# Geology

# Re-Os dating of pyrite confirms an early diagenetic onset and extended duration of mineralization in the Irish Zn-Pb orefield --Manuscript Draft--

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Corresponding Author:	Danny Hnatyshin University of Alberta Edmonton, Alberta CANADA
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	University of Alberta
Corresponding Author's Secondary Institution:	
First Author:	Danny Hnatyshin
First Author Secondary Information:	
Order of Authors:	Danny Hnatyshin
	Robert A Creaser
	Jamie J Wilkinson
	Sarah A Gleeson
Order of Authors Secondary Information:	
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Abstract:	The Irish Midlands contains one of the world's largest hydrothermal Zn-Pb ore districts, but uncertainty exists in the timing of mineralization relative to host rock ages. Consequently, genetic models for ore formation are poorly constrained and remain controversial. Here, we use Re-Os geochronology to show that ore-stage pyrite from the Lisheen deposit formed at $346.6 \pm 3.0$ Ma, shortly after host rock deposition. Pyrite from the Silvermines deposit returns an age of $334.0 \pm 6.1$ Ma, indicating that at least some mineralization occurred during later burial. These age determinations show that the much younger paleomagnetic ages reported for the Irish Zn-Pb deposits reflect remagnetization during the Variscan orogeny, a process that we suggest impacts paleomagnetic dating more widely. The Re-Os ages overlap with the ages of Lower Carboniferous volcanic rocks in the Midlands, which are the product of magmatism that has been invoked as the driving force for hydrothermal activity. The relatively low initial Os ratios for both Lisheen (0.253 $\pm$ 0.045) and Silvermines (0.453 $\pm$ 0.006) are compatible with derivation of Os from these magmas, or from the Caledonian basement that underlies the ore deposits.
Response to Reviewers:	

- 1 Re-Os dating of pyrite confirms an early diagenetic onset and extended duration
- 2 of mineralization in the Irish Zn-Pb orefield
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- 4 Danny Hnatyshin<sup>1</sup>, Robert A. Creaser<sup>1</sup>, Jamie J. Wilkinson<sup>2,3</sup>, and Sarah A.
- 5 Gleeson<sup>1</sup>
- 6
- <sup>7</sup> <sup>1</sup>Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, AB
- 8 T6G 2R3, Canada
- <sup>9</sup> <sup>2</sup>Department of Earth Science and Engineering, Imperial College London, South
- 10 Kensington Campus, Exhibition Road, London SW7 2AZ, United Kingdom
- <sup>11</sup> <sup>3</sup>Department of Earth Sciences, Natural History Museum, Cromwell Road, London SW7
- 12 5BD, United Kingdom
- 13

- 14 Abstract
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16 The Irish Midlands contains one of the world's largest hydrothermal Zn-Pb ore districts, 17 but uncertainty exists in the timing of mineralization relative to host rock ages. 18 Consequently, genetic models for ore formation are poorly constrained and remain 19 controversial. Here, we use Re-Os geochronology to show that ore-stage pyrite from the 20 Lisheen deposit formed at 346.6 ± 3.0 Ma, shortly after host rock deposition. Pyrite from 21 the Silvermines deposit returns an age of  $334.0 \pm 6.1$  Ma, indicating that at least some 22 mineralization occurred during later burial. These age determinations show that the 23 much younger paleomagnetic ages reported for the Irish Zn-Pb deposits reflect 24 remagnetization during the Variscan orogeny, a process that we suggest impacts 25 paleomagnetic dating more widely. The Re-Os ages overlap with the ages of Lower 26 Carboniferous volcanic rocks in the Midlands, which are the product of magmatism that 27 has been invoked as the driving force for hydrothermal activity. The relatively low initial 28 Os ratios for both Lisheen (0.253  $\pm$  0.045) and Silvermines (0.453  $\pm$  0.006) are 29 compatible with derivation of Os from these magmas, or from the Caledonian basement 30 that underlies the ore deposits.

