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ICP-MS ANALYSIS
OF RHENIUM AND OSMIUM ISOTOPES
FROM THE COLDWELL ALKALINE COMPLEX

ICP-MS Analysis of Rhenium and Osmium Isotopes from the Coldwell Alkaline Complex

by
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Abstract

The Coldwell Alkaline Complex on the north shore of lake Superior is an intrusion which consists of rings of gabbroic and syenitic material. Analysis of Re and Os isotopes (by ICP-MS) from four samples (three chalcopyrite and one whole rock) of gabbroic material from the outermost ring shows indications of mixing with the surrounding archean terrane. The Re data is obscured however by a large amount of W in the sample. This W seems to come from the process used to prepare the samples and indicates that either separation with sodium polytungstate should be discontinued or a better chromatographic separation should be effected.

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INTRODUCTORY REMARKS

With renewed tensions in South Africa, exploration for alternate supplies of Pt group elements is increasing in Canada. At present there are several companies exploring the Coldwell Alkaline Complex, including Fleck Resources. The Coldwell Complex is a large alkaline intrusion, on the northern shores of Lake Superior near the town of Marathon, consisting of mostly gabbroic and syenitic material. The genesis is uncertain, in the past it has been suggested that the Complex was formed as the result of a failed rifting event[3]. It has also been suggested that the sulfides of the rocks being studied were formed by assimilation of the surrounding Archean terrane[15]. Neither hypothesis, however, has been conclusively proven.

Re and Os are metals that are among the least abundant crustal components. ^{187}Re decays to ^{187}Os with a half life of 4.23×10^{10} years[16] and as transition metals are the only elements that can be used for a geochronometer for the direct dating of sulphide minerals. Os is a compatible element[21] and Re is partially incompatible in a mantle setting. This means that the Re/Os ratio varies depending on the source of the rocks. As both elements commonly occur as sulphide minerals or alloys, Os isotopic systematics pertain to the metallic minerals of a rock (e.g. chalcopyrite, pyrrhotite) and can thus potentially determine the timing and genesis of ore deposits. Furthermore Re and Os are highly refractory metals and are not as easily mobilized as Sr and Ar which are presently used to ascertain the genesis of ores.

Several techniques have been used in the determination of Re/Os. The technique used in this study utilizes Inductively Coupled Plasma Mass Spectrometry (ICP-MS) which ionizes significant portions of the Re and Os content in a plasma[17] and can produce accurate Re/Os even though their elemental abundances are often in the ppb range[16].

The most abundant sulphide mineral in the Coldwell Alkaline Complex is chalcopyrite, which has previously been used by Dr. J.M. Richardson in Os isotopic work at McMaster University. Thus this mineral was used to assess the Os isotopic character of the Coldwell Alkaline Complex.

