pmd*CRC H1 Project

Application of Re-Os isotopes to Geochronology, Ore Forming models and Exploration Models

Final report

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Executive Summary

Contents:

1. Introduction and Background

The H1 project was initiated in July 2003 in order to apply the Re-Os isotopic system to the investigation of the timing of mineralised systems within the Mt Isa Inlier. The approach was to establish the veracity of the Re-Os isotopic system as a geochronometer in mineralised portions of a polydeformed, multiply metasomatised Proterozoic terrain. To this end a range of deposit types of differing ages were initially targeted (George Fisher, Mt Isa Cu and Ernest Henry IOCG) with a view to developing a geochronological toolkit for the key sulphide phases present in these areas.

The results of the first year of this project provided some tantalising evidence of significantly younger mineralising processes and/or open system behaviour within the (specifically) Mt Isa Cu system, prompting a need for further work to evaluate fully the relative sources, budgets and evolution of Re and Os within the terrain as whole. It was hoped that a more holistic approach to the terrain, rather than focussing wholly upon the mineralised portions, would provide constraints on relative crustal vs mantle sources of PGE (and by inference any base metals travelling with them) and a means by which to evaluate the potential for particularly mafic lithologies, such as the Eastern Creek Volcanics, to provide a source for the mineralisation in the terrain. Further more, it was anticipated that some first order constraints on the age of deposition of unaltered host mineralisation lithologies might also be obtained.

Therefore, overall, the H1 project was designed to push the limits of the then existing Re-Os technology in a terrain of interest to pmd*CRC sponsors, with a view to establish a robust chronometer of mineralisation with Precambrian terranes.

2. The Mt Isa Cu system

Sampling Methodology

A range of samples were selected from within the orebody itself with a view to representing the different zones within the system and indeed the peripheral alteration. Hence four whole rock ore samples were analysed (plus a duplicate analysis, see table 2.1) in addition to a whole rock sample from the alteration halo comprising mag+bt with minor po+sph. These whole rock analyses were complemented by various mineral separates; namely two samples of separated cpy from the central ore body, and sph and asp from within the Cu ore zone. Finally, for the purposes of comparison, sph mineral separate from the Pb-Zn ore zone was also analysed.

Mt Isa ore		Re (ppb)	Os (ppb)	$^{187}Os/^{188}Os$	2SEM	$^{187}Re/^{188}Os$	2SEM
MG03041a	Isa Cu-ore	2.01	0.044	16.267	0.789	684.1	10.3
MG03041b	duplicate	1.93	0.048	14.675	0.115	566.3	8.5
MG04014	Isa Cu-ore	0.092	0.010	1.3409	0.0250	50.6	0.8
MG02070	Edge Cu-ore body	0.462	0.403	0.43541	0.01441	5.74	0.09
AW02025	Core Cu-ore body	0.183	0.283	0.45044	0.02635	3.24	0.05
MG02393	Magnetite alteration	1.35	0.038	8.6729	0.0530	360.8	5.5
2208/90	Chalcopyrite	0.159	0.010	1.5958	0.0804	91.0	1.4
2208/91	Chalcopyrite	0.065	0.007	0.2300	0.0021	45.9	0.7
2364	Sphal from Pb-Zn	3.78	0.315	1.5777	0.0903	68.7	1.0
2401 sph	Sphal in Cu ore zone	0.555	0.057	0.3822	0.0431	48.5	0.7
2401 sph	duplicate	0.526	0.056	0.3753	0.0236	47.0	0.7
2401 aspy	Arsenopyrite in Cu ore zone	5.95	0.139	18.080	0.107	690	10

Figure 2.1: Summary table of Re-Os isotopic for the Mt Isa ore body.

Data quality and evaluation

Overall the data produced was of reasonable precision, and displayed excellent reproducibility through duplicate analyses of both whole rock ore (MG3041) and mineral separate (2401 sph) analyses. This was slightly surprising given anticipated nugget effects due to heterogeneous distribution of high Re and Os bearing phases within the ore system.

