LEAD AND STRONTIUM ISOTOPE STUDY OF FIVE VOLCANIC AND INTRUSIVE ROCK SUITES AND RELATED MINERAL DEPOSITS, VANCOUVER ISLAND, BRITISH COLUMBIA

by

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ABSTRACT

Lead isotope compositions have been obtained from five major volcanic and intrusive rock suites and several ore deposits on Vancouver Island. Lead, uranium and thorium concentrations and strontium isotope ratios have been obtained for a subset of these samples. The rock suites examined are the Paleozoic Sicker Group, Triassic Karmutsen Formation, Jurassic Island Intrusions and Bonanza Group volcanic rocks, and the Eocene Catface intrusions.

Isotope geochemistry of the Sicker Group is consistent with the interpretation that it formed as an island arc. Relatively high 207Pb/204Pb ratios indicate sediment involvement in the subduction process, which suggests that the Sicker Group formed close to a continent. Buttle Lake ore deposits display decreasingly radiogenic lead isotope ratios with time, suggesting that the associated magmas become increasingly primitive. This supports the hypothesis that these deposits formed during the establishment of rifting in a back-arc environment.

Karmutsen Formation flood basalts display isotopic mixing between an ocean island-type mantle source and average crust. Isotopic evidence is used to support a Northern Hemisphere
origin for these basalts.

Mixing is apparent in the lead and strontium isotope signatures of the Island Intrusions and Bonanza Group volcanic rocks, between depleted mantle and crustal (possibly trench sediments) components. This is consistent with formation of these rocks in an island arc environment.

Eocene Catface intrusions have relatively high $^{207}\text{Pb}/^{204}\text{Pb}$ indicating that crustal material was involved in their formation. There are two groups of plutons corresponding to an east belt and west belt classification. Galena from the Zeballos mining camp related to the Eocene Zeballos pluton indicates that the mineralization was derived from the pluton.

Galena lead isotope data from Vancouver Island may be interpreted in a general way by comparison with data from deposits elsewhere of known age and origin. No single growth curve model can be applied. Lead isotope characteristics of Vancouver Island are clearly different from those of the North American craton, reflecting the oceanic affinities of this terrane.

A new technique has been developed to compare $^{207}\text{Pb}/^{204}\text{Pb}$ ratios between samples with differing $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. The
procedure projects $^{207}\text{Pb}/^{204}\text{Pb}$ ratios along suitable isochrons until they intersect a reference value of $^{206}\text{Pb}/^{204}\text{Pb}$. This technique can be used for interpreting lead isotope data from old terranes, in which lead and uranium may have undergone loss or gain, and if lead and uranium abundances have not been measured.
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CHAPTER 1

INTRODUCTION

1.1 SCOPE OF THESIS

This thesis uses lead and strontium isotope systems as geochemical tracers to: 1) isotopically characterize each of five major plutonic and volcanic rock suites from Vancouver Island, 2) delineate some of the relationships that exist between them, 3) interpret the plate tectonic settings of these rock units by comparison with the isotope characteristics of modern analogues, and 4) provide a framework within which to interpret galena lead isotope data from ore deposits in Vancouver Island. This is the first combined lead and strontium isotope study of rocks on Vancouver Island, but similar studies have been done using neodymium, strontium and lead isotope systems for rocks further to the east in the Canadian Cordillera (Ghosh 1986; Smith 1986).

Vancouver Island was chosen for its apparent geological simplicity with clearly defined discrete rock packages that form the island. It has an interesting present-day geological
setting--adjacent to a subduction zone. Vancouver Island was also investigated by the 1984-1985 LITHOPROBE geotraverse (Clowes 1984) which sought to combine geological mapping, petrochemistry, geochronology, radiogenic and stable isotope studies with deep seismic, gravity, magnetotelluric, and geomagnetic surveys in an effort to understand a modern, active continental margin. Preliminary results from LITHOPROBE have augmented this research. A number of the geochronology samples and oxygen isotope samples that were analysed by LITHOPROBE participants were from this thesis.

The section of this thesis dealing with the Buttle Lake camp volcanogenic massive sulphide ore deposits forms part of a collaborative study with S. Juras at the University of British Columbia. This study emphasizes the significance of lead isotopes and chemical petrology of the Sicker Group in the mine sequence, while Juras' study focused on a detailed stratigraphy and petrochemistry of the volcanic rocks.

1.2 GENERALIZED GEOLOGY OF VANCOUVER ISLAND

Syntheses of the geology of Vancouver Island have been made by Muller (1977), Muller et al. (1974) and Sutherland Brown and Yorath (1985). Various aspects have been reported by
Fyles (1955), Yole (1969), Muller and Carson (1969), Northcote and Muller (1972), Carson (1973), Muller (1971, 1980), Yorath et al. (1985a, 1985b) and in numerous theses of students and geological reports for mining companies. The magmatic history of Vancouver Island can be simplified into four major episodes: 1) Paleozoic volcanic arc formation (Sicker Group rocks), 2) extrusion of Triassic tholeiitic flood basalt (Karmutsen Formation basalts), 3) Mesozoic volcanic arc formation (Bonanza Group and Island Intrusions), and 4) Tertiary tectonic and plutonic activity. Each episode is separated from the next by sediment deposition or limestone formation.

Sicker Group volcanic and volcaniclastic rocks and greywackes (Fig. 1.1) represent the Paleozoic arc. The top of the Sicker Group is delimited by the Buttle Lake limestone, which contains Middle Pennsylvanian fusulinids (Sada and Danner 1974) to Early Permian conodont assemblages (Brandon et al. 1986).

Massive outpouring of tholeiitic basalts of the Karmutsen Formation (Fig. 1.1) occurred in the Late Triassic. These basalts unconformably overlie the Sicker Group, forming a thick (up to 6 km) sequence of massive, pillowed and brecciated basalts and sills. Locally there are rhyodacite flows at the top of the Karmutsen Formation; these may represent a change in
Figure 1.1 Geological sketch map of Vancouver Island. Taken from Muller et al. (1974).
tectonic regime (Marten 1984). The Karmutsen Formation is overlain conformably by the Late Triassic Quatsino and Parsons Bay Formations, dominantly of limestone and shale respectively.

An Early to mid-Jurassic island arc assemblage is made up of volcanic and volcaniclastic rocks known as the Bonanza Group (Fig. 1.1). Coeval with Bonanza volcanism was the intrusion of major quartz diorite to granodiorite batholiths, known as the Island Intrusions (Fig. 1.1). Cretaceous sedimentary rocks of the Nanaimo and Queen Charlotte Groups are in marked angular unconformity against all preceding units.

The most recent in the series of tectonic events involved the truncation of Vancouver Island to the west and south, and the accretion of several small terranes. The Pacific Rim complex, a Mesozoic subduction complex analogous to the Franciscan of California, was accreted along the western margin of Vancouver Island during the Paleocene (65 Ma to 55 Ma--Brandon and Massey 1985). Rusmore and Cowan (1985) have identified a small terrane known as the Pandora Peak unit, that was emplaced south of the San Juan fault (Fig. 1.1) during the Late Cretaceous or early Tertiary (83 Ma to 40 Ma). The Leech River complex (Fig. 1.1) was accreted to the south of the San Juan fault in the Late Eocene or Early Oligocene (40 Ma to 30 Ma--Rusmore and Cowan 1985). The paleogeography of southern
Vancouver Island was further modified by the accretion of the Eocene Metchosin volcanic rocks (Fig. 1.1) south of the Leech River fault (post 40 Ma).

Relationships between these tectonic events, and the intrusion in the Eocene (approximately 40 Ma, Table 5.1) of several small quartz diorite plutons (Catface intrusions) throughout Vancouver Island, are enigmatic. Ewing (1981), Sutherland Brown and Yorath (1985), Isachsen (1984), and Armstrong et al. (in press) relate the occurrence of these intrusions to Cenozoic subduction. They occur in the arc-trench gap between the subducting plate and coeval Kamloops Group volcanism (Ewing 1981). They are also coeval with amphibolite grade metamorphism in the Leech River complex (Rusmore and Cowan 1985), and with a major reorganization of plate motions in the Pacific (Ewing 1981; Brandon and Massey 1985).

Paleozoic and Mesozoic rock packages of Vancouver Island comprise a large allochthonous terrane known as Wrangellia (Jones et al. 1977). Characteristic of Wrangellian stratigraphy is the thick sequence of Triassic tholeiitic flows and pillow lavas, which overlie a Paleozoic arc, and which are overlain by platform carbonates (Jones et al. 1977). Wrangellia extends northwards through the Queen Charlotte Islands into the Wrangell Mountains of south-central Alaska. Triassic rocks exposed in the
Hell's Canyon region of Eastern Oregon (45.3° N, 116.8° W) are regarded by some (Jones et al. 1977; Coney et al. 1980; Hillhouse et al. 1982) to be a possible southeastern extension of Wrangellia. This, however, is disputed by others (Scheffler 1983).

The West Shasta district of California in the Eastern Klamath Mountains consists of a Devonian arc sequence which sits on a mid-Silurian ophiolite complex. Comparisons have been made between the major volcanogenic ore bodies of the West Shasta District and the Buttle Lake ore deposits on Vancouver Island. Muller (1980) tentatively correlates the Myra Formation of the Sicker Group with the Balaklala Rhyolite (West Shasta District), and the Nitinat Formation with the Copley Greenstone (West Shasta District). Lead isotope studies of the West Shasta ore bodies, the Balaklala Rhyolite, and the Copley Greenstone have been made by Slawson (1983) and Doe et al. (1985), allowing direct comparison of the isotopic characteristics of these two Paleozoic arc sequences in western North America. Results in Chapter 2 do not support the tentative correlation by Muller.

1.3 SAMPLE SUITE

Five important rock units from each of four major magmatic
episodes were sampled in this study. These are: the Sicker Group, Karmutsen Formation, Bonanza Group, Island Intrusions, and Catface intrusions. Where possible, strontium isotope data and lead isotope data were obtained for the same samples.

Lead, uranium and thorium concentration analyses were done for a subset of samples by isotope dilution, neutron activation analysis, delayed neutron counting, or gamma ray spectroscopy. The thorium isotope dilution technique attempted here was found to be unreliable due to interfering ions, and has only been used in one case.

Galena from a number of mines and showings on Vancouver Island was obtained and analysed. Several samples are from the Kuroko-type massive sulphide ore bodies at Buttle Lake, and at Mount Sicker. Quartz-gold veins related to the Tertiary Catface intrusions and two showings within the Karmutsen Formation were also sampled. The Island Copper porphyry deposit in Bonanza Group hypabyssal intrusive rocks yielded some galena from late veins which provided a sampling of lead from the Jurassic arc episode.
1.4 USE OF LEAD AND STRONTIUM ISOTOPES AS GEOCHEMICAL TRACERS

Recognition that igneous rocks associated with different tectonic environments have different geochemistry was closely followed by the understanding that lead and strontium isotopes could be used as tracers of geochemical environment (Slawson and Austin 1962; Gast et al. 1964). Isotopes have an advantage over trace elements because the degree of partial melting and magmatic fractionation are not known to significantly alter the isotope ratios of the resulting magmas. Thus, for example, the isotope ratios of mantle-derived magmas reflect the isotope ratios of the mantle.

The study of lead isotope ratios of rocks and ores within the plate tectonic framework has come to be known as plumbotectonics (Doe and Zartman 1979) after their important attempt to describe lead evolution in three different reservoirs: the upper crust, lower crust, and mantle, and a fourth 'mixed' environment called the orogene. This study follows this approach, recognizing the contribution of lead and strontium from different reservoirs to volcanic and plutonic rocks and ores in a variety of plate tectonic environments.

More recently neodymium isotopes have been studied (Richard et al. 1976) and the combined Nd-Sr-Pb isotope systems are now
being used to further explore geochemical variations between volcanic rocks erupted in different plate tectonic settings (e.g. Cohen et al. 1980; Dupre and Allegre 1980; Allegre et al. 1982; Cohen and O'Nions 1982; Carlson 1984; Zartman 1984).

1.4.1 Mid-ocean ridges

Mid-ocean ridge basalts (MORBs) have been extensively analyzed for their lead and strontium isotope compositions and trace element patterns since the mid-1960's. MORBs are depleted in large ion lithophile elements (LILEs) and are believed to represent melts from a mantle source which has become 'depleted' due to repeated extraction of melts.

$^{87}\text{Sr}/^{86}\text{Sr}$ values for MORBs are in the range 0.702-0.703 (Basaltic Volcanism Study Project 1981). However, the Rb/Sr ratio for typical MORB is 0.01, which is not high enough to support the observed $^{87}\text{Sr}/^{86}\text{Sr}$ ratios unless there has been some depletion of Rb relative to Sr in the source. A positive correlation has been found between $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ for Atlantic MORBs (Cohen et al. 1980; Dupre and Allegre 1980).

The general field of MORB analyses is shown in Figure 1.2. The linear trends in both $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams correspond to apparent ages of between 1 and 2 Ga. In general, $^{206}\text{Pb}/^{204}\text{Pb}$ is less than
Figure 1.2 $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagram for abyssal basalts (MORBs) and rocks from ocean islands (OIBs). Taken from Tatsumoto 1978.
18.7 and $^{207}\text{Pb}/^{204}\text{Pb}$ is less than 15.5. MORBs have low $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios relative to average crustal growth curves such as that of Stacey and Kramers (1975). They plot to the right of the Geochron indicating enrichment in U/Pb relative to a single stage source, which is in contradiction to both Sr and Nd isotope systems.

1.4.2 Ocean islands

Ocean island basalts (OIBs) have been interpreted as products of a mantle source, which is tapped by hot spots or mantle plumes (Wilson 1963; Morgan 1971; Schilling 1973). This mantle source has different isotopic characteristics than MORB-type mantle and has larger concentrations of LILEs. It is relatively enriched in the light rare earth elements. Speculations on the nature and location of this type of mantle vary from 'primitive' mantle (DePaulo 1979) to recycled ocean crust (Chase 1981; Hofmann and White 1982), from shallower than MORB-type mantle (Allegre and Bottinga 1977; Hedge 1978; Tatsumoto 1978; Anderson 1982) to deeper (Schilling 1973; DePaulo and Wasserburg 1977; Hofmann and Hart 1978; Hamelin et al. 1984a), and to adjacent to MORB-type mantle (Gill 1984).

Lead isotope analyses have been made for numerous ocean islands (e.g. Oversby and Gast 1970; Oversby 1972a, 1972b; Sun 1980; Weis 1983). Each ocean island has a range of lead isotope
values, but variation in isotope ratios is much greater between islands than within a single island. Most islands show a linear trend in the data in both of the conventional lead isotope plots. They tend to have more radiogenic values than MORBs (206Pb/204Pb > 18.5, and 207Pb/204Pb > 15.5), but fall on approximately the same trend. Published fields for several OIBs are shown in Figure 1.2. The very variable lead signatures displayed by OIBs show that the mantle is heterogeneous and that heterogeneities are preserved for long periods of time. The OIB field has been generalized in following illustrations.

Strontium is also more variable and generally more radiogenic in OIBs than in MORBs (Basaltic Volcanism Study Project 1981). Rb/Sr ratios are typically 0.03 in OIBs--large enough to support the range of 87Sr/86Sr values, assuming closed system isotopic evolution of a chondritic initial ratio since the time of formation of the earth.

1.4.3 Island arcs

Island arcs form above subducting plates. It has been suggested that sediment on the downgoing plate is recycled into the mantle and is involved in production of island arc magmas (Tatsumoto 1969; Armstrong and Cooper 1971; Kay et al. 1978; Nohda and Wasserburg 1981). Lead isotopes provide a useful way of tracing this type of contamination. Continentally-derived
sediments contain high concentrations of lead relative to the concentration of lead in ocean crust and the mantle. They also have higher 207Pb/204Pb ratios than MORBs and OIBs. Consequently, even a small quantity of lead derived from sediments can be detected in the lead signatures of island arc magmas. The island arc field occupies an intermediate position between those of ocean sediments and MORBs (see Fig. 2.3). Several studies of island arcs demonstrate this relationship well (Armstrong and Cooper 1971; Oversby and Ewart 1972; Meijer 1976; Kay et al. 1978).

Strontium isotope ratios for island arc magmas are also more radiogenic reflecting sediment involvement in subduction. Meijer (1976) and Kay et al. (1978) noted a positive correlation between lead and strontium isotope compositions and concentrations. This provides strong support for the sediment plus mantle (and/or slab) mixing hypothesis.

1.4.4 Use of lead and strontium isotopes as tracers of ancient geological environments

Although there is little or no difference in the lead and strontium daughter:reference isotope ratios between the source and magma, there is a significant change in the parent:daughter ratios. Thus it is necessary to correct for in situ isotope evolution in rocks older than approximately 20 Ma.
This study examines the lead and strontium isotope characteristics of island arc, ocean island, and possibly back arc environments that range in age from older than 300 Ma to approximately 40 Ma. Initial ratios are calculated using measured $^{238}\text{U}/^{204}\text{Pb}$ ($\mu$), $^{232}\text{Th}/^{238}\text{U}$ ($k$), and $^{87}\text{Rb}/^{86}\text{Sr}$ values, and independent isotopic or fossil age estimates. Mobility of lead, uranium, thorium, rubidium and strontium in rocks due to surface weathering, seawater alteration or metamorphism may make these initial values unreliable. Galena from syngenetetic sulphide ore deposits has been analysed to provide independent estimates of the lead isotope initial values for each rock suite.

Where comparisons are made between lead isotope initial values for Vancouver Island rock suites and analyses of modern plate tectonic environments, the modern fields have been projected back using Stacey and Kramers' growth curve (Stacey and Kramers 1975). This is only an approximation, since it is unreasonable to assume that all of the fields evolved at the same rate. Furthermore, since these adjustments are greater for the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios than for the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio, the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio is the most useful tracer in old allochthonous terranes and ophiolites (Hamelin et al. 1984b). It is for this reason that the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio has been singled out for plotting against lead concentration and against
$^{87}$Sr/$^{86}$Sr initial ratios to reveal mixing patterns.

1.5 ANALYTICAL TECHNIQUES

Analytical techniques are described for all of the data reported in this thesis. In many instances computer programs are used in order to calculate the reported data from the raw data. These programs are referred to by name (capital letters in quotation marks) throughout this section. All of the programs are listed in Appendix D unless otherwise stated. Table D.1 (Appendix D) summarizes the inputs and outputs of these programs.

1.5.1 Galena lead isotope ratios

Most galena samples were prepared and analyzed by the author following procedures outlined in Appendix A. Analyses of samples conducted over the same period of time as the whole rock lead samples were analyzed using the "UBCZPB" mass spectrometer measuring program (Appendix B); raw data were corrected for mass fractionation using the same factors as for the whole rock samples (Appendix B, Table B.2). Several samples (Zeballos gold veins, and others) were analyzed over a two month period in 1983, using either the "MSCOPB" or "UBCZPB" measuring programs (Appendix B). Raw data for these analyses were
corrected using mass fractionation factors determined by repeated analyses of Broken Hill Standard #1 measured over the same time span (see Appendix A).

A one sigma estimate of the error associated with a single analysis was obtained by adding within-run precision at one standard deviation to the fractionation variation between runs and the uncertainty in the mass fractionation factors. This was done by adding the squares of each of the uncertainties and taking the root. Uncertainties in mass fractionation factors and in mass fractionation variation between runs are estimated in Appendices A and B.

Samples from the Myra deposit at Buttle Lake and from Lenora and Tyee deposits at Mount Sicker are reported in Chapter 2. These were analyzed by B. Ryan following procedures outlined by Andrew (1982: Appendix A), using the mass spectometer in the Department of Geophysics and Astronomy, the University of British Columbia.

1.5.2 **Whole rock lead isotope ratios**

Whole rock samples were analyzed following the procedures outlined in Appendix B. Raw data were corrected using mass fractionation factors determined from 25 runs of the Broken Hill Standard #1 (Appendix B: Table B.1). The one sigma errors quoted
in brackets after each of the reported isotope ratios are the sums of within-run precision, fractionation variation between runs, and uncertainty in mass fractionation factors. They are calculated using the program "WRPBIC" (Appendix D). These values are generally less than 0.1%. Uncertainties in the values of a single sample were also estimated by the method of sum of squares of the residuals of several duplicate analyses (Appendix B: Tables B.7, B.8 and B.9). These show that the uncertainty associated with a single analysis is of the order of 0.1%. Geological variation was estimated using different samples of the same rock units, and was found to be 0.2% (Appendix B: Table B.10) for homogeneous rock types using samples that were separated by more than 100 m.

Accuracy was tested by analysing the BCR-1 standard. The isotopic composition measured agreed with the published values (Tatsumoto et al. 1972) to within 0.15% (Appendix B: Table B.11).

1.5.3 Lead concentration by isotope dilution

Lead concentrations were determined for several samples using the procedures outlined in Appendix B. Mixed spike 84-3 (Appendix C) was added to the samples. Uncertainties in the concentration were determined by error propagation (Rees 1984), using a program called "WRPBID" (listed in Appendix D). The
Uncertainties calculated in this way are 0.01 to 0.03 ppm.

Uncertainty in the measured lead concentrations was also estimated using duplicate analyses (Appendix B: Table B.12). The uncertainty measured in this way is 0.1 ppm, much larger than that estimated by error propagation. This suggests that there are uncertainties not being considered in the error propagation calculations. The uncertainty calculated by duplicate analyses is more representative of analytical conditions. The discrepancy might be due to sample heterogeneities, or incomplete dissolution. Such errors can be reduced by the use of high pressure bombs in the dissolution process, or by spiking the sample after dissolution. The data are interpreted with these errors in mind.

Accuracy was tested by analyzing the Columbia River Basalt standard (BCR-1). The lead concentrations measured for the standard (Appendix B: Table B.11) agree well with the published value of Tatsumoto et al. (1972).

1.5.4. Uranium concentration by isotope dilution

Uranium concentrations were determined following procedures outlined in Appendix B. Error propagation (Rees 1984) was used to determine the uncertainty associated with each analysis (using the same principles as for lead concentrations: section
1.5.3. It was found that the results of uranium determination by isotope dilution were consistently less than by neutron activation analysis or gamma ray spectroscopy (Appendix B: Table B.13). A similar discrepancy was reported by Tilton (1973). Tilton (1973) chose to use the neutron activation numbers rather than those by isotope dilution. In this study, I have chosen to accept the isotope dilution numbers and have reduced the neutron activation analysis and gamma ray analysis numbers by a factor of 1.0935 (determined by comparison of several samples with two methods of determination, Appendix B: Table B.13) for the purposes of calculating an internally consistent set of μ values. This approach is supported by close agreement of uranium values by isotope dilution with recent analyses by L. Erdman using neutron activation analysis at the TRIUMF reactor in Vancouver (Tables 2.2 and 3.2).

Uncertainties were calculated using the error propagation program "UCALC", listed in Appendix D. These were generally better than 1%, in agreement with one pair of duplicate analyses for sample 683421 (Chapter 4). Dissolution problems might make actual uncertainties somewhat larger.

1.5.5. Thorium by isotope dilution

Thorium was determined following the procedure outlined in Appendix B. Interfering ions caused instability in the mass
spectrometry. In only one case is the thorium value reported by this method. Error propagation calculations were made using the program "THCALC" (Appendix D). The thorium concentration determined by isotope dilution is approximately 15% lower than that obtained by gamma ray spectroscopy. This may be due to incomplete dissolution of the sample, or to the same effect noted for uranium analyses (section 1.5.4).

1.5.6. Uranium by delayed neutron counting

Ten samples were submitted for uranium analysis to Neutron Activation Services Ltd. (N.A.S.), Ontario. Five gram samples were irradiated for 60 seconds using an enriched uranium reactor. A neutron detector was used to count samples for 60 seconds. The detection limit is 0.01 ppm. Counting statistics were not available from the laboratory, however, typical uncertainties for this method are 10%.

1.5.7. Thorium by neutron activation analysis

Ten samples were submitted to Neutron Activation Services Ltd. for thorium analysis at a detection limit of 0.05 ppm. One gram samples were irradiated for 60 minutes then cooled for 7 to 10 days. Counting was done for 1,000 seconds on the protoactinium peak using a gamma ray counter. The peak is at 311 keV. Counter resolution is 1.8 keV in the 1,332 keV range. Corrections were made for interference. Typical uncertainties
for this method are 12% (Erdman 1985).

1.5.8. Urnium and thorium by gamma ray spectroscopy

All samples of the Island Intrusions were analyzed for uranium and thorium concentrations by gamma ray spectroscopy by T.J. Lewis in 1976 at the Geological Survey of Canada Earth Physics Branch laboratory in Ottawa. This method, originally described by Lewis (1974), is updated in Lewis et al. (1983).

Gamma ray spectra were acquired from powdered rock samples (330 to 800 g), using solid state, Ge(Li) detectors. The equipment used consists of two detectors with efficiencies of 13 to 16% and resolutions at 1.33 meV of 1.8 to 1.9 keV (peak width at half height), an EGG-Ortec model 1710 multi-channel analyzer system, and a DEC PDP 11/23 computer system. Resolution checks were run at least once each month and standards were re-measured four times a year. Original standards were obtained from the New Brunswick Laboratories of the US Atomic Energy Commission, and comparison of results from standard samples have been published by Lewis (1974).

Accuracy is estimated to be approximately 10% at 1 ppm U and Th. Most samples were measured for a few hours. This is usually longer than necessary to achieve a 10% precision from the counting statistics.
1.5.9. Rubidium and strontium determinations

Strontium isotopic ratios were determined at the University of British Columbia. Some measurements were made by K. Scott or P. Holbek using a National Bureau of Standards-type, 30 cm radius, 60° sector solid source mass spectrometer constructed by Henry Faul (PhD) of the University of Pennsylvania and automated with a Data-General Nova 1210 minicomputer. Later measurements were made by A. Andrew or S. Juras using a Vacuum-Generators Isomass 54R solid source mass spectrometer automated with a Hewlett-Packard HP-85 computer. Measured ratios have been normalized to a $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194, and corrected for interlaboratory bias by adjusting the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio so that the National Bureau of Standards standard SrCO$_3$ (SRM 987) gives a ratio of $0.71020 \pm 0.00002$, and the Eimer and Amend Sr standard a ratio of $0.70800 \pm 0.00002$. The precision of a single $^{87}\text{Sr}/^{86}\text{Sr}$ is $0.0001$ (one sigma).

Rubidium and strontium concentrations were also determined by K. Scott, P. Holbek, S. Juras or A. Andrew at the University of British Columbia by X-ray fluorescence (XRF) using a Philips PW 1410 spectrometer with a Mo X-ray tube and a 3kW generator. Replicate analyses were carried out on whole-rock powder pellets using international standards for calibration. Rb/Sr ratios have a precision of 2% (one sigma) where Rb concentrations exceed 50 ppm, 3% at 33 ppm, and 10% at 10 ppm.
CHAPTER 2

ISOTOPE GEOCHEMISTRY OF THE SICKER GROUP, VANCOUVER ISLAND

SYNOPSIS

Whole rock lead isotope analyses have been obtained for a variety of lithologies from the Sicker Group in the Cowichan - Horne Lake and Buttle Lake Uplifts. Sicker Group lead isotope ratios are consistent with the hypothesis that it formed as an island arc. Relatively high values of $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ suggest that large quantities of crustal lead must have been involved in the formation of the Sicker volcanics. Thus it is proposed that the trench related to the Paleozoic island arc had a substantial input of continental detritus and may have lain near a continent. Speculative models involving anomalously radiogenic mantle may also be invoked to explain the data.

Galena lead isotope signatures from the volcanogenic ore deposits at the Buttle Lake mining camp are uniform within each of the major ore bodies. Slight differences in composition are, however, observable between the different ore bodies, which
suggest that the initial ratios for the Sicker Group become
decreasingly radiogenic with time. This has major significance
in terms of ore genesis for these important deposits.

There are significant differences in isotopic composition
between the Sicker Group and Devonian island arc type rocks in
the Shasta District, California. This rules out the possibility
that there are direct correlations between the rock units of
these two areas.

2.1 INTRODUCTION

The Sicker Group was first mapped by Clapp (1912) and is
named after Mount Sicker (Fig. 2.1) where it is exposed. It is
the name given to the oldest rocks on Vancouver Island, which
are exposed in three main areas (Fig. 2.1): the Cowichan - Horne
Lake, Buttle Lake, and Nanoose Uplifts. The group is made up of
volcanic, volcanioclastic and sedimentary rocks, which have been
metamorphosed to greenschist facies.

The oldest formation in the Sicker Group has been identified
by Muller (1980) as the Nitinat, which is made up of mafic
agglomeratic and tuffaceous volcanic rocks, basaltic pillow
lavas and brecciated pillows with some cherty horizons. Basalts
Figure 2.1 Distribution of three major uplifts of Sicker Group rocks, Vancouver Island, B.C., showing sample locations detailed in Table 2.1
containing distinctive uralitized pyroxene phenocrysts are exposed in the Maple Bay area in the Cowichan Lake - Horne Lake Uplift, and have been sampled in this study. A K-Ar age of 421 ± 36 Ma was obtained for a sample of Nitinat tuff, but it had a low K content and may therefore be anomalous (Brandon et al. 1986). Other K-Ar data for Nitinat rocks give reset Permian ages (Brandon et al. 1986).

Saltspring Intrusions, intrusive into the Nitinat Formation, are quartz feldspar porphyry and granodiorite bodies, that previously have been called the Tyee quartz-feldspar porphyry and, more generally, the Tyee intrusions. They occur on Saltspring Island and east of Cowichan Lake. Zircon analyses from these intrusions are highly discordant, but give a best estimate of 393 ±25/-10 Ma (Brandon et al. 1986). In this study, these intrusions have been sampled at Maple Bay.

K-Ar dating of sericite from a sericitic quartz porphyry of the Saltspring Intrusions (Muller 1980) gave a metamorphic age of 180 ± 8 Ma, the time of intrusion of major batholiths known as the Island Intrusions. Deep seismic profiles obtained as part of the LITHOPROBE project have been interpreted by Yorath et al. (1985b) as showing that the Sicker Group sits within these batholiths as roof pendants; so it is likely that the isotope systems were at least partially reset in the Jurassic.
Overlying the Nitinat in the Buttle Lake Uplift is the Myra Formation. It is the Myra Formation that is host to the major Kuroko-type massive sulphide ore deposits near the south end of Buttle Lake. It contains basaltic and andesitic flows, rhyolite domes, rhyolitic and dacitic volcaniclastic layers, black argillites, siltstones and greywackes (Walker 1980). A preliminary zircon Pb-Pb age of greater than 370 Ma age for the H-W quartz feldspar porphyry member of the Myra Formation (Brandon et al. 1986), has recently been revised to 365 \pm 3 Ma (R. Parrish in press). This age is in good agreement with a second zircon age from the top of the Myra at Buttle Lake which is 370 \pm 18/-6 (S. Juras in prep.). Several lithological types have been sampled from the Myra Formation together with galena from the associated ore deposits.

A chert horizon containing Early Mississippian microfossils, disconformably overlies the Nitinat Formation in the Cowichan Lake area (Brandon et al. 1986). These are the oldest fossils yet found in the Sicker Group. The overlying volcanic strata have previously been correlated with the Myra Formation, but are now considered to be younger (Brandon et al. 1986). This interpretation requires that the ore deposits at Mount Sicker are younger than those at Buttle Lake.
The top of the Sicker Group is marked by the Buttle Lake Formation, a fossiliferous limestone unit. Conodont assemblages indicate that the Buttle Lake Formation spans the interval between Early Permian and Middle Pennsylvanian (Brandon et al. 1986). Because the oldest fossils in the Buttle Lake Uplift are Early Permian (Yole 1969), the underlying volcanic strata cannot be younger than 280 Ma, using the DNAG (Decade of North American Geology) timescale (Palmer 1983).

Lithologies and the calc-alkaline nature of the Sicker volcanics are suggestive of an island arc environment, and it has been considered to be a Paleozoic island arc since the first major plate tectonic synthesis for the Western Cordillera (Monger et al. 1972). Similarities between the Paleozoic Sicker Group and other Paleozoic arc-type rocks such as those at Shasta, California, have been considered by Muller (1980). This is discussed further here by comparing data on the lead isotope compositions of rocks and ore deposits of the Shasta District (Slawson 1983; Doe et al. 1985) to data from Sicker Group rocks and ores.

Whole rock lead isotope analyses have been obtained for a variety of Sicker Group rocks from the Maple Bay, Buttle Lake mine, Mount Sicker, and Mount Brenton areas (Fig. 2.1, Tables
2.1 and 2.2). Uranium, thorium and lead concentrations were obtained for a subset of samples by isotope dilution, neutron activation analysis, or slow neutron counting.

This study focuses on the interpretation of whole rock and galena analyses (Tables 2.2 and 2.3). The whole rock analyses are compared with those of the Shasta Paleozoic island arc, California, and with those of modern island arcs. A description of the isotopic data is presented for Buttle Lake, Maple Bay, and Lenora and Tyee rocks and ores, followed by a discussion of the Sicker Group as a whole.

2.2 BUTTLE LAKE CAMP

2.2.1 Introduction

Westmin Resources Ltd., Vancouver, mines several volcanogenic polymetallic ore deposits in the Buttle Lake camp at the southern end of Buttle Lake in Strathcona Provincial Park, central Vancouver Island (Fig. 2.1). Ore deposits occur at more than one stratigraphic level and are associated with massive or brecciated felsic horizons (Walker 1980).

There is general agreement amongst geologists that the Buttle Lake ore deposits are Kuroko-type volcanogenic deposits (Carvalho
TABLE 2.1 Locations and brief descriptions of analyzed samples of Sicker Group rocks from Vancouver Island, B.C. General location is on Figure 2.1.

<table>
<thead>
<tr>
<th>SAMPLE NAME</th>
<th>LAT. DECIMAL DEGREES</th>
<th>LONG. DECIMAL DEGREES</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maple Bay</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MB1</td>
<td>48.85</td>
<td>123.68</td>
<td>Uralite porphyry</td>
</tr>
<tr>
<td>MB2</td>
<td>48.85</td>
<td>123.68</td>
<td>Quartz eye porphyry (Tyee)</td>
</tr>
<tr>
<td>MB3</td>
<td>48.85</td>
<td>123.68</td>
<td>Quartz eye porphyry (Tyee)</td>
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<tr>
<td>MB3A</td>
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<td>Quartz porphyry with epidote and hornblende</td>
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<td>MB3B</td>
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<td>123.68</td>
<td>Quartz porphyry near uralite contact</td>
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<td>MB3D</td>
<td>48.85</td>
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<td>Pink-banded chert in mafic unit</td>
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<td>MB3E</td>
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<td>Fragmental uralite</td>
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<td><strong>Buttle Lake</strong></td>
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<td></td>
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<tr>
<td>GRHY</td>
<td>49.58</td>
<td>125.61</td>
<td>Upper Lynx pit - silicified andesite or G rhyolite</td>
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<tr>
<td>R78</td>
<td>49.57</td>
<td>125.58</td>
<td>HW massive black rhyolite. W143 2357'</td>
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<tr>
<td>R90</td>
<td>49.57</td>
<td>125.58</td>
<td>HW massive black rhyolite. W143 1631'</td>
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<td>R91</td>
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<td>125.58</td>
<td>HW massive black rhyolite. W143 1773'</td>
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<tr>
<td>R128</td>
<td>49.57</td>
<td>125.58</td>
<td>Quartz feldspar porphyry (QFP) dome in HW rhyolite. P13-306 1188'</td>
</tr>
<tr>
<td>R129</td>
<td>49.57</td>
<td>125.58</td>
<td>QFP dome in HW rhyolite. P13-306 1323'</td>
</tr>
<tr>
<td>R130</td>
<td>49.57</td>
<td>125.58</td>
<td>QFP dome in HW rhyolite. P13-306 1411'</td>
</tr>
<tr>
<td>R131</td>
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<td>125.58</td>
<td>QFP dome in HW rhyolite. P13-306 1428'</td>
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<tr>
<td>W149</td>
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<td>125.61</td>
<td>Rhyolite unit at top of mine sequence; G hanging wall rhyolite. W149 270'</td>
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<td><strong>Lenora/tyee mine area</strong></td>
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<td>LT1</td>
<td>48.87</td>
<td>123.78</td>
<td>Diorite sheet, possibly not Sicker</td>
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<td>Quartz porphyry (Tyee)</td>
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<td>Chert horizon</td>
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<td>Diorite sheet, possibly not Sicker</td>
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<td>LT5</td>
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<td>123.78</td>
<td>Intermediate tuff</td>
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<td>LT6</td>
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<td>123.78</td>
<td>Felsic tuff</td>
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<td>123.82</td>
<td>Meta-andesite (Appendix I in Holbek 1980)</td>
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<td>H16</td>
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<td>123.82</td>
<td>Lithic tuff (Appendix I in Holbek 1980)</td>
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<td>123.82</td>
<td>Tyee quartz feldspar porphyry</td>
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<td><strong>Sicker General - Armstrong suite</strong></td>
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<td>STQE</td>
<td>48.89</td>
<td>123.71</td>
<td>Quartz eye sericite schist</td>
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<td>S3</td>
<td>48.86</td>
<td>123.72</td>
<td>Hornblende porphyry</td>
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### TABLE 2.2. Lead, uranium and thorium data from the Sicker Group volcanic rocks, Vancouver Island, B.C.