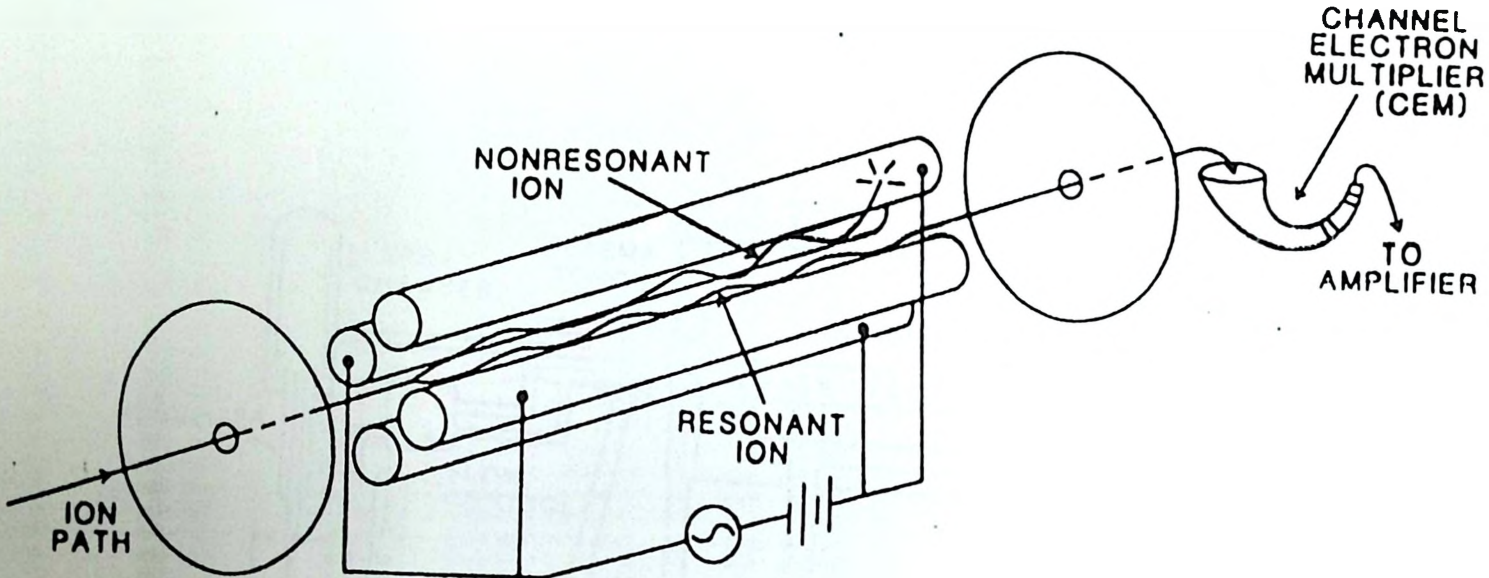


FIGURE 1: FROM STRONG AND LONGERICH, 1985

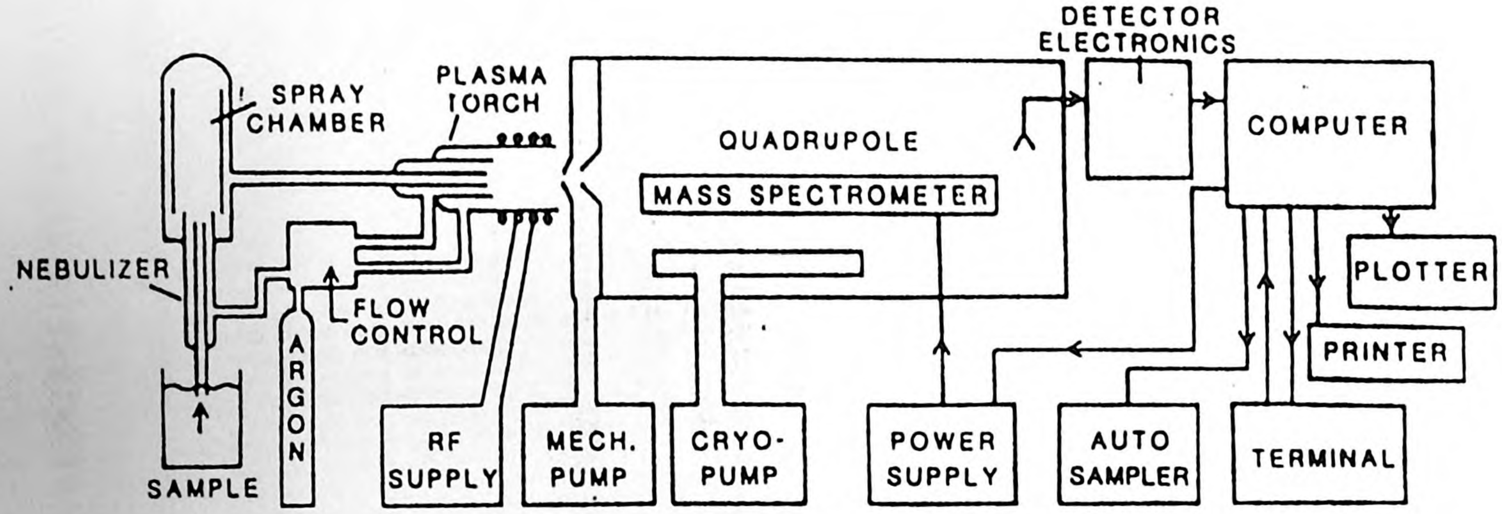


FIGURE 2: FROM STRONG AND LONGERICH, 1985

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

The technique of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is an addition to the stable of hyphenated techniques that have already been developed (e.g. GC-MS). In ICP-MS an RF (radio frequency) produced Ar plasma (the ICP) is connected to a quadrupole mass spectrometer (see figure 1) with a tiny hole interfacing the two to allow the sample (which is at atmospheric pressure) to be precisely analyzed by the mass spectrometer (which requires pressures of no more than 10^{-5} torr). The liquid sample is usually introduced via a nebulizer (see figure 2). An argon gas flow entrains the tiny nebulized droplets of sample and carries them to the torch where the plasma is located. The sample is then almost completely ionized by the plasma (which reaches temperatures up to 7500 K). The ions then pass through the interface to reduce the pressure of the ionized sample and Ar gas flow. Once the pressure has been reduced to about 10^{-5} torr the sample is channelled into the quadrupole mass

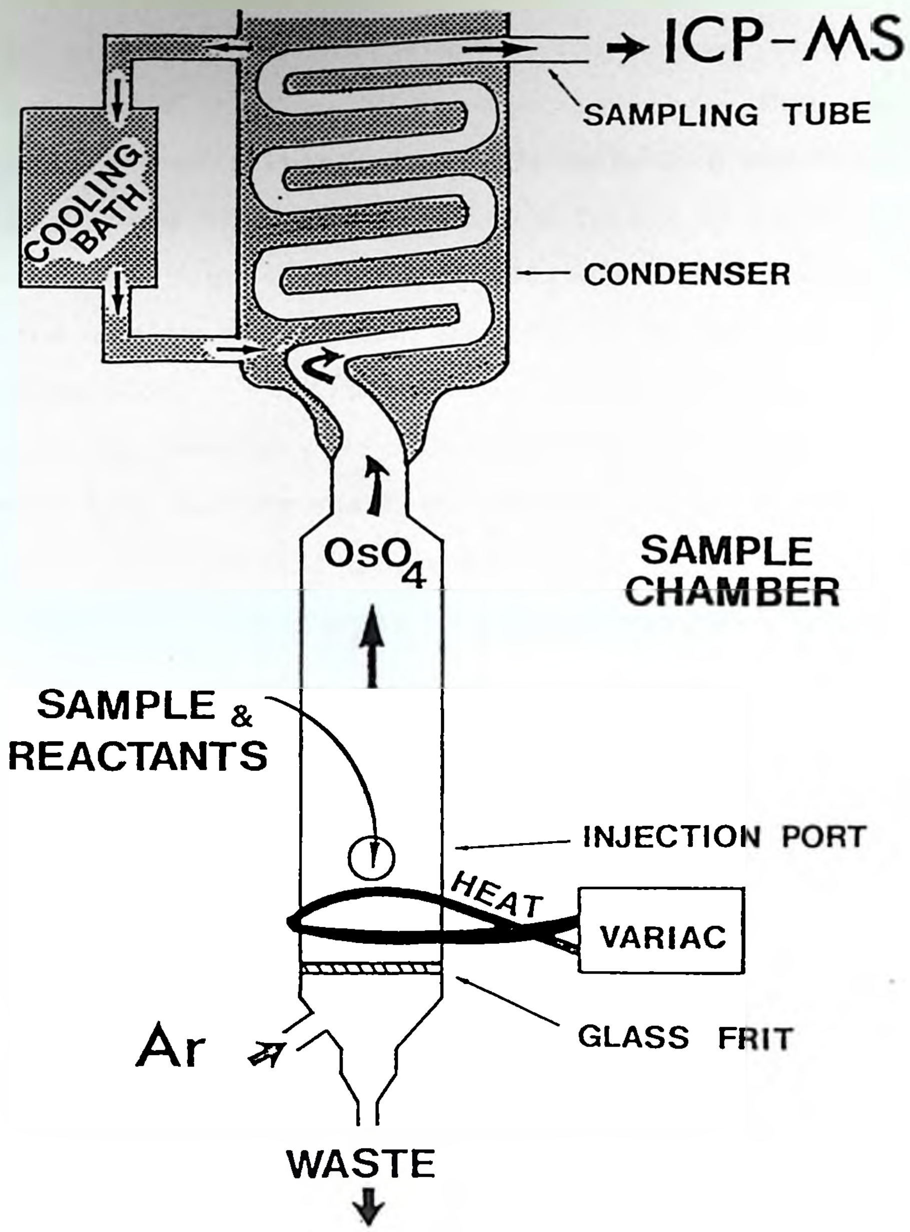


FIGURE 3: FROM RICHARDSON ET. AL., 1989

spectrometer (i.e. a mass spectrometer which uses ellipsoidal, charged rods to guide the ions to the ion counter). This analyzes the ions rapidly and efficiently for their abundance and type. For analyzing Os, instead of a nebulizer the solution is injected into an Os generator (see figure 3). Quantitative analysis is performed by spiking the sample with known amounts of Re and Os on known isotopic composition. The ICP-MS can detect isotopes down to abundances of a few tens of parts per trillion. This technique is thus a powerful tool for the quantitative analysis of low abundance isotopes, especially refractory elements like Re and Os which are not easily isotopically analyzable by most other common techniques.

Sample Type	^{187}Os/^{186}Os	^{187}Re/^{186}Os	Reference
Shale	6.2	3000-4000	18
Komatiite	1.3-2	1.5-38	19
Dolerite Dike	80-570	1200-14000	19
Tholeiite	108	1780	19
Komatiite	0.873	15-30	21
G-Chromitite	0.895	0.17-0.22	22
J-M Reef	1.32	12-20	22
Osmiridium	0.9-1.02		24
Laurite	1.45		24
Chondrite(C1)		3.3	24
Chondrite(H,L,E)		3.4	24
Iron Meteorites		3.2	24
Whole Mantle		3.2	24
Granite		400	24
Basaltic Tholeiite		1100	24
Peridotite		3.2	24
Shale	1.12		28

Table 3: Isotopic Ratios for Selected Rocks

GEOCHEMISTRY OF Re AND Os

The isotope ^{187}Re decays to ^{187}Os by beta decay with a half life of $(4.23 \pm 0.13)\times10^{10}$ years[23]. In the mantle it has been found that Re is an incompatible element and Os is a compatible element which means that Re is selectively enriched in crustal material and Os, for the most part, remains in the mantle. Since ^{187}Re is partitioned away from ^{186}Os (which remains in the mantle) there is a significant variation in the ^{187}Os/^{186}Os and ^{187}Re/^{186}Os ratios in rocks, depending on the age of occurrence and upon the source material (e.g. recycled crust, depleted mantle, mantle etc.). As Os is compatible it does not matter whether material was derived from chondritic or from depleted mantle sources. This is because both have a fairly constant ^{187}Os/^{186}Os ratio. Over time, only crustal development or mixing should significantly alter this ratio. Thus Os becomes more radiogenic in most crustal rocks as compared to mafic rocks, e.g. the more mafic the rock the smaller the ^{187}Os/^{186}Os ratio as compared to more acidic rocks (see table 3). Thus the use of the Re-Os

