LEAD SYSTEMATICS OF THE SUDBURY NICKEL ORES: SUDBURY, ONTARIO, CANADA

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LEAD SYSTEMATICS OF THE SUDBURY NICKEL ORES: SUDBURY, ONTARIO CANADA

by

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ABSTRACT

Lead isotope ratios have been determined by a VG.354 thermal ionization mass spectrometer on Sudbury Igneous Complex sulphide ores. The isotopic ratios are contrasted with the lead isotope profile of selected country rocks in the vicinity of the complex. South Range data form a linear array whose slope indicates an age of approximately 1.85 Ga, the published age of the igneous complex. They also indicate a magmatic origin for lead in the ore. North Range data describe a parallel isochron, with lower ²⁰⁶Pb/²⁰⁴Pb and 207Pb/204Pb ratios. The South and North Range data are similar to the lead-isotope composition of country rocks close to them, and indicate rather different crustal-source rocks for sulphide ores in these regions of the complex. This fact suggests that the Sudbury Igneous Complex was generated by a meteorite impact which occurred at the edge of the Huronian succession overlying the Southeast edge of the Superior Province.

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CHAPTER 1

INTRODUCTION

1. GENERAL STATEMENT

The decay of uranium and thorium to stable isotopes of lead has proven to be of value in determining the history, processes and sources involved in the formation of ore deposits.

In this study, Pb abundance and isotopic ratio determinations have been successfully achieved by thermal ionization-mass spectrometry for samples analysed for Re/Os (Dickin et al., 1992; Beneteau. 1990) and other samples collected from the Sudbury Igneous Complex (hereafter abbreviated SIC).

Sm-Nd and Re-Os isotopes provide strong support for the crustal origin of the SIC. However, they cannot resolve components from two crustal reservoirs which may be involved in the genesis of the complex, namely the Levack gneisses and the overlying units of the Huronian super group. Firstly. the sedimentary strata of the Huronian super group were largely derived by erosion of the Superior basement. also. igneous units within the Huronian succession were contaminated by the Superior basement. The Sm/Nd system is significantly fractionated by such intra-crustal not differentiation processes, while the preliminary Re/Os data

available suggest very variable but overlapping isotope ratios in the two crustal reservoirs.

However, it has been demonstrated that the U/Pb system is one isotopic system very sensitive to intra-crustal differentiation. This system is fractionated during high-grade metamorphism to yield uranium-depleted lower crustal gneisses, as well as a uranium-enriched upper crust of the Huronian super group. Over time these systems should generate different lead isotope profiles in the two crustal reservoirs which may be involved in the genesis of the SIC.

The Sudbury igneous complex was chosen as a test because, this complex has been the centre of many geologic controversies and its origin is still discussed.

1.1 Theoretical Background.

A detailed discussion of the theoretical basis and the isotope geochemistry of Pb, Th, and U has been provided in detail by Doe (1970), Faure (1977, 1986). Lead, atomic number 82, is the most metallic of the group IV-B elements. Lead forms a divalent ion having a larger radius than uranium and thorium and has four naturally occurring isotopes: ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁶Pb. The latter three are radiogenic as a result of radioactive decay, with ²³⁶U producing ²⁰⁶Pb, ²⁰⁵Pb and ²⁰⁷Pb and ²⁰²Th generating ²⁰⁶Pb. The ²⁰⁴Pb has no long-lived radioactive parent and is often used as a stable reference isotope. The modes of decay are complex.

each parent-daughter series involving many relatively short-lived radioactive intermediate daughters before the stable Pb isotope is reached. Intermediate daughter products are not important for this discussion. The relative abundance of the three radiogenic isotopes are generally expressed as ratios with ²⁰⁴Pb such as ²⁰⁶Pb/²⁰⁴Pb. The rate of radioactive decay of the parents given by the half-lives t1/2 differ significantly. Abundance, half-lives and decay constants of the principal naturally occurring isotopes of uranium and thorium are given in Table 1.1).

Uranium has atomic number 92 and is now known to be the third member of the Actinide series of elements. Uranium (Z=92) (Z=90) and thorium have similar geochemical properties. They both form tetravalent ions with similar ionic radii (U^{+4} = 1.5 A°; Th⁺⁴ = 1.10 A°) and thus substitute for each other. which accounts for their geochemical coherence.

The U-Th-Pb isotopic system can potentially yield information about the mean ages, as well as information about the very early history of the earth, since the half lives in this system range from 0.7 Ga to 14 Ga. The first reliable age of meteorites (4.5 Ga) was a lead isochron age (Patterson, 1956; Murthy & Patterson, 1962).

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1.2 Geochemical Behaviour of Uranium, Thorium and Lead.

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Uranium, thorium and lead belong to the group of the large-ion lithophiles (while lead has strong chalcophillic tendencies) which were accumulated predominantly in the crust and fractionated significantly during the earth's history. Their concentration in the mantle is lower. Upper crustal rocks are enriched in U compared to lower crustal or mantle rocks (Doe, 1970). Uranium is preferentially mobilized from the lower continental crust during high-grade metamorphism and accumulates in the upper crust. This causes the crust to become stratified in U/Pb ratio.

According to Armstrong (1968), 68% of U, 79% of Th, and 53% of Pb are concentrated in the crust. On the other hand, when compared to the depleted mantle, Allegre et al. (1988) estimated that 80% of uranium, 70% of lead and 90% of thorium now reside in the continental crust.

The most extensive account of the occurrence and distribution of lead and uranium in igneous metamorphic and sedimentary rocks has been described in detail by Wedepohl (1978). The values are given in Table 1.2. The increase of lead concentrations from ultrabasic to granitic rocks is almost as steep as that of uranium. Therefore, the U/Pb ratio of the common magmatic rock units is rather uniform, although it decreases slightly from granitic to ultrabasic rocks. The average lead content of argillaceous sediment (20 ppm) and granitic rocks (23 ppm) is only slightly higher than that of granulites.

The upper continental crust mainly consists of magmatic intrusives and metamorphic rocks, and minor sedimentary material buried during a thrusting event (Wedepohl, 1978). The lower continental crust consists mainly of high-grade metamorphic rocks of intermediate chemical composition. These rocks are relatively depleted in U (Lambert & Heier, 1967), but probably not in Pb.

Table 1.1. Abundances, half-lives and decay constants of the principal naturally occurring isotopes of Uranium and Thorium (modified from Faure, 1986).

ISOTOPE	ABUNDANCE	HALF-LIFE (years)	DECAY CONSTANT (per year)
2380	99.2743	4.468 x 10°	1.55125 x 10-10
2350	0.7200	0.7038 x 10°	9.8485 x 10-10
234U	0.0057	2.47 x 10 ⁵	2.806 x 10-6
232Th	100.0000	1.401 x 10 ^e	4.9475 x 10 ⁻¹¹

Table 1	1.2.	Average	cond	centrations	; of	the	РЬ	and	U	ratio
		in igneo	us,	sedimentar	y a	nd m	etan	norph	nic	rocks
		(Wedepoh	1, 1	1978).						

ROCK TYPE	Pb	(bbw)	(mqq) U
Ultra basic		3	0.014
Basic		6	0.4
Intermediate (calcalkaline)		10	1
Intermediate (alkaline)		12	6
Granodiorite		15	2.6
Granite		23	3.9
Granulite		18.7	1.4
Argillaceous sediment		20	4
Arenaceous sediment		7	0.45
Calcereous & dolomitic sediments		9	1.95
Troilite		5.9	0.009
Ordinary chondrites		0.45	0.01
Achondrites		0.44	0.07

1.3. The Geology of the Sudbury Igneous Complex.

The general geology of the Sudbury basin is illustrated in Figure 1.1. Many of the details can be found in Pye et al. The Sudbury Ianeous Complex (SIC) is the world's (1984). greatest producer of nickel, and is located in the southern Canadian Shield between the early Proterozic Huronian supra crustal rocks of the Southern province and the Archean rocks of the Superior province. The Sudburv plutonic structure has an elliptical outcrop pattern, approximately 27 kilometres on its short axis and about 60 kilometres on its long axis. This is due to tectonic shortening in a northerly direction during the Penokean and subsequent orogenies (Rousell, 1984) by Southerly dipping thrusts, defined recently in seismic images (Milkereit et al.. 1992). This thrusting event is responsible for several faults (parallel to the strike of rock units within the central Sudbury basin) cutting across the SIC from the Southwest to the Southeast (Dressler, 1984b).

The SIC is a differentiated and layered tholeiitic intrusion (Naldrett et al., 1970), which is overlain by the Onaping Tuff and underlaid by a "contact sublayer" (Naldrett et al., 1984) which is composed of differentiated norite, sulphide-bearing ore and brecciated rock. A lower zone of norite, a middle zone of quartz gabbro and an upper zone granophyre make up its "main mass".

Figure 1.1 Geological setting of the Sudbury Intrusive Complex relative to the three nearby geological provinces. The main mass of the complex is hatched. (From Pye et al., 1984)

Mines:	Creighton	=	()
	Falconbridge East	=	()
	Strathcona	=	()
	Whistle Pit	=	()
Silicates:	Main Mass	=	()
	Onaping Tuff	=	()
	Huronian	=	(•)
	Nipissing Diabase	=	(\diamond)
	Levack Gneiss	=	(¥)
	Sudbury Breccia	=	(Ó)
	Archean Granite	=	($\check{\bigtriangleup}$)



Φ

The sublayer is the lower-most unit of the Igneous and intrudes along the contact between the main mass Complex of the Complex and the footwall rocks as discontinuous lenses, sheets and embayments referred to as the "contact sublayer" (Naldrett et al., 1984) and forms several dikes (quartz-diorite) in the surrounding rocks known as offset dikes. Indeed, it hosts many of the nickel-copper ore bodies of the Sudbury area. Pattison (1979) described the sublaver in general and Naldrett et al. (1984) described the contact sublayer in detail. Grant & Bite (1984) have documented the field and major element characteristics of the offset dikes. They suggested a genetic relationship between the offset dikes and the main mass magma. The contact sublayer and the offset dikes are composed of gabbro to guartz diorite and feature two main groups of inclusions (Naldrett et al., 1984).

Inclusions in the contact sublayer are chiefly derived from the footwall rocks (felsic gneiss, quartzites, and amphibolites) and those composed of mafic and ultramafic rocks (Scribbins et al., 1984). Mafic and ultramafic inclusions are derived from hidden layered intrusions that have fractionated at moderate depths in the crust (Scribbins et al., 1984). Naldrett (1984) has suggested that these hidden intrusions are related genetically to the SIC.

Geologists are not in agreement about the correct geological interpretation of the Sudbury Igneous Complex.

Its origin, structure and associated ores have long been a subject of controversy (Pye et al., 1984). Opinions are divided between an endogenic volcanic explosion (Speers, 1957; Muir, 1984) and meteorite impact (Dietz, 1964; French, 1968, 1970; Peredery & Morrison, 1984). Various features of the SIC, such as the extreme brecciation of country rocks around the Complex, the presence of shock metamorphic features in the Onaping formation and in the footwall rocks, and overturned strata at the rim of the structure were argued by Dietz (1964) to support an origin by meteorite impact. Peredery (1972) developed this model by proposing that the Onaping formation was a fallback breccia resulting from the impact.

1.4. Geochemistry and isotope geochemistry of the Sudbury Igneous Complex.

1.4.1. Geochronology.

The age relationships in the Sudbury structure are exceedingly complex, as different events in the past have occurred in it, and since it lies at the "junction" of three structural provinces of the Canadian Shield. In particular, the Superior, Southern and the Grenville provinces were affected by Penokean and Grenville orogenies (see Figure 1.2).

Numerous geochronologic studies have been carried forth in the Complex. The first important isotopic age results for Sudbury structure were based on the K-Ar and Rb-Sr the methods, involving both mineral and whole-rock ages. Later studies focused on using U-Pb determinations on zircon baddeleyite. Earlier norite biotite analyses by Aldrich et (1959) give consistent K-Ar and Rb-Sr ages of about 1770 al. Myr. Rb-Sr whole-rock analysis by Faure et al. (1964) found an age for the norite granophyre of about 1704 ± 19 Myr. Fairbairn et al. (1968) obtained an Rb-Sr whole rock age for samples of granophyre and norite at about 1705 ± 19 Myr. A similar age of 1785 ± 126 Myr was obtained for the felsic norite by Hurst & Wetherill (1974). Rb-Sr studies of the SIC by Gibbins & McNutt (1975a) yield an age of 1680 ± 30 and 1956 + 98 Myr for the granophyre and norite, respectively, whereas Hurst & Farhat (1977) reported a Rb-Sr norite whole Figure 1.2

Location of the Sudbury Structure with respect to structural province boundaries and major fault systems. (From Card and Hutchinson, 1972.)



rock age of 1883 ± 136 Myr. An age of 1850 ± 1 Myr, obtained on U-Pb zircon and baddeleyite separated from the norite and granophyre respectively (Krogh et al., 1984), is perhaps the best age yet determined. U/Pb data are reliable because they were analyzed on abraded zircons (Krogh, 1982).