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<th>SAMPLE NAME</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
<th>Pb PPM (I.D.)2,3</th>
<th>U PPM (I.D.)2,4</th>
<th>U PPM (N.A.A.)5</th>
<th>Th PPM (D.N.)5</th>
<th>μ6</th>
<th>k7</th>
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<tr>
<td>MB1</td>
<td>18.596 (0.013)</td>
<td>15.583 (0.012)</td>
<td>38.105 (0.037)</td>
<td>5.17</td>
<td>0.90 (0.01)</td>
<td>0.97</td>
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<td>11.1</td>
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<td>MB2</td>
<td>25.754 (0.016)</td>
<td>15.973 (0.009)</td>
<td>44.569 (0.032)</td>
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<td>nd</td>
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<td>6.6</td>
<td>161.6</td>
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<td>15.820 (0.009)</td>
<td>42.190 (0.031)</td>
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<td>nd</td>
<td>nd</td>
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<tr>
<td>MBJA</td>
<td>21.588 (0.018)</td>
<td>15.742 (0.015)</td>
<td>39.809 (0.041)</td>
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<td>nd</td>
<td>nd</td>
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<td>MB3B</td>
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<td>nd</td>
<td>nd</td>
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<tr>
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<tr>
<td>GR138</td>
<td>19.351 (0.015)</td>
<td>15.630 (0.014)</td>
<td>38.627 (0.039)</td>
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<td>nd</td>
<td>nd</td>
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<tr>
<td>GR142</td>
<td>19.412 (0.007)</td>
<td>15.624 (0.008)</td>
<td>38.631 (0.026)</td>
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<td>nd</td>
<td>nd</td>
<td>nd</td>
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<tr>
<td>GR142-AVG</td>
<td>19.382 (0.012)</td>
<td>15.627 (0.011)</td>
<td>38.630 (0.033)</td>
<td>5.08</td>
<td>1.42 (0.05)</td>
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<tr>
<td>R78</td>
<td>19.561 (0.016)</td>
<td>15.596 (0.015)</td>
<td>38.934 (0.040)</td>
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<td>nd</td>
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<tr>
<td>R78-AVG</td>
<td>19.519 (0.007)</td>
<td>15.644 (0.008)</td>
<td>38.970 (0.028)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
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<tr>
<td>R90</td>
<td>19.512 (0.011)</td>
<td>15.641 (0.010)</td>
<td>39.047 (0.032)</td>
<td>5.11</td>
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<td>R91</td>
<td>19.430 (0.010)</td>
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<td>38.865 (0.030)</td>
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<td>R91-AVG (N=2)</td>
<td>19.444 (0.007)</td>
<td>15.620 (0.008)</td>
<td>38.900 (0.028)</td>
<td>2.66</td>
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<td>39.267 (0.061)</td>
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<tr>
<td>R128-AVG (N=2)</td>
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<td>15.601 (0.012)</td>
<td>39.070 (0.035)</td>
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<td>nd</td>
<td>nd</td>
<td>nd</td>
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<tr>
<td>R129</td>
<td>19.530 (0.019)</td>
<td>15.630 (0.017)</td>
<td>39.067 (0.097)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
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<tr>
<td>R129-AVG (N=2)</td>
<td>19.603 (0.007)</td>
<td>15.635 (0.008)</td>
<td>39.101 (0.028)</td>
<td>nd</td>
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<td>nd</td>
<td>nd</td>
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<tr>
<td>R130</td>
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<td>4.61</td>
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<tr>
<td>R131</td>
<td>19.868 (0.029)</td>
<td>15.621 (0.023)</td>
<td>39.362 (0.062)</td>
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<td>R131-AVG (N=4)</td>
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Note: μ6 and k7 values are not provided in the table.
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<th>SAMPLE NAME</th>
<th>206pu/204pu</th>
<th>207pu/204pu</th>
<th>208pu/204pu</th>
<th>Pb PPM (I.D.)</th>
<th>U PPM (I.D.)</th>
<th>U PPM (N.A.A.)</th>
<th>Th PPM (D.N.)</th>
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<th>k7</th>
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<td>W149</td>
<td>18.756 (0.007)</td>
<td>15.571 (0.008)</td>
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<td>W149-AVG (N=2)</td>
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<td>15.569 (0.009)</td>
<td>38.237 (0.029)</td>
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<td>LENORA AND TYEE</td>
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<td>1/T1</td>
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<td>15.597 (0.008)</td>
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<td>1/T2</td>
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<td>15.673 (0.011)</td>
<td>39.248 (0.034)</td>
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<td>38.522 (0.028)</td>
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<td>1/T4</td>
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<td>0.9</td>
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<td>15.677 (0.013)</td>
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<td>38.055 (0.030)</td>
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<td>0.54 (0.01)</td>
<td>0.6*</td>
<td>0.9*</td>
<td>6.3</td>
<td>1.6</td>
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1. Figures given in brackets are the one sigma uncertainties based on the addition of in-run precision and mass fractionation uncertainties. For average values (n>2) the figures in brackets are the one standard error of the mean value.
2. I.D. is isotope dilution analysis (Appendix H). nd = not determined.
3. Uncertainties based on duplicate analyses are estimated to be 0.1 ppm (Appendix B; Table B.12).
4. Figures given in brackets are the one sigma uncertainties calculated by error propagation using "WRUCLC" (Appendix D).
5. N.A.A. stands for Neutron Activation Analysis. D.N. is delayed neutron counting. Details of techniques used and uncertainties are given in Chapter 1. An asterisk marks samples analysed at TRIUMF by L. Erdman, all others were done by Neutron Activation Services Ltd., Hamilton, Ontario.
6. μ values (238pu/204pb) are calculated using U(I.D.) values where possible or U(N.A.S.) values which have been reduced by a factor of 1.0935 (Appendix B). na = not applicable.
7. k values (232Th/238u) are calculated using U(N.A.S.) and Th(N.A.S.) values. na = not applicable.
TABLE 2.3  Galena-Lead Isotope Analyses from Buttle Lake, Lenora, Tyee and Port Alberni Volcanogenic Ore Deposits, Vancouver Island, B.C.

<table>
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<th>Sample Name</th>
<th>Anal. Number</th>
<th>Deposit Name</th>
<th>Map Name</th>
<th>North</th>
<th>East</th>
<th>Lead Isotope Ratios (two sigma uncertainty)</th>
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<td>206/204</td>
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<td>G-Hanging wall sulphide</td>
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<td>UG-101</td>
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<td>W162, 319-342 ft</td>
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<td>125.61</td>
<td>18.539 (.003)</td>
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<td>125.61</td>
<td>18.614 (.012)</td>
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<td>G and S-Zone sulphides</td>
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<td>G Zone from Lynx pit</td>
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<td>125.61</td>
<td>18.544 (.008)</td>
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<td>GZ-107r</td>
<td>1</td>
<td>G Zone from Lynx pit</td>
<td>G27r</td>
<td>49.58</td>
<td>125.61</td>
<td>18.544 (.008)</td>
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<td>GZ-110</td>
<td>1</td>
<td>G Zone from Lynx pit</td>
<td>G210</td>
<td>49.58</td>
<td>125.61</td>
<td>18.551 (.008)</td>
</tr>
<tr>
<td>GZ-110r</td>
<td>1</td>
<td>G Zone from Lynx pit</td>
<td>G210r</td>
<td>49.58</td>
<td>125.61</td>
<td>18.563 (.004)</td>
</tr>
<tr>
<td>SZ-111</td>
<td>1</td>
<td>S Zone from Lynx pit</td>
<td>S11</td>
<td>49.58</td>
<td>125.61</td>
<td>18.554 (.004)</td>
</tr>
<tr>
<td>GS-AVG (n=5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HW ore</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HW-103</td>
<td>1</td>
<td>HW 20 level 049 hole 1698'</td>
<td>HW3</td>
<td>49.57</td>
<td>125.57</td>
<td>18.548 (.008)</td>
</tr>
<tr>
<td>HW-104</td>
<td>1</td>
<td>HW 20 level 049 hole 1679'</td>
<td>HW4</td>
<td>49.57</td>
<td>125.57</td>
<td>18.573 (.010)</td>
</tr>
<tr>
<td>HW-108</td>
<td>1</td>
<td>HW 20 level 049 hole 108 m</td>
<td>HW8</td>
<td>49.57</td>
<td>125.57</td>
<td>18.559 (.005)</td>
</tr>
<tr>
<td>HW-108r</td>
<td>1</td>
<td>HW 20 level 049 hole 108 m</td>
<td>HW8r</td>
<td>49.57</td>
<td>125.57</td>
<td>18.546 (.004)</td>
</tr>
<tr>
<td>HW-AVG (n=4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Myra ore</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MY-001</td>
<td>1</td>
<td>Myra</td>
<td>MO1</td>
<td>49.58</td>
<td>125.60</td>
<td>18.480 (.006)</td>
</tr>
<tr>
<td>G79WM-001</td>
<td>2</td>
<td>Myra</td>
<td>WM1</td>
<td>49.58</td>
<td>125.60</td>
<td>18.506 (.011)</td>
</tr>
<tr>
<td>G79WM-002</td>
<td>2</td>
<td>Myra</td>
<td>WM2</td>
<td>49.58</td>
<td>125.60</td>
<td>18.488 (.011)</td>
</tr>
<tr>
<td>G79WM-003</td>
<td>2</td>
<td>Myra</td>
<td>WM3</td>
<td>49.58</td>
<td>125.60</td>
<td>18.493 (.011)</td>
</tr>
<tr>
<td>MY-AVG (n=4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lenora and Tyee ores</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G79LN-AVG</td>
<td>2</td>
<td>Lenora</td>
<td>LN</td>
<td>48.87</td>
<td>123.78</td>
<td>18.546 (.011)</td>
</tr>
<tr>
<td>C79TY</td>
<td>2</td>
<td>Tyee</td>
<td>TY</td>
<td>48.87</td>
<td>123.78</td>
<td>18.558 (.015)</td>
</tr>
<tr>
<td>Showing 12 km southeast of Port Alberni</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30457-001</td>
<td>1</td>
<td>Showing</td>
<td>S457</td>
<td>49.125</td>
<td>18.350 (.005)</td>
<td>15.572 (.004)</td>
</tr>
</tbody>
</table>

1. Analyses by A. Andrew were done in the Geochronology Laboratory, The University of British Columbia;
2. Analyses by B. Ryan, reported in Andrew (1982) were done in the Geophysics Laboratory, The University of British Columbia.
There are many similarities between these and the well described Kuroko deposits of Japan. Both are associated with submarine, calc-alkaline felsic volcanics in the waning stages of a mafic to felsic volcanic cycle. The yellow ore, black ore, hematitic chert, siliceous and stringer ore types that characterize the Japanese deposits are all found in the Buttle Lake deposits.

2.2.2 Sample suite

Galena samples were collected from the H-W deposit (structurally and stratigraphically the lowest), from the G hanging wall, G, and S zones of the Lynx deposit, and from the Myra deposit. Whole rock samples were collected from the massive H-W rhyolite (samples R78, R90 and R91), and from a fragmental quartz feldspar porphyry unit within this rhyolite (samples R128, R129, R130 and R131). A sample of siliceous rock was taken from the Lynx pit, directly beneath the G zone ore (sample GRHY). Sample W149 was taken at the top of the mine sequence from the uppermost quartz feldspar porphyry, the G hanging wall rhyolite. This sample contained some sulphide mineralization. Figure 2.2 shows locations of the ore bodies named here, and of the samples analyzed.

2.2.3 Results

Galena and whole rock lead isotope data (Tables 2.2 and 2.3)
Figure 2.2 Map showing the locations of the Buttle Lake ore deposits named in the text and projected locations of whole rock and galena samples analysed (Tables 2.2 and 2.3).
are shown in Figures 2.3 and 2.4. Analyses of three rocks from the H-W massive black rhyolite group together, whereas the results from rocks of the fragmental quartz feldspar porphyry unit spread along a line, which may be an isochron; however, the line is not long enough to give a meaningful age estimate for these rocks (calculated age is $180 \pm 250$ Ma). The H-W galena plots at the least radiogenic end of the line in both Figures 2.3 and 2.4. Variation in ratios for the H-W galena (0.06%) is within the analytical error.

Galena from the Myra ore deposit at Buttle Lake has isotopic ratios that are slightly different than the H-W ore deposit. Using a two-tailed students $t$ statistical test the $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the Myra and H-W ores are different at the 0.05 level of significance. It seems reasonable to assume that there is also a real difference in $^{207}\text{Pb}/^{204}\text{Pb}$ between these ore bodies, as suggested in Figures 2.3 and 2.4. Galena can therefore be used to distinguish between different ore bodies in this camp, and to aid stratigraphic correlation of ore horizons. This is particularly useful in this type of deposit where ore horizons are separated by faults and folds.

The H-W ore is the most radiogenic (with the exception of one sample of G hanging wall sulphide) despite its position at the base of the mine sequence. Further up the sequence the ores
Figure 2.3 207Pb/204Pb versus 206Pb/204Pb plot of galena (solid circles; Table 2.3) and whole rock present (solid triangles; Table 2.2) and initial ratios at 370 Ma (open triangles; Table 2.4) from Buttle Lake Uplift. Three galena samples from the Cowichan - Horne Lake Uplift (S457, LN, TY) are also shown. Galena (open circles) and whole rock (inverted triangles) analyses from the Paleozoic volcanogenic ore deposits of Shasta, California are taken from Slawson (1983) and Doe et al. (1985). A solid diamond marks the estimated composition of Devonian mantle (Doe et al. 1985). Major fields of whole rocks from modern mid-ocean ridge basalts, ocean islands and ocean sediments are taken from the literature as follows: mid-ocean ridge basalts (Church and Tatsumoto 1975, Brevart et al. 1981, Vidal and Clauer 1981); ocean islands (Sun and Jahn 1975, Sun 1980, Tatsumoto 1978, Weis 1983); island arcs (Oversby and Ewart 1972, Church 1975, Meijer 1976, Kay et al. 1978); Pacific sediments (Church 1976, Sun 1980, and Vidal and Clauer 1981). These fields have been adjusted for 370 Ma lead evolution using the growth curve of Stacey and Kramers (1975).
Figure 2.4  $^{208}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb plot of Buttle Lake galena and whole rock data. See Figure 2.3 for explanation of symbols and source of data. Isotopic fields for MORB, island arcs, ocean islands and Pacific sediments have been adjusted for 370 Ma lead evolution using Stacey and Kramers (1975) growth curve.
become less enriched in $^{207}\text{Pb}/^{204}\text{Pb}$. Whole rock sample W149, taken from the top of the mine sequence, has the lowest $^{207}\text{Pb}/^{204}\text{Pb}$ value of all rocks sampled. Correspondingly, galena from the stratigraphically high Myra deposit has the least radiogenic ratios of the Buttle Lake ores sampled (Figs. 2.3 and 2.4).

Differences in isotopic composition of galena between the Myra ore and the H-W deposits are not simply due to an age difference between the deposits, because the oldest of the deposits has the most radiogenic ratios, and because the isotopic differences are not in the direction of a suitable isochron. Rather differences must be attributed to variations in the isotopic compositions of the source magmas. In an island arc setting, mixing of crustal lead with mantle-derived magmas is to be expected (Meijer 1976; Kay et al. 1982). Involvement of greater quantities of crustal lead in the production of the H-W rocks and ores, than for the Myra ore, can explain the higher $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of the former.

Decrease of $^{207}\text{Pb}/^{204}\text{Pb}$ with time in the Myra Formation rocks and ores is significant and supports a new model for the formation of the Buttle Lake ores being proposed by S. Juras (in preparation). Based on a detailed stratigraphy of the mine sequence, he suggests that the ores form in a back-arc rifting
environment. According to this hypothesis the back-arc magmas become increasingly primitive as rifting progresses. Early magmas in the back-arc are relatively enriched in $^{207}$Pb/$^{204}$Pb due to the involvement of arc crustal material. As the arc splits, the crust in the back-arc thins and the magmas show less crustal involvement, and concomittantly lower $^{207}$Pb/$^{204}$Pb values. A similar model, based on neodymium and strontium studies, has been proposed for the formation of the Kuroko ore deposits in Japan (Nohda and Wasserburg 1986).

There are many implications of this new model for ore genesis for Kuroko-type volcanogenic massive sulphides in terms of exploration strategy. A specific tectonic setting is required, namely the initial stages of back-arc rifting in a mature island arc. Thus, an increasingly primitive volcanic pile can be an exploration target. At Buttle Lake, the largest ore deposit is at the base of the mine sequence and has the most radiogenic lead, whereas the highest grade ore is higher up in the sequence and has less radiogenic lead characteristics.

Variation in initial ratios for different stratigraphic levels of the Myra Formation, marked by galena lead isotope analyses, illustrates one fundamental problem in using whole rock common lead age determinations. Isochron age calculations rely on the assumption that the initial ratios of the rocks were
homogeneous. If this assumption is not true, the slope of the linear array of evolved ratios is not only due to the age of the array, but is partly controlled by initial inhomogeneities.

2.2.4 Comparison of Myra Formation whole rock initial ratios and galena

Whole rock initial ratios for the Buttle Lake Uplift, calculated using an assumed age of 370 Ma (Table 2.4), are plotted with galena analyses in Figures 2.3 and 2.4. The galena samples have more radiogenic ratios than the whole rock initial ratios. There are three possible explanations for this:

1) The whole rock initial ratios were never the same as the galena ratios. The assumption that volcanic rocks and syngentic ore deposits have the same initial ratios has been shown to be reasonable (Brevart et al. 1981). However, small differences between whole rock initial ratios and ore lead ratios were found in the Kuroko deposits of Japan (Fehn et al. 1983). Church et al. (1986) also note that ores from Cascade porphyry deposits have greater 206Pb/204Pb values than the volcanic rocks with which they are associated. The discrepancy here is larger than is reasonably explained in this way.

2) The assumed age for the rocks is too old so that the initial ratios are underestimated. This is unlikely since the age of the Myra Formation is based on two zircon age estimates which show good agreement (S. Juras pers. comm. 1986). An age of
TABLE 2.4 Initial ratios for the Sicker Group, Vancouver Island, B.C. Age corrections are for assumed age of 370 Ma. μ and k values used in the calculations are listed in Table 2.2.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>206Pb/204Pb1</th>
<th>207Pb/204Pb1</th>
<th>208Pb/204Pb1</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB1</td>
<td>17.94 (0.02)</td>
<td>15.55 (0.01)</td>
<td>37.55 (0.08)</td>
</tr>
<tr>
<td>MB2</td>
<td>16.21 (1.04)</td>
<td>15.46 (0.06)</td>
<td>36.21 (1.34)</td>
</tr>
<tr>
<td>GRHY</td>
<td>18.32 (0.04)</td>
<td>15.57 (0.01)</td>
<td>not applicable</td>
</tr>
<tr>
<td>R90</td>
<td>18.16 (0.15)</td>
<td>15.57 (0.01)</td>
<td>37.86 (0.19)</td>
</tr>
<tr>
<td>R129</td>
<td>18.82 (0.12)</td>
<td>15.59 (0.02)</td>
<td>not applicable</td>
</tr>
<tr>
<td>R130</td>
<td>18.17 (0.37)</td>
<td>15.55 (0.01)</td>
<td>37.76 (0.11)</td>
</tr>
<tr>
<td>R131</td>
<td>18.33 (0.09)</td>
<td>15.56 (0.02)</td>
<td>37.99 (0.24)</td>
</tr>
<tr>
<td>H10A</td>
<td>18.81 (0.09)</td>
<td>15.60 (0.01)</td>
<td>38.29 (0.10)</td>
</tr>
<tr>
<td>H16</td>
<td>18.63 (0.04)</td>
<td>15.62 (0.01)</td>
<td>38.38 (0.05)</td>
</tr>
<tr>
<td>H58B</td>
<td>17.75 (0.31)</td>
<td>15.54 (0.01)</td>
<td>37.59 (0.29)</td>
</tr>
<tr>
<td>S3</td>
<td>18.16 (0.04)</td>
<td>15.57 (0.01)</td>
<td>37.87 (0.04)</td>
</tr>
</tbody>
</table>

Average 370 Ma = 18.05 (0.73) 15.56 (0.05) 37.67 (0.64)

---

1. Figures in brackets are the one sigma estimates of uncertainty calculated using the error propagation program "T1CORR" (Appendix D).
approximately 300 Ma is required to allow better agreement between galena and whole rock initial ratios. This seems to be too young based on other age estimates.

3) Recent uranium gain or lead loss has occurred in the Myra Formation rocks, causing the measured $\mu$ values to be too high. This is the most likely possibility since it is unlikely that the Sicker Group rocks have behaved as a closed system since their time of formation—particularly since they have been subjected to metamorphism at least once in the Mesozoic. The variation in initial ratios is support for this possibility. If the rocks had remained closed systems, the initial ratios would probably define a more cohesive field.

2.2.5 Comparison of Sicker Group rocks and ores with those of the West Shasta District of California.

An Early Devonian volcanic sequence is exposed in the Eastern Klamath Mountains. Here, Kuroko-type massive sulphides occur in the Balaklala Rhyolite (Kinkel et al. 1956), which is made up of siliceous metavolcanic rocks overlying a low K, tholeiitic basalt to andesite series known as the Copley Greenstone. Muller (1980) tentatively correlated the Copley Greenstone with the Nitinat Formation, and the Balaklala Rhyolite with the Myra Formation. The ore deposits of the West Shasta district are overlain by black shales of the Kennett Formation, which in turn are overlain by a Permian limestone unit apparently correlative with the Buttle
Lake Formation (Muller 1980). Detailed trace element and rare earth element analyses of the Copley Greenstone and the Balaklala Rhyolite indicate that this volcanic sequence represents an immature island arc related to a back-arc basin, similar to the present day Mariana island arc (Lapierre et al. 1985).

Lead isotope studies of the Shasta district (Slawson 1983; Doe et al. 1985), provide data for comparison with the Sicker Group volcanic rocks and ores. Data from Slawson (1983) and Doe et al. (1985) have been plotted with Sicker Group ores and rocks from Buttle Lake camp in Figures 2.3 and 2.4. It is apparent that the majority of ore samples from West Shasta are isotopically distinct from those from the Buttle Lake camp. Lead isotope signatures also show that the Copley Greenstone is not the same unit as the Nitinat Formation, and that the Balaklala Rhyolite is not the same as the Myra Formation. The Sicker Group rocks have higher 207Pb/204Pb ratios than the West Shasta rocks, indicating a greater crustal component in the former. This evidence makes it unlikely that these two areas were part of the same Paleozoic volcanic belt.

There are a few outliers in the Shasta data of Slawson (1983) which plot closer to the values of the Sicker ore deposits. There is, however, some doubt about the correctness of
these outliers (as expressed by Doe et al. 1985 because of their inability to reproduce the outlying values for the Balaklala A and B ore deposits).

2.3 MAPLE BAY

2.3.1 Geology

Pillowed basaltic units and tuffaceous rocks of the Nitinat Formation are exposed at Maple Bay (Muller 1980). They are complexly folded with a quartz feldspar porphyry. Muller (1980) correlates the porphyry with the Myra Formation, but Brandon et al. (1986) interpret it as being one of the Saltspring Intrusions. The rocks in this area have been metamorphosed to upper greenschist facies (Brandon et al. 1986).

2.3.2 Sample suite

Samples were taken from the mafic unit, the quartz feldspar porphyry, and from a chert horizon within the mafic unit (Table 2.1, Fig. 2.5).

2.3.3 Results

Lead isotope compositions for the Maple Bay samples are listed in Table 2.2, and shown in conventional lead-lead plots in Figures 2.6 and 2.7. The spread in $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios
Figure 2.5 Detailed geology of Maple Bay area (from Muller 1980, figure 15) showing whole rock sample locations (Table 2.1).
Figure 2.6  $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plot of whole rock and galena data from the Sicker Group, Vancouver Island, B.C. Squares are samples from the Cowichan - Horne Lake Uplift. Triangles are for samples from the Buttle Lake Uplift. Open symbols mark initial ratios (Table 2.4) calculated at 370 Ma. Solid symbols are for present ratios (Table 2.2). Solid circles are for galena samples (Table 2.3). The best fit line to the whole rock data, excluding samples LT1, LT4, H16, H58B, H10A, SQE, S3, using York (1969) least squares regression has the parameters: slope = 0.057120, intercept = 14.516. This corresponds to an age of 496 Ma $\pm$ 76 Ma. The growth curve, marked "S & K", is that of Stacey and Kramers (1975).
Figure 2.7  208Pb/204Pb versus 206Pb/204Pb plot of whole rock and galena data (Tables 2.2, 2.3 and 2.4) from the Sicker Group, Vancouver Island, B.C. For explanation of symbols see Figure 2.6.
between samples and the linearity of the plots suggest that an isochron age can be calculated for these rocks (using equation #1, Table 2.5). Taking all of the Maple Bay samples \((t_2 = 0)\), the estimated age \((t_1)\) is \(320.75^{+75/-80}\) Ma (least squares regression after York 1969) and \(k\) (equation #2, Table 2.5) is \(3.0^{+0.2/-0.3}\). Calculated separately, the felsic unit gives an age of \(424^{+97/-103}\) Ma, and the mafic Nitinat tuff gives \(700^{+275/-335}\) Ma; \(k\) values are \(3.4^{+0.4/-0.5}\) and \(2.9^{+0.3/-0.4}\), respectively.

The large uncertainties associated with each age calculation indicates that common lead age determination is not a suitable method for these rocks. Common lead isotope isochrons can only be used with confidence if the age of the rocks is sufficient to nullify the effects of inhomogeneous initial ratios, and to produce a wide spread in values due to in situ addition of radiogenic lead.

2.4 MOUNT SICKER - LENORA AND TYEE MINE AREA

2.4.1. Geology and sample suite.

Lenora and Tyee massive sulphide ore deposits occur on the flanks of Mount Sicker (Fig. 2.1). These mines, which are similar to those of the Buttle Lake Uplift, were productive from
TABLE 2.5 Equations used in calculating isochron ages using common lead isotope analyses.

Equation #1:

Isochron slope in $^{207}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb = $m_{207-206}$

$$m_{207-206} = \frac{1}{137.88} \frac{e^{\lambda_{1}t_{1}} - e^{\lambda_{2}t_{2}}}{e^{\lambda_{1}t_{1}} - e^{\lambda_{1}t_{2}}}$$

Equation #2:

Isochron slope in $^{208}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb = $m_{208-206}$

$$m_{208-206} = k \frac{e^{\lambda_{3}t_{1}} - e^{\lambda_{3}t_{2}}}{e^{\lambda_{1}t_{1}} - e^{\lambda_{1}t_{2}}}$$

$\lambda_{1} = 0.155125 \times 10^{-9}$ Jaffey et al., 1971

$\lambda_{2} = 0.98485 \times 10^{-9}$ Jaffey et al., 1971

$\lambda_{3} = 0.049475 \times 10^{-9}$ LeRoux and Glendenin, 1963

137.88 = present ratio $^{238}$U/$^{235}$U
1898 to 1964. The ore is hosted by tuffaceous rocks of the Sicker Group, thought by Muller (1980) to belong to the Myra Formation. Samples were collected from a compositional variety consisting of: tuffaceous rocks, a chert horizon, and a diorite sheet, which may be either contemporaneous or a later intrusive unrelated to the Sicker Group. All of these rocks were extremely altered. No lead, uranium or thorium determinations were made on this sample suite; only lead isotope compositions were measured. Galena lead isotope analyses for a few samples of the ore are reported in Andrew et al. (1982).

2.4.2 Results.

Lead isotope compositions of samples LT1 to LT6 (Table 2.2) are plotted on Figures 2.6 and 2.7. The data are not sufficiently spread to allow the calculation of a meaningful isochron age. The diorite sheet has a uniform isotopic composition indicated by the similarity in ratios from a sample taken from the top of the sheet (sample LT1) and another from the bottom (sample LT4). It is not possible, however, to tell conclusively from the data whether or not the sheet belongs to the Sicker Group or to Tertiary intrusives (Chapter 5), because there is an overlap in their isotopic compositions.

The marked similarity in the isotopic composition of the galena from the Lenora and Tyee ore deposits to those of the
Westmin ore deposits at Buttle Lake, suggests that both camps are of the same age and origin (Andrew 1982). Brandon et al. (1986) recently concluded that the Myra Formation does not occur in the Cowichan Lake Uplift, and that there must be a minimum age difference of 20 Ma years between the Myra Formation in the Buttle Lake Uplift (minimum age 370 Ma) and the rocks overlying the Nitinat tuff in the Cowichan Lake Uplift (maximum age 350 Ma). Given their estimate of a minimum age difference of 20 Ma between the two ore forming events, the galena lead isotope ratios for the Lenora and Tyee ore deposits should be more radiogenic than those of the Buttle Lake ore deposits. They are not. Therefore, contrary to Brandon et al. (ibid), galena lead data support the existence of Myra Formation correlatives in the Cowichan Lake Uplift.

2.5. DISCUSSION OF THE SICKER GROUP AS A WHOLE

2.5.1 Augmented sample suite
Several whole rock analyses of rocks from pre-existing collections are included in this discussion. These include two rocks from R.L. Armstrong, one sample of the Tyee quartz porphyry, and a sample of uralite porphyry (samples S1QE, and S3). Three rocks from the B.Sc thesis collection of P. Holbek (1980) were also analyzed. These were all from the Mount Brenton
area of the Cowichan - Horne Lake Uplift (samples H10A, H16 and H58B). All of these samples had been crushed and analysed for rubidium and strontium. Their lead isotope compositions are therefore regarded with suspicion for reasons outlined in Chapter 1. A galena analysis from near Port Alberni, provided by Westmin Resources Ltd., is also discussed below.

2.5.2 Plate tectonic setting of the Sicker Group

Figures 2.2 and 2.3 show typical lead isotope ratios for modern plate tectonic environments, which have been projected back by 370 Ma using an average crustal growth curve (Stacey and Kramers 1975). The Sicker Group (represented in this figure by galena samples and whole rock samples from Buttle Lake Uplift) has higher 207Pb/204Pb ratios than for MORBs, and resembles other island arc type environments—although direct comparison is difficult to make because of the age difference. Also shown is the value for the Devonian mantle proposed by Doe et al. (1985) based on analyses from the West Shasta district of the eastern Klamath mountains.

Sicker Group rocks must have incorporated relatively large amounts of lead from sedimentary rocks in order to produce the observed ratios. This implies that the subduction zone, which produced the Sicker arc, must have been sediment-rich, and therefore was probably near to a supply of continental detritus.
Alternatively, contribution to the arc of mantle which is anomalously radiogenic, relative to the estimated Devonian mantle value (Doe et al. 1985), is required to explain the data.

2.5.3. Age considerations

Analyses of all of the Sicker Group rocks sampled in this study (Table 2.2) are plotted in Figures 2.6 and 2.7. These figures show the general colinearity of the whole rock data. The best fit line through all of the data in Figure 2.6, using the least squares regression method of York (1969), gives an isochron age of 496 Ma ± 76 Ma. The large error in this age estimate reflects the variation in initial ratios for Sicker Group rocks shown by the Buttle Lake galena data.

Whole rock modified Concordia method (Russell et al. 1967; Ulrych 1969) using the primordial lead composition of Tatsumoto et al. (1973) gives an age of 416 ± 90 Ma for the lower intercept, and an upper intercept age of 4379 ± 17 Ma (Table 2.6, Fig. 2.8). This method relies upon the assumptions that initial ratios were homogeneous and that lead evolution occurred in a closed system. Neither assumption can be shown to be appropriate for the Sicker Group, hence the large uncertainties associated with the age determination.

Rubidium and strontium isotope data for the Sicker Group
TABLE 2.6. Data for the Concordia plot (Fig. 2.8). Primordial lead composition is from Tatsumoto et al. (1973) as follows: \( \frac{206\text{Pb}}{204\text{Pb}} = 9.307, \frac{207\text{Pb}}{204\text{Pb}} = 10.294, \frac{208\text{Pb}}{204\text{Pb}} = 29.476. \) Figures given in brackets are one sigma uncertainties, based on propagation of errors associated with the lead isotope data and the \( \mu \) values, from the program "CONCORD" (Appendix D).

<table>
<thead>
<tr>
<th>SAMPLE NAME</th>
<th>( \frac{238\text{U}}{204\text{Pb}} )</th>
<th>( \frac{206\text{Pb}}{238\text{U}} )</th>
<th>( \frac{207\text{Pb}}{235\text{U}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB1</td>
<td>11.08 (0.27)</td>
<td>0.838 (0.020)</td>
<td>65.817 (1.573)</td>
</tr>
<tr>
<td>MB2</td>
<td>161.58 (17.38)</td>
<td>0.102 (0.010)</td>
<td>4.846 (0.471)</td>
</tr>
<tr>
<td>GRHY</td>
<td>17.98 (0.60)</td>
<td>0.560 (0.018)</td>
<td>40.896 (1.323)</td>
</tr>
<tr>
<td>R90</td>
<td>22.96 (2.47)</td>
<td>0.444 (0.043)</td>
<td>32.110 (3.119)</td>
</tr>
<tr>
<td>R129</td>
<td>12.59 (1.84)</td>
<td>0.815 (0.104)</td>
<td>58.459 (7.456)</td>
</tr>
<tr>
<td>R130</td>
<td>17.07 (0.57)</td>
<td>0.577 (0.019)</td>
<td>42.915 (1.389)</td>
</tr>
<tr>
<td>R131</td>
<td>26.90 (0.50)</td>
<td>0.394 (0.008)</td>
<td>27.417 (0.509)</td>
</tr>
<tr>
<td>H10A</td>
<td>13.93 (0.12)</td>
<td>0.741 (0.006)</td>
<td>52.955 (0.461)</td>
</tr>
<tr>
<td>H16</td>
<td>5.37 (0.59)</td>
<td>1.795 (0.178)</td>
<td>137.315 (13.596)</td>
</tr>
<tr>
<td>H58B</td>
<td>47.12 (5.28)</td>
<td>0.238 (0.024)</td>
<td>15.751 (1.587)</td>
</tr>
<tr>
<td>S3</td>
<td>6.32 (0.05)</td>
<td>1.464 (0.012)</td>
<td>115.627 (0.929)</td>
</tr>
</tbody>
</table>

1. \( \mu \) values and their uncertainties are calculated using the program "WRUCLC" (Appendix D) for U ppm determined by isotope dilution (Table 2.2), and using "MUCALC" for U ppm determined by neutron activation analysis.
Figure 2.8. Whole rock Concordia plot for samples from the Sicker Group, Vancouver Island, B.C. Data are in Table 2.6. Open squares represent samples from Cowichan - Horne Lake Uplift; open triangles represent samples from Buttle Lake Uplift.
(Table 2.7) do not provide age information, because of the scattered nature of the analyses. This is probably due to the fact that many of the rocks have been metamorphosed since their time of formation so the isotope system has been at least partially reset. It is also possible that the Sicker Group does not have a single initial $^{87}\text{Sr}/^{86}\text{Sr}$, but that there is a range of appropriate values. This is true for many island arcs.

One analysis of galena from the Alberni area (sample S457, Table 2.3, Figs. 2.2 and 2.3) has a less radiogenic lead isotope signature than do the syngenetic massive sulphide ore deposits of both the Buttle Lake mine and the Mount Sicker ores. This may mean one of two things, either the Alberni sample is from an older mineralization event, or the initial ratios within the Sicker Group are more variable than suggested by the galena lead isotope ratios of the Buttle Lake, and Lenora and Tyee ore deposits.

The time difference represented in the $^{206}\text{Pb}/^{204}\text{Pb}$ difference between sample S457 and the H-W ore is 100 to 150 Ma (using $\mu$ values of between 8 and 12). If the H-W ore is correctly dated at 365 Ma, an older mineralization event in the Sicker at 465-515 Ma is required to explain the galena S457. This seems highly unlikely since rocks of this age have not yet been identified in the Sicker Group. Unfortunately the geology
TABLE 2.7. Rubidium and strontium isotope data for the Sicker Group, Vancouver Island, B.C. Initial ratios are calculated at 370 Ma, using decay constants recommended by Steiger and Jager (1977).

<table>
<thead>
<tr>
<th>SAMPLE NUMBER</th>
<th>Sr ppm</th>
<th>Rb ppm</th>
<th>Rb/Sr</th>
<th>87Rb/86Sr</th>
<th>INITIAL</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ALTERNATIVE)</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MB1 (MB001)</td>
<td>295</td>
<td>1.0</td>
<td>0.003</td>
<td>0.010</td>
<td>0.7050</td>
<td>0.7049</td>
</tr>
<tr>
<td>MB2 (MB002)</td>
<td>143</td>
<td>21.5</td>
<td>0.150</td>
<td>0.434</td>
<td>0.7068</td>
<td>0.7045</td>
</tr>
<tr>
<td>R78 (SJR78)</td>
<td>50</td>
<td>14.1</td>
<td>0.283</td>
<td>0.818</td>
<td>0.7086</td>
<td>0.7043 S. Juras (in progress)</td>
</tr>
<tr>
<td>R90 (SJ90)</td>
<td>105</td>
<td>47.1</td>
<td>0.448</td>
<td>1.297</td>
<td>0.7094</td>
<td>0.7026 S. Juras (in progress)</td>
</tr>
<tr>
<td>R131</td>
<td>307</td>
<td>54.8</td>
<td>0.179</td>
<td>0.517</td>
<td>0.7067</td>
<td>0.7040</td>
</tr>
<tr>
<td>H10A (79H-10A)</td>
<td>374</td>
<td>18.0</td>
<td>0.048</td>
<td>0.139</td>
<td>0.7056</td>
<td>0.7049 Holbek (1980)</td>
</tr>
<tr>
<td>H16 (79H-16)</td>
<td>364</td>
<td>14.2</td>
<td>0.039</td>
<td>0.113</td>
<td>0.7058</td>
<td>0.7052 Holbek (1980)</td>
</tr>
<tr>
<td>H58B (79H-58B)</td>
<td>222</td>
<td>54.3</td>
<td>2.450</td>
<td>7.101</td>
<td>0.7272</td>
<td>0.6898 Holbek (1980)</td>
</tr>
<tr>
<td>S1QE (Sicker1QE)</td>
<td>223</td>
<td>4.5</td>
<td>0.020</td>
<td>0.058</td>
<td>0.7039</td>
<td>0.7036 Armstrong et al., 1986</td>
</tr>
<tr>
<td>S3 (Sicker 3)</td>
<td>39.6</td>
<td>1.2</td>
<td>0.003</td>
<td>0.009</td>
<td>0.7055</td>
<td>0.7055 Armstrong et al., 1986</td>
</tr>
</tbody>
</table>
of the rocks associated with the anomalous sample has not been disclosed (Walker pers. comm. 1985). Further work is required to establish the nature of the difference in isotopic composition between the anomalous sample (S457) and the productive massive sulphides in the Sicker Group.

2.6. CONCLUSIONS

The Sicker Group volcanic rocks have been isotopically characterized by whole rock and galena lead isotope analyses. Common lead age determination methods are too imprecise to contribute to an understanding of the absolute age of the Sicker Group. However, a number of conclusions can be drawn from the isotopic data:

1) Sicker Group lead isotope ratios are typical of those of an island arc.

