nelson batholith, ore-leads from deposits associated with this batholith, and ore-leads from New Mexico (analyzed by J. Blenkinsop) were apparently derived from a primary system characterized by a present-day value of the

U^{238}/Pb^{204} ratio (the μ -value) equal to 8.7 to 8.8₅. The significance of the isotopic composition of rock-lead from New Mexico was not revealed by the one sample studied. On the other hand, ore-lead from one of the stratiform deposits at Balmat was apparently derived from a primary system with a μ -value of 9.0. This value agrees with the one obtained in this laboratory by R.G. Ostic for stratiform deposits selected by R.L. Stanton in accordance with geological criteria. It is also consistent with A.J. Sinclair's interpretation of the isotopic abundances of lead from the Sullivan mine and from deposits located in the Kootenay arc north and south of the Nelson batholith. In addition, both rock-leads and ore-leads from Broken Hill appear to reflect the existence of this higher μ system.

The present study has therefore provided, for the first time, definitive evidence relative to the existence of two distinct distributions of primary μ -values. Several geophysical models are discussed in an attempt to reconcile this difference, and explain in general terms the evolution of lead isotope ratios in the earth.

Also, for the first time, analyses of Nelson rocks and ores have provided clear evidence of a genetic relationship between ore deposits and granitic rocks. At the same time, lead isotope abundance patterns in plutonic rocks of batholithic dimensions were investigated.

TABLE OF CONTENTS

ABSTRACT	ii
LIST OF FIGURES	v
LIST OF TABLES	vi
ACKNOWLEDGEMENTS	vii
CHAPTER 1 INTRODUCTION	1
Objectives of the Present Investigation	1
Scope of the Present Investigation	6
CHAPTER 2 EXPERIMENTAL TECHNIQUES	8
Extraction of Lead from Potassium Feldspars	8
Preparation of Tetramethyllead	13
Gas Chromatographic Purification of Tetramethyllead	17
Contamination	21
Mass Spectrometry	24
Sample Size, Precision, and Reproducibility	26
CHAPTER 3 ANALYSES AND INTERPRETATIONS	36
Choice of Samples	36
Nelson, British Columbia	36
Balmat, New York	38
Broken Hill, New South Wales, Australia	40
West-Central New Mexico	42
Balmat, N.Y.	43
Nelson, B.C.	53
West-Central New Mexico	65
Broken Hill, Australia	70
CHAPTER 4 CONCLUSIONS	80
BIBLIOGRAPHY	89

LIST OF FIGURES

FIGURE 2-1	SCHEMATIC DIAGRAM OF MICRO-LEAD APPARATUS	14
FIGURE 2-2	TRIMETHYLLEAD SPECTRUM FROM APPROXIMATELY 500 MICROGRAMS OF TETRAMETHYLLEAD	30
FIGURE 3-1	ISOTOPIC COMPOSITION OF BALMAT LEADS	45
FIGURE 3-2	ISOTOPIC COMPOSITION OF KOOTENAY ARC AND NELSON LEADS	55
FIGURE 3-3	APPROXIMATE SAMPLE LOCATIONS, NELSON AREA, BRITISH COLUMBIA	57
FIGURE 3-4	ISOTOPIC ABUNDANCES OF NEW MEXICO LEADS	68
FIGURE 3-5	SURFACE GEOLOGICAL PLAN BROKEN HILL MINE AREA AND APPROXIMATE SAMPLE LOCATIONS	73
FIGURE 3-6	ISOTOPIC ABUNDANCES OF BROKEN HILL LEADS	74
FIGURE 3-7	ISOTOPIC COMPOSITION OF LEAD FROM THE MUNDI MUNDI GRANITE	77

LIST OF TABLES

TABLE 2-1	REPRODUCIBILITY OF ANALYSES ON THE BASIS OF LOOP CLOSURE ERRORS	33
TABLE 2-2	REPLICATE ANALYSES OF BALMAT 500 GALENA	34
TABLE 3-1	ISOTOPIC COMPOSITION OF BALMAT LEADS	44
TABLE 3-2	LEAD ISOTOPE RATIOS, URANIUM AND LEAD CONCENTRATIONS OF BALMAT ROCKS AND MINERALS	51
TABLE 3-3	ISOTOPIC COMPOSITION OF NELSON LEADS	56
TABLE 3-4	ISOTOPIC COMPOSITION OF LEADS FROM THE KOOTENAY ARC AND FROM SULLIVAN MINE	58
TABLE 3-5	ISOTOPIC COMPOSITION OF NEW MEXICO LEADS	66
TABLE 3-6	OBSERVED ISOTOPIC COMPOSITION OF BROKEN HILL LEADS	71
TABLE 4-1	APPARENT URANIUM/LEAD RATIOS FOR LEADS FROM CERTAIN STRATIFORM DEPOSITS	83

ACKNOWLEDGEMENTS

The writer thanks Dr. R.D. Russell for his help in formulating the present thesis, and also for his guidance during the course of the entire investigation. Technical achievements finally attained would not have been possible without the advice and encouragement at various times of Dr. W.F. Slawson, Dr. T.J. Ulrych, Dr. A.J. Sinclair and Mr. J. Blenkinsop. The latter shared with the writer the joys and sorrows of mass spectrometry during the past two years, and, in addition, helped Dr. Russell successfully reduce invaluable isotopic data stored on paper and magnetic tapes.

The writer also wishes to acknowledge the many helpful discussions with Dr. J.R. Richards of the Australian National University. Discussions began during the latter's visit to this university in 1965 and were continued in letters exchanged after his return to Canberra.

The writer is grateful to all who helped supply samples for this study; individual acknowledgements are included in the thesis proper. Mineral separation facilities were provided by Dr. W.H. White, Dr. R.E. Delavault, and Dr. Sinclair of the Department of Geology. The general co-operation of this department throughout the investigation was appreciated. Technical assistance in the art of glass-blowing was provided in many emergencies by Mr. J. Lees and by Mr. E. Williams; Miss S. Newman kindly prepared three of the Nelson ore-leads for the writer; Mr. J.M. Ozard critically reviewed a draft of the present

thesis which was subsequently typed by Miss J. Kalmakoff.

The present research was supported by National Research Council of Canada grants to R.D. Russell, W.F. Slawson and A.J. Sinclair, and to a lesser extent, by a National Science Foundation grant to W.F. Slawson. Personal financial assistance for three years in the form of a National Research Council Studentship was also appreciated.

CHAPTER 1
INTRODUCTION

Objectives of the Present Investigation

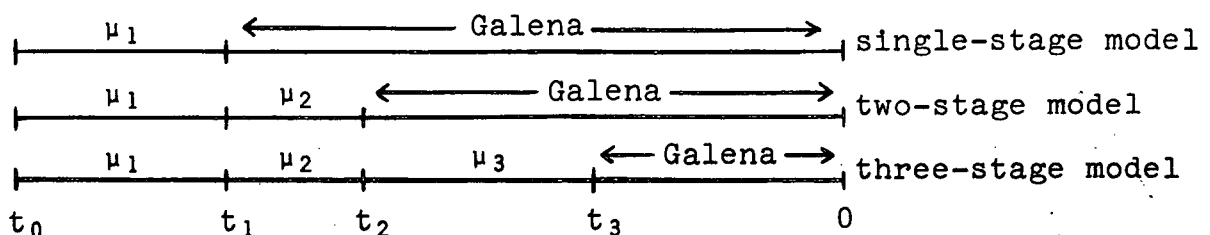
The study of the variations of lead isotope abundances in natural minerals has long been of interest to geophysicists and geochemists in their attempts to understand the chemistry and history of the outer parts of the earth. Lead occurs in trace quantities in practically all types of rocks and, in addition, is found in massive concentrations in the form of the ore mineral galena (PbS).

During the past seven years geophysicists at this university have been studying isotopic variations in ore-leads, and have postulated two basic models. It appears that some ore-leads have developed from a common initial time (the 'age' of the earth) in a single system closed with respect to the transfer of uranium, thorium and lead and that they have subsequently had relatively little isotopic alteration in crustal rocks. Leads from most of the stratiform* deposits originally selected by Stanton and studied here by Ostic and Russell (Stanton and Russell, 1959; Ostic, et al, 1967) seem to belong in this classification. The measured lead isotope ratios, Pb^{206}/Pb^{204} , Pb^{207}/Pb^{204} , and Pb^{208}/Pb^{204} for these samples have been used to calculate the present-day uranium/lead and

* In this thesis, for brevity, the term 'stratiform' will always refer to this particular group of deposits. It is recognized that this is a narrower definition than is normally accepted.

thorium/uranium ratios of this primary lead system, $\mu \equiv U^{238}/Pb^{204} = 8.99 \pm 0.05$, $Th/U = 3.89 \pm 0.04$ (Ostic, et al, 1967)**. Apparently this source material is remarkably uniform on a world-wide scale with respect to these three elements, and it has been suggested that the leads from these stratiform deposits come from a deep (probably subcrustal) source and are transported to the crust by volcanic action.

The second basic model used to explain ore-lead variations postulates a single-stage history in the primary system as described above, and subsequent histories in crustal systems. Hence radiogenic lead produced by the decay of uranium and thorium in crustal rocks is added to the primary lead and an anomalous lead suite is produced. Kanasewich (1962) and others have shown that in many instances the leads have apparently seen only one or two crustal systems and hence straight line relationships are often observed when Pb^{207}/Pb^{204} is plotted as a function of Pb^{206}/Pb^{204} . The slopes of these lines can be interpreted to give age and geochemical information.



** In this thesis, the primeval ratios, a_0 and b_0 , and the age of the earth, t_0 , are assigned the values 9.56, 10.42, 4.55×10^9 yr respectively (Murthy and Patterson, 1962).

Hence, ore-leads are either single-stage primary leads or multi-stage anomalous leads and the latter can often be recognized by doing a sufficient number of precise isotopic analyses from a given district.

Investigators in other laboratories have been studying rock-leads and, in general, have observed rather large variations in isotopic composition. These variations can be interpreted to mean that rock-leads in the earth's crust are products of heterogeneous systems open with respect to lead, uranium and thorium. Geological activity in the crust for over two-thirds of the earth's lifetime may account for these open systems.

On the other hand, observed isotopic variations may be due to experimental errors and to calibration uncertainties. Presently available rock-lead data have been obtained from a number of different mass spectrometers that have not been rigorously calibrated in order to remove possible interlaboratory differences. In addition, samples have been analyzed by solid-source techniques on various filament materials (usually rhenium or tantalum), and it has been shown (Doe, et al, 1965) that the isotopic composition of the lead depends to some extent on the type of filament material used. Much of the earlier data are also in question because of uncertain adjustments for mass discrimination effects in electron multipliers. Although present solid-source techniques are capable of good isotopic analyses of only a few micrograms of

lead, Doe, et al (1967) have pointed out that mass spectrometer fractionation is always present. The effect of this fractionation cannot be quantitatively removed from the isotope ratios and may not remain constant from one run to the next. Hence the reproducibility of the data is poor. A recent modification of the solid-source technique by Catanzaro (1967) seems to have solved the fractionation problem. However, the new method has not as yet been fully tested and no new rock-lead data have been produced.

The solid-source data do, however, suggest that the rock-leads originated in a system that has a distinctly lower U/Pb ratio than the one associated with the stratiform ores ($\mu = 9.0$). For example, Cooper and Richards (1966) have analyzed the lead extracted from 25 modern volcanic extrusives. Single-stage μ -values calculated for these samples range between 8.47 and 8.91 and the mean value is 8.70. The average μ -value calculated from Zartman's (1965a) analyses of 12 microclines from igneous and metaigneous rocks from the Llano Uplift, Texas, is 8.55 (8.47 - 8.65).

The low lead content of most rocks (~ 15 ppm for igneous rocks) has been one of the factors that has so far prevented the study of rock-leads in this laboratory. However, it is of particular interest at this time to obtain more reliable rock-lead data in order to clarify this apparent discrepancy. If the above difference is not due to experimental uncertainties or to lack of interlaboratory calibration

(cf. Richards, 1967), but is a real phenomenon, then a fundamentally different source material is required to account for the isotopic abundances of trace leads in rocks. In other words, the lead in these stratiform ores is not genetically related to lead in rocks.

The present research originated in the belief that it was desirable to make a study of the relationships between ore-leads and their associated rocks. There are only two published examples of correlated studies of rocks and ores. In the earlier of these, Murthy and Patterson (1961) found that the lead in the ore deposits of Butte, Montana was isotopically similar to that in potassium feldspars of the Boulder batholith, the host rock of the ore. However, the lead in one quartz sample from an associated igneous intrusion was different and the authors therefore concluded that the feldspar leads had been contaminated by ore-leads and that there was not a parental relationship between the hydrothermal ores and the host rock.

The second investigation was carried out by Doe (1962) on ore deposits and rocks near Balmat, New York. The study of Balmat leads was continued by the present writer (see Chapter 3). ..

The purpose of this thesis, then, is to report new precise analyses that help clarify rock-lead relationships and also relationships between ores and adjacent rocks.

Scope of the Present Investigation

The present study is restricted to gas-source mass spectrometer analyses of ore-leads and of leads extracted from potassium feldspars.

The ore mineral galena contains 'common lead', lead which has not been in contact with its parent elements uranium and thorium since the time of crystallization, and hence has not changed its isotopic composition since that time. In order to make a comparative rock-lead study, one must know the isotopic composition of the lead that existed in the rock at the time of its last crystallization - the common lead component. The mineral potassium feldspar (KAlSi_3O_8) has the highest lead/uranium ratio of any of the common rock-forming minerals (typically ~ 100 in granitic rocks), and hence uranium decay in this mineral will be least effective in altering the common lead isotope ratios. It is believed (cf. Sorrell, 1962) that the lead (ionic radius 1.20) substitutes for the potassium (radius 1.33) in the crystal lattice forming in effect a lead feldspar ($\text{PbAl}_2\text{Si}_2\text{O}_8$). In order to obtain the exact common lead component it is necessary to calculate the amount of radiogenic lead produced by the in situ decay of uranium and thorium in the feldspars from the time of crystallization to the present. To do this one needs to know the lead, uranium and thorium concentrations as well as the present-day isotopic abundances. This correction is usually small for potassium feldspars and can be safely neglected for rocks less than

500 m.y. old. Even in the case of the 1000 m.y. old igneous rocks studied by Zartman (1965a), the correction applied to the Pb^{206}/Pb^{204} ratio ranged from only 0.25 to 0.50 per cent; corrections to the Pb^{207}/Pb^{204} ratio were less than 0.10 per cent.

In addition to having a low uranium/lead ratio, potassium feldspars also contain more lead (~ 35 ppm) than any of the other common minerals. Hence it is possible to obtain from about 15 grams of sample the 500 micrograms of lead that are required for a satisfactory gas-source mass spectrometer analysis. In addition, the time spent on mineral separations is kept to a minimum.

Lead isotope abundances were determined by means of gas-source mass spectrometry of tetramethyllead to ensure a consistency with ore-lead data obtained in this laboratory. Gas-source measurements here have been refined to the extent that the techniques are well understood and capable of producing highly precise data (see, for example, Ostic, 1963, for a detailed discussion). Whittles (1964) has claimed that mass spectrometer fractionation, the major uncertainty in the solid-source work, is not a problem with gas sources providing one maintains a sample line pressure sufficient to produce viscous flow through the constriction (or 'leak') leading into the source region of the spectrometer. A sample line pressure of at least 10 mm is recommended for the present leak.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

Extraction of Lead from Potassium Feldspars

Potassium feldspars were separated from the whole-rock samples by the following methods. A small portion of each sample was initially passed through the entire crushing apparatus to clean the system. Clean hand specimens of the sample were then crushed, washed thoroughly, and sifted through clean brass screens. For the majority of the samples, the -50, +70 and -70, +100 mesh fractions were found to be the most convenient to use, and these were subsequently passed through a Franz isodynamic separator which removed most of the dark minerals. The K-feldspars were then floated in an acetone-bromoform solution adjusted to a specific gravity of approximately 2.58. The purity of the K-feldspar concentrate was estimated by staining with sodium-cobaltinitrite solution and was found to be typically 85-95 per cent. Impurities remaining were mainly plagioclase and quartz. Doe and Tilling (1967) have shown that quartz contains much less lead than either K-feldspar or plagioclase, and that plagioclase usually contains less than one-half as much lead as coexisting K-feldspar. In addition, these authors have shown that the leads from coexisting feldspar pairs are, in general, grossly similar in isotopic composition. Hence, contamination due to impurities in the K-feldspar concentrates should be inconsequential.

The feldspar sample was ground to a very fine powder in an agate mortar and was subsequently immersed in warm

6 N HCl for about 30 minutes followed by 30 minutes in warm 8 N HNO₃. This step was adopted from the procedures followed by Doe (1962), Zartman (1965a), and others, to remove lead and uranium loosely held on the surface of the mineral grains. "In general, the leachable lead is more radiogenic than that more tightly bound in the crystal lattice. A considerable increase in the Pb/U ratio and a better agreement of isotopic data result after the acid pre-treatment" (Zartman, 1965a). In addition, the acid-wash will remove any lead contamination due to handling of the mineral separates. Doe and Tilling (1967) have recently pointed out in this regard that the lead content of bromoform may be as high as several hundred ppm and furthermore, that it is very difficult to remove all traces of this from the sample by merely washing repeatedly with acetone.

The quantitative extraction of lead from rocks and minerals is generally accomplished by one of two methods. In the most popular procedure, the sample is dissolved in hydrofluoric and perchloric acids and the lead is subsequently isolated and purified by means of ion exchange columns and dithizone extractions. Marshall and Hess (1958), Masuda (1962), Cooper and Richards (1966), Tatsumoto (1966) and others, however, have extracted lead by heating the sample either in a vacuum or in a stream of hydrogen at temperatures of the order of 1000 °C. The volatile material is collected on a cold finger or on a cool portion of the quartz furnace tube.

The lead can then be purified by the usual chemical techniques.