1.4.2. Isotopic Geochemistry.

In the literature there are two main interpretations of the One interpretation is that isotopic geochemistry. the Complex crystallized primarily from mantle-derived basaltic magma that was crustally contaminated (Kuo & Crocket, 1979; Naldrett & Hewins, 1984; Naldrett et al., 1986; Naldrett & et al., 1991). Evenson. 1987; Walker The other interpretation is that the Sudbury Complex is overwhelmingly crustal and no direct mantle-derived component was apparently involved in its origin (Ding & Schwarcz, 1984; Faggart et al., 1985; Deutsch et al., 1990; Dickin et al., 1992). However, there have been doubts about the nature of the crustal component in the Complex, since it is located between the Superior province to the north and northwest and overlying sediments (Huronian super group) to the south and southeast.

Faggart et al. (1985) presented Nd isotope data for the silicate rocks of the SIC, showing that they contained remarkably strong crustal signature, with an epsilon value at 1.85 Ga averaging -7.5. They interpreted this to

mean that the Complex crystallized from a melt with homogeneous Nd isotopic systematics. Naldrett et al. (1986) noted a more heterogeneous Nd isotope with epsilon values ranging from -5 to -9; accordingly, they preferred a "mixing model", which indicates a mantle-derived magma mixing with "partial" impact melting of crustal lithologies in the Superior province of the Sudbury region.

Dickin et al. (1992) presented a compilation of previous Nd isotope data for different Sudbury mines and possible country rock sources (see Figure 1.3). These results demonstrated that the silicate rocks from these mines are consistent with a model of 100% crustal derivation of the SIC, either from the Levack gneisses in the Superior province or a mixture of sedimentary and metavolcanic rocks from the Huronian supra crustals of the Southern province.

Recent Re/Os isotopic studies of sulphide ores from four Sudbury mines also indicated a crustal signature (Walker et al., 1991; Dickin et al., 1992). Initial Os isotope data from these mines, along with Levack gneiss and Huronian super group data at 1.85 Ga are presented in histogram form in Figure 1.4. The data from the Creighton, Levack West and Falconbridge mines are consistent with 100% crustal source from these country rocks. In contrast, the Strathcona

Figure 1.3

Histogram of calculated Neodymium (Nd) isotopic data for silicate samples from sublayer ores and for country rocks at 1.85 Ga.

N=Nipissing diabase, L=Huronian Lavas, S=Huronian Sedimentary Formations, Stars=depleted mantle composition at 1.85 Ga.

(After Dickin et al., 1992)



mine is not generally consistent with this model. Dickin et al. (1992) have argued that gross disturbances of Re-Os systems were obvious after 1.85 Ga, and they excluded the Strathcona mine from consideration on these grounds.

The ^{e7}Sr/^{ee}Sr (T = 1.85 Ga) ratios of the Igneous Complex (Gibbins & McNutt, 1975; Hurst & Farhat, 1977; Rao et al., 1984) are somewhat higher than the mantle-derived magma and implies that the complex-producing magma was a crustal melt prior to crystallization. On the basis of their REE study, Kuo & Crocket (1979) indicated significant amounts of crustal interaction.

Isotopic and geochemical studies have indicated that the rocks and ores of the SIC have a crustal signature. The mechanism by which this catastrophic event occurred, an endogenic volcanic explosion or meteoritic impact, is still discussed.

Figure 1.4 Histogram of calculated osmium (Os)
isotopic data for sulphide ores and
country rocks at 1.85 Ga.
Double boxes represent the range of
values found in replicate analysis of
ores. Crustal units are as follows:
Solid boxes = Walker et al., 1991
LG = Levack gneiss
Gow = Gowganda Formation

Open boxes = Dicken et al., 1992

MK = McKim fm

ST = Stobie formation.



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CHAPTER 2

SUDBURY ORES

2.1 Introduction

As mentioned in Chapter 1 and shown in Figure 1.1, the ores of Sudbury are located at the margin of the Sudbury Igneous Complex, whose major faults divide the Complex and its environment into the North Range and South Range areas.

Naldrett (1984) subdivided the deposits into five groups, as follows:

- (1) South Range deposits
- (2) North Range deposits
- (3) Offset deposits
- (4) Fault-related deposits, and
- (5) Miscellaneous deposits

In this study, sulphide ores were analyzed from the Creighton mine (a typical example of South Range deposits), from the Falconbridge East mines of the South Range which belong to the so-called "fault-related deposits" and from the Strathcona mine and Whistle Pit of the North Range (see Figure 1.1). The collection and preparation of the samples is discussed in Chapter 3 below, while the analytical results may be found below in Table 5.1 and the sample descriptions can be found in Appendix A.

The Sudbury ore deposits are unique and constitute the largest known concentration of nickel-copper sulphides on earth. Their genetics have been studied by many authors and were thought to be magmatic in origin (e.g., Hawley, 1965; Naldrett et al., 1984) or of hydrothermal origin (Phemister, 1925; Yates, 1938, 1948). Naldrett (1984) advocated a magmatic origin of the mineralization in which sulphide precipitation was triggered by the contamination of a mafic magma through the assimilation of SiO2-rich country rock. Dietz (1972) suggested that the sulphide ores represent meteoritic material. They could alternatively represent an aggregation of pre-existing sulphide phases from melted country rocks, or might be derived from small components of a mantle-derived melt, generated by decompression melting.

2.2 The Creighton Mine

2.2.1. Geology.

Creigton mine is located in the South Range, on the southern limb of the SIC (see Figure 1.1). The massive ore body at Creighton has the largest number of ore varieties (Souch et al., 1969) and includes a series of individual sheet-like ore bodies that extend downward to a depth of approximately 3 kilometres (Yates, 1948; Souch et al., 1969) and a trough-like depression at the base of the Sudbury Igneous Complex (SIC).

The Creighton ore zone has been described in detail by Hewley (1962) and Souch et al. (1969). The ore zone is shown in detail in Figure 2.1 below and consists of three ore types. Quartz-rich norite irregularly comes into contact with the underlying ore zone or sublayer, and occasionally contains enough minor sulphide to form low-grade ore. In the upper part of the sublayer, disseminated sulphide ores occur, but becomes more massive toward the lower contact and is intruded into the footwall rocks of Elsie Mountain greenstone and Creighton granite. The massive ore deposits contain large angular xenoliths of the country rock lithologies and norite, along with exotic gabbroic ultramafic inclusions such those described by Scribbins et al. (1984). as Both magmatic textures and textures suggestive of assimilation are common. The ore is associated with a shear zone in the

norite above, which passes into the underlying rocks (all see Figure 2.1).
Figure 2.1 Geologic setting; Creighton mine looking west. After Souch et al., 1969.



2.2.2. Sampling.

Massive and disseminated ores were sampled from both the 4200 7200-foot levels and from а variety of different environments. This was done in an attempt to test for al., 1992) and for lead isotope initial osmium (Dickin et heterogeneity of the ore (this study). Sample descriptions and localities are given in Appendix A.1.

2.2.3. Isotope Geochemistry of the Creighton Ore.

Dickin et al. (1992) presented a compilation of initial neodymium-isotope data for the Creighton samples (Figure 2.2). These are age corrected. It can be seen that the silicate rocks associated with the sublayer ores from Creighton mine are consistent with a model of 100% crustal derivation of the SIC, from a mixture of sedimentary and metavolcanic rocks from the Huronian units.

Re/Os isotope results from the sulphide ores of Creighton mine also strongly point to a crustal sionature al.. 1991: Dickin et (Walker et al.. 1992). Initial Os-isotope data from the Creighton mine fall within the range of estimated crustal compositions at 1.85 (see Figure Ga 2.3). Double-lined boxes represent the total range of initial ratios determined by duplicate analyses of the same sample.

The agreement of the initial ratios ¹⁰⁷Os/¹⁰⁰Os (T = 1.85 Ga) from disseminated sulphide and contact-sublayer samples from Creighton is good evidence that the main mass and the contact sublayer are cogenetic. This agrees with previous geochemical evidence that the sulphide and silicate melts were cogenetic (Naldrett, 1984). Initial ¹⁰⁷Os/¹⁰⁰Os ratios of the Creighton mine cluster around 0.6 with a few lower initial ratios (see Figure 2.3). This distribution to lower initial ratios does not correlate with the lithological environment, thus Dickin et al. (1992) suggested that the low ratios are accounted for by the loss of radiogenetic osmium, probably associated with mid-proterozoic or Grenville orogenic events.

Figure 2	2.2	Histo	gram	of	calc	ula	ted	neod	ymiur	n (No	D)
		isoto	pe d	ata	for	sil	icat	e sa	mple	s fro	om
		Creiq	hton	Min	e an	d f	or c	ount	ry re	ocks	\mathbf{at}
		1.85	Ga.								

N = Nipissing diabase

L = Huronian lavas

- S = Huronian sedimentary formations
- Stars = depleted mantle composition at

1.85 Ga (after Dickin et al., 1992)



Figure 2.3 Histogram of calculated osmium (Os) isotopic data for Creighton sulphide ores and country rocks at 1.85 Ga (after Dickin et al., 1992)



2.3 Falconbridge East mine

2.3.1. Geological setting.

Falconbridge East mine ore deposits occur at the Southeastern margin of the Sudbury Igneous Complex (SIC) in Falconbridge Township (Figure 1.1). The deposits occur within fault zones between the base of the SIC and the metavolcanic and sedimentary rocks of the Stobie Formation in the lower Huronian group (see Figure 2.4).

The Falconbridge East mine deposits have been described by Davidson (1948) and Lochhead (1955). Much of the ore at Falconbridge is emplaced along faults, and the ore zone dips steeply north to vertical in the upper levels and vertical to 70 degrees in the middle and lower levels. The ore body is a narrow sheet of sulphides within the contact between the main mass norite and metavolcanic rocks of the Stobie Formation (see Figure 2.5).

Lochhead (1955) suggested that the fault was active during the crystallization of the SIC. The ore zone at the East mine varies in width from a few centimeters to 28 meters with an average of about 5 meters in width, and is composed of pyrrhotite, pentlendite and chalcopyrite (Davidson, 1948). Figure 2.4 Geology and location of the Falconbridge East mine, Falconbridge Township (after Burrows & Rickaby, 1934; from Beneteau, 1990).





STREET

Twp.

Figure 2.5 Cross-section through the Falconbridge East mine showing geological relationships and dominant lithologies (after Davison, 1948; from Beneteau, 1990)

Also shown is the approximate location of the sample transect.

(See Appendix A.1)



2.3.2. Sampling.

Samples were collected on a traverse which cross-cut the quartz-rich norite, the sublayer at the Falconbridge East open pit mine and the contact Stobie Formation (see Figure 2.6) (Beneteau, 1990). Sample descriptions are given in Appendix A.1. Selected samples (less disturbed Re/Os isochron systematics) were analyzed. Seven sublayer ores (F2, F3, F4, F5, F6, F24, F28), one disseminated ore in norite (F1) and one sample from the Stobie Formation (F22), are chosen from Figure 2.6.

2.3.3. Isotope Geochemistry of the Falconbridge Mine.

Recent studies have postulated that the sulphide ores from Falconbridge East mine have a large crustal component. Analysis of sulphide ores has yielded initial '*70s/'**0s ratios of about 0.54 for samples interpreted as undisturbed since the formation of the SIC (Beneteau et al, 1991). Some of the sublayer ores have disturbed Re/Os isochron systematics (Beneteau, 1990; Beneteau et al., 1991), possibly due to the effects of the Grenville orogeny (see Figure 2.7).

Beneteau (1990) has suggested that the Re/Os isotopic systematics at the Falconbridge East mine recorded at minimum three geological processes. First, there was contamination of an ultramafic magma with crust material to yield a mafic magma with a strongly radiogenic crustal signature. Secondly, there was crystallization of the sublayer sulphides. And finally, there was alteration by fluids during the Grenville orogeny. He also mentioned that the strongly radiogenic initial 1070s/1000s ratio of 0.54 ± 0.10 rules out principal derivation of the ore from the mantle or from meteoritic sources (see Figure 2.7).