2) High $^{207}\text{Pb}/^{204}\text{Pb}$ ratios relative to an estimated Devonian mantle value indicates crustal involvement in the formation of the Sicker Group volcanic rocks. This suggests that continental detritus was available to the trench related to subduction and arc-formation, and that the arc formed close to a continental land mass. Alternatively, an anomalous mantle source is required.

3) A decrease in the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio of both ores and rocks
with time in the Myra Formation at Buttle Lake supports the hypothesis that the magmas producing these ores became more primitive with time, and favours a back-arc origin for Kuroko-type volcanogenic massive sulphides.

4) The Sicker Group rocks are not direct equivalents of the West Shasta volcanic rocks. There are significant isotopic differences between the two areas.

5) Galena lead isotope ratios for the Lenora and Tyee ore deposits in the Cowichan Lake Uplift are so similar to those of the Buttle Lake ore deposits that it seems unlikely that there is an age difference of 20 Ma or more between them, as required by the interpretation of Brandon et al. (1986). The galena lead isotope information, here, should be reconciled in any age estimations for the Sicker Group.
ISOTOPE GEOCHEMISTRY OF THE KARMUTSEN VOLCANICS

SYNOPSIS

Lead isotope ratios of the Triassic flood basalts of the Karmutsen Formation are heterogeneous. Evidence for isotopic mixing suggests that one end-member has a low lead content, low 207Pb/204Pb and 87Sr/86Sr, but high 206Pb/204Pb and 208Pb/204Pb relative to a second lead-rich end-member. The data can be explained in terms of crustal contamination of a thorium enriched mantle source.

3.1 INTRODUCTION

The Karmutsen Formation is a Late Triassic sequence of subaqueous to subaerial tholeiitic volcanic rocks of predominantly basaltic composition, reaching a thickness of 6,000 m (Muller 1977). It overlies the Paleozoic Sicker Group and is overlain by Late Triassic (Late Karnian to Early Norian) carbonates (Carlisle and Suzuki 1974; Muller et al. 1974;
Jeletsky 1970). It forms a major part of the outcrop of Vancouver Island and is a dominant and characteristic feature of Wrangellia (Jones et al. 1977).

Concordant zircon dates of 217 to 222 Ma have been obtained for a Karmutsen-related intrusive rock (Isachsen et al. 1985). This sample (S1AM) provides an isotopic estimate of the age of these rocks which agrees well with the fossil age of between 228 and 232 Ma using the DNAG timescale of Palmer (1983). Sample S1AM was analysed for its common lead isotopic composition in this study (see Table 3.2).

Karmutsen Formation rocks are generally accepted as the equivalents of the Nikolai Greenstone of Alaska (Muller 1977). Chilkat basalts from the Taku terrane, Alaska, are also thought to belong to the same group of basalts (Davis and Plafker 1985).

Major element geochemical analyses fail to discriminate adequately between plate tectonic settings for these volcanic rocks (Barker et al. 1985). On various discriminant diagrams they plot as mid-ocean ridge basalts (MORB), back-arc, within plate or island arc tholeiites. The purpose of this study is to isotopically fingerprint the Karmutsen Formation and to use isotopic composition and the concentrations of lead, uranium and thorium to further discriminate between plate tectonic settings.
for this type of basalt.

Samples were obtained from several locations on Vancouver Island (Fig. 3.1 and Table 3.1). The Buttle Lake mine road, central Vancouver Island, provided a suitable transect along which to collect samples from different stratigraphic levels (Fig. 3.1 and Table 3.1: samples KAR1, KAR2, KAR7 and KAR10, and K008). Basalt samples were also obtained from Piper's Lagoon on the east coast of Vancouver Island, about 10 km north of Nanaimo (Fig. 3.1 and Table 3.1: samples K005 and K007). Whole rock samples K609, K610, K612, K613 and S1AM were obtained, in powdered form, from the collections of J. Muller and R.L. Armstrong. One sample of rhyodacite from the Malksope River area (Fig. 3.1 and Table 3.1: sample K101) was analyzed.

Two galena samples (Fig. 3.1 and Table 3.1) were available from deposits of probable vein type within the Karmutsen Formation. Lead mineralization is very rare in these volcanics probably reflecting the low concentrations of lead in the rocks (Table 3.2).
Figure 3.1 Distribution of Karmutsen Formation rocks (patterned) on Vancouver Island, B.C., with whole rock (circles) and galena (squares) sample locations (Table 3.1).
### TABLE 3.1 Whole rock and galena sample locations (see Fig. 3.1) and brief descriptions.

<table>
<thead>
<tr>
<th>NAME</th>
<th>LAT.</th>
<th>LONG.</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>K005</td>
<td>49.23</td>
<td>123.95</td>
<td>Basalt. Piper's Lagoon</td>
</tr>
<tr>
<td>K007</td>
<td>49.23</td>
<td>123.95</td>
<td>Basalt. Piper's Lagoon</td>
</tr>
<tr>
<td>K008</td>
<td>49.79</td>
<td>125.60</td>
<td>Pillow basalt. Buttle Lake Road</td>
</tr>
<tr>
<td>K101</td>
<td>50.17</td>
<td>127.35</td>
<td>Rhyodacite. Malksope River</td>
</tr>
<tr>
<td>K609</td>
<td>49.94</td>
<td>124.62</td>
<td>Basalt. Upper Campbell Lake, East side, 7 km south southeast of dam, Buttle Lake Road.</td>
</tr>
<tr>
<td>K610</td>
<td>49.31</td>
<td>124.74</td>
<td>Basalt, somewhat altered. Between Marshy and Lucy lakes.</td>
</tr>
<tr>
<td>K613</td>
<td>49.25</td>
<td>124.87</td>
<td>Basalt. Sproat Lake road, east of Stirling Arm.</td>
</tr>
<tr>
<td>K616</td>
<td>49.23</td>
<td>124.94</td>
<td>Basalt. South of Stirling Arm, Sproat lake.</td>
</tr>
<tr>
<td>KAR1</td>
<td>49.67</td>
<td>125.53</td>
<td>Sill-like massive basalt. Buttle Lake Road.</td>
</tr>
<tr>
<td>KAR2</td>
<td>49.69</td>
<td>125.55</td>
<td>Massive basalt. Buttle Lake Road</td>
</tr>
<tr>
<td>KAR7</td>
<td>49.85</td>
<td>125.62</td>
<td>Amygdaloidal, scoriaceous basalt. Buttle Lake Road</td>
</tr>
<tr>
<td>KAR10</td>
<td>49.94</td>
<td>125.61</td>
<td>Massive basalt near Dolly Varden Point, Buttle Lake Road.</td>
</tr>
<tr>
<td>KAR11</td>
<td>49.99</td>
<td>125.41</td>
<td>Massive, fine-grained basalt, Echo Lake, Buttle Lake Road.</td>
</tr>
<tr>
<td>S1AM</td>
<td>48.87</td>
<td>123.71</td>
<td>Hornblende gabbro dyke intrusive into Sicker Group rocks - 2.9 km south of Chemainus River bridge, Highway 1</td>
</tr>
<tr>
<td>K314</td>
<td>49.06</td>
<td>124.71</td>
<td>Galena - Starlight prospect</td>
</tr>
<tr>
<td>K335</td>
<td>49.75</td>
<td>124.59</td>
<td>Galena - Nutcracker prospect (Texada Island)</td>
</tr>
</tbody>
</table>

1. All rock samples were collected by C.I. Godwin, except S1AM which is from the collection of R.L. Armstrong. Galena samples are from the Economic collection at the University of British Columbia.
### TABLE 3.2 Lead, uranium and thorium data from Karmutsen volcanic rocks and related galena lead isotope analyses, Vancouver Island, B.C. Data sites are located in Figure 3.1 and Table 3.1.

<table>
<thead>
<tr>
<th>SAMPLE NAME</th>
<th>$^{206}$Pb/$^{204}$Pb</th>
<th>$^{207}$Pb/$^{204}$Pb</th>
<th>$^{208}$Pb/$^{204}$Pb</th>
<th>Pb PPM</th>
<th>U PPM</th>
<th>TH PPM</th>
<th>(N.A.A.)</th>
<th>(D.N.)</th>
<th>μ6</th>
<th>k1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Whole rock samples</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K005</td>
<td>19.183(0.012)</td>
<td>15.605(0.011)</td>
<td>38.814(0.033)</td>
<td>1.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.224(0.009)</td>
<td>15.618(0.009)</td>
<td>38.081(0.030)</td>
<td>1.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K005-AVG (n=2)</td>
<td>19.204(0.011)</td>
<td>15.612(0.010)</td>
<td>38.848(0.032)</td>
<td>1.39</td>
<td>0.31(0.01)</td>
<td>0.34</td>
<td>0.95</td>
<td>14.2</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>K007</td>
<td>19.741(0.013)</td>
<td>15.629(0.010)</td>
<td>39.238(0.031)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.658(0.023)</td>
<td>15.584(0.017)</td>
<td>39.370(0.049)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K007-AVG (n=3)</td>
<td>19.711(0.022)</td>
<td>15.605(0.013)</td>
<td>39.270(0.051)</td>
<td>0.91</td>
<td>0.32(0.01)</td>
<td>0.36</td>
<td>0.97</td>
<td>22.1</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>K008</td>
<td>19.696(0.037)</td>
<td>15.590(0.029)</td>
<td>39.364(0.078)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>19.672(0.013)</td>
<td>15.599(0.008)</td>
<td>39.345(0.029)</td>
<td></td>
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<tr>
<td>K008-AVG (n=3)</td>
<td>19.676(0.011)</td>
<td>15.581(0.014)</td>
<td>39.324(0.031)</td>
<td>0.54</td>
<td>0.23(0.01)</td>
<td>nd</td>
<td>nd</td>
<td>27.1</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>K101 #1</td>
<td>21.506(0.008)</td>
<td>15.772(0.008)</td>
<td>40.151(0.030)</td>
<td>1.52</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>K101 #2</td>
<td>20.262(0.009)</td>
<td>15.675(0.008)</td>
<td>39.509(0.028)</td>
<td>1.52</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>K609</td>
<td>18.575(0.031)</td>
<td>15.407(0.025)</td>
<td>38.298(0.069)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
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<tr>
<td>K610</td>
<td>18.449(0.029)</td>
<td>15.427(0.025)</td>
<td>37.852(0.063)</td>
<td></td>
<td></td>
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<tr>
<td>K610-AVG (n=2)</td>
<td>18.361(0.021)</td>
<td>15.428(0.019)</td>
<td>37.760(0.050)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>K612</td>
<td>19.306(0.061)</td>
<td>15.627(0.050)</td>
<td>38.747(0.125)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>K613</td>
<td>17.946(0.010)</td>
<td>15.379(0.010)</td>
<td>37.679(0.031)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
<tr>
<td>KAR1</td>
<td>19.361(0.013)</td>
<td>15.601(0.012)</td>
<td>38.860(0.037)</td>
<td>1.86</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
<td></td>
</tr>
</tbody>
</table>

The table includes data on lead, uranium, and thorium concentrations, along with various isotopic ratios and measurements such as Pb PPM, U PPM, TH PPM, and μ6. The data is presented for whole rock samples labeled K005, K007, K008, K009, K010, K011, K609, K610, K612, and KAR1, with specific values for each sample provided in the table.
TABLE 3.2 (continued)

<table>
<thead>
<tr>
<th>SAMPLE NAME</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
<th>PB PPM (I.D.)</th>
<th>U PPM (I.D.)</th>
<th>U PPM (N.A.A.)</th>
<th>Th PPM (D.N.)</th>
<th>p6</th>
<th>k7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole rock samples (continued)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAR2</td>
<td>19.000(0.013)</td>
<td>15.599(0.012)</td>
<td>38.568(0.036)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAR2-AVG (n=2)</td>
<td>18.998(0.009)</td>
<td>15.596(0.011)</td>
<td>38.564(0.033)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>KAR7</td>
<td>19.397(0.015)</td>
<td>15.592(0.014)</td>
<td>38.951(0.039)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAR7-AVG (n=2)</td>
<td>19.416(0.011)</td>
<td>15.587(0.010)</td>
<td>38.975(0.033)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>KAR10</td>
<td>18.715(0.011)</td>
<td>15.551(0.010)</td>
<td>38.144(0.031)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAR10-AVG (n=2)</td>
<td>18.728(0.010)</td>
<td>15.561(0.008)</td>
<td>38.176(0.030)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>KAR11</td>
<td>18.991(0.007)</td>
<td>15.583(0.008)</td>
<td>38.325(0.028)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KAR11-AVG (n=2)</td>
<td>18.928(0.012)</td>
<td>15.598(0.011)</td>
<td>38.313(0.013)</td>
<td>1.23</td>
<td>0.44(0.01)</td>
<td>nd</td>
<td>nd</td>
<td>22.9</td>
<td>na</td>
</tr>
<tr>
<td>S1AM</td>
<td>18.748(0.008)</td>
<td>15.614(0.009)</td>
<td>38.469(0.029)</td>
<td>5.37</td>
<td>nd</td>
<td>0.7*</td>
<td>1.4*</td>
<td>8.31</td>
<td>2.1</td>
</tr>
<tr>
<td>Galena Samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K314</td>
<td>18.661(0.003)</td>
<td>15.569(0.004)</td>
<td>38.233(0.015)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K335</td>
<td>18.707(0.007)</td>
<td>15.574(0.009)</td>
<td>38.268(0.020)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Figures given in brackets are one sigma uncertainties based on the addition of in-run precision and mass fractionation uncertainties, except where given for average values. Figure given in brackets following averaged values is one standard error of the mean value for n > 2. If n=2 the pooled standard deviation is given.
2. I.D. is isotope dilution analysis (Appendix B). nd = not determined.
3. Uncertainties are estimated to be 0.1 ppm based on duplicate analyses (Appendix B: Table B.12).
4. Figures given in brackets are uncertainties based on error propagation calculations, using program "WRRUC" (Appendix D).
5. N.A.A. stands for Neutron Activation Analysis. D.N. is delayed neutron counting. Details of techniques used and uncertainties are in Chapter 1. Analyses marked with an asterix were analyzed at TRIUMF by L. Erdman. All others were done by Neutron Activation Services Ltd., Hamilton, Ontario.
6. 238U/204Pb values are calculated using U (I.D.) ppm. na = not applicable.
7. k values (232Th/238U) are calculated using U (N.A.A.) and Th (D.N.) values. na = not applicable.
3.2 ISOTOPIC DATA

3.2.1 Lead isotope compositions for rocks and ores

Whole rock lead isotope compositions for the Karmutsen Formation (Table 3.2) are plotted in Figure 3.2. Several initial values (Table 3.3) are also shown. These have been calculated using measured $\mu$ and $k$ values (Table 3.2) and an assumed age of 220 Ma. The galena analyses (Table 3.2) plot with the whole rock initial values. This condition is to be expected if the lead in the galena has the same age and source as the lead in the rocks.

Three of the samples (K609, K610 and K613) have low $^{207}\text{Pb}/^{204}\text{Pb}$ values, which were not duplicated by any of the freshly crushed rocks, despite the fact that KAR10 was obtained from a similar location as K609. Several possibilities exist to explain this apparent discrepancy:

1) There are real, major heterogeneities in the Karmutsen lead data. Similar large ranges in $^{207}\text{Pb}/^{204}\text{Pb}$ values exist in the data from the Deccan flood basalts (Allegre et al. 1982).

2) The old rock powders are contaminated. This may have occurred during storage or during the crushing stage, which was not done specifically for lead isotope analyses. Old sample powders from the Bonanza Group rock suite also have low $^{207}\text{Pb}/^{204}\text{Pb}$ signatures which were not duplicated by the fresh rocks. This, therefore, seems the most probable reason.
Figure 3.2  a) 207Pb/204Pb versus 206Pb/204Pb and b) 208Pb/204Pb versus 206Pb/204Pb plot of whole rock lead isotope data (Tables 3.2 and 3.3) from the Karmutsen Formation and related galena samples (Table 3.2). Vectors join present values to initial values of the same rock, based on a 220 Ma age and measured μ values. Duplicated or triplicated analyses are enclosed within dashed lines. The growth curve, marked "S & K", is that of Stacey and Kramers (1975). A solid line encloses whole rock initial ratios and galena analyses. Open circles mark estimated compositions of two possible end-members that may contribute lead to the rocks (see text for details).
TABLE 3.3 Initial lead isotope ratios at 220 Ma for the Karmutsen Formation volcanic rocks, Vancouver Island, B.C.
Initial ratios, calculated from data in Table 3.2, are plotted in Figures 3.2 and 3.3.

<table>
<thead>
<tr>
<th>NAME</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>K005</td>
<td>18.71 (0.01)</td>
<td>15.59 (0.01)</td>
<td>38.40 (0.07)</td>
</tr>
<tr>
<td>K007</td>
<td>18.94 (0.04)</td>
<td>15.57 (0.03)</td>
<td>38.60 (0.14)</td>
</tr>
<tr>
<td>K008</td>
<td>18.74 (0.06)</td>
<td>15.53 (0.01)</td>
<td>not applicable</td>
</tr>
<tr>
<td>KAR11</td>
<td>18.17 (0.01)</td>
<td>15.55 (0.01)</td>
<td>not applicable</td>
</tr>
<tr>
<td>S1AM</td>
<td>18.46 (0.03)</td>
<td>15.60 (0.01)</td>
<td>38.28 (0.04)</td>
</tr>
</tbody>
</table>

MEAN (1S) 18.61 (0.30) 15.57 (0.03) 38.43 (0.16)

1. Figures in brackets are the one sigma uncertainties calculated using the error propagation program "T1CORR" (Appendix D). These represent analytical uncertainties, but geological uncertainty, arising from the unknown history of uranium and thorium since time of formation, is not included.
3) The fresh rocks are contaminated. This is unlikely because of the special care taken during crushing. Contamination during analysis by addition of lab blank is not a possible explanation because of good agreement between duplicate analyses done at different times. Also, the galena samples have lead signatures which agree with the higher $^{207}\text{Pb}/^{204}\text{Pb}$ values of the fresh rocks. Poor duplication of sample K101 (Fig. 3.2) is probably due to sample inhomogeneity.

3.2.2 Comparison of Karmutsen Formation lead isotopic data with those of well known basalts

Representative fields for basalts from several different plate tectonic environments are shown with the Karmutsen Formation lead isotope data in Figures 3.3 and 3.4. All fields have been adjusted to 220 Ma using the lead evolution model of Stacey and Kramers (1975). This approximation facilitates comparison of the Karmutsen whole rock initial ratios with ratios for younger basalts.

Karmutsen Formation initial ratios partially overlap most of the fields shown (Figs. 3.3 and 3.4). Higher $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios than MORBs for most of the samples rule out an origin of Karmutsen Formation basalts at a mid-ocean ridge. There are similarities in the isotopic fields of the Karmutsen Formation with island arc tholeiites and ocean island basalts.
Figure 3.3 Comparison of Karmutsen Formation whole rock initial ratios at 220 Ma (open triangles) and Karmutsen galena (open squares) with $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ fields adjusted to 220 Ma (using Stacey and Kramers 1975 growth curve, "S & K") of ocean island basalts (Sun and Jahn 1975; Sun 1980; Tatsumoto 1978; Weis 1983); island arcs (Oversby and Ewart 1972; Meijer 1976; Kay et al. 1978; Church 1976); mid ocean ridge basalts (Church and Tatsumoto 1975; Brevart et al. 1981; Vidal and Clauer 1981); Pacific sediments (Church 1976; Sun 1980; Vidal and Clauer 1981).
Figure 3.4 Comparison of Karmutsen initial ratios at 220 Ma (open triangles) and Karmutsen galena (open squares) with 208\text{Pb}/204\text{Pb} and 206\text{Pb}/204\text{Pb} fields, adjusted to 220 Ma (using Stacey and Kramers 1975 growth curve, "S & K"), of mid-ocean ridges, island arcs, ocean island basalts and Pacific sediments. For references to source of data see Figure 3.3.
(Figs. 3.3 and 3.4), and with various continental flood basalts (Figs. 3.5 and 3.6). Figure 3.5 shows considerable overlap between the isotopic ratios of the Karmutsen Formation, and Chilcotin basalts, some types of Columbia River flood basalts (Imnaha and Picture Gorge basalts), and Deccan Trap basalts.

The fields for several continental flood basalts are separated in Figure 3.6 due to highly variable 208Pb/204Pb ratios. The Karmutsen Formation initial ratios plot with some of the Columbia River basalts, but are intermediate between the Chilcotin and Deccan flood basalts.

3.2.3 Lead, uranium and thorium concentrations

Lead, uranium and thorium concentrations are reported for MORBs, OIBs, island arc tholeiites and Chilcotin flood basalts (Table 3.4). There are differences in the absolute abundances of these elements in each tectonic environment. Comparison of lead, uranium and thorium concentrations of the Karmutsen basalts with other basalts (Table 3.4; Fig. 3.7) shows that they are richer in lead than MORBs, yet poorer in lead than typical island arcs. There is a close similarity in the lead, uranium and thorium content of Karmutsen basalts with the Chilcotin basalts and with ocean island basalts. This comparison does, however, assume that the lead, uranium and thorium concentrations have remained relatively unchanged since the time of formation of basalts of
Figure 3.5  207Pb/204Pb versus 206Pb/204Pb diagram showing generalized fields of isotope data from continental flood basalts (adjusted to 220 Ma using Stacey and Kramers 1975 growth curve, "S & K"), and Karmutsen Formation initial ratios at 220 Ma (open triangles: Table 3.3) and galena (open squares: Table 3.2). Data are from Leeman and Manton (1972), Allegre et al. (1982), Bevier (1982), Carlson (1984), and Church (1985). The Columbia River Basalts field has been divided into two. Field #1 contains analyses from the Imnaha, Grande Ronde, Picture Gorge, and Wanapum formations. Field #2 contains analyses of the Saddle Mountains basalts.
Figure 3.6 208Pb/204Pb versus 206Pb/204Pb diagram showing generalized fields for continental flood basalts (adjusted to 220 Ma using Stacey and Kramers 1975 growth curve, "S & K") and Karmutsen Formation whole rock initial ratios at 220 Ma. See Figure 3.5 for explanation of symbols and source of data.
TABLE 3.4  Typical lead, uranium and thorium concentrations, with maximum ranges for various oceanic and continental basalts.

<table>
<thead>
<tr>
<th>BASALT TYPE</th>
<th>REFERENCE</th>
<th>PB PPM</th>
<th>U PPM</th>
<th>TH PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continental Flood Basalts</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chilcotin</td>
<td>Bevier (1982)</td>
<td>1.5(1.1-2.1)</td>
<td>0.4(0.2-1.0)</td>
<td>1.0(0.6-3.5)</td>
</tr>
<tr>
<td>Columbia River</td>
<td>Carlson (1984)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mid-Ocean Ridge Basalts</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leg 37 Atl.</td>
<td>Cumming (1980)</td>
<td>0.5(0.4-0.7)</td>
<td>0.2(0.1-0.3)</td>
<td>0.6(0.4-0.9)</td>
</tr>
<tr>
<td>Juan de Fuca</td>
<td>Church and Tatsumoto (1975)</td>
<td>0.5(0.2-1.0)</td>
<td>0.2(0.1-0.5)</td>
<td>0.3(0.1-0.9)</td>
</tr>
<tr>
<td>Reykjanes</td>
<td>Sun &amp; Jahn (1975)</td>
<td>0.5(0.4-0.7)</td>
<td>0.1(0.1-0.2)</td>
<td>0.4(0.4-0.5)</td>
</tr>
<tr>
<td>Island Arc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mariana</td>
<td>Meijer (1976)</td>
<td>1.9(0.6-3.0)</td>
<td>0.2(0.2-0.3)</td>
<td>0.7(0.4-1.1)</td>
</tr>
<tr>
<td>Aleutians</td>
<td>Kay et al. (1978)</td>
<td>5.0(3.8-8.2)</td>
<td>1.0(0.5-1.7)</td>
<td>2.0(0.9-4.0)</td>
</tr>
<tr>
<td>Japan</td>
<td>Tatsumoto (1969)</td>
<td>1.7(1.7-7.1)</td>
<td>0.2(0.1-0.4)</td>
<td>0.2(0.1-0.4)</td>
</tr>
<tr>
<td>Tonga-Kermadec</td>
<td>Oversby and Ewart (1972)</td>
<td>2.2(0.3-4.2)</td>
<td>0.2(0.1-0.4)</td>
<td></td>
</tr>
<tr>
<td>Ocean Islands</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iceland</td>
<td>Sun and Jahn (1975)</td>
<td>1.4(1.0-1.6)</td>
<td>0.4(0.3-0.6)</td>
<td>1.3(0.9-1.3)</td>
</tr>
<tr>
<td>Hawaii Kilauea</td>
<td>Sun (1980)</td>
<td>1.7(1.3-2.0)</td>
<td>0.5(0.4-0.6)</td>
<td>1.4(1.0-2.0)</td>
</tr>
<tr>
<td>Mauna Kea</td>
<td>Sun (1980)</td>
<td>1.2</td>
<td>0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Mauna Loa</td>
<td>Sun (1980)</td>
<td>0.8</td>
<td>0.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Figure 3.7 Average lead, uranium and thorium concentrations for various basalt types. See Table 3.4 for source of data.
the Karmutsen Formation.

3.2.4 Strontium data

Initial strontium ratios vary from 0.703-0.704 (Table 3.5; Armstrong et al. in press). This is higher than for MORBs and for the Chilcotin basalts (Bevier 1982), and lower than for continental crust, but otherwise not useful in discriminating between tectonic environments. Strontium and rubidium data for the samples studied in this thesis are in Table 3.4. Other data for the Karmutsen Formation is in Armstrong et al. (in press).

3.2.5 Evidence for isotopic mixing

U-Pb and Th-Pb isochron plots are shown in Figure 3.8 with the 220 Ma isochron for reference. The $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{235}\text{U}/^{204}\text{Pb}$ plot (Fig. 3.8b) clearly shows that the Karmutsen volcanics are not simply derived from a single source, which had a homogeneous initial ratio that remained a closed system until the present. Rather, mixing must be invoked to explain the apparently negative slope.

Mixing is also evident in Figure 3.9, which shows the initial lead ratios plotted against the reciprocal of lead concentration. Using least squares regression, it is possible to determine the best fit lines to the data for each of the ratios (Fig. 3.10) and hence to estimate the end-member compositions.
TABLE 3.5 Rubidium and strontium isotope data for the Karmutsen Formation, Vancouver Island, B.C. Initial ratios are calculated for an age of 220 Ma, using decay constants recommended by Steiger and Jager (1977). All data have been reported in Armstrong et al. (in press).

<table>
<thead>
<tr>
<th>SAMPLE NUMBER</th>
<th>Sr PPM</th>
<th>Rb PPM</th>
<th>$^{87}\text{Rb}/^{86}\text{Sr}$</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
<th>AGE (ASSUMED)</th>
<th>INITIAL $^{87}\text{Sr}/^{86}\text{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K005 (G84VI005)</td>
<td>241</td>
<td>10.8</td>
<td>0.129</td>
<td>0.7040</td>
<td>220 Ma</td>
<td>0.7036</td>
</tr>
<tr>
<td>K007 (G84VI007)</td>
<td>223</td>
<td>17.8</td>
<td>0.231</td>
<td>0.7040</td>
<td>220 Ma</td>
<td>0.7033</td>
</tr>
<tr>
<td>K609 (IGC5A2)</td>
<td>368</td>
<td>13.8</td>
<td>0.107</td>
<td>0.7044</td>
<td>220 Ma</td>
<td>0.7041</td>
</tr>
<tr>
<td>K610 (63-12N)</td>
<td>182</td>
<td>8.2</td>
<td>0.130</td>
<td>0.7043</td>
<td>220 Ma</td>
<td>0.7039</td>
</tr>
<tr>
<td>K612 (63-78A)</td>
<td>270</td>
<td>32.0</td>
<td>0.341</td>
<td>0.7055</td>
<td>220 Ma</td>
<td>0.7044</td>
</tr>
<tr>
<td>Leached</td>
<td>170</td>
<td>19.6</td>
<td>0.336</td>
<td>0.7048</td>
<td>220 Ma</td>
<td>0.7037</td>
</tr>
<tr>
<td>K613 (63-87D)</td>
<td>263</td>
<td>5.8</td>
<td>0.064</td>
<td>0.7041</td>
<td>220 Ma</td>
<td>0.7039</td>
</tr>
<tr>
<td>K616 (67-20C)</td>
<td>288</td>
<td>3.6</td>
<td>0.036</td>
<td>0.7040</td>
<td>220 Ma</td>
<td>0.7039</td>
</tr>
<tr>
<td>KAR11</td>
<td>473</td>
<td>11.6</td>
<td>0.071</td>
<td>0.7040</td>
<td>220 Ma</td>
<td>0.7038</td>
</tr>
<tr>
<td>K101 (BP-SELCO)</td>
<td>29.9</td>
<td>70.9</td>
<td>6.870</td>
<td>0.7235</td>
<td>220 Ma1</td>
<td>0.70201</td>
</tr>
<tr>
<td>S1AM</td>
<td>223</td>
<td>5.5</td>
<td>0.058</td>
<td>0.7039</td>
<td>220 Ma</td>
<td>0.7037</td>
</tr>
</tbody>
</table>

1. Using a two point isochron with one point at K101 and the other at the average value for the basalt samples with $^{87}\text{Sr}/^{86}\text{Sr} = 0.7040 \pm 0.0001$ and $^{87}\text{Rb}/^{86}\text{Sr} = 0.122 \pm 0.079$, the age is $203 \pm 5$ Ma.
Figure 3.8. U-Pb and Th-Pb isochron plots for the Karmutsen Formation, Vancouver Island, B.C. Data is in Table 3.2. The 220 Ma reference isochron is drawn, in each case, through the mean initial value (Table 3.3). Error bars mark the one sigma analytical uncertainties in the lead ratios (Table 3.2), and one sigma uncertainties in U/Pb and Th/Pb ratios of 10% and 14% respectively.
Figure 3.9 a) Initial $^{208}\text{Pb}/^{204}\text{Pb}$ versus $1/\text{Pb}$ (ppm), b) initial $^{207}\text{Pb}/^{204}\text{Pb}$ versus $1/\text{Pb}$ (ppm) and c) initial $^{206}\text{Pb}/^{204}\text{Pb}$ versus $1/\text{Pb}$ (ppm) plot for Karmutsen Formations rocks, Vancouver Island, B.C. Data are in Tables 3.2 and 3.3. Error bars mark the one sigma uncertainties in the initial ratios and lead concentrations calculated by error propagation (Table 3.3). Best fit lines by least squares regression and correlation coefficients ($r$) are shown for each plot. Estimated end-member isotopic compositions (circles) are shown for $1/\text{Pb} = 0.1$ (10 ppm) and $1/\text{Pb} = 2.0$ (0.5 ppm).
$^{208}\text{Pb}/^{204}\text{Pb}$ (initial)

$^{207}\text{Pb}/^{204}\text{Pb}$ (initial)

$^{208}\text{Pb}/^{204}\text{Pb}$ (initial)
Figure 3.9b shows a correlation (correlation coefficient \(r=-0.87\)) between \(^{207}\text{Pb}/^{204}\text{Pb}\) and \(1/\text{Pb}\). Taking a value of 10 ppm for the lead-rich end-member, which is a suitable value for ocean sediments, the corresponding \(^{207}\text{Pb}/^{204}\text{Pb}\) ratio is 15.602 (Fig. 3.9b). Choice of a different lead content for this end-member would not significantly change the isotope ratio. A lead-poor end-member with a lead content of 0.5 ppm, which is a suitable mantle value, has a corresponding \(^{207}\text{Pb}/^{204}\text{Pb}\) value of 15.523. Lower \(^{207}\text{Pb}/^{204}\text{Pb}\) values can be achieved by choosing a lower lead content for this end-member.

The initial \(^{208}\text{Pb}/^{204}\text{Pb}\) versus \(1/\text{Pb}\) diagram (Fig. 3.9a) shows that the lead-rich end-member has a lower \(^{208}\text{Pb}/^{204}\text{Pb}\) ratio than the lead-poor end-member. The correlation coefficient (\(r\)) for this relationship is 0.97, but is based on only three samples. Using the best-fit line (Fig. 3.9a), the \(^{208}\text{Pb}/^{204}\text{Pb}\) compositions are 38.231 and 38.884 for the lead-rich and lead-poor end-members respectively.

Correlation between initial \(^{206}\text{Pb}/^{204}\text{Pb}\) and \(1/\text{Pb}\) in Figure 3.9c is poorer than for the other ratios (\(r=0.44\)). This is probably because the post-formation in situ addition of radiogenic lead is greatest for this ratio. Any uranium or lead loss or gain since the time of formation will tend to obscure
the original relationship by making it impossible to calculate the correct initial ratios. There is, however, a suggestion that the lead-rich end-member has a lower $^{206}\text{Pb}/^{204}\text{Pb}$ ratio than the lead-poor one. Using the same criterion as above the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are 18.425 and 18.833 for the lead-rich and lead-poor sources respectively.

The estimated end-member lead isotope compositions are shown in Figure 3.2. The lead-rich end-member plots close to the 220 Ma point on the average crustal lead growth curve of Stacey and Kramers (1975) in both figures. Pacific ocean sediments also have a similar isotopic composition. The lead-poor end-member plots close to the mantle (MORB) trend in Figure 3.2a, at higher $^{206}\text{Pb}/^{204}\text{Pb}$ values than for MORB. It therefore resembles an OIB-type mantle source. It does not plot at the end of the array of initial data in Figure 3.2b, and has higher $^{208}\text{Pb}/^{204}\text{Pb}$ values than OIB-type mantle. This is possibly because the $^{208}\text{Pb}/^{204}\text{Pb}$ end-members were chosen on the basis of only three samples. If the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios were determined using the same three samples, the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio required for the lead-poor end-member would be higher, producing a more suitable end-member composition, but still with higher $^{208}\text{Pb}/^{204}\text{Pb}$ than typical OIB-type mantle. Alternatively, if initial $^{208}\text{Pb}/^{204}\text{Pb}$ data were available for more samples, the $^{208}\text{Pb}/^{204}\text{Pb}$ estimate for the lead-poor end-member might be lower.
Figure 3.10 shows a positive correlation (r=0.90) of $^{238}\text{U}/^{204}\text{Pb}$ with $1/\text{Pb}$. Thus the lead-rich end-member has a lower $\mu$ value (10 at 10ppm) than the lead-poor end-member (31 at 0.5 ppm). These values are appropriate for ocean sediments and enriched mantle respectively.

The relationship between initial strontium and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios is illustrated in Figure 3.11. The higher initial strontium values, which presumably represent the crustal end-member, have lower $^{206}\text{Pb}/^{204}\text{Pb}$ values. This confirms that the lead-rich (presumably crustal) end-member has a lower $^{206}\text{Pb}/^{204}\text{Pb}$ value than the lead-poor (presumably mantle) end-member.

Samples K609, K610 and K613 must have initial ratios that are lower than their present values. They do not fit the correlation diagrams, because low $^{207}\text{Pb}/^{204}\text{Pb}$ values are associated with low $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values. They require the involvement of a third component, perhaps similar to depleted mantle, unless they are unreliable samples as suggested in section 3.2.1.

In the absence of the lead and uranium concentration data required to calculate initial ratios, it would still be possible
Figure 3.10  $^{238}\text{U}/^{204}\text{Pb}$ versus $1/\text{Pb (ppm)}$ for the Karmutsen Formation, Vancouver Island, B.C. A best fit line by least squares regression is shown, with estimated end-member isotopic compositions for $1/\text{Pb (ppm)} = 0.1$ (10 ppm) and $1/\text{Pb} = 2.0$ (0.5 ppm). Error bars mark one sigma uncertainties in the $238\text{U}/204\text{Pb}$ of the greater of 10% or error propagation using "MUCALC", and one sigma uncertainty in $1/\text{Pb (ppm)}$ of the greater of 3% or error propagation using "WRPBID".
Figure 3.11 $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagram for the Karmutsen Formation, Vancouver Island, B.C. Present ratios (filled triangles) are connected to initial ratios (open triangles) at 220 Ma by correction vectors. The MORB correlation line is that of Hamelin et al. (1984a). A correlation line adjusted to 220 Ma using a Rb/Sr value of 0.01 and mu value of 10 is also shown. Data are in Tables 3.2, 3.3 and 3.5.
to observe the mixing relationship by using a simple technique
to adjust $^{207}\text{Pb}/^{204}\text{Pb}$ ratios. This technique is described in
Appendix E.

3.3 DISCUSSION

Any petrogenetic model for the Karmutsen Formation has to
explain the following general observations:
1) Most of the data display mixing between two end-members. The
lead-poor source has lower $^{207}\text{Pb}/^{204}\text{Pb}$, and initial $^{87}\text{Sr}/^{86}\text{Sr}$,
but higher $^{206}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, and $^{238}\text{U}/^{204}\text{Pb}$ than the
lead-rich source.
2) The lead-rich source has the characteristics of average
crust, by comparison with Stacey and Kramers (1975) growth
curve.
3) The lead-poor source has higher $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$
than MORB.

Crustal contamination of a mantle-derived magma can explain
these observations. Oxygen isotope data for the Karmutsen
Formation are in the range $\delta^{18}O=7.6$ to 14.9 per mil (Muhlenbachs,
written communication, 1986); consistent with the crustal
contamination hypothesis. There are several possible types of
crustal contaminants, mantle sources and contamination
mechanisms, each of which are discussed below.

3.3.1 Crustal contaminant

The lead-rich end-member has an isotopic composition that plots close to the 220 Ma point on Stacey and Kramers (1975) crustal lead growth curve (Fig. 3.2). Pacific sediments at 220 Ma are of a suitable isotopic composition (Figs. 3.3 and 3.4).

The laboratory blank lead isotopic composition also has similar values (Appendix B), which raises the question of contamination during analysis. Duplicate analyses are good in general for the Karmutsen samples ruling out the possibility of variable blank contamination during analysis. Contamination prior to analysis is unlikely because of the care taken during the crushing and subsequent stages. The samples with the least lead would be expected to be the most contaminated, whereas it is the samples with the highest lead contents which show the greatest degree of contamination with the 'crustal' lead component. It is extremely unlikely, therefore, that the contamination did occur during analysis.