The second method was chosen for the present research as it avoids excessive handling of the sample in a laboratory not designed for work with small quantities of lead, and also the necessity of obtaining quantities of lead-free chemicals. One major problem that could arise with this technique is the possibility of isotopic fractionation during the volatilization. Starik and co-workers (Starik, et al, 1957) have demonstrated such a fractionation when uranium minerals or granites were sublimated in vacua. Their data indicate, however, that there are different modes of lead occurrence in minerals and rocks, rather than an actual fractionation of the lead existing within a single mode. Khlopin (1956), on the other hand, did not observe isotopic fractionation with granites at $\sim 1000^{\circ}\text{C}$. The acid-washed feldspar samples volatilized in the present study should contain only the lead held within the crystal lattice of a single mineral, hence fractionation should not be a problem.

Finely powdered graphite (Fisher Scientific Co., Grade #38), previously purified in a hydrogen stream at 1000°C , was thoroughly mixed with the feldspar sample. The weight ratio of rock powder to graphite was approximately 30:1. The sample was then loaded into a quartz combustion boat which was, in turn, inserted into a quartz tube approximately 30 cm long, 15 mm in diameter. This tube was carefully placed inside a larger diameter (25 mm) thick-walled quartz tube which forms

part of the heavy-duty, resistance furnace. Combustion boats not more than one-half the length of the furnace element were used to ensure uniform heating of the sample. The furnace reached a temperature of 1000°C in about one hour and was held at this temperature for five hours. A hydrogen flow of approximately 150 cm³ per minute was maintained through the furnace during the heating period. The volatile material in the sample appears as a thin metallic mirror about 1 cm long on the inside of the inner quartz tube which extends into the cooler region of the furnace. The mirror was allowed to cool in a hydrogen atmosphere before the quartz tube was removed from the furnace. The boat size limited the amount of feldspar that could be volatilized on a single loading to about 6 or 7 grams; hence, for most samples, several runs were required.

Baskova and Novikov (1957) volatilized rock samples in vacua for 1.5 to 2.5 hours at 1050-1100°C. They used a weight ratio of rock powder to carbon of 1:1, believing that the reduction to metallic lead by the carbon increased the yield of the process. An 88 per cent yield at the ten ppm level (chemical methods = 100 per cent) was obtained in the case of feldspars. Masuda (1962) reduced this ratio to 30:1, pointing out that the vapour pressure of lead (II) oxide is in fact higher than that of the metal. The main purpose of the carbon, he believes, is to prevent the rock particles from cohering to form a hard mass. Both Masuda and the present writer have found that without carbon the sublimation process

is impeded and hence the yield is reduced. Masuda heated his samples in vacua for about one hour at 1000-1100°C and obtained yields comparable to those of Baskova and Novikov. Cooper and Richards (1966) have recently used this technique to extract lead from basaltic rocks by heating finely powdered rock-graphite mixes in vacua for five hours at 1000°C. The methods employed in the present study as described earlier should give yields comparable to the above.

Whittles (1964) was troubled by the formation of a lead oxide silicate of the form $x\text{PbO} \cdot \text{SiO}_2$, a black compound which could not be reduced to free lead in the hydrogen furnace or dissolved in nitric acid. In some cases over 50 per cent of the lead in the sample was lost. Whittles solved this problem by keeping his lead mirrors at all times in an oxygen free environment. Fortunately, during the present research, this silicate was never observed to form, despite the fact that the lead mirrors were exposed to the atmosphere for brief periods. It may be that its formation required some trace element in the sulfides studied by Whittles that was not present in the feldspars of this study. Alternatively, it may reflect slight differences in the properties of the quartz tubing used in the two studies.

Because of the small sample size and a large lead background in the laboratory, it was necessary to take precautions to avoid contamination. Feldspar samples were acid-washed in new pyrex beakers which had been thoroughly cleaned

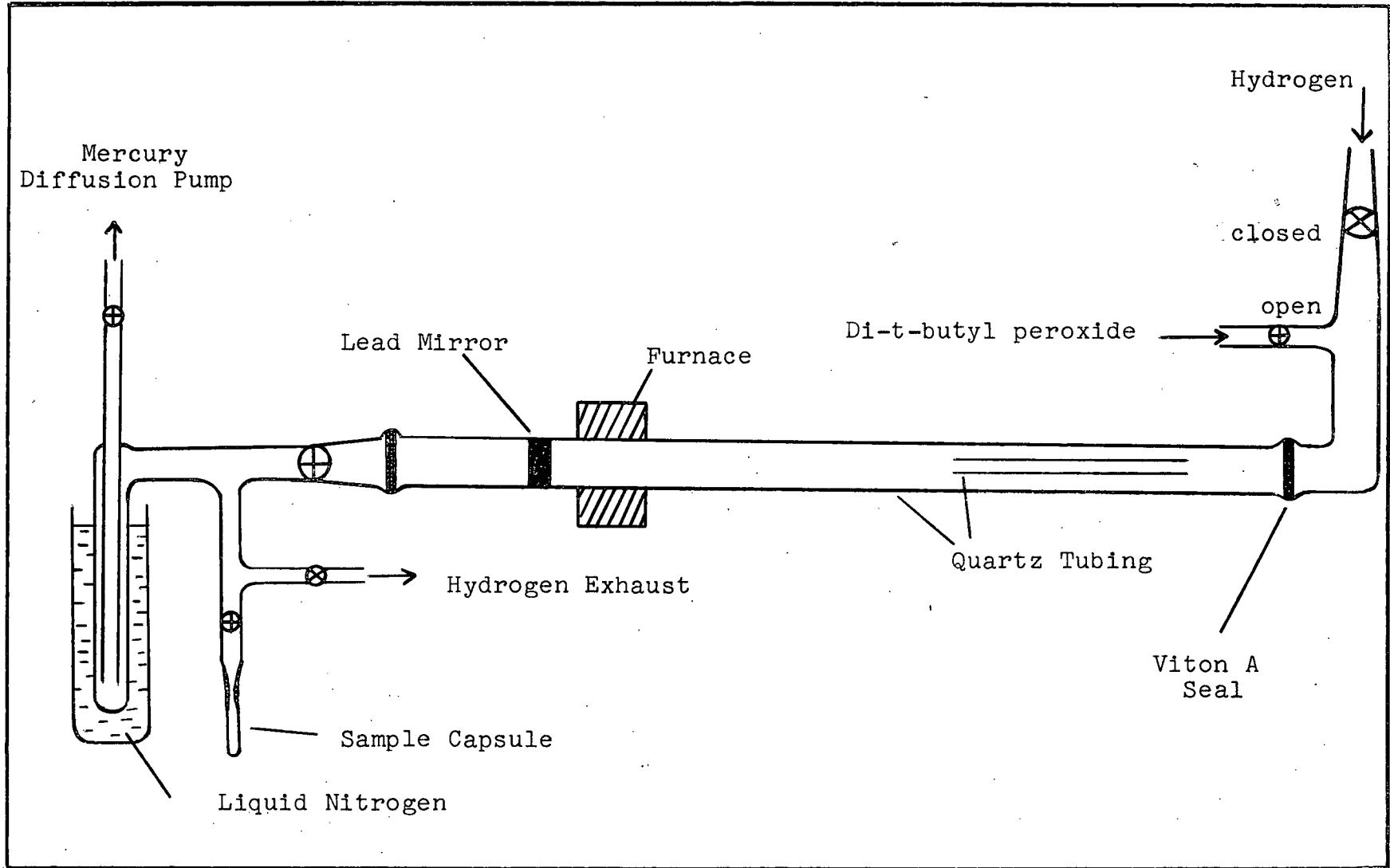
in hot 3 N HNO₃ and rinsed with distilled water prior to use. The samples were rinsed with distilled and doubly-distilled water to remove all traces of the acid, covered with a clean beaker and dried at 250°F. They were kept covered until used to prevent contamination from lab dust, etc.

The inner quartz tubing was wholly immersed in 6 N HNO₃ for at least twelve hours, flushed with distilled water and dried. If there remained a residue on the tube from a previous run, the inside of the tube was cleaned for 5-10 minutes with 10% HF. The quartz boats were similarly cleaned with nitric acid. The heavy furnace tubing was cleaned briefly in dilute nitric acid, flushed with distilled water and dried. The large quartz tubing and sample cold trap of the micro-lead apparatus (described in the following section) were cleaned each time for several hours in 3 N HNO₃, flushed and dried. All stopcocks that come in contact with the tetramethyllead were cleaned and regreased. Disposable plastic gloves were used to handle the clean glassware.

Preparation of Tetramethyllead

The reader is referred to the thesis of Whittles (1964) for a detailed description of the 'micro-lead apparatus' used to prepare tetramethyllead. A schematic diagram of the apparatus is shown in Figure 2-1. Only a brief description of the free radical technique and the main departures from Whittles' procedure are given here.

FIGURE 2-1 SCHEMATIC DIAGRAM OF MICRO-LEAD APPARATUS



After the volatilization, the small quartz tube was inserted into the large tubing of the micro-lead apparatus and the system was pumped down with a mercury diffusion pump. Hydrogen was then admitted to the system at atmospheric pressure and the flow rate adjusted to approximately 150 cm³/min. The mirror was moved progressively down the tube by heating at 750°C for about 15 minutes in each position. Eventually the lead was isolated from the other volatile material and formed a pure mirror near the end of the furnace on the inside of the outer quartz tube. In addition to this lead mirror, with some of the feldspars a faint bluish mirror was also observed.

In practice, the mirror had to be moved only four or five times in order to obtain sufficient purity and it was found that it was not necessary to move it at a reduced hydrogen pressure (1 to 2 cm of mercury). This step in the procedure was initiated by Ulrych (1962) in order to remove iron contamination from the lead, and was continued by Whittles who believed that it tended to give more consistent results because of increased mirror purity. An advantage of working at atmospheric pressure is that the lead does not become too dispersed on the tube and hence is more easily observed.

The lead mirror is removed by the action of free methyl radicals produced from the thermal decomposition of di-tertiary-butyl peroxide. This source material was

originally chosen by Ulrych and was also used by Whittles after the latter had carefully considered other possibilities. It is quite suitable from the point of view of high radical yield, absence of interfering radicals, freedom from undesirable impurities, and the relative ease with which the decomposition products (methane, ethane, acetone, higher boiling ketones) can be separated from the tetramethyllead. A decomposition temperature of approximately 700°C was chosen. At this temperature all of the peroxide is decomposed and the removal of the mirror seems most efficient. The peroxide was admitted to the system by means of a glass leak calibrated to give a pressure of one mm of mercury in the region of the furnace. The tetramethyllead along with the decomposition products were collected in a liquid nitrogen trap and later transferred to a small glass capsule. Lead mirrors were usually removed in from 1 to 4 minutes; the best results were obtained when the mirror was slightly hot to the touch and the separation between the mirror and furnace was about one cm.

In some cases there appeared to be insufficient mass flow towards the cold trap, and hence some of the tetramethyllead would diffuse back into the hot region of the furnace and decompose to form a second mirror. This backflow was easily removed by retracting the furnace several centimetres and cooling the new mirror with a blower. In order to be certain that all of the lead had been removed, hydrogen

was re-admitted to the system and any remaining lead was moved to a fresh position further down the tube. This final mirror was then removed as described above.

It is believed that this procedure consistently recovers greater than 90 per cent of the lead. The problem of backflow can be at least partially eliminated by increasing the mass flow in the system, that is, by admitting more of the peroxide source material. This is readily accomplished by using an adjustable needle valve instead of a glass leak. The disadvantage is the greater difficulty in separating by gas chromatography a larger quantity of the decomposition products. The glass leak was normally used in this research.

Gas Chromatographic Purification of Tetramethyllead

The methods here were developed from the work of Ulrych (1960, 1962) who was the first to successfully apply gas chromatographic techniques in the purification of tetramethyllead for isotopic analysis. Ulrych was able to produce samples containing a few milligrams of tetramethyllead of sufficient purity to give precise mass spectrometric analyses. He employed a pyrex column five feet long with an internal diameter of 10 mm. This column was packed with 40-60 mesh ground firebrick coated with 25 per cent by weight white paraffin oil. Use of firebrick as a solid support is not recommended by authorities in this field (J. Cornelius, Varian Aerograph, personal communication) because of its

large adsorptive surface area. Ulrych, therefore, probably lost considerable lead by adsorption on the solid support. However, his samples were relatively large so that he could afford significant loss without losing mass spectrometer sensitivity.

Whittles, working with about one order of magnitude less lead than Ulrych, felt that losses in the column would be too severe, and hence developed a vacuum distillation technique. He found, however, that when he pumped on his samples at dry ice temperatures, considerable lead was lost so that in practice he had to reach a compromise between desired purity and size of sample. This meant that for many of the samples, the pressure inside the mass spectrometer was several times higher than normal, and hence larger and probably more uncertain corrections were required.

Neither method as it existed was believed adequate for the present work. Gas chromatography, however, seemed to be capable of producing the more consistent results if only the lead loss in the column could be reduced to a tolerable level. This can be accomplished by minimizing the losses on (a) the solid support and (b) the liquid phase.

A support is required that has a small and non-adsorptive surface area. The support chosen was 45-60 mesh Chromosorb G, an oyster white, very hard, dense diatomaceous earth with a surface area of only 0.5 square metres per gram. A column packed with this support will have a total surface

area approximately three to four times smaller than that of a typical firebrick column. Chromosorb W is a highly recommended support that would give a still smaller area, but it is considerably more expensive. The Chromosorb was acid-washed by the manufacturer (Varian Aerograph) and was also coated with dimethyldichlorosilane (DMCS) to reduce surface active sites in the diatomaceous earth material, and hence reduce adsorption on the support. Others have found that the Chromosorb supports are very suitable from this point of view. Bonelli and Hartman (1963), for example, using a column packed with Chromosorb W were able to detect lead alkyls in the 10^{-10} gram range. Blenkinsop (personal communication) has recently shown that there is negligible cross-contamination of large (~ 100 mgm) tetramethyllead samples; hence column losses are probably small (since cross-contamination has been found to be associated with large column losses). His tests were made with a column packed with Chromosorb W coated with 15 per cent by weight dinonyl phthalate.

Adsorption on the liquid phase can be minimized by using the lightest possible loading. The maximum recommended loading for Chromosorb G is five per cent. When greater liquid loadings are used, column efficiency is reduced; that is, the peaks on the chromatogram become broader. Initially, the present writer attempted to use a five per cent loading but found that the samples passed through the column too rapidly (in about seven minutes), and the separation from the decomposition

products was not complete. A 10-15 per cent loading proved to be satisfactory and was used throughout the present research.

Ethane and methane are both very volatile and hence easily separated from tetramethyllead in a chromatographic column. The critical separation is between the large quantity of acetone and the much smaller quantity of tetramethyllead. Type 2044 white paraffin oil has a high solvent efficiency for these two substances (that is, the two peaks are well resolved) and was chosen as the stationary liquid.

A pyrex column five feet long with an internal diameter of 10 mm was used. A column temperature of about 75°C was maintained by means of a heated oil bath. The carrier gas, helium, was passed through an activated charcoal trap held at liquid nitrogen temperatures at a flow rate of approximately 70 cm³/min. Although this trap was apparently not capable of removing all traces of water vapour from the helium, resulting contamination of samples was insignificant. The thermal conductivity detector has been described in detail by Ulrych (1962).

The sample was admitted to the column by crushing the glass capsule in a section of thick-walled tygon tubing. This method of introduction is non plug-like and hence not ideal, but does not in practice seem to adversely affect the overall performance of the column. The use of tygon tubing in a chromatographic system is not recommended as it tends to break down readily and may cause contamination. It has,

however, been used successfully in this laboratory for several years and was found to be satisfactory. The tetramethyllead was subsequently collected in a liquid nitrogen trap and transferred to a break-seal tube for analysis on the mass spectrometer.

The column packing was changed for each sample as an added precaution against cross-contamination. The column glassware, cold trap, etc. were cleaned each time by the methods described earlier.

Ulrych's chromatographic procedures were therefore adapted to meet the requirements of the present study. In particular, special attention was given to the problem of lead loss in the column, and hence a better quality solid support and a smaller percentage of stationary liquid were used. A quantitative determination of the amount of lead actually lost was not made; however, it would appear that this revised chromatographic technique is capable of producing larger mass spectrometer ion beams from a given sample than the vacuum distillation method of Whittles. In addition, the mass spectrometer operating pressures are much lower.

Contamination

In order to check the efficiency of the cleaning procedure, a 'blank' sample (consisting of a small amount of the purified graphite in a quartz boat) was prepared. No peaks were detectable in the mass range 248-255 above the

usual background in the mass spectrometer. This background, due to residual amounts of tetramethyllead in the machine, is always present to some extent, but can be minimized by thoroughly cleaning the source assembly and sample line of the instrument. The background spectrum is no larger than 0.5 per cent of the smallest sample beam intensity and causes negligible contamination.

A considerably larger background spectrum can, however, be produced by flushing the instrument with di-tertiary-butyl peroxide. Apparently this is due to the formation of tetramethyllead in the source region of the spectrometer by the action of free methyl radicals on metallic lead deposited from previous samples. The heat supplied by the filament would be sufficient to decompose both tetramethyllead and di-t-butyl peroxide. Fortunately, a strong 'masking' effect was observed, since the isotopic composition of this background could be changed to a value close to that of a new sample by simply flushing this sample through the machine for 1-2 hours before beginning the analysis. This flushing technique was employed with all samples, and, in addition, samples of significantly different composition were not analyzed in succession. This procedure effectively prevented cross-contamination of samples.

Lead contamination resulting from the preparation procedure is therefore less than that due to the machine background. The latter can be controlled by periodic cleaning of

source and sample line and by flushing before each analysis.

Whittles (1964) reported a contaminant that was characterized by three peaks in the 280 mass range and by a series of peaks at all masses between 240 and 248. In addition, there were peaks at masses 249 and 250 in the trimethyllead spectrum. He believed that this contaminant resulted in some way from the use of hydrofluoric acid in the cleaning of the quartz tubing, and found that it apparently did not form if the tubing was baked in an oxygen stream at 950°C after the cleaning. Although this contaminant was not observed during the present study, as a precaution, the quartz tubing was baked in oxygen whenever this acid was used.

An unknown material was sometimes produced in the free-radical process that was eluted from the chromatographic column at about the same time as the tetramethyllead. This substance did not have any mass fragments in the trimethyllead spectrum, so a small quantity of it in a sample was not serious.