Instead, the data have shown that 60-70% of the Os in Falconbridge East ores is of crustal origin. Similar results were obtained by Walker et al. (1991) who proposed that the composition of the ores suggested a process of mixing between mantle-derived magma and Levack gneiss. However, the undisturbed ores fall entirely within the envelope of the estimated crustal compositions (Figure 2.8). Owing to that, Dickin et al. (1992) did not agree with this model and argued instead that the ores could be derived entirely by crustal melting.

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Figure 2.6 Schematic diagram illustrating host lithologies of the Falconbridge East Mine. Diagram also delineates sample locations (from Beneteau, 1990).



Figure 2.7 1070s/1000s vs. 107Re/1000s isochron diagram for Chalcopyrite and magnetic (pyrrhotite-pentlandite) separates from the Falconbridge East mine, Sudbury. Errors are 20 and plot within the symbols. Circled symbols represent samples not used in regressions (from Beneteau, 1990).



Figure 2.8 Histogram of calculated osmium (Os) isotopic data for (Falconbridge) sulphide ores and country rocks at 1.85 Ga (from Dickin et al., 1992).



 $^{\omega}_{4}$

2.4. Strathcona mine.

2.4.1. Geological setting.

The Strathcona mine is located in Levack Township on the northern margin of the Sudbury Igneous Complex (see Figure 1.1). The geology of the deposit has been documented by Naldrett & Kullerud (1967), Cowan (1968), and Abel etal. (1979). Cowan (1968) has described the ores at Strathcona mine and subdivided them into three major ore zones. The hanging-wall ores occur in a norite with local xenolith-rich ores, and the main zone occurs in a late granite breccia, a tectonic breccia containing many footwall gneiss fragments and norite. Finally, the deep ore zone lies well below the base of the norite, and is completely emplaced in the granitic gneiss complex by the injection of a sulphide magma to form a mass of stream veins which locally make high-grade This deep ore zone represents a deposit that ore. has remained tectonically undisturbed since the time of its original settling (Naldrett & Kullerud, 1967). The deep ore zone contains a higher percentage of chalcopyrites and nickeliferous pyrrhotites, pentlandites, magnetites and different zoning patterns of the nickel represents in sulphides than in the main zone (Naldrett & Kullerud, 1967).

Figure 2.9 is a schematic showing a vertical section thorugh the Strathcona deposit. The sublayer (late granite

breccia) with its disseminated sulphides (hanging wall zone breccia) is underlaid by the granitic gneiss complex. Most of the sulphide ore occurs in the deep zone and in late granite breccia.

2.4.2. Sampling.

Strathcona ores examined for this study are chalcopyrite and pyrrhotite separates from the deep ore zone. Sample descriptions and localities are given in Figure 2.9 and Appendix A.2. Figure 2.9 Strathcona Mine, Geological Section showing location of D1 Stope (from Schindler, 1975).

D1 refers to the stope from which the sample was collected (see Figure 2.9).



ω

2.4.3. Isotope Geochemistry of the Strathcona samples.

(1991) have presented a model and suggested Walker et al. that Re/Os isotopic systematics at the Strathcona mine ores indicate open-system behaviour to several tens of millions of vears following magmatic crystallization. Four Strathcona samples repress to give an age less than the accepted age for the Complex. See Figure 2.10. However, this isochron is defined by two types of ores, corresponding to a shallow ore zone and a deep ore zone. Therefore, Walker et al. (1991)suggested that the young "age" may be the result of combining ores that crystallized with slightly different initial Os isotopic compositions. Their modelling suggested that the Strathcona ores are at least 90% crustal in origin.

Dickin et al. (1992) suggested that the large variation of calculated initial osmium isotope ratios in the Strathcona mine is due to post-crystallization, open-system behaviour of the Re/Os system (see Figure 2.11). They suggested also that unradiogenic osmium isotope ratios from the deep ore zone can surely be attributed since to this process. their geochemistry is not consistent with a direct mantle-derived origin. Dickin et al. (1992) also speculated that the Re/Os systematics of the shallow ore zone may have been reset. The effect of this event on Pb-isotope systematics will he discussed later.

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Figure 2.10

1870s/1860s versus 187Re/1860s plot

for Sudbury ores. Data for ores from three mines, Levack West, Falconbridge and Strathcona, define isochron apex of 1840 \pm 60 Ma, 1780 \pm 110 Ma and 1770 \pm 60 Ma, respectively. Error bars are smaller than the size of the symbols, or as shown (after Walker et al., 1991).



ω9

Figure 2.11 Histogram of calculated osmium (Os) isotopic data for Strathcona sulphides, ores and country rocks.

Solid boxes = Walker et al., 1991 Open boxes = Dickin et al., 1992 (after Dickin et al., 1992)



2.5. Whistle Pit.

The Whistle deposit is at the extreme northeast corner of the Sudbury Igneous Complex (SIC)(Figure 1.1). Pattison (1979) has thoroughly documented the geology of this area (Figure 2.12). Sublayer rocks at Whistle Pit filled a funnel-shaped depression in the footwall. The distribution of rock types shows an outward zoning toward the main mass of norite. Along the deposit the contact sublayer is closely associated with rocks that form the different facies of the footwall (Figure 2.12). As the footwall contacts are breccia rock is approached. the sublayer seen to be orthopyroxene-rich and some olivine is present. The Whistle deposit is the only area at Sudbury Basin where olivine has ever been observed in rocks belonging to the SIC (Naldrett et al.. 1984). According to them. xenoliths and sulphide minerals occur throughout the contact sublaver from the oliving-bearing to the guartz-rich contact sublayer: and iron-enrichment is accompanied by an increase in quartz. The samples analysed in this study are from the sublayer sulphides (See Appendix A.2). There is no established information concerning isotopes about the Whistle Pit in the literature.

Figure 2.12 Plan of the Whistle property at the extreme north-eastern corner of the SIC (after Pattison, 1979).



2.6 Main Mass of the Sudbury Iqneous Complex (SIC)

The main mass of the SIC comprises a sequence of a lower unit norite. and an upper unit of granophyre (formerly called of micropegmatite) separated by a transition zone (middle unit) guartz gabbro (Naldrett et al., 1970; Pye et al., 1984; of Dressler, 1984b; Naldrett & Hewins, 1984). Each of these be subdivided and may show differences units mav further between North and South Range varieties (Naldrett et al.. 1970) as illustrated in Figure 2.13) and as described below. The norites of the South Range are different petrologically from the norites of the North Range but the chemistry is similar (Chai & Eckstrand, 1994). The South Range norite is medium-to-coarse grained black rock containing plagioclase a and hyperstheme. as well as guartz, magnetite and augite. The guartz-rich norite is fine-grained and contains guartz and biotite. On the North Range, felsic norite is the main rock type of the lower unit while the mafic norite is at the base of the Complex.

The granophyre of the South Range is very similar to the North Range granophyre. Unlike the norite there are only slight differences in texture or mineralogy due to the generally strong deformation and alteration of the South Range. Granophyre, or "micropeqmatite", is characterized by a fine-grained intergrowth of guartz and alkali feldspar (Barker, 1970), minor amounts of augite, green hornblende, biotite, epidote, chlorite, and opaque oxide minerals. Peredery & Naldrett (1975) have described the granophyre and recognized two distinct rock types, the granophyre-rich phase (termed the "granophyric micropegmatite", typical of the main mass of the granophyre) and the rich plagioclase (termed the plagioclase-rich phase).

The quartz gabbro of the North Range (middle unit) is very similar to the quartz gabbro of the South Range, except that in the former there is more opaque oxide minerals. The other minerals in the unit are placioclase, augite and apatite. Figure 2.13 Comparison and correlation of partially idealized sections through the rocks of the North and South Ranges. The Columns indicate variation in modal composition of the rocks (after Naldrett et al. 1970; from Naldrett & Hewins, 1984).


2.7. Unaping Formation

The Onaping Formation is a 1.6 kilometre thick fragmental succession that consists of breccias and igneous-textured rocks that are divided into three members. From the base upward, they are the Basal member, the Grey member and the Black member (Muir & Peredery, 1984). The contacts are with conformably overlying Onwatin slate and the generally conformable underlying granophyre.

The Basal member consists of medium to coarse breccias consisting of fragments of country rocks. In the North Range, the Basal member is discontinuous. The Grev Onaping consists of abundant anoular to round fragments of country rock, fluidal glass in a very fine-grained formation, and sulphides. The country rock fragments comprise various types derived from the Archean (granitic gneiss rocks) and the Proterozoic (metavolcanic and metasediments). Thece fragments account for about 20-30% of the total volume of the Grey and Black members (Muir & Peredery, 1984). Some fragments are euhedral to subhedral and appear similar to phenocrysts, while others are composite ranges from a few millimetres to a few metres in diameter and comprise combinations of breccia, fluidal-textured material and glass (Muir & Peredery, 1984). The country rock fragments have shock metamorphic features (French, 1968, 1972).

The transition to Black Onaping is of a gradual increase

in the amount of carbonaceous material which imparts a black colour to the rock (Peredery, 1972). The Black Onaping is similar to the Grey Onaping in that the individual units of breccia have similar characteristics. The composite fragments have similar features and the glasses have similar overall characteristics (Muir & Peredery, 1984).

The origin of the Onaping Formation is closely related with the origin of the Sudbury Basin. There has been prolonged controversy as to whether the Onaping is of volcanic origin (Thomson, 1957; Williams, 1957; Stevenson, 1972), or represents impact-generated fall-back breccias and melt bodies (French, 1967; Dence, 1972; Peredery, 1972).

CHAPTER 3

A REVIEW OF COUNTRY ROCKS ADJACENT TO THE SUDBURY IGNEOUS COMPLEX.

3.1. Huronian volcanism and sedimentation in the Southern Provinces.

The Huronian supergroup of the Southern province forms an early Proterozoic assemblage of volcanics and dominantly clastic sediments which lie unconformably on Archean rocks of the Superior province (Stockwell et al., 1970). The results of radiometric dating (Fairbairn et al., 1960; Lowden et al., 1962; Van Schmus, 1965, 1976; Corfu & Andrews, 1986)suggested that the deposition of the supergroup occurred between 2500 Ma and 2219 Ma. The rocks in the area have been affected by orogeny prior to Nipissing magmatism (Pye et al., 1984), the lower amphibolite facies metamorphism during the Penokean orogeny at 1.8-1.9 Ga (Card, 1978), the 1.85 Ga Sudbury event (Krogh et al., 1982), the post-Sudbury event deformation at 1.6 Ga to 1.3 Ga (Shanks & Schwerdtner, 1989), and the 1 Ga - 1.2 Ga Grenville orogeny (Davidson, 1986).

The Huronian samples were collected between the Proterozoic granitoid suite of the Grenville front tectonic zone and the mafic rock of the Sudbury Igneous Complex (SIC) (See Figure 3.1).

The dominant structures of the area are the Murray fault and numerous other faults, and gentle folds. Rocks South of the Murray fault are cut by several faults in parallel with the Murray (Thomson, 1961). On the south side, the Stobie formation and the Elsie Mountain formation are adjacent to the SIC and are followed in turn to the south by the Copper Cliff, the McKim, the Ramsey Lake, and the Mississaqi formations. The Elsie Mountain, Stobie, and Copper Cliff formations represent one major mafic-felsic volcanic cycle. A detailed account of the Southern province can be found in Card et al. (1972). The sample localities and descriptions are shown in Figures 1.1 and 3.1, and in Appendix A.4. Figure 3.1 Sample localities from Huronian super group and Nipissing diabase (from Pye et al., 1984).



3.1.1. Elsie Mountain and Stobie Formations.

The volcanic rocks of the Elsie Mountain and Stobie are lithologically similar to one formations another. consisting of massive and foliated fine- to coarse-grained mafic metavolcanic and lesser amounts of metasedimentary material. The rocks are black to dark green and have a foliated texture. The most dominant minerals are amphibolites (both hornblend and actinolite), variable amounts of guartz, magnesium-rich chlorite, and calcite. Minor constituents include pyrite, magnetite, and sericite (See Appendix A.4). Sulphide minerals occur as disseminations, stratiform layers, and concentrations along joints and fracture surfaces (Innes. 1972). Accordingly, the present mineralogy of the Stobie and Elsie Mountain formations are indicative of upper greenschist to amphibolite facies associated with 1.9 Ga Penokean orogeny (Card, 1964: Zolnai et al., 1984) and/or the emplacement of the sublayer at 1.85 Ga (Krooph et al., 1984).

A sample of the Stobie Formation (H1) was collected near the Murray fault and was found to consist of irregular quartz grains, very fine-grained elements of micaeous minerals and very small and thin pyrite dykes (See Appendix A.4).