Notably, different samples of the same mineral phase recorded significant variations in Re and Os (and hence $^{187}Os/^{188}Os_m$), implying local controls over Re and Os partitioning into specific phases, rather than a mineral controlled distribution effect. For example, sphalerites from the Pb-Zn ore body contain a factor of six times more Re than those from the Cu ore. So too, chalcopyrite contains highly variable Re abundances from different portions of the Cu ore.

Geochronological information:

Overall the Mt Isa Cu samples record scattered Os isotopic systematics, implying post mineralisation open system behaviour, or a very late age of formation of the ore body. Whole rock ore samples, which should theoretically be the least susceptible to resetting due to their large sample volumes, show considerable scatter about reference isochrons younger than ~1440 Ma. Such isochrons are controlled largely by highly radiogenic ore samples, and the radiogenic magnetite alteration halo. Addition of an asp separate from the Cu ore zone (2401 asp) to the regression produces a slightly older age (~1480 Ma), but highlights that the source
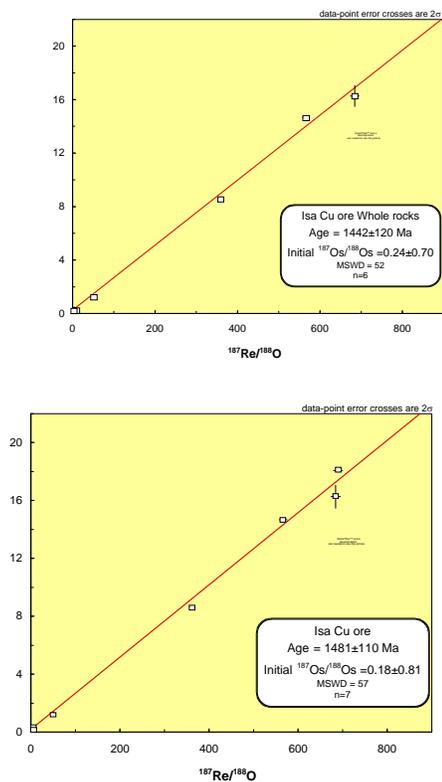
Figure 2.1: a) Isochron regression for whole rock Cu ore samples b) Whole rock samples with arsenopyrite mineral separate, suggesting that asp is the phase carrying highly radiogenic Os in the whole rocks.
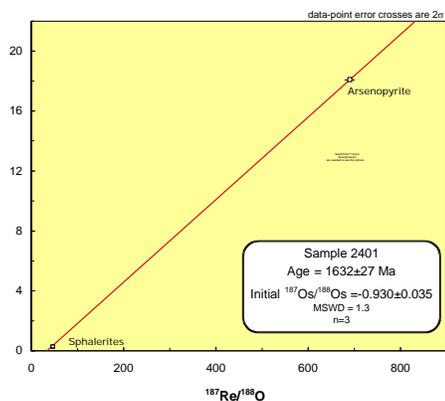

Figure 2.2: Mineral separates from sample MG02401. Sphalerite is unradiogenic with respect arsenopyrite, effectively resulting in a 2 point isochron with a negative initial ratio, suggesting it contains no geologically meaningful information.

of the highly radiogenic Os isotopes in the whole rock ores may well be due to presence of arsenopyrite, or inclusions contained within arsenopyrite.

Significantly, both regressions produce lines of best fit which overlap with the age of peak metamorphism, but also extend to significantly younger ages. Such regressions also project to geologically meaningful initial $^{187}Os/^{188}Os$ ratios, and they contain a statistically valid number of data points in the regression (figure 2.1). Therefore, despite the large amount of excess scatter (as recorded in the model 3 isochron), such whole rock arrays are likely to reflect geologically real open system behaviour on the whole rock scale within the ore body. Hence it would appear that the Mt Isa Cu ore deposit did not close with respect to Os isotopes on a whole rock scale until after ~1500Ma, however the calculated errors on the regressions do permit open system behaviour during (and even prior to) the Isan Orogeny.