Both Ulrych (1962) and Whittles (1964) were troubled by the presence of trimethyl bismuth in some of their samples. This material has the same boiling point as tetramethyllead and hence would not likely be removed in the column purification. It gives rise to an increased abundance of mass 254, a peak which is measured to correct for the presence of C^{13} . In practice, the C^{12}/C^{13} ratio for the particular methyl radical source is sufficiently well known so that the mass 254 peak could be ignored if bismuth were found to be present.

The only other metal alkyl that could contaminate the trimethyllead spectrum is trimethylthallium which would give peaks at masses 248 and 250. Up and down mass 'tailing' from these peaks (including the effects of C^{13} and hydrogen loss) would contaminate the very important 249 peak. The size of the mass 250 peak (measured to correct for the loss of a hydrogen atom from one of the methyl groups) depends only on the mass spectrometer source potentials. Hence, the presence of thallium would be clearly revealed by abnormally large mass 250 peaks.

Throughout the present work, neither bismuth nor thallium was observed in any of the samples.

Mass Spectrometry

The mass spectrometer used in this study was the 90°-sector 12-inch radius, gas-source instrument designed and built by F. Kollar and R.D. Russell and subsequently used by Ulrych (1962), Whittles (1964) and others. The routine mass spectrometer operating procedures have been described in detail by Ostic (1963). A brief summary here emphasizes the procedures that are important when the sample size is small.

To determine the difference in isotopic composition between two samples A and B, sample A is first analyzed, then sample B is analyzed, and finally sample A is reanalyzed. The average of the two A analyses is then compared with the

B analysis. When possible, two samples of similar isotopic composition were chosen for comparison in order to minimize the effects of any cross-contamination. Ostic and others have shown that it is very important to maintain the same mass spectrometer operating conditions throughout a given comparison (usually one day) in order to obtain a meaningful difference in isotopic composition between the two samples. Hence source potentials, operating pressures, etc. must be held approximately constant during the day. This is only possible with two samples of about the same size and purity. While this is relatively easy to achieve with large, pure samples (~ 100 mgm of tetramethyllead), a special effort must be made with small, relatively impure samples (~ 1 mgm of tetramethyllead).

A check on the precision of the isotopic comparison of two samples is made by a routine intercomparison or looping technique (for a detailed discussion, see Ostic, et al, 1967). Three samples, A, B and S are included in each loop and over three days each sample in turn is compared with the other two samples in the manner described above. The isotopic differences (A-B, B-S, S-A) are added algebraically to determine the loop closure error, ϵ , for each isotope ratio. These total errors are then distributed evenly among the analyses of the three days. In this way, the isotopic compositions of the two samples, A and B are obtained relative to a standard sample, S. In addition, it can be shown that

the quantity $\epsilon/\sqrt{3}$ approximates the standard deviation of a measured isotope ratio and hence provides an estimate of the reproducibility of the analyses on a day-to-day basis.

All samples were ultimately intercompared with the laboratory standard, Broken Hill #1, a split of the original University of Toronto sample T1003 from the main lode ore-body at Broken Hill. Isotope ratios for this sample were given by Kollar, et al (1960): $\text{Pb}^{206}/\text{Pb}^{204} = 16.116$, $\text{Pb}^{207}/\text{Pb}^{204} = 15.542$, $\text{Pb}^{208}/\text{Pb}^{204} = 36.068$.

Sample Size, Precision, and Reproducibility

The sulfide samples which were analyzed by Ulrych (1962) generally produced several milligrams of tetramethyllead and he was able to claim a precision of approximately 0.05 per cent in the measurement of isotope ratios relative to lead-204. In other words, the sum of the percentage standard deviations of the mean trimethyllead peak heights $\left\{ \sqrt{\frac{\sum (x_i - \bar{x})^2}{n(n-1)}} \right\}$ is 0.05 per cent for each of the isotope ratios. Ulrych's precision on a single analysis compares then quite favourably with that obtained by Ostic (1963) who used sample sizes about two orders of magnitude larger. Ostic, however, found that in order to obtain a reproducibility of measured isotope ratios on the basis of replicate analyses that was comparable with the above precision, he had to use the intercomparison technique described above. Ulrych's analyses, on the other hand, were not intercompared in this

in this manner and it is not clear what reproducibility he obtained. Whittles (1964) subsequently analyzed samples containing less than 100 micrograms of lead to a precision of about 0.40 per cent. Intercomparison techniques were not used in this study either and, although Whittles claims to have obtained a comparable reproducibility, this was not convincingly demonstrated.

In this study, it is necessary to make highly reproducible measurements. Doe's (1962) analyses of Balmat rocks and ores are at least 0.8 per cent deficient in the Pb^{207}/Pb^{204} ratio in comparison with the locus of the stratiform ores studied by Ostic, et al (1967). Since his Pb^{207}/Pb^{204} ratios are reproducible to within only 0.8 per cent at the 95 per cent confidence level, more accuracy is clearly needed to verify this difference. The ore-leads appear to have, on the average, slightly higher Pb^{207}/Pb^{204} ratios than the feldspar leads. However, the maximum range in this ratio for five of the seven samples amounts to only 0.5 per cent.

Since the mass spectrometer operating conditions must not be changed during a day's analyses, the tetramethyllead samples prepared for the present study must be sufficiently large so that the ion beams produced in the mass spectrometer can be measured to a high precision (say ~ 0.05 per cent) and, in addition, there must be sufficient residue of unused sample to be recovered and analyzed a second time under the same conditions. If the sample is too small,

the ion beam intensity decreases very rapidly during the first analysis and the source potentials must then be adjusted in order to produce a satisfactory beam intensity for the second analysis.

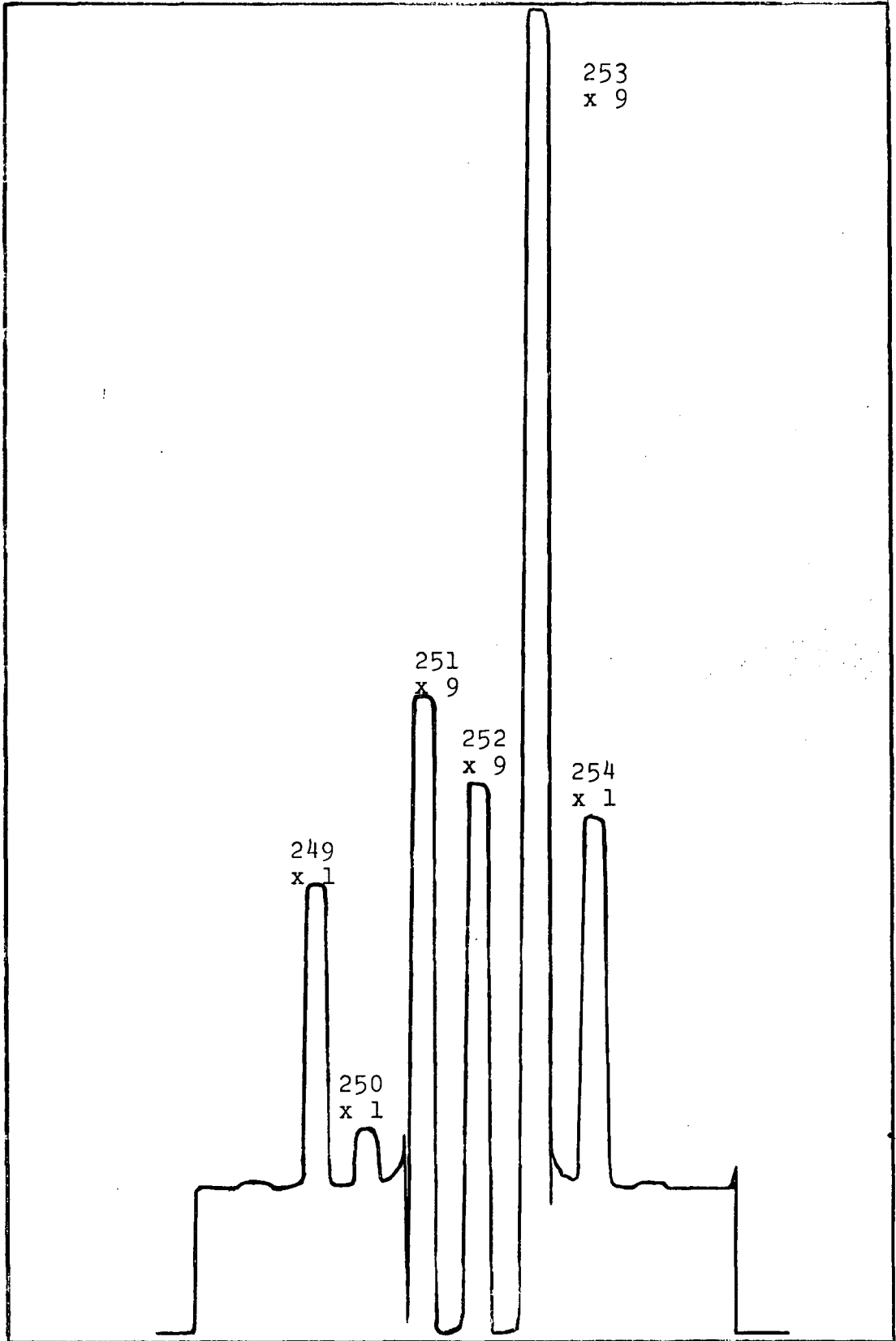
The minimum sample size required to fulfil the above conditions was determined to a large extent by the capabilities of the data reduction system. The output of the mass spectrometer measuring system consists of the shaft rotation of a ten-turn high-precision potentiometer. Ostic used a three inch recording dial mounted on the end of this shaft, and the trimethyllead ion currents were measured by reading this dial. Weichert (1965), following a suggestion made by Kollar (1960), modified the system by replacing the dial with a ten-turn, 1000 counts per turn encoder (Perkin Elmer Model 10/1000). The encoder provides input to a four decimal digit memory; twice a second, on command, the contents of the memory along with the scan direction and 'shunt' selector value are recorded on punched paper tape. Weichert also programmed an IBM 7040 computer to filter and reduce the data. Recently, this automatic reduction system has been modified to incorporate a Precision Instrument incremental tape recorder and the reduction program has been revised and streamlined by Russell and Blenkinsop (Weichert, et al, 1967), so that a complete analysis can be reduced in about 40 seconds.

This automatic reduction system in its present form greatly assisted the writer in his attempts to make precise

analyses of small samples of tetramethyllead. The standard deviations of the individual peak measurements are approximately a factor of two lower than those obtained with the dial-recording system. In addition, human errors in the data reduction calculations are eliminated and the time taken to obtain the final isotopic abundances is greatly reduced.

A main asset of the system is its ability to calculate meaningful pressure scattering coefficients. This 'tailing' in the mass spectrum is probably due to the presence of gas molecules of various kinds in the analyser tube and accumulated corrections, typically of the order of 0.5 per cent of the lead isotope ratios, are required. Whittles (1964) found that he could not measure the actual coefficients for each run from the chart recorder spectrum because the peak amplitudes become too small when the sample size is reduced. Ultimately, he had to rely on an empirical correction based on the reading of the ionization gauge. The difficulty with this method is that the gauge is not uniformly sensitive to all gases and hence true pressure comparisons are only possible with samples of uniform purity. Therefore, coefficients obtained by the above method may not be consistent. The auto-reduction program calculates one and two mass pressure coefficients from the digitally recorded data according to the formulas given by Ostic (1963). The half-mass factor is obtained by measuring the 'valley' between the mass 251 and mass 252 peaks. The values obtained for small samples

FIGURE 2-2 TRIMETHYLLEAD SPECTRUM FROM APPROXIMATELY 500 MICROGRAMS OF TETRAMETHYLLEAD



during the course of the present research compare favourably with typical values obtained for large amplitude spectra. The data therefore should not be significantly in error because of this correction factor. At very low ion beam intensities, even the automatically computed factors become unsatisfactory.

The present writer found that in order to satisfy the requirements given above a minimum of 500 micrograms of tetramethyllead were required. The sample preparation system was quantitatively calibrated from the preparations of the Balmat rock samples since their lead contents have been determined (Doe, 1962). Five hundred micrograms of tetramethyllead give rise to a mass spectrometer ion current of approximately 2×10^{-13} amperes for the least abundant isotope at mass 249 (that is, lead-204). If the feedback voltage* in the measuring system is 3 volts, this current corresponds to a peak height on the chart recorder approximately 20 per cent of the full scale value (Figure 2-2). The precision of measurement of isotope ratios with respect to lead-204 on the basis of a single analysis ranged between 0.05 per cent and 0.10 per cent for samples of this site. The ore-lead analyses were generally somewhat more precise. In order to obtain at least 500 micrograms of sample, a maximum of 30 grams of feldspar was processed. In other words, feldspars containing less than about 20 ppm lead were not analyzed. This practical

*The current sensitivity of the measuring system can be increased by lowering this voltage, but to the detriment of servo characteristics.

lower limit did not exclude any of the chosen samples.

A reproducibility of analyses on a day-to-day basis was achieved that was comparable with the above precision of a single analysis. The quantity, $\epsilon/\sqrt{3}$, where ϵ is the loop closure error, has an average value of about 0.08 per cent for the intercompared samples of the present study (Table 2-1). Some of the smaller samples were not fully intercompared and hence loop closure errors are not available. This is due to the fact that some of these samples were too small after they had been analyzed once or twice, and thus it was not possible to analyze them successfully a third time. However, the abundances as determined from a single day's analyses are probably not in error by more than 0.10 per cent.

Another estimate of the day-to-day reproducibility can be obtained from the replicate analyses of a standard sample over a significantly long time interval. In this study, the Balmat 500 galena was chosen as a secondary standard and approximately 10 milligrams of tetramethyllead were prepared using the free radical technique. This sample was analyzed eleven times during a five month period, and towards the end of this time it had become comparable in size (~ 1 mgm) to most of the rock-lead samples. The isotopic ratios, means and standard deviations for these analyses are given in Table 2-2. The standard deviations of the three isotope ratios range between 0.10 per cent and 0.15 per cent, and are only slightly higher than values quoted by Ostic

TABLE 2-1

REPRODUCIBILITY OF ANALYSES ON THE BASIS OF LOOP CLOSURE ERRORS

Loop	Sample	Percent Standard Deviation ($\epsilon/3$)		
		Pb ²⁰⁶ /Pb ²⁰⁴	Pb ²⁰⁷ /Pb ²⁰⁴	Pb ²⁰⁸ /Pb ²⁰⁴
1	1 Broken Hill			
	500 Balmat	0.07	0.03	0.06
	84 Balmat	0.07	0.03	0.06
2	1 Broken Hill			
	500 Balmat	0.03	0.04	0.02
	qbg Balmat	0.03	0.04	0.02
3	500 Balmat			
	ccg Balmat	0.07	0.05	0.05
	ccgp Balmat	0.07	0.05	0.05
4	500 Balmat			
	R14 Nelson	0.33	0.12	0.12
	R9 Nelson	0.33	0.12	0.12
5	Blue Star, Nelson			
	Scranton	0.10	0.08	0.07
	Victor	0.10	0.08	0.07
Means		0.12%	0.06%	0.06%

TABLE 2-2

REPLICATE ANALYSES OF BALMAT 500 GALENA

Date of Analysis	Observed Isotope Ratios			Feedback Voltage
	Pb ²⁰⁶ /Pb ²⁰⁴	Pb ²⁰⁷ /Pb ²⁰⁴	Pb ²⁰⁸ /Pb ²⁰⁴	
Nov. 29, 1966	16.830	15.528	36.614	12
	16.833	15.537	36.624	12
Dec. 5, 1966	16.817	15.499	36.544	3
	16.829	15.510	36.498	3
Jan. 9, 1967	16.840	15.534	36.659	12
Mar. 19, 1967	16.827	15.503	36.547	3
Apr. 4, 1967	16.806	15.491	36.499	3
Apr. 9, 1967	16.808	15.484	36.496	3
Apr. 13, 1967	16.845	15.487	36.541	3
Apr. 19, 1967	16.860	15.497	36.576	3
Apr. 23, 1967	16.849	15.481	36.512	3

Means and Standard Deviations*:

All data	16.831 ± 0.017 (0.10%)	15.505 ± 0.020 (0.13%)	36.555 ± 0.056 (0.15%)
3-volt data	16.830 ± 0.020 (0.12%)	15.494 ± 0.010 (0.07%)	36.527 ± 0.030 (0.08%)
12-volt data	16.834 ± 0.005 (0.03%)	15.533 ± 0.005 (0.03%)	36.632 ± 0.024 (0.07%)

*
$$\sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}}$$

(1963, p. 32) for replicate analyses of large samples over a one month period. The above estimate of reproducibility is probably pessimistic as the data in Table 2-2 suggest that the measured ratios are a function of the feedback voltage in the measuring system. The 3-volt data and the 12-volt data treated separately give significantly lower deviations for the Pb^{207}/Pb^{204} and Pb^{208}/Pb^{204} ratios.

In summary, small samples (less than one milligram of lead) have been precisely analyzed for the first time. In spite of a difference in sample size of at least two orders of magnitude, the rock-lead data are only slightly less precise than the best ore-lead data from this laboratory.

CHAPTER 3

ANALYSES AND INTERPRETATIONS

Choice of Samples

With one exception, the rock samples that were chosen for this study are associated with lead ores that have been analyzed in this laboratory. In the one case (Balmat, N.Y.) where this is not true, both ore-leads and rock-leads were analyzed. In addition, these ore studies are all classic examples of 'type' interpretations of lead isotope abundances. That is, the data support the two basic models described in an earlier chapter. The ores at Balmat and at Broken Hill (N.S.W., Australia) belong to the special class of stratiform deposits defined in Chapter 1 and by Stanton (1960). Anomalous lead suites have been found in the Broken Hill district (Thackaringa-type deposits), near Nelson, British Columbia (Kootenay arc deposits), and in the West-Central New Mexico area. The Balmat area is one of a very few from which there have been published ore-rock studies.

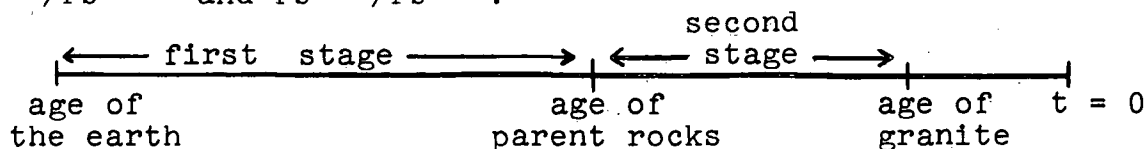
Nelson, British Columbia

Samples were collected by the writer from the Nelson batholith, a large and relatively young (~ 150 m.y. old) granitic body located in south-eastern British Columbia. For these young rocks it is not necessary to correct for in situ uranium and thorium decay in the potassium feldspars.