3.1.2. Copper Cliff Formation.

The Copper Cliff formation conformably overlies the Stobie formation and is conformably overlain by the McKim Burrows & Rickaby (1934) recognized its volcanic formation. connection and included it with other volcanics of the area. Phemister (1956) described rhyolite of the Copper Cliff formation as granite. The normal rhyolite is grey to pink. medium- to fine-grained, and has a fairly well-developed foliation. The felsic metavolcanics of the Copper Cliff formation are composed of a fine-grained feldspar, guartz and sericite with minor biotite, chlorite, carbonate, epidote, iron oxides and sulphide minerals, mainly pyrite and pyrrhotite.

A sample from the Copper Cliff formation (H2) was collected near the Murray fault. This sample consisted of very fine grained sericite in 60%, 15% guartz and minor constituents are chlorite, muscovite, biotite, magnetite and pyrite. Some alterations are observed in the sample that biotite altered to chlorite. The flow structures of the magnetite and pyrite are in the same direction. All these minerals are the products of metamorphic recrystallization under conditions corresponding to the amphibolite and upper green-schist facies of regional metamorphism.

3.1.3. McKim Formation.

The McKim formation is a thick accumulation of greywacke, siltstone, and aluminous pelite of the uppermost formation in the Elliot Lake group (Robertson et al., 1969a, 1969b). In the Sudbury area, it conformably overlays the Matinenda and Copper Cliff formations. The rocks consist mainly of guartz, muscovite, potassic feldspar, chlorite, biotite and plagioclase.

Samples of the McKim formation (H3 and MKE) were collected near Sudbury and Espanola, respectively. They show similar mineralogy and are composed of subangular to subrounded and irregular guartz in shape, poorly developed plagioclase, fine-grained biotite of irregular shape with irregular orientations, chlorite, and opaque minerals. There are also minor amounts of zircon with pleochroic evidence of halo in the biotite.

3.1.4. Ramsey Lake Formation.

The Ramsey Lake formation (conglomerate) is the lower-most formation of the Hough Lake Group (Roscoe, 1969). It consists mainly of massive or poorly bedded conglomeratic rocks consisting of scattered plutonic rock fragments in a feldspathic grey wacke matrix. The conglomerate generally has much more matrix than pebbles. Card (1978) interpreted the conglomerates of the Ramsey Lake formation to be debris flows. Most of the other researchers recommended a glacial origin (Roscoe, 1969; Robertson, 1976).

A sample from the Ramsey Lake formation (H4) is collected from southeast of Kelly Lake and consists of an approximately 50% quartz matrix which contains very few inclusions, very fine-grained potassic feldspar and weakly altered and coarse-grained plagioclase and lithic fragments are present in about 22% of the sample. Minor constituents of the sample are biotite, chlorite, and sulphide. The chlorite appears to be of secondary, after the biotite.

3.1.5. Mississagi Formation.

The Mississagi formation forms the uppermost unit of the Hough Lake Group (Thomson, 1962). It consists mainly of moderately well sorted, medium-to-coarse grained subarkose to arkose (Long, 1976), composed mainly of quartz with variable amounts of plagioclase, potash feldspar, biotite, muscovite, chlorite and rock fragments.

Samples of from the Mississagi formation (H5, H6, H7, H8, and H9) were collected between the Sudbury basin and the Grenville province (See Figure 1.1 and 3.1) and involve identical mineralogy. These consist of fine- to coarse-grained 50% guartz, K-feldspar 10%, trace amounts of plagioclase, sericite and sulphides mainly in the form of pyrite and magnetite. Metamorphism has produced biotite and

has generally produced weakly altered foliations and lineations in the samples.

3.2. Nipissing Diabase.

dykes. Sills. and core-sheets of tholeiitic gabbro, collectively termed the Nipissing Diabase, are the most abundant and widespread igneous rocks intruding into the Huronian sequence of the South province. (Van Schmus, 1965; Fairbairn et al., 1969). The Nipissing gabbro sills from the Gowganda area have yielded a U-Pb baddeleyite age of 2219 Ma (Corfu & Andrews, 1986). The Diabase is generally intruded into Huronian metasediments, although some bodies cut the Archean basement and are possibly also represented in the Northwestern Grenville province (Lumbers, 1975). Their emplacement was controlled by pre-existing structures such as major faults of the Murray and Onaping system (Card & Pattison, 1973). In the Sudbury area the Nipissing diabases have undergone metamorphism from the lower greenshist to the lower almandine-amphibolite facies (Card & Pattison, 1973).

Three samples from the Nipissing Diabase (NIP1, NIP3, NIP4) were collected from the same road cut near the Worthington offset (See Figures 1.1 and 3.1). They consist of about 35% plagioclase, feldspars, sulphides (chalcopyrite, pyrite and minor pyrrhotite) quartz, amphibole, calcite, chlorite and euhedral pyroxene. There is also some

plaqioclase altered to clay minerals and calcite and in some areas altered to amphiboles and trace amounts of chlorite.

3.3. Superior Province.

North and East of the Sudbury Igneous Complex (SIC) is the terrain underlain by Archean rocks (a variety of gneisses, granites and diabase dykes) (See Figure 1.1). The Superior province was formed during the Kenoran orogeny about 2.7 Ga (Hurst & Farhat, 1977; Krogh et al., 1984). For a more detailed description of the geology of the area see Pye et al. (1984).

3.3.1. Levack Gneiss Complex.

The Levack Gneiss complex constitutes part of the Archean basement beneath the northern area of the Sudbury Igneous Complex in the immediate area of the contact. Rocks of the Levack Gneiss include migmatitic rocks and tonalitic to quartz dioritic gneisses, with irregularly shaped zones of upper amphibolite and lower granulite facies (Card et al., 1984). The Levack Gneiss Complex contains lower crustal rocks of pyroxene granulite facies (Grieve et al., 1991).

Two samples (LG3.1 and LG4.9) are of relatively homogeneous grey Levack gneiss and are composed mainly of plagioclase, guartz, pyroxene and minor amounts of opague minerals such as pyrite and magnetite. Sample localities are shown in Figure 1.1.

3.3.2. Archean Granite.

In the north, the Sudbury Igneous Complex intrudes into Archean granitic rocks, generally of guartz monzonite composition, which occur as discrete enveloped homogeneous plutons enveloped by migmatite (Card et al., 1984).

In this study a sample (LGC) of Archean granite is represented by a granite formation north of Capreol (Figure 1.1), overlain to the east by basal Huronian units.

3.3.3. Sudbury Breccias in the North Range.

Sudbury Breccias in the North Range occur on the fringe of the Sudbury Igneous Complex in the Archean gneisses and granites of the Superior province. Gabbroic fragments and diabase clasts are very common within these breccias (Dressler, 1984a). The matrix of the Sudbury breccia is black or grey (Peredery & Morrison, 1984). Sudbury breccia is attributed to the shock-induced melting of crustal rocks, and its geochemistry has been shown to characterize the average footwall rock in the region (Dressler, 1984a). Speers (1957) found some trace elements enriched in the breccia relative to the country rock, in particular, lead and vanadium.

Samples of Sudbury breccias (SB4.9, SB5.6, and SB8.6) were collected from Highway 144. The fragments of these samples are probably derived from the host rocks.

CHAPTER 4

METHODOLOGY

4.1. Sample Preparations.

The materials analyzed in this research include ore minerals. especially sulphides, and whole rock samples. Detailed sample preparation is outlined in Appendix C.1. Sulphide ores were analyzed from the Creighton and Falconbridge East mines of the South Range (Dickin et al., 1992; Beneteau, 1990), and from the Strathcona (Schindler, 1975) and Whistle Pit mines of the North Range (Figure 1.1). A porite sample from near Creighton was also analyzed to assess the relationship between the main mass and the sulphide ores. Seven samples of the Onaping Tuff were also sampled from the interior of the Complex. Eleven country rock samples were collected from different formations of the Huronian super group, mostly from south of the Sudbury Igneous Complex (SIC), along with three samples of the Nipissing Diabase from a large body near Worthington. Two samples of relatively homogeneous grey Levack Gneiss were analyzed from northwest of the SIC. However, in view of the gross heterogeneity displayed by the Levack gneisses on an outcrop scale, an attempt was made to achieve a more representative regional sample by analysis of the devitrified glassy matrix of the so-called "Sudbury breccia". This material is attributed to shock-induced melting of crustal rocks, and its geochemistry has been shown elsewhere to approximate a regional average of the wall rocks (Dressler, 1984a). One sample of Superior province basement is represented by a granite taken just north of Capreol, which is overlain to the east by basal Huronian units. Sample localities and description are presented in Appendices A.1, A.2, A.3, A.4, A.5 and in Figures 1.1 and 3.1.

4.2. Dissolution and Anion Exchange.

All chemical processing was carried forth in clean laboratories of the Department of Geology at McMaster University. Columns of samples were prepared for analysis, using the Dowex Bio-Rad anion-exchange resin, by a procedure described in Appendix C.2.1. Specifically, two sets of columns of different volume (small and medium) were used, Appendix C.2.2, Table C.2 and C.3. There were two steps in the use of the column-anion exchange resin. The first involved separation of lead from other elements, while the second involved separating the uranium from all elements.

4.3. Mass spectrometry.

The isotopes of Pb and U were analyzed on a VG 354 Thermal Ionization Mass Spectrometer with a 27 cm radius and 90° magnet sector. It has one fixed and four externally adjustable Faraday collectors and one Daly multiplier detector.

Fourteen samples and two international lead standards (NBS SRM 981) or two U natural were loaded simultaneously in a "clean" laminar-flow work-bench station. Loading technique is presented in Appendix C.3.1. After loading, the samples are introduced into the solid-source thermal ionization mass spectrometer, and normally samples are run only when the vacuum is at approximately 2×10^{-7} mbars (1.5 $\times 10^{-7}$ Torr). Then, isotope ratios were measured sequentially on the 16 samples.

The general peak jumping system was used for lead and uranium analysis. Only the main or axial collector was used to measure ion beams: to calculate ratios the beam was adjusted to allow each of the peaks to strike alternately on the collector. Measurement of the uranium isotopes was achieved by using the Daly detector. All analyses were run in automatic mode using the HP 9121 computer.

4.3.1. Lead Isotope.

Lead was loaded on single Re filaments (Figure 4.A, Appendix C.3.2) with silica gel and phosphoric acid technique (Cameron et al., 1969). This was thought to form a blanket over the sample which effectively restrains Pb volatilisation so that the filament can be raised to a higher temperature. The isotopic measurements have been carried out between 1150°-1250°C with the aid of a pyrometer to monitor temperature. The program used was called the 'Pb Dynamic Temp GpJ' and is listed in Appendix C.3.3.

The beam size was not controlled, but was allowed to find its own level according to the size of the Pb sample. In most cases, sample amounts were chosen to yield 100-500 ng mass-spectrometer loads. Some of the samples contained substantially smaller amounts of lead, resulting in increased measuring error. Samples were analyzed in duplicate to assure reproducibility.

The two main errors that affect lead isotopes are fractionation in the mass spectrometer and the uncertainty in measurement of the least abundant isotopic ²⁰⁴Pb. During the study, this researcher carried out 50 measurements of the lead isotope standard NBS SRM 981 to monitor the reproducibility of the working conditions. Table 4.1. Lead Isotope Ratios.

Isotope ratio	Mean	Standard deviation
20000/204Pb	36.539	± 0.058
207РБ/204РБ	15.443	± 0.023
206₽Ъ/204₽Ъ	16.893	± 0.009

The mass fractionation level was 0.10% per mass unit. Analytical errors are discussed in more detail in Appendix C.3.4. The total processing blanks use about 1 ng, which is negligible relative to the sample size of several micrograms. Figure 4.A (Single Re filament Bead)

Lead was loaded on single Re filaments.

Figure 4.B (Double filament Bead)

Uranium was loaded on the side of a double filament



4 A



DOUBLE FILAMENT BEAD

4.3.2. Uranium Isotopes.

Uranium was loaded on the side of a double filament (Figure 4.B, Appendix C.3.2). While the side filament is tantalum, the centre filament is rhenium (zone-refined). The filaments were out-gassed for 15 minutes at 2.7 A under vacuum before samples of uranium were loaded. As mentioned previously, uranium was analyzed by axial peak jump to measure ion beams. The beam was measured with the high sensitivity Dalv detector rather than with the less sensitive Faraday detector. Only the uranium ratio of ²⁹⁰U/²⁹⁵U was taken for the purpose of finding the uranium concentration. The program used was called 'UID Axial Peak Jump' and is listed in Appendix C.3.5.

Uranium and lead concentrations were determined by isotope dilution using a mixed 295U-200Pb spike. A 295U spike was used for uranium and a ²⁰⁰Pb spike was used for lead. The program used is listed in Appendix C.3.6.