On a scale smaller than that of the whole rock, detailed analysis was undertaken on sulphide mineral separates from within a single sample within the Cu ore zone. Arsenopyrite and two splits of sphalerite from sample MG02401 were analysed to investigate whether solely the sulphide portion of the ore body was open to Re and Os exchange. This analysis produced an analytically sound regression (MSWD = 1.3), however it is based on only three data points, two of which plot on top of each other resulting in a two point isochron. Further, the regression projects to a negative initial isotopic ratio, implying that despite inferred

precision, this isochron can have no geological significance since the samples could never have been in isotopic equilibrium with each other. Given that all sulphides used in this regression were obtained from the same sample, it seems that isotopic equilibrium has not been maintained since development of the textural association preserved in the hand specimen.

It is also possible to construct numerous other isochronous regressions from the Mt Isa Cu ore data set, which result in various degrees of precision, however none of the arrays generated can be considered to be robust geologically as they require either a) choosing a mixture of whole rock samples and mineral separates from different samples, or b) projecting to negative initial ratios which are not within error of geologically possible $^{187}Os/^{188}Os$ ratios.

Therefore it is possible to conclude that isochronous arrays calculated for the Mt Isa Cu ore body show clear evidence for open system behaviour on both the whole rock and mineral separate scale, and that the timing of this behaviour is comparatively young with respect to the age of deformation recorded elsewhere within the inlier. Hence these ages may reflect either i) differential cooling through the closure temperature of Os in different portions of the ore body, ii) focussing of fluid flow through different ore body zones during the waning stages of ore formation over a protracted history, or iii) a later, completely independent thermal event which partially reset the Os isotopic system. If the latter were the case, such an event could even be associated with hydrocarbon and/or hydrothermal fluid migration through system during exhumation after the Isan Orogeny, which could involve aspects of i and ii.

2.1 Urquhart Shale
In order to investigate the role the Urquhart Shale played with respect to the mineralisation, a series of samples of varying proximity to mineralised systems were investigated. This was undertaken in order to:

a) attempt to determine an age of deposition for the least altered, more distal portions of the Urquhart Shale,
b) determine the Os isotopic initial ratio at the time of mineralisation in order to investigate whether the Urquhart Shale was a potential source of mineralisation
c) compare the Os isotopic signature of the host Urquhart Shale with other potential metal sources, such as the Eastern Creek Volcanics (see below)

To this end, whole rock analyses were undertaken on low metamorphic grade samples from adjacent mineralisation within both the Mt Isa and George Fisher systems in addition to a suite of samples from Transmitter Hill located outside of the mineralisation footprint of the Mt Isa orebody.
All samples preserved high $^{187}Re/^{188}Os$ ratios as is typical of highly reducing shales, however there was apparent non-systematic variation in Re and Os contents between samples in localities both proximal to mineralised regions and those from the more distal Transmitter Hill location (Table 2.2).

Urquhart Shale		Re (ppb)	Os (ppb)	^{187}Os/^{188}Os	2 SEM	^{187}Re/^{188}Os	2 SEM
MG02096	At Mt Isa	0.039	0.008	0.68718	0.04002	26.1	0.4
MG02106	At Mt Isa	0.535	0.014	8.1086	0.2979	384.8	5.2
2208/119 WR	Transmitter Hill	0.948	0.026	9.1758	0.0605	376.2	5.7
2208/120 WR	Transmitter Hill	0.447	0.010	9.7820	0.0486	472.9	7.1
2208/121 WR	Transmitter Hill	0.202	0.031	0.64004	0.00206	33.8	0.5
2208/123 WR	Transmitter Hill	0.280	0.018	2.2114	0.1013	93.9	1.4
2208/125 WR	Transmitter Hill	0.186	0.029	0.91327	0.00665	33.7	0.5
2208/77 dark	George Fisher	0.241	0.017	2.4902	0.0082	90.8	1.4
2208/77 light	George Fisher	0.352	0.013	3.1414	0.0106	179.3	2.7
2208/79 WR	George Fisher	3.21	0.089	7.0858	0.0308	330.4	5.0