Evidence for a metasomatic origin of at least some of the Nelson plutonic rocks (Little, 1960, p. 98) has been

discredited as a result of detailed field mapping by J.V. Ross and A.J. Sinclair (personal communication, 1967). However, this does not preclude derivation from melting of pre-existing rocks as opposed to mechanical injection of new material from a deep source. Low initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratios (0.705 - 0.710) for rocks from this area (Fairbairn, et al, 1964) do, however, imply that the granitic magma has not been derived from typical rubidium-enriched crustal material.

The Nelson granites should, in any case, contain a common lead component characteristic of the parent rocks and, in addition, uranium and thorium in these rocks should have produced a radiogenic component. If complete mixing of lead isotopes occurred when the batholith was formed, potassium feldspars from different regions will then contain lead of uniform isotopic composition. On the other hand, partial mixing of isotopes will be revealed by a linear relationship (a two-stage anomalous lead line) between the isotope ratios $\text{Pb}^{207}/\text{Pb}^{204}$ and $\text{Pb}^{206}/\text{Pb}^{204}$.



Rock-lead isotopic analyses for part of the southern California batholith (Patterson, et al, 1956) indicated a uniform composition throughout. Doe (1967), however, has recently found isotopic variations as high as 8 per cent among the different rock-types that make up the Boulder batholith. The present research continues the study of lead isotope

abundance patterns in plutonic rocks of batholithic dimensions.

An important reason for analyzing lead in the Nelson granites was to investigate a possible genetic relationship between these rocks and spatially related mineral deposits. Mineralization in the Nelson area is known to have occurred after emplacement of the batholith, and a genetic relationship between the two has been suggested by several authors (Schofield, 1920; Cairnes, 1934; Irvine, 1957).

The present study was facilitated by the fact that the mineral deposits associated with the Nelson batholith occur in the structural belt known as the Kootenay arc. The first lead isotope analyses reported from this area are given by Russell and Farquhar (1960). Sinclair (1966) has subsequently reported more precise analyses of ore-leads from this region. His data suggest that all leads from the Kootenay arc have had grossly similar isotopic histories that can be explained by a modified two-stage anomalous lead model.

Balmat, New York

A more precise study of the lead in Balmat rocks and ores was made possible by Dr. B.R. Doe who kindly supplied the four feldspar and two galena samples that were analyzed in his own investigation.

From Doe's study, it appeared that a genetic link between the ores and at least some of the rocks in the area

was possible, but radiogenic lead (that is, primarily lead-206) must have been added to the potassium feldspars subsequent to the formation of the ores for this to be so.

The ore deposits at Balmat are of the stratiform type studied by Ostic, et al (1967). However, on the basis of Doe's analyses, the ore-leads were derived from a primary system characterized by a μ -value of about 8.7 rather than 9.0, the value calculated from Ostic's data. A clarification of this apparent difference will be a main contribution of the present thesis.

Doe's analyses of Balmat rock-leads suggest that they too are related to a primary system with a μ -value of 8.7 or lower. With the exception of one highly anomalous sample, these leads have a rather small range in isotopic composition and Doe (1962) therefore states that "it is very likely that these bodies were formed with lead from a common source". Within the analytical uncertainty (95 per cent confidence limits are approximately 0.8 per cent of isotope ratios with respect to lead-204), Doe's results also suggest that the Balmat ore-leads were derived from this same source material. Doe (1962) concludes that "the data from both minerals (i.e. galena and potassium feldspar) fit the normal growth curves equally well".

More precise isotopic analyses of the Balmat rocks and ores are required in order to verify this conclusion.

Broken Hill, New South Wales, Australia

The writer is grateful to Mr. J.L. Liebelt and to Mr. H.F. King of the Zinc Corporation, Limited, for supplying samples of Mundi Mundi granite and lode pegmatite. The lode pegmatite sample, consisting primarily of green potassium feldspar (amazonite), came from within the B-lode orebody (No. 9 in the Mine Sequence of Carruthers and Pratten, 1961), on the No. 15 level, New Broken Hill Consolidated Limited. This orebody is one of the zinc lodes and typically grades about 5% lead, 18% zinc. The sample of Mundi Mundi granite was collected from an outcrop 18 miles northwest of Broken Hill. This outcrop, an elliptical mass measuring 1 mile x $\frac{1}{2}$ mile, is one of a number of small granitic bosses which intrude the Willyama Complex, the metamorphosed sediments which are the host rocks for the Broken Hill orebodies.

The writer is also grateful to Dr. S.E. Shaw of the Geology Department, University of New South Wales at Broken Hill for supplying samples of the Upper Granite and "Potosi" gneisses (numbers 13 and 5 respectively in the Mine Sequence). Mineral separations for six of the above samples were carried out by H. Berry and R. Rudowski under the direction of Dr. J.R. Richards at the Australian National University, Canberra.

Ore-leads from the Broken Hill area have been used on many occasions to illustrate the two basic models employed in lead isotope interpretations. The lead deposits can be

divided into two types, Broken Hill or stratiform type and Thackaringa or vein type. The Broken Hill type is represented by the massive main lode at the city of Broken Hill and by other smaller deposits in the area. Ostic, et al (1967) have suggested that these stratiform deposits contain a primary-like lead. On the basis of a single-stage model, this lead has an apparent age of 1600 million years and has developed in a source material characterized by a μ -value of 9.0. The Thackaringa deposits contain lead that is genetically related to lead of the main lode type (Russell, et al, 1961). Kanasewich (1962) further suggested that the radiogenic component of the Thackaringa leads was generated in source rocks between the times 1600 m.y. ago and 500 m.y. ago, and that at this later time mixing of the radiogenic and primary components occurred and the Thackaringa deposits were formed.

The rock types chosen for the present study are located at different distances from the main orebody. For example, the lode pegmatite sample came from within an ore formation, while the samples of Mine Sequence gneisses were collected at distances of 1000 feet or more from the main ore zone. The sample of Mundi Mundi granite came from an outcrop about 18 miles from Broken Hill. Hence, rock-ore relationships in the Broken Hill area can be examined as a function of distance from the main orebody.

K-A and Rb-Sr age determinations (Richards and Pidgeon, 1963; Pidgeon, 1967) suggest that the Mine Sequence

gneisses and the Mundi Mundi granite have had a chronological history similar to that of the Thackaringa-type ores. For example, the 500 m.y. ages for biotites from these rocks can be correlated with the event which caused the emplacement of the Thackaringa deposits. It is of interest to see if the trace lead in the rocks has had a similar history.

West-Central New Mexico

The sample of Precambrian Bosque del Apache granite which was analyzed in this study was collected by Dr. C.F. Austin.

Associated with this granite is a small, contact pyrometasomatic ore deposit. The isotopic abundances of lead from this deposit have been reported by Slawson and Austin (1962) as part of their study of ore-leads associated with the Zuni lineament. Recently, Blenkinsop and Slawson (1967) have reported more precise isotopic analyses for a number of these New Mexico leads. The above studies have suggested that the anomalous leads in this region are the product of a single crustal system and, moreover, that they are genetically related to a lead which has an isotopic composition similar to that of the Bosque ore.

Sinclair (1964, p. 44) has suggested that ore-rock relationships can be simply and directly studied by comparing ore-lead from such a contact metasomatic deposit with the common lead in the adjacent 'parent' rocks.

Balmat, New York

A detailed description of the Balmat samples has been given by Doe (1962). Results from the present study are given in Table 3-1 along with Doe's earlier data.

Pb^{207}/Pb^{204} and Pb^{208}/Pb^{204} versus Pb^{206}/Pb^{204} diagrams for all of the data are shown in Figure 3-1.

The new analyses presented in this thesis show clearly relationships between the samples that could not be shown by Doe's measurements. Both ore-leads have significantly higher Pb^{207}/Pb^{204} ratios than the feldspar leads. Therefore the possibility that the ores were derived directly from any of the igneous rocks is precluded since a negative amount of lead-207 would have had to have been added to the feldspars subsequent to the formation of the ores in order to account for the difference. Doe (1962a) concluded that rocks similar to the marbles surrounding the orebodies are an unlikely source of the relatively isotopically uniform ore-lead since a large difference in isotopic composition was observed between two marble samples. Hence, the ores do not appear to be related to any of the associated rocks so far examined.

The ore-lead from the no. 2 mine (Pb 84, F19) was apparently derived from a similar primary system as the lead in stratiform deposits studied by Ostic, et al (1967). The Pb^{207}/Pb^{206} single-stage model age for this sample is 1100 m.y. A μ -value (see page 1) of 9.0 was calculated for

TABLE 3-1

ISOTOPIIC COMPOSITION OF BALMAT LEADS

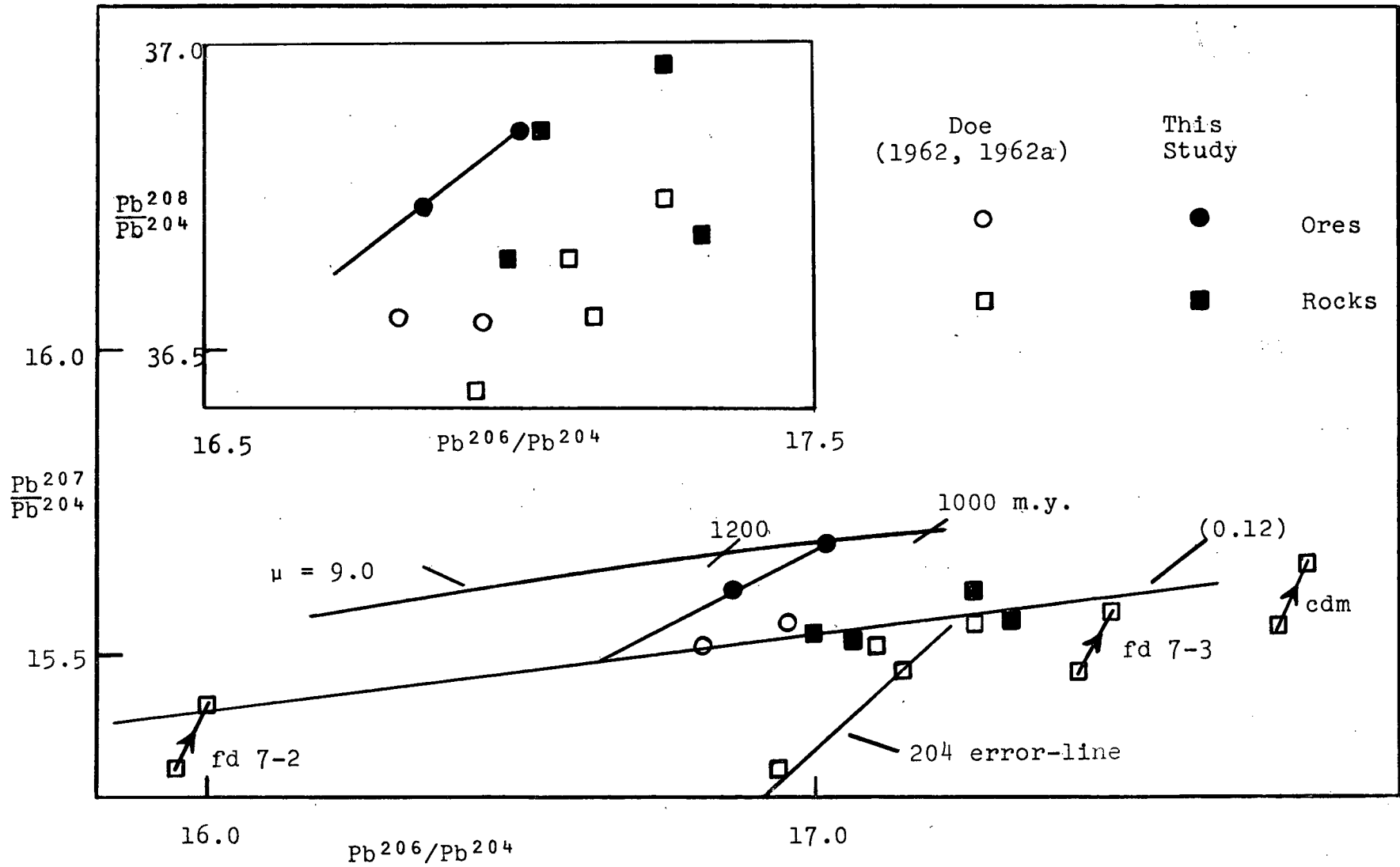
Sample	†Lead ppm	Observed Lead Isotope Abundances					
		This Study		Doe (1962, 1962a)			
		$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{207}}{Pb^{204}}$	$\frac{Pb^{208}}{Pb^{204}}$	$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{207}}{Pb^{204}}$	$\frac{Pb^{208}}{Pb^{204}}$
84, F19 galena		17.019	15.677	36.857	16.96	15.55	36.54
500, 26N galena		16.864	15.605	36.733	16.82	15.51	36.55
ccg K-feldspar	30	17.054	15.520	36.857	16.94	15.31	36.43
ccgp K-feldspar	25	17.260	15.599	36.962	17.26	15.54	36.74
qbg K-feldspar	50	17.320	15.551	36.685	17.14	15.47	36.55
hpg K-feldspar	113	16.997	15.527	36.641	17.10	15.51	36.64
cdm 14-p K-feldspar	9				18.99 *17.76 **17.81	15.63 *15.54 **15.64	37.12
fd 7-2 marble	3.2				17.98 *15.95 **16.00	15.46 *15.32 **15.42	36.32
fd 7-3 marble	0.48				19.22 *17.43 **17.48	15.60 *15.47 **15.57	36.64

† Data from Doe (1962, 1962a)

* corrected for 1000 m.y. in situ uranium decay

** adjusted to the UBC standard as explained in text

FIGURE 3-1 ISOTOPIC COMPOSITION OF BALMAT LEADS



the source material of the lead, in precise agreement with Ostic's value.

If the two ore-leads were derived at the same time from the same source they should, according to the model described in Chapter 1, have the same isotopic composition. But, the lead from the no. 3 mine (Pb 500, 26N) could only have developed in a single, closed system with a μ -value distinctly lower than 9.0. It is more likely that there was one primary mineralization 1100 m.y. ago and that the isotopic differences between the mines are explained by subsequent contamination of the lead in one of them. Doe (1962a) has shown that the no. 3 mine has a much lower lead concentration (< 10 ppm) than the no. 2 mine (> 5000 ppm) and hence that the former was more likely to show significant contamination from lead "released from the carbonate minerals replaced by the sulfides". In addition, Doe's data suggest that the no. 2 mine has the more uniform lead isotopic composition. Contamination of the lead in the no. 3 mine by older lead from a different source is consistent with the following interpretation of the rock-lead data.

On the basis of Doe's analyses, isotopic variations among the four feldspar leads appear to be primarily in a direction corresponding to errors in the measurement of the lead-204 abundances (that is, lines passing through the origin in Figure 3-1). The apparent Pb^{207}/Pb^{204} variations among these four samples have been considerably reduced by

the present analyses. Model ages and μ -values calculated on the basis of a single-stage model range from 730 m.y. to 950 m.y. and from 8.7 to 8.8 respectively. These model ages would be increased if corrections for in situ uranium decay were made. However, the corrections must be small and the ages should still be younger than the Rb-Sr and K-Ar mineral ages (~ 1050 m.y.). In addition, there would still be a significant variation in isotopic composition among the samples. Hence, a single-stage model is not adequate and a multi-stage model must be adopted to explain the observed abundances.

It has been shown (Russell and Farquhar, 1960) that the slope R of a linear relationship between the ratios Pb^{207}/Pb^{204} and Pb^{206}/Pb^{204} for common leads is given by:

$$R = \frac{1}{\alpha} \frac{(e^{\lambda' t_1} - e^{\lambda' t_2})}{(e^{\lambda t_1} - e^{\lambda t_2})} \dots\dots\dots(3-1)$$

$$\text{where } \alpha = (U^{238}/U^{235})_{t=0}$$

$$\lambda' = 0.9722 \times 10^{-9} \text{y.}^{-1}$$

$$\lambda = 0.1537 \times 10^{-9} \text{y.}^{-1}$$

These anomalous leads contain a mixture of radiogenic lead developed between times t_1 and t_2 , with a single common lead. Isotopic alteration after time t_2 (for example, as a result of in situ uranium decay) is assumed negligible.

The Balmat data are most readily interpreted by means of a short-period anomalous lead model (Kanasewich, 1962a). In terms of this model, the duration of the second (or most recent) stage of development in uranium-rich crustal environments is only a few hundred million years. The limiting

case occurs when $t_1 \rightarrow t_2 = t_1$. Equation (3-1) then reduces to:

$$R = \frac{\lambda'}{\alpha\lambda} e^{(\lambda' - \lambda)t_1} \dots\dots\dots(3-2)$$

The least-squares line (a weighted fit as suggested by York (1966)) through the four feldspar lead points in Figure 3-1 has a slope of 0.19 ± 0.12 . From equation (3-2), the time t_1 is 1740^{+600}_{-1300} m.y. The sample, ccgp, has a higher Pb^{207}/Pb^{204} ratio than the others. If this sample is omitted, the slope becomes 0.10 ± 0.03 , and the time t_1 is 900 ± 450 m.y. A better estimate of this time can be obtained by including in the above calculation the two marble samples and the one feldspar sample (cdm 14-p) which were analyzed by Doe but were not included in the present study. Two corrections were first applied to the observed abundances: (a) a correction for in situ uranium decay to 1000 m.y. ago, and (b) a correction to compensate for interlaboratory differences. The latter correction was made by comparing the present analyses of the Balmat rocks and ores with Doe's earlier data and hence calculating the mean displacement vector. The isotopic abundances of the samples were then adjusted by this amount. This correction changed the Pb^{207}/Pb^{204} ratios by about 0.6 per cent and the Pb^{206}/Pb^{204} ratios by 0.3 per cent (Figure 3-1). The slope of the least-squares line through the five feldspar leads and two marble leads is 0.12 ± 0.03 and the corresponding time is 1200 ± 300 m.y.