CHAPTER 5

RESULTS

5.1. LEAD ISOTOPIC DETERMINATION.

5.1.1. Sudbury Ores.

Twelve sublayer ores from the Falconbridge East mine and the Creighton cluster measure close to the 1.85 Ga reference line in Figure 5.1. This result suggests that Pb was incorporated into these ores at the time of the emplacement of the Sudbury Igneous Complex (dated at 1.85 Ga by U/Pb zircon analysis, Krogh et al., 1984).

Some of the sublayer ores (Table 5.1) have disturbed Re/Os isochron systematics (Beneteau. 1990: Beneteau et al.. 1991; Dickin et al., 1992), possibly due to the effects of the Grenville orogeny. All samples analysed have incoherent U/Pb isochron systematics (Table 5.1), but only two samples from the Creighton and Falconbridge mines have disturbed Ph/Ph isochron systematics. The sample from Creighton (C9) has a texture indicating secondary sulphide replacement and represents massive chalcopyrite-rich ore. The other ore sample from Falconbridge (F6) is a PGE-rich cross-cutting vein. which is obviously not co-genetic with the sublayer. while both of them lie off the main array. Falconbridge East mine shows higher lead isotopic ratios than the Creighton mine but still have the same age.

Figure 5.1. Pb - Pb isochron diagram.

Shows present-day compositions of Sudbury ores and Onaping Tuff relative to the 1.85 Ga and 1.0 Ga reference lines.

Symbols:

- (A) Creighton mine
- (▼) Falconbridge East mine
- (I) Strathcona mine
- () Whistle pit
- (•) Onaping Tuff

Analytical errors are smaller than the size of the symbols.



Ore samples from the Strathcona and Whistle Pit mines lie along a shorter array, of similar 1.85 Ga slope age, but displaced to lower ^{20GPb/204Pb} and ^{207Pb/204Pb} ratios (Figure 5.1). The Strathcona samples also have lower ^{20GPb/204Pb} ratios than any other ores. The unradiogenic Pb in these samples has probably not been disturbed by the later resetting events which have opened Re/Os systems in this mine (because isotope ratios are more resistant than elemental ratios to disturbance).

5.1.2. Main Mass.

Two samples, one disseminated ore in norite (from Falconbridge East) and a norite whole-rock (near Creighton), also lie in the same Pb/Pb array of the ores. This succests that Pb in the ores is co-genetic with the silicate rocks of the SIC. Similar results were obtained from the Re/Os analysis of Sudbury ores (Walker et al., 1991; Dickin et al., 1992). Textural evidence also supports a magmatic origin for the sulphide ores. Both samples (F1 disseminated and SR7 whole rock) are collected from the South Range. In contrast, two samples of granophyre and three samples of guartz gabbro from the South and North Ranges lie off the main array (not shown in the diagram).

The scatter of data points may be due to open system metamorphism caused by the same thermal episode that affected

the granophyric micropegmatite (1680 ± 31 My, Gibbins & McNutt, 1975). Another explanation may be that the elemental chemistry of the main mass cannot be formed from an individual batch of magma by the melting of the crustal rocks, but rather that it was the result of a convective mixing of components during the prolonged cooling of the overlying silicon magma.

Silicate samples of the Onaping Tuff lie close to a 1 Ga Pb/Pb reference line (Figure 5.1). This result suggests that the U/Pb systematics in these presumed uranium-rich fine-grained rocks were disturbed during the Grenville orogeny, which was the latest event in the area.

Table 5.1

Pb isotope data for ore samples and silicates from the SIC and country rock

		SoebP	207Pb	208Pb	207Pb	Pb	U	
Sample		204Pb	204Pb	204Pb	204Pb	ppm	DDW	Lithology
					1.85 Ga			
Falcont	prid	lge						
F1		17.700	15.636	39.397	15.448	-	-	disseminated
F2		19.282	15.830	39.814	15.471	9.7	0.24	sublayer
F3		17.267	15.538	36.693	15.372	6.9	0.60	sublayer
F4		18.480	15.704	38.722	15.421	-	-	sublayer
F5		17.356	15.587	37.510	15.428	6.5	0.32	* sublayer
F22		23.213	16.310	44.008	15.517	33.4	0.28	* sublayer
F24		20.514	15.958	41.746	15.442	-		* sublayer
F28		16.741	15.557	36.637	15.494		-	* sublayer
F6		22.585	16.362	45.559	15.697	46.4	0.42	vein
Creight	00							
C1		16.458	15,486	36, 927	15,437	_	- 1	sublaver
62		18,872	15,765	39.467	15,449	7.3	0.23	sublaver
63		16.370	15,463	37.031	15,420	10.7	0.24	* sublaver
C9		17,158	15,422	38.694	15,218	5.6	0.19	* sublaver
C12E	>	15,892	15.453	35.819	15,479	14.6	0.19	* sublaver
C120		15,907	15,480	36.049	15.524	20.0	0.23	* sublaver
SR7		17.707	15.644	38.410	15,490	-	-	norite
0.07			101011	our irv	101 100			1101 2 0 2
Stratho	ona	a						
PO		14.901	15.128	35.209	15.152	_	_	deep ore zone
CP		14.899	15.124	35.184	15.137	_	-	deep ore zone
Whistle	2							
W5		14.867	15.027	35.177	14.925	-	-	sublayer
WЭ		15.936	15.228	35.187	15.126	-	_	sublayer
Onaning	1 TI	ıff						
OT1		41, 195	17.773	47, 185	6 2 AN	-		**
012		23.735	16,129	40.023	15,619		_	**
013		21.701	15.954	37.955	15.551	_		**
OTA		26.137	16,287	40,901	15.378		_	**
0.0		22.636	16,101	38,451	15.649	_	_	**
0110	5	22.486	15,992	39,223	15.537	1 × 12 3	-	**
OTI	1	23.350	16,132	38.839	15.632	_		**

Table 5.1 (continued)

	20ePb	207Pb	soepb	207Pb	Pb	U	
Sample	204Pb	204Pb	204Pb	204Pb	DDW	ppm	Lithology
				1.85 Ga			
Superior	prov.						
L63.1	13.957	14.692	33.710	14.648			grey gneiss
LG4.9	14.563	14.846	34.779	14.769	-		qrey qneiss
SB5.6	16.046	15.157	39.747	15.031		-	matrix
SB.86	16.037	15.260	39.323	15.162	-	-	matrix
SB4.9	14.973	15.009	39.928	14.950	-	-	matrix
LGC	16.530	15.334	39.019	15.174	-	-	granite
Southern	prov.						
McKim	20,830	16.091	39.060	15.612	22.5		McKim
H1	26.040	16.661	47.159	15.573	18.5		Stobie
H2	31.475	17.306	49.497	15.615	18.1		Copper cliff
HЗ	20,280	15.956	39.167	15.493	12.5	-	McKim
H4	32.174	17.910	45.672	15.279	16.7		Ramsey Lake
HS	20.442	15.987	38.479	15.513	-		Mississagi
H6	21.044	16.085	38.605	15.514	-	-	Mississaqi
H7	22.086	16.215	41.330	15.549	-	_	Mississaqi
HB	28.977	17.051	37.929	15.698	_	×.,	Mississagi
H9	22.316	15.264	41.984	15.599	_		Mississaqi
H12	20.716	16.029	39.259	15.518			Elsie Mountain
NIP1	18.105	15.761	36.578	15.574	5.4		diabase
NIP3	17.978	15.789	36.286	15.629		_	diabase
NI23	18.174	15.826	36.537	15.656	_	-	diabase
Main mas	5						
NRA	28.511	16.668	49.872	15.156	_	-	granophyre
SR13	26.510	16.464	49.590	15.186	_	_	granophyre
SR15	20.599	15.847	40.930	15.259	i -		quartz gabbro
NRB	23.019	16.131	45.014	15.284	-		quartz gabbro
NRC	19.942	15.806	41.123	15.318	-	_	quartz gabbro

* Re/Os- disturbed system

** 207Pb/204Pb 1.0 Ga

5.1.3. Country Rocks in the Southern and Superior provinces.

The country rocks to the North and South of the Sudbury Complex display markedly different Pb isotope signatures: 25 predicted from their stratigraphic levels in the crust. Levack gneisses have very unradiogenic Pb, but the matrix samples of Sudbury breccia are somewhat more radiogenic, and approach the Archean granite composition (Figure 5.2). The collinearity of Sudbury breccia samples with the country rocks suggests that they were derived by closed-system melting of the Superior province crust. Arguably, this represents bulk melts of fusible granitic units (Grieve et al., 1991), rather than the more tonalitic grey gneisses. The samples have Pb-isotope profiles similar to those found in the North Range ores (shown by a line in Figure 5.2).

Huronian super groups have much more radiogenic Pb, and most samples, along with the Nipissing diabase, fall close to the 1.85 Ga reference line through the South Range ores. The shallow slope of the Huronian array may be viewed as rather unusual, since these rocks were derived from Superior province. Most of these samples are very fine-grained. However, the conglomerate sample (H4) from the Ramsey Lake formation lies far above the 1.85 Ga array, suggesting an older sample as compared with the other Huronian units. This result suggests that the U/Pb systems in the fine-grained samples were largely reset at 1.85 Ga along with the matrix (but not the clasts) of the Ramsey Lake conglomerate.

A combination of possible factors may have caused this resetting event:

(1) Thermal heating by the Penokean orogeny (Gibbins & McNutt, 1975: Hu et al., 1991);

(2) Heating from the postulated impact;

.

(3) Fluid migration in the vicinity of the Murray fault. This last factor may explain the more radiogenic Pb in samples within 1 kilometre of the fault. These samples show many alterations. Figure 5.2. Pb - Pb isochron diagram.

Shows measured (present-day) compositions of country rocks relative to reference lines from fig. 2.

Symbols: (♦) Huronian units

(\$) Nipissing diabase

- Levack gneiss
 Sudbury breccia cutting levack gneiss
- (Δ) Archean granite



5.2. U/Pb Variation.

The Pb isotope variations of all the samples and selected samples analysed for U and Pb concentrations were listed in Table 5.1. The Pb concentrations of the Creighton mine found the maximum Pb content in the sample C12C and the minimum in the sample C9. While the minimum Pb content at Falconbridge East mine are in the samples, F5 and F3, which are from the middle of the sublayer, the maximum in the sample, F6, is from a cross-cutting vein.

Lead concentrations of selected country rocks (Huronian and Nipissing diabase) were also analysed (Table 5.1) and found the maximum Pb content in the sample McKim and the minimum in the sample NIP1.

The few uranium concentration data (Table 5.1), ranging from 0.19 to 0.60 ppm, are not representative of all samples. Uranium and thorium concentrations in most of the samples were not measured and no attempt was made to produce age-corrected isotopic compositions for the ²⁰⁰Pb data. The ²⁰⁰Pb/²⁰⁴Pb versus the ²⁰⁰Pb/²⁰⁴Pb data from the SIC show no pronounced correlation (Figure 5.3, Table 5.1), but they do show the ordered mobility of thorium and uranium in near-surface crustal rocks. Figure 5.3 200pb/204Pb versus 206Pb/204Pb ratios of Sudbury ores, silicates and country rocks.

Symbols: (x) Falconbridge

- (λ) Creighton
- (⊗) Strathcona
- (•) Whisttle
- (O) Dnaping
- (() Huronian
- ([®]) Levack
- () Breccia
- $(_{\otimes})$ Granite


CHAPTER 6

DISCUSSION

6.1. Lead Model.

For the purpose of providing a petrogenetic evaluation of the Pb isotope data, one must estimate the initial Pb isotope ratio at 1.85 Ga. Unfortunately, the open-system behaviour of uranium prevents the direct calculation of these ratios. However, coupled ²⁹⁵U-²⁰⁷Pb and ²⁹⁶U-²⁰⁶Pb systems are used for this study to model the initial Pb isotope ratio by projecting the data back parallel to the 1.85 Ga reference line in Figure 5.1. Since all samples were ultimately derived from the Superior basement, they should lie, at 1.85 Ga, along a 2.7 Ga reference line.

Initial ²⁰⁷Pb/²⁰⁴Pb data at the 1.85 Ga line were calculated by projecting the present-day composition back to a chord linking the 2.7 Ga and 1.85 Ga compositions of the growth curve of Stacey & Kramers (1975). A similar method was used by Taylor et al. (1980) to model initial ratios of the Nuk gneiss system in Western Greenland.