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## 34 INTRODUCTION

Hvdrothermal ore deposits hosted by sedimentary rocks supply the majority of the 35 world's lead, zinc, and a significant proportion of copper. Although general models for 36 37 ore formation are well established (e.g., Gustafson and Williams, 1981; Goodfellow et 38 al., 1993; Leach et al., 2005; Wilkinson, 2014), significant controversy remains over 39 fundamental aspects of their genesis. Some ores are thought to have formed during, or 40 soon after, deposition of the host sediments (syngenetic/early diagenetic mineralization), whereas others formed after - in some cases hundreds of millions of years after -41 42 lithification of the host rocks (epigenetic mineralization). For a number of Zn-Pb 43 deposits, such as the Carboniferous ores of central Ireland (Hitzman and Beaty, 1996), 44 both models have been proposed. This dichotomy stems from difficulties in determining with confidence the relative timing of sulfide precipitation, and the paucity of 45 hydrothermal minerals amenable to radiogenic isotope dating. 46

The lack of certainty regarding the timing of Zn-Pb mineralization has numerous 47 impacts, including on the understanding of geodynamic controls on deposit location, on 48 49 the development of fluid flow models, and on identifying viable sulfide precipitation 50 mechanisms. In a wider context, inferred ages of ore deposition, in particular those 51 obtained by paleomagnetic methods, have been used to argue for a link between the 52 formation of sediment-hosted Zn-Pb deposits and supercontinent assembly cycles (Leach et al., 2001). However, if paleomagnetic methods date orogenic events rather 53 54 than mineralization, then this interpretation is invalid. Finally, mineral exploration is 55 guided by deposit models: a syngenetic interpretation will focus efforts on specific stratigraphic horizons, whereas an epigenetic model allows for deposits to occur in 56 57 receptive host rocks of any age.

Here we use Re-Os dating of ore-stage pyrite, an approach not previously applied to carbonate-hosted Zn-Pb ores, to test models for the timing and genesis of mineralization in the Irish orefield – questions that have been vigorously debated for 50 years but have yet to be answered convincingly.

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# 63 **IRISH OREFIELD**

In Ireland during the Early Mississippian, a marine transgression across the Laurussian continental margin deposited thick limestone units (Figs. 1, 2). Hydrothermal fluids subsequently precipitated tens of millions of tons of zinc and lead within these carbonate rocks, making the Irish orefield one of the most intensely mineralized Zn districts on Earth (Singer, 1995). The giant Navan Zn-Pb deposit forms the largest resource, but economic Zn-Pb deposits also formed at Tynagh, Silvermines, Galmoy, and Lisheen (Fig. 1).

Early syngenetic models, such as the extension and convection model of Russell (1978), were largely discounted in the 1990s in favor of epigenetic interpretations involving lateral, topographically-driven fluid flow (Hitzman and Beaty, 1996), similar to the widely accepted model for Mississippi Valley-type (MVT) Zn-Pb deposits. Significantly, the past decade has seen movement away from this concept, as new regional data sets and analytical techniques have become available (Wilkinson and Hitzman, 2014).

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#### 79 **STUDY SITES**

Lisheen is the second-largest base-metal deposit in Ireland and has a welldefined geologic setting (e.g., Wilkinson et al., 2005). The Silvermines deposit has been

central to the development of syngenetic models (e.g., Boyce et al., 2003) and presents an opportunity to test an existing Rb-Sr sphalerite age ( $360 \pm 5$  Ma; Schneider et al., 2007) and a much younger paleomagnetic age ( $269 \pm 4$  Ma; Symons et al., 2007).

85 Sulfide mineralization at Lisheen (Fig. 2) occurs principally within a hydrothermal 86 dolomite breccia located at the base of the Waulsortian Limestone Formation (WLF). A 87 minor proportion of ore is hosted by an oolitic unit (Lisduff Oolite Member - LOM) within 88 underlying argillaceous bioclastic limestones (Ballysteen Limestone Formation - BLF). 89 Mineralization forms three stratabound ore bodies: the Main, Derryville, and Bog zones, 90 each of which are controlled by a major normal fault (Hitzman et al., 2002). 91 Mineralization primarily occurs in the hanging-wall of these faults within the WLF; 92 footwall mineralization is mainly developed within the LOM.