The short-period model adequately explains the observed isotopic variations (primarily in the Pb^{206}/Pb^{204} ratios) among the feldspar leads. It is suggested that this short-term crustal development took place in a whole-rock system of age t_1 which was subsequently metamorphosed at time t_2 when mixing of lead isotopes occurred among the various mineral phases. Zartman's (1965) Rb-Sr study of whole rocks and minerals from the Llano Uplift, Texas provides an appropriate comparison. He has shown that there was a primary event in that area of Texas about 1120 m.y. ago followed by a metamorphic event about 100 m.y. later. Ulrych and Reynolds (1966) subsequently showed that the whole-rock and mineral lead isotope abundances could be interpreted to give the same age information.

On the basis of the Rb-Sr and K-Ar mineral ages, the last metamorphism (t_2) in the Balmat area occurred about 1050 m.y. ago. The age of the whole-rock system has not been measured by the Rb-Sr technique; however, this age can be estimated if it is assumed that the least radiogenic common lead is the product of a single-stage system. The single-stage model age and the apparent μ -value for the marble sample, fd 7-2 (corrected for 1000 m.y. of in situ decay and adjusted to compensate for interlaboratory differences), are 1590 m.y. and 8.7₆ respectively. This age, based on a single marble sample, seems unacceptable when compared with the uranium-lead age calculated by the method of Ulrych (in press) which

is described in the following section. Incorrect adjustment for in situ decay is a likely explanation for this discrepancy.

Ulrych (in press) and Russell, et al (in press) have recently shown how the measured lead isotope ratios and uranium and lead concentrations for a U/Pb system can be applied to an assumed two-stage model in order to calculate age and geochemical information. In this model it is assumed that the lead now observed in a mineral or rock existed in a primary system ($\mu = \mu_1$) until the time t_1 when it was transported to its present environment ($\mu = \mu_2$, as observed). The Balmat leads, however, are apparently the product of three environments: a primary system until t_1 , a short-term exposure to a crustal system until t_2 , and the presently observed system. But, if it is assumed that the second stage is very short (that is, $t_1 \approx t_2$), the Ulrych model is a reasonable approximation and the age, t_1 and the primary μ -value, μ_1 can be calculated using the observed isotopic abundances and the U/Pb ratios. The uranium and lead concentrations have been determined by Doe for the two marbles (dolomites) and for two of the feldspars at Balmat and are given in Table 3-2 along with the observed lead isotope abundances. The isotopic ratios for the three samples not analyzed in the present study were adjusted by the method described above in order to compensate for interlaboratory differences. An age of 970 ± 300 m.y. and a primary μ -value of 8.80 ± 0.53 have been calculated for these four samples

TABLE 3-2

LEAD ISOTOPE RATIOS, URANIUM AND LEAD CONCENTRATIONS
OF BALMAT ROCKS AND MINERALS

Sample	Observed Isotope Ratios			U ppm	Pb ppm	V = (U ²³⁵ /Pb ²⁰⁴) _{obs.}
	Pb ²⁰⁶ /Pb ²⁰⁴	Pb ²⁰⁷ /Pb ²⁰⁴	Pb ²⁰⁸ /Pb ²⁰⁴			
cdm-14-p* (K-feldspar)	19.04	15.73	37.33	1.17	9.9	0.054
hpg(K-feldspar)	17.00	15.53	36.64	0.324	113.	0.0013
fd 7-2 (marble)*	18.03	15.56	36.53	0.64	3.2	0.0885
fd 7-3 (marble)*	19.27	15.70	36.85	0.083	0.48	0.0786

*Isotope Ratios from Doe (1962, 1962a), adjusted as explained in text. All chemical determinations of U and Pb by Doe.

using the parameters $a_0 = 9.56$, $b_0 = 10.42$, $t_0 = 4.55 \times 10^9$ y. This calculation is less sensitive to the U/Pb ratio of any particular sample and hence is more reliable than the one described above that is based on a single marble sample.

If it is assumed that the ore-lead from the no. 3 mine was contaminated by lead from this rock system, a minimum age of the system can be calculated from the intersection of the anomalous lead line in Figure 3-1 with the line through the two ore-leads. These lines intersect on the 1230 m.y. old primary isochron at a point corresponding to a μ -value of 8.7; that is, $t_1 \approx 1230$ m.y. Hence, despite high standard deviations, the average age of about 1200 ± 300 m.y. obtained above for the rock system from the slope of the anomalous lead line is consistent with other age information.

Evidence given above suggests that on the basis of a single-stage model the common lead which was incorporated into the Balmat rocks at the time of their formation had developed in a system characterized by a μ -value of 8.75 ± 0.05 . This is significantly lower than 9.0, the value associated with the stratiform ores studied by Ostic. It is, of course, possible that this common lead did not develop in a single, closed system but rather that it has had a multi-stage history. However, it is not possible to suggest a multi-stage model based on the primary ($\mu = 9.0$) growth curve which would yield the observed isotopic

abundances without at the same time postulating the existence of very much older (at least 2000 m.y.) rock systems in the Balmat area. There is no evidence to suggest that there are rocks of this age; hence, the existence of a primary system with a lower μ -value is postulated. This subject is developed in the following chapter.

Summary and Preferred Interpretation

On the basis of the new analyses presented in this thesis, the Balmat ores formed from lead isotopically of the type observed by Ostic and others (1967) in certain stratiform deposits. In a case where there is a low concentration of lead in the ore, contamination of the ore-lead by lead from a rock system is apparent. The rock-leads (from potassium feldspars and from marbles) form a suite of short-period anomalous leads apparently derived from a source material with a μ -value of about 8.7₅. This short-term development took place between approximately 1050 m.y. ago and ~ 1230 m.y. ago. It is clear that the primary system postulated for the rock-leads ($\mu = 8.7_5$) is distinctly different from the one associated with the ores ($\mu = 9.0$); hence the ore-lead is not genetically related to the lead in the rock system.

Nelson, B.C.

Four rock samples from different localities in the Nelson batholith were chosen for the present study. In addi-

tion, the writer analyzed four galena samples from ore deposits located in the Nelson granite or in adjacent sedimentary rocks. The sample locations are shown in Figure 3-3 and isotopic abundances, approximate lead contents of the potassium feldspars, and sample descriptions are given in Table 3-3. The galena sample from the Blue Star mine was collected by the writer. Samples from the Lakeshore showing and from the Scranton and Victor mines were collected by Sinclair. Sinclair (1966) has also reported preliminary isotopic analyses for these three samples.

Sinclair (1966) made precise intercomparison analyses of eight samples from seven mines located in the Kootenay arc north and south of the Nelson batholith. The present writer re-calculated the isotopic ratios from the raw data (see Table 3-4) and also the least-squares line (York, 1966) through the points in Figure 3-2. The slope of this line is 0.1022 ± 0.0085 when weights inversely proportional to the squares of the analytical uncertainties are assigned to each co-ordinate, and 0.1024 ± 0.0083 when all co-ordinates are given equal weight. The isotopic abundances of lead from the Sullivan mine (East Kootenay district), re-calculated from Sinclair's data (Table 3-4), plot on the anomalous lead line in Figure 3-2. Hence, a genetic relationship between Kootenay arc leads and Sullivan-type lead is suggested. Sinclair (1966) similarly concluded that "Kootenay arc leads were formed by addition of variable amounts of radiogenic lead to lead of Sullivan isotopic composition".

FIGURE 3-2 ISOTOPIC COMPOSITION OF KOOTENAY ARC AND NELSON LEADS

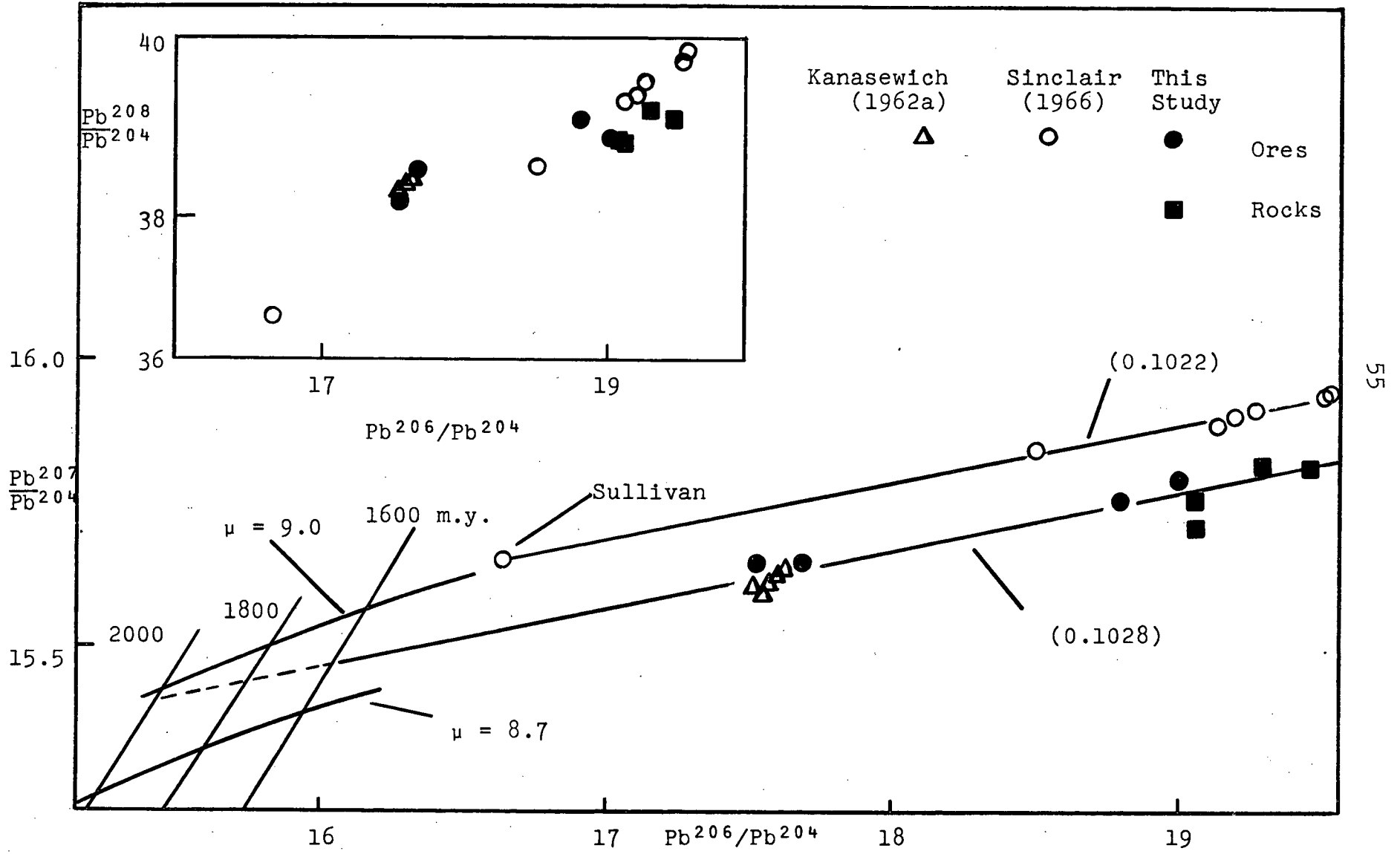
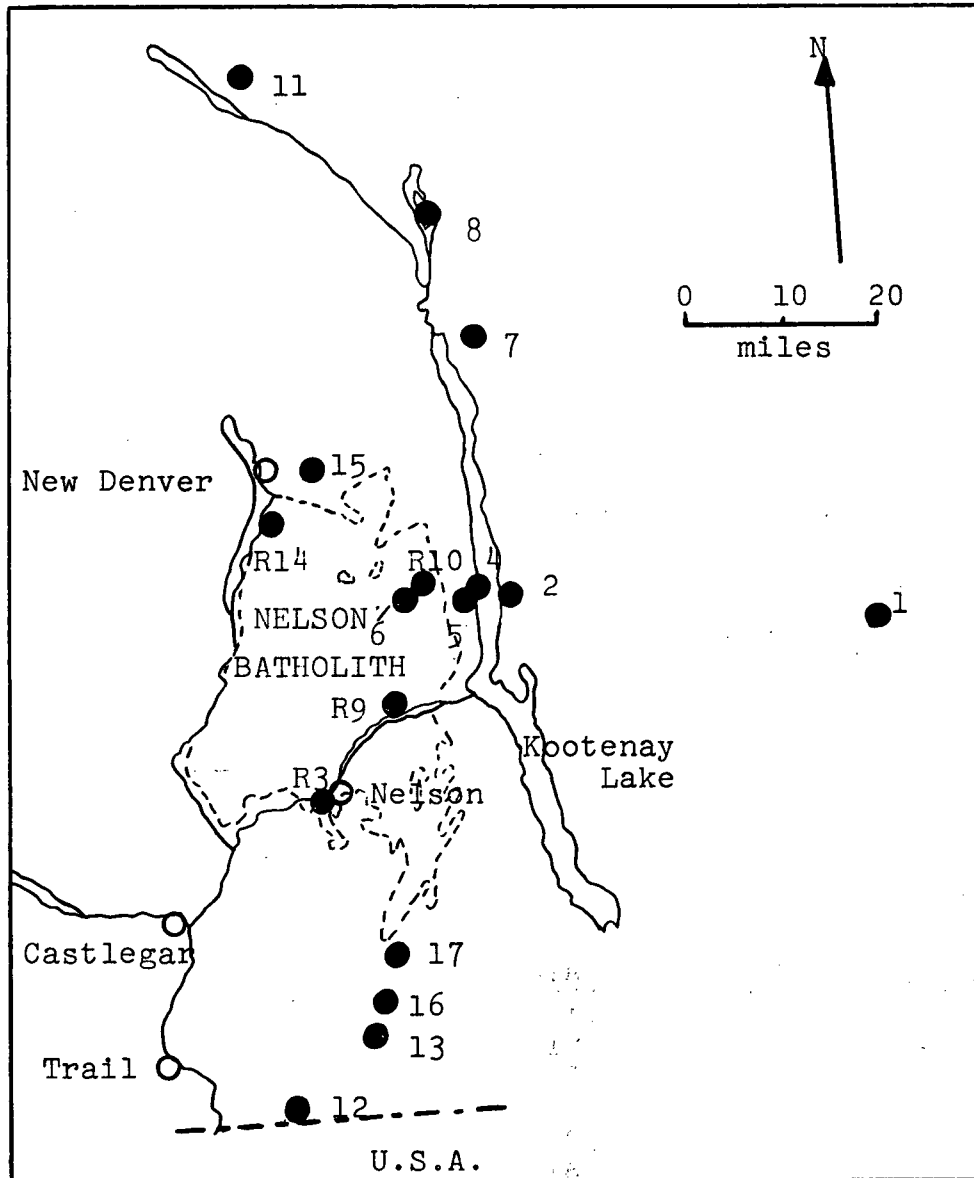


TABLE 3-3

ISOTOPIC COMPOSITION OF NELSON LEADS

Sample	Description	ppm lead	Pb ²⁰⁶ /Pb ²⁰⁴	Pb ²⁰⁷ /Pb ²⁰⁴	Pb ²⁰⁸ /Pb ²⁰⁴
R14	K-feldspar from porphyritic granite	50	19.466	15.812	39.348
R 3	K-feldspar from porphyritic quartz monzonite	40	19.076	15.756	39.043
R10	K-feldspar from pegmatite associated with foliated diorite	30	19.287	15.815	39.486
R 9	K-feldspar from porphyritic granite	40	19.066	15.711	39.078
Blue Star Mine	Galena		17.528	15.641	38.188
182 Lakeshore	Galena		17.682	15.649	38.631
294 Victor	Galena		18.802	15.757	39.368
295 Scranton	Galena		19.000	15.798	39.090
Bluebell 226	Bluebell galena data from		17.59	15.62	38.42
228	Kanasewich (1962a)		17.57	15.61	38.38
229			17.52	15.60	38.26
230			17.55	15.59	38.31
237			17.62	15.63	38.48

FIGURE 3-3 APPROXIMATE SAMPLE LOCATIONS, NELSON AREA,
BRITISH COLUMBIA



- | | |
|----------------------|---------------------------|
| 1. Sullivan Mine | R10. Pegmatite |
| 2. Bluebell Mine | 11. Mollie Mac Showing |
| R3. Quartz Monzonite | 12. Reeves Macdonald Mine |
| 4. Blue Star Mine | 13. Jersey Mine |
| 5. Lakeshore Showing | R14. Granite |
| 6. Scranton Mine | 15. Victor Mine |
| 7. Sal Showings | 16. H.B. Mine |
| 8. Duncan Mine | 17. Jackpot Showings |
| R9. Granite | |

TABLE 3-4

ISOTOPIC COMPOSITION* OF LEADS FROM THE KOOTENAY ARC
AND FROM SULLIVAN MINE

Sample	Pb ²⁰⁶ /Pb ²⁰⁴	Pb ²⁰⁷ /Pb ²⁰⁴	Pb ²⁰⁸ /Pb ²⁰⁴
318 Mollie Mac	18.495	15.836	38.70
300 Jersey Mine	19.266	15.918	39.87
288 Jersey Mine	19.258	15.921	39.82
286 HB Mine	19.250	15.915	39.85
284 Jackpot	19.134	15.886	39.62
293 Reeves Macdonald	19.192	15.907	39.72
291 Sal A Zone	19.529	15.937	40.15
282 Duncan Lake	19.555	15.944	40.26
321 Sullivan	16.638	15.658	36.623
323 Sullivan	16.639	15.653	36.582

*re-calculated from raw data of Sinclair

The origin of the Sullivan orebody is a subject that is continually debated. Sinclair (1964) suggested an epigenetic origin and a probable genetic relationship of the Sullivan ore fluids with the source magma of the Precambrian Moyie Intrusions. Others have suggested that a syngenetic origin more readily explains the conformable nature of the orebody. On the basis of analyses by Leech and Wanless (1962) and by Sinclair (1966), this large deposit contains lead of apparently uniform isotopic composition. In addition, the isotopic ratios are on the locus defined by leads from the stratiform deposits studied by Ostic, et al (1967). A single-stage model age of 1340 m.y. is calculated for the Sullivan lead. According to this model, this age gives the time of extraction of the lead from the source material, and, in addition, the probable time of mineralization at Sullivan.