6.2. Lead Sources.

²⁰⁷Pb/²⁰⁴Pb ratios computed at 1.85 Ga are plotted as histograms in Figure 6.1. These results confirm observations made above that ores from the Strathcona mine and Whistle Pit and from the Falconbridge East and Creighton mines have distinct lead-isotope signatures, resembling Superior province granitic material and Huronian metasediments, respectively. There is no reason to believe that any mantle-derived lead component in the Sudbury ores exist. Osmium-isotope data do not require a mantle-derived component (Dickin et al., 1992) despite the larger osmium content of the mantle relative to crustal rocks. Since lead is more enriched in the crust than in the mantle, the crustal lead component would totally swamp any hypothetical mantle-derived component.

Two samples from the norite (main mass, South Range) discussed above also reflect the local Pb isotope composition of the Huronian super group (along with the Nipissing diabase). But the other samples from the main mass (granophyre and guartz gabbro) have similar initial ratios, on the South and North Ranges (See Figure 6.2). As discussed previously, this may be due to open-system metamorphism caused by the same thermal episode that affected the granophyric micropegmatite (1580 ± 31 My, Gibbins & McNutt, 1975). Another theory may be that the elemental chemistry of the main mass cannot be formed from an individual batch of magma by melting the crustal rocks, but rather that it was the result of a convective mixing of components during the prolonged cooling of the overlying silicon magma.

Figure 6.1. Histogram of the calculated ²⁰⁷Pb/²⁰⁴Pb ratios for Sudbury ores and for country rocks at the 1.85 Ga SIC.

Legend V: vein

V: vein

D: disseminated ore

N: norite

Q: disturbed sample (C9)

Country rocks:

- N: Nipissing diabase
- L: Levack gneiss
- B: Sudbury breccia matrix

G: Archean granite



Figure 6.2. Histogram of the calculated initial ²⁰⁷Pb/²⁰⁴Pb ratios for the main mass and for country rocks at 1.85 Ga.

Symbols:



Norite granophyre Quartz gabbro

Country rocks:

- N: Nipissing diabase
- L: Levack gneiss
- B: Sudbury breccia matrix
- G: Archean granite



CHAPTER 7

SUMMARY

7.1. Model for the Sudbury Igneous Complex.

The Pb isotope data are consistent with the impact of a meteorite at about 1.85 Ga (evidence from shocked zircons. Krooh et al., 1984) on the Huronian/sedimentary apron of the Superior craton. This sediment thickens to the South, so that after vaporising the uppermost Huronian crust, the impact must have generated a crater in the Archean basement on the North Range, but this crater was contained within the basal Huronian strata on the South Range. This impact would also melt upper crustal materials of different rocks to produce the Sudbury magmas. Such a large proportion of crustal (sulphide-rich) magmatic segregations generated the locality of the ores.

Therefore, the ores on the North and South Ranges apparently reflect the local Pb isotope compositions in the melted country rocks. Within the same time-frame, material ejected from the complex would begin to fall, some of it back into the complex, and some outside, to form a fall-back breccia generated by the impact (Peredery, 1972). The silicate main mass (norite, granophyre, and guartz gabbro) may not be formed as an individual batch of magma by in-situ melting the crustal rocks: rather, this main mass is the result of magma mixing of the North and South Range signatures and subsequent differentiation. Figures 7.1a and 7.1b show a schematic cross section of the Sudbury complex before formation and afterwards.

Lead contents in the ores are similar to the source (country) rocks and probably represent a "frozen in" isotopic signature acquired during early segregation of sulphide liquids from the overlying impact-generated silicate melt. Subsequent modifications by orogenesis and erosion produced the Sudbury structure seen today.

7.2. Conclusions.

(1) The Pb isotope data are consistent with the impact of a meteorite on the Huronian sedimentary apron of the Superior craton. These data are also consistent with a 100 percent crustal source from either Superior province or Huronian units.

(2) Lead isotope compositions reflect the geographic distinction between the opposing provinces (Southern and Superior). Samples from the Superior province have lower ²⁰⁶Pb/²⁰⁴Pb ratios than those of Huronian units. The ores on the North and South Ranges apparently reflect the local Pb

isotope compositions of melted country rocks. In contrast, the elemental chemistry of the main mass implies convective mixing of the components during the prolonged cooling of the silicate magma.

(3) Sublayer ores from mines of the Sudbury Igneous Complex cluster close to the 1.85 Ga reference line. This suggests that Pb was incorporated into these ores at the time of emplacement of the Complex, dated at 1.85 Ga by U/Pb zircon analysis (Krogh et al., 1984).

Figure 7.1a & b. Schematic cross-section of the Sudbury structure before and after formation.



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APPENDICES

APPENDIX A.1

Sampling details and descriptions collected from the South Range, Sudbury Igneous Complex, Sudbury, Ontario.

Abbreviations:

cpy = chalcopyrite

po = pyrrhotite

FALCONBRIDGE EAST MINE, SUDBURY, ONTARIO.

F1 1.0 M above hanging wall (quartz-rich norite)

Disseminated cpy and po in medium-to-coarse grained ouartz-rich norite. Sample appears more felsic than at Murray Mine road cut. Po and cpy are disseminated interstitially as blebs. Sulphides 20%, po 80%, cpy 20%. Bluish-white quartz comprises 20% of sample. Some fractures appear chloritized.

F2 0.5 M below hanging wall (ore)

Wispy 1-5 cm quartz segregations and veinlets of quartz and in hanging-wall breccia. Feldspar (?) is white and pink. Quartz is white to grey. Cpy-rich ore, cpy 60%, po 40%. Inclusions 1mm-5cm in size appear; to be strongly altered hornfels after partially assimilated. Cpy is usually near inclusion rather than po.

F3 3.0 M above footwall sublayer (ore)

Massive ore containing numerous small (0.3mm-3.0cm) inclusions of felsic rocks. pegmatitic and guartz-rich

material. Sulphides comprise 85%: 95% po, 5% cpy, silicates 15%. Po and cpy occur as lacy intergrowths, not blebs. Sample is highly oxidized and is from the old mine workings that are now at the surface. Cpy occurs in veins in one inclusion. Larger inclusions have dark rims of cpy.

F4 Right at hanging wall (ore)

Sulphides 95%: 95% po, 5% cpv, silicates 5%. Small inclusions 1 cm from massive ore beneath the norite. Inclusions appear to be from both hanging wall mafic metavolcanic rocks and guartz-rich norite. Mafic metavolcanic rocks are more assimilated than the guartz-rich norite. Cpy occurs nearer to inclusions.

F5 3.0 M below hanging wall (ore)

Massive sulphides; 98% po, 2% silicate blebs. No cpy is visible. Sample is highly oxidized. Silicate inclusions are 1-15mm in size and are mainly quartz-rich norite in composition. Some assimilation textures are present.

F6 Vein 1.0 M below hanging wall (ore)

Sample was taken from a cpy-rich zone in hanging wall of pit. Small annular biotite inclusions, rimmed and assimilated by 50% cpy and 50% po. Sample also contains a small veinlet of galena. Sample thought to be PGE-rich.

F22 0.2 M from the contact in F.W. (ore)

Breccia ore with 90% sulphides and 10% clasts. Clasts are quartz and chloritized fragments (mafic metavolcanic rocks), range in size from 2mm-50cm. Sulphides 90% po, 10% cpy. Cpy tends to be concentrated around clast margins and inside clasts.

F24 1.0 M into sublayer from F.W.-S.L. contact (ore)

Breccia ore: 85% sulphides 15% clasts. Clasts are dominantly chloritized with some being quartz. Sulphides: 80% po, 20% cpy. Wispy veins of cpy and po found in clasts. Clasts range in size from 1 mm to 80cm. Clasts are rounded and have sharp boundary contacts.

F28 Middle of sublayer (ore)

Clasts in ore range from 2mm-50cm. Clasts of quartz material and mafic metavolcanic rock fragments. Clast boundaries sharp. Some mafic metavolcanic rock clasts exhibit remnant foliation. Some clasts show assimilation by sulphides. Other clasts contain sulphide stringers. Sulphides 90%: 90% po. 10% cpy. Most cpy occurs in and/or around clast margins.

CREIGHTON MINE

Abbreviations:

cpy = chalcopyrite

po = pyrrhotite

C1 L4600 13185 N 4100E sub

Sublayer massive sulphides: 90% po, 10% coy, with small angular hornfels inclusions. Stringers of coy and po in clasts. Fragments brecciated and can be visually fit back together. No alteration or assimilation on the margins, some inclusions rimmed by coy.

C2 L4600 13275N 4150E

Medium grained exotic gabbro clasts with large disseminated sulphide blebs. Silicates 80%, sulphides 20% (80% po, 20% cpy). C=cpy usually marginal to po blebs. Eutectic textures common.

C3 L4600 13275N 4150E

Fine-grained black disseminated ore (60% po, 40% cpy) around silicates (mainly fine-grained norite). Some large sulphide blebs.

C9 L4600 13350N 4200E sub small

Massive sulphides in sublayer. Small cpy-rich sample (50% po, 50% cpy). Two clasts are present; one is partially assimilated by cpy at margins.

C12 (M. Cpy) L7000 6400N 4400E sub

Massive sublayer ore. Some blebs of quartz 2mm in size. Some assimilated silicates in cpy-rich areas.

SILICATE (MAIN MASS)

All kilometre-ages measured going South from intersection of NW bypass with Hwy 144 at Chelmsford.

SR13 Granophyre (upper zone) 7.7km (near Small Lake on East

side of road)

Felsic, more pink, course-to-medium grained (3-4mm) micropegmatite, massive textured 25% cpy, minor mineral, chlorite and guartz. Also fewer guartz veins (Pegmatitic segregations).

SR15 Quartz gabbro (Middle zone) 9.7km

Massive, medium-grained diorite, no segregations, no hematite alteration, some of feldspar, pyrite veins, minor amount of hematite, sulphide.

APPENDIX A.2

Sampling details and descriptions collected from North Range. Sudbury Igneous Complex, Sudbury, Ontario.

STRATHCONA MINE

Abbreviations:

coy = chalcopyrite

po = pyrrhotite

DIC (po) Pyrrhotite

Po separate containing 2-3 model percent pentlandite, obtained from deep ore zone comprised of 75% po. magnetite cpy 15% from D1 stope, 2750 level.*

DIC (cpy) Chalcopyrite

Cpv separate from same mass as that from which po obtained.

* D1 refers to the stope from which the sample was collected (see Figure 2.4). The letter C indicates a particular sample from this stope.

WHISTLE PIT

W.5

Sublayer sulphide, 60% po 40% cpy, blebs rounded, contains 1-3cm inclusions of Hornfels footwall clasts. No sulphides in clasts.

W.9

Sublayer fine-grained, non-porphyritic, ultra mafic inclusion 20cm diameter, contains minor disseminated po and cpy. Rimmed appears assimilated on margins by po-rich sublayer (95% po 5% cpy).

SILICATE (MAIN MASS)

NRA Granophyre

Felsic more pink coarse-to-medium grained. massive texture. Essential minerals K-feldspar, plagioclase. hornblende, and minor biotite. No visible sulphides.

NRB Quartz gabbro

Massive structure, with coarse-to-medium grained, massive texture, essential minerals K-feldspar, plagioclase, pyroxene, hornblende, minor biotite, and sulphides.

NRC Quartz gabbro

Massive structure coarse-to-medium grained, light areas and plaqioclase, dark areas are Augite and hypersthene (pyroxene).

APPENDIX A.3

ONAPING TUFF

NORTH RANGE

OT1 Dowling township

Large sample, few sulphides, and appear to be mostly rims. Matrix with heterogenous texture, an euhedral guartz.

SOUTH RANGE

OT2 Blezard township

Fine grained, no apparent sulphide clasts, 1-4mm po occurs as clasts that can rim guartz grains.

OT3 Capreol township

Fine grained, clasts bearing po, matrix fine-grained with medium-grained detail. Intergrowth of guartz and potassic feldspar.

OT6 Capreol township

Grey, contains sulphide clasts, angular to subrounded fragments of several varieties of arkose and guartz.

OT9, OT10 Creighton township

Consisting mostly of white to cream-coloured quartz, and rounded quartz pebbles, the fragments of quartz pebbles.
OT11 Rayside township

Matrix is light-to-medium grey and weakly foliated to massive. The fragments consist of white guartz and large fragments are virtually absent.

APPENDIX A.4

SOUTH RANGE COUNTRY ROCKS: HURONIAN SUPER GROUP

H1

Black to dark grev metavolcanic, fine-grained, mainly irregular guartz grains and very fine-grained of micaceous minerals (sericite), amphibolies, and very small and thin pyrite dyke also present. Minor amounts of magnetite, chlorite, zircon and epidite also present.