Sample Type	[Os] ppb	[Re] ppb	Reference
River and Shelf Sediments	0.01-0.07		18
Shale	1-3	50-300	18
Komatiite	5-7	0.2-4	19
Tholeiite	0.0413	1.84	19
Dolerite	0.004-0.06	1.5-1.8	19
Dunite	3.9		20
Harzburgite Dunite	6.7		20
Kimberlite	5		20
Chromite	112-1680		20
Komatiite flows	1-2.2	0.545-1.27	21
Mantle	3.1		21
Chromitite	26.5	0.113	22
Hawaiian Basalts		1	22
Chondrites (C1)	420	35	24
Chondrites (H,L,E)	660	37	24
Iron Meteorites	2500	30000	24
Granite	0.06	0.6	24
Basaltic Tholeiite	0.03	0.84	24
Peridotite	5.3	0.43	24
NiCu Sulphide	0.440	0.448	25
Syenogabbro		3.6	30
Syenite		1.8	30
Granite	2.0	6.7	30
Diabase	4.6	7.1	30
Hawaiian Basalt	3.0		30
Dunite	11.4		30

Table 2: Re and Os Concentrations in Selected Rocks

system could be a valuable aid in modelling of mantle and crustal processes once there is sufficient data.

The compatibility of Os results in a separation of daughter and parent isotopes during the initial formation of the rocks. This is unlike the other common isotopic tracer techniques like Rb/Sr, Sm/Nd and U/Pb, where both the elements are incompatible to the mantle[21].

It has been found that the Re-Os system is theoretically open to resetting in fluids that transport noble metals[21]; however, no unambiguous examples of this have been published yet (so far Re/Os have been found resistant to greenschist grade metamorphism[21]).

One problem with Re/Os is that the elements occur in such low abundance (most crustal materials contain less than 1 ppb of Os[19] (see table 2)) that even just a very small amount of a mineral concentrated in Os can severely skew results. For example the presence of one 20 cubic micrometer grain of laurite $(Ru, Os, Ir)S_2$ (containing 9 weight % Os) per gram of sample would increase the whole rock concentration of Os by 5 ppb[22]. Thus if rocks analyzed are too low in PGE's then information is difficult to acquire, and if the PGE concentration is too high in the sample, then there is a possibility that the sample is too heterogeneous for a precise determination of the Os content.

There is a low abundance of Os in naturally occurring rocks (see table 2). Usually those rocks likely to have a large amount of Os are chosen for analysis. It has been found that there are higher PGE values associated with ultramafic rocks. Also there is a close association of PGE's with chromite and sulfides[20]. The fractional crystallization of basic magmas leads to a concentration of Os in early crystallizing fractions[20]. Thus most of the analyses so far have dealt with PGE rich sources (Bushveld, Stillwater etc.).