Some of the Kootenay arc leads, however, do not fit the model proposed by Sinclair (1966). In particular, the new analyses of the four galenas from deposits associated with the Nelson batholith plot significantly below Sinclair's anomalous lead line (Figure 3-2). The Blue Star and Lakeshore samples appear to have slightly lower Pb^{207}/Pb^{204} ratios and slightly higher Pb^{206}/Pb^{204} ratios than Sullivan lead. Hence, a direct genetic relationship with the latter is precluded. In comparison with the present results, the isotopic abundances reported by Sinclair (1966) for the Lakeshore, Scranton, and Victor samples appear to be in error by about 0.75 per cent. The

least-squares line through these four ore-lead points has a slope of 0.1031 ± 0.0084 . This value is in good agreement with that obtained from Sinclair's data. Therefore, ore-leads associated with the Nelson batholith apparently have had a chronological history similar to that of leads in the Kootenay arc north and south of the batholith. However, the batholith leads do not incorporate a Sullivan-type component.

Significant variations in isotopic composition (± 2 per cent for the Pb^{206}/Pb^{204} ratio) were obtained for the feldspar leads from the batholith. Hence, complete mixing of lead isotopes did not occur when the batholith was formed. However, there is some evidence that partial mixing did take place. Rock samples R3 and R9, for example, are very similar in isotopic composition and are from the same area of the batholith. Sample R14, on the other hand, from the opposite side of the batholith, has a distinctly different isotopic composition. Moreover, it is significant that the general trend of the rock-lead points in Figure 3-2 is in a direction approximately parallel to the Sinclair anomalous lead line.

Five samples from the Bluebell mine, located on the east shore of Kootenay Lake about $2\frac{1}{2}$ miles east of Lakeshore, were analyzed in this laboratory by Kanasewich (1962a). Their isotopic compositions are similar to those obtained in the present study for the Blue Star and Lakeshore samples (Figure 3-2, Table 3-3). There are, however, significant Pb^{207}/Pb^{204} variations among these seven samples.

It seems likely that the leads in the Nelson rocks and the leads in the associated orebodies (including Bluebell) have developed in the same source rocks during the same time interval. The slope of the weighted least-squares line through the 13 points in Figure 3-2 (4 rock-leads, 4 ore-leads, 5 Bluebell leads) is 0.1028 ± 0.0094 . This is in excellent agreement with the value obtained above (0.1031) when only the four ore-leads were considered, and also with the value calculated from Sinclair's data (0.1022). The Pb^{207}/Pb^{204} variations among the ore-leads are again observed in the rock-lead data. The resultant scatter about the least-squares line suggests that the leads contain an isotopically heterogeneous common lead component.

Several authors (for example, Schofield, 1920, p.36) have suggested that the ore deposits in the Nelson area are genetically related to granitic bodies. Irvine (1957, p.97), for example, concerning the origin of Bluebell ore states:

"Ore deposition is probably related to one or another of the granitic bodies which surround the mine, but so far no direct evidence links the deposits to any one body".

Lead isotope data now suggest that the Bluebell ore-leads and the Nelson rock-leads were derived from the same source rocks. Cairnes (1934) believed that mineral deposits in the Slocan district (for example, Victor and Scranton) were formed from ore solutions derived from the Nelson batholith. Hedley and Fyles (1956), however, point out that "no evidence has been

found that any one deposit is genetically related to a specific part of the [Nelson] batholith". Lead isotope abundances suggest that individual deposits cannot be related to a specific part of the batholith on a geographical basis. For example, lead from Scranton mine is isotopically similar to rock-leads R3 and R9 (Table 3-3), but Scranton is geographically closer to rock sample R10 which has a distinctly different isotopic composition. This result was not unexpected since a given ore deposit was not formed until the corresponding part of the batholith had consolidated, and therefore the ore-lead and nearby rock-lead probably did not originate in the same region of the source rock system.

Mineralization in the Nelson area is believed to have occurred shortly after the emplacement of the Nelson batholith (Hedley, 1952). The batholith was emplaced approximately 150 million years ago on the basis of the K-Ar age determinations recently carried out by Khanh (in preparation) on biotites and hornblendes from the Nelson rocks. From equation (3-1) the time t_1 is 1620 ± 170 m.y. when $R = 0.1028 \pm 0.0094$ and $t_2 = 150$ m.y. Hence the source rocks of the anomalous leads are at least 1600 million years old.

Sinclair (1966) has suggested that either Lower Purcell (Beltian) rocks or rocks of the Churchill geological province could have been the source of the radiogenic

component of Kootenay arc leads. He points out that Lower Purcell strata are at least 1500 million years old since they are intruded by Moyie sills, dikes, and stocks which have K-Ar ages of about 1500 m.y. (Hunt, 1961). Recently, however, Obradovich and Peterman (1967) have reported Rb-Sr whole-rock ages for Beltian rocks from Montana which suggest that there were three distinct episodes of sedimentation at approximately 1300, 1100 and 900 m.y. ago. These sediments rest on a metamorphosed basement that has been dated at 1600-1850 m.y., apparently the time of major Churchill orogeny (Goldich, et al, 1966). If the K-Ar age of 1500 m.y. for the Moyie Intrusions is not accepted, then the maximum age of the Lower Purcell series may be only about 1300 m.y. Therefore, the source rocks of the anomalous leads may be the metamorphic rocks of the Churchill province or perhaps a mixture of Churchill and Lower Purcell rocks.

All of the Kootenay arc leads contain a single radiogenic component developed between 1600 m.y. ago and 150 m.y. ago, possibly in rocks of the Churchill province. Then, about 150 m.y. ago, ore deposits were formed north and south of the Nelson batholith that apparently contain mixtures of this radiogenic lead and Sullivan-type lead. At the same time the Nelson batholith and associated ore deposits were formed which, however, did not incorporate significant amounts of Sullivan-type lead. They did incorporate a common lead component (perhaps derived from various mineral phases

in the Churchill rocks) that is distinctly different in isotopic composition from the Sullivan lead. Figure 3-2 shows clear evidence for a direct genetic association between the trace lead in the batholith and the ores in its immediate proximity.

The isotopic composition of the common lead component in the rocks of the batholith can be calculated if it is assumed that this lead is the product of a single, closed system. The lower anomalous lead line in Figure 3-2 intersects the 1600 m.y. isochron at the point (16.05, 15.47) which corresponds to a μ -value of 8.85. It is possible, of course, that this common lead component is not a single-stage lead, but rather was produced in a number of uranium-lead systems (for example, in reconstituted crustal systems). This anomalous lead line intersects the locus of the Ostic-Russell-Stanton stratiform ore-leads ($\mu = 9.0$) at a time greater than 2000 m.y. Hence, any multi-stage model based on this growth curve requires leads older than 2000 m.y. The presence of rocks of this age in the Nelson area appears less likely than the presence of rocks with an average age of about 1600 m.y. Therefore, the existence of a 1600 m.y. old primary lead is postulated. The scatter about the lower anomalous lead line (Figure 3-2) may be due to small variations in the isotopic composition of the 1600 m.y. old common lead. It may be, however, that some of the scatter is also due to contamination of these rocks and ores by small amounts

of Sullivan-type lead.

Summary and Preferred Interpretation

All of the Kootenay arc leads contain a radiogenic component which developed between 1600 m.y. ago and 150 m.y. ago. At least some of the ore-leads north and south of the Nelson batholith are genetically related to Sullivan-type primary lead ($\mu = 9.0$). On the other hand, rock-leads from the Nelson batholith and ore-leads from deposits closely associated with the batholith contain a different common lead component. This common lead could be derived from a single-stage system characterized by a μ -value of about 8.8.

The analyses reported in this thesis provide, for the first time, clear evidence of a genetic relationship between ore deposits and granitic rocks.

Incomplete mixing of lead isotopes occurred when the Nelson batholith formed.

West-Central New Mexico

The isotopic ratios of the Bosque rock-lead are given in Table 3-5 along with sample descriptions and isotopic abundances for the 8 ore-leads studied by Blenkinsop and Slawson (1967). These data are plotted in Figure 3-4.

The slope of the weighted least-squares line (York, 1966) through 7 of the ore-leads (omitting the Bosque sample)

TABLE 3-5

ISOTOPIC COMPOSITION OF NEW MEXICO LEADS

Sample	Sample Description	Observed Isotopic Abundances*		
		Pb ²⁰⁶ /Pb ²⁰⁴	Pb ²⁰⁷ /Pb ²⁰⁴	Pb ²⁰⁸ /Pb ²⁰⁴
501 La Bonita	vein deposit in Precambrian granite	25.27	16.34	42.53
504 Hansonburg	deposit associated with silicified limestone	22.26	16.05	40.50
502 Box Canyon	vein deposit in fault contact of Precambrian granite with Paleozoic limestone	20.64	15.89	39.80
508 Kelly	vein and replacement deposits in limestone adjacent to a stock	18.74	15.73	38.82
507 Linchburg	contact pyrometasomatic deposit in limestone	18.55	15.74	38.72
532 Orogrande		18.92	15.74	39.19
530 Modoc		18.21	15.68	39.07
505 Bosque del Apache ore-lead	contact pyrometasomatic deposit	16.19	15.46	36.03
Bosque del Apache rock-lead	potassium feldspar from granite, ~ 20 ppm lead	24.60	16.01	41.31

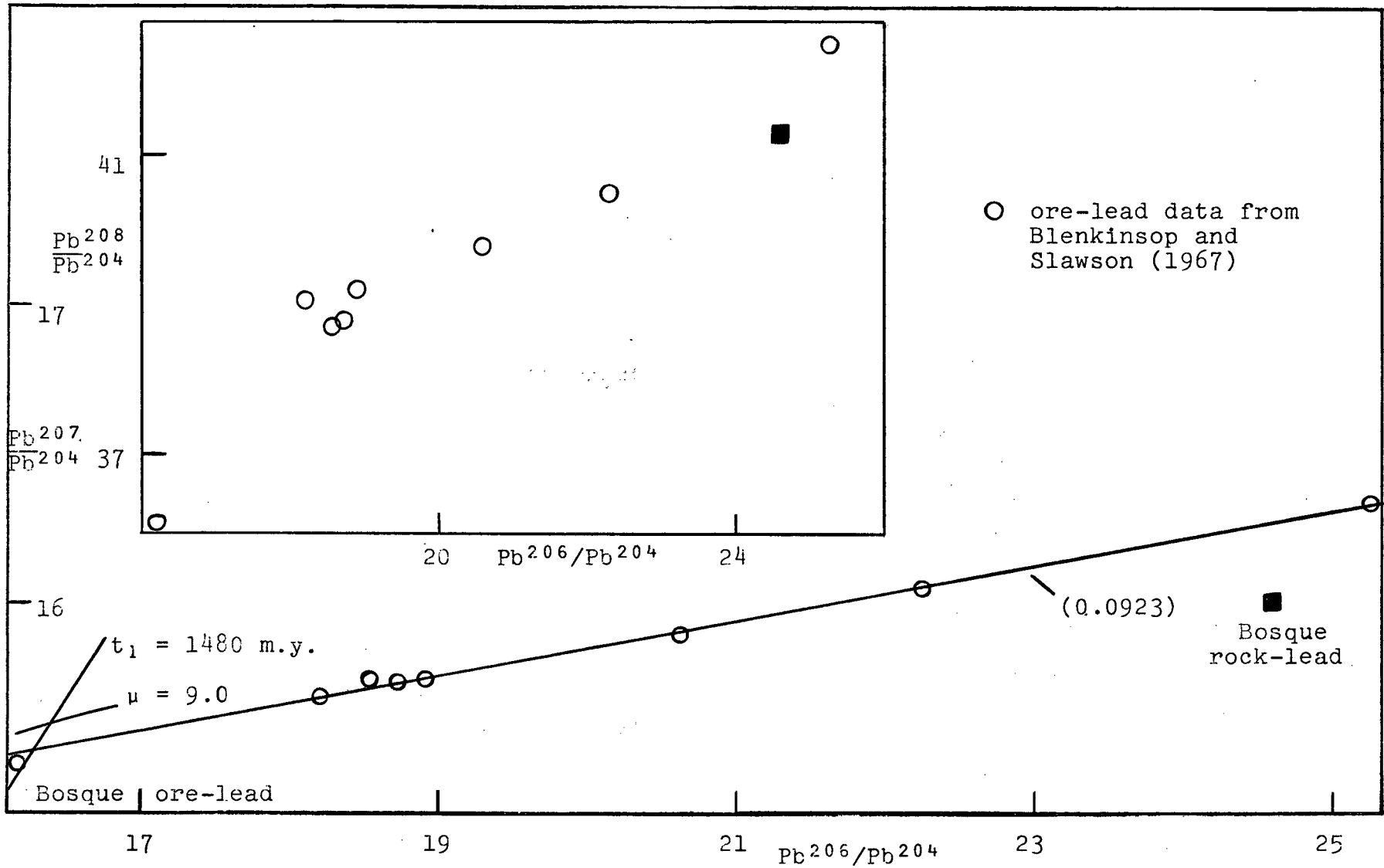
*Ore data from Blenkinsop and Slawson (1967)

in Figure 3-4 is 0.0923 ± 0.0021 . If the time of anomalous lead mineralization, t_2 , is 30 m.y. (on the basis of K-Ar ages by Weber and Bassett, 1963), the time t_1 from equation (3-1) is 1480 ± 40 m.y. This value for the age of the source rocks of the anomalous leads is in good agreement with concordant U/Pb ages of 1450 m.y. recently reported by Tilton and Grunenfelder (1967) for rocks from the Sandia Mountains to the northeast.

The slope of the line in Figure 3-4 is 0.0941 ± 0.0022 if the Bosque sample is included in the calculation. Therefore, a genetic relationship between the Bosque sample and the other ore-leads is not precluded despite the fact that the "mineralogy and appearance of this deposit suggest a distinctly different condition of mineralization from that which resulted in the other deposits sampled" (Slawson and Austin, 1962). The single-stage model age and the apparent μ -value calculated for the Bosque ore-lead are 1500 m.y. and 8.8 respectively. If the Bosque sample is not considered, the least squares line in Figure 3-4 intersects the primary isochron $t_1 = 1480$ m.y. at a point which corresponds to a μ -value of approximately 8.8 (5). Hence, if the lead in the source rocks 1480 m.y. ago was the product of a single-stage system, this system is characterized by a μ -value lower than 9.0, the value associated with certain stratiform ores.

The Bosque rock-lead and the Bosque ore-lead are

FIGURE 3-4 ISOTOPIC ABUNDANCES OF NEW MEXICO LEADS



very different in isotopic composition. In addition, the rock-lead does not plot on the anomalous lead line in Figure 3-4; hence its isotopic composition cannot be explained by the two-stage model postulated above for the ore-leads. It is, however, not possible to preclude the possibility that the Bosque ore-lead is genetically related to the Bosque rock-lead; that is, that they were derived from the same source material. The isotopic composition of the rock-lead was subsequently altered by the addition of large quantities of radiogenic lead from the crust, while the ore-lead appears to be relatively uncontaminated by crustal lead. It is noteworthy in this regard that the Bosque rock-lead and the ore-lead in a nearby vein deposit (La Bonita, 501) are similar in isotopic composition (Table 3-5).

The New Mexico ore-leads that were studied by Blenkinsop and Slawson are genetically related to a 1500 m.y. old common lead. If interpreted by a single-stage model, this lead has an isotopic composition similar to that of the Bosque ore and is characterized by a μ -value lower than the one associated with the stratiform ores studied by Ostic. The Bosque rock-lead does not belong to the above suite of ore-leads. However, the true significance of the isotopic abundances of this lead cannot be determined without analyses of additional samples.

Broken Hill, Australia

The lode pegmatites at Broken Hill appear concordant with the orebodies and with the surrounding gneisses and are, in general, closely associated with the main lode galena. It is therefore very difficult to obtain potassium feldspar separates that are entirely free of ore-lead. The feldspar analyzed in the present study was first hand-picked from cleavage fragments and ground to a very fine powder in an agate mortar. The sample was then washed and the K-feldspar was floated in an acetone-bromoform solution. This feldspar was subsequently leached for 24 hours in warm 6 N HCl. Since at this stage a microscopic examination revealed no visible galena, the remaining lead in the sample was separated by the volatilization technique and analyzed on the mass spectrometer.

The sample contained approximately 2000 ppm lead of isotopic composition identical to that of the main lode galena (Table 3-6). This result was not unexpected since previous authors (Andrews, 1922; Stillwell, 1959) have suggested that a close genetic relationship exists between the lode pegmatites and the orebodies. Rb-Sr analyses by Pidgeon (1967) of whole rocks and potassium feldspars from the lode pegmatites give an approximate age of 1650 m.y. for these rocks ($\lambda = 1.39 \times 10^{-11} \text{y.}^{-1}$), in good agreement with the model lead age of 1600 m.y.