3.3.2 Mantle source

The isotopic composition of the lead-poor source has a low $^{207}\text{Pb}/^{204}\text{Pb}$ ratio, and plots with typical oceanic mantle (Fig. 3.2a). The $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are, however,
higher than typical MORB, so the mantle source more closely resembles an OIB-type source. A mantle source enriched in thorium is required to explain the higher $^{208}\text{Pb}/^{204}\text{Pb}$ values than typical OIB mantle.

The lowest $^{207}\text{Pb}/^{204}\text{Pb}$ samples (K609, K610, and K613), also have low $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, and may therefore represent a second mantle source, which resembles depleted mantle (Figs. 3.3 and 3.4). Nd analyses of the same rocks would help to determine the nature of the mantle source or sources.

3.3.3 Mixing mechanisms

There are several possible ways for isotopic mixing to have taken place. Three of these are:
1) Assimilation of crustal material by mantle-derived magmas.
2) Shallow recycling of subducted sediments into a back-arc environment
3) Deep recycling of subducted sediments.

Rocks from the Devonian island arc assemblage do not have a suitable isotopic composition to be the crustal contaminant. Assimilation of Sicker Group material is not, therefore, a possible explanation for the isotopic mixing observed in the Karmutsen Formation basalts. Pelagic sediments interbedded with the Karmutsen lava flows may have had a suitable isotopic
composition, but it is unlikely that lead from these sediments could have become incorporated into the volcanic rocks in the subaqueous environment.

Recycling of subducted crustal material into the mantle is a more likely possibility. Church (1984) explains 'mixed' isotopic characteristics of the Columbia River Basalts of Washington and Oregon, by invoking shallow recycling of sediments introduced into the back arc environment by subduction. Deep recycling of sedimentary material is proposed to explain neodymium, lead and strontium characteristics of back-arc basalt glasses in the South Sandwich Islands (Cohen and O'Nions 1982). The isotopic data available so far can not adequately distinguish between these possibilities.

3.3 CONCLUSIONS

Lead isotope data has been obtained from several whole rock and galena samples from the Karmutsen Formation volcanic rocks of Vancouver Island. These, combined with strontium isotope analyses of some of the same rocks, lead to the following general conclusions:
1) The Karmutsen Formation did not originate at a mid-ocean ridge. $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios
are too high.

2) Lead, uranium and thorium concentrations are greater in Karmutsen basalts than in MORBs, but less than island arc tholeiites. They are similar to those of ocean islands and continental flood basalts.

3) Whole rock initial ratios (except for three low $^{207}\text{Pb}/^{204}\text{Pb}$ samples) plot with two galena samples in both $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams.

4) All but three samples can be described in terms of isotopic mixing between two end-members.

5) A lead-poor end-member has lower $^{207}\text{Pb}/^{204}\text{Pb}$ and initial $^{87}\text{Sr}/^{86}\text{Sr}$, but higher $^{206}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{238}\text{U}/^{204}\text{Pb}$ than a lead-rich end-member. It resembles ocean island mantle.

6) The lead-rich end-member has average crustal isotopic characteristics.

7) A third end-member, possibly similar to depleted mantle, is required to explain three, low $^{207}\text{Pb}/^{204}\text{Pb}$ samples, but these samples may be contaminated.

8) Isotopic data for the Karmutsen Formation can be explained in terms of the crustal contamination of magma from thorium-enriched mantle, but the contamination mechanisms cannot be uniquely identified.

9) Isotopic data are consistent with the origin of the Karmutsen Formation basalts in a similar manner to those of other flood basalts, such as the Columbia River Basalts and the
Chilcotin basalts, in a back-arc rifting environment.
CHAPTER 4

ISOTOPE GEOCHEMISTRY OF THE BONANZA GROUP AND ISLAND INTRUSIONS

SYNOPSIS

Lead isotope analyses of five plutonic rocks from the Island Intrusions and six volcanic rocks from the Bonanza Group support a comagmatic origin for the two Jurassic rock suites. Lead and strontium isotope systems cannot adequately distinguish between an island arc or an oceanic island origin for these rocks. Calculated initial lead isotope ratios fall on a linear trend in both $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plots. If interpreted as a mixing line, the more radiogenic end-member has a composition which is lower in $^{207}\text{Pb}/^{204}\text{Pb}$ and higher in $^{206}\text{Pb}/^{204}\text{Pb}$ than typical upper continental crust. Assimilation of Sicker Group material during emplacement of the intrusions may explain the mixing trend.

Galena lead isotopes from a vein within the Island Copper porphyry deposit plot with the initial ratios for Bonanza Group volcanics and Island Intrusions, confirming the hypothesis that this mineralization is related to the Jurassic island arc.
volcanic event.

4.1 INTRODUCTION

The Bonanza Group, named by Gunning (1932), is a sequence of calc-alkaline pyroclastic, extrusive and hypabyssal volcanic rocks with minor intercalated sediments. The sediments contain Early Jurassic fossils (Muller et al. 1974), which give an age range of 204 to 187 Ma using the DNAG timescale (Palmer 1983). The volcanic rocks range in composition from basaltic andesite and dacite at the base, to rhyolitic and rhyodacitic rocks that are interbedded with basaltic andesite and andesite higher in the sequence (Northcote and Muller 1972). They overlie basalts of the Triassic Karmutsen Formation and limestone and shale of the Triassic Quatsino and Parson Bay Formations.

The Island Intrusions, thought to be the plutonic equivalents of the later stages of Bonanza volcanism (Northcote and Muller 1972), are mainly granodioritic, and underlie 30% of Vancouver Island (Fig. 4.1). Chemical variation diagrams show that both intrusive and volcanic suites follow the same differentiation trends (Northcote and Muller 1972). Age estimates for both Bonanza Group volcanic rocks and Island Intrusions are summarized in Table 4.1. K-Ar ages obtained for
Figure 4.1 Distribution of Bonanza Group volcanic rocks (dotted) and Island Intrusions (igneous pattern) on Vancouver Island, B.C. Whole rock sample locations for Bonanza Group rocks are marked with squares, and Island Intrusions are marked with circles. The Island Copper porphyry deposit is marked with a cross. Sample details are in Table 4.2.
both suites show considerable overlap, with Bonanza volcanic ages ranging from 138 Ma to 164 Ma (Northcote and Muller 1972), and Island Intrusions from 145 Ma to 184 Ma (Muller 1977). More recent zircon analyses by Isachsen (1984), and Rb-Sr isochrons (Armstrong et al. in press), suggest that 190 Ma is a better estimate of the age of these rocks, the previous ages being minimum estimates.

Northcote and Muller (1972) and Souther (1977) proposed that the Bonanza Group volcanic rocks and Island Intrusions are comagmatic and represent an island arc volcanic assemblage. In this study lead and strontium isotopes are used as tracers to test this hypothesis, to fingerprint these two rock suites isotopically, and to compare their isotopic characteristics with those of modern plate tectonic settings.

Five samples from the Island Intrusions, and six from the volcanic rocks of the Bonanza Group have been analyzed for lead and/or strontium isotopic compositions. Sample locations are in Figure 4.1. Table 4.2 locates the coordinates of the samples together with brief sample descriptions. Analyses are in Table 4.3. All samples of the Island Intrusions have uranium and thorium concentrations measured by gamma ray spectroscopy, and lead concentrations obtained by isotope dilution. Details of experimental procedures for lead isotope compositions and
TABLE 4.1 Summary of age determinations for the Bonanza Group and Island Intrusions, Vancouver Island, B.C.

<table>
<thead>
<tr>
<th>METHOD</th>
<th>AGE (MA)¹</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Island Intrusions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zircon Pb/Pb</td>
<td>187 ± 6</td>
<td>Armstrong et al. in press</td>
</tr>
<tr>
<td>U-Pb</td>
<td>126 to 175</td>
<td>Armstrong et al. in press</td>
</tr>
<tr>
<td>K-Ar</td>
<td>145 to 184</td>
<td>Muller 1977, Carson 1972, Northcote and Robinson 1972</td>
</tr>
<tr>
<td>Rb-Sr</td>
<td>183 ± 7</td>
<td>Armstrong et al. in press</td>
</tr>
<tr>
<td>Bonanza Group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K-Ar</td>
<td>138 to 164</td>
<td>Northcote and Muller 1972</td>
</tr>
<tr>
<td>Rb-Sr</td>
<td>179 ± 5</td>
<td>Armstrong et al. in press</td>
</tr>
</tbody>
</table>

¹ Ages published prior to 1977 have been adjusted to the new decay constants of Steiger and Jager (1977).
TABLE 4.2 Locations and brief descriptions of samples from the Bonanza Group and Island Intrusions, Vancouver Island, B.C. Analyses are reported in Table 4.3.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>LAT.</th>
<th>LONG.</th>
<th>DESCRIPTION</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>NORTH</td>
<td>WEST</td>
<td></td>
</tr>
<tr>
<td>Bonanza Group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT59</td>
<td>50.71</td>
<td>127.97</td>
<td>Altered andesite.</td>
</tr>
<tr>
<td>MT360</td>
<td>50.65</td>
<td>127.83</td>
<td>Altered andesite.</td>
</tr>
<tr>
<td>B619</td>
<td>50.46</td>
<td>128.06</td>
<td>Andesite. 1.5 to 3.5 km northwest of Cape Parkins.</td>
</tr>
<tr>
<td>B620</td>
<td>50.47</td>
<td>128.06</td>
<td>Basalt. Location is same as B619.</td>
</tr>
<tr>
<td>B621</td>
<td>50.47</td>
<td>128.06</td>
<td>Basalt. Location is same as B619.</td>
</tr>
<tr>
<td>B625</td>
<td>50.11</td>
<td>127.14</td>
<td>Rhyolite. North shore of Tahsish Inlet.</td>
</tr>
<tr>
<td>Island Intrusions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>681381</td>
<td>50.24</td>
<td>126.46</td>
<td>Quartz monzonite. Nimpkish batholith 5 km northeast of Hoomak Lake.</td>
</tr>
<tr>
<td>682122</td>
<td>50.19</td>
<td>126.37</td>
<td>Quartz diorite. Nimpkish batholith 10 km E, 1 km South of Hoomak Lake.</td>
</tr>
<tr>
<td>683171</td>
<td>50.03</td>
<td>127.09</td>
<td>Quartz monzonite. Amai Inlet pluton.</td>
</tr>
<tr>
<td>683421</td>
<td>50.31</td>
<td>125.58</td>
<td>Granodiorite. Pye Lake pluton on road to Rock Bay.</td>
</tr>
<tr>
<td>692131</td>
<td>50.31</td>
<td>126.06</td>
<td>Granodiorite. Adam River pluton, northeast of Mount Juliet.</td>
</tr>
<tr>
<td>Island Copper galena</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ISCU</td>
<td>50.61</td>
<td>127.48</td>
<td>Galena from veins in Island Copper porphyry copper-molybdenum mine.</td>
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TABLE 4.3 Lead, uranium and thorium data from the Bonanza Group volcanic rocks, and Island Intrusions, Vancouver Island, B.C. Locations of samples are in Table 4.2.

<table>
<thead>
<tr>
<th>SAMPLE NAME</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
<th>Pb PPM (I.D.)</th>
<th>U PPM (G.R.)</th>
<th>U PPM (G.R.)</th>
<th>Th PPM (I.D.)</th>
<th>Th PPM (I.D.)</th>
<th>μ6</th>
<th>k7</th>
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<tr>
<td>Bonanza Group volcanic rocks</td>
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</tr>
<tr>
<td>MT59</td>
<td>18.535(0.007)</td>
<td>15.548(0.008)</td>
<td>38.070(0.028)</td>
<td>4.06</td>
<td>0.21(0.01)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>3.3</td>
<td>na</td>
</tr>
<tr>
<td>MT360</td>
<td>18.835(0.008)</td>
<td>15.556(0.008)</td>
<td>38.170(0.029)</td>
<td>5.24</td>
<td>1.47(0.15)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>17.7</td>
<td>na</td>
</tr>
<tr>
<td>MT360-AVG</td>
<td>18.830(0.022)</td>
<td>15.557(0.019)</td>
<td>38.161(0.052)</td>
<td>5.30</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>B619g</td>
<td>18.332(0.007)</td>
<td>15.505(0.008)</td>
<td>37.729(0.028)</td>
<td>nd</td>
<td></td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>B620g</td>
<td>17.657(0.009)</td>
<td>15.456(0.010)</td>
<td>37.279(0.031)</td>
<td>nd</td>
<td></td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>B621g</td>
<td>18.225(0.010)</td>
<td>15.453(0.010)</td>
<td>37.627(0.032)</td>
<td>nd</td>
<td></td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
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<tr>
<td>B625g</td>
<td>19.680(0.010)</td>
<td>15.560(0.010)</td>
<td>38.854(0.032)</td>
<td>2.16</td>
<td></td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
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<tr>
<td>Island Copper Galena</td>
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<tr>
<td></td>
<td>18.527(0.011)</td>
<td>15.555(0.009)</td>
<td>38.088(0.024)</td>
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<td>681381</td>
<td>19.480(0.007)</td>
<td>15.594(0.008)</td>
<td>38.879(0.028)</td>
<td>4.12</td>
<td>1.47(0.02)</td>
<td>1.68</td>
<td>5.02</td>
<td>nd</td>
<td>23.1</td>
<td>3.1</td>
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<tr>
<td>682122</td>
<td>19.049(0.007)</td>
<td>15.578(0.008)</td>
<td>38.511(0.029)</td>
<td>2.73</td>
<td>nd</td>
<td>0.82</td>
<td>2.10</td>
<td>nd</td>
<td>16.6</td>
<td>2.7</td>
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<tr>
<td>683171</td>
<td>19.721(0.020)</td>
<td>15.645(0.017)</td>
<td>38.985(0.049)</td>
<td>5.60</td>
<td>nd</td>
<td>2.71</td>
<td>7.41</td>
<td>nd</td>
<td>27.1</td>
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<tr>
<td>683171-AVG</td>
<td>19.734(0.015)</td>
<td>15.633(0.013)</td>
<td>38.961(0.040)</td>
<td>5.11</td>
<td>1.04(0.01)</td>
<td>1.13</td>
<td>5.71</td>
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<tr>
<td>692131</td>
<td>18.976(0.007)</td>
<td>15.566(0.008)</td>
<td>38.311(0.027)</td>
<td>6.28</td>
<td>2.12(0.02)</td>
<td>2.29</td>
<td>5.16</td>
<td>4.91</td>
<td>21.6</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

1. Figures given in brackets are the one sigma uncertainties based on the addition of in-run precision and mass fractionation uncertainties.
2. I.D. is isotope dilution analysis (Appendix B). nd = not determined.
3. Uncertainty in this value is estimated at 0.1 ppm (Appendix B; Table B.12).
4. Figures given in brackets are uncertainties based on error propagation calculations using the program "WRUCALC" (Appendix D).
5. G.R. stands for gamma ray spectroscopy. Details of techniques used and uncertainties are in Chapter 1. nd = not determined.
6. μ values (238U/204Pb) are calculated using U (I.D.) ppm, or U (G.R.) ppm which has been reduced by a factor of 1.0935 (Appendix B; Table B.13). na = not applicable.
7. k values (232Th/238U) are calculated using U (G.R.) and Th (G.R.) values. na = not applicable.
8. Samples B619, B620, B621 and B625 were previously crushed for Rb-Sr analyses. These unusually low 207Pb/204Pb signatures could not be duplicated by newly crushed rocks, so the powders are probably contaminated.
isotope dilution techniques are in Appendices A and B. Other methods are outlined in Chapter 1. The two Bonanza samples, MT59 and MT360, have uranium and lead concentration data by isotope dilution, but they were not analyzed for strontium. Several Bonanza samples from similar locations have previously been analyzed for strontium (Armstrong et al. in press). The lead isotope data acquired from four of these samples are reported, but the lead signatures could not be duplicated by freshly crushed samples, therefore it is likely that the results are unreliable.

4.2 RESULTS

Lead isotope ratios of the Bonanza Group volcanic rocks and Island Intrusions (Table 4.3) are plotted in Figures 4.2 and 4.3. Initial lead ratios (Table 4.4) are shown for a 190 Ma time correction, using μ values obtained by isotope dilution methods where possible. Some of the Island Intrusion samples are corrected using μ values for which the uranium concentrations were determined by gamma ray spectroscopy. All of these μ values have been reduced by a factor of 1.0935 to be consistent with μ values for which the uranium was determined by isotope dilution (see Chapter 1).
Figure 4.2. 207Pb/204Pb versus 206Pb/204Pb plot of whole rock samples (Table 4.3) from the Island Intrusions (circles) and Bonanza Group volcanic rocks (diamonds), Vancouver Island, B.C. One galena analysis from Island Copper porphyry is also plotted (open square). Analyses marked by an "x" are unreliable (see text). Initial values (open symbols) calculated for an age of 190 Ma (Table 4.4) are connected to the present values (solid symbols) by correction vectors. The growth curve shown, marked "S & K", is that of Stacey and Kramers (1975). Field boundaries define present and initial ratios of the Island Intrusions.
Figure 4.3  $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plot of whole rock samples (Table 4.3) from the Island Intrusions (circles) and Bonanza Group volcanic rocks (diamonds), Vancouver Island, B.C. One galena analysis from Island Copper porphyry is also plotted (open square). Analyses marked by an "x" are unreliable (see text). Initial values (open symbols) calculated for an age of 190 Ma (Table 4.4) are connected to the present values (solid symbols) by correction vectors. The growth curve shown, marked "S & K", is that of Stacey and Kramers (1975). Field boundaries define present and initial ratios of the Island Intrusions.
mass fractionation

± 0.1%
TABLE 4.4 Initial lead isotope ratios for the Bonanza Group and Island Intrusions, Vancouver Island, B.C. Ratios have been corrected for an assumed Early Jurassic age of 190 Ma. Decay constants used are those recommended by Steiger and Jager (1977). μ and k values are in Table 4.3.

<table>
<thead>
<tr>
<th>NAME</th>
<th>206pb/204pb</th>
<th>207pb/204pb</th>
<th>208pb/204pb</th>
<th>(+ Error)</th>
<th>(+ Error)</th>
<th>(+ Error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT59</td>
<td>18.44 (0.02)</td>
<td>15.54 (0.01)</td>
<td>not applicable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MT360</td>
<td>18.30 (0.06)</td>
<td>15.53 (0.02)</td>
<td>not applicable</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>681381</td>
<td>18.79 (0.01)</td>
<td>15.56 (0.01)</td>
<td>38.20 (0.09)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>682122</td>
<td>18.55 (0.05)</td>
<td>15.55 (0.01)</td>
<td>38.09 (0.08)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>683171</td>
<td>18.92 (0.09)</td>
<td>15.59 (0.01)</td>
<td>38.24 (0.14)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>683421</td>
<td>18.72 (0.01)</td>
<td>15.57 (0.01)</td>
<td>38.10 (0.09)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>692131</td>
<td>18.33 (0.01)</td>
<td>15.53 (0.01)</td>
<td>37.84 (0.07)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Numbers in brackets are estimated errors based on the propagation of uncertainties in measured isotopic compositions, and in μ and k values. The program "T1CORR" (Appendix D) was used to calculate these values.
All of the data plot below Stacey and Kramer's (1975) curve for average crustal lead evolution, but with higher $^{207}\text{Pb}/^{204}\text{Pb}$ values than for the oceanic trend of Church and Tatsumoto (1975) (Figs. 4.2 and 4.3).

The initial ratios for the Island Intrusions have a linear trend in both the $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plots (Figs. 4.2 and 4.3). This linear relationship can be shown to be more significant for the initial ratios than for the uncorrected data by comparing correlation coefficients. The correlation coefficients for the uncorrected data (excluding Island Copper galena) are 0.94 and 0.89 for Figures 4.2 and 4.3 respectively. Initial lead ratios display improved correlation coefficients of 0.95 and 0.96 despite the overall shortening of the length of the lines (Figs. 4.2 and 4.3). Addition of radiogenic lead to the rocks from 190 Ma to 0 Ma has tended to obscure the original linearity.

Initial lead isotope ratios for two of the Bonanza Group volcanic rocks are colinear with those of the Island Intrusions in both $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, and $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plots, supporting a comagmatic origin for these two rock units. Bonanza Group volcanic rocks have lower $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios than those from plutonic rocks of the Island Intrusions.
Isotopic ratios of galena from the Island Copper porphyry deposit near Port Hardy is colinear with the initial ratios of both Bonanza Group volcanics and Island Intrusions, indicating a comagmatic origin for the mineralization. This supports the Jurassic age for the deposit determined by Rb-Sr age determination, and by K-Ar on biotite from the Rupert Inlet stock (Northcote and Robinson 1972).

Generalized plots of data from various tectonic environments are shown in Figures 4.4 and 4.5 with the lead data for the Island Intrusions and Bonanza Group volcanics. Direct comparison cannot be made between the lead isotope initial ratios and modern tectonic environments, so the modern lead isotope fields have been projected back 190 Ma using Stacey and Kramers (1975) growth curve. Island Intrusions and Bonanza Group volcanic lead data overlap with the fields for both ocean islands and island arcs.

Strontium isotope data are in Table 4.5. Initial strontium ratios are in the range 0.7033-0.7042, which is within the typical ranges (Basaltic Study Project 1981) of both ocean islands (>0.703) and island arcs (0.7027-0.7062). Those Bonanza Group volcanic rocks, which have lead ratios resembling depleted mantle values (Figs. 4.4 and 4.5), do not have correspondingly
Figure 4.4  207Pb/204Pb versus 206Pb/204Pb plot of initial ratios (Table 4.4) for whole rock data from the Island Intrusions (open circles), Bonanza Group volcanic rocks (diamonds) and galena from Island Copper porphyry deposit (open square), Vancouver Island, B.C. Typical fields for modern mid-ocean ridge basalts (Church and Tatsumoto 1975; Brevart et al. 1981; Vidal and Clauer 1981), island arcs (Oversby and Ewart 1972; Meijer 1976; Kay et al. 1978), ocean islands (Sun and Jahn 1975; Sun 1980; Tatsumoto 1978; Weis 1983) and Pacific sediments (Church 1976; Sun 1980; Vidal and Clauer 1981) are also shown. All fields have been adjusted to 190 Ma using Stacey and Kramers' (1975) growth curve, marked "S & K". Whole rock lead isotope values for Sicker Group volcanic rocks, corrected back to 190 Ma using measured μ values (Table 2.3), are plotted as inverted triangles.
Figure 4.5  $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plot of initial ratios (Table 4.4) for whole rock data from the Island Intrusions (open circles) and Bonanza Group volcanic rocks (diamonds), and galena data from Island Copper porphyry deposit (open square), Vancouver Island, B.C. The typical fields for mid-ocean ridge basalts, island arc volcanic rocks, ocean islands and Pacific sediments (see Fig. 4.4 for references) are also shown. Whole rock lead isotope values for the Sicker Group volcanic rocks, corrected back to 190 Ma using measured $\mu$ and $k$ values (Table 2.3), are plotted as inverted triangles. Bonanza volcanic initial ratios (open diamonds) have been determined using measured $\mu$ values (Table 4.3) and an assumed $k$ value of 3. These are shown connected to the present ratios (solid diamonds) with correction vectors.
TABLE 4.5 Rubidium and strontium isotope data for the Island Intrusions and Bonanza Group volcanic rocks, Vancouver Island, B.C. Initial ratios are calculated for an age of 190 Ma, using decay constants recommended by Steiger and Jager (1977). Sample locations are in Table 4.2.

<table>
<thead>
<tr>
<th>SAMPLE NUMBER</th>
<th>SR PPM (ALTERNATIVE)</th>
<th>RB PPM</th>
<th>(87\text{Rb}/86\text{Sr})</th>
<th>(87\text{Sr}/86\text{Sr})</th>
<th>AGE (ASSUMED)</th>
<th>INITIAL (87\text{Sr}/86\text{Sr})</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Island Intrusions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>681381 (68138II)</td>
<td>252</td>
<td>74.5</td>
<td>0.856</td>
<td>0.7056</td>
<td>190 Ma</td>
<td>0.7033</td>
<td>Armstrong et al. (1986)</td>
</tr>
<tr>
<td>682122 (68212O)</td>
<td>373</td>
<td>31.9</td>
<td>0.249</td>
<td>0.7044</td>
<td>190 Ma</td>
<td>0.7037</td>
<td>Armstrong et al. (1986)</td>
</tr>
<tr>
<td>683171 (68317O)</td>
<td>179</td>
<td>103</td>
<td>1.670</td>
<td>0.7084</td>
<td>190 Ma</td>
<td>0.7039</td>
<td>Armstrong et al. (1986)</td>
</tr>
<tr>
<td>683421 (68342O)</td>
<td>253</td>
<td>47.4</td>
<td>0.541</td>
<td>0.7050</td>
<td>190 Ma</td>
<td>0.7035</td>
<td>Armstrong et al. (1986)</td>
</tr>
<tr>
<td>692131 (68213K)</td>
<td>330</td>
<td>68.8</td>
<td>0.603</td>
<td>0.7050</td>
<td>190 Ma</td>
<td>0.7034</td>
<td>Armstrong et al. (1986)</td>
</tr>
<tr>
<td><strong>Bonanza Group</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B619 (69S119L)</td>
<td>460.1</td>
<td>37.7</td>
<td>0.237</td>
<td>0.7048</td>
<td>190 Ma</td>
<td>0.7042</td>
<td>Armstrong et al. (1985)</td>
</tr>
<tr>
<td>B620 (69S125A)</td>
<td>291.7</td>
<td>5.4</td>
<td>0.052</td>
<td>0.7037</td>
<td>190 Ma</td>
<td>0.7036</td>
<td>Armstrong et al. (1985)</td>
</tr>
<tr>
<td>B621 (69S126A)</td>
<td>367.8</td>
<td>10.5</td>
<td>0.081</td>
<td>0.7038</td>
<td>190 Ma</td>
<td>0.7036</td>
<td>Armstrong et al. (1985)</td>
</tr>
<tr>
<td>B625 (6822C)</td>
<td>46.1</td>
<td>65.8</td>
<td>4.134</td>
<td>0.7145</td>
<td>190 Ma</td>
<td>0.7033</td>
<td>Armstrong et al. (1985)</td>
</tr>
</tbody>
</table>

1. Age assumed for the Island Intrusions is based on zircon analyses of the Island Intrusions (see text).
low initial strontium values. All the Bonanza Group samples were altered to some extent so that the strontium ratios measured may not be reliable. There is a positive correlation between initial 207Pb/204Pb and initial 87Sr/86Sr for data from the Island Intrusions (Fig. 4.6).

4.3 DISCUSSION

Lead and strontium isotope ratios are consistent with the origin of the Bonanza Group volcanic rocks and the Island Intrusions either in an oceanic island or an island arc tectonic setting. Both possibilities are explored further in the following sections.

4.3.1 An ocean Island?

Lead isotope data from modern ocean islands tend to display linear arrays in Pb-Pb plots, which may be secondary isochrons (Oversby and Gast 1970; Russell 1972; Tatsumoto 1978; Chase 1981) or mixing lines (Anderson 1982). Chase (1981) discovered a systematic relationship between the data arrays for seven different oceanic islands. He found that each island is consistent with secondary enrichment in U/Pb of a single primary reservoir, with a μ value of 7.91 ± 0.04, at a specific time between 2.5 Ga and 1 Ga ago. Applying the secondary isochron
Figure 4.6 Initial $^{87}\text{Sr}/^{86}\text{Sr}$ versus initial $^{207}\text{Pb}/^{204}\text{Pb}$ plot for the Island Intrusions (circles), and Bonanza Group volcanic rocks (diamond), Vancouver Island, B.C. Two mixing curves are shown for mixing between a mid-ocean ridge type mantle source and two different crustal sources. The MORB end-member has: $^{207}\text{Pb}/^{204}\text{Pb} = 15.43$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7022$, Sr = 100 ppm, Pb = 0.5 ppm. Average Sicker Group material at 190 Ma (solid square) has: $^{207}\text{Pb}/^{204}\text{Pb} = 15.60$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7056$, Sr = 200 ppm, and Pb = 5 ppm. Typical upper continental crust (ringed circle) has: $^{207}\text{Pb}/^{204}\text{Pb} = 15.70$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7070$, Sr = 400 ppm, and Pb = 20 ppm.
model to the Island Intrusions, the calculated $\mu$ value for the primary reservoir is 7.97 and the time at which secondary enrichment of U/Pb occurs is 1.37 Ga (Table 4.6). Good agreement of these values with those of other oceanic islands is support for the origin of the Island Intrusions in an oceanic island setting.

The apparent correlation between initial $^{207}$Pb/$^{204}$Pb and initial $^{87}$Sr/$^{86}$Sr displayed by the Island Intrusions neither confirms nor denies the origin of the Island Intrusions in an oceanic island. The model of Chase (1981) does not require that these values be correlated, however, a model proposed by Anderson (1982) does require correlated initial lead and strontium ratios in ocean island rocks. Anderson (1982) suggested that the lead, strontium and neodymium isotope data from mid-ocean ridge basalts and ocean island basalts can be resolved in terms of mixing of depleted and enriched mantle sources.

4.3.2 An Island Arc?

Lead isotope data from island arcs often display linear arrays on Pb-Pb plots, and a correlation of initial lead and strontium ratios (Tatsumoto and Knight 1969; Armstrong and Cooper 1971; Church and Tilton 1973; Meijer 1976; Kay et al. 1978; Tsunakawa 1981). In most cases the linear trends have a
Table 4.6 Calculations for secondary isochron model, Island Intrusions, Vancouver Island, B.C.

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope of best fit line to initial lead data</td>
<td>0.92787</td>
</tr>
<tr>
<td>Age given by slope, assuming 190 Ma for intrusion</td>
<td>1.37 Ga</td>
</tr>
<tr>
<td>Slope of primary isochron assuming the age of the earth is 4.57 Ga, and t2 is 1.37 Ga</td>
<td>0.78636</td>
</tr>
<tr>
<td>Intersection of primary and secondary isochrons</td>
<td>0.8768</td>
</tr>
<tr>
<td>206Pb/204Pb</td>
<td>15.648</td>
</tr>
<tr>
<td>207Pb/204Pb</td>
<td>15.280</td>
</tr>
<tr>
<td>µ value for first stage, assuming Earth had the composition of troilite lead (Tatsumoto et al. 1973) at 4.57 Ga</td>
<td>7.97</td>
</tr>
</tbody>
</table>
steeper slope (approximately 0.3) than those of ocean islands (approximately 0.1) on Pb-Pb plots (Kay et al. 1978). They are interpreted as mixing lines between lead-rich, high 207Pb/204Pb subducted or assimilated crustal lead, and lead-poor, low 207Pb/204Pb oceanic mantle (Church 1973 and 1976; Kay et al. 1978; Meijer 1976).

If the Island Intrusions and Bonanza Group volcanic rocks are to be interpreted as an island arc assemblage, the low slope of the mixing line (approximately 0.1) must be explained in terms of the compositions of the two end-members. This places important constraints on the lead-rich and strontium-rich 'crustal' end-member.

It is possible to determine the nature of the end-members by constructing mixing hyperboli in the initial 207Pb/204Pb versus initial 87Sr/86Sr plot (Fig. 4.6). The end-members selected were: a typical MORB (at 190 Ma) with 207Pb/204Pb = 15.43, 87Sr/86Sr = 0.7022, Pb = 0.5 ppm, Sr = 100 ppm (Tsunakawa 1981), and two estimates of a crustal component. These were curve 1, average Sicker Group rocks at 190 Ma, with 207Pb/204Pb = 15.60, 87Sr/86Sr = 0.7056, Pb = 5 ppm, and Sr = 200 ppm, and curve 2, average upper North American continental crust, with 207Pb/204Pb = 15.7 (from the Shale Curve lead growth curve model of Godwin and Sinclair 1982 at 190 Ma), 87Sr/86Sr = 0.707, Pb =
20 ppm (typical upper continental crustal lead concentration estimated by Doe and Zartman 1979), Sr = 400 ppm (O'Nions et al. 1979; Weaver and Tarney 1980).

The resulting hyperboli, calculated using the general equation of Langmuir et al. (1978), are shown in Figure 4.6. It can be seen that the high 207Pb/204Pb signature of upper continental crust precludes its involvement in the formation of the Island Intrusions and Bonanza Group volcanics. Rather, a suitable candidate for the crustal end-member is detritus from the pre-existing Paleozoic Sicker Group arc volcanic rocks, which have lower lead concentrations (Table 2.2) and 207Pb/204Pb ratios than the specific upper continental crustal type used in the calculation.

The envelopes to the demonstrated hyperboli (Fig. 4.6) indicate the variation in mixing that is possible given the variation in end-member compositions. Thus Sicker Group material cannot uniquely be identified as the crustal end-member because many other continental crustal and ocean sediment compositions would be suitable candidates. It is, however, possible to rule out contamination by sediments that were derived from the miogeosynclinal part of the Canadian Cordillera, which are characterized by high 207Pb/204Pb values (Godwin and Sinclair 1982; Andrew et al. 1984).
Suitability of Sicker Group rocks for contributing lead to the mantle-derived Bonanza Group and Island Intrusions magmas is further illustrated in Figures 4.4 and 4.5. In both figures the Sicker Group lead data (adjusted to 190 Ma using measured $\mu$ and $k$ values) plot at the radiogenic ends of the mixing lines. Island Intrusions show a greater degree of contamination than do the Bonanza Group volcanic rocks. It is therefore possible that part (or all) of the mixing trend is due to assimilation of Sicker material by the intrusions.

The Cretaceous Sierra Nevada batholith, which is a granodioritic body at the root of a magmatic arc, is a suitable analogue to the Island Intrusions. Lead isotope data from the Sierra Nevada batholith have a linear pattern on conventional lead isotope plots (Doe and Delevaux 1973), which is steeper than that of the Island Intrusions (apparent secondary isochron age is 2900 Ma). This reflects the nature of the crustal end-member for the Sierra Nevada batholith which is more continental in character than that for the Island Intrusions. Correlation between lead and strontium isotope data which is apparent for the Island Intrusions is also apparent for the Sierra Nevada batholith (Doe and Delevaux 1973). De Paulo (1981) found that in the Sierra Nevada, the intrusions are consistently more radiogenic than the volcanic rocks. Neodymium, strontium,
oxygen and lead isotope data combine to indicate that mantle-derived magmas have assimilated old continental crust during the formation of the Sierra Nevada magmatic arc (De Paulo 1981). The conclusion that assimilation of old crust is an important process in the formation of magmatic arcs (De Paulo 1981) is supported by the lead and strontium data obtained here for the Island Intrusions and Bonanza Group volcanic rocks.

4.3.3 Geological considerations

Most ocean islands are predominantly basaltic with minor amounts of differentiated silicic rocks. The Bonanza Group volcanic rocks and the Island Intrusions are more typical of rocks associated with island arcs because of their calc-alkaline chemistry and felsic nature. The interpretation that these Jurassic rocks formed an island arc assemblage therefore seems to be most reasonable.

It is possible that neodymium isotope analyses of the same rocks analyzed in this study would help to distinguish between island arc and ocean island origins for these Jurassic igneous rocks. Island arc data are usually displaced away from the mantle array (DePaulo and Wasserburg 1977) to higher, more positive, values of $\varepsilon_{\text{Sr}}$ (the deviation in parts in 10$^4$ of a rock's initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from the ratio in a model reservoir thought to be representative of the total earth) in
the Nd-Sr correlation diagram (Basaltic Volcanism Study Project 1981). This displacement has been observed for island arcs which show contamination by normal upper continental crustal sediments, so it is possible that the specific crustal type required to explain the lead isotope data may not significantly displace the data away from the mantle array. Neodymium analyses would, however, help to further describe and identify the crustal contaminant.

4.3.4 A model

One possible explanation for the isotopic characteristics of the Bonanza Group volcanics and Island Intrusions is as follows:

1) Subduction of an oceanic plate beneath another plate carrying the Paleozoic Sicker Group and Triassic Karmutsen Formation occurs away from a supply of continental detritus so that the trench is starved.

2) Partial melting occurs in the upper part of the downgoing slab and/or in the mantle wedge above the subducting plate. The isotope signature of the melt is approximately the same as for depleted mantle.

3) Magmas rise into the upper plate. Explosive Bonanza volcanism precludes the contamination of Bonanza magmas by crustal materials, except for oceanic sediments introduced into the magma by subduction.

4) Magmas residing in the upper plate assimilate Sicker Group
and other material while cooling slowly; this produces a heterogeneous, mixed lead isotope signature in the Island Intrusions with more radiogenic isotope values than for the Bonanza Group volcanics.

5) In situ addition of radiogenic lead between 190 Ma and the present causes the original linear mixing trend to be partially obscured.

4.4 CONCLUSIONS

Lead isotope data have been obtained for rocks from the Island Intrusions and Bonanza Group volcanic rocks. Several general conclusions can be drawn from these, and from strontium isotope analyses of the same rocks:

1) Lead isotope data support a comagmatic origin for the Island Intrusions and Bonanza Group volcanic rocks.

2) The Island Intrusions contain lead which is more radiogenic than in the Bonanza Group volcanic rocks.

3) Lead and strontium isotope data alone cannot distinguish between island arc and ocean island tectonic settings for these rocks. Lithologies are more typically those of an island arc.

4) The initial lead data form a linear array in the Pb-Pb plots. If interpreted as a mixing line, the radiogenic end-member has to have a lower than typical crustal value of 207Pb/204Pb.
The Sicker Group Paleozoic rocks into which the Island Intrusions are emplaced are of a suitable lead and strontium composition. 

5) Galena from the Island Copper porphyry deposit supports a Jurassic age for the deposit.
CHAPTER 5

ISOTOPE GEOCHEMISTRY OF THE CATFACE TERTIARY INTRUSIONS

SYNOPSIS

Lead and strontium isotope ratios from the Catface Tertiary intrusions in Vancouver Island occupy a narrow range of values, indicating a homogeneous or well mixed source. Within this range, the lead isotope data fall into two distinct clusters, corresponding to an eastern and a western belt geographically. Initial strontium ratios for these intrusions show little variation about a mean value of 0.7039 ± 0.0002.