Sulfide ore at Silvermines is generally restricted to two stratigraphic levels: the
Upper G and B Zones within the dolomitized base of the WLF (Fig. DR2), and the Lower
G, K, and P Zones hosted by dolomitized portions of the BLF (Taylor, 1984). All ore
zones are spatially associated with normal faults (Taylor, 1984).

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## 98 **Re-Os GEOCHRONOLOGY**

At Lisheen, massive pyrite from the early main ore-stage in the LOM (sample LK 8S08FW: Panel 8, Stope 8 in the Main Zone orebody) was selected for analysis. At Silvermines, massive pyrite from the B Zone orebody (samples B18, B15) was chosen (see Appendix DR1 for sample descriptions). All pyrite separates were produced and analyzed using the procedures described by Morelli et al. (2010), some additional details are described in Appendix DR2. Twelve pyrite separates were analyzed from the Lisheen sample, with Re and Os concentrations of 2-8 ppb and 15-280 ppt, respectively.

For Silvermines, twelve pyrite separates from B18 and one from B15 were analyzed; these contain 0.5-2.5 ppb Re and 85-400 ppt Os. Detailed analytical results are provided in Tables DR1, DR2, and DR3.

The Lisheen sample yields a Re-Os isochron age of  $346.6 \pm 3.0$  Ma, whereas the Silvermines samples produce a younger Re-Os isochron age of  $334.0 \pm 6.1$  Ma. (Fig. 3) The Silvermines isochron shows some scatter beyond calculated analytical uncertainties (MSWD = 19); this scatter can be accounted for by only a 1% variation in initial  $^{187}Os/^{188}Os$  (IOs) of the fluid from which pyrite formed.

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# 115 TIMING AND DURATION OF MINERALIZATION

116 The early ore-stage pyrite samples from both Lisheen and Silvermines yield Early 117 Mississippian Re-Os ages that place the timing of sulfide mineralization within ~15 myr 118 of host rock deposition. The Re-Os age from Lisheen (346 ± 3.0 Ma) overlaps with the 119 probable depositional age range (353-347 Ma; Waters et al. 2011) for the WLF (Fig. 4). 120 We conclude that Zn-Pb mineralization at Lisheen most likely developed during the latter 121 depositional stages of the WLF, or during deposition of the overlying Crosspatrick 122 Formation (CF) at a depth of no more than 200 meters below the paleo-seafloor. This 123 interpretation is consistent with arguments that the thickening of the WLF and CF above 124 the ore zone was due to subsidence of the seafloor during mineralization-related host 125 rock dissolution (Wilkinson et al., 2011).

Previous interpretations of the timing of mineralization at Silvermines concluded that syngenetic and near-seafloor mineralization took place based on the occurrence of exhalative features (e.g., Boyce et al. 1983), vent fauna (e.g., Boyce et al., 2003), sedimentary reworking of sulfides (Lee and Wilkinson, 2002) and a sphalerite Rb-Sr age

(Schneider et al., 2007). Our result does not exclude a syngenetic component to the hydrothermal system, but clearly shows that significant mineralization occurred during later stages of host rock burial (e.g. Reed and Wallace, 2004). Likewise, the Re-Os age obtained for Lisheen does not exclude later mineralization at greater burial depths as has been suggested based on sulfur isotope data (Wilkinson et al., 2005). Together, the new Re-Os ages provide concrete evidence for a protracted, and probably episodic, history of mineralization in the Irish Zn-Pb orefield (Wilkinson and Hitzman, 2014).