TABLE 3-6

OBSERVED ISOTOPIC COMPOSITION OF BROKEN HILL LEADS

Sample	Description	$\frac{\text{Pb}^{206}}{\text{Pb}^{204}}$	$\frac{\text{Pb}^{207}}{\text{Pb}^{204}}$	$\frac{\text{Pb}^{208}}{\text{Pb}^{204}}$	Lead ppm
1*	Main lode galena	16.116	15.542	36.068	
70	ore-leads from	17.40	15.69	38.54	
45	Thackaringa-	17.81	15.71	38.62	
68	type deposits	17.89	15.72	38.87	
67		17.95	15.74	39.09	
69		17.97	15.75	38.93	
66		18.02	15.75	38.93	
65		19.55	15.96	39.85	
Mundi Mundi granite	K-feldspar	39.709	18.221	51.967	15
BH6, BH9	K-feldspar from Upper granite gneiss	17.029	15.642	37.328	30
Lode pegmatite	K-feldspar	16.108	15.542	36.011	2000

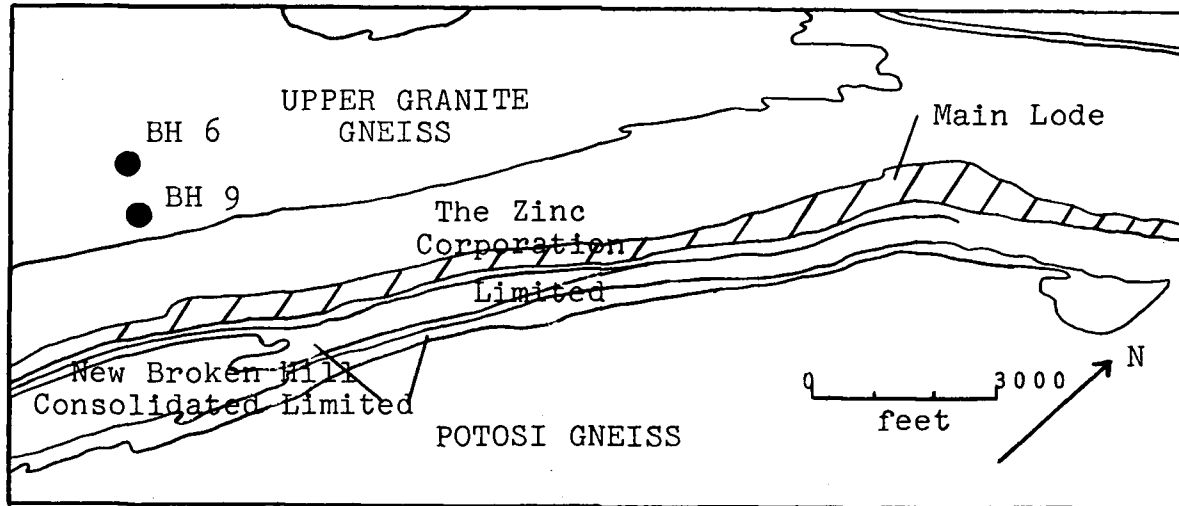
* Isotopic Abundances from Kollar, et al (1960).

**Isotopic Abundances from Russell, et al (1961).

Since the samples from the Mine Sequence gneisses were not directly associated with the lode material, routine mineral separation procedures were adequate. It was not possible for the writer to analyze the feldspar samples individually since only a limited amount of each (6 - 11 grams) was available. In order to obtain sufficient lead for one adequate mass spectrometer analysis, two samples from the Upper Granite Gneiss (BH 6 and BH 9) were combined and the isotopic abundances of the composite sample were determined. Sample BH 9 was collected from a bore core at a depth of 146 feet and at a location given by the mine coordinates 9500' S, 1000' E. BH 6 was collected at the surface at 9500' S, 300'E. Hence the separation of the two samples is only about 700 feet, a negligible distance compared to the scale of the Broken Hill mine area (Figure 3-5).

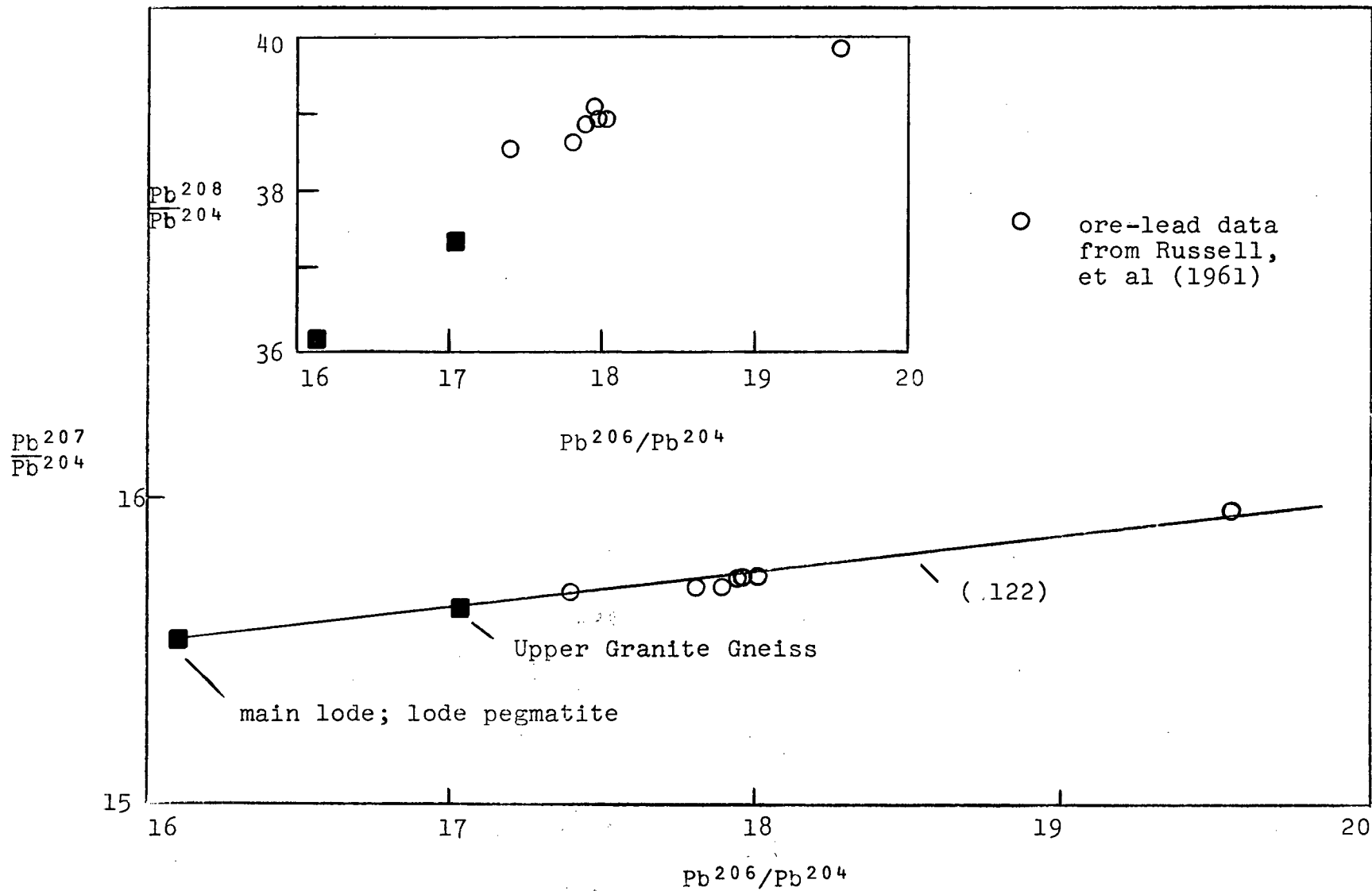
The isotopic ratios for this composite sample and for the Broken Hill ore-leads are given in Table 3-6 and are plotted in Figure 3-6. The feldspar lead plots on the anomalous lead line defined by the ore-leads, or, in other words, the lead from the gneiss has had a history similar to that of the Thackaringa-type ores. The rock-lead is therefore genetically related to lead of the main lode type and, in addition, contains a radiogenic component generated in source rocks between 1600 m.y. ago and 500 m.y. ago.

FIGURE 3-5 SURFACE GEOLOGICAL PLAN
BROKEN HILL MINE AREA*
AND APPROXIMATE SAMPLE
LOCATIONS



*from Lewis, Forward, and Roberts (1965)

FIGURE 3-6 ISOTOPIC ABUNDANCES OF BROKEN HILL LEADS



Pidgeon (1967) has reported a mean whole-rock Rb-Sr age of 1640 ± 40 m.y. ($\lambda = 1.39 \times 10^{-11} \text{y.}^{-1}$) for three of the gneiss rock units (sillimanite, Potosi, Alma) from the Mine Sequence. The Alma Gneiss is located about a mile away from the main lode but has suffered the same high-grade (granulite facies) metamorphism. In addition, Pidgeon has calculated an age of 1750 m.y. for the Upper Granite Gneiss. This age is based on only four whole-rock samples and he believes that the Upper Granite may not be significantly older than the other three types. Pidgeon further suggests that the gneiss whole rock age of 1640 ± 40 m.y. gives the time of the high-grade metamorphism in the Broken Hill area and that "almost complete redistribution of strontium isotopes occurred within a rock unit at this time". In Palaeozoic time, these rocks were affected by a relatively mild regional metamorphism as indicated by the 500 m.y. K-Ar and Rb-Sr ages reported by Richards and Pidgeon (1963) and by Pidgeon (1967). Pidgeon (1967) has, in addition, interpreted the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratios calculated for the gneiss units to give the original age of sedimentation or emplacement of the Willyama rocks. The maximum age of deposition was estimated to be 1820 ± 100 m.y. However, this result is not very reliable principally because it depends on the assumption that each of the gneiss units has remained a closed system with respect to rubidium and strontium since the time of original deposition. It is

therefore concluded that when all of the assumptions and inherent uncertainties in the lead and strontium models are considered (for example, in the age of the earth and in the rubidium decay constant), there are no demonstrable differences among the model lead age of 1600 m.y., the 1640 m.y. whole rock Rb-Sr age of the gneisses and the 1820 m.y. maximum age of deposition.

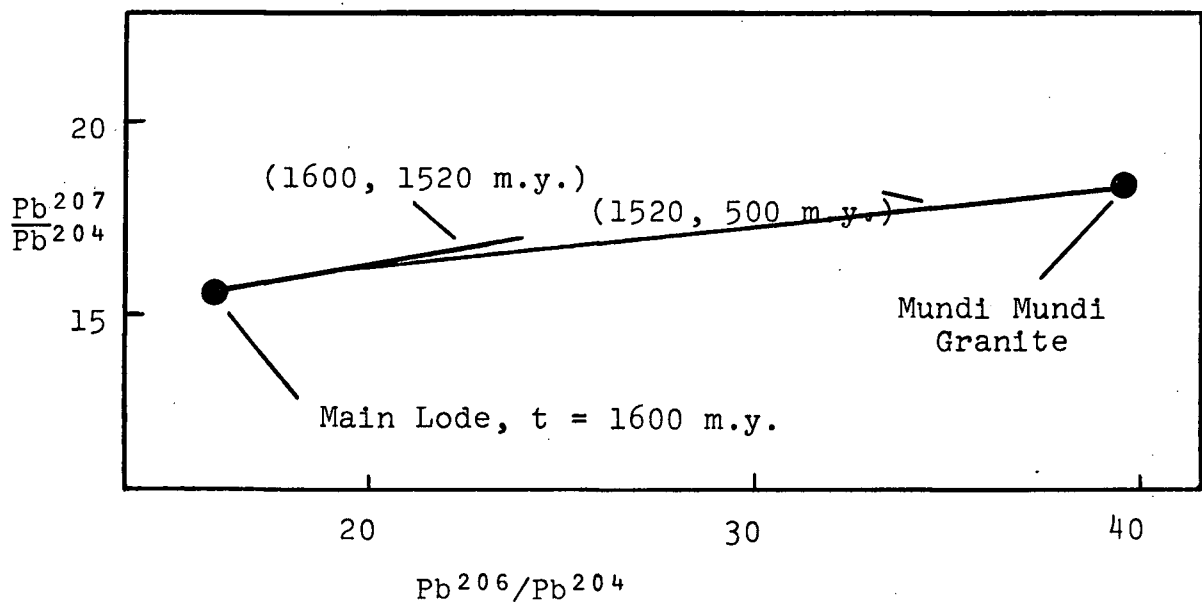
On the assumption that the one composite sample from the Upper Granite Gneiss is broadly representative of the whole body, the results from the present study suggest that the lead that was incorporated into these rocks at the time of their formation (approximately 1600 m.y. ago) had an isotopic composition very similar to that now observed in the main lode orebody. Radiogenic lead generated in the uranium-rich phases of the gneiss was mixed with this primary lead and incorporated into the potassium feldspars at the time of the 500 m.y. metamorphism. In situ uranium decay in the potassium feldspars during the past 500 m.y. should be negligible.

The genetic relationship observed between trace lead in the gneiss and the lead from the main lode suggests that the Broken Hill orebody had a syngenetic origin. If, for example, barren sediments were metamorphosed to form the gneiss, and the ore-lead was introduced at a later time, one would not expect to observe a large ore-lead component in the gneissic rocks unless significant isotopic exchange

occurred between the gneiss and the ore solutions.

The observed isotope ratios for the potassium feldspar from the Mundi Mundi granite are given in Table 3-6. Pb^{207}/Pb^{204} and Pb^{206}/Pb^{204} ratios are plotted in Figure 3-7. The whole-rock Rb-Sr age for these granites is 1520 ± 40 m.y. (Pidgeon, 1967; $\lambda = 1.39 \times 10^{-11} y.^{-1}$), and on the basis of K-Ar and Rb-Sr biotite ages (Richards and Pidgeon, 1963; Pidgeon, 1967) these rocks were also disturbed by the mild regional metamorphism about 500 million years ago.

FIGURE 3-7 ISOTOPIC COMPOSITION OF LEAD FROM THE MUNDI MUNDI GRANITE



A three-stage model is postulated to explain the observed lead isotope abundances of this sample. (The above two-stage model is considered less probable since it would not reflect the well established 1520 m.y. event.) The initial stage began about 1600 m.y. ago in a rock system that contained lead of the main lode type, uranium and thorium. The lead isotope ratios grew in this system for about 80 m.y. to points along the line defined by the two times 1600 and 1520 m.y. (Equation 3-1, Figure 3-7). Then, about 1520 m.y. ago the Mundi Mundi granite was formed. Radiogenic lead was produced by the decay of uranium and thorium in the granite between the times 1520 m.y. ago and 500 m.y. ago, and was incorporated into the potassium feldspars at the time of the 500 m.y. metamorphism. The third stage in the development, the in situ uranium decay in the feldspars during the past 500 m.y., is assumed to be inconsequential. The precursor of the granite, according to the model illustrated in Figure 3-7, apparently had an average μ -value of approximately 100. The average value in the granite during the second stage was about 120.

The model proposed to explain the observed lead isotope abundances in the Mundi Mundi granite is consistent with information provided by previous lead isotope studies and by K-Ar and Rb-Sr geochronology. Since only one sample of granite was available, analyses of samples from other localities are desirable.

It is concluded from this study that the lode pegmatites and the orebodies have had a common origin. Probably all of the granitic and gneissic rocks within 20 miles of the main orebody contain a common lead component that is identical to the 1600 m.y. old lead of the main lode type. In addition, these rocks contain a radiogenic component generated between about 1600 m.y. ago and 500 m.y. ago. These two components were mixed when the rocks were mildly disturbed at the time of the 500 m.y. regional metamorphism. The above interpretation is consistent with previous lead isotope, Rb-Sr and K-Ar studies.

CHAPTER 4

CONCLUSIONS

The objective of this thesis was to provide definitive evidence relative to the existence of systematic differences between the isotopic abundances of lead from rocks and lead from certain stratiform ores. Interlaboratory differences and large analytical uncertainties have previously precluded a clear answer to this question. Using an identical experimental technique for both rocks and ores, the writer has analyzed samples from Balmat (New York), Nelson (British Columbia), Broken Hill (New South Wales), and from West-Central New Mexico. The precision of analyses (approximately 0.15 per cent at the 95 per cent confidence level) was sufficient to resolve the differences in question.

A clear separation of rock-lead and ore-lead patterns was resolved in the cases of Balmat and Nelson. In both localities, some ores were apparently derived from a primary system for which the calculated present-day value of the U^{238}/Pb^{204} ratio (the μ -value) is 9.0. This agrees identically with the value for the stratiform deposits studied by Ostic, et al (1967). However, a different primary system with a μ -value of 8.7 to 8.8₅ is required to explain the observed abundances of feldspar leads from Balmat and Nelson and ore-leads from New Mexico.

The difference between these μ -values is significant, about five times the analytical uncertainty, and must be

explained by any valid geophysical model. However, the absolute numerical values quoted may be two or three per cent high because no correction for mass spectrometer discrimination has been made. For a gas-source mass spectrometer, the discrimination can be estimated from the laws of gas flow, and is constant if operating conditions are reproduced.

All of the rock-leads and ore-leads from the Broken Hill district reflect only the existence of the higher μ system. Lead from this system (that is, isotopically of the main lode type) was apparently incorporated into the granitic and gneissic rocks at the time of their formation. Lead characteristic of the lower μ system was not detected, even in the case of rocks 20 miles distant from the main orebody.

For each of the Balmat, Nelson, and New Mexico suites, it is assumed that a two-stage model adequately describes the observed isotopic variations. (For the feldspar leads, a third stage corresponding to in situ uranium decay is neglected.) In other words, it is assumed that the observed anomalous lead lines can be interpreted as the addition of radiogenic lead to lead produced in a single, closed environment. Adequate independent age information from these three areas might help to verify the above model as it has in the case of the Broken Hill leads. However, the generally good fit of the data to the anomalous lead lines suggests that the two-stage model is a reasonable

approximation. Since the calculated μ -values are rather insensitive to small deviations from the assumed model, they are unlikely to be significantly in error.

It is therefore the conclusion of this thesis that the primary lead system required to explain the observed lead isotope abundances of certain stratiform ore deposits is not applicable to rock-leads and to ore-leads in general. Apparent μ -values for the stratiform deposits studied by Ostic, et al (1967) are given in Table 4-1 along with the values obtained in the present study for the ore-leads from Balmat, N.Y. and from the Sullivan mine, B.C. The average μ -value is 8.96 ± 0.13 . There is evidence to suggest, however, that the samples from Manitouwadge and from Read Rosebery have been significantly contaminated by radiogenic crustal lead (Ostic, et al, 1967). If these samples are omitted from the calculation, the average μ is 9.00 ± 0.05 . It is perhaps significant that while the average μ -value for these deposits is significantly higher than the average obtained in this study for rock-leads (that is, about 8.75), the range in values for each group (8.70 - 8.85 for the rock-leads and 8.93 - 9.09 for the stratiform ore-leads) suggests that the two distributions may overlap. An acceptable geophysical model must, however, explain the apparent existence of two distinct distributions of μ -values.

Ostic, et al (1967), following the earlier work of Stanton and Russell (1959), suggest that the leads from

TABLE 4-1

APPARENT URANIUM/LEAD RATIOS FOR LEADS FROM
CERTAIN STRATIFORM DEPOSITS*

Sample	$\mu \equiv (U^{238}/Pb^{204})_{t=0}$	
Mount Isa	9.09	
Sullivan mine	9.05	
Cobar, C.S.A.	9.00	
Bathurst	9.00	
Balmat	9.00	
Broken Hill	8.98	
Captain's Flat	8.98	
Cobar, lower horizon	8.97	
Hall's Peak	8.93	
Read Rosebery	8.93	
Manitouwadge	8.61	
Mean \pm std dev.	8.96 \pm 0.13	all samples
	9.00 \pm 0.05	excluding Manitouwadge, Read Rosebery

*All data, except Balmat and Sullivan from Ostic, et al (1967).

these stratiform deposits originated in a primary system that is probably subcrustal. The leads are transported to the crust by island arc volcanism and deposited syngenetically in associated sediments without significant contamination by radiogenic leads from crustal rocks.