H2

Felsic pyroclastic rocks, sericite is present as very fine to fine grains. Sericite makes up as much as 60%. About 15% is guartz. The matrix surrounding the fragments consists mainly of chlorite, guartz, muscovite and biotite. Some of the biotite altered to chlorite, minor sulphides of magnetite, and pyrite is also present. Flow structure is in same direction.

H3 Siltstone

Quartz is subangular to subrounded and irregular in shape. Plagioclase (about 1%) poorly developed twinning. Biotite (about 13%) fine-grained and occurs grains of irregular shape with irregular in Chlorite (about 10%). Chlorite grains are orientation. fine-grained and blended, and generally occur as replacement of biotite. Matrix makes up nearly 40% of the sample. It contains silt-sized grains of guartz.

feldspar, muscovite, with minor amounts of chlorite, biotite, and opaque minerals. Minor amounts of zircon with pleochroic halo in the biotite.

MK (= McKim) Espanola area

Contains nearly 25-35% guartz, which is subangular to subrounded in shape. Plagioclase and K-feldspars are present to the extent of about 10%. Matrix accounts for nearly 40% of the sample. It contains muscovite, chlorite and biotite, with minor amounts of opague minerals.

H4 Conglomerate

Contains nearly 50% quartz, which is subrounded and oval and contains very few inclusions. About 10% of potassium feldspar of fine-to-medium grained detail and weaklv altered. About 3% olacioclase which is fine-to-coarse grained. Lithic fragments account for about 22% of the sample. Medium-to-coarse grained lithic fragments are present, and are graded into pebble-sized clasts. About 2% is muscovite, and there are minor amounts of biotite and chlorite. The chlorite appears to be secondary after biotite. Finally, there are minor sulphides.

H5. Sub arkosic Wacke to Arkosa H6.H7 H7.H8.H9

> Quartz (about 50%) fine-to-coarse grained, K-feldspar (about 11%), 3% plagioclase, feldspars are fine-coarse grained, and are weakly altered. Minor amounts of detrital biotite and chlorite. The matrix makes nearly 31% of the wackes. It consists of silt-sized particles of muscovite, biotite, guartz, feldspar, and minor amounts of sulphides. The chlorite present after the biotite. Samples H6 & H9 have more feldspar and guartz, as sericite.

H12 Elsie Mountain sample

Very fine-grained, mainly irregular guartz grains and biotite and minor hornblende. Matrix is 9-20% of the sample. Minor amounts of garnet, apatite, pyrite, magnetite, plagioclase, and chlorite. NORTH RANGE COUNTRY ROCKS

LG3.1 Levack gneiss

Contains mainly plagioclase, quartz pyroxene and minor amounts of sulphides (pyrite and magnetite).

LG4.9 Grey Levack gneiss

The following Matrix samples were collected along Highway 144:

SB4.9 Matrix of breccia

Consists primarily of small stubby plagioclase laths, rounded quartz grains.

SB5.6 Matrix

Dark grev to black, vesicles make up nearly 25% of matrix, very fine grained matrix includes guartz and plagioclase.

SB8.6 Matrix

About 80% matrix, very fine grained plagioclase, vesicular.

LGC Hutton township granite, North of Capreol

Equigranular, medium-to-coarse grained quartz monzonite granite.

APPENDIX B

LEAD MODEL CALCULATION

B.1 MODEL CALCULATIONS, CONSTANTS AND SYMBOLS USED IN LEAD-LEAD AGE

lead isotope data follows The interpretation of the procedures described by Faure (1986). Constants and symbols are listed in Table B.1. Constants vary from one lead evolution model to another. In this study, the model of Stacey & Kramers (1975) was used. They suggested that 3.7 x 10^{+9} years ago the U/Pb ratio of the source reservoir Was modified by geochemical differentiation, setting a new starting time and new initial lead isotope ratios for the modeling of radiogenic lead, thus establishing a two-stage evolution. The generally accepted values for the isotope ratios of primeval lead are those of Tatsumoto et al. (1973)who analyzed Pb in troilite from the Canyon Diablo iron meteorite which contains lead but negligible amounts of U and Th. Thus, the isotopic composition has not changed since its time of formation.

Symbol	Meaning	Value	Ref
λ1	Decay constant for 238U	$1.55125 \times 10^{-10}/year$	1
λ2	Decay constant for $235_{\rm U}$	9.8485 x 10^{-10} /year	1
к	Present day ratio 238U/235U	137.88	
a _O	Primeval 206pb/204pb	9.307	2
bo	Primeval 207 _{pb} /204 _{pb}	10.294	2
т	Age of the Earth	4.55 x 10 ⁹ years	3
Т*	Date of geochemical	3.7×10^9 years	
	differentiation in Stacey's		
	and Kramer's model (1975)		
a'	Initial 206pb/204pb in	11.152	
	Stacy's and Kramer's model		
	(1975)		
b'	Initial 207pb/204pb in	12.998	
	Stacy's and Kramer's model		
	(1975)		
м	Slope of a secondary		
	isochron		

Table B.1 Constant and symbols used in the pb-pb age and model calculation. Ref 1=Steiger and Jager, 1977; 2=Tatsumoto et al., 1973; 3=Patterson, 1956. Section B.2 Calculation of the Secondary isochron fitting the distribution of the lead isotope ratios of the lead isotope ratios of the Ore Samples and silicates from the SIC:

Faure (1986) gives a detailed discussion of the equations which define multi-stage leads. For a two-stage Pb (if a sample of Pb is passed through U-bearing systems characterized by different ²³⁰U/²⁰⁴Pb ratios [u1 and u2]), then the ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb ratios of that sample are given

$$(206\text{pb}/204\text{pb}) = a_0 + u_1(e^{\lambda 1}T_{-e^{\lambda 1}t_1}) + u_2(e^{\lambda 1}t_{-e^{\lambda 1}t_2}) \mapsto (B.1)$$

$$(207 \text{pb}/204 \text{pb}) = b_0 + (u_1/\kappa)(e^{\lambda 2}T_{-e}\lambda 2_{t1}) + (u_2/\kappa)(e^{\lambda}t_{1-e}\lambda 2_{t2}) \mapsto (B \cdot 2)$$

- Where: T = age of the earth and corresponds to the singlestage model and can be exchanged with T* for Stacey's and Kramers' model (1975).
 - t1 = the time in the past when Pb was removed from system 1 and transferred to system 2.
 - t2 = the time in the past when Pb was removed from system 2 after which its isotopic composition remained constant.

Now, t2 = 0, since the Pb isotopic evolution continues to the present, when the isotopic composition is determined.

Simplifying the initial first stage component and equations B.1 and B.2 with A&B respectively. Thus we obtain.

$${}^{(206_{Pb}/204_{Pb})} = A + \mu_2(e^{\lambda_1 t_1} - 1) \rightarrow (B.3)$$

 ${}^{(207_{Pb}/204_{Pb})} = B + (\mu_2/k) (e^{\lambda_2 t_1} - 1) \rightarrow (B.4)$

We then combine both equations to eliminate u2, resulting in:

This equation (B.5) represents a family of straight lines passing through a point with A and B as coordinates, and with a slope M given by: $\lambda 2t1$

$$M = \frac{1(e^{\lambda 2 t t} - 1)}{K(e^{\lambda 1 t t} - 1)} \longrightarrow (B \cdot 6)$$

In other words, the straight lines are known as secondary isochrons which pass through (coordinates A and B) and the growth curve of system 1 and whose slope depends only on the internal of time t1, t2 during which the lead resided in system 2 (see Figure B.2).

In this study, $t1 - t2 = 1.85 \times 10^{+9}$ years. The above value and equation (B.6) were used to calculate the slope of the secondary isochron fitting the distribution of the lead isotopic composition from the ores and the country rocks (whole rocks). That slope has a value of 0.1131. Figure B.2 Diagram showing the coordinates of points A and B.



APPENDIX C

C.1. SAMPLING AND CRUSHING

Previously prepared at McMaster University using standard separation techniques, the samples used in this research are listed below:

No.	Locality	Material used	References
1	Falconbridge East mine	Sulphide ores	Beneteau, 1990
2	Creighton mine	Sulphide ores	Dickin et al., 1992
З	Strathcona mine	Sulphide ores	Schindler, 1975
4	Superior province (Levack gneiss)	Country rock (LG3.1)	Dickin et al., 1992

The remaining samples were prepared by the author. The samples weighing about 5-10kg were further refined in the rock crushing laboratory at McMaster University. The weathered material was removed by a sledge hammer and no visible signs of alteration, such as hydrothermal veining, appeared. Some care was exercised in ensuring that only unaltered material was incorporated in samples. Rock samples were cleaned with a wire brush and then were broken into pieces suitable for the jaw crusher with first a hammer and later with a hydraulic splitter.

The next step in sample reduction was to crush the pieces further, using a jaw crusher to achieve chips sizes approximately 6mm in diameter. Prior to using the jaw crusher, the instrument was first pre-contaminated with some of the sample in order to avoid any contamination from previous samples. The chips were split several times with a table-top divider until one sixteenth of the total whole-rock sample remained. This representative aliquot was loaded into a tungsten carbide disc mill, which was then placed on shatterbox vibration. A Spex tungsten-carbide shatterbox was operated in vibration mode for approximately five minutes. Then the entire sample was removed from the disc mill and poured onto a clean sheet of white paper. Here the powder was split into two equal parts and one part was reloaded into the disc mill while the remaining part was discarded. The shatter box was then operated for another eight minutes until a fine powder of approximately 200-300 mesh was produced. The resulting powder was stored in 125 ml glass bottles.

To prevent contamination of the samples, all pieces of equipment and working surfaces were thoroughly cleaned after each operation. The cleaning operation was a two-phase process involving first a vacuum cleaner and secondly disposable paper towels. Polyethylene gloves were worn before operating the tungsten-carbide shatter box. All work was carried out in an area where incoming air passed through a high-quality particulate filter.

C.2. Chemistry

C.2.1. Dissolution

Approximately 100-400 mg (milligrams) of powdered sample were weighed into clean Teflon bombs and containers of known weight. Two different kinds of samples, silicates and sulphides, were analyzed during this study. In each bomb of silicates approximately 10 ml (millilitres) of concentrated HF (48%) was added. The Teflon bombs were then tightly sealed and placed into Teflon safety jackets. The safety jackets and bombs were placed in an oven and and left for 3 days at 120°C. After 3 days the bombs were removed, cooled, and the HF was evaporated on hot plates enclosed in a laminar flow hood. When the samples were dry, about 5 ml of concentrated HNO₂ was added to each bomb to remove any insoluble flourides.

Then this solution was evaporated to dryness and 5 ml of 6N HCl (warm dilute) was added, and then bombs were put back into the safety jackets and replaced in the oven overnight to remove any sulphide component. Next day the samples were cooled and diluted with approximately 5 ml of Milli-Q-Water if there were no undissolved residues remaining.

All samples of nominally pure sulphides (ores) were dissolved in 5 ml of 7.5N HNO_{2} and heated for a while, then evaporated to dryness and added 10 ml (6m HCL). Each solution was subsequently split, into two aliquots. To one was added isotopically enriched U and Pb from a mixed 295U-208Pb spike. Both the spiked and unspiked aliquots were evaporated to dryness and subsequently taken into solution with 2 ml of 1m HBr and transferred to plastic test tubes and centrifuged for 10 minutes. Centrifugation was performed in order to prevent undissolved solids, if any, from being loaded into the anion exchange columns.

Dowex Bio-Rad AG 50W, 200-400 mesh, anion exchange resin in polyethylene columns were used in this study. The ion-exchange resin was washed and rinsed with distilled water in a Teflon bottle. The mixture was allowed to stand for a few minutes and the suspension containing fine particles decanted. Then the clean resin was stored in water until use.

C.2.2. Column anion exchange

Two sets of columns of different volume (small and medium) were used. Medium and small columns were made of polyethylene tubing with clean cotton wool placed at the bottom of the columns to retain the resin. The resin was discarded after each use to avoid anv problems of inter-sample contamination and in order to obtain high purity material for analysis.

The first step in column anion exchange 15 the separation of lead from other elements. Columns were WAYA cleaned with 3m1 solutions, in order (See Table C.2). The cleaning procedure was repeated. Each sample was loaded into the columns, washed in with 1 ml of 1M HBr. and eluted with 3 ml of 1M HBr. Then Pb was collected with 6 ml of a 6M HCl solution and then evaporated. The columns were then cleaned once again, and the sample was pass through a second anion-exchange column, in order to obtain high-purity samples for analysis.

The second step was separation of uranium from thorium. Uranium was collected with the eluting HBr uranium rock solution and evaporated gently, especially near the end of the process. Then 1 ml of 7M HNO₂ was added.