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#### 138 **OSMIUM SOURCE**

139 The precise IOs obtained for pyrite isochrons from both Lisheen (0.253  $\pm$  0.045) and 140 Silvermines  $(0.453 \pm 0.006)$  reflect the source(s) of Os in the hydrothermal fluids that 141 formed the deposits. These relatively low values invite the possibility that the fluids contained a mixture of mantle-derived Os (<sup>187</sup>Os/<sup>188</sup>Os ~0.13; Meisel et al., 2001) and 142 crustal Os (187Os/188Os >>0.13; Ehrenbrink and Jahn, 2001). Alternatively, the IOs 143 144 values may reflect derivation of Os from the immediate basement rocks of the Irish 145 deposits, which were largely derived from early Paleozoic (Caledonian) volcanic arcs 146 (480-380 Ma; Chew and Stillman, 2009). We estimate average crustal source rock ages 147 for Os at Lisheen (363 Ma) and Silvermines (412 Ma) by assuming the IOs of the 148 Caledonian arc rocks was 0.2, similar to that reported in porphyry systems (e.g. Zimmerman et al., 2014), combined with a <sup>187</sup>Re/<sup>188</sup>Os ratio of 190 calculated from 149 150 average crustal concentrations of Re (2 ppb) and Os (50 ppt) (Peucker-Ehrenbrink and 151 Jahn, 2001; Sun et al., 2003). These estimates are compatible with Os, like Pb and 152 other metals, being sourced from the early Paleozoic basement (Dixon et al., 1990;

Wilkinson et al., 2005; Wilkinson, 2014) and/or the overlying Devonian Old RedSandstone.

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# 156 A POSSIBLE LINK BETWEEN VOLCANISM AND ZN-PB MINERALIZATION

157 The possibility of a genetic link between the Irish orefield and early Carboniferous 158 volcanism (e.g. Strogen, 1995) has been a lingering but largely undocumented issue. 159 However, evidence for a mantle input into the Zn-Pb deposits has recently been 160 proposed based on He isotope data derived from fluid inclusions from all the main ore 161 deposits (Davidheiser-Kroll et al., 2014), and from the intimate association of 162 mineralization and mantle-derived igneous rocks in the Stonepark area, Limerick (Fig. 2: 163 McCusker and Reed, 2013). Our Re-Os ages overlap with these Chadian-Asbian 164 volcanic rocks and, therefore, are consistent with a new genetic model (Wilkinson and 165 Hitzman, 2014) that invokes magmatic heat derived from underplating and mid-crustal 166 sills as a driver for regional fluid flow. Such a magmatic-related model may explain the 167 unusually high fluid temperatures documented in the province (~70-280°C; Wilkinson, 168 2010), compared to those documented for sediment-hosted Zn-Pb deposits elsewhere, 169 and the extraordinary regional extent of Zn-Pb mineralization.

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# 171 IMPLICATIONS FOR DATING OF CARBONATE-HOSTED ZN-PB ORES

Paleomagnetic dating at Silvermines (Symons et al., 2007), Galmoy (Pannalal et al., 2008b), and Lisheen (Pannalal et al., 2008a) yields ages of  $269 \pm 4$ ,  $290 \pm 9$  Ma, and 277  $\pm$  7 Ma, respectively (Fig. 4). However, paleomagnetic studies do not readily discriminate between primary magnetization ages (e.g. mineralization), and remagnetization ages. Consequently, we interpret the disparity between our Re-Os pyrite ages and the systematically younger paleomagnetic ages from the Irish orefield to be a result of widespread remagnetization that took place during Variscan orogenic activity. The preservation of well-defined Re-Os isochrons (Fig. 3), despite a Variscan overprint in southern and central Ireland, suggests that the Re-Os isotope system in pyrite was little affected by these tectonothermal processes, and is therefore a robust system for dating weakly metamorphosed, sediment-hosted Zn-Pb deposits.

183 Globally, paleomagnetic ages have been used to implicate major collisional 184 orogenies that developed during supercontinent assembly cycles as principal drivers for 185 MVT mineralization (Leach et al., 2001). However, if paleomagnetic ages reflect younger 186 orogenic events rather than the age of mineralization, as we observe in the Irish orefield, 187 then this interpretation is invalid. We propose, therefore, that application of pyrite Re-Os 188 geochronology may help resolve the large age discrepancies and competing 189 geodynamic models reported for several MVT districts (e.g., Tennessee, USA and 190 Upper Silesia, Poland: e.g. Leach et al., 2005).