The source of these intrusions can not be identified uniquely using lead and strontium isotope data alone, but two possibilities can be ruled out. 207Pb/204Pb, 208Pb/204Pb and initial strontium ratios are all too high to be from solely mantle-derived magmas. Initial strontium ratios are too low and the 208Pb/204Pb and 232Th/238U ratios too high for the Catface intrusions to be the products of melting of pre-existing Sicker Group rocks.
Galena from quartz-gold veins related to the Zeballos pluton has a lead isotopic composition similar to that of the Zeballos pluton. Consequently, if lead and gold have the same origin, the source of the gold is the intrusion, rather than the host rocks.

5.1 INTRODUCTION

The Catface Tertiary intrusions of Vancouver Island are small quartz diorite plutons, which intrude a variety of rock units. They have come to be known as the Catface intrusions after the type pluton near Tofino. Carson (1973) divided the intrusions into an eastern and a western belt based on geographic distribution. West belt intrusions tend to have a foliation which is absent in East belt plutons. Plutons from both belts were sampled (Fig. 5.1, Table 5.1).

A concordant Eocene age of $41 \pm 1$ Ma has been obtained on zircons from the Catface intrusion (Isachsen 1984). K-Ar ages (circa 45 Ma) have been determined (Table 5.2) for each of the samples here analyzed for lead. Two age groupings exist, one at 50-55 Ma and another at 38-42 Ma. The uncertainty in the age for the Zeballos pluton is such that it could belong to either of the two groups. However, it seems likely that the east belt plutons are generally younger than the west belt plutons. Sample
Figure 5.1 Distribution of Eocene Catface intrusions (shaded areas), Vancouver Island, B.C. Dots with abbreviated sample names mark whole rock sample locations (Table 5.1). Galena sample locations (Table 5.1) are shown as crosses, except for six samples from the Zeballos mining camp marked ZB. Present locations of plate boundaries are indicated. Diamond symbols mark named Paleozoic ore deposits. Squares locate towns.
TABLE 5.1 Locations (Fig. 5.1) and brief descriptions of whole rock samples from the Catface Tertiary intrusions, and galena from related mineralization. Sample symbols are used in Figures 5.1 and 5.2.

<table>
<thead>
<tr>
<th>SAMPLE NAME (SYMBOL)</th>
<th>LAT.</th>
<th>LONG.</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole rock samples</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catface (CT)</td>
<td>49.24</td>
<td>125.95</td>
<td>Quartz diorite, west belt</td>
</tr>
<tr>
<td>Faith Lake (FL)</td>
<td>49.65</td>
<td>125.41</td>
<td>Quartz diorite, east belt</td>
</tr>
<tr>
<td>Mt. Washington (MW)</td>
<td>49.77</td>
<td>125.29</td>
<td>Quartz diorite, east belt</td>
</tr>
<tr>
<td>Stubbs Island (SI)</td>
<td>49.16</td>
<td>125.93</td>
<td>Quartz diorite, west belt</td>
</tr>
<tr>
<td>Zeballos (ZB)</td>
<td>50.04</td>
<td>126.78</td>
<td>Quartz diorite, west belt</td>
</tr>
<tr>
<td>Zeballos gold-quartz veins</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30317 (LS)</td>
<td>50.02</td>
<td>126.79</td>
<td>Galena, Lone Star/Rey Oro</td>
</tr>
<tr>
<td>30318 (WS)</td>
<td>50.03</td>
<td>126.81</td>
<td>Galena, White Star</td>
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<td>30320 (PR)</td>
<td>50.04</td>
<td>126.84</td>
<td>Galena, Peerless</td>
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<td>30349 (PV)</td>
<td>50.03</td>
<td>126.81</td>
<td>Galena, Privateer</td>
</tr>
<tr>
<td>30484 (CZ)</td>
<td>50.04</td>
<td>126.78</td>
<td>Galena, Central Zeballos</td>
</tr>
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<td>30487 (BP)</td>
<td>50.04</td>
<td>126.78</td>
<td>Galena, Bragg property</td>
</tr>
<tr>
<td>Miscellaneous vein deposits</td>
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</tr>
<tr>
<td>30319 (WW)</td>
<td>49.03</td>
<td>124.70</td>
<td>Galena, WWW showing</td>
</tr>
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<td>JS (JS)</td>
<td>48.94</td>
<td>123.76</td>
<td>Galena, J and S showing</td>
</tr>
<tr>
<td>30483 (BJ)</td>
<td>49.47</td>
<td>126.42</td>
<td>Galena, Brown Jug claim</td>
</tr>
<tr>
<td>30486 (LC)¹</td>
<td></td>
<td></td>
<td>Galena, Livingston claims</td>
</tr>
</tbody>
</table>

¹. Cowichan Lake District. Exact location unknown.
TABLE 5.2 Summary of K-Ar ages obtained for Catface Tertiary intrusions, Vancouver Island, B.C., for the samples that were analyzed for lead in this study. Original ages have been corrected to modern constants of Steiger and Jager (1977). Other K-Ar ages for Tertiary intrusions on Vancouver Island are in Carson (1973).

<table>
<thead>
<tr>
<th>NAME</th>
<th>AGE (Ma)</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catface</td>
<td>49 ± 12</td>
<td>Wanless et al. (1967), p.15</td>
</tr>
<tr>
<td>Faith Lake</td>
<td>40 ± 7</td>
<td>Wanless et al. (1968), p.29</td>
</tr>
<tr>
<td>Mt. Washington</td>
<td>36 ± 6</td>
<td>Wanless et al. (1968), p.29-30</td>
</tr>
<tr>
<td>Stubbs Island</td>
<td>51 ± 5</td>
<td>Wanless et al. (1968), p.30-31</td>
</tr>
<tr>
<td>Zeballos</td>
<td>39 ± 14</td>
<td>Wanless et al. (1967), p.16</td>
</tr>
</tbody>
</table>
locations and descriptions are in Table 5.1 and Figure 5.1.

Quartz veins related to the Zeballos pluton are of economic interest since they contain important values in gold. Several mines were productive in the 1930's in the Zeballos area. Comparison of lead isotope ratios from galena in the veins to whole rock lead ratios from the pluton provides a method for determining the source of the lead in the veins. Galena lead isotope analyses (Table 5.1, Fig. 5.1) were obtained for eight vein deposits.

Plate tectonic reconstructions of western North America during the Tertiary suggest that volcanic and plutonic activity at this time was largely related to a general regime of easterly subduction of oceanic plates beneath North America (Atwater 1970, Byrne 1979, Ewing 1981). A magmatic arc existed in the Coast Mountains during the Eocene, between approximately 53 and 42 Ma (Ewing 1981, Souther 1977). Volcanic rocks erupted at this time include the Sloko volcanics in northern B.C., Ootsa Lake Group volcanic rocks in central B.C., and Marron Formation volcanics, Kamloops Group volcanic rocks and Coryell province volcanics in southern B.C. The Catface intrusions occur seaward of these volcanic belts in a fore-arc setting.

At approximately 42 Ma, which is similar to the age of some
of the Catface intrusions, a change in plate motions occurred (Byrne 1979; Ewing 1981). South of 50° N, Cascade volcanism was initiated in response to the easterly subduction of the Farallon (now Juan de Fuca) plate (Ewing 1981; Brandon and Massey 1985). North of 50° N the Pacific plate motion was taken up along the Queen Charlotte transform fault (Ewing 1981). This overall plate configuration (Fig. 5.1) has continued to the present day (Atwater 1970; Riddihough 1977; Byrne 1979). The Garibaldi volcanic belt represents the present magmatic arc associated with subduction of the Juan de Fuca plate (Ewing 1981); it occurs about 250 km inland from the trench.

The Eocene was also the time of accretion of the Metchosin volcanic rocks to southern Vancouver Island, south of the Leech River fault (Rusmore and Cowan 1985). It is therefore difficult to attribute a specific plate tectonic setting to the Catface intrusions given the complex tectonic history of the area at the time they were intruded.

5.2 RESULTS

Lead isotope compositions for the whole rock and galena samples (Tables 5.3 and 5.4) are plotted in Figure 5.2. They occupy a narrow range of values despite the small size of the
TABLE 5.3  Lead, uranium and thorium data for the Catface intrusions, Vancouver Island, B.C. Sample sites are located in Figure 5.1 and Table 5.1.

<table>
<thead>
<tr>
<th>SAMPLE NAME</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
<th>Pb PPM</th>
<th>U PPM</th>
<th>U PPM</th>
<th>TH PPM</th>
<th>μ6</th>
<th>k7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole rock data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catface (CT)</td>
<td>18.997(0.032)</td>
<td>15.622(0.026)</td>
<td>38.657(0.066)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Faith Lake (FL)</td>
<td>18.753(0.009)</td>
<td>15.583(0.007)</td>
<td>38.400(0.021)</td>
<td>1.28</td>
<td>0.25(0.03)</td>
<td>0.39</td>
<td>1.5</td>
<td>12.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Mount Washington (MW)</td>
<td>18.734(0.010)</td>
<td>15.588(0.008)</td>
<td>38.179(0.021)</td>
<td>1.93</td>
<td>0.21(0.16)</td>
<td>nd</td>
<td>nd</td>
<td>7.0</td>
<td>na</td>
</tr>
<tr>
<td>Stubbs Island (SI)</td>
<td>19.093(0.004)</td>
<td>15.608(0.004)</td>
<td>38.694(0.013)</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>Zeballos (Z)</td>
<td>19.055(0.004)</td>
<td>15.602(0.004)</td>
<td>38.608(0.013)</td>
<td>3.71</td>
<td>1.10(0.16)</td>
<td>1.29</td>
<td>4.2</td>
<td>19.0</td>
<td>3.4</td>
</tr>
</tbody>
</table>

1. Figures given in brackets are the one sigma uncertainties based on the addition of in-run precision and mass fractionation uncertainties, calculated using program "WRP3BIC" (Appendix D).
2. I.D. is isotope dilution analysis (Appendix B); nd = not determined
3. Estimated uncertainty for this value is 0.1 ppm (Appendix B; Table B.12).
4. Figures given in brackets are uncertainties based on error propagation calculations, using the program "WRU3LC" (Appendix D).
5. N.A.A. stands for neutron activation analysis, D.N. is delayed neutron counting. These samples were analyzed by Neutron Activation Services Ltd., Hamilton, Ontario. Uncertainties are estimated at 10%.
6. μ values (238U/204Pb) are calculated using U ppm (I.D.); na = not applicable.
6. k values (232Th/238U) are calculated using U (N.A.A.) and Th (D.N.) values; na = not applicable. Uncertainties are assumed to be 14% based on 10% uncertainties in each of U and Th concentrations.
TABLE 5.4  Galena lead isotope data from Vancouver Island, B.C., for quartz-gold veins related to the Eocene Zeballos pluton and miscellaneous galena samples from veins of probable Tertiary age. Samples are located in Table 5.1 and Figure 5.1. Numbers in brackets are estimated one sigma errors, based on the sum of errors of in-run precision and uncertainties in the mass fractionation factors. Data are plotted in Figure 5.2.

<table>
<thead>
<tr>
<th>SAMPLE LABEL</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galena from quartz-gold veins related to the Zeballos pluton</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30317 LS</td>
<td>18.979(0.003)</td>
<td>15.601(0.004)</td>
<td>38.551(0.016)</td>
</tr>
<tr>
<td>30318 WS</td>
<td>18.985(0.002)</td>
<td>15.605(0.004)</td>
<td>38.584(0.015)</td>
</tr>
<tr>
<td>30320 PR</td>
<td>19.003(0.003)</td>
<td>15.583(0.005)</td>
<td>38.534(0.014)</td>
</tr>
<tr>
<td>30349 PV</td>
<td>18.983(0.004)</td>
<td>15.601(0.007)</td>
<td>38.560(0.024)</td>
</tr>
<tr>
<td>30484 CZ</td>
<td>18.980(0.004)</td>
<td>15.606(0.004)</td>
<td>38.568(0.014)</td>
</tr>
<tr>
<td>30487 BP</td>
<td>19.005(0.002)</td>
<td>15.611(0.005)</td>
<td>38.588(0.015)</td>
</tr>
<tr>
<td>Galena from miscellaneous vein deposits of probable Tertiary age</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30319-1 WW</td>
<td>18.993(0.003)</td>
<td>15.577(0.005)</td>
<td>38.533(0.014)</td>
</tr>
<tr>
<td>30319-2 WW</td>
<td>19.009(0.002)</td>
<td>15.604(0.004)</td>
<td>38.636(0.014)</td>
</tr>
<tr>
<td>JS</td>
<td>18.725(0.004)</td>
<td>15.584(0.004)</td>
<td>38.283(0.012)</td>
</tr>
<tr>
<td>30483 BJ</td>
<td>18.957(0.003)</td>
<td>15.614(0.004)</td>
<td>38.551(0.016)</td>
</tr>
<tr>
<td>30486 LC</td>
<td>18.967(0.004)</td>
<td>15.598(0.006)</td>
<td>38.556(0.016)</td>
</tr>
</tbody>
</table>
Figure 5.2  \(^{207}\text{Pb}/^{204}\text{Pb}\) versus \(^{206}\text{Pb}/^{204}\text{Pb}\), and \(^{208}\text{Pb}/^{204}\text{Pb}\) versus \(^{206}\text{Pb}/^{204}\text{Pb}\) plots of whole rock and galena lead isotope data from Tertiary intrusions and related ore deposits, Vancouver Island, B.C. Solid squares mark present whole rock ratios (Table 5.2); open squares are initial values (Table 5.6). Present and initial ratios are linked by correction vectors. Triangles mark galena analyses. Abbreviated labels are defined in Table 5.2.
plutons and their wide geographic separation. In detail the lead data plot in two clusters in Figure 5.2, which correspond to the east and west belt classification of Carson (1972). Within each cluster the isotopic data are identical within analytical precision. The east belt plutons (Faith Lake and Mount Washington) are less radiogenic than the others, despite their younger age. Both clusters plot well above the oceanic trend defined by mid-ocean ridge basalts and oceanic islands (Church and Tatsumoto 1975; Figure 5.2).

Initial strontium ratios (Table 5.5) average 0.7039 ± 0.0002. Taken separately, the east belt plutons have an initial ratio of 0.7041 ± 0.0001 which is slightly higher than for the west belt plutons (0.7038 ± 0.0001). There is, therefore, an inverse relationship between 206Pb/204Pb and initial strontium ratios.

Galena samples from the vein deposits in the Zeballos area (Table 5.4) have remarkably homogeneous lead ratios. They form a tight cluster close to the Zeballos pluton initial ratios (Table 5.6), which were calculated using the measured μ value and an assumed age for the pluton of 40 Ma.
TABLE 5.5  Rubidium and strontium isotope data for the Catface Intrusions, Vancouver Island, B.C. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are calculated using an assumed age of 40 Ma. Samples are located in Figure 5.1 and Table 5.1.

<table>
<thead>
<tr>
<th>SAMPLE NAME</th>
<th>Sr PPM</th>
<th>Rb PPM</th>
<th>$^{87}\text{Rb}/^{86}\text{Sr}$</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$ (INITIAL)</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catface¹</td>
<td>414</td>
<td>23.5</td>
<td>0.164</td>
<td>0.7038</td>
<td>Isachsen (1984)</td>
</tr>
<tr>
<td>Faith Lake</td>
<td>548</td>
<td>20.9</td>
<td>0.110</td>
<td>0.7043</td>
<td>Armstrong et al. (in press)</td>
</tr>
<tr>
<td>Mount Washington</td>
<td>595</td>
<td>16.9</td>
<td>0.082</td>
<td>0.7041</td>
<td>Armstrong et al. (in press)</td>
</tr>
<tr>
<td>Zeballos</td>
<td>381</td>
<td>39.3</td>
<td>0.299</td>
<td>0.7040</td>
<td>Armstrong et al. (in press)</td>
</tr>
</tbody>
</table>

1. Catface sample is not the same sample analyzed in this study for lead. Details of this sample are in Isachsen (1984)
TABLE 5.6 Initial ratios for the Catface Intrusions, Vancouver Island, B.C. Age corrections are for an assumed age of 40 Ma. One sigma uncertainties given in brackets are based on error propagation using the program "T1CORR" (Appendix D). μ and k values used in the calculations are in Table 5.3. Data are plotted in Figure 5.2.

<table>
<thead>
<tr>
<th>SAMPLE NAME</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faith Lake</td>
<td>18.68 (.01)</td>
<td>15.58 (.01)</td>
<td>38.30 (.04)</td>
</tr>
<tr>
<td>Mt. Washington</td>
<td>18.69 (.01)</td>
<td>15.59 (.01)</td>
<td>not applicable</td>
</tr>
<tr>
<td>Zeballos</td>
<td>18.94 (.02)</td>
<td>15.60 (.01)</td>
<td>38.48 (.04)</td>
</tr>
</tbody>
</table>
5.3 DISCUSSION

5.3.1 Origin of the Catface intrusions

Tertiary intrusions on Vancouver Island appear to belong to two different magmatic events, thus the name 'Catface intrusions' may be wrongly applied to all of them, masking important differences. Faith Lake and Mount Washington plutons have less radiogenic lead than the other plutons, despite their younger age, but slightly higher initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Uniformity of lead isotope ratios within each cluster implies a homogeneous or well mixed source for each magmatic event.

Initial strontium, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ are all too high with respect to $^{206}\text{Pb}/^{204}\text{Pb}$, for the intrusions to have formed directly from oceanic mantle. A component of crustal lead, perhaps from subducted sediments, from underplated material, or from basement rocks, must have been involved in their formation.

Sicker Group basement rocks are not of a suitable isotopic composition to be the major crustal component in the formation of the Catface intrusions. Strontium ratios of the Sicker Group are too high (as previously pointed out by Isachsen 1984, and illustrated by Armstrong et al. in press, figure 10). Uranium and thorium data also support this conclusion. Th/U values are
higher in the Catface intrusions (>3, Table 5.3) than in the Sicker Group (<3, Table 2.2). If melting of the Sicker Group were to take place, the Th/U value in the melt would tend to be lower than in the residue, since uranium is more efficiently transferred into the liquid phase (Seitz 1973; Tatsumoto 1978; Anderson 1982). Finally, the 208Pb/204Pb ratio is slightly higher in the Tertiary intrusions than would be expected if the crustal lead component was Sicker Group material.

Deep seismic reflection profiles of southern Vancouver Island show a zone of underplated material (Yorath et al. 1985b; Clowes et al. 1987), which has been interpreted as being associated with the most recent subduction regime that was initiated in late Eocene, at about the same time as the intrusions were being emplaced. This is, therefore, one possible source for these intrusions.

The lead isotope composition of Pacific ocean sediments (Church 1976) is of a suitable composition to be the crustal component in the Tertiary intrusions (Figure 5.3). Introduction of these sediments into the site of magma genesis by subduction, therefore, is the most likely explanation for their origin. The Catface intrusions occupy the isotopic fields characteristic of island arcs in Figures 5.3 and 5.4, supporting this hypothesis. The variation in isotope ratios between the East belt and West
Figure 5.3 207Pb/204Pb versus 206Pb/204Pb plot showing present day (solid squares; Table 5.3) and initial (open squares; Table 5.6) whole rock lead isotope compositions for the Tertiary intrusions, Vancouver Island, B.C. Also shown are present day generalized fields for mid-ocean ridge basalts (Church and Tatsumoto 1975; Brevart et al. 1981; Vidal and Clauer 1981), ocean islands (Sun and Jahn 1975; Tatsumoto 1978; Sun 1980; Weis 1983), island arcs (Oversby and Ewart 1972; Church 1975; Meijer 1976; Kay et al. 1978) and ocean sediments (Church 1975; Vidal and Clauer 1981; Sun 1980). The growth curve for reference is that of Stacey and Kramers (1975).
Figure 5.4. $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plot showing present day (filled squares; Table 5.3) and initial (open squares; Table 5.6) whole rock lead isotope compositions for the Tertiary intrusions, Vancouver Island, B.C. Also shown are present day generalized fields for mid-ocean ridge basalts, ocean islands, island arcs and Pacific sediments (see Fig. 5.3 for source of data). The growth curve for reference is that of Stacey and Kramers (1975).
belt plutons is more problematic and may be due to modification during emplacement into different host rocks. Geographical variations in isotope ratios are found in the Andes in Peru (Barreiro and Clark 1984), and in the Cascades (Church et al. 1986). In both cases variation in crustal thickness or type are invoked to explain observed differences.

The hypothesis of crustal contamination of mantle type lead with upper crustal lead could be further tested using Nd isotopes. Deviation from the mantle array in the Nd-Sr correlation diagram towards higher Sr values would be expected. The consistency of the inverse relationship between initial strontium ratios and 206Pb/204Pb could also be tested. If the East belt plutons have higher 87Sr/86Sr initial ratios than the West belt ones they should also have lower 144Nd/143Nd ratios.

5.3.2 Galena lead isotope data

Similarity in the initial lead ratios of the Zeballos batholith with galena from quartz-gold veins, and the uniformity of those ratios argue strongly for a plutonic source for the gold, assuming that lead and gold have a common origin. This contradicts a conclusion arrived at by Andrew et al. (1982) in the absence of whole rock lead data, thus pointing out the advantages of interpreting galena lead isotope data with data from whole rock lead. The implication that the host rock to the veins is an
unimportant factor in locating gold-rich veins related to Tertiary intrusions is supported by a statistical study by Hansen and Sinclair (1984).

Knowledge of the isotopic composition of Tertiary intrusions and vein deposits provides a useful means of identifying Tertiary mineralization on Vancouver Island. Galena from the Brown Jug claim near Tofino can be shown to be related to the Tertiary intrusions by simple comparison. It therefore represents a possible gold producer. Similarly, lead from the J and S prospect might be related to Tertiary intrusions of the eastern belt because of its similarity in isotopic composition with Faith Lake and Mount Washington plutons. It is unlikely that the J and S prospect is related to a Paleozoic massive sulphide deposit, because of the differences in composition between it and the Paleozoic Buttle Lake and Lenora and Tyee ore deposits. Livingston Claims, a Pb-Zn ore deposit in Cowichan limestone, and the WWW ore deposit near Alberni, both have lead isotope ratios indistinguishable from those of the Zeballos-related deposits, implying that these are Tertiary deposits related to the Eocene intrusive event.

A lead isotope study of mineral deposits associated with Tertiary plutons in the Cascade Range of Washington and Oregon by Church et al. (1986) shows that they have extremely
homogeneous lead isotope ratios in the same range as those of Vancouver Island. All the deposits were younger (20 Ma to 6.5 Ma) and related to the Cascade subduction regime (Church et al. 1986). Geographical variations in isotope ratios were also found and related to crustal basement variations. The lead isotope features of these pluton-related ore deposits are the same as for those of Vancouver Island. The genetic interpretation of these deposits as containing metals originating in subducted sediments, is the favoured interpretation for the lead in the Catface intrusions and associated gold deposits. The coincidence of lead isotope ratios of Tertiary pluton-related ore deposits over a wide geographic area stretching from Vancouver Island along the west coast to Oregon is of major significance. Specifically, Tertiary mineralization, commonly associated with gold, can be identified easily using lead isotope analyses.

5.5 CONCLUSIONS

Catface Tertiary intrusions include two groups of plutons, each with a homogeneous lead isotope signature. The groups correspond to a geographically distinct east belt and west belt.

The origin of these plutons is not completely resolved.
Initial strontium, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios rule out oceanic mantle as the only source. Strontium, uranium and thorium data preclude the direct genesis of the plutons from Sicker Group basement rocks. Lead isotope data are consistent with the origin of the intrusions from a well mixed combination of mantle, and upper crustal sediments introduced by subduction. Strontium initial ratios are, however, rather low. Nd isotopes may help to resolve this inconsistency.

Galena lead isotope ratios from Tertiary quartz-gold veins in Vancouver Island indicate that the origin of the gold is in the plutons, and that ultimately the metals are derived from recycled crustal material rather than the mantle. The homogeneity of lead isotope signatures from pluton-related Tertiary ore deposits in the Pacific northwest region of North America simplifies the identification of Tertiary gold-related mineralization by lead isotope analysis throughout the western Cordillera.
CHAPTER 6

PLUMBOTECTONICS OF VANCOUVER ISLAND

SYNOPSIS

Paleozoic rocks of Vancouver Island are characterized by higher $^{207}\text{Pb}/^{204}\text{Pb}$ ratios than Mesozoic volcanic and plutonic rocks, indicating greater involvement of upper crustal material in their formation. The Mesozoic volcanic rocks are depleted in $^{207}\text{Pb}/^{204}\text{Pb}$ and there is evidence of isotopic mixing in both the Triassic and Jurassic episodes. In the Triassic, the mantle source resembles an ocean island basalt source and the crustal contaminant has the features of average crust. Jurassic Island Intrusions display mixing between a depleted mantle source and an oceanic or arc-type crustal source, which may be Sicker Group material. There is a return to greater crustal involvement in the formation of the Tertiary Catface intrusions.

Galena and whole rock lead isotope compositions from Vancouver Island are characterized by higher $^{206}\text{Pb}/^{204}\text{Pb}$, and lower $^{207}\text{Pb}/^{204}\text{Pb}$ ratios than those of cratonic North America. No single lead isotope growth curve model can be applied to Vancouver Island because it is a mosaic of different tectonic
environments. Interpretation of age of deposits from galena lead isotope data can be made by comparison with data from known ore deposits. This is difficult, however, in the ranges $^{206}\text{Pb}/^{204}\text{Pb} = 18.5-18.8$, and $^{207}\text{Pb}/^{204}\text{Pb} = 15.55-15.60$, where some Tertiary, Mesozoic and Paleozoic ore deposits fall. Galena with $^{206}\text{Pb}/^{204}\text{Pb} > 18.8$ is Tertiary.

6.1 INTRODUCTION

Each of the volcanic and plutonic episodes that made up the history of Vancouver Island has its own isotopic characteristics. Several different mantle sources have been tapped during the development of the island, and various types of crustal material have contributed to the isotopic heterogeneity of Wrangellia through changes in provenance or volume of trench sediments, assimilation, and recycling of continental detritus into the mantle.

This chapter synthesizes the isotopic information from each of the volcanic and plutonic episodes that have been discussed in the preceding chapters. Major isotopic characteristics of each of these episodes are summarized and compared. Recognition of isotopic differences between rock suites provides a means of identifying the mineralization source and age for galena samples
related to these volcanic and plutonic episodes. A method of distinguishing between mineralization ages using galena lead isotope analyses is described. Major differences between the isotopic characteristics of Vancouver Island and those of the North American craton are considered.

6.2 ISOTOPIC COMPARISONS BETWEEN SAMPLE SUITES

Sicker Group volcanic rocks are generally more enriched in $^{207}\text{Pb}/^{204}\text{Pb}$ than rocks from the Jurassic volcanic and plutonic episode. If both these episodes are related to island arc formation, then the difference in isotopic composition may be explained by a difference in the provenance of the sediments involved in the subduction process. Higher $^{207}\text{Pb}/^{204}\text{Pb}$ ratios in the Sicker Group rocks suggest that continentally-derived, $^{207}\text{Pb}/^{204}\text{Pb}$-rich material was involved in their formation. The Sicker Group may have formed above a trench filled with sediment from an adjacent continent. Unfortunately there is little evidence to suggest where Wrangellia was during the Paleozoic, but faunal similarities have been found between the Early Permian fossils in the Sicker Group, and those of Australia, Timor and the Urals in Russia (Danner 1977).

Typical upper continental crustal sediments were not
involved in the formation of the Island Intrusions and Bonanza Group magmas (Chapter 4), suggesting that the Early Jurassic arc was intra-oceanic or cut off from continental detritus by a sediment trap.

The Catface Tertiary intrusions have lead isotope ratios which plot along the Sicker Group trend in $^{207}$Pb/$^{204}$Pb versus $^{206}$Pb/$^{204}$Pb diagrams. This similarity implies a similarity in the sources of these different rock units. If the Tertiary intrusions are related to subduction, as suggested in Chapter 5, the relatively high $^{207}$Pb/$^{204}$Pb ratios (higher than for the Island Intrusions) may be due to an abundance of craton-derived trench sediments. The uplift of the Rocky Mountains in the Late Jurassic to Early Tertiary may have allowed abundant continental detritus to reach the trench.

There is considerable overlap in the initial ratios of the Triassic Karmutsen Formation volcanic rocks with those of the Jurassic Island Intrusions and Bonanza Group volcanic rocks. Despite the apparent similarity between these two Mesozoic episodes, there are major isotopic differences in detail. Both display isotopic mixing, but the end-members are quite different. There is a shift from an enriched mantle (high $^{206}$Pb/$^{204}$Pb) source in the Triassic to a depleted (MORB-type) mantle in the Jurassic. The crustal component looks like average crust in the Triassic, but has the features of island arc-type
material in the Jurassic Island Intrusions and Bonanza Group volcanic rocks.

There are several possible explanations for these differences. If the crustal component in the Karmutsen basalts was introduced into the mantle source by shallow recycling of subducted sediments, the same crustal material may not have been available to the trench in the Jurassic. Allochthonous terranes were accreted to the margin of western North America during the period between the Triassic and Early Jurassic. Thus it is possible that isotopic differences between Triassic and Jurassic rocks reflect changes in paleogeography. If, however, the crustal component in the Karmutsen Formation is due to deep recycling, differences in paleogeography are irrelevant. Differences in the mantle sources of these two Mesozoic episodes then would be due to the heterogeneous nature of the mantle, and/or derivation of the magmas from different depths in a layered mantle.

6.3 VANCOUVER ISLAND AND THE DUPAL ANOMALY

The Dupal anomaly (Hart 1984) is a globe-encircling region from the equator to 60° south within which ocean islands and ocean ridges display $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios higher than their Northern Hemisphere counterparts. Lead isotope analyses of rocks from the Ninety-east Ridge are clearly
anomalous when compared to the Northern Hemisphere Reference Line (NHRL: Hart 1984). These rocks are now 40° further north than they were at the time they formed (approximately 85 Ma ago). Restoring them to their original position puts them within the present position of the Dupal anomaly, indicating that the anomaly has not changed position significantly—at least not in 85 Ma. Hart (1984) proposed that this region of anomalous mantle may have existed for more than three billion years, although its location, beyond 85 Ma, is open to question. If, however, the Dupal anomaly existed throughout the Mesozoic close to its present position in the Southern Hemisphere, there are important implications for Vancouver Island.

The isotopic composition of mantle that could have been involved in the generation of the Karmutsen Formation has been estimated in Chapter 3. This estimated composition falls close to the NHRL in Figure 6.1. Thus, there is no evidence of a Dupal anomaly in the mantle source for these rocks.

Paleomagnetic data show that the Karmutsen Formation formed at approximately 17° north or south of the equator (Yole and Irving 1980; Swartz et al. 1980; Hillhouse and Gromme 1984). If it formed at the southerly latitude, it would be expected to
Fig. 6.1 $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plot showing the Northern Hemisphere reference line (NHRL; Hart 1984), estimated mantle value for the Karmutsen Formation (K; Figure 3.9), and approximate composition of anomalous mantle (Dupal anomaly; Hart 1984).
display the enriched $^{207}\text{Pb}/^{204}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios characteristic of the Dupal anomaly in Southern Hemisphere mantle. Since this is not the case, the northerly latitude is favoured here for the origin of the Karmutsen Formation. Paleontological evidence based on ammonite zonation during the Mesozoic (Taylor et al. 1984) also favours the northern latitude.

6.4 INTERPRETATION OF GALENA LEAD ISOTOPE DATA

Galena lead isotope analyses from the ore deposits, discussed in earlier chapters, are shown on Figure 6.2, with four growth curves for reference. Also shown are the fields of whole rock initial ratios of the Island Intrusions and the Tertiary intrusions. These fields represent potential galena lead isotope ratios for mineralization related to these plutonic episodes. Sicker Group whole rock initial ratios are not shown because of the uncertainty involved in calculating these values for rocks which have undergone changes in the relative abundances of uranium, thorium and lead since their time of formation.

One of the original objectives of this study was to produce a growth curve model for the interpretation of galena lead
Figure 6.2 Vancouver Island galena lead isotope data shown with reference growth curves representing "North American" lead. These are the "shale" curve (Godwin and Sinclair 1982) and Bluebell curve (Andrew et al. 1984). Stacey and Kramers (1975) two-stage growth curve which represents average crustal lead growth and the mantle curve of Doe and Zartman (1979) are also shown. Fields of whole rock initial values are shown for the Jurassic Island Intrusions and the Tertiary Catface intrusions.
isotope ratios from ore deposits on Vancouver Island. The galena data, however, do not display a systematic change in ratios with age along a well-defined trend (Fig. 6.2), because Vancouver Island is made up of several different tectonic environments—each with its own isotopic characteristics produced by different combinations of various mantle and crustal lead types. Growth curve models work well where a particular environment has persisted for a long time, so that mineralization events occurring at different times have lead isotope ratios which change smoothly as a function of time. Since this is not the case for Vancouver Island a single growth curve model is inappropriate.

Galena lead isotope data from ore deposits of unknown age and origin can be interpreted in a general way by comparing them to the data from known deposits. This method is complicated by the fact that there is an area on the \( \frac{207\text{Pb}}{204\text{Pb}} \) versus \( \frac{206\text{Pb}}{204\text{Pb}} \) plot within which there are small differences in isotopic composition between ore deposits of widely different ages. This area occupies the range \( \frac{206\text{Pb}}{204\text{Pb}} = 18.5 \) to 18.8 and \( \frac{207\text{Pb}}{204\text{Pb}} = 15.55 \) to 15.60, and contains ore deposits of Paleozoic, Mesozoic and Tertiary age. Outside this area it is possible to identify Tertiary mineralization (\( \frac{206\text{Pb}}{204\text{Pb}} > 18.8 \)) from Paleozoic and Mesozoic mineralization (\( \frac{206\text{Pb}}{204\text{Pb}} < 18.5 \)).
Jurassic plutonic activity is isotopically distinct from the Tertiary plutons (Fig. 6.2b), so it is possible to distinguish between these mineralization ages for cases in which the mineralization is related to the plutons. Tertiary mineralization is characterized by higher $^{208}\text{Pb}/^{204}\text{Pb}$ (>38.25) than the Jurassic mineralization (<38.25).

Paleozoic mineralization can be identified by comparison with the Buttle Lake, Lenora and Tyee ore deposits and sample S457 (Chapter 2). These ratios ($^{206}\text{Pb}/^{204}\text{Pb}$ < 18.6 and $^{207}\text{Pb}/^{204}\text{Pb}$ > 15.56) can be distinguished from Jurassic mineralization that has a lower $^{207}\text{Pb}/^{204}\text{Pb}$ ratio, and Tertiary mineralization that has a greater $^{206}\text{Pb}/^{204}\text{Pb}$ ratio (Fig. 6.2). There is no clear separation between mineralization syngeneric with the Triassic Karmutsen Formation, and Sicker-related mineralization; although in general the Karmutsen mineralization has lower $^{207}\text{Pb}/^{204}\text{Pb}$ and greater $^{206}\text{Pb}/^{204}\text{Pb}$ ratios.

There is considerable overlap between the initial ratio fields for whole rock samples from the Karmutsen Formation (not shown in Fig. 6.2) with those of the Tertiary intrusions, the Island Intrusions and Bonanza Group volcanic rocks, and the Paleozoic galena samples. This means that Triassic
mineralization cannot be positively identified by lead isotopes alone.

6.5 VANCOUVER ISLAND VERSUS NORTH AMERICAN LEAD

6.5.1 North American lead

A model for the evolution of lead in the Selwyn shale basin was proposed by Godwin and Sinclair (1982). This three-stage lead isotope growth curve known as the 'shale' curve was found to be generally applicable to the miogeosynclinal part of the Canadian Cordillera for ore deposits of upper crustal origin (Andrew et al. 1984). A second curve known as the 'Bluebell' curve was developed to describe the evolution of a second lead reservoir, possibly the lower crust, which contributed lead to ore deposits in the southwestern part of the miogeosyncline. Many ore deposits in the Canadian Cordillera can be interpreted in terms of mixing of lead from the upper and lower crust (Andrew et al. 1984). Both of these North American lead isotope growth curves are shown in Figure 6.2.

6.5.2 Vancouver Island lead

The lead isotope characteristics of ore deposits from Vancouver Island are high $^{206}\text{Pb}/^{204}\text{Pb}$ and low $^{207}\text{Pb}/^{204}\text{Pb}$ relative to ore deposits occurring in the upper continental crust in cratonic North America. Figure 6.2 shows the field of
Vancouver Island ore deposits plotted with the upper continental crustal 'shale' curve (Godwin and Sinclair 1982) and the 'Bluebell' or lower crustal common lead growth curve (Andrew et al. 1984). The Vancouver Island field occupies an area which is higher in 206Pb/204Pb than a chord joining the two growth curves at 0 Ma. The same pattern of high 206Pb/204Pb and low 207Pb/204Pb relative to an ore lead growth curve was shown by Russell (1972) to be typical of oceanic lead. The lead characteristics of Vancouver Island are those of oceanic and arc volcanic lead--clearly different from cratonic lead.

Three distinct lead isotope provinces have been recognized in the Western United States (Zartman 1974). Vancouver Island lead falls into category III of Zartman (1974), having the same features of eugeosynclinal lead (207Pb/204Pb < 15.7, 206Pb/204Pb > 18.7), while the 'North American' lead described in the previous section falls into categories I and II. Thus, the boundaries between isotopic provinces can be traced northwards into Western Canada.

6.6 SUGGESTION FOR FURTHER WORK

The lead and strontium isotope signatures obtained for five
rock suites from Vancouver Island may be compared with those of other volcanic and plutonic rock suites which are thought to be related in some way. For example, Tipper and Richards (1976) proposed that during the Mesozoic, the Bonanza and Hazelton volcanic belts were continuous. If this was the case, isotopic similarities would be expected between these units; the hypothesis can be tested by analyzing Hazelton volcanic rocks for their lead isotope compositions.