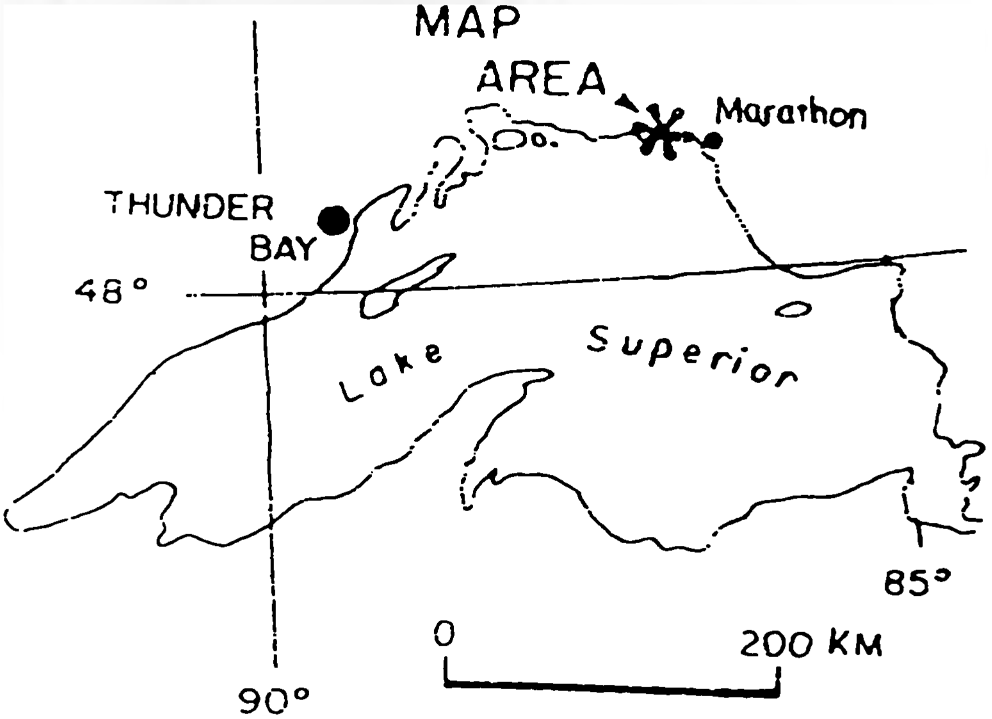


FIGURE 4: FROM MITCHELL AND PLATT, 1982

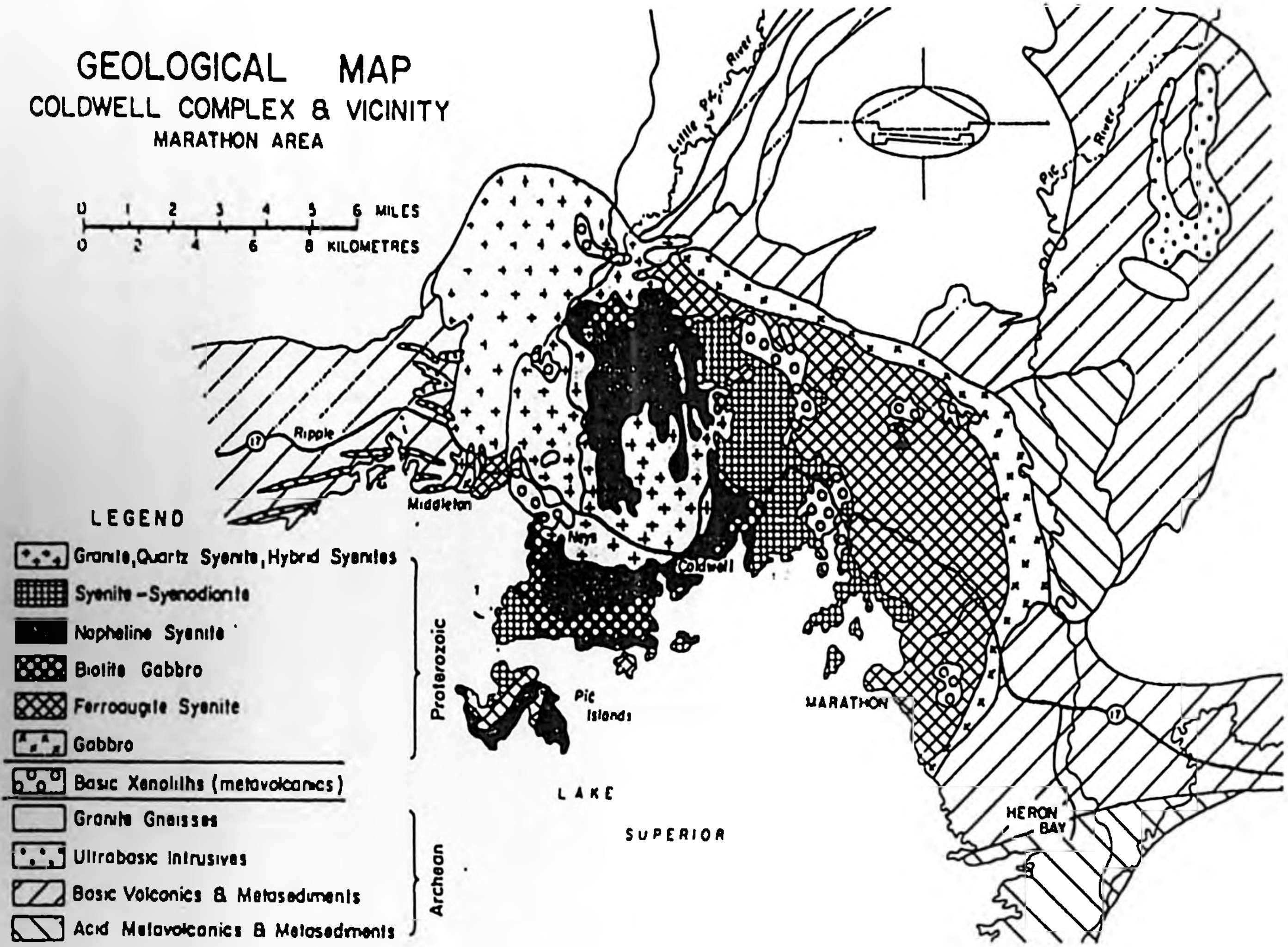


FIGURE 5: FROM PLATT AND MITCHELL, 1982

GEOLOGY OF THE COLDWELL REGION

The Coldwell Alkaline Complex is a partial ring structure located on the north shore of Lake Superior near the town of Marathon (see figure 4). The complex is about 25 km in diameter and is the largest alkaline complex intrusion in North America. It is of Neohelikian age (1044.5 ± 6.2 Ma (2 sigma): Rb/Sr whole rock isochron[1]) and intrudes the Wawa-Abitibi Greenstone Belt of the Superior Structural Province (see figure 5). The complex is slightly younger than the majority of the Keweenawan igneous events that occur in the Lake Superior basin around that time.

The Coldwell Alkaline Complex is located at a 'hinge point' between the Mamainse Michipicoten volcanic sequence and the North Shore Osler volcanic sequence (see figure 6). The Complex is associated with nearby alkaline intrusions that occur in a roughly N-S belt with the Coldwell Complex forming the southernmost member. The Coldwell complex is similar to complexes formed in continental rift zones (e.g. Oslo rift, Gardar rift, Kenyan rift)[2] and is considered to have originated