Table 2.2: Summary of whole rock Re-Os isotopic data from the Urquhart Shale, Mt Isa region.
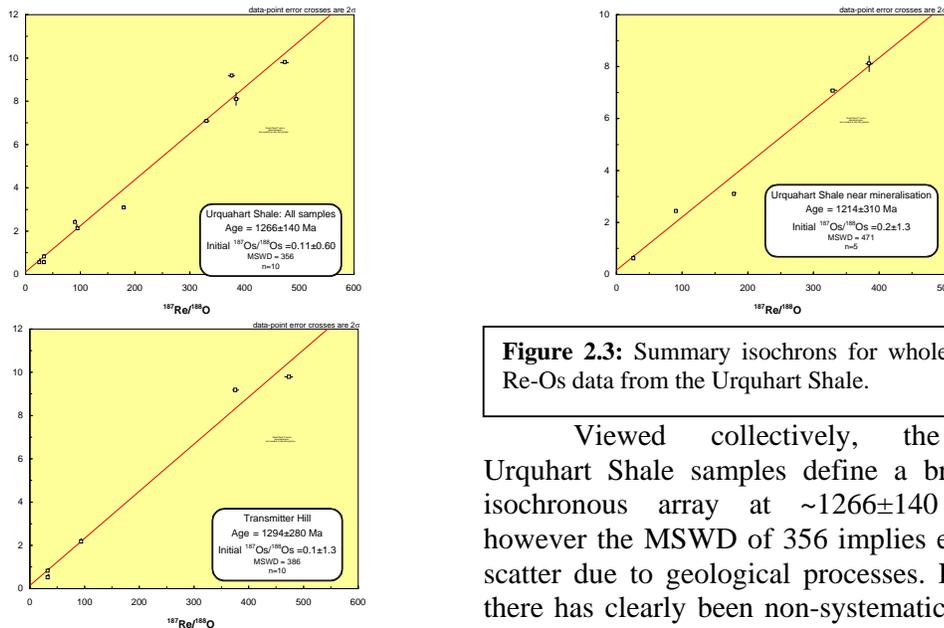

Figure 2.3: Summary isochrons for whole rock Re-Os data from the Urquhart Shale.

Viewed collectively, the 10 Urquhart Shale samples define a broadly isochronous array at ~1266±140 Ma, however the MSWD of 356 implies excess scatter due to geological processes. Hence there has clearly been non-systematic open system behaviour since deposition of the sediments. This is not surprising given that they have been through the Isan Orogeny at least one mineralisation event and had multiple phases of magmatism pass through them.

Those samples adjacent the mineralised systems define an even less precise array corresponding to 1214±310 ma, with an even higher MSWD (471 on five samples). This indicates that equilibration on a whole rock scale has not occurred between these samples, and it may be concluded that the Urquhart Shale has been variably open to isotopic exchange for a protracted period(s) of time after the end of the Isan Orogeny.

So too those samples more distal from the mineralised systems show no systematic shift in Os isotopes from those more proximal. There is no apparent geological age significance in the regression for the Transmitter Hill data (Figure 2.3). The only point of note is that the apparent initial ratios for whole rock samples closer to the mineralised systems may be slightly higher than for those more distal. However caution should be exercised when evaluating this as they errors on such measurements are large, and overlap both sample sets considerably.

On the basis of these results it would appear that there is no systematic Os isotopic anomaly associated with the footprint of mineralised systems in the Urquhart Shale, or, if there is one, it is of such a scale that it is of no use for exploration or targeting.