Analyses of basalts of known age in allochthonous terranes in the Western Canadian Cordillera may reveal isotope signatures that do or do not display the Dupal anomalous mantle signature. In some instances this may help to decide the provenance of allochthonous terranes.

Major differences in isotopic characteristics between rocks and ores of the allochthonous terranes, and those within the North American craton, show that the edge of the ancient craton can be delineated using isotopic criteria. This has been done using the 0.706 initial strontium ratio (Armstrong 1979). Lead isotope data are another expression of this boundary (cf Ghosh 1986; Zartman 1974).
CHAPTER 7

CONCLUSIONS

Five suites of rocks from Vancouver Island have been characterized isotopically by using whole rock lead and strontium isotope systems. Paleozoic Sicker Group rocks have lead isotope ratios which cover the range $^{206}\text{Pb}/^{204}\text{Pb} = 18.5$ to $26.0$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.55$ to $16.00$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.0$ to $45.0$. Initial ratios indicated by galena from volcanogenic ore deposits at Buttle Lake, Mount Sicker, and Port Alberni occupy the range $^{206}\text{Pb}/^{204}\text{Pb} = 18.3$ to $18.6$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.55$ to $15.60$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.0$ to $38.2$. A small but significant difference in the isotopic ratios of galena samples from two ore horizons at Buttle Lake indicate a decrease in crustal component with time, supporting the hypothesis that the mine sequence developed during initiation of back-arc spreading.

Karmutsen Formation volcanic rocks have heterogeneous lead isotope ratios. Isotope mixing is apparent between two end-member compositions which are estimated at: 1) $^{206}\text{Pb}/^{204}\text{Pb} = 18.425$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.602$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.231$, and 2) $^{206}\text{Pb}/^{204}\text{Pb} = 18.833$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.523$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.884$. The former has the composition of average crust, whereas the latter
possibly represents ocean island basalt type mantle. Contamination of a mantle-derived magma by sedimentary material, which may have been introduced by subduction, is a possible explanation. The mantle source does not display the Dupal anomaly, supporting a Northern Hemisphere origin for these basalts.

Initial ratios for the Bonanza Group volcanic rocks and Island Intrusions at 190 Ma occupy the ranges $^{206}\text{Pb}/^{204}\text{Pb} = 18.3$ to $18.9$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.53$ to $15.59$, $^{208}\text{Pb}/^{204}\text{Pb} = 37.8$ to $38.3$, and $^{87}\text{Sr}/^{86}\text{Sr} = 0.703$ to $0.704$. The Bonanza volcanic rocks are less radiogenic than the Island Intrusions, but are colinear on $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plots indicating that they are comagmatic. Galena from the Jurassic Island Copper porphyry deposit plots with the whole rock initial ratios, showing that it formed during the same magmatic event. Isotopic mixing between a mantle source and a crustal source is partly attributed to assimilation of Sicker Group material by the Island Intrusions, but may be due to the subduction of island arc-type detritus. The linear array of initial ratios corresponds to a secondary isochron age of $1.37$ Ga, which agrees well with those of modern ocean islands. It is not possible to distinguish between an island arc and an ocean island origin for these rock suites, based on isotopic evidence alone.

Catface intrusions fall into two groups isotopically,
corresponding to an east and west geographical location. The East belt plutons occupy the ranges $^{206}\text{Pb}/^{204}\text{Pb} = 18.73$ to $18.75$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.58$ to $15.59$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.38$ to $38.40$. The West belt plutons are more radiogenic with: $^{206}\text{Pb}/^{204}\text{Pb} = 18.99$ to $19.09$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.60$ to $15.62$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.60$ to $38.66$. Strontium initial ratios are in the range 0.7038 to 0.7042, and are slightly more radiogenic in the East belt plutons than in the West belt. The apparent inverse relationship between lead and strontium isotope data is not easily explained. Galena from gold veins in the Zeballos mining camp has a similar isotopic composition to that of the pluton, which strongly suggests that the mineralization has its origin in the pluton.

Differences in the isotopic characteristics of each of the rock packages analyzed are due to the changing tectonic regimes that built Vancouver Island. A greater contribution of crustal lead in the Paleozoic Sicker Group rocks than in the Mesozoic rock suites is perhaps due to the nearness of Wrangellia to a continent in the Devonian. Triassic and Jurassic rock suites all indicate less involvement of crustal material and/or lack of a Dupal anomaly. Higher $^{207}\text{Pb}/^{204}\text{Pb}$ ratios in the Catface Tertiary intrusions indicate a return to greater crustal involvement.

It is inappropriate to apply a single growth curve model to describe lead isotope evolution on Vancouver Island. However, age
determinations can be made in a general way by comparing galena isotope data with the initial values of the various rock suites. Some ambiguities in this "fingerprinting" method occur because of the overlap of fields of initial values. Tertiary mineralization, however, can be distinguished clearly from Jurassic and Paleozoic mineralization.

The data base provided by this study can be used in comparing major rock suites from Vancouver Island to rock suites in other parts of Wrangellia, or in different terranes throughout the Cordillera and/or world. A major difference exists in isotopic features of rocks and ore deposits associated with the miogeosynclinal part of the Canadian Cordillera, and those of Vancouver Island. This difference may be general to the allochthonous terranes, allowing a boundary to be drawn which marks the edge of the North American craton.
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APPENDIX A

LABORATORY PROCEDURES FOR GALENA LEAD ISOTOPE ANALYSIS

A.1 GALENA LEAD SAMPLE PREPARATION

Galena crystals selected from rock or ore samples are stored in plastic vials. Approximately 10 mg of grains of clean galena are picked out, using a needle and a binocular microscope, and put into a disposable 10 ml polypropylene beaker.

A clean glass beaker (10 ml) and the sample are both covered in Parafilm. The sample container is weighed, then the contents emptied into the glass beaker and the container is reweighed. The weight of the sample indicates the amount of water that must be added to the lead chloride crystals prior to loading.

Approximately 8 ml 2N HCl is added to the sample in the glass beaker, which is then left overnight on a hotplate in a laminar air flow hood in front of a fume hood. The lead sulphide is converted to lead chloride with the production of hydrogen sulphide.

The dry PbCl₂ crystals are rinsed in 4N HCl three times, using a glass pipette to decant the excess liquid. Most of the impurities are readily dissolved in 4N HCl, but PbCl₂ is least soluble at this normality. Cleaned lead chloride crystals are dried by returning the beaker to the hotplate for a few minutes.

A solution containing 1 μg Pb per 2 μl aqueous solution is prepared by adding a calculated amount of quartz distilled water allowing for the loss of 30% of the sample due to non-dissolution of some of the galena and loss of lead chloride during rinsing.

A.2 PREPARATION AND LOADING OF FILAMENTS

Pre-cleaned rhenium ribbon 1.5 cm long is spot-welded to single filament posts. The filaments are transferred to the laminar air flow hood where they are mounted onto the filament holder six at a time, then rinsed with 2-bottle water, then 2-bottle acetone.

A micropipette with disposable tips is used to load 2 μl of sample onto each filament, using a new tip for each sample. Samples are dried at 1 Amp. 4 μl of silica gel-phosphoric acid solution is loaded on top of the dry sample. This is left to dry at 1.1 Amp, then the current is gradually increased until the load dissolves and reprecipitates. This process can be observed using the binocular microscope. When recrystallization is
complete, the current is slowly increased until white smoke is
given off and the load turns white. The current can then be
turned up to 2 Amps or higher to allow the load to glow gently
for a few seconds, then off. The entire loading procedure should
take about an hour if done properly.

Samples are loaded into the VG isomass 54R mass
spectrometer, six at a time, and analyzed using the measuring
program "UBCZPB" which is loaded into the HP85 mini computer.
Early galena runs (pre-1983) were occasionally analyzed using
"MSCOPB" which has a different peak measuring sequence. Both of
these programs are described in Appendix B. "UBCZPB" has been
updated by J. Gabites since the galena analyses included in this
thesis were obtained. The new program is called "UBCGPB". It has
the same peak measuring sequence as "UBCZPB" but automatically
converts the measured ratios to the more useful 206\text{Pb}/204\text{Pb},
207\text{Pb}/204\text{Pb} and 208\text{Pb}/204\text{Pb} ratios and corrects them for mass
fractionation.

Raw data were corrected for mass fractionation using mass
fractionation factors determined by repeated analyses of Broken
Hill Standard #1. For analyses obtained in 1983, these are given
in Tables A.1 and A.2. All others were analysed over the same
timespan as the whole rock samples, and were therefore corrected
in the same way as for whole rock isotope composition runs
(Appendix B).

The within-run precision for each analysis is added to the
fractionation variation between runs and the uncertainty in the
mass fractionation factors determined from the analyses of
Broken Hill Standard (Tables A.1, A.2, B.1, B.2 and Figs. A.1
and B.1), using the equation:
\[ s^2 = x^2 + y^2 + z^2 \]
where: \( s \) = standard deviation of one analysis, \( x \) = within-run
precision, \( y \) = fractionation uncertainty between runs, \( z \) =
uncertainty in mass fractionation factors.
TABLE A.1 Broken Hill standard measurements for the period January 1983 to March 1983.

<table>
<thead>
<tr>
<th>DATE</th>
<th>TEMPOC</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>09/01/83</td>
<td>1150</td>
<td>15.959(0.003)</td>
<td>15.318(0.003)</td>
<td>35.431(0.007)</td>
</tr>
<tr>
<td>17/01/83</td>
<td>1150</td>
<td>15.967(0.006)</td>
<td>15.322(0.005)</td>
<td>35.471(0.014)</td>
</tr>
<tr>
<td>23/01/83</td>
<td>1150</td>
<td>15.961(0.005)</td>
<td>15.326(0.005)</td>
<td>35.434(0.011)</td>
</tr>
<tr>
<td>02/02/83</td>
<td>1150</td>
<td>15.964(0.003)</td>
<td>15.323(0.002)</td>
<td>35.434(0.006)</td>
</tr>
<tr>
<td>03/02/83</td>
<td>1150</td>
<td>15.964(0.005)</td>
<td>15.323(0.008)</td>
<td>35.445(0.021)</td>
</tr>
<tr>
<td>25/02/83</td>
<td>1150</td>
<td>15.964(0.002)</td>
<td>15.324(0.002)</td>
<td>35.448(0.004)</td>
</tr>
<tr>
<td>25/02/83</td>
<td>1150</td>
<td>15.962(0.001)</td>
<td>15.321(0.001)</td>
<td>35.435(0.003)</td>
</tr>
</tbody>
</table>

MEAN VALUES (N=7)  15.963  15.322  35.443
STD. DEV. (S1) 0.002  0.002  0.013
MEAN WITHIN-RUN (S2) 0.004  0.004  0.009
FRACTIONATION VARIATION BETWEEN RUNS (S3) 0.000  0.000  0.009
WHERE S32 = S12 - S22

1. S3 cannot be negative. The fractionation variation between runs is considered to be negligible for the 206Pb/204Pb and 207Pb/204Pb ratios.
Table A.2. Calculation of mass fractionation factors using five published values of the Broken Hill Standard #1: 1983.

<table>
<thead>
<tr>
<th>REFERENCE</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Coopers et al. (1969)</td>
<td>16.003 (0.011)</td>
<td>15.390 (0.013)</td>
<td>35.660 (0.036)</td>
</tr>
<tr>
<td>2) Richards et al. (1981) best double-spiked</td>
<td>16.004 (0.006)</td>
<td>15.390 (0.007)</td>
<td>35.651 (0.017)</td>
</tr>
<tr>
<td>3) Richards et al. (1981) bias corrected</td>
<td>16.007 (0.012)</td>
<td>15.395 (0.010)</td>
<td>35.665 (0.046)</td>
</tr>
<tr>
<td>4) Richards and Blockley (1984) Canberra</td>
<td>16.003 (0.013)</td>
<td>15.386 (0.013)</td>
<td>35.640 (0.040)</td>
</tr>
<tr>
<td>5) Richards and Blockley (1984) Edmonton (Cumming)</td>
<td>16.005 (0.013)</td>
<td>15.387 (0.018)</td>
<td>35.651 (0.055)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MEAN PUBLISHED VALUE</th>
<th>16.004 (0.002)</th>
<th>15.390 (0.004)</th>
<th>35.653 (0.010)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEAN MEASURED VALUE (TABLE A.1)</td>
<td>15.963 (0.002)</td>
<td>15.322 (0.002)</td>
<td>35.443 (0.013)</td>
</tr>
</tbody>
</table>

| FRACTIONATION FACTORS¹ | 1.002593 | 1.004412 | 1.005937 |
| STD. DEV. | 0.000093 | 0.000204 | 0.000242 |

¹ These fractionation factors and uncertainties were used in the determination of fractionation corrected data and their uncertainties (see text). These are not perfectly mass dependent.
Figure A.1 Graphical representation of the determination of mass dependent fractionation factors using York (1969) least squares linear regression. For perfect mass dependent fractionation, the line must pass through the origin. The fractionation factors determined in Table A.2 do not fit the line well, so it was assumed that fractionation for this time period was not perfectly mass dependent. Therefore, fractionation factors determined in Table A.2 were used in data reduction, rather than the 0.139% per mass unit determined here.
A.3 REAGENT PREPARATION

A.3.1 Hydrochloric acid
Hydrochloric acid is diluted to 6N using distilled water, then is once distilled, using a one litre distillation flask. 2N, 4N, and 6N wash bottles are made up by diluting to the required strength with quartz distilled water.

A.3.2. Nitric Acid
Reagent grade nitric acid (18N) is diluted to 9N with distilled water and used directly for cleaning glassware.

A.3.3. Silica gel - phosphoric acid
A 1N solution of phosphoric acid is prepared using Ultrex ultrapure phosphorus pentoxide and 2-bottle water. Fumed silica is added to this and the mixture shaken then left in an ultrasonic bath for several hours. After leaving to settle for two days the supernate is decanted and kept in a clean teflon bottle. The rest is discarded.

A.3.4. Quartz distilled water (Q-water)
Distilled water is used as feed for the quartz distillation process.

A.3.5. Two-bottle water
Quartz distilled water is used as feed for the two-bottle (2B) sub-boiling distillation apparatus described in Mattinson (1971).

A.3.6. Rhenium ribbon
Zone refined rhenium ribbon (0.001" x 0.030") is obtained from The Rembar Company, 67 Main Street, Dobb's Ferry, New York. This is cut into strips 1.5 cm long and boiled in two-bottle 2N HCl, then rinsed in two-bottle H2O and dried under an infrared lamp in a clean air hood. See Appendix B for preparation of two-bottle distilled reagents.

A.3.7. Fumed Silica
Fumed silica was obtained from BDH Chemicals Ltd.
APPENDIX B

LAB PROCEDURES FOR ROCK LEAD, URANIUM AND THORIUM ISOTOPE ANALYSIS

B.1 SAMPLE PREPARATION

Rock samples are broken using a hydraulic rock-splitter until they are of a suitable size for crushing (7 to 8 cm diameter). As much of the outer surface as possible is discarded at this stage. The rock chips obtained after crushing with a jaw-crusher are cleaned using distilled 2N HCl in an ultrasonic bath. After rinsing three times with quartz-distilled water, the rock chips are dried under infrared lamps in a laminar flow hood.

Cleaned rock chips are ground using a tungsten carbide ring mill (5 minutes) until the powder does not feel gritty. The mill is cleaned between samples using distilled water and compressed air. The first two loads of rock powder are discarded, and third and subsequent loads of rock powder are saved for analysis.

B.2 SAMPLE DISSOLUTION

Approximately 0.6 g of each sample rock powder is accurately weighed into a 15 ml Savillex beaker (teflon). Suitable quantities of mixed spike 84-3 or thorium spike 84-2 are added for isotope dilution runs.

Samples are digested in 5 ml two-bottle distilled (2B) HF and 1ml concentrated 2B HNO₃ in covered beakers. The beakers are heated for at least three days on a hot plate at 50°C, then the lids are removed and the liquid allowed to evaporate. Concentrated 2B HNO₃ (2 ml) is added to dried sample residues and samples are again taken to dryness. Two to 3 ml 2N HCl are added to each beaker and evaporated down to a moist paste (Arden and Gale 1974). The HCl puts Pb and U into solution easily, but for Th analyses the residue has to be completely dissolved by several leachings with 6N HCl. Eight to 10 ml 1N HBr is then added to the nearly dry chlorides in preparation for anion exchange column separation of lead, uranium and thorium.

B.3 ANION EXCHANGE COLUMN PROCEDURES

Initial separation of lead, uranium and thorium is achieved using disposable anion exchange columns containing 4 ml clean
AG1X8 100-200 mesh resin (Kraus and Nelson 1958), and the column procedure described by Oversby (1975). Columns are cleaned using two column volumes (CV's) of quartz-distilled water, followed by two CV's of two-bottle (2B) 6N HCl and two CV's 2B H2O. Columns are prepared using two CV's 1N HBr, then the sample, in 1N HBr, is loaded. For isotope dilution (ID) runs the sample elute, containing U and Th, is saved. Three 2 ml aliquots then a further CV of 1N HBr are passed through and saved for further purification of U and Th (ID runs only) or discarded in the case of lead isotopic composition analysis (IC). Two 2 ml aliquots of 2N HCl are added and discarded, then lead is eluted from the column in one CV 6N HCl, into a small (5 ml) Savillex beaker.

After evaporation to dryness the lead sample is taken up in 2 ml HBr and passed through the same column procedure for a second time using smaller columns with a 1 ml resin bed. The sample, collected in 2 ml 6N HCl is evaporated to dryness and is then ready to be loaded onto a clean rhenium filament.

B.4 URANIUM AND THORIUM COLUMN PROCEDURE

Uranium and thorium are further cleaned using the column procedure of Tatsumoto (1966). The solution containing U and Th in HBr is evaporated to dryness and cooled completely. Concentrated 2B HNO3 is added to cover the bottom of the beaker and is warmed to destroy Br\(^-\). This process is repeated twice. Two to 3 ml 7N 2B HNO3 are added to dissolve the sample for loading onto the column.

Small anion exchange columns, containing 1 ml clean AG1X8 100-200 mesh resin, are cleaned as before, and then preconditioned with 2 CV's of 7N HNO3. The sample is loaded then rinsed with two small aliquots of 7N HNO3. Uranium and thorium are collected in one CV of 2B H2O followed by one CV of 2B 6N HCl. Further cleanup is achieved by redissolving the sample in 7N HNO3 and passing it through a clean column a second time following the same procedure.

B.5 PREPARATION AND LOADING OF FILAMENTS

B.5.1 Lead
Rhenium filaments are prepared and loaded following the procedure described under galena lead isotope analysis.

B.5.2 Uranium
Rhenium filaments are prepared, then baked out for 15 minutes at 3.2 Amps in a vacuum (2.0 x 10⁻⁵ torr). Tantalum
oxide is used to enhance ionization of the oxides. A drop of tantalum oxide is loaded onto each filament and allowed to dry at 1.0 Amp. A uranium sample is taken up in 0.1N HNO₃ and loaded on top of the tantalum oxide coating, using a clean pipette tip for each sample. When dry, a drop of 1N phosphoric acid (H₃PO₄) is loaded on top and the filament gradually heated to 2.0 amps. The final load should appear white after white fumes of H₃PO₄ have been given off.

B.5.3 Thorium

Thorium samples are loaded onto outgassed rhenium filaments using colloidal graphite to enhance metal ionization (Arden and Gale 1974). A drop of colloidal graphite is dried onto the filament at 1 amp, then the thorium sample is loaded in a drop of 1N HNO₃ and allowed to dry. A drop of phosphoric acid, followed by a second drop of colloidal graphite, are loaded on top. The filament is heated until white fumes of phosphoric acid are given off, but the filament should not reach red heat. The load should be black and matte.

An alternative, simpler and equally effective loading method is to take up the sample in 2B H₂O or 1N HNO₃ and dry it onto a baked out tantalum filament. Oxide peaks are then measured.

B.6 MASS SPECTROMETRIC PROCEDURES

All of the reported analyses were done in the Geochronology Laboratory at the Department of Geological Sciences, U.B.C., using a VG Isotopes Isomass 54R mass spectrometer linked to a HP-85 microcomputer.

B.6.1 Lead isotope composition

Lead samples are heated to 11500-12500°C and require frequent focusing for the first few blocks of data. The isotopic composition is measured using either "MSCOPB" OR "UBCZPB" programs. The former, used initially for galena analyses, measures ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb ratios directly in sets of five per block. Due to the uncertainty in measuring the ²⁰⁴Pb peak, it was found to be preferable to measure the ²⁰⁷Pb/²⁰⁶Pb, ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁴Pb/²⁰⁷Pb ratios using "UBCZPB". In this program the ²⁰⁴Pb/²⁰⁷Pb ratio is measured twice as often as the other two ratios, improving the statistics on the ratio.

Background counts are measured at mass 206.5 at the beginning of each block three times, and before and after the first two sets of five ratios. The background is measured at mass 204.5 before and after the ²⁰⁷Pb/²⁰⁴Pb ratio.
Raw data is converted to the $\text{Pb}^{206}/\text{Pb}^{204}$, $\text{Pb}^{207}/\text{Pb}^{204}$ and $\text{Pb}^{206}/\text{Pb}^{204}$ ratios, then normalized to absolute values using correction factors determined by repeated analyses of the Broken Hill Standard (Tables B.1 and B.2). Each analysis is reported with an associated error based on a combination of the fractionation variation between runs, the uncertainty in mass fractionation factors (Table B.2; Fig. B.1), and within-run precision. The conversion of raw data, normalization and combination of errors is done using the program "WRPBIC" (Appendix D).

**B.6.2 Lead isotope dilution**

Isotope dilution runs are measured using "UBCOPB". This program measures the $\text{Pb}^{208}/\text{Pb}^{207}$ and $\text{Pb}^{206}/\text{Pb}^{208}$ ratios. Background measurements are made at 206.5 before and after each set of five ratios. The data are corrected for mass fractionation, then used to calculate lead concentrations using the following equation:

$$208\text{Pb} \mu\text{moles} = \text{wt.} 84-3 \times 207\text{Pb}84-3 \times A$$

$$A = (1 - \frac{208\text{Pb}/204\text{Pb}84-3 \times 207\text{Pb}/208\text{Pb}^{\text{I.D.}}}{207\text{Pb}/208\text{Pb}^{\text{I.D.}} - 207\text{Pb}/208\text{Pb}^{\text{I.C.}}})$$

where: $208\text{Pb} \mu\text{moles} = \mu\text{moles} 208\text{Pb} \text{ in the sample}$,
$207\text{Pb}84-3 = \mu\text{moles/g} 207\text{Pb} \text{ in the spike 84-3}$,
$208\text{Pb}/207\text{Pb}84-3$ is the ratio in the spike 84-3,
$207\text{Pb}^{\text{I.D.}}/208\text{Pb}^{\text{I.D.}}$ is the ratio in the ID run,
$207\text{Pb}/208\text{Pb}^{\text{I.C.}}$ is the ratio in the sample, and
$\text{wt.} 84-3 = \text{weight of 84-3 used in the ID run}$.

Total lead is found by dividing the number of moles of $208\text{Pb}$ by the fraction of $208\text{Pb}$ determined from the IC run (atomic proportions and the atomic weight of the sample are calculated from the IC data in the conventional way). The result is divided by the weight of the sample and multiplied by the atomic weight of the sample lead to give the lead concentration in ppm. This can be checked using a similar equation which uses the $206\text{Pb}/207\text{Pb}$ ratios for the IC and ID runs and the $207\text{Pb}/206\text{Pb}$ ratio of the 84-3 spike. The preparation, isotopic composition, and lead concentration of mixed spike 84-3 are given in Appendix C.

For lead concentrations less than 1.3 ppm the isotopic composition is adjusted for blank lead of measured composition (n=2):

$$206\text{Pb}/204\text{Pb} = 18.329 \pm 0.010$$
$$207\text{Pb}/204\text{Pb} = 15.619 \pm 0.011$$

<table>
<thead>
<tr>
<th>DATE</th>
<th>TEMPOC</th>
<th>206pb/204pb</th>
<th>207pb/204pb</th>
<th>208pb/204pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>18/12/83</td>
<td>1150</td>
<td>15.961(0.002)</td>
<td>15.323(0.002)</td>
<td>35.467(0.005)</td>
</tr>
<tr>
<td>18/12/83</td>
<td>1150</td>
<td>15.958(0.002)</td>
<td>15.318(0.001)</td>
<td>35.438(0.005)</td>
</tr>
<tr>
<td>23/12/83</td>
<td>1200</td>
<td>15.954(0.001)</td>
<td>15.295(0.001)</td>
<td>35.371(0.004)</td>
</tr>
<tr>
<td>09/01/84</td>
<td>1150</td>
<td>15.950(0.002)</td>
<td>15.307(0.002)</td>
<td>35.400(0.005)</td>
</tr>
<tr>
<td>02/02/84</td>
<td>1100</td>
<td>15.957(0.001)</td>
<td>15.321(0.001)</td>
<td>35.442(0.003)</td>
</tr>
<tr>
<td>20/02/84</td>
<td>1140</td>
<td>15.955(0.003)</td>
<td>15.314(0.003)</td>
<td>35.423(0.006)</td>
</tr>
<tr>
<td>24/02/84</td>
<td>1150</td>
<td>15.961(0.003)</td>
<td>15.320(0.003)</td>
<td>35.435(0.006)</td>
</tr>
<tr>
<td>02/03/84</td>
<td>1150</td>
<td>15.952(0.034)</td>
<td>15.320(0.033)</td>
<td>35.436(0.076)</td>
</tr>
<tr>
<td>02/03/84</td>
<td>1150</td>
<td>15.959(0.008)</td>
<td>15.323(0.008)</td>
<td>35.453(0.018)</td>
</tr>
<tr>
<td>16/03/84</td>
<td>1150</td>
<td>15.950(0.002)</td>
<td>15.313(0.002)</td>
<td>35.414(0.005)</td>
</tr>
<tr>
<td>22/03/84</td>
<td>1150</td>
<td>15.960(0.002)</td>
<td>15.314(0.001)</td>
<td>35.429(0.005)</td>
</tr>
<tr>
<td>29/03/84</td>
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<td>15.972(0.003)</td>
<td>15.319(0.001)</td>
<td>35.447(0.006)</td>
</tr>
<tr>
<td>02/04/84</td>
<td>1150</td>
<td>15.970(0.001)</td>
<td>15.320(0.001)</td>
<td>35.455(0.003)</td>
</tr>
<tr>
<td>17/04/84</td>
<td>1150</td>
<td>15.945(0.007)</td>
<td>15.299(0.007)</td>
<td>35.367(0.016)</td>
</tr>
<tr>
<td>30/05/84</td>
<td>1150</td>
<td>15.950(0.002)</td>
<td>15.308(0.002)</td>
<td>35.398(0.005)</td>
</tr>
<tr>
<td>31/05/84</td>
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<td>15.951(0.001)</td>
<td>15.311(0.001)</td>
<td>35.412(0.003)</td>
</tr>
<tr>
<td>29/06/84</td>
<td>1150</td>
<td>15.958(0.004)</td>
<td>15.321(0.003)</td>
<td>35.442(0.009)</td>
</tr>
<tr>
<td>29/06/84</td>
<td>1150</td>
<td>15.958(0.002)</td>
<td>15.320(0.002)</td>
<td>35.441(0.005)</td>
</tr>
<tr>
<td>14/08/84</td>
<td>1150</td>
<td>15.950(0.004)</td>
<td>15.313(0.003)</td>
<td>35.416(0.009)</td>
</tr>
<tr>
<td>16/08/84</td>
<td>1150</td>
<td>15.959(0.004)</td>
<td>15.319(0.003)</td>
<td>35.440(0.010)</td>
</tr>
<tr>
<td>16/08/84</td>
<td>1150</td>
<td>15.945(0.006)</td>
<td>15.304(0.005)</td>
<td>35.383(0.019)</td>
</tr>
<tr>
<td>28/10/84</td>
<td>1150</td>
<td>15.953(0.004)</td>
<td>15.307(0.002)</td>
<td>35.422(0.013)</td>
</tr>
<tr>
<td>14/12/84</td>
<td>1150</td>
<td>15.948(0.010)</td>
<td>15.310(0.009)</td>
<td>35.387(0.019)</td>
</tr>
<tr>
<td>15/01/85</td>
<td>1150</td>
<td>15.963(0.005)</td>
<td>15.323(0.004)</td>
<td>35.446(0.013)</td>
</tr>
<tr>
<td>26/01/85</td>
<td>1150</td>
<td>15.949(0.002)</td>
<td>15.310(0.002)</td>
<td>35.407(0.006)</td>
</tr>
</tbody>
</table>

**MEAN VALUES (N=25)**
- 15.955
- 15.314
- 35.423

**STD. DEV. (S1)**
- 0.007
- 0.008
- 0.027

**WEIGHTED MEAN**

**WITHIN-RUN (S2)**
- 0.004
- 0.004
- 0.010

**FRACTIONATION VARIATION BETWEEN RUNS (S3)**
- 0.006
- 0.007
- 0.025

**WHERE S3^2 = S1^2 - S2^2**

<table>
<thead>
<tr>
<th>REFERENCE</th>
<th>206Pb/204Pb</th>
<th>207Pb/204Pb</th>
<th>208Pb/204Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Coopers et al. (1969)</td>
<td>16.003 (0.011)</td>
<td>15.390 (0.013)</td>
<td>35.660 (0.036)</td>
</tr>
<tr>
<td>2) Richards (1981)</td>
<td>16.004 (0.006)</td>
<td>15.390 (0.007)</td>
<td>35.651 (0.017)</td>
</tr>
<tr>
<td>3) Richards (1981) bias corrected</td>
<td>16.007 (0.012)</td>
<td>15.395 (0.010)</td>
<td>35.665 (0.046)</td>
</tr>
<tr>
<td>4) Richards and Blockley (1984)</td>
<td>16.003 (0.013)</td>
<td>15.386 (0.013)</td>
<td>35.640 (0.040)</td>
</tr>
<tr>
<td>5) Richards and Blockley (1984) Edmonton (Cumming)</td>
<td>16.005 (0.013)</td>
<td>15.387 (0.018)</td>
<td>35.651 (0.055)</td>
</tr>
</tbody>
</table>

MEAN PUBLISHED VALUE | 16.004 (0.002) | 15.390 (0.004) | 35.653 (0.010) |

MEAN MEASURED VALUE | 15.955 (0.007) | 15.314 (0.008) | 35.423 (0.027) |

FRACTIONATION FACTORS¹ | 1.003096 | 1.004937 | 1.006503 |
STD. DEV. | 0.000105 | 0.000229 | 0.000271 |

¹. Graphical representation of these fractionation factors (Fig. B.1) suggests that they are mass dependent. Assuming perfect mass dependence, the fractionation factor is 0.159 ± 0.004% per mass unit (see Fig. B.1). Fractionation factors used in calculations were 1.0032 ± 0.0002, 1.0048 ± 0.0003, and 1.0064 ± 0.0004 for the 206Pb/204Pb, 207Pb/204Pb and 208Pb/204Pb ratios respectively.
Figure B.1 Graphical representation of the determination of mass dependent fractionation factors, using York (1969) least squares linear regression. For perfect mass dependent fractionation, the line must pass through the origin. The fractionation factors determined in Table B.2 fit the line well, so it was assumed that fractionation for this time period was mass dependent. The 0.16% per mass unit fractionation factor determined here was used in data reduction.
\[ \frac{208\text{pb}}{204\text{pb}} = 38.065 \pm 0.011 \]

The uncertainty in the analysis is then adjusted to include the uncertainties in the amount of lead subtracted and in the composition of the blank lead, using the program "BLANKSUB" (Appendix D).

**B.6.3 Uranium isotope dilution**

Uranium is measured at 1300–1400°C using the program "UBCU" which measures the ratio of the uranium oxide peaks. A mass fractionation factor of 0.006% per mass unit, based on repeated measurements of NBS U500 equal atom uranium standard (Table B.3) is applied to the measured ratios. Uranium concentrations are calculated using the equation:

\[
238\text{U}_\text{umoles} = 235\text{U}_\text{umoles} \times \text{wt. 84-3} \left[ \frac{238\text{U}/235\text{U}_{84-3} - 238\text{U}/235\text{U}_\text{I.D.}}{238\text{U}/235\text{U}_\text{I.D.} \times 1/137.88 - 1} \right]
\]

Where: 238\text{U}_\text{umoles} = \text{umoles 238U in the sample,}  
235\text{U}_\text{umoles} = \text{umoles/g 235U in the spike (Appendix C),}  
wt. 84-3 = \text{weight in grams of the 84-3 mixed spike,}  
238\text{U}/235\text{U}_{84-3} = \text{ratio in the spike (Appendix C),}  
238\text{U}/235\text{U}_\text{I.D.} = \text{ratio in the isotope dilution run, and}  
1/137.88 = 235\text{U}/238\text{U} in natural samples.

**B.6.4 Thorium isotope dilution**

Thorium isotopes are measured as metal ions in the case of colloidal graphite loading, or as oxides for tantalum filaments, at 1800°C or more, using the program "UBCTH". Mass fractionation was not determined for thorium because no thorium standard was available. However, it can be assumed to be quite small if similar to the fractionation factor for uranium (Table B.3). Thorium concentrations are then given by the equation:

\[
\text{Th \ umoles/g} = 232\text{Th}_{84-2} \times \text{wt.84-2} \left[ \frac{230\text{Th}/232\text{Th}_{84-2} - 230\text{Th}/232\text{Th}_\text{I.D.}}{230\text{Th}/232\text{Th}_\text{I.D.} \times \text{wt. sample}} \right]
\]

Where:  
230\text{Th}/232\text{Th}_{84-2} = \text{ratio in spike 84-2 (Appendix C),}  
232\text{Th}_{84-2} = \text{umoles/g 232Th in spike (Appendix C),}  
230\text{Th}/232\text{Th}_\text{I.D.} = \text{ratio in isotope dilution run,}  
wt.84-2 = \text{weight of added spike in grams.}

In many runs of natural rock samples, the relative sizes of the thorium isotope peaks changed with time. The 232\text{Th} peak decreased to background level within a few blocks and the 230\text{Th} peak increased dramatically. This instability indicates that there are interfering ions, since it is not possible for a
TABLE B.3 Mass fractionation factor for uranium determined by analyses of the U500 NBS standard (zircon laboratory, UBC). The results were compared to the certified values as follows:

<table>
<thead>
<tr>
<th>DATE</th>
<th>235U/238U</th>
</tr>
</thead>
<tbody>
<tr>
<td>02/02/84</td>
<td>1.000048 (0.000051)</td>
</tr>
<tr>
<td>02/02/84</td>
<td>0.999649 (0.000439)</td>
</tr>
<tr>
<td>01/14/85</td>
<td>1.000126 (0.001433)</td>
</tr>
</tbody>
</table>

Mean (n=3) 0.999941 (0.000148)

Certified Value 0.999698 (0.00199)

Mass fractionation factor = 1.000243 or 0.006% per mass unit
single element to display this type of behaviour. The ions involved were not identified, but the problem may be eliminated by using a more rigorous column separation for thorium. The problem did not arise in measurements of the spike alone.
B.7 REAGENT PREPARATION

B.7.1 Quartz-distilled water
Distilled water from the geochemistry laboratory, room 311, Department of Geological Sciences, U.B.C., is further distilled using a quartz still in the Geochronology laboratory, Department of Geological Sciences, U.B.C.

B.7.2 Two-bottle water
A two-bottle still of the type described by Mattinson (1971) is used to produce ultrapure water using the quartz-water as feed.

B.7.3 Hydrochloric acid
Reagent grade hydrochloric acid is diluted to 6N (1:1) with distilled water. This is then distilled once using a quartz still. The distillate is diluted as required for galena analyses, and used as feed for the sub-boiling still (Mattinson 1971) for whole rock lead analysis. The two-bottle 6N HCl is diluted to 2N HCl using two-bottle water, for use in anion exchange column separations.

B.7.4 Nitric acid
Reagent grade nitric acid is distilled once, at full strength, using a conventional still. Once distilled nitric acid is used in washing procedures diluted 1:1 with distilled water. Ultrapure nitric acid is produced by the two-bottle sub-boiling distillation of once distilled nitric acid. Two-bottle 7N nitric acid is obtained by diluting two-bottle concentrated nitric acid with two-bottle water.

B.7.5 Hydrobromic acid
Reagent grade hydrobromic acid (approximately 9N) is distilled using the two-bottle sub-boiling apparatus (Mattinson 1971). The distillate is then diluted to 1N using two-bottle water.

B.7.6 Hydrofluoric acid
Reagent grade hydrofluoric acid is distilled using the two-bottle sub-boiling still (Mattinson 1971).

B.7.7 Silica gel - phosphoric acid
A 1M solution of phosphoric acid was prepared in a clean teflon bottle using ultrex phosphorus pentoxide, and two-bottle water. Fumed silica (BDH Chemicals Ltd., Toronto) was added to the solution and shaken for several minutes. The solution was further shaken ultrasonically for an hour. The mixture was left to stand for 24 hours, then the supernatent colloidal solution was decanted into a clean teflon bottle for use in the loading procedure.
B.7.8 Colloidal graphite

Aquadag colloidal graphite was provided by Dr. Hooley, Department of Chemistry, the University of British Columbia.

B.8 MEASUREMENT OF BLANKS

Lead is a pervasive contaminant, so it is essential to assess the contribution of blank lead to the analyses by measuring the content of lead in each of the reagents, the dissolution process, the column procedures and finally in the loading process. Total procedural blanks are routinely measured by adding a known amount of a spike solution to a beaker and treating it in the same way as a sample. The change in the isotopic composition of the spike lead is then proportional to the amount of contaminant or blank lead in the process. This can be accurately measured using the isotope dilution equation and the isotopic composition of the blank lead (see page 203). Total blanks are listed in Table B.4.

Reagent blanks were measured by adding spike lead to two different volumes of each reagent. A graph was then drawn for each. The slope of the line gives the concentration of blank lead per ml, and the intercept should be the loading plus handling blank. Using this technique (Patterson in press) the reagent blanks were measured (Table B.5). An assessment of the contribution of reagent and other blanks to the total blank is made in Table B.6. It was found that the reagents, HBr in particular, provide a large proportion of lead to the total blank, so a reduction in the quantity of reagents used would significantly reduce the blank.