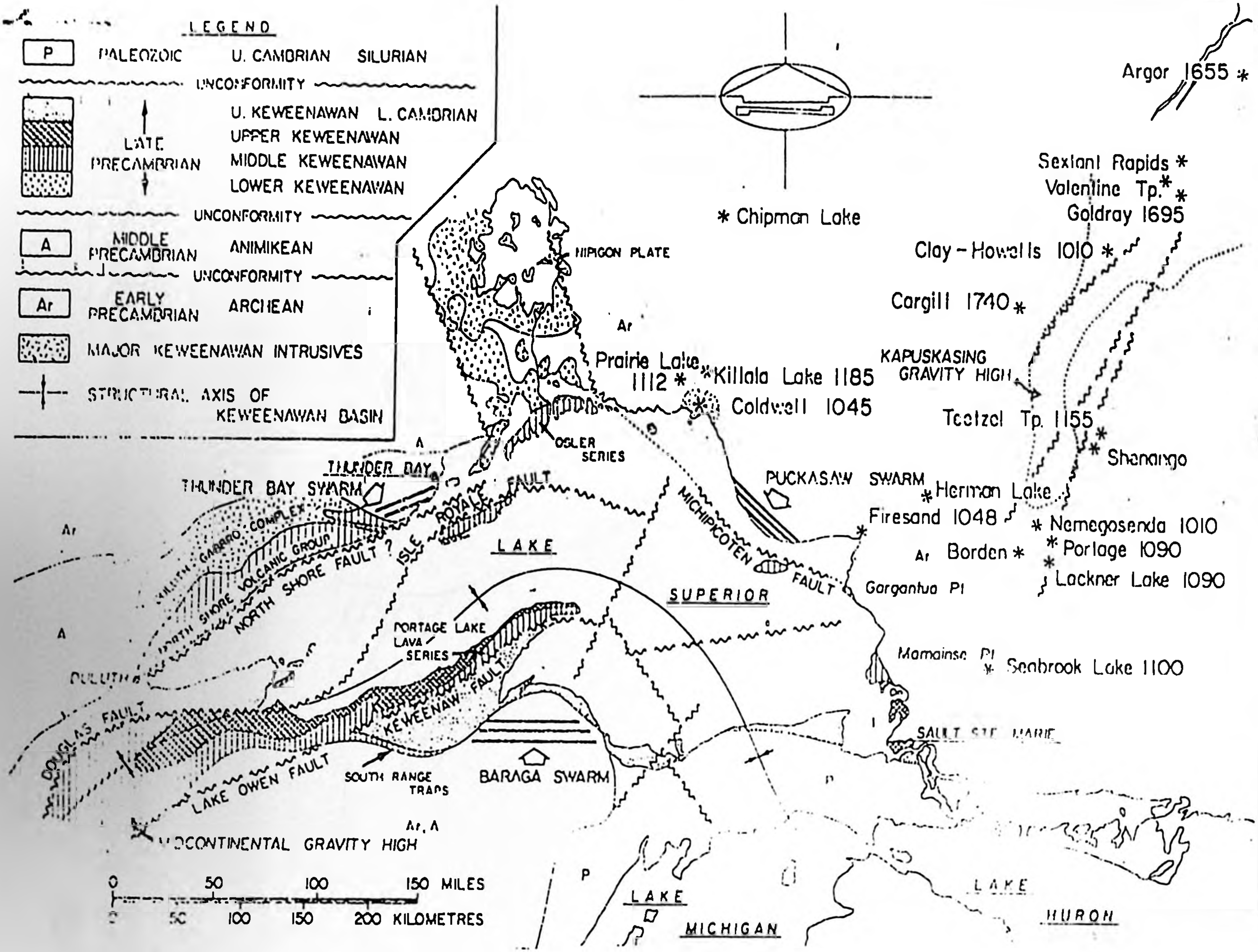


FIGURE 6: FROM MITCHELL AND PLATT 198

MARATHON PROPERTY

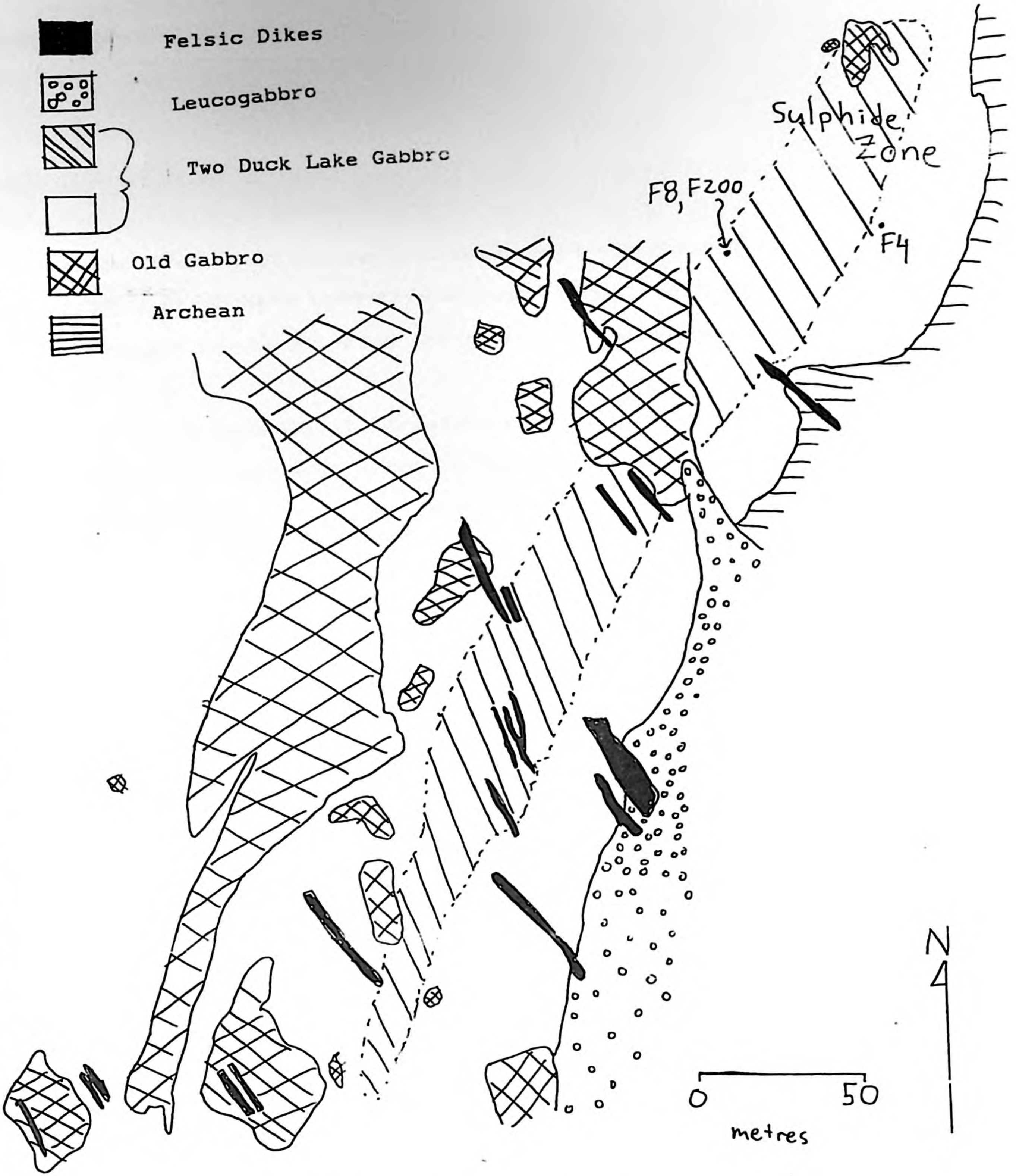


Figure 7: Drafted by Dave Good

as a result of the partial melting of subcontinental upper mantle at a plume-generated triple junction[3]. The Coldwell Complex is thought to characterize the failed arm of a spreading centre.[3]

The Wawa-Abitibi Greenstone belt, host rocks of the Coldwell Alkaline Complex, consists of supracrustal metavolcanic and metasedimentary rocks. The metavolcanic units are composed of calc-alkalic pyroclastic rocks, schists, gneisses and mafic (iron rich) tholeiitic volcanic rocks. The metasedimentary rocks contain graded turbidites, mudstones, schists, conglomerates and wackes. Two periods of folding and faulting are reported and the metamorphic grade is greenschist to amphibolite facies[4].

The Coldwell Complex comprises three separate intrusions. The first and oldest intrusion contains saturated alkalic rocks and peralkaline oversaturated residua (material formed before the intrusion). This intrusive centre comprises the eastern gabbro and consists of ferroaugite syenite. The second intrusion (the western gabbro, biotite gabbro, ferroaugite syenite and nepheline syenite units) contains miaskitic alkaline rocks with undersaturated residua. The latest identifiable intrusion contains alkaline rocks characterized by oversaturated residua. This final intrusion is only seen on the Pic Islands and the nearby Coldwell peninsula[13,6].

The internal structure of the Coldwell Complex consists of an interlocking system of gabbroic ring dikes and conical sheets of syenite[5]. The central portion of the complex contains more xenoliths than the outer portion and is thought to be a downfaulted block that is bounded by the Little Pic River Fault and the Redsucker Fault Zone[6]. Each magmatic centre represents a particular subsidence event with a general regional westward trend of subsidence over time[7].

A recent gravity survey over the Coldwell Complex showed a 50-60 mgal positive anomaly[8] . However the rock exposed at the surface consists of mostly low density syenite and minor gabbro. To account for the anomaly, Mitchell ***et al.*** (1983) proposed that the 3-5 km of felsic rocks at the surface is underlain by 3-5 km of gabbro. They postulated that 3 km of peridotite or pyroxenite lies beneath this gabbro.

Within the Coldwell Complex, there are several platinum group element (PGE) deposits and showings. The Fleck deposit is presently being explored by Fleck Resources LTD. for Cu, Ni, Pd, Pt, Au, and Ag. The deposit is located in the Two Duck Lake gabbro and is bordered to the east by Archean rocks of the Abitibi-Wawa greenstone belt and to the west by ferroaugite syenite of the Coldwell Alkaline Complex. The mineralogy of the deposit consists of olivine(Fo_{67-49}), plagioclase(An_{60-35})[9], biotite, magnetite, ilmenomagnetite, sulphide minerals, apatite, augite and clinopyroxene[10]. In the sulphide rich zones, Cu, platinum group metals (PGM), Ag, Au, Co, and Ni are found.

The Two Duck Lake Gabbro which hosts the Fleck deposit intrudes an older gabbro to the west. The eastern edge of the Two Duck Lake Gabbro intrudes the Heron Bay Greenstone Belt. Internally, the Two Duck Lake Gabbro consists of three distinct phases of gabbro: a pegmatitic gabbro which occurs at the contact

Mineral Name	Mineral Formula
chalcopyrite	$CuFeS_2$
pyrite	FeS_2
pyrrhotite	$Fe_{1-x}S$ (x= 0-0.17)
pentlandite	$(Fe,Ni)_9S_8$
merenskyite	$(Pd,Pt)(Te,Bi)_2$
hollingworthite	$(Rh,Pt,Pd)AsS$
cubanite	$CuFe_2S_3$
temagemite	Pd_3HgTe_3
kotulskite	$Pd(Te,Bi)$
altaite	$PdTe$
isomertierite	$Pd_{11}Sb_2As_2$
mertierite II	$Pd_8(Sb,As)_3$
atokite	$(Pd,Pt)_3Sn$
zvyagintsevite	$(Pd,Pt,Au)_3(Pb,Sn)$
sperrylite	$PtAs_2$
electrum	(Au,Ag)
clausthalite	$PbSe$
bornite	Cu_5FeS_4
michenerite	$(Pd,Pt)BiTe$
stannopalladinite	$(Pd,Cu)_3Sn_2$
guanglinite	Pd_3As
majakite	$PdNiAs$
empressite	$AgTe$
hessite	Ag_2Te
melonite	$NiTe_2$
muthamannite	$(Ag,Au)Te$
altaite	$AgTe$
naumannite	Ag_2Se

Table 1: Metallic Minerals of the Coldwell Complex

with the older gabbro, a coarse grained gabbro which occurs to the east of the older gabbro and a light coloured pegmatitic phase which seems to be a very chemically altered constituent of the pegmatite.