Recent geophysical observations have given strong support to theories that postulate a spreading of the sea floors as a result of convection currents in the upper mantle (see, for example, Vine, 1967). Armstrong (1967) has suggested a steady-stage model based on these ideas to explain the evolution of lead isotope ratios in the earth. In this model, sialic material continuously eroded from the continents forms oceanic sediments that are subsequently carried down into the mantle by means of convection currents. This down-welling of crustal material takes place along volcanic island arcs and marginal trenches. For example, Oliver and Isacks (1967) have shown from seismological studies that in the Tonga-Fiji region intermediate and deep earthquake foci occur in a section of the lithosphere (about 100 km thick) that has been thrust 600-700 km into the mantle. Armstrong suggests that a degree of isotopic equilibration takes place between this crustal section and the upper mantle before the material is returned to the surface in the form of volcanic matter. Crustal material has been continuously recycled in this manner through the upper mantle, and the continental volumes have therefore remained constant since

the time very early in the earth's history (probably less than 100 m.y. after formation) when differentiation into core, mantle, and crust was completed. The continents themselves, however, are frequently broken up, moved and fused together by the convection currents in the mantle. Armstrong defines the upper mantle as the mantle above 500 km, the depth at which convective mixing ceases. Recent calculations on the viscosity of the mantle by McConnell (1967) suggest that convection must be negligible below about 200 km. This correction, if valid, will not, however, have a bearing on the qualitative aspects of the Armstrong model.

From abundance data for various rock types believed to be representative of crustal and upper mantle material, Armstrong has calculated an apparent μ -value of 8.5 for the mixed crust-plus-upper-mantle system. This value, derived from only a semi-quantitative model, is in remarkably good agreement with values determined by lead isotope methods. Therefore, such a long-term mixing of crustal and upper mantle material appears to be a possible mechanism to explain the evolution of lead isotopes in the earth.

The rather special status of certain stratiform ore deposits is not, however, immediately explained by this mixing model. Armstrong (1967) believes that the lead from these deposits represents the "best mixed crust plus upper mantle lead". It is of interest to point out here that ore-leads from South Africa, recently analyzed in this laboratory

by J. Blenkinsop and reported by Ulrych, et al (1967), apparently originated in a primary system with a μ -value of about 9.5. This value, when averaged with the lower value obtained in the present study for rock-leads (≈ 8.8) gives some support to this 'best mixed' model for stratiform ores. (It should be noted that μ -values calculated for these very old, > 3000 m.y., South African leads are sensitive to the uncertainties in the values of the primeval ratios, a_0 and b_0 .)

Armstrong considers that the lead in modern pelagic sediments (including manganese nodules) plots on an extension of the stratiform ore-lead growth curve ($\mu = 9.0$). This lead, produced by the chemical weathering of continental crustal rocks, is well mixed and transported to marine sediments by sea water. It therefore approximates an average crustal-plus-upper-mantle lead according to the Armstrong model. Isotopic analyses of lead in pelagic sediments have been reported by Chow and Patterson (1959, 1962), but until more precise analyses of such samples are made and inter-laboratory differences removed, one cannot be sure that they lie on an exact extension of the stratiform growth curve. Therefore, the mixing model as proposed by Armstrong to account for the origin of these stratiform deposits requires further experimental verification.

If a 'best mixed' model for these leads is rejected, then either a 'preferentially mixed model' or a 'homogeneous

source' model must be considered. Ostic, et al (1967) propose the latter and suggest a subcrustal source. This model would be rejected on the basis of the abundance data compiled by Armstrong since the μ -value for the upper mantle alone (≈ 6.4) is much too low. However, Armstrong's model for the upper mantle is based on the observed abundances of uranium and thorium in oceanic tholeiites, and Ulrych (in press) has argued that these rocks are the result of a fairly recent differentiation (in general, less than 250 m.y. ago), and hence are not truly representative of upper mantle material. Therefore, the homogeneous source model cannot be ruled out.

A preferential but thorough mixing in an island arc, marginal trench environment of sialic crustal material ($\mu \approx 10.4$; Armstrong, 1967) with material from the upper mantle also appears to be a possible mechanism capable of producing the observed abundances of the stratiform ores. It is of interest to note that lead from White Island, New Zealand has an apparent μ -value of 8.89 (Ostic, et al, 1967). White Island is an active andesitic volcano located on the margin of a trench that is associated with many of New Zealand's deep-focus earthquakes. This possible mixture of stratiform ore-lead ($\mu = 9.0$) and granitic rock-lead ($\mu = 8.8$) can be interpreted to give support to the above mixing model.

Zartman (personal communication, 1967) has recently suggested a model that attempts to explain the observed

abundances of 1000 m.y. old leads solely on the basis of crustal phenomena. In terms of this model, a more or less complete melting of crustal material down to a depth of about 35 km occurred at this time and the lead isotope ratios were partially homogenized. Zartman would produce the stratiform ore deposits by preferential melting and homogenization of the upper relatively uranium-rich sections of this crustal block. Previous authors (Alpher and Herman, 1951; Shaw, 1957) have agreed that an efficient mixing of continental material can provide the apparently uniform source that is required to explain the observed abundances. Calculations carried out by Russell, et al (1966) emphasize the fact that a very thorough mixing of heterogeneous crustal systems is required in order to produce leads that can be interpreted by means of a single-stage model.

It is clear from the above discussion that there exists a wide choice of possible models and mechanisms to explain the evolution of lead isotopes in the earth. On the basis of data presently available, none of these appear to be entirely satisfactory. The contribution of this thesis is to prove for the first time that there is a significant difference between the primary lead system associated with certain stratiform ore deposits and the one apparently associated with granitic rocks, and to suggest that this finding has important geophysical consequences.

BIBLIOGRAPHY

- Alpher, R.G. and R.C. Herman. The primeval lead isotope abundances and the age of the earth's crust. *Phys. Rev.*, 84, 1111 (1951)
- Andrews, E.C. Geology of the Broken Hill district. *Mem. Geol. Surv. N.S.W.*, 8, 1 (1922)
- Armstrong, R.L. A model for Sr and Pb isotope evolution in a dynamic earth. Privately distributed manuscript, Geology Department, Yale University (1967)
- Baskova, Z.A. and G.I. Novikov. The evolution of small amounts of Pb by a reducing calcination in vacuum. *Geochemistry*, 678 (1957)
- Blenkinsop, J. and W.F. Slawson. Geophysical evidence of the Zuni Lineament. *Earth and Planetary Science Letters*, accepted for publication.
- Bonelli, E.J. and H. Hartmann. Determination of lead alkyls by gas chromatography with the electron capture detector. Paper presented to Gulf Coast Spectroscopic Group, Baton Rouge, Louisiana (1963)
- Cairnes, C.E. Slocan mining camp, British Columbia. *Geol. Surv. Can. Mem.* 173 (1934)
- Carruthers, D.S. and R.D. Pratten. Stratigraphic succession and structure in Zinc Corp. Ltd. and New Broken Hill Consolidated Ltd., Broken Hill, N.S.W. *Econ. Geol.*, 56, 1088 (1961)
- Catanzaro, E.J. Triple-filament method for solid-sample lead isotope analysis. *J. Geophys. Res.*, 72, 1325 (1967)
- Chow, T.J. and C.C. Patterson. Lead isotopes in manganese nodules. *Geochim. et Cosmochim. Acta*, 17, 21 (1959)
- Chow, T.J. and C.C. Patterson. The occurrence and significance of lead isotopes in pelagic sediments. *Geochim. et Cosmochim. Acta*, 26, 263 (1962)
- Cooper, J.A. and J.R. Richards. Lead isotopes and volcanic magmas. *Earth and Planetary Science Letters*, 1, 259 (1966)
- Doe, B.R. Relationships of lead isotopes among granites, pegmatites, and sulfide ores near Balmat, N.Y. *J. Geophys. Res.*, 67, 2895 (1962)

- Doe, B.R. Distribution and composition of sulfide minerals at Balmat, New York. *Geol. Soc. Amer. Bull.*, 73, 833 (1962a)
- Doe, B.R., Tilton, G.R. and C.A. Hopson. Lead isotopes in feldspars from selected granitic rocks associated with regional metamorphism. *J. Geophys. Res.*, 70, 1947 (1965)
- Doe, B.R. The bearing of lead isotopes on the source of granitic magma. *J. Petrol.*, 8, 51 (1967)
- Doe, B.R. and R.I. Tilling. The distribution of lead between coexisting K-feldspar and plagioclase. *Amer. Mineral.*, 52, 805 (1967)
- Doe, B.R., Tatsumoto, M., Delevaux, M.H. and Z.E. Peterman. Isotope-dilution determination of 5 elements in G-2 (granite), with a discussion of the analysis of lead. U.S. Geol. Surv. Prof. Paper 575B (1967)
- Fairbairn, H.W., Hurley, P.M. and W.H. Pinson. Initial $\text{Sr}^{87}/\text{Sr}^{86}$ and possible sources of granitic rocks in southern B.C. *J. Geophys. Res.*, 69, 4889 (1964)
- Goldich, S.S., Lidiak, E.G., Hedge, C.E. and F.G. Walthall. Geochronology of the midcontinent region, United States. *J. Geophys. Res.*, 71, 5389 (1966)
- Hedley, M.S. Geology and ore deposits of the Sandon area, Slocan mining camp, British Columbia. *B.C. Dept. Mines Bull.*, 29 (1952)
- Hedley, M.S. and J.T. Fyles. Localization of lead-zinc ore in the Kootenay arc. Paper presented to Pacific Northwest Regional Conference, Amer. Inst. Min. Eng., Seattle, Washington (1956)
- Hunt, G.H. The Purcell eruptive rocks. Ph.D. Thesis, Univ. of Alberta (1961)
- Irvine, W.T. The Bluebell mine. Structural geology of Canadian ore deposits, *Can. Inst. Min. Met.*, 2, 95 (1957)
- Kanasewich, E.R. Approximate age of tectonic activity using anomalous lead isotopes. *Royal Astron. Soc. Geophys. J.*, 7, 158 (1962)
- Kanasewich, E.R. Quantitative interpretations of anomalous lead isotope abundances. Ph.D. Thesis, Univ. of B.C. (1962a)

- Khanh, N.K. M.Sc. Thesis, Univ. of B.C.(in preparation)
- Khlopın, V.G. Determination of isotopic composition of lead in rocks. *Doklady Akademii Nauk, SSSR*, 111, 395 (1956)
- Kollar, F. The precise intercomparison of lead isotope ratios. Ph.D. Thesis, Univ. of B.C. (1960)
- Kollar, F., Russell, R.D. and T.J. Ulrych. Precision inter-comparisons of lead isotope ratios: Broken Hill and Mount Isa. *Nature*, 187, 754 (1960)
- Leech, G.B. and R.K. Wanless. Lead-isotope and potassium-argon studies in the East Kootenay district, British Columbia. *Geol. Soc. Amer.*, Buddington Volume, 241 (1962)
- Lewis, B.R., Forward, P.S. and J.B. Roberts. Geology of the Broken Hill lode, reinterpreted. *Geology of Australian Ore Deposits*, 1, Eighth Commonwealth Mining and Metallurgical Congress, 319 (1965)
- Little, H.W. Nelson map-area, west half, British Columbia. *Geol. Surv. Can. Mem.*, 308 (1960)
- Marshall, R.R. and D.C. Hess. Lead from some stone meteorites. *J. Chem. Phys.*, 28, 1258 (1958)
- Masuda, A. Experimental method for determination of isotopic composition of lead in volcanic rocks. *Earth Sci. Nagoya Univ.*, 10, 117 (1962)
- McConnell, R.K. Jr. Earth's equatorial bulge and viscosity of the mantle. (Abstract) *Trans. Amer. Geophys. Union*, 48, 212 (1967)
- Murthy, V.R. and C.C. Patterson. Lead isotopes in ores and rocks of Butte, Montana. *Econ. Geol.*, 56, 59 (1961)
- Murthy, V.R. and C.C. Patterson. Primary isochron of zero age for meteorites and the earth. *J. Geophys. Res.*, 67, 1161 (1962)
- Obradovich, J.D. and Z.E. Peterman. Geochronology of the Belt Series, Montana. Paper presented to conference on geochronology of Precambrian stratified rocks. Geology Department, Univ. of Alberta, Edmonton (1967)
- Oliver, J. and B.L. Isacks. Some evidence on the structure of the mantle near an island arc. (Abstract) *Trans. Amer. Geophys. Union*, 48, 219 (1967)

- Ostic, R.G. Isotopic investigation of conformable lead deposits. Ph.D. Thesis, Univ. of B.C. (1963)
- Ostic, R.G., Russell, R.D. and R.L. Stanton. Additional measurements of the isotopic composition of lead from stratiform deposits. *Can. J. of Earth Sciences*, 4, 245 (1967)
- Patterson, C.C., Silver, L. and C. McKinney. Lead isotopes and magmatic differentiation. (Abstract) *Intern. Geol. Congr.*, 20, 221 (1956)
- Pidgeon, R.T. A rubidium-strontium geochronological study of the Willyama Complex, Broken Hill, Australia. *J. Petrol.*, 8, 283 (1967)
- Richards, J.R. and R.T. Pidgeon. Some age measurements on micas from Broken Hill, Australia. *J. Geol. Soc. Australia*, 10, 243 (1963)
- Richards, J.R. Lead isotopes at Dugald River and Mount Isa, Australia. *Geochim. et Cosmochim. Acta*, 31, 51 (1967)
- Russell, R.D. and R.M. Farquhar. Lead Isotopes in Geology, Interscience Publishers Inc., New York (1960)
- Russell, R.D., Ulrych, T.J. and F. Kollar. Anomalous leads from Broken Hill, Australia. *J. Geophys. Res.*, 66, 1495 (1961)
- Russell, R.D., Kanasewich, E.R. and J.M. Ozard. Isotopic abundances of lead from a "frequently-mixed" source. *Earth and Planetary Science Letters*, 1, 85 (1966)
- Russell, R.D., Slawson, W.F., Ulrych, T.J. and P.H. Reynolds. Further applications of concordia plots to rock lead isotope abundances. Submitted for publication.
- Schofield, S.J. Geology and ore deposits of the Ainsworth mining camp, British Columbia. *Geol. Surv. Can. Mem.*, 117 (1920)
- Shaw, D.M. Comments on the geochemical implications of lead isotope dating of galena deposits. *Econ. Geol.*, 52, 570 (1957)
- Sinclair, A.J. A lead isotope study of mineral deposits in the Kootenay arc. Ph.D. Thesis, Univ. of B.C. (1964)
- Sinclair, A.J. Anomalous leads from the Kootenay arc, British Columbia. C.I.M. Special Volume No. 8, 249 (1966)

- Slawson, W.F. and C.F. Austin. A lead isotope study defines a geological structure. *Econ. Geol.*, 57, 21 (1962)
- Sorrell, C.A. Solid state formation of Ba, Sr, and Pb feldspars in clay-sulfate mixtures. *Amer. Mineral.*, 47, 291 (1962)
- Stanton, R.L. and R.D. Russell. Anomalous leads and the emplacement of lead sulfide ores. *Econ. Geol.*, 54, 588 (1959)
- Stanton, R.L. General features of the conformable "pyritic" orebodies. *Trans. C.I.M.*, 63, 22 (1960)
- Starik, I.E., Sobotovich, E.V., Lovtsyus, G.P., Lovtsyus, A.V. and G.V. Avdzeiko. Modes of lead occurrence in nature. *Geochemistry*, 683 (1957)
- Stillwell, F.L. Petrology of the Broken Hill lode and its bearing on ore genesis. *Proc. Aust. Inst. Min. Met.*, 190, 1 (1959)
- Tatsumoto, M. Isotopic composition of lead in volcanic rocks. *J. Geophys. Res.*, 71, 1721 (1966)
- Tilton, G.R. and M.H. Grunenfelder. Isotopic lead ages of sphene. (Abstract) *Trans. Amer. Geophys. Union*, 48, 243 (1967)
- Ulrych, T.J. The preparation of lead tetramethyl for mass spectrometer analysis. M.Sc. Thesis, Univ. of B.C. (1960)
- Ulrych, T.J. Gas source mass spectrometry of trace leads from Sudbury, Ontario. Ph.D. Thesis, Univ. of B.C. (1962)
- Ulrych, T.J. and P.H. Reynolds. Whole-rock and mineral leads from the Llano Uplift, Texas. *J. Geophys. Res.*, 71, 3089 (1966)
- Ulrych, T.J., Burger, A. and L.O. Nicolaysen. Least radiogenic terrestrial leads. *Earth and Planetary Science Letters*, 2, 179 (1967)
- Ulrych, T.J. Oceanic basalt leads: a new interpretation and an independent age for the earth. *Science*, accepted for publication.
- Vine, F.J. Spreading of the ocean floor: new evidence. *Science*, 154, 1405 (1966)
- Weber, R.H. and W.A. Bassett. K-Ar ages of Tertiary volcanic and intrusive rocks in Socorro, Catron, and Grant Counties, New Mexico. New Mexico Geol. Soc. Guidebook, Fourteenth Field Conference, 220 (1963)

- Weichert, D.H. Digital analysis of mass spectra. Ph.D. Thesis, Univ. of B.C. (1965)
- Weichert, D.H., Russell, R.D. and J. Blenkinsop. A method for digital recording for mass spectra. *Can. J. Phys.*, 45, 2609 (1967)
- Whittles, A.B.L. Trace lead isotope studies with gas source mass spectrometry. Ph.D. Thesis, Univ. of B.C. (1964)
- York, D. Least-squares fitting of a straight line. *Can. J. Phys.*, 44, 1079 (1966)
- Zartman, R.E. Rb-Sr age of some metamorphic rocks from Llano Uplift, Texas. *J. Petrol.*, 6, 28 (1965)
- Zartman, R.E. Isotopic composition of lead in microclines from Llano Uplift, Texas. *J. Geophys. Res.*, 70, 965 (1965a)