Blanks were not determined for uranium and thorium isotope dilution runs. Several attempts were made to measure the total procedural uranium blank, but in each case the $^{238}\text{U}$ peak was not found. This indicates that the blank levels are insignificant.
### TABLE B.4 Total procedural blanks for 1983 to 1985

<table>
<thead>
<tr>
<th>DATE</th>
<th>BEAKER TYPE</th>
<th>SAMPLE SIZE</th>
<th>BLANK (ng)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28/09/83</td>
<td>30ml teflon</td>
<td>1.0g</td>
<td>24.0a</td>
</tr>
<tr>
<td>11/10/83</td>
<td>30ml teflon</td>
<td>1.0g</td>
<td>22.7a</td>
</tr>
<tr>
<td>03/11/83</td>
<td>30ml teflon</td>
<td>1.0g</td>
<td>48.0a</td>
</tr>
<tr>
<td>27/11/83</td>
<td>30ml teflon</td>
<td>1.0g</td>
<td>8.3</td>
</tr>
<tr>
<td>17/02/84</td>
<td>15ml savillex</td>
<td>0.6g</td>
<td>7.7</td>
</tr>
<tr>
<td>19/03/84</td>
<td>15ml savillex</td>
<td>0.6g</td>
<td>7.7</td>
</tr>
<tr>
<td>17/04/84</td>
<td>15ml savillex</td>
<td>0.6g</td>
<td>8.2</td>
</tr>
<tr>
<td>24/05/84</td>
<td>15ml savillex</td>
<td>0.6g</td>
<td>21.5b</td>
</tr>
<tr>
<td>30/05/84</td>
<td>15ml savillex</td>
<td>0.6g</td>
<td>10.4b</td>
</tr>
<tr>
<td>11/07/84</td>
<td>15ml savillex</td>
<td>0.6g</td>
<td>4.5</td>
</tr>
<tr>
<td>11/07/84</td>
<td>15ml savillex</td>
<td>0.6g</td>
<td>8.1</td>
</tr>
<tr>
<td>10/01/85</td>
<td>15ml savillex</td>
<td>0.6g</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Maximum and minimum blanks for various part processes:
- Loading blank (n=8): 0.069-0.386ng
- Beaker blanks (includes loading, n=7): 0.127-0.350ng
- Dissolution blank (n=1): 0.755ng
- Large column blank (n=4): 7.6-9.3ng
- Small column blank (n=2): 2.8-9.8ng

---

a. These high, variable blanks were the result of a hole in the filter of the clean air hood.

b. High blanks were measured after an unfortunate accident with the clean air hood. No samples were measured at this time.
### TABLE B.5 Reagent blanks for 1983 to 1985

<table>
<thead>
<tr>
<th>DATE</th>
<th>REAGENT</th>
<th>BLANK(^1)</th>
<th>SLOPE(^2)</th>
<th>INTERCEPT(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nov 83</td>
<td>2B H2O</td>
<td>0.043 ng/ml</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jan 84</td>
<td>2B H2O</td>
<td>0.045 ng/ml</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jan 85</td>
<td>2B H2O</td>
<td>0.017 ng/ml</td>
<td>0.005 ng/ml</td>
<td>0.292 ng</td>
</tr>
<tr>
<td>Nov 83</td>
<td>Q H2O</td>
<td>0.107 ng/ml</td>
<td>0.066 ng/ml</td>
<td>0.197 ng</td>
</tr>
<tr>
<td>Nov 85</td>
<td>HF</td>
<td>0.074 ng/ml</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mar 84</td>
<td>HF</td>
<td>0.085 ng/ml</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nov 83</td>
<td>conc. HNO(_3)</td>
<td>0.045 ng/ml</td>
<td></td>
<td>0.027 ng/ml 0.465 ng</td>
</tr>
<tr>
<td>Feb 84</td>
<td>conc. HNO(_3)</td>
<td>0.105 ng/ml</td>
<td></td>
<td>0.065 ng/ml 0.438 ng</td>
</tr>
<tr>
<td>Jan 85</td>
<td>conc. HNO(_3)</td>
<td>0.147 ng/ml</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nov 83</td>
<td>6N HCl</td>
<td>0.019 ng/ml</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mar 84</td>
<td>6N HCl</td>
<td>0.054 ng/ml</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jan 85</td>
<td>6N HCl</td>
<td>0.037 ng/ml</td>
<td>0.029 ng/ml</td>
<td>0.178 ng</td>
</tr>
<tr>
<td>Nov 83</td>
<td>1N HBr</td>
<td>0.104 ng/ml</td>
<td>0.058 ng/ml</td>
<td>0.459 ng</td>
</tr>
<tr>
<td>Mar 84</td>
<td>1N HBr</td>
<td>0.158 ng/ml</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jan 85</td>
<td>1N HBr</td>
<td>0.100 ng/ml</td>
<td>0.088 ng/ml</td>
<td>0.476 ng</td>
</tr>
<tr>
<td>Mar 84</td>
<td>2N HCl</td>
<td>0.145 ng/ml</td>
<td>0.077 ng/ml</td>
<td>0.544 ng</td>
</tr>
<tr>
<td>Jan 85</td>
<td>2N HCl</td>
<td>0.130 ng/ml</td>
<td>0.038 ng/ml</td>
<td>2.291 ng</td>
</tr>
</tbody>
</table>

1. Blank is calculated by dividing the blank by the volume of reagent on which the blank was determined. Where two volumes were determined, the blank quoted is for the larger volume.
2. This column is for blanks which have been determined by measuring blank levels in two different volumes of reagent. The blank is then found by dividing the difference in blank values by the difference in volume.
3. The blank value in this column should be approximately constant for different reagents, and should represent the blank due to sample loading and handling.
TABLE B.6 Summation of blanks measured from 1983 to 1985

<table>
<thead>
<tr>
<th></th>
<th>Summation of blanks measured from 1983 to 1985</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DISSOLUTION:</strong></td>
<td></td>
</tr>
<tr>
<td>1 Beaker (10 ml)</td>
<td>0.127 ng/ml</td>
</tr>
<tr>
<td>2B HF 5 ml @ 0.027 ng/ml</td>
<td>0.135 ng/ml</td>
</tr>
<tr>
<td>2B conc. HNO3 3 ml @ 0.147 ng/ml</td>
<td>0.441 ng/ml</td>
</tr>
<tr>
<td><strong>LARGE COLUMN:</strong></td>
<td></td>
</tr>
<tr>
<td>2B 2N HCl 3 ml @ 0.130 ng/ml</td>
<td>0.390 ng/ml</td>
</tr>
<tr>
<td>2B 1N HBr 25 ml @ 0.088 ng/ml</td>
<td>2.200 ng/ml</td>
</tr>
<tr>
<td>2B 6N HCl 8 ml @ 0.029 ng/ml</td>
<td>0.232 ng/ml</td>
</tr>
<tr>
<td><strong>SMALL COLUMN:</strong></td>
<td></td>
</tr>
<tr>
<td>2B 1N HBr 10 ml @ 0.088 ng/ml</td>
<td>0.880 ng/ml</td>
</tr>
<tr>
<td>2B 2N HCl 1 ml @ 0.130 ng/ml</td>
<td>0.130 ng/ml</td>
</tr>
<tr>
<td>2B 6N HCl 4 ml @ 0.029 ng/ml</td>
<td>0.116 ng/ml</td>
</tr>
<tr>
<td>Small beaker (5 ml)</td>
<td>0.127 ng/ml</td>
</tr>
<tr>
<td><strong>LOADING:</strong></td>
<td></td>
</tr>
<tr>
<td>Total loading procedure</td>
<td>0.070 ng/ml</td>
</tr>
</tbody>
</table>

Sum of blanks as above = 4.721 ng
Total blank measured = 4.3 ng (for Jan. 1985)

Most of the measured blank can be accounted for by the reagents. Decreasing the quantities of reagents used would significantly reduce the total blank.
B.9 DATA QUALITY

B.9.1 Lead isotope composition

Within-run mass-spectrometer precision is usually better than 0.03%. Reproducibility (1 sigma) of the Broken Hill Galena Standard (Table B.1) is 0.025% for the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio, 0.052% for the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio and 0.090% for the $^{208}\text{Pb}/^{204}\text{Pb}$ ratio based on 25 analyses of the standard over the period during which all of the rock lead analyses were done. Uncertainty in mass fractionation is added to the measured within-run precision for each analysis by the process of error propagation (Rees 1984).

Duplicate analyses of sample powders for ten rocks (Tables B.7, B.8 and B.9) indicate that the one sigma error in each of the ratios is as follows:

- $^{206}\text{Pb}/^{204}\text{Pb} = 0.14\%$
- $^{207}\text{Pb}/^{204}\text{Pb} = 0.08\%$, and
- $^{208}\text{Pb}/^{204}\text{Pb} = 0.06\%$.

This is comparable to the propagated errors based on mass spectrometry and mass fractionation errors alone. It includes sample inhomogeneity and/or dissolution differences between samples.

Geological sampling error was assessed by comparing results for three rocks from different locations within the same homogeneous rhyolite dome (samples R78, R90 and R91), and two rocks (L/T1 and L/T4) from the same diorite sheet (Table B.10). Approximate error limits were determined as follows:

- $^{206}\text{Pb}/^{204}\text{Pb} = 0.22\%$
- $^{207}\text{Pb}/^{204}\text{Pb} = 0.08\%$, and
- $^{208}\text{Pb}/^{204}\text{Pb} = 0.15\%$.

This includes all possible sources of error.

Accuracy was assessed by analyzing BCR-1 rock standard and comparing the results to those of Tatsumoto et al. (1972). Results (Table B.11) are 0.10% to 0.15% higher than the standard value.

B.9.2 Lead concentration

Lead concentrations are precise to ± 0.1 ppm or 3% based on six duplicate analyses (Table B.12). Propagation of errors using "WRPBID" predicts a precision of 0.3% based on uncertainties in spike concentration and composition, weighing errors, mass spectrometry and mass fractionation. Weighing errors and the uncertainty in the concentration of lead in the spike are the major contributing factors to the overall uncertainty in lead concentrations. The difference in uncertainties calculated from duplicate analyses, and predicted
TABLE B.7  Uncertainty in 206Pb/204Pb Ratios

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>NO. 1</th>
<th>NO. 2</th>
<th>1-2</th>
<th>(1-2)^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H10A</td>
<td>19.626</td>
<td>19.639</td>
<td>-0.013</td>
<td>0.000169</td>
</tr>
<tr>
<td>W149</td>
<td>18.756</td>
<td>18.748</td>
<td>0.008</td>
<td>0.000064</td>
</tr>
<tr>
<td>GRHY</td>
<td>19.351</td>
<td>19.412</td>
<td>-0.061</td>
<td>0.003721</td>
</tr>
<tr>
<td>R78</td>
<td>19.561</td>
<td>19.519</td>
<td>0.042</td>
<td>0.001764</td>
</tr>
<tr>
<td>R91</td>
<td>19.430</td>
<td>19.444</td>
<td>-0.014</td>
<td>0.000196</td>
</tr>
<tr>
<td>K005</td>
<td>19.183</td>
<td>19.224</td>
<td>-0.041</td>
<td>0.001681</td>
</tr>
<tr>
<td>KAR2</td>
<td>19.000</td>
<td>18.998</td>
<td>0.002</td>
<td>0.000004</td>
</tr>
<tr>
<td>KAR7</td>
<td>19.397</td>
<td>19.416</td>
<td>-0.019</td>
<td>0.000361</td>
</tr>
<tr>
<td>KAR10</td>
<td>18.715</td>
<td>18.728</td>
<td>-0.013</td>
<td>0.000169</td>
</tr>
<tr>
<td>KAR11</td>
<td>18.999</td>
<td>18.928</td>
<td>0.071</td>
<td>0.005041</td>
</tr>
</tbody>
</table>

TOTAL = 0.013170

S2 = (0.013170)/(2(N-1))

S = 0.027 (0.14%)
### TABLE B.8  Uncertainty in $^{207}\text{Pb}/^{204}\text{Pb}$ ratios

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>NO. 1</th>
<th>NO. 2</th>
<th>1-2</th>
<th>(1-2)$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H10A</td>
<td>15.644</td>
<td>15.643</td>
<td>0.001</td>
<td>0.000001</td>
</tr>
<tr>
<td>W149</td>
<td>15.571</td>
<td>15.566</td>
<td>0.005</td>
<td>0.000025</td>
</tr>
<tr>
<td>GRHY</td>
<td>15.630</td>
<td>15.635</td>
<td>-0.005</td>
<td>0.000025</td>
</tr>
<tr>
<td>R78</td>
<td>15.596</td>
<td>15.644</td>
<td>-0.048</td>
<td>0.002304</td>
</tr>
<tr>
<td>R91</td>
<td>15.602</td>
<td>15.630</td>
<td>-0.018</td>
<td>0.000324</td>
</tr>
<tr>
<td>K005</td>
<td>15.605</td>
<td>15.618</td>
<td>-0.013</td>
<td>0.000169</td>
</tr>
<tr>
<td>KAR2</td>
<td>15.599</td>
<td>15.596</td>
<td>0.003</td>
<td>0.000009</td>
</tr>
<tr>
<td>KAR7</td>
<td>15.592</td>
<td>15.587</td>
<td>0.005</td>
<td>0.000025</td>
</tr>
<tr>
<td>KAR10</td>
<td>15.551</td>
<td>15.563</td>
<td>-0.012</td>
<td>0.000144</td>
</tr>
<tr>
<td>KAR11</td>
<td>15.583</td>
<td>15.588</td>
<td>-0.005</td>
<td>0.000025</td>
</tr>
</tbody>
</table>

\[ \text{TOTAL} = 0.003051 \]

\[ S^2 = \frac{0.003051}{2(N-1)} \]

\[ S = 0.013 \ (0.08\%) \]
TABLE B.9: Uncertainty in $^{208}$Pb/$^{204}$Pb ratios

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>NO. 1</th>
<th>NO. 2</th>
<th>1-2</th>
<th>(1-2)$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H10A</td>
<td>38.933</td>
<td>38.937</td>
<td>-0.004</td>
<td>0.000016</td>
</tr>
<tr>
<td>W149</td>
<td>38.245</td>
<td>38.229</td>
<td>0.016</td>
<td>0.000256</td>
</tr>
<tr>
<td>GRHY</td>
<td>38.627</td>
<td>38.633</td>
<td>-0.006</td>
<td>0.000036</td>
</tr>
<tr>
<td>R78</td>
<td>38.934</td>
<td>38.970</td>
<td>-0.036</td>
<td>0.001296</td>
</tr>
<tr>
<td>R91</td>
<td>38.865</td>
<td>38.900</td>
<td>-0.035</td>
<td>0.001225</td>
</tr>
<tr>
<td>K005</td>
<td>38.814</td>
<td>38.881</td>
<td>-0.067</td>
<td>0.004489</td>
</tr>
<tr>
<td>KAR2</td>
<td>38.568</td>
<td>38.569</td>
<td>-0.001</td>
<td>0.000001</td>
</tr>
<tr>
<td>KAR7</td>
<td>38.951</td>
<td>38.975</td>
<td>-0.024</td>
<td>0.000576</td>
</tr>
<tr>
<td>KAR10</td>
<td>38.144</td>
<td>38.176</td>
<td>-0.032</td>
<td>0.001024</td>
</tr>
<tr>
<td>KAR11</td>
<td>38.325</td>
<td>38.313</td>
<td>0.012</td>
<td>0.000144</td>
</tr>
</tbody>
</table>

TOTAL = 0.009063

$S^2 = (0.009063)/2(N-1)$

$S = 0.022 \ (0.06\%)$
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>RATIO</th>
<th>MEAN</th>
<th>DIFF.</th>
<th>DIFF.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>R78</td>
<td>19.540</td>
<td>19.496</td>
<td>0.044</td>
<td>0.001936</td>
</tr>
<tr>
<td>R90</td>
<td>19.512</td>
<td>19.496</td>
<td>0.016</td>
<td>0.000256</td>
</tr>
<tr>
<td>R91</td>
<td>19.437</td>
<td>19.496</td>
<td>0.059</td>
<td>0.003481</td>
</tr>
<tr>
<td>L/T1</td>
<td>18.958</td>
<td>18.930</td>
<td>0.028</td>
<td>0.000784</td>
</tr>
<tr>
<td>L/T4</td>
<td>18.902</td>
<td>18.930</td>
<td>0.028</td>
<td>0.000784</td>
</tr>
</tbody>
</table>

\[ 206pb/204pb \ s^2 = \frac{0.007241}{4} \]
\[ s = 0.043 \ (0.22\%) \]

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>RATIO</th>
<th>MEAN</th>
<th>DIFF.</th>
<th>DIFF.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>R78</td>
<td>15.620</td>
<td>15.624</td>
<td>0.004</td>
<td>0.000016</td>
</tr>
<tr>
<td>R90</td>
<td>15.641</td>
<td>15.624</td>
<td>0.017</td>
<td>0.000289</td>
</tr>
<tr>
<td>R91</td>
<td>15.611</td>
<td>15.624</td>
<td>0.013</td>
<td>0.000169</td>
</tr>
<tr>
<td>L/T1</td>
<td>15.597</td>
<td>15.608</td>
<td>0.011</td>
<td>0.000121</td>
</tr>
<tr>
<td>L/T4</td>
<td>15.619</td>
<td>15.608</td>
<td>0.011</td>
<td>0.000121</td>
</tr>
</tbody>
</table>

\[ 207pb/204pb \ s^2 = \frac{0.000716}{4} \]
\[ s = 0.014 \ (0.08\%) \]

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>RATIO</th>
<th>MEAN</th>
<th>DIFF.</th>
<th>DIFF.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>R78</td>
<td>38.952</td>
<td>38.962</td>
<td>0.010</td>
<td>0.000100</td>
</tr>
<tr>
<td>R90</td>
<td>39.047</td>
<td>38.962</td>
<td>0.075</td>
<td>0.007225</td>
</tr>
<tr>
<td>R91</td>
<td>38.888</td>
<td>38.962</td>
<td>0.074</td>
<td>0.004489</td>
</tr>
<tr>
<td>L/T1</td>
<td>38.559</td>
<td>38.530</td>
<td>0.029</td>
<td>0.000841</td>
</tr>
<tr>
<td>L/T4</td>
<td>38.501</td>
<td>38.530</td>
<td>0.029</td>
<td>0.000841</td>
</tr>
</tbody>
</table>

\[ 208pb/204pb \ s^2 = \frac{0.013496}{4} \]
\[ s = 0.058 \ (0.15\%) \]
Table B.11. Accuracy assessment using BCR-1 standard

<table>
<thead>
<tr>
<th>Date</th>
<th>206pb/204pb</th>
<th>207pb/204pb</th>
<th>208pb/204pb</th>
<th>Pb (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>March 1985</td>
<td>18.819 (0.006)</td>
<td>15.633 (0.008)</td>
<td>38.715 (0.027)</td>
<td>13.40 (0.03)</td>
</tr>
<tr>
<td>May 1985</td>
<td>18.810 (0.008)</td>
<td>15.626 (0.008)</td>
<td>38.693 (0.029)</td>
<td>13.89 (0.05)</td>
</tr>
</tbody>
</table>

Tatsumoto et al. 1972

1) Double spike corrected
2) silica gel--0.15% mass fractionation correction

Measured isotopic compositions of BCR-1 are 0.1-0.15% greater than published values of Tatsumoto et al. 1972. Measured lead concentrations are within the uncertainties quoted for the standard value.
TABLE B.12: Reproducibility in lead concentrations measured in whole rock samples

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>NO. 1</th>
<th>NO. 2</th>
<th>1-2</th>
<th>(1-2)^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>683421</td>
<td>5.112</td>
<td>5.016</td>
<td>0.096</td>
<td>0.009216</td>
</tr>
<tr>
<td>K005</td>
<td>1.421</td>
<td>1.362</td>
<td>0.059</td>
<td>0.003481</td>
</tr>
<tr>
<td>R90</td>
<td>5.359</td>
<td>5.114</td>
<td>0.243</td>
<td>0.059049</td>
</tr>
<tr>
<td>MT. W.</td>
<td>1.887</td>
<td>1.932</td>
<td>0.045</td>
<td>0.002025</td>
</tr>
<tr>
<td>MT59</td>
<td>4.058</td>
<td>3.907</td>
<td>0.151</td>
<td>0.022801</td>
</tr>
<tr>
<td>MT360</td>
<td>5.236</td>
<td>5.354</td>
<td>0.118</td>
<td>0.013924</td>
</tr>
</tbody>
</table>

\[
\text{TOTAL} = 0.110496
\]

\[
S^2 = \frac{(0.110496)}{2(N-1)}
\]

\[
S = 0.105 \text{ ppm (approximately 3%)}
\]
from error propagation, may be due to inhomogeneity in sample powders, or incomplete dissolution. However, the accuracy of the BCR1 analysis argues against the latter, at least for basalts.

Accuracy was tested by analyzing BCR-1 rock standard. The measured values (Table B.11) were within one sigma of the standard value of Tatsumoto et al. (1972).

B.9.3 Uranium concentration

One duplicate analysis of sample 643421 indicates that the precision might be as good as ± 0.01 ppm or 1%. Error propagation by the method of Rees (1984) suggests that the uranium analyses are precise to about 1% depending on weighing errors, uncertainties in the spike calibration and mass spectrometry. A consistent bias is detectable between data from neutron activation analysis or gamma ray spectroscopy and isotope dilution data. This is probably due to the different analytical techniques. Neutron activation and gamma ray spectroscopy numbers are unlikely to be more precise than 10%, therefore it was thought to be reasonable to adjust these numbers by a suitable factor to be more consistent with the results of isotope dilution analysis. An adjustment factor was determined by comparing the results of nine samples that have uranium values determined by both isotope dilution and neutron activation or gamma ray analysis (Table B.13).

B.9.3. Thorium concentration

There are insufficient data to assess the error limits on thorium analyses, other than by error propagation, which suggests that the error is quite small, in the order of 1%. This is the minimum error associated with an analysis, since both lead and uranium concentrations have actual uncertainties which are larger than those estimated by error propagation.
TABLE B.13 Bias in uranium concentrations measured by different methods. I.D. = isotope dilution; "other" is gamma ray spectroscopy or neutron activation analysis.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>I.D.</th>
<th>other</th>
<th>other/I.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R131</td>
<td>1.16</td>
<td>1.63</td>
<td>1.4052</td>
</tr>
<tr>
<td>ZEBALLOS</td>
<td>1.10</td>
<td>1.29</td>
<td>1.1727</td>
</tr>
<tr>
<td>681381</td>
<td>1.47</td>
<td>1.68</td>
<td>1.1429</td>
</tr>
<tr>
<td>683421</td>
<td>1.04</td>
<td>1.13</td>
<td>1.0865</td>
</tr>
<tr>
<td>692131</td>
<td>2.12</td>
<td>2.29</td>
<td>1.0802</td>
</tr>
<tr>
<td>K005</td>
<td>0.31</td>
<td>0.32</td>
<td>1.0323</td>
</tr>
<tr>
<td>K007</td>
<td>0.32</td>
<td>0.34</td>
<td>1.0625</td>
</tr>
<tr>
<td>MB001</td>
<td>0.90</td>
<td>0.97</td>
<td>1.0778</td>
</tr>
<tr>
<td>FAITH LAKE</td>
<td>0.25</td>
<td>0.39</td>
<td>1.5600</td>
</tr>
</tbody>
</table>

Mean value\(^1\) (n=7) = 1.0935 ± 0.0196

+ one std. error

---

1. Samples R131 and Faith Lake were excluded from the mean because their factors were in excess of 2 sigma from the mean value.
APPENDIX C

SPIKE CALIBRATIONS

C.1 CALIBRATION OF STOCK (300 PPM) 207Pb SPIKE

Stock 207Pb spike was found on the shelf in the zircon lead chemistry lab in the Department of Geophysics and Astronomy, U.B.C., labelled: .238256 g Pb(NO₃)₂ per 500 ml (300 ppm). 50 ml of this solution was decanted into a clean teflon bottle and relabelled "84-2 conc. 207Pb spike". This was then calibrated as follows.

C.1.1 Isotopic Composition

The isotopic composition of this spike was determined as in Table C.1.

<table>
<thead>
<tr>
<th>Date</th>
<th>208Pb/207Pb</th>
<th>206Pb/208Pb</th>
<th>204Pb/206Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/11/83</td>
<td>0.058928(0.000054)</td>
<td>0.389318(0.000263)</td>
<td>0.004464(0.000017)</td>
</tr>
<tr>
<td>25/11/83</td>
<td>0.058915(0.000009)</td>
<td>0.389480(0.000032)</td>
<td>0.004744(0.000210)</td>
</tr>
</tbody>
</table>

Mean : 0.058922(0.000039) 0.389399(0.000187) 0.004464(0.000017)

1. The 204Pb/206Pb ratio for 25/11/83 was excluded from the mean value because of its poor in-run precision.

Ratios were converted and corrected for 0.16% per mass unit mass fractionation. Giving:

1. Absolute Ratios:
   - 206Pb/204Pb = 224.731 ± 0.856,
   - 207Pb/204Pb = 5809.865 ± 37.405, and
   - 208Pb/204Pb = 576.939 ± 2.206.

2. Atomic weight = 207.009001.

3. Atom percent: 206Pb = 0.021172,
   - 207Pb = 0.924192,
   - 208Pb = 0.054542, and
   - 204Pb = 0.000094.

C.1.2 Isotope dilution

The concentration of lead in the spike solution was determined by isotope dilution using a standard solution of
NBS981 previously calibrated by Pat Shore (see zircon lab book of standards and spikes, 1979). The concentration of NBS981 79-2 standard was taken to be 10.734877 +/- 0.004561. Errors are based on the maximum possible weighing errors (P.J. Shore). The isotopic composition of NBS981 is given by the National Bureau of Standards. Results of four isotope dilution runs are in Table C.2.

### Table C.2 Isotope dilution runs for spike 84-2

<table>
<thead>
<tr>
<th>Run</th>
<th>84-2 (g)</th>
<th>NBS981 (g)</th>
<th>raw $^{208}\text{Pb}/^{207}\text{Pb}$</th>
<th>Total Pb (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00339</td>
<td>3.6008</td>
<td>2.132449(0.000169)</td>
<td>307.568</td>
</tr>
<tr>
<td>2</td>
<td>0.00320</td>
<td>1.5336</td>
<td>1.895208(0.002122)</td>
<td>315.361</td>
</tr>
<tr>
<td>3</td>
<td>0.00916</td>
<td>0.5750</td>
<td>0.849568(0.000204)</td>
<td>309.001</td>
</tr>
<tr>
<td>4</td>
<td>0.00961</td>
<td>0.6888</td>
<td>0.918939(0.005904)</td>
<td>309.067</td>
</tr>
</tbody>
</table>

Runs 3 and 4 in Table C.2 were considered most reliable because they were not swamped by NBS981 lead. The concentration is taken to be 309 ppm.

### C.2 Preparation of 84-3 Mixed $^{207}\text{Pb}$ and $^{235}\text{U}$ Spike

Spike 84-3 was prepared from 79-2 $^{235}\text{U}$ concentrated stock solution with a concentration of 1143.5 ppm (P.J. Shore) and 84-2 $^{207}\text{Pb}$ spike with a concentration of approximately 309 ppm. Required concentrations are: $^{235}\text{U} = 2$ ppm, and $^{207}\text{Pb} = 2$ ppm. A 500 ml final solution requires 1000 µg $^{235}\text{U}$ (0.8745 g of spike 79-2) and 1000 µg $^{207}\text{Pb}$ (3.236 g of spike 84-2). Calculations for mixed spike 84-3 are:

1. weight of clean teflon beaker + $^{235}\text{U}$ 79-2 spike = 10.2421, weight of beaker = 9.3590,
2. nominal weight of $^{235}\text{U} = 0.8831 \times 1143.5 = 1009.82$ µg,
3. weight of clean teflon beaker + $^{207}\text{Pb}$ 84-2 spike = 12.3562, weight of beaker = 9.3750,
4. nominal weight of lead = 2.9812 \times 309 = 921.19 µg.

All of the above weighings were done in the zircon lab using a Mettler balance. The two solutions were transferred into a weighed 500 ml screw-top volumetric flask with TFE telon cap liner, and diluted to 500 ml with 2N HNO3. Relevant calculations are:

1. volumetric flask + label + cap = 179.095 g (1200 g P300 balance),
2. final solution = 713.340 (Mettler P1200 balance),
3. weight of solution = 534.245, and
4. nominal concentrations of Pb = 1.721 ppm, and U = 1.887 ppm.

C.3 CALIBRATION OF 84-3 MIXED SPIKE

C.3.1 Isotope composition of lead in spike 84-3
The isotopic composition of lead in 84-3 was determined by the repeated analyses in Table C.3.

TABLE C.3 Composition of lead in spike 84-3; 1984.

<table>
<thead>
<tr>
<th>Date</th>
<th>208pb/207pb</th>
<th>206pb/208pb</th>
<th>204pb/206pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>13/2/84</td>
<td>0.058932</td>
<td>0.390159</td>
<td>0.004519</td>
</tr>
<tr>
<td>1/7/84</td>
<td>0.058934</td>
<td>0.389827</td>
<td>0.004351</td>
</tr>
<tr>
<td>2/7/84</td>
<td>0.058940</td>
<td>0.390181</td>
<td>0.004503</td>
</tr>
<tr>
<td>1/8/84</td>
<td>0.058934</td>
<td>0.389982</td>
<td>0.004481</td>
</tr>
<tr>
<td>2/8/84</td>
<td>0.058936</td>
<td>0.390229</td>
<td>0.004597</td>
</tr>
<tr>
<td>3/11/84</td>
<td>0.058922</td>
<td>0.390235</td>
<td>0.004314</td>
</tr>
<tr>
<td>16/11/84</td>
<td>0.058905</td>
<td>0.390071</td>
<td>0.004488</td>
</tr>
<tr>
<td>10/12/84</td>
<td>0.058893</td>
<td>0.390033</td>
<td>0.004425</td>
</tr>
<tr>
<td>11/12/84</td>
<td>0.058910</td>
<td>0.389845</td>
<td>0.004446</td>
</tr>
</tbody>
</table>

MEAN1: 0.058934 0.390062 0.004458
(0.000016) (0.000154) (0.000087)

Converted ratios, corrected for 0.16% mass fractionation (per mass unit), are:
206pb/204pb = 225.034      208pb/207pb = 0.059028
207pb/204pb = 9804.828     206pb/208pb = 0.388818
208pb/204pb = 578.758

Atomic weight = 207.0089702
Atomic proportions are: 206pb = 0.021210373
207pb = 0.924145068
208pb = 0.054550304
204pb = 0.000094254

1. The mean value and one standard deviation is given for each ratio.

C.3.2 Isotope dilution calculations for lead in spike 84-3
Three isotope dilution runs were done using each of two calibrated solutions; 79-3 mixed 235U and 208Pb spike (zircon laboratory), and NBS981 standard solution 79-3 (zircon laboratory). The following spike constants were used for the
mixed spike from calibrations by P Van der Heyden, zircon laboratory spikes and standards book, 1984:

1. atomic proportions: 
   \[ \begin{align*}
   \text{208Pb} &= 0.990854254, \\
   \text{207Pb} &= 0.006958367, \\
   \text{206Pb} &= 0.002148874, \text{ and} \\
   \text{204Pb} &= 0.000038505.
   \end{align*} \]

2. Concentration of lead = 1.08596 ppm

NBS certified values were used for the isotopic composition of NBS981 79-3 standard, and the concentration as before (see calibration of spike 84-2). Isotope dilution conditions and results are in Table C.4.

<table>
<thead>
<tr>
<th>RUN</th>
<th>79-3 (g)</th>
<th>84-3 (g)</th>
<th>208Pb/207Pb</th>
<th>Total Pb conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5555</td>
<td>0.4113</td>
<td>0.939626 x 1.0016</td>
<td>1.762</td>
</tr>
<tr>
<td>2</td>
<td>0.4909</td>
<td>0.5040</td>
<td>0.696130 x 1.0016</td>
<td>1.757</td>
</tr>
<tr>
<td>3</td>
<td>0.5886</td>
<td>0.3481</td>
<td>1.161474 x 1.0016</td>
<td>1.760</td>
</tr>
<tr>
<td>NBS981 (g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.8149</td>
<td>0.9842</td>
<td>1.321013 x 1.0016</td>
<td>1.758</td>
</tr>
<tr>
<td>5</td>
<td>0.2204</td>
<td>0.4335</td>
<td>1.038981 x 1.0016</td>
<td>1.764</td>
</tr>
<tr>
<td>6</td>
<td>0.1852</td>
<td>0.3243</td>
<td>1.105313 x 1.0016</td>
<td>1.765</td>
</tr>
</tbody>
</table>

Mean value (n=6) = 1.761 +/- 0.003 ppm

C.3.3 Isotope composition of uranium in spike 84-3

The isotopic composition of 84-3 spike was taken to be the same as that of the stock concentrated 235U spike solution. The 235U/238U ratio for 79-2 uranium spike has been found to be 8742 (P. Van der Heyden, zircon laboratory spikes and standards book 1984).

C.3.4 Isotope dilution calculations for uranium in spike 84-3

Spike 84-3 was calibrated against 79-5 U500 equal atom standard (NBS), which has a concentration of 24.9117 ppm (P. Shore, spikes and standards book, 1979). Results are in Table C.5.
TABLE C.5 Isotope dilution results for uranium in spike 84-3.

<table>
<thead>
<tr>
<th>RUN</th>
<th>U500 (g)</th>
<th>84-3 (g)</th>
<th>235U/238U (RAW)</th>
<th>U ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.7408</td>
<td>1.9560</td>
<td>1.422314</td>
<td>1.981</td>
</tr>
<tr>
<td>2</td>
<td>.6713</td>
<td>1.9982</td>
<td>1.483982</td>
<td>2.014</td>
</tr>
<tr>
<td>3</td>
<td>.6649</td>
<td>1.9955</td>
<td>1.481986</td>
<td>1.989</td>
</tr>
<tr>
<td>4</td>
<td>.8427</td>
<td>0.9689</td>
<td>1.185258</td>
<td>1.996</td>
</tr>
</tbody>
</table>

Mean (n=4) = 1.995 ± 0.014 ppm

Mass fractionation corrections of 0.006% per mass unit were made, based on repeated analyses of the U500 equal atom standard (Table B.3).

C.4 PREPARATION OF 230TH SPIKE 84-1

Spike 84-1 was prepared from 230Th as ThO₂ from Oak Ridge, batch number RD 1542, 1968 Th230-130A as follows:

1. weight of beaker + ThO₂ = 15.2008 g, with
   Beaker = 15.1920 g, and
3. ThO₂ = 0.0088 g.

ThO₂ was dissolved using 5 ml two-bottle (2B) HF and a few drops HClO₄. It was left covered and heated overnight. The cover was then removed to allow evaporation. Subsequently more HClO₄ was added and heated uncovered until fuming. A few drops of concentrated HNO₃ were added (to drive off the HClO₄) and the sample was evaporated to dryness. The residue was taken up in 2B distilled water, and diluted to 100 ml in a screw-topped flask.

The isotopic composition of the spike was determined by four runs using the program "UBCTH" which measures the 230Th/232Th ratio. Two loading methods were used and found to give the same results. A drop of spike solution was evaporated onto a baked out tantalum filament and the oxide peaks were measured at approximately 1800°C. Alternatively a drop of colloidal graphite (prepared from Aquadag colloidal graphite) was dried onto a baked out rhenium filament, then a drop of the spike solution added on top, and heated to dryness. In this case the metal peaks were measured.

The four isotope composition runs were as follows:
1) 230Th/232Th = 11.361
2) 230Th/232Th = 11.383
3) 230Th/232Th = 11.425 MEAN (n=4) 11.406 (0.042), where
4) 230Th/232Th = 11.456 0.042 is the standard deviation.

0.042 is the standard deviation.
Other parameters are:
1. Atomic proportions are: $^{230}\text{Th} = 0.919394$, and $^{232}\text{Th} = 0.080606$
3. Weight of thorium in spike = $230.1948/262.1936 \times 0.0088$ g
   = 0.007726 g
4. Weight of 100 ml solution $\text{H}_2\text{O} + \text{ThO}_2 = 167.39$ g
5. Weight of 100 ml screw-top flask = 68.10 g
6. Nominal concentration of Th in spike = $0.007726/99.29$
   = 77.812 $\mu$g Th/g solution
   = 0.033802675 $\mu$moles Th
   = 0.031077977 $\mu$moles $^{230}\text{Th}$
   = 71.4896 ppm $^{230}\text{Th}$
   = 6.3224 ppm $^{232}\text{Th}$

C.5 PREPARATION OF 84-2 DILUTE $^{230}\text{Th}$ SPIKE

Spike 84-2 was prepared from 84-1 concentrated $^{230}\text{Th}$ spike as follows:
1. Required concentration = 10 ppm
2. 100 ml solution requires 1000 $\mu$g Th, approximately 12.85 g 84-1
3. Weight of beaker + spike = 30.6349 g
4. Weight of empty beaker = 17.7337 g
5. Weight of 84-1 = 12.9012 g
6. Weight of Th in new spike = $12.9012 \times 77.812$ $\mu$g
   = 1003.868174 $\mu$g
7. Spike was diluted to 100 ml with two-bottle distilled 2N HNO$_3$
in a clean teflon bottle.
8. Final weight of bottle plus spike = 151.1057 g
9. Initial weight of teflon bottle = 37.4733 g
10. Weight of solution = 113.6324 g
11. Nominal concentration of Th = 8.834 ppm

C.6 CALIBRATION OF 84-2 DILUTE $^{230}\text{Th}$ SPIKE

C.6.1 Isotope composition of spike 84-2

The isotope composition of 84-2 is assumed to be the same as for 84-1.

C.6.2 Isotope dilution determinations for spike 84-2

Spike 84-2 was calibrated using 84-4 $^{232}\text{Th}$ standard which
was prepared from specpure ThO$_2$ as $^{232}\text{Th}$ in the same way as
given for 84-1. Neutron activation analysis (by Neutron
Activation Services Ltd, Hamilton, Ontario) showed the
concentration to be 97 ppm. Three isotope dilution runs were
measured and are reported in Table C.6.