The Two Duck Lake gabbro contains silicate, sulphide, telluride, and PGE minerals. The common sulfides are chalcopyrite, pyrrhotite, pentlandite and pyrite. Other minerals are listed in Table 1[12,11,14]. The PGE's are concentrated asymmetrically along the eastern and western boundaries of the Two Duck Lake gabbro. PGE's are associated with the Cu rich sulphide minerals, but no PGE's have yet been identified in pyrrhotite[11]. Some crystals of hollingworthite are zoned and have high Ir contents in the centre and elevated Os and Rh at the margins[12].

SAMPLE DESCRIPTIONS

In the field season of 1989 Dave Good traveled to the Two Duck Lake gabbro of the Coldwell Alkaline Complex to collect samples for his Ph.D. thesis. Upon returning, samples F4, F8 and F200 (see figure 7) were chosen for Re/Os analysis. These samples were slabbed and subsequently F8 was divided into a pegmatite and a coarse grained portion. Sample F200 was divided into a white and a dark portion (samples F8P, F8C, F200W and F200D respectively). The samples were subdivided along a 1 cm wide gradational boundary and the subdivisions were believed to be comagmatic.

From the field geology it was advised that samples F8 and F200 were collected in a sulphide rich zone. Scattered through this zone were roundish pods of pegmitite mixed with the more coarse grained gabbro.

Upon examination of the thin sections a rough mineralogy was devised along with a relative time scale of formation for the major minerals (see figure 7). Sample F4 and F8C were fresh coarse grained gabbros consisting of plagioclase, olivine, amphibole, pyroxene and a trace of pyrrhotite and magnetite. They consisted mostly of plagioclase, pyroxene and amphibole with scattered grains of olivine and about 5% sulphides (chalcopyrite and pyrrhotite). Sample F200D consisted of roughly the same mineralogy but there was less plagioclase and more sulphides and olivine. In addition there was some alteration of some of the grains and there seemed to be an overall form of large clumps of pyroxene, amphibole and sulphide crystals. Sample F200W was quite light compared to F200D and contained a little more plagioclase, less pyroxene, less sulphides (barely visible), a little calcite and a fair amount of intersitial material that was unidentifiable. Lastly sample F8P was more like sample F8C however the grains were two to three times larger, euhedral chlorite was reacting with some of the grains, calcite occurred in fair sized chunks and the grains seem more altered (see appendix).

ANALYTICAL METHOD

Crushing and Mineral Separation

The samples F200, F8 and F4 were cut into 3-0.5 cm slabs on a water cooled diamond saw. The slabs were then examined with a hand lens, described and any weathering was removed with a diamond blade saw. Next sample F200 was divided into a light portion and a dark portion and F8 was divided into a pegmatite portion and a coarse grained portion. The samples were then cleaned in an ultrasonic bath.

The samples were crushed in a Braun Chipmunk jaw crusher, split into two portions and stored in labelled plastic bags. About 150g of each sample was then crushed finely in a tungsten carbide shatterbox and placed in bags for fire assay analysis.

Samples F200, F8 and F4 were sieved using plastic sieves. Material that was greater than 30 mesh was removed and stored.

The samples were then divided into size fractions of -30+70 mesh, -70+100 mesh, -100+140 mesh, -140+200 mesh and less than 200 mesh. This material was stored in Ziploc plastic bags for mineral separation.

The samples had a strongly magnetic portion separated by hand magnet. These were then were separated into heavy and light minerals using liquid sodium polytungstate (2.94 g/cm^3) in separatory funnels. Both heavy and light portions were washed with water to remove adhering sodium polytungstate (tungsten can interfere with Re and Os data acquisition on a mass spectrometer due to the nearness of the ^{186}W to the Re and Os isotopes). The heavier material was then run through a magnetic separator (slope 15 degrees, tilt 30 degrees) and at an amperage of 1A only chalcopyrite and plagioclase remained.

Chemical Preparation

The sulphide separates were then weighed and a precise amount of spike material was added to each. The spike material consisted of a $^{190}Os/^{192}Os$ ratio of 51.5 ± 0.9, $^{187}Os/^{188}Os$ ratio of 0.063 ± 0.006 and a $^{185}Re/^{187}Re$ ratio of 17.04 ± 0.41. This material is used to precisely quantify the amount of Os and Re in the sample. The samples were then dissolved in concentrated HNO_3 and placed on a hot plate at a low temperature for 3 days. The resulting solution was filtered and half of the solution was placed in a refrigerator for Os analysis. The other half of the solution was dried on a hot plate to remove all HNO_3. This was then dissolved in concentrated HCl and set aside for ion exchange.

To clean the Re part of the solution of excess Ni, Cu and other elements which might interfere with the ICP-MS, the solution was washed down a column of -100+200 mesh anion exchange resin (Bio-Rad AG-1X8). The resin was then washed with 50 mL of 1M HCl. The resin was next washed with 70 mL of 6M HCl and divided into three portions (0-5 mL, 5-65 mL, 65-70 mL) then the HCl was boiled off and the residue redissolved in 2 mL of 1M HCl.

Fire Assay

The sample F200W (the light coloured F200 portion), was mixed with 3 g silica, 1.21 g of sulphur, 2.47 g of Ni, 12.29 g of Na_2CO_3 and 24.62 g of Na_2BO_4 in a crucible. The crucible was put in a furnace for 16 hours at 1100 degrees celsius. Once cool the crucible was separated from the metal bead (which contains most of the Os) and the flux (which contains most of the Re). The bead was crushed in an agate mortar and subject to dissolution as previously described in the Chemical Preparation section. The flux was then crushed in the tungsten carbide shatterbox and the resultant powder was placed in a beaker with concentrated HCl. After a day the HCl was decanted, set aside to boil to a smaller volume, and additional HCl was added to the powder. This process was repeated 7 times and the HCl was boiled down to a volume of 100mL whereupon it was washed down the ion exchange column as previously described.