The cleaning and separation procedures are outlined in Table C.3.

In this procedure. a medium column was first used, followed by use of a small column. This procedure was successful for all the samples and the total procedure blank was 1 ng, which is negligible compared the sample size of several micrograms. It was assumed that some of the samples had low Pb concentrations, and consequently that more sample might be needed for further measurement.

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Small Columns	
Length	2.2 cm
Capacity	0.25
Resingrade	200-400
Cleaning	
H ₂ O	3ml
6M HCL	3ml
H ₂ O	3ml
6M HCL	3ml
H ₂ O	3ml
1M Hbr	3ml
Loading	
1M HBR	1M
Washing	
1M HBR	1M
Elution	
1M HBR	3M*
Collection	
6M HCL	6ml

Table C.2: Quantities used in the Ion-Exchange pb Procedures

* for uranium separation form Thorium.

	Medium Columns	Small Columns
Length	5.5 cm	2.2 cm
Capacity	.2 ml	0.25 ml
Resingrade	200 - 400	200 400
Cleaning		
H ₂ O	4 ml	3 ml
2m HN03	4 ml	3 ml
0.5n HCL	4 ml	3 ml
Н2О	4 ml	3 ml
If leaving more that	an 24 hours columns	must be brought to
this stage and left	in water.	
Conditioning		
7.5 m HN03	4 ml	3 ml
Loading: Sample is d	lissolved in the foll	owing columns of:
7.5m HNO3	1 ml	0.2 ml
Washing		
7.5 M HN03	1 ml	0.3 ml
7.5 M HN03	2 ml	0.5 ml
Elution		
H ₂ O	2 ml	
1m HBR	6 ml	
6m HCL	4 ml (Th)	
		1.
Collect		
1m HBR	4 ml (U)	

Table C3: Quantities used in the ion exchange uranium procedure:

C.3.1 Loading Technique

The samples were loaded in filtered air in a laminar flow cabinet.

(a) Gloves were worn at all times.

- (b) For lead, a single rhenium filament bead was placed on the centre insert of the current power supply, and, for uranium, a double filament with side filament at the bottom was used.
- (c) One ul of 1/3 or 0.3M H_BPO₄ was pipetted onto the filament and was evaporated until almost complete dryness.
- (d) For lead Standard: One ul of silica gel was pipetted onto the filament and likewise evaporated to almost complete dryness, as the current was very slowly increased to a maximum of 1.15 A (amperes). If sample starts drying, the current is then lowered to 1.00 A.
- (e) One ul of the NBS 981 Standard was loaded and evaporated to dryness at a current of 1.5 A. Then the current was very slowly until the filament has a red glow or begins to smoke, so that the surface is smooth and has no bubbles. In the case of uranium, a current of 1.3 A was used, and the observational test for reducing current was a small puff of outgassing acid. The sample was then let dry for about a minute.

(f) With test samples the procedure was slightly different. These were picked up in H₃PO₄ and loaded onto the filament (Step C). Otherwise, the procedure was the same as above.

C.3.2. Filaments.

Cathoden Ltd. single and double filaments were used. They were cleaned in boiling de-ionized water for about 10 minutes prior to use. Different filament configurations were used for Pb and U analysis. Lead was loaded onto single rhenium filaments (Figure 4A) while uranium was loaded onto the side of a double filament. The double filament consists of two metallic ribbons, one side filaments onto which the sample is loaded and one centred filament used for ionization. A rhenium filament was used as the centre and a Tantalum filament was used as the side filament (Figure 4B). Filaments were outgassed for 15 minutes at a current of 2.7 A under vacuum (5 x 10^{-6} Torr) prior to loading. All filament ribbons (H.Cross Co.) were measured 25 micrometres thick and 760 micrometres wide. For uranium analysis, zone-refined rhenium ribbons (purity 99.9%) were used.

C.3.3. Lead dynamic temperature

Procedure name: Pb DYNAMIC 1250 C GPJ Type: AXIAL Peak Jump

----ENTER----------SIDE--------WARMUP TIMES (mins)--P-heat Init Max P-heat Init Max Filament Preheat Hold Measure 0.00 0.00 0.00 Currents 0.00 1.70 2.20 00.0 00.0 05.0Pyrometer Initial Z-bias Z-focus Slit D-focus D-bias Extract Source 500 1250 C values 500 400 600 700 700 050 Rhenium aiming current 0.0E+00 Beam growth limit -2.5 to +2.5 % in 10 sec. 2 3 4 5 Sequence 1 6 Detector (F/D) F F D F F F Aiming current 1.0E-13 1.0E-13 1.0E-13 0.0E-00 0.0E-00 0.0E-00 No. of runs 00 00 00 01 01 10 No. of cycles 02 02 15 00 00 00

19

00

00

00

Daly bias +0.000E+00 Faraday bias +0.000E+00

19

Start Grand Totals at Sec. No. 3

Sequence type

C.3.4. Analytical errors.

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Reproducibility of lead isotope ratios is very good for all samples. Replicate analyses of the standard NBS SRM 981 obtained in the course of the entire research were compared with the recommended value for NBS SRM 981. See Table C.4.

The two main errors affecting lead isotope analysis are mass-dependent isotopic fractionation in the mass spectrometer and the accuracy of measurement of the small ²⁰⁴Pb peak. In a ²⁰⁷Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb diagram, both errors yield theoretical error lines (Doe et al., 1966) having slopes of 1.23 for mass fractionation and 0.82 for the inaccuracy in the ²⁰⁴Pb measurement.

Fifty measurements of the lead standard NBS SRM 981 also define an array in a ²⁰⁷Pb/²⁰⁴Pb versus ²⁰⁶Pb/²⁰⁴Pb diagram (Figure C.3). This "error line" has a slope of 1.01, which is intermediate between the two theoretical error lines, thus indicating both that analytical errors have been affected more or less equally in the lead isotopic measurements and consequently that they can be explained either hv physico-chemical fractionation or by uncertainties in the measurement of 204Pb. Therefore, all data have heen correlated for mass isotopic fractionation using the following formula:

- CC = MC / (1 f (n/100)), where
- CC = Corrected composition
- MC = Measured composition
- f = Percentage fractionation per atomic mass unit.
- n = Mass speed of ratio considered in the correction procedure.

For example, a common value for 206Pb/204Pb will be n = 2.

The percentage fractionation per atomic mass unit can be deduced by comparing the measured lead composition of the Standard NBS SRM 981 with the recommended value. In the present study, the difference between these two values was found to be about 0.10%, on average. Figure C.3 Experimental error line defined by replicate analyses of the NBS Standard SRM 981. Small black dots: Measurement of NBS 981 in the present study. Open star: the recommended lead isotope composition of the Standard NBS 981.



C.3.5

^orocedure name: U ID GPJ Type: AXIAL Peak Jump ----ENTER----------SIDE--------WARMUP TIMES (mins)--P-heat Init Max Filament P-heat Init Max Preheat Hold Measure Currents 0.00 4.60 6.20 0.00 0.80 2.80 00.0 00.0 05.0^Pyrometer Initial Z-bias Z-focus Slit D-focus D-bias Extract Source 500 400 600 700 0000 C values 500 700 050 Rhenium aiming current 0.0E+00 Beam growth limit -9.5 to +9.5 % in 10 sec. 2 Sequence 3 4 5 6 1 F F)etector (F/D) F D F F 0.0E-00 0.0E-00 0.0E-00 limina current 1.0E-14 5.0E-14 1.0E-13 No. of runs 01 01 10 00 00 ŌŌ. No. of cycles 10 20 20 00 00 00 Sequence type 30 30 30 00 00 00

)aly bias +0.000E+00 Faraday bias +0.000E+00

Start Grand Totals at Seq. No. 3

```
20 INPUT "SAMPLE NAME".A$
21 INPUT "SAMPLE NAME".A$
22 LPRINT A$
30 LPRINT
40 INPUT "ENTER wt of: powder".W1
50 LPRINT W1
60 INPUT "ENTER wt of:beaker empty:beaker+soln:spiked soln.",W3,W4,W5
70 LPRINT W3, W4, W5
80 INPUT "ENTER wt of spike", W9
90 LPRINT W9
100 INPUT "ENTER 238/235", R1
110 LPRINT R1
120 INPUT "ENTER Pb comp. 6/4. 7/4. 8/4. ID 6/4".R2.R3.R4.R5
130 LPRINT R2.R3.R4.R5
140 A1=203.973
150 A2=205.974
160 A3=206.976
170 A4=207.977
180 A5=235.044
190 A6=238.051
200 S1=7.7
210 S2=2.31
220 53=.0000011
230 $4=.0088342
240 $5=.0143054
250 $6=.0000046
260 W8=W1*W5/(W4-W3)
270 R6=(R5-R2)*A2
280 R7=A1+A2*R2+A3*R3+A4*R4-R6*S3/S4
290 CONCPB=S1*R7/R6*W9/W8
300 R8=1/R1-1/137.88
310 CONCU=S2/R8*A6/A5*W9/W8/(1+S6/S5)
330 LPRINT
340 LPRINT "Conc. U=",CONCU," ppm
350 LPRINT
360 LPRINT "CONC. PB=", CONCPB, " ppm
370 GOTO 20
380 END
```

Lead Isotope Ratios of standard NBS981 run during the course of this research

		zoepp		20769		SoebP	
Temp		204Pb	s.d.	204Pb	s.d.	204Pb	s.d.
1250	C	16,907	0.018	15.449	0.017	36.556	0.018
		16.912	0.024	15.458	0.031	36.600	0.029
		16.899	0.015	15.445	0.016	36.523	0.018
		16.907	0.040	15.445	0.040	36.543	0.043
		16.840	0.028	15.387	0.027	36.385	0.031
		16.900	0.013	15.448	0.016	36.571	0.016
#14		16.919	0.032	15.475	0.033	36.621	0.028
		16.895	0.037	15.448	0.038	36.568	0.040
		16.888	0.025	15.445	0.026	36.560	0.026
		16.901	0.003	15.442	0.003	36.553	0.003
		16.902	0.072	15.447	0.080	36.565	0.085
		16.888	0.081	15.446	0.086	36.562	0.090
		16.895	0.131	15.447	0.136	36.600	0.037
		16.893	0.033	15.444	0.033	36.550	0.031
1230	С	16.892	0.080	15.432	0.079	36.520	0.071
		16.882	0.027	15.434	0.027	36.527	0.029
#4		16,901	0.022	15.439	0.091	36.545	0.022
		16.909	0.020	15.462	0.180	36.609	0.021
1150	C	16.870	0.011	15.423	0.011	36.496	0.011
		16.906	0.072	15.453	0.073	36.599	0.069
#32		16.917	0.011	15.469	0.009	36.625	0.009
		16.917	0.064	15.430	0.064	36.509	0.068
		16.904	0.008	15.455	0.008	36.550	0.009
		16.883	0.012	15.443	0.014	36.557	0.015
		16.889	0.028	15.446	0.028	36.566	0.028
		16.885	0.054	15.445	0.058	36.514	0.058
		16.909	0.038	15.469	0.034	36.624	0.035
		16.904	0.019	15.450	0.015	36.589	0.014
		16.867	0.011	15.411	0.014	36.465	0.014
		16.866	0.014	15.415	0.015	36.483	0.017
		16.893	0.010	15.443	0.010	36.552	0.010
		16.888	0.005	15.433	0.005	36.513	0.007
		16.894	0.013	15.441	0.013	36.539	0.011
		16.889	0.009	15.430	0.008	36.511	0.009
		16.914	0.018	15.456	0.018	36.5/5	0.019
		16.89/	0.024	15.443	0.026	36.006	0.025
		16.892	0,006	15.442	0.008	36.552	0.010
		19.308	0.005	15.45/	0.005	36.580	0.006

Table C.4 (continued)

	206Pb		207Pb		зоврь	
Temp	204Pb	s.d.	204Pb	5.d.	204Pb	s.d.
	16.868	0.008	15.413	0.008	36.465	0.010
	16,903	0.058	15.443	0.058	36.540	0.080
	16.934	0.024	15.500	0.024	36.733	0.021
	16,919	0.034	15.465	0.037	36.542	0.011
	16.927	0.038	15.489	0.009	36.659	0.034
	16.898	0.008	15.441	0.016	36.539	0.019
	16.846	0.033	15.402	0.035	36.458	0.039
	16.899	0.020	15.445	0.016	36.545	0.018
	16.865	0.022	15.412	0.016	36.460	0.023
	16.883	0.009	15.436	0.007	36.530	0.008
	16.914	0.009	15.467	0.099	36.618	0.007
	16.858	0.029	15.412	0.027	36.481	0.029

s.d. = internal standard deviation

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