TABLE C.6 Determination of the concentration of thorium in spike 84-2.

<table>
<thead>
<tr>
<th>84-2 g</th>
<th>84-4 g</th>
<th>232Th/230ThID</th>
<th>Th ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1077</td>
<td>2.8778</td>
<td>30.137</td>
<td>9.0492</td>
</tr>
<tr>
<td>1.2954</td>
<td>1.2461</td>
<td>11.276</td>
<td>8.9989</td>
</tr>
<tr>
<td>2.0581</td>
<td>1.0061</td>
<td>5.770</td>
<td>9.0044</td>
</tr>
</tbody>
</table>

MEAN (n=3) = 9.018 (0.028) ppm (1 std. dev.)

The following isotope dilution equation was used:

\[ 230\text{Th}_{84-2} = 232\text{Th}_{84-4} \times \frac{(230\text{Th}/232\text{Th}_{84-4} - 230\text{Th}/232\text{Th}_{ID})}{(232\text{Th}/230\text{Th}_{84-2} \times 230\text{Th}/232\text{Th}_{ID} - 1)} \]

where:
- \( 230\text{Th}_{84-2} \) is the µmoles \( 230\text{Th} \) in spike 84-2
- \( 232\text{Th}_{84-4} \) is the µmoles/g \( 232\text{Th} \) in standard 84-4
- \( 230\text{Th}/232\text{Th}_{84-4} \) is the ratio in the standard
- \( 230\text{Th}/232\text{Th}_{ID} \) is the ratio in the isotope dilution run
- \( 232\text{Th}/230\text{Th}_{84-2} \) is the ratio in spike 84-2
APPENDIX D

PRINTOUTS OF COMPUTER PROGRAMS USED IN CALCULATION OF DATA

A summary of each of the listed programs is given in Table D.1
<table>
<thead>
<tr>
<th>PROGRAM</th>
<th>INPUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>WRPBIC</td>
<td>Raw data with in-run precision</td>
</tr>
<tr>
<td></td>
<td>$^{207}\text{Pb} / ^{206}\text{Pb} \pm i$</td>
</tr>
<tr>
<td></td>
<td>$^{208}\text{Pb} / ^{206}\text{Pb} \pm i$</td>
</tr>
<tr>
<td></td>
<td>$^{204}\text{Pb} / ^{207}\text{Pb} \pm i$</td>
</tr>
<tr>
<td>WRPBID</td>
<td>$^{206}\text{Pb} / ^{204}\text{Pb} \pm s$</td>
</tr>
<tr>
<td></td>
<td>$^{207}\text{Pb} / ^{204}\text{Pb} \pm s$</td>
</tr>
<tr>
<td></td>
<td>$^{208}\text{Pb} / ^{204}\text{Pb} \pm s$</td>
</tr>
<tr>
<td></td>
<td>spike weight $\pm 0.0003g$</td>
</tr>
<tr>
<td></td>
<td>sample weight $\pm 0.0003g$</td>
</tr>
<tr>
<td></td>
<td>raw $^{208}\text{Pb} / ^{207}\text{Pb}$ (ID run) $\pm i$</td>
</tr>
<tr>
<td>BLANKSUB</td>
<td>output from WRPBIC $\pm s$</td>
</tr>
<tr>
<td></td>
<td>Pb ppm $\pm 0.1$ ppm</td>
</tr>
<tr>
<td></td>
<td>sample weight $\pm 0.0003g$</td>
</tr>
<tr>
<td></td>
<td>amount of blank to be subtracted</td>
</tr>
<tr>
<td>WRUCLC</td>
<td>Raw $^{235}\text{U} / ^{238}\text{U} + i$</td>
</tr>
<tr>
<td></td>
<td>spike weight $\pm 0.0003g$</td>
</tr>
<tr>
<td></td>
<td>sample weight $\pm 0.0003g$</td>
</tr>
<tr>
<td></td>
<td>$^{204}\text{Pb}$ micromoles $\pm$ uncertainty based on 0.1 ppm total uncertainty in lead content</td>
</tr>
<tr>
<td>MUCALC</td>
<td>U(GR) or U(NAA) $\pm 10%$</td>
</tr>
<tr>
<td></td>
<td>divided by 1.0935</td>
</tr>
<tr>
<td></td>
<td>$^{204}\text{Pb}$ micromoles $\pm$ uncertainty based on 0.1 ppm total uncertainty in lead content</td>
</tr>
<tr>
<td>TICORR</td>
<td>$^{206}\text{Pb} / ^{204}\text{Pb} \pm s$</td>
</tr>
<tr>
<td></td>
<td>$^{207}\text{Pb} / ^{204}\text{Pb} \pm s$</td>
</tr>
<tr>
<td></td>
<td>$^{208}\text{Pb} / ^{204}\text{Pb} \pm s$</td>
</tr>
<tr>
<td></td>
<td>$^{238}\text{U} / ^{204}\text{Pb} \pm s$</td>
</tr>
<tr>
<td>WRTHCLC</td>
<td>raw $^{230}\text{Th} / ^{232}\text{Th} + i$</td>
</tr>
<tr>
<td></td>
<td>spike weight $\pm 0.0003g$</td>
</tr>
<tr>
<td></td>
<td>sample weight $\pm 0.0003g$</td>
</tr>
<tr>
<td></td>
<td>Age correction</td>
</tr>
<tr>
<td>CONCORD</td>
<td>$^{238}\text{U} / ^{204}\text{Pb} \pm s$</td>
</tr>
<tr>
<td></td>
<td>$^{206}\text{Pb} / ^{204}\text{Pb} \pm s$</td>
</tr>
<tr>
<td></td>
<td>$^{207}\text{Pb} / ^{204}\text{Pb} \pm s$</td>
</tr>
</tbody>
</table>

---

**TABLE D.1. Summary of data reduction programs.**

<table>
<thead>
<tr>
<th>PROGRAM</th>
<th>INPUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>WRPBIC</td>
<td>Mass fractionation factors, fractionation variations between runs.</td>
</tr>
<tr>
<td>WRPBID</td>
<td>Spike 84-3 isotopic composition and concentration, mass fractionation, all uncertainties associated with the input data.</td>
</tr>
<tr>
<td>BLANKSUB</td>
<td>blank composition, all uncertainties associated with input data.</td>
</tr>
<tr>
<td>WRUCLC</td>
<td>Spike 84-3 isotopic composition and concentration, uranium mass fractionation, all uncertainties associated with the input data.</td>
</tr>
<tr>
<td>MUCALC</td>
<td>Uncertainties associated with input data.</td>
</tr>
<tr>
<td>TICORR</td>
<td>Uncertainties associated with input data.</td>
</tr>
<tr>
<td>WRTHCLC</td>
<td>Spike 84-1 composition and concentration, mass fractionation, input data.</td>
</tr>
<tr>
<td>CONCORD</td>
<td>Uncertainties associated with input data.</td>
</tr>
</tbody>
</table>

---

1. $i =$ in-run precision (standard error). $s =$ estimated uncertainty based on propagation of errors (one sigma).
D.1 WRPBIC

10 REM PROGRAM WRPBIC TO CALC 6/4, 7/4 AND 8/4 RATIOS FROM
20 REM RAW DATA USING FRACTIONATION FACTORS 0.16% PMU
30 REM AND FRACTIONATION VARIATION BETWEEN RUNS
40 REM DETERMINED FROM REPEATED ANALYSES OF BHS
50 REM FRACTIONATION VARIATION ADDS .006, .007 AND .025
60 REM TO 6/4 7/4 8/4 RATIOS RESPECTIVELY.
70 PRINT "TYPE IN 7/6 RATIO, ERROR"
80 INPUT R76, ERR1
90 PRINT "TYPE IN 8/6, ERROR"
100 INPUT R86, ERR2
110 PRINT "TYPE IN 4/7, ERROR"
120 INPUT R47, ERR3
125 PRINT "TYPE SAMPLE NAME"
126 INPUT A$
130 ERR1P=(ERR1/R76)*100
140 ERR2P=(ERR2/R86)*100
150 ERR3P=(ERR3/R47)*100
160 R74=1/R47
170 E74=(ERR3P*R74)/100
180 S=R76*R47
190 R64=1/S
200 E64=ERR1P^2+ERR3P^2
210 E64A=SQR(E64)
220 E64=(E64A*R64)/100
230 R84=R86*R64
240 E84=ERR2P^2+E64A^2
245 E84=SQR(E84)
247 E84=(E84*R84)/100
250 REM NOW MULTIPLY RAW RATIOS BY FRACTIONATION FACTORS
260 REM AND ADD FRACTIONATION VARIATION ERRORS AND
270 REM FRACTIONATION FACTOR UNCERTAINTY TO IN-RUN ERRORS
280 R64=R64*1.0032
290 R74=R74*1.0048
300 R84=R84*1.0064
305 REM FRACTIONATION VARIATION BETWEEN RUNS (ABSOLUTE) FV1-3
310 FV1=.006
320 FV2=.007
330 FV3=.025
335 REM UNCERTAINTY IN ABSOLUTE BHS VALUE (STD DEV) FFU1-3
340 FFU1=.002
350 FFU2=.004
360 FFU3=.01
370 E64=E64^2+FV1^2+FFU1^2
380 E64=SQR(E64)
390 E74=E74^2+FV2^2+FFU2^2
400 E74=SQR(E74)
410 E84=E84^2+FV3^2+FFU3^2
420 E84=SQR(E84)
422 LPRINT "INPUT",A$
423 LPRINT "207PB/206PB ="R76 "("ERR1")"
424 LPRINT "208PB/206PB ="R86 "("ERR2")"
425 LPRINT "204PB/207PB ="R47 "("ERR3")"
426 LPRINT "RESULTS"
427 LPRINT "206PB/204PB ="R64 "("E64")"
428 LPRINT "207PB/204PB ="R74 "("E74")"
429 LPRINT "208PB/204PB ="R84 "("E84")"
430 PRINT A$,R64,E64,R74,E74,R84,E84
440 PRINT "MORE DATA ? Y=1,N=2"
450 INPUT Y
460 IF Y=1 THEN 10
470 END
D.2 WRPBID

10 REM WRPBID PROGRAM CALCULATES PB PPM AND ASSOCIATED ERRORS
20 DIM X(15), Y(15), S(7,15)
50 PRINT "TYPE IN SAMPLE NAME"
60 INPUT A$
70 PRINT "TYPE IN 6/4, ERROR"
80 INPUT X(1), Y(1)
90 PRINT "NOW 7/4, ERROR"
100 INPUT X(2), Y(2)
110 PRINT "8/4, ERROR PLEASE"
120 INPUT X(3), Y(3)
130 PRINT "MASS FRACTIONATION IS .16%+/-.01%"
240 REM WEIGHTS OF EACH PB ISOTOPE ARE AS FOLLOWS:
250 WT4=203.973044#
260 WT6=205.974468#
270 WT7=206.975903#
280 WT8=207.97665#
290 IF Y=1 THEN 500
300 REM SPIKE CONSTANTS ARE; 8/7, 6/8, 4/6
310 X(4)=.059017#
320 Y(4)=.000017#
330 X(5)=.388818#
340 Y(5)=.000166#
350 X(6)=.044444#
360 Y(6)=8.700000000000005D-05
365 REM SPIKE CONCENTRATION
370 X(7)=1.761
380 Y(7)=.003
400 X(8)=1.0016
410 Y(8)=.0001
420 PRINT "ENTER WT SPIKE, WEIGHING ERROR, WT SAMPLE, ERROR"
430 INPUT X(9), Y(9), X(10), Y(10)
440 PRINT "ENTER 8/7 ID, ERROR"
450 INPUT X(11), Y(11)
500 REM ZERO VARIABLES BEFORE CALCS
510 FOR I=0 TO 3
520 FOR J=0 TO 11
530 S(I,J)=0
540 NEXT J
550 NEXT I
560 X(0)=0
570 Y(0)=0
580 FOR J=0 TO 11
590 X(J)=X(J)+Y(J)
600 REM BEGIN CALCULATIONS
620 A=X(1)
630 B=X(2)
640 C=X(3)
REM NOW CALC ATOMIC WEIGHT AND ATOMIC PROPORTIONS FOR SAMPLE
TOT=1+A+B+C
AT4=1/TOT
AT6=A/TOT
AT7=B/TOT
AT8=C/TOT
AWT=AT4*WT4+AT6*WT6+AT7*WT7+AT8*WT8
S(1,J)=AWT
IF Y=1 THEN 940
REM CALCULATE SPIKE CONSTANTS
SP64=1/X(6)
SP84=1/(X(6)*X(5))
SP74=(1/X(4))*SP84
REM SPIKE ATOMIC PROPORTIONS
TOTSP=1+SP64+SP84+SP74
AT4SP=1/TOTSP
AT6SP=SP64/TOTSP
AT7SP=SP74/TOTSP
AT8SP=SP84/TOTSP
AWTSP=AT4SP*WT4+AT7SP*WT7+AT6SP*WT6+AT8SP*WT8
REM CORRECT ID RATIO TO 7/8 AND MASS FRACTIONATION
ID78=1/(X(11)*X(8))
IC78=B/C
IC78=X(9)*X(7)*AT7SP*(1-(X(4)*ID78))/(ID78-IC78)
P8#=(PB8/AWTSP)
TOTPB=(P8#/AT8)/X(10)
P4#=TOTPB*AT4
S(2,J)=TOTPB
S(3,J)=P4#
REM RESTORE VARIABLES TO FORMER VALUE
X(J)=X(J)-Y(J)
NEXT J
REM ERROR SUMMATION
PRINT "ERRORS >0.5% ; I,J"
FOR I=1 TO 3
E=0
FOR J=1 TO 11
IF Y(J)=0 THEN 1590
IF ABS(S(I,J)-S(I,0))<.005*S(I,0) THEN 1580
PRINT I,J
E=E+(S(I,J)-S(I,0))^2
NEXT J
S(I,1)=SQR(E)
NEXT I
PRINT
1640 PRINT "RESULTS AND ERRORS FOR "A$":"
1650 LPRINT "RESULTS AND ERRORS FOR "A$":"
1680 PRINT "ATOMIC WT OF SAMPLE: ", S(1,0) S(1,1)
1690 LPRINT "ATOMIC WEIGHT OF SAMPLE: ", S(1,0) S(1,1)
1695 IF Y=1 THEN 1740
1700 PRINT "TOTAL PB IN ROCK" S(2,0) "+/-" S(2,1) "PPM"
1710 LPRINT "TOTAL PB IN ROCK" S(2,0) "+/-" S(2,1) "PPM"
1720 PRINT "204PB IN MICROMOLES " S(3,0) S(3,1)
1730 LPRINT "204PB IN MICROMOLES " S(3,0) S(3,1)
1740 PRINT "MORE DATA ? Y=1, N=2"
1750 INPUT N
1760 IF N=1 THEN 50
1770 END
D.3 WRUCLC

10 REM WRUCLC A PROGRAM TO CALC. UPPM, MU AND ASSESS THE ERROR IN EACH
20 REM THE FOLLOWING CONSTANTS ARE ASSUMED
30 U8NAT=.9928
40 UAW=238.0291503#
50 A5=235.044
60 A8=238.051
70 REM DECLARE VARIABLES
80 DIM X(7), Y(7), S(2,7)
90 REM CORRECTION FACTOR
100 X(1)=1.000243#
110 Y(1)=.000257#
120 PRINT "CORRECTION FACTOR IS 1.000243 +/- .000257"
130 PRINT "TYPE IN SAMPLE NAME"
140 INPUT A$
150 PRINT "TYPE IN 5/8 U RATIO (RAW) AND ERROR "
160 INPUT X(2), Y(2)
190 REM SPIKE CONSTANTS ARE AS FOLLOWS
200 X(3)=.00011439#
205 REM THAT WAS 238U ATOMIC PROPORTION
210 Y(3)=4.070000000000001D-06
270 REM SPIKE CONCENTRATION
280 X(4)=1.995
290 Y(4)=.014
300 PRINT "TYPE IN WT OF 84-3 USED, MAX WEIGHING ERROR"
310 INPUT X(5), Y(5)
320 PRINT "TYPE IN WT OF SAMPLE, WEIGHING ERROR"
330 INPUT X(6), Y(6)
340 PRINT "TYPE IN 204PB MICROMOLES, ERROR"
350 INPUT X(7), Y(7)
1000 REM BEGIN CALCULATIONS, FIRST ZERO EVERYTHING
1010 FOR I=0 TO 2
1020 FOR J=0 TO 7
1030 S(I,J)=0
1040 NEXT J
1050 NEXT I
1060 Y(0)=0
1070 X(0)=0
1075 FOR J=0 TO 7
1080 X(J)=X(J)+Y(J)
1081 ID85=1/X(2)
1082 ID85=ID85*X(1)
1083 X3=1/X(3)
1084 XT=1+X3
1086 AT5SP=X3/XT
1087 AT8SP=1/XT
1088 AWTSP=AT5SP*A5+AT8SP*A8
1089 REM THAT WAS THE ATOMIC WEIGHT OF THE SPIKE
1090 U8=(((X(4)*AT5SP*X(5))/(AWTSP))*((X(3)-ID85)/(ID85*(1/137.88)-1)))
1100 U8=U8/X(6)
1110 TOT = (U8/U8NAT)*UAW
1120 MU = U8/X(7)
1130 S(1,J)=TOT
1140 S(2,J)=MU
1150 X(J)=X(J)-Y(J)
1160 NEXT J
1500 REM ERROR SUMMATION
1510 PRINT "ERRORS > .5% FOR "A$"I,J"
1515 LPRINT
1516 LPRINT "ERRORS > .5% FOR "A$"I,J"
1520 FOR I=1 TO 2
1530 E=0
1540 FOR J=1 TO 7
1550 IF Y(J)=0 THEN 1590
1560 IF ABS(S(I,J)-S(I,0))<.005*S(I,0) THEN 1580
1570 PRINT I,J
1580 E=E+(S(I,J)-S(I,0))^2
1590 NEXT J
1600 S(I,1)=SQR(E)
1610 NEXT I
1620 PRINT "U PPM FOR "A$" = "S(1,0)"+-"S(1,1)
1630 PRINT "MU = "S(2,0)"+-"S(2,1)
1640 LPRINT "U PPM FOR "A$" = "S(1,0)"+-"S(1,1)
1650 LPRINT "MU = "S(2,0)"+-"S(2,1)
1660 END
D.4 WRTHCLC

10 REM WRTHCLC A PROGRAM TO CAL PPM, K AND ASSESS THE ERROR IN EACH
20 REM THE FOLLOWING CONSTANTS ARE ASSUMED
30 THNAT=1
40 THAW=232.038
50 A0=230.033
60 A2=232.038
70 REM DECLARE VARIABLES
80 DIM X(8), Y(8), S(3,8)
90 REM CORRECTION FACTOR
100 X(1)=1.00016
110 Y(1)=.00016
120 PRINT "CORRECTION FACTOR IS 1.00016 +/- .00016"
130 PRINT "TYPE IN SAMPLE NAME"
140 INPUT A$
150 PRINT "TYPE IN 0/2 TH RATIO (RAW) AND ERROR"
160 INPUT X(2),Y(2)
190 REM SPIKE CONSTANTS ARE AS FOLLOWS
200 X(3)=11.40600000000001#
205 REM THAT WAS 232TH/230TH SPIKE ATOMIC PROPORTION
210 Y(3)=.042
270 REM SPIKE CONCENTRATION
280 X(4)=9.018
290 Y(4)=.028
300 PRINT "TYPE IN WT OF 84-2 USED, MAX WEIGHING ERROR"
310 INPUT X(5),Y(5)
320 PRINT "TYPE IN WT OF SAMPLE, WEIGHING ERROR"
330 INPUT X(6),Y(6)
340 PRINT "TYPE IN MU, ERROR"
350 INPUT X(7),Y(7)
360 PRINT "TYPE IN 204PB MICROMOLES, ERROR"
370 INPUT X(8),Y(8)
1000 REM BEGIN CALCULATIONS, FIRST ZERO EVERYTHING
1010 FOR I=0 TO 2
1020 FOR J=0 TO 8
1030 S(I,J)=0
1040 NEXT J
1050 NEXT I
1060 Y(0)=0
1070 X(0)=0
1075 FOR J=0 TO 8
1080 X(J)=X(J)+Y(J)
1082 ID02=X(2)*X(1)
1083 X3=X(3)
1084 XT=1+X3
1086 AT0SP=X3/XT
1087 AT2SP=1/XT
1088 AWTSP=AT0SP*A0+AT2SP*A2
1089 REM THAT WAS THE ATOMIC WEIGHT OF THE SPIKE
1090  TH2=((X(4)*AT2SP*X(5))/(AWTSP))*((X(3)-ID02)/(ID02))
1100  TH2=TH2/X(6)
1110  TOT=(TH2/THNAT)*THAW
1120  W=TH2/X(8)
1123  S(2,J)=W
1125  K=(TH2/(X(8)*X(7)))
1127  S(3,J)=K
1130  S(1,J)=TOT
1150  X(J)=X(J)-Y(J)
1160  NEXT J
1500  REM ERROR SUMMATION
1510  PRINT "ERRORS > .5% FOR "A$"I,J"
1515  LPRINT
1516  LPRINT "ERRORS > .5% FOR "A$"I,J"
1520  FOR I=1 TO 3
1530  E=0
1540  FOR J=1 TO 8
1550  IF Y(J)=0 THEN 1590
1560  IF ABS(S(I,J)-S(I,0))<.005*S(I,0) THEN 1580
1570  PRINT I,J
1580  E=E+(S(I,J)-S(I,0))^2
1590  NEXT J
1600  S(I,1)=SQR(E)
1610  NEXT I
1620  PRINT "TH PPM FOR "A$" = "S(1,0)+/-"S(1,1)
1630  PRINT "W = "S(2,0)+/-"S(2,1)
1640  LPRINT "TH PPM FOR "A$" = "S(1,0)+/-"S(1,1)
1650  LPRINT "W = "S(2,0)+/-"S(2,1)
1660  PRINT "K =" S(3,0)+/-"S(3,1)
1670  LPRINT "K = "S(3,0)+/-"S(3,1)
1680  END
D.5 T1CORR

10 REM THIS PROGRAM (T1CORR) CORRECTS WHOLE ROCK LEAD DATA
20 REM FOR THE MEASURED MU AND K VALUES
30 REM THE DECAY CONSTANTS USED ARE AS FOLLOWS:
40 L1=1.55125E-10
50 L2=9.8485E-10
60 L3=4.9475E-11
65 DIM X(7),Y(7),S(4,7)
70 PRINT "TYPE IN THE SAMPLE NAME, AND THE AGE OF THE ROCK, ERROR"
80 INPUT A$,X(1),Y(1)
85 LPRINT X(1),Y(1)
90 T2=0
100 PRINT "TYPE IN MEASURED MU, ERROR"
110 INPUT X(2),Y(2)
115 LPRINT "MU IS:" X(2)+"-"Y(2)
120 PRINT "NOW ENTER 6/4, ERROR, 7/4, ERROR"
125 INPUT X(3),Y(3),X(4),Y(4)
130 PRINT "DO YOU WISH TO CORRECT FOR TH AS WELL? Y=1, N=2"
140 INPUT Y
150 IF Y=2 THEN 165
155 PRINT "TYPE IN K, ERROR, 8/4, ERROR"
160 INPUT X(5),Y(5),X(6),Y(6)
165 REM ZERO VARIABLES
170 FOR I=0 TO 3
180 FOR J=0 TO 6
190 S(I,J)=0
200 NEXT J
210 NEXT I
220 X(0)=0
230 Y(0)=0
240 FOR J=0 TO 6
250 X(J)=X(J)+Y(J)
260 T1=X(1)*1E+06
270 A1=X(3)-X(2)*(EXP(T1*L1)-EXP(T2*L1))
280 B1=X(4)-(X(2)/137.88)*(EXP(T1*L2)-EXP(T2*L2))
290 IF Y=2 THEN 320
300 C1=X(6)-(X(5)*X(2))*(EXP(T1*L3)-EXP(T2*L2))
310 S(3,J)=C1
320 S(1,J)=A1
330 S(2,J)=B1
340 X(J)=X(J)-Y(J)
350 NEXT J
360 REM ERROR SUMMATION
370 FOR I=1 TO 3
380 E=0
390 FOR J=1 TO 6
400 E=E+(S(I,0)-S(I,J))^2
410 NEXT J
420 S(I,1)=SQR(E)
430 NEXT I
1080 PRINT "TIME CORRECTED VALUES FOR "A$
1090 LPRINT "TIME CORRECTED VALUES FOR "A$
1100 PRINT S(1,0),S(1,1)
1110 LPRINT S(1,0),S(1,1)
1120 PRINT S(2,0),S(2,1)
1130 LPRINT S(2,0),S(2,1)
1140 IF Y=2 THEN 1170
1150 PRINT S(3,0),S(3,1)
1160 LPRINT S(3,0),S(3,1)
1170 LPRINT.
1180 PRINT "MORE DATA? Y=1, N=2"
1190 INPUT N
1200 IF N=1 THEN 70
1210 END
D.6 BLANKSUB

10 REM PROGRAM BLANKSUB TO SUBTRACT BLANKS FROM IC RUNS
15 REM ERROR CALCULATED
20 REM THE FOLLOWING CONSTANTS ARE ASSUMED
30 A4=203.973044#
40 A6=205.974468#
50 A7=206.975903#
60 A8=207.97665#
70 DIM X(12), Y(12), S(5,12)
71 PRINT "TYPE IN PB PPM IN SAMPLE, ERROR"
72 INPUT X(4), Y(4)
73 PRINT "TYPE IN WT SAMPLE, ERROR"
74 INPUT X(5), Y(5)
75 PRINT "INPUT AMT OF BLANK TO BE SUBTRACTED"
76 INPUT X(9), Y(9)
77 X(6)=18.329
78 Y(6)=.01
79 X(7)=15.619
80 Y(7)=.011
81 X(8)=38.065
82 Y(8)=.011
89 PRINT "TYPE IN SAMPLE NAME"
90 INPUT A$
100 PRINT "TYPE IN 6/4, ERROR"
110 INPUT X(1), Y(1)
120 PRINT "TYPE IN 7/4, ERROR"
130 INPUT X(2), Y(2)
140 PRINT "TYPE IN 8/4, ERROR"
150 INPUT X(3), Y(3)
151 FOR I=1 TO 3
152 FOR J=0 TO 9
153 S(I,J)=0
154 NEXT J
155 NEXT I
156 X(0)=0
157 Y(0)=0
158 FOR J=0 TO 9
159 X(J)=X(J)+Y(J)
160 REM THE ATOMIC PROPORTIONS OF SAMPLES ARE:
170 SAMTOT=1+X(1)+X(2)+X(3)
180 AP4=1/SAMTOT
190 AP6=X(1)/SAMTOT
200 AP7=X(2)/SAMTOT
210 AP8=X(3)/SAMTOT
220 AWTSAM=AP4*A4+AP6*A6+AP7*A7+AP8*A8
230 TOTMOL=X(5)*X(4)/AWTSAM
240 MOL4=AP4*TOTMOL
250 MOL6=AP6*TOTMOL
260 MOL7=AP7*TOTMOL
270 MOL8=AP8*TOTMOL
310 REM BLANK COMPOSITION TO BE SUBTRACTED IS:
360 BLKTOT=1+X(6)+X(7)+X(8)
370 BAP4=1/BLKTOT
380 BAP6=X(6)/BLKTOT
390 BAP7=X(7)/BLKTOT
400 BAP8=X(8)/BLKTOT
410 AWTBLK=BAP4*A4+BAP6*A6+BAP7*A7+BAP8*A8
420 REM AMT OF BLANK IN MOLES TO BE SUBTRACTED IS SUBBLK
430 SUBBLK=X(9)/AWTBLK
440 NEW4=MOL4-SUBBLK*BAP4
450 NEW6=MOL6-SUBBLK*BAP6
460 NEW7=MOL7-SUBBLK*BAP7
470 NEW8=MOL8-SUBBLK*BAP8
480 SAM1=NEW6/NEW4
490 SAM2=NEW7/NEW4
500 SAM3=NEW8/NEW4
510 S(1,J)=SAM1
520 S(2,J)=SAM2
530 S(3,J)=SAM3
540 X(J)=X(J)-Y(J)
550 NEXT J
1000 REM ERROR SUMMATION
1010 PRINT "ERRORS> .5%, I,J"
1020 FOR I=1 TO 3
1025 E=0
1030 FOR J=1 TO 9
1040 IF Y(J)=0 THEN 1090
1050 IF ABS(S(I,J)-S(I,0))<.005*S(I,0) THEN 1080
1060 PRINT I,J
1070 E=E+(S(I,J)-S(I,0))^2
1080 NEXT J
1090 S(I,1)=SQR(E)
1100 NEXT I
1120 PRINT
1130 LPRINT
1140 PRINT "RESULTS AND ERRORS FOR "A$":"
1150 LPRINT "RESULTS AND ERRORS FOR "A$":"
1160 PRINT "BLANK CORRECTED RATIOS 6/4, 7/4, 8/4" S(1,0),
S(1,1),S(2,0),S(2,1),S(3,0),S(3,1)
1170 LPRINT "BLANK CORRECTED 6/4, 7/4, 8/4 RATIOS"S(1,0),
S(1,1),S(2,0),S(2,1),S(3,0),S(3,1)
1180 PRINT "MORE DATA , INPUT Y=1, N=2"
1190 INPUT N
1200 IF N=1 THEN 71
D.7 CONCORD

10 REM PROGRAM CONCORD TO CALC ERRORS ON COORDS
20 REM USING TATSUMOTO PRIMORDIAL LEAD
30 REM 6/4=9.307, 7/4=10.294
70 DIM X(12), Y(12), S(5,12)
75 X(4)=9.307
76 Y(4)=.001
77 X(5)=10.294
78 Y(5)=.001
89 PRINT "TYPE IN SAMPLE NAME"
90 INPUT A$
100 PRINT "TYPE IN 6/4, ERROR"
110 INPUT X(1),Y(1)
120 PRINT "TYPE IN 7/4, ERROR"
130 INPUT X(2),Y(2)
140 PRINT "TYPE IN MU, ERROR"
150 INPUT X(3),Y(3)
151 FOR I=1 TO 2
152 FOR J=0 TO 5
153 S(I,J)=0
154 NEXT J
155 NEXT I
156 X(0)=0
157 Y(0)=0
158 FOR J=0 TO 5
159 X(J)=X(J)+Y(J)
160 REM COORDS ARE GIVEN AS FOLLOWS
170 P6U8=(X(1)-X(4))/X(3)
180 P7U5=((X(2)-X(5))/X(3))*137.88
190 S(1,J)=P6U8
200 S(2,J)=P7U5
540 X(J)=X(J)-Y(J)
550 NEXT J
1000 REM ERROR SUMMATION
1010 PRINT "ERRORS>.5%, I,J"
1020 FOR I=1 TO 2
1025 E=0
1030 FOR J=1 TO 5
1040 IF Y(J)=0 THEN 1090
1060 IF ABS(S(I,J)-S(I,0))<.005*S(I,0) THEN 1080
1070 PRINT I,J
1080 E=E+(S(I,J)-S(I,0))^2
1090 NEXT J
1100 S(I,1)=SQR(E)
1110 NEXT I
1120 PRINT
1130 LPRINT
1140 PRINT A$,S(1,0) S(1,1),S(2,0) S(2,1)
1180 PRINT "MORE DATA , INPUT Y=1, N=2"
1190 INPUT N
1200 IF N=1 THEN 75
1210 END
D.8 MUCALC

10 REM PROGRAM MUCALC TO CALC MU AND ITS ERROR
20 DIM X(3),Y(3)
30 PRINT "TYPE IN UPPM, ERROR"
40 INPUT X(1),Y(1)
50 PRINT "TYPE IN 204PB MICROMOLES, ERROR"
60 INPUT X(2),Y(2)
70 REM BEGIN CALCULATIONS - FIRST CALC 238U MICROMOLES
80 U8=X(1)*.9928
90 U8=U8/238.0291503#
100 Y(1)=(Y(1)*.9928)/238.0291503#
110 ERR1P=Y(1)*100/U8
120 ERR2P=Y(2)*100/X(2)
130 MU=U8/X(2)
140 Y(3)=(ERR1P)^2+(ERR2P)^2
150 Y(3)=SQR(Y(3))
160 Y(3)=(MU*Y(3))/100
170 PRINT "MU IS"MU,"ERROR IS "Y(3)
180 PRINT "AGAIN? Y=1,N=2"
190 INPUT Y
200 IF Y=1 THEN 30
210 END
Mixing of crustal and mantle lead in the sources of island arc magmas has been documented by several authors and has been found, in this thesis, to be a reasonable explanation for the isotopic signatures of the Karmutsen Formation and the Island Intrusions. Generally, mixing relationships are found by discovering linear relationships in the initial lead isotope data. Often, however, uranium and lead determinations are not made, so the initial ratios can not be determined (\(\mu\) values are required to calculate initial ratios), or the initial ratios are unreliable due to the mobility of uranium and lead. A simple technique, described here, projects \(207\text{pb}/204\text{pb}\) ratios along isochrons to a reference value of \(206\text{pb}/204\text{pb}\) may be used in order to determine relative enrichment or depletion of \(207\text{pb}/204\text{pb}\) in a suite of rocks. The degree of enrichment or depletion can then be used to decipher mixing relationships in the isotope data.

The \(207\text{pb}/204\text{pb}\) ratio is singled out for projection because it is the most indicative of relative crustal involvement in
volcanic rocks that originate in the mantle. Paleozoic or younger additions of radiogenic 207Pb are small due to the relatively small proportion of 235U remaining, in comparison to 238U and 232Th. Any significant differences in 207Pb/204Pb ratios between reservoirs must be due to long term differences in isotopic history. High 207Pb/204Pb ratios are generated in continental rocks due to long term (greater than 2 Ga) high $\mu$ evolution. Mantle lead, on the other hand has low 207Pb/204Pb ratios because the evolution took place in a low $\mu$ environment and increases in $\mu$ have occurred relatively recently (less than 2 Ga). It is, therefore, useful to order a rock suite by rank of 207Pb/204Pb. The projection technique described here standardizes all 207Pb/204Pb ratios by projecting them onto a single value of 206Pb/204Pb. This lessens the effects of in situ lead evolution, allowing the original 207Pb/204Pb ordering to be seen, even if the absolute initial ratios are not known.

In order to determine the projected value, the age of the rocks must be known by isotopic or palaeontological methods. The slope of the isochron along which the projected (and initial) ratio must lie, can then be calculated using the secondary isochron equation of Kanasewich (1968), equation 1:

$$\text{Slope } M = 1 \times \frac{(e^{\lambda_1 t_1} - e^{\lambda_2 t_2})}{137.88 (e^{\lambda_1 t_1} - e^{\lambda_2 t_2})}$$

where: $\lambda_1 = \text{decay constant for } 238\text{U} = 0.98485 \times 10^{-9}$ (Jaffey et
Figure E.1 Graphical representation of projected values for a rock suite with an age of 220 Ma. Present $^{207}\text{Pb}/^{204}\text{Pb}$ ratios (x's numbered 1 to 5) are projected onto a $^{206}\text{Pb}/^{204}\text{Pb}$ reference value of 19.0. Slope of projection vectors is uniquely calculated using equation 1, with $t_1 = 220$ Ma and $t_2 = 0$ Ma.
\lambda_2 = \text{decay constant for } ^{235}\text{U} = 0.155125 \times 10^{-9} \text{ (Jaffey et al. 1971)}

t_1 = \text{age of the rock}

t_2 = \text{zero Ma (time of analysis)}

The isochron is projected through the present \(^{207}\text{Pb}/^{204}\text{Pb}\) value until it intersects a reference value of \(^{206}\text{Pb}/^{204}\text{Pb}\). This point of intersection is the projected value. Figure E.1 illustrates the determination of projected values for samples from a rock unit with an age of 220 Ma, and a reference \(^{206}\text{Pb}/^{204}\text{Pb}\) value of 19.0.

Figure E.2 shows both present (Chapter 3: Table 3.2) and projected (Table E.1) \(^{207}\text{Pb}/^{204}\text{Pb}\) ratios for samples from the Karmutsen Formation plotted against 1/Pb. No linear relationship is apparent between the present values (x's) and lead concentration, but a negative correlation is apparent when the projected \(^{207}\text{Pb}/^{204}\text{Pb}\) values (triangles) are used. The same negative correlation is illustrated using the initial \(^{207}\text{Pb}/^{204}\text{Pb}\) values in Chapter 3. Only five initial ratios were used in Figure 3.9b, because these were the only samples with measured uranium and lead concentrations. Projected \(^{207}\text{Pb}/^{204}\text{Pb}\) values can be determined for all samples for which lead isotopic compositions have been determined. Figure E.2 shows that
Figure E.2 Present 207Pb/204Pb (crosses) and projected 207Pb/204Pb (open triangles) versus 1/Pb (ppm) for Karmutsen Formation rock samples (cf Chapter 3). The line shown is the best fit line to the projected data and has a correlation coefficient of 0.70.
TABLE E.1  

<table>
<thead>
<tr>
<th>SAMPLE NAME</th>
<th>PROJECTED 207Pb/204Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>K005</td>
<td>15.602</td>
</tr>
<tr>
<td>K007</td>
<td>15.569</td>
</tr>
<tr>
<td>K008</td>
<td>15.547</td>
</tr>
<tr>
<td>K101-1</td>
<td>15.645</td>
</tr>
<tr>
<td>K101-2</td>
<td>15.611</td>
</tr>
<tr>
<td>KAR1</td>
<td>15.583</td>
</tr>
<tr>
<td>KAR2</td>
<td>15.598</td>
</tr>
<tr>
<td>KAR7</td>
<td>15.569</td>
</tr>
<tr>
<td>KAR10</td>
<td>15.571</td>
</tr>
<tr>
<td>KAR11</td>
<td>15.585</td>
</tr>
<tr>
<td>S1AM</td>
<td>15.627</td>
</tr>
</tbody>
</table>
projected $^{207}\text{Pb}/^{204}\text{Pb}$ values are just as useful as initial ratios in revealing the linear relationship between lead concentration and isotopic composition.