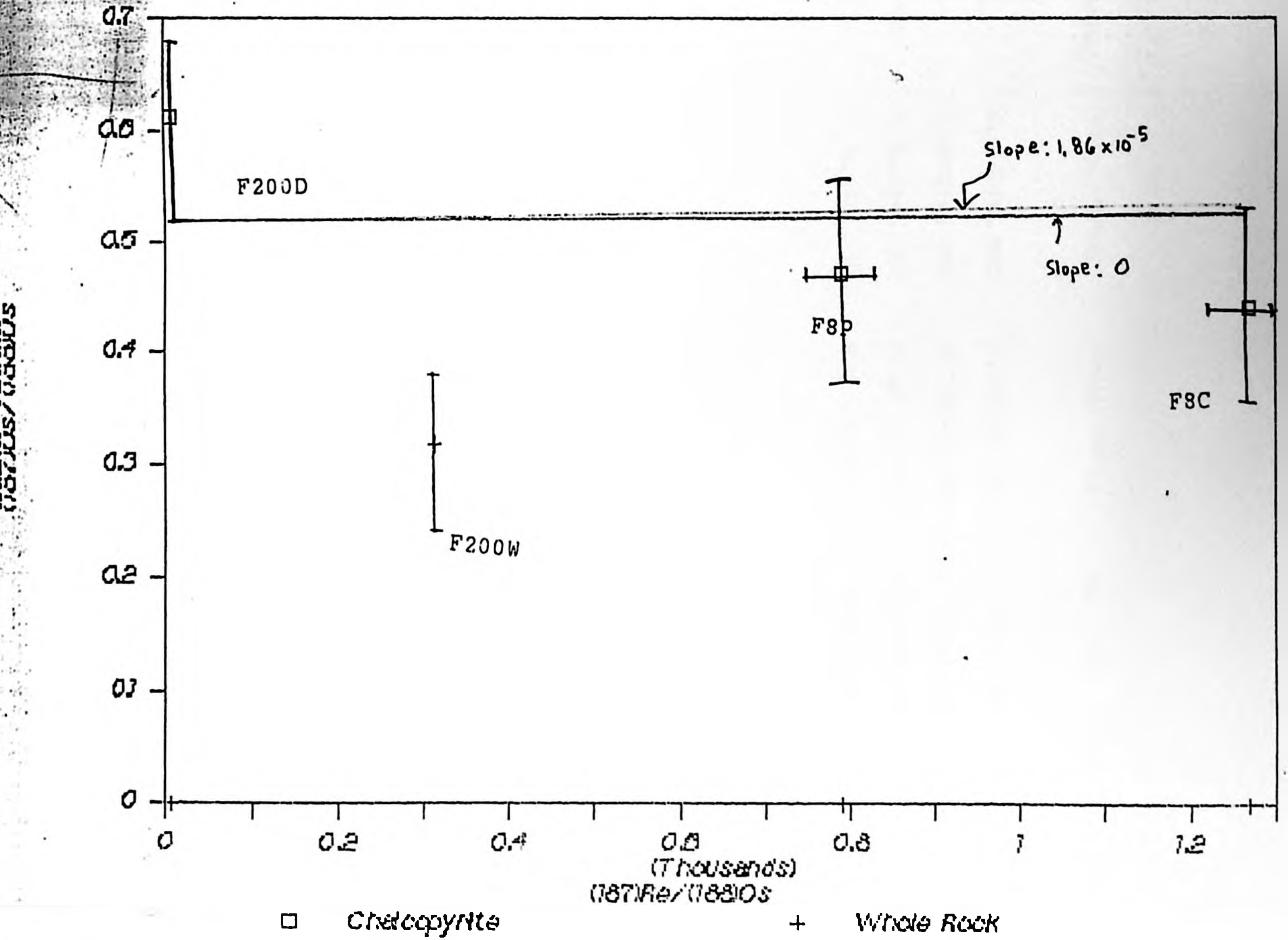
Mass Spectrometry

For Os analysis the ICP-MS was optimized for the analysis of Os using a solution of 10 ppb of Re. This enabled the positioning of the torch (in this case a long torch was used) such that the ions were quantitatively passed to the quadrupole mass spectrometer. The optimized lens settings were: lens B=36, lens E1=75, lens P=22 and lens S2=44. The flow of the Ar was also optimized and this resulted in gas flows of: Nebulizer=1.0 L/min, Auxiliary=2.0 L/min. and Plasma=12 L/min. The total nebulizer pressure was 9.5 p.s.i., the power was 1.2 Kw and the running pressure of the mass spectrometer was 2×10^{-5}.

After the optimization a blank consisting of HIO_4 was injected into Osmium generator (see fig. 5) to provide a background spectrum. After rinsing with water 1 mL of HIO_4 was injected into the generator followed by 1 mL of the Os solution. The HIO_4 strongly oxidized the solution converting the Os to $OsO_4(g)$ which was carried up to the plasma with a flow of Ar and from the torch into the quadrupole mass spectrometer for analysis. The generator was again washed with water and the procedure repeated for 5 injections of Os solution. Between switches in solution all the glassware was cleaned by soaking in aqua regia for 1 hour. The data was stored on a 3 1/2" disc for further analysis.

For Re analysis the solution was introduced into a nebulizer for analysis and the drained solution was recycled back to the nebulizer through the same container. The mass spectrometer took 80 analyses of each sample and between samples the nebulizer was cleaned by running 3M HCl and water through it. Again the data was stored on 3 1/2" discs for data analysis.

Re and Os Isotopic Values



Sample	^{187}Os/^{188}Os	^{185}Re/^{187}Re	Os (ppb)	Re(ppb)
F8P	0.473+0.085	2.674±0.064	1.35±0.68	51.8±1.2
F8C	0.442±0.096	2.730±0.048	1.77±0.64	96.6±1.7
F200D	0.613±0.099	9.68 ±0.24	1.96±0.28	3.46±0.09
F200W	0.319±0.078	8.9 ±1.9	0.13±0.04	0.73±0.11

Sample	^{187}Os/^{186}Os	^{187}Re/^{186}Os	^{187}Os(ppt)	^{187}Re(ppb)
F8P	3.93±0.88	791 ±40	8.43±0.53	14.1 ±0.56
F8C	3.68±0.95	1270±95	9.01±0.47	25.9 ±1.6
F200D	5.09±0.98	6.17±0.49	321 ±24	0.324±.025
F200W	2.65±0.57	315 ±10	.741±.019	0.733±.019

Table 4: Raw Data

All errors are calculated to 2 sigma

ANALYTICAL RESULTS

The results are presented in two tables (one is data from the printouts and the other has been mathematically manipulated) and one graph. The trend of data plotted on the graph suggests that ^{187}Re is indirectly proportional to Os in a sample. As well, if instead of following this trend you try to plot a positive slope (as should be expected in decay) then it is not possible to get a slope greater than about 1.86×10^{-5}. However previous work[1] requires a slope on the order of 0.0183. Another point is that sample F200W does not seem to correlate very well with the other points on the graph. Lastly the position of F200D seems to indicate that an initial ^{187}Os/^{188}Os value of at least about 0.52 is expected. This correlates to an ^{187}Os/^{186}Os value of 4.3 (which is a much higher value than that for mantle derived material (table 3)).

The tabulated results have a number of interesting features. The sample F200D has Re concentrations greater than Os concentrations. However the concentrations of ^{187}Re and ^{187}Os are practically equal. The values of Re and Os cluster for F8 however

F200D and F200W have only similar ^{185}Re/^{187}Re values. Sample F200W has a combination of low Re and Os concentrations while F8 and F200D have higher Re and Os values with sample F8 having much higher Re concentrations than F200.

DISCUSSION

It is most likely that F200W is not collinear with any of the other analyzed samples because it was the only sample to be analyzed by whole rock analysis. In the other samples only the chalcopyrite was analyzed. Thus the differing chemistries of the samples would lead to varying initial Re and Os

The fact that the data does not fall on a straight line could be explained in several ways. Firstly the evening before the Re analysis was run the ICP-MS detector was unnecessarily strained by careless use. The background was noticeably larger the next day so the Re analyses might be totally incorrect and thus the graph could be meaningless. Alternatively the lack of linearity could be due to ^{187}Re/^{188}Os values for F8 that are erroneously large. The Re analysis of this sample also showed that more W was present than Re or Os. This apparent excess could be from one (or more) of three sources; a)contamination during crushing, b) the mineral separation with sodium polytungstate or c) the rocks themselves. In any event the excess mass at 183 and especially at 184 and 186

(14%, 31%, 29% respectively) could overlap into the 186, 187 and especially the 185 positions if there is an overwhelming amount of W in the system. This overlap would make the data analysis program see extra ^{187}Re and especially ^{185}Re (due to an overlap with both 184 and 186). This would produce ^{187}Re/^{188}Os peaks which were much larger than the actual ^{187}Re/^{188}Os value especially if the Os values were not very large.