3. George Fisher

George Fisher		Re (ppb)	Os (ppb)	$^{187}Os/^{188}Os$	2 SEM	$^{187}Re/^{188}Os$	2 SEM
2208/71 whole rock	Gn breccia + carb clasts + pyritic siltstone	0.87	0.209	0.5424	0.0028	20.96	0.32
2208/70: whole rock	Galena breccia	1.179	0.1247	1.3230	0.0087	52.65	0.79
sphalerite		0.790	0.1102	0.9931	0.0019	38.43	0.58
galena		0.491	0.0735	0.9323	0.0037	35.55	0.54
2208/74 whole rock	Galena + Sphalerite breccia	1.23	0.022	2.0601	0.0226	343.0	5.2
galena		0.24	0.241	0.2176	0.0006	4.93	0.07
sphalerite		0.62	0.146	5.0847	0.0380	33.92	0.51
2208/142 whole rock	Sphal + galena bx	0.68	0.198	0.4996	0.0054	17.43	0.26
2208/72 whole rock	Sphal bands siltstone	0.936	0.1197	1.1365	0.0044	42.62	0.64
sphalerite		0.426	0.0674	0.7738	0.0021	33.01	0.50
2208/73 Sphalerite	Sphal band in siltstone	0.2676	0.0835	0.4609	0.0012	16.11	0.24
2208/76 whole rock	Sphal bands	1.704	0.0447	4.2740	0.0167	283.1	4.3
2208/140 whole rock	Sphal bands + Gn tension gashes + Pyrite	0.44	0.188	0.3719	0.0015	11.59	0.17
2208/138 whole rock		1.53	0.207	1.1218	0.0068	40.25	0.61
2208/137 whole rock		0.48	0.017	3.7778	0.0277	201.89	3.04

Table 3.1: Summary of Re-Os isotopic data for the George Fisher Pb-Zn deposit

Considerable analytical effort was directed towards the George Fisher deposit over multiple analytical campaigns in order to address some issues arising from what were initially considered to be "anomalously young" Re-Os ages. To this end a total of 15 whole rock and mineral separate samples from the ore body were analysed.

One immediately striking feature is that a small subset of the dataset contain exceedingly high $^{187}Os/^{188}Os$ ratios (>2) with respect to the rest of the data. These samples (2208/74 wr and sphalerite separate, 2208/76 wr and 2208/137 wr) clearly contain a component not sampled in the rest of the data which is behaving in a non-systematic manner with respect to the rest of the mineralised system, and these are considered no further here. Since a galena separate from 2208/74 was also analysed, this data cannot also be used as it

cannot be demonstrated whether the galena separate has been affected by the component observed in the sphalerite and whole rock fractions of the same sample. It must also be noted that the three fractions analysed from 2208/74 do not record any geochronological information in themselves, further supporting non-systematic, open system behaviour in this sample. Therefore a total of 10 samples from the George Fisher orebody are available for data reduction.
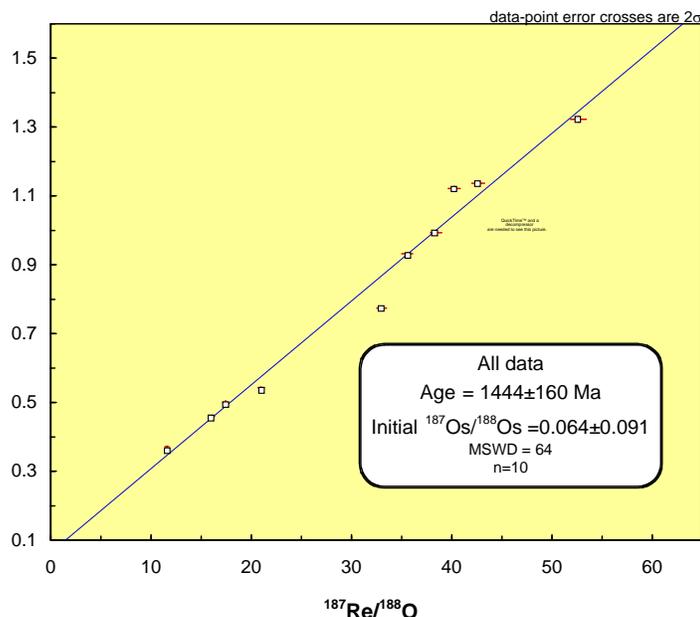

Figure 3.1: Isochron diagram displaying all relevant data for the George Fisher deposit. Note that although overall the dataset define a broadly linear array, there is a large amount of scatter and concomitantly large error.