That the possible interpreted initial ^{187}Os/^{186}Os value is about 5 times larger than it would be if it was mantle derived (see table 3) indicates that some mixing with crustal material must have occurred between the escape from the mantle and the collection of samples. In fact the ^{187}Re/^{188}Os ratio (which is about one tenth the value of ^{187}Re/^{186}Os) indicates (at least for F200D and F200W which had relatively low amounts of tungsten) that there must have been a great deal of mixing with the surrounding crustal rocks because the ratio is so very large (see table 3).

The very odd equality of concentrations of ^{187}Os and ^{187}Re (considering the half life of 4.23×10^{10} years) in sample F200D could be explained in three ways. First perhaps the Re was mobilized, however this is unlikely as it is more likely that the

Os would be mobilized[31]. Second perhaps Os was mobilized, however if this was the case then one must explain why there is so little Os in the nearby samples. Last possible the samples were collected from near the site of a completely digested xenolith. If a xenolith had been incorporated into the gabbro it likely would have strongly affected the chemistry the area where it was dissolved but would have had little affect on adjacent areas. If the xenolith originated from rocks that were very much older than the intrusion, there would have been time for considerable ^{187}Os to be produced and if this migrated it could enrich a sample at a different locality in ^{187}Os relative to ^{187}Re.

Re and Os values for F8P and F8C are relatively similar because the two subsamples of F8 consist of coarse grained and pegmatitic versions of the same rock. F200W is distinctly chemically and mineralogically different from F200D and hence would not be expected to have similar Re and Os values. Another probable explanation for the dissimilarity in Re and Os content of the F200 Samples is that F200D is from a chalcopyrite separate and F200W is based on a whole rock analysis.

The foregoing discussion pertains to 8 analyses (2 for each sample), 4 of which are in doubt (e.g. Re). As there is some doubt as to the accuracy of some of the results this discussion was meant to outline possible trends in the data.

CONCLUSION AND RECOMMENDATIONS

In conclusion 4 samples were analyzed for Re and Os by ICP-MS. The data showed good precision (as seen in the 2 sigma errors, Table 4) but poor accuracy (as seen in the graph). The main problem with obtaining accurate values seems to be due to the method for analyzing Re. In Re analysis the whole solution is nebulized whereas for the more accurate Os analysis only that part of the solution volatile at low temperatures and pressures was analyzed (mostly OsO_4). This can lead to poor Re results especially if there is too much W in the solution. The tungsten can get into solution from the crushing procedure (tungsten carbide steel), the mineral separation procedure (using the heavy liquid sodium polytungstate) or from the rock itself. Since tungsten has a significant percentage of its natural abundance at masses very close to the mass positions for Re and Os it is critical that as little tungsten as possible be introduced or if accidentally introduced that it be removed as efficiently as possible. The present procedure however does none of these. It is suggested that crushing be done using other metals. It is also suggested that other heavy liquids should be used until a better method of evaluating how much sodium polytungstate is left in the sample after mineral separation (presently it is done by eye which is clearly a poor method as illustrated by these results)

The addition of Re and Os from various aspects of the analytical procedure should be looked into much more extensively. The use of materials (especially metals or substances contained in metals) with unknown Re and Os contents in all aspects of sample preparation and analyses is risky when analyzing at the low ppb and high ppt range because a small amount of contamination could lead to very erroneous results.

The final and most important recommendation concerning analytical procedure is that the chromatographic separation by ion exchange procedure be changed. Rocks containing tungsten will be completely unanalyzable unless this is done and any samples contaminated with tungsten will likely give erroneous Re values. Use of sodium polytungstate along with tungsten carbide crushers makes the process faster and safer than using other heavy liquids and ceramic crushers, but as long as this procedure is followed tungsten contamination will be a recurring problem. On the other hand by using better chromatographic technique the safety and speed need not be sacrificed and rocks that are high in heavier elements will be easily analyzed. Towards this end it is suggested that perhaps investment of research time in coupling HPLC to the nebulizer could be of great value in not only analyzing Re but almost any other element could be separated from the matrix (with the appropriate gradient conditions) and saved for more precise analysis after a preliminary analysis.

On the geological side unfortunately due to the time it took to carry out the procedures, problems with obtaining machine time, and delays due to mechanical breakdown and other difficulties, it was only possible to analyze 4 samples for Re and Os and the Re values (especially for F8) are suspect. This limits the amount that can be said with confidence about the Coldwell Complex. It is however suggested that the sulphide zone in the Two Duck Lake Gabbro might have been significantly mixed with less mafic rocks. Whether this mixing is limited to the sulphide zone (the only part analyzed) or extends to the whole of the Two Duck Lake Gabbro is not known.

The samples should be reanalysed for Re once the ICP-MS is back on line. If more plausible values were obtained then it is likely that the anomalous values were due to a faulty detector. If the anomalous Re values are due to excess tungsten then separating the Re on a chromatographic column should clear up the trouble.

If further time is available to work on samples from Coldwell, I would recommend analyzing sample F4. From the results of this analysis it might be possible to determine if the mixing is limited in area. It is suggested that extensive work on samples from the Archean rock, the Old Gabbro, as well as from the sulphide zone and the rest of the Two Duck Lake Gabbro might well determine if sulphide genesis is due to incorporation of a xenolith, due to general mixing with Archean or Old Gabbro or a completely unrelated event. This could be accomplished by comparing whole rock analyses which can indicate how much Re and Os came from the different mixing end members. If however mixing endmembers cannot be found then possibly remnants of the strata were removed by erosion or else the missing end member has not yet been exposed.

Thus although various problems limited the usefulness of the data in this report if further work is done the Re and Os analyses could be improved and the petrogenesis of the Two Duck Lake Gabbro may be conclusively determined.

APPENDIX

Sample descriptions based on thin sections

Sample F4

Mineral	Abundance(%)	Crystal Form
Plagioclase	30	Euhedral
Olivine	15	Anhedral
Clinopyroxene	20	Subhedral
Amphibole	25	Subhedral
Pyrrhotite	3	Anhedral
Chalcopyrite	7	Anhedral

Sample F8P

Mineral	Abundance(%)	Crystal Form

Plagioclase	20	Euhedral
Olivine	5	Anhedral
Clinopyroxene	15	Subhedral
Amphibole	10	Subhedral
Pyrrhotite	2	Anhedral
Chalcopyrite	10	Anhedral
Calcite	5	Subhedral
Chlorite	8	Euhedral

Special Features:

-sericitization and chloritization of plagioclase, olivine, clinopyroxene, and amphibole

-chlorite grows euhedrally into calcite grains

-chalcopyrite occasionally contains some odd multi coloured dendritic growths on their surfaces

Sample F8C

Mineral	Abundance(%)	Crystal Form

Special Features:

-matrix consists of a lot of altered, unidentifiable minerals around a few large, altered grains of amphibole and plagioclase

-graphic intergrowth of amphibole and plagioclase with the matrix

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