Overall the data define a broadly isochronous array (Figure 3.1), although there is clearly scatter beyond that attributable to analytical error. This implies that mineralised system has experienced open system behaviour on the scale of the deposit. Therefore, in order to evaluate the significance (or otherwise) of any ages generated, it is necessary to investigate the system in more detail.

Firstly, the whole rock samples alone define a poorly resolved isochron of ~1459 Ma, with significant scatter and an unfeasibly low initial ratio (figure 3.2, panel a). Further, the mineral separates alone define an even more poorly constrained isochronous array at ~1383 Ma, with an even larger MSWD and corresponding error. Two conclusions can be drawn from these observations; i) the mineralised system has been open to exchange of Re and/or Os over a range of length scales, and ii) the exchange is not specific to a single mineralised phase; ie, both sphalerite and galena exhibit non-systematic behaviour with respect to each other within the ore body. Therefore not all sulphides within the mineralised system closed to the Re-Os system simultaneously, and the length scale of such variation in Os isotopic signature was greater than the size of the samples collected for whole rock analysis. Further, regression of just the sphalerite separates (not illustrated) produces no geologically

meaningful data, further emphasising that even different portions of the same mineral phase closed at different times.
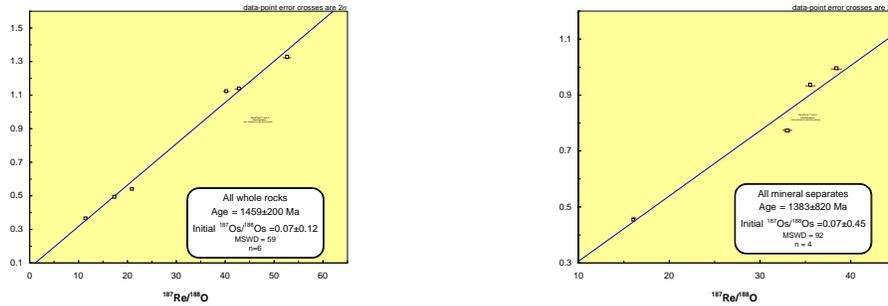

Figure 3.2: Isochron diagrams for whole rock (left) and mineral separate (right) samples for George Fisher. The mineral separate plot is comprised of three sphalerite and one galena split.
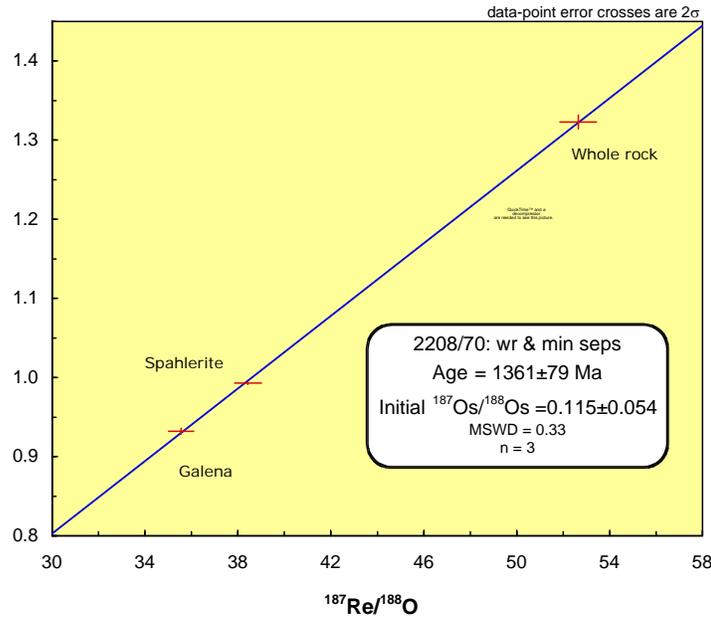

Figure 3.3: Three point isochron for sample 2208/70 composed of whole rock, sphalerite and galena analyses.

The greatest level of precision attainable in this sort of system should be that obtained from a single specimen and its constituent components. Hence there were two attempts to generate individual sample isochrons through analysis of galena and sphalerite separates from a single whole rock. One sample (2208/74) displayed non-systematic variable behaviour under the influence of an unidentified highly radiogenic phase, and so was of no use in this analysis. The other, (2207/70) produced a robust regression with a very low MSWD (<1) implying that all error within the sample is from the analytical procedure, and not from geological factors (figure 3.3). Although the isochron fits particularly well, the precision on the age obtained is

comparatively poor (±79 Myr), as there is only a limited spread in the range of $^{187}Re/^{188}Os$ ratios. With these considerations in mind, this still represents the best age for closure of the Os isotopic system at George Fisher.

4. Ernest Henry

Sample		Re (ppb)	Os (ppb)	$^{187}Os/^{188}Os$	2 SEM	$^{187}Re/^{188}Os$	2 SEM
2208/68	Chalcopyrite	66.5	2.46	2.94829	0.06858	178.5	2.7
2208/68	Pyrite	136	2.04	5.25964	0.01250	537.4	8.1
2208/68	Magnetite	140	3.69	10.3352	0.0155	427.4	6.4
2208/68	Whole rock	151	3.46	18.5149	0.2027	716.4	10.8
2208/68	High Mag	102	0.985	74.0438	1.5439	5330.4	80.8
2208/68	Residual phases	146	2.36	171.299	0.257	6944.6	104.7
2208/69	Whole rock	116	3.09	15.6606	0.0235	549.4	8.3
2208/69	Magnetite	202	12.2	3.39506	0.01143	113.9	1.7
2208/69	Chalcopyrite	37.5	8.87	0.849771	0.002268	22.3	0.3
2208/69	Pyrite	46.5	7.67	25.7289	0.0943	126.7	1.9
2208/172	Whole rock	106	3.92	4.80140	0.03044	209.0	3.1
2208/173	Whole rock	84.5	4.71	1.01678	0.01915	96.4	1.5
2208/174	Whole rock	86.3	1.54	30.5650	0.1510	1338.8	20.2
2208/171	Whole rock	34.4	16.2	2.16253	0.00740	12.9	0.2

Table 4.1 Summary of Re-Os isotopic data for Ernest Henry

A combination of approaches were applied to the Ernest Henry mineralised system over several analytical campaigns. The first was to thoroughly analyses the constituent components of two mineralised samples, in order to ascertain what geochronological information could be obtained with respect to the mineralised assemblage. The second, subsequent phase, involved whole rock analysis from varying portions of the orebody in order to evaluate whether isotopic homogenisation had taken place on broad scale during mineralisation.
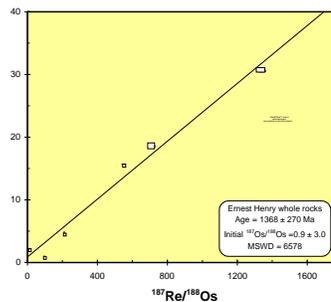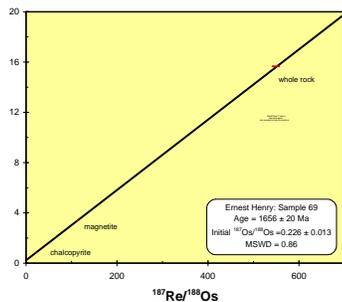
The results are somewhat equivocal; the whole rocks scatter about a comparatively "young" reference line, whereas chalcopyrite, magnetite and the whole rock from 2208/69 define an isochron with a mildly radiogenic initial ratio and an age of 1656±20 Ma; older than the diorite that is host to the mineralisation. Given that the mineral isochron is defined to a large extent by the comparatively radiogenic whole rock point, this implies that the age is a reflection of an unidentified, highly radiogenic phase, possibly molybdenite. This is

corroborated by the very high $^{187}Re/^{188}Os$ ratios of half of the whole rock samples analysed, suggesting a large component of potentially inherited molybdenite.

A similar relationship can be observed in the constituent phases for 2208/68 (not illustrated) whereby the whole rock is more radiogenic than not only the sulphides, but also the magnetite, as in the case for 2208/69. Given that Re is generally highly compatible in magnetite when it forms, the presence of other, unidentified high Re/Os phases suggests that they were already present at the time of magnetite growth and were effectively locking up the Re inventory available for incorporation during the formation of the mineralising assemblage. If this is the case, then it is not appropriate to consider the whole rock analyses in conjunction with the ore minerals that formed subsequently within them, and hence no geochronological information can be gleaned from the Ernest Henry data. Further, there is clear isotopic evidence that not all portions of the same phase were forming simultaneously; for example, magnetites from different samples do not all plot on the same isochron; so too chalcopyrites and so on.

Therefore it is possible to conclude that the Os budget within the Ernest Henry ore body is dominated by inherited, highly radiogenic components, possibly molybdenites derived from the host diorite, with only partial equilibration taking place between mineralising phases during ore body formation.

5. Eastern Creek Volcanics and mafic magmatism of uncertain affinities

Sample		Re (ppb)	Os (ppb)	$^{187}Os/^{188}Os$	2 SEM	$^{187}Re/^{188}Os$	2 SEM
Eastern Creek Volcanics							
8520-6026(1)	Cromwell Metabasalt	0.630	0.033	3.71675	0.02319	134.7	2.0
8520-6026 dup	Cromwell Metabasalt	0.463	0.042	2.41679	0.03376	69.4	1.0
7820-3528	Cromwell Metabasalt	1.04	0.042	5.36932	0.03821	200.9	3.0
7820-3534	Cromwell Metabasalt	1.87	0.039	52.0429	0.3451	1791.8	26.9
7820-3502	Cromwell Metabasalt	1.86	0.032	52.3648	0.4147	2163.0	32.4
7820-3509(1)	Cromwell Metabasalt	1.59	0.057	8.20340	0.14853	275.1	4.1
7820-3509 dup	Cromwell Metabasalt	1.69	0.041	16.0050	0.1045	619.2	9.3
7820-3525(1)	Pickwick Metabasalt	0.190	0.078	0.512324	0.00897	12.2	0.2
7820-3525 dup	Pickwick Metabasalt	0.198	0.100	0.392037	0.00117	9.93	0.15
7820-3535(1)	Pickwick Metabasalt	1.65	0.058	9.52979	0.05044	303.6	4.6
7820-3535 dup	Pickwick Metabasalt	1.72	0.057	7.38441	0.04636	285.0	4.3
7820-3537	Pickwick Metabasalt	0.086	0.120	0.234003	0.00265	3.51	0.05
MG04018	Dolerite	0.580	0.015	17.5509	0.0950	606.0	9.1
MG04019	Dolerite	0.341	0.060	1.77698	0.00399	33.1	0.5
MG04020	Dolerite	0.470	0.057	3.30490	0.01110	56.5	0.8

Table 5.1: Summary Re-Os data for the Eastern Creek Volcanics and unassigned dolerites. All analyses are whole rock analyses. "dup" signifies total procedural duplicate analysis of the sample as a measure of external reproducibility. Sample localities can be found in Gregory (2006).