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# 199 **Figure captions**

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Figure 1. Map of Ireland (modified from Wilkinson, 2010) showing selected Zn-Pb ore deposits, volcanic rocks, and approximate northwestern limit of major deformation associated with the Variscan orogeny (Hitzman, 1999).

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Figure 2. Basic stratigraphy of the Lisheen (L) and Silvermines (S) areas (modified from
Wilkinson et al., 2005).

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Figure 3. Model 3 Re-Os isochron plots based on data for ore-stage pyrite separates from Lisheen (top) and Silvermines (bottom), created using Isoplot v3.00 (Ludwig, 2001). All uncertainties shown are  $2\sigma$ .

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212 Figure 4. Age constraints of major events associated with the Irish Zn-Pb orefield. Key to 213 sources of data: 1 - Waters et al. (2011); 2 - Strogen (1995); Sommerville et al. (1992) 3 - Reed 214 and Wallace (2004); 4 – Quinn et al. (2005); Hitzman (1999); 5 – Hitzman et al. (2002); 215 Wilkinson et al. (2011); 6 – Pannalal et al. (2008a); 7 – Boyce et al. (1983); Lee and Wilkinson 216 (2002); 8 - Symons et al. (2007); 9 - Schneider et al. (2007); 10 - Symons et al. (2002); 11 -217 Anderson et al. (1998); 12 – Pannalal et al. (2008b); 13 – McCusker and Reed (2013). Methods: 218 Re-Os (rhenium-osmium), Rb-Sr (rubidium-strontium), PM (paleomagnetism), GA (geological 219 arguments).

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![](_page_21_Figure_0.jpeg)

# **Appendix DR1: Sample Descriptions**

8S08FW – This sample of massive pyrite was collected by Jamie Wilkinson from the southern part of the Lisheen Main Zone orebody (Panel 8, Stope 8; Figure DR1) where the ore zone is very thick. The sample came from the footwall of the Killoran Fault at a depth of 176m, within the Lisduff Oolite Member of the Ballysteen Limestone Formation. Ore is locally developed in the footwall oolite at Lisheen and its approximate contiguity with the hangingwall ore zone has been used to argue for a post-faulting timing for mineralization (Hitzman et al., 2002). The sample processed (Fig. DR2) is primarily composed of massive pyrite that is crosscut by calcite veins. A minor amount of sphalerite and fine grained galena (<10 µm) is observed in thin section and back scattered electron images (Figure 1). Such pyrite-rich zones are typical within the high grade cores of the ore lenses at Lisheen (e.g. Fusciardi et al., 2003).

B15 – This sample was collected by John Ashton (Ashton, 1975) from the Silvermines Bzone in the barite ore zone (haulage 4932). The following description is based on his field notes of the sampling locality. The ore zone contains fine grained massive sulfide composed of ~40-45% pyrite, 5-10% galena, and a variable mixture of barite and sphalerite. Pyrite occurs typically as elongate crystals that occasionally show slight deformation. Sphalerite has replaced pyrite, and galena typically has replaced sphalerite. The sample processed (Fig. DR3) is composed of massive pyrite with cracks infilled by quartz and carbonate. No barite occurs within this sample and galena is present in cracks or as a replacement of pyrite. Pyrite-rich ore was often mined within the B zone at Silvermines, and this pyritic massive sulfide (Taylor and Andrew, 1978) is generally interpreted as an early mainstage mineralization ore type.

B18 – This sample was collected by John Ashton (Ashton, 1975) from the Silvermines Bzone (Location: Stope Hanging Wall Drift 48-1S; Fig DR1). The following description is based on his field notes of the sampling locality. The sample comes from the central part of the B zone in a Pb-rich area close to the B-fault where stratiform massive pyrite and semi-massive pyrite with dolomite breccia overlie siderite- or barite-hosted sulfides. Locally, the massive pyrite is mineralized and was mined. The sample processed (Figure 3) is composed primarily of fine grained (0.5-2mm), massive pyrite. Sphalerite and galena are present in smaller amounts and show the same general paragenesis as B15, with sphalerite after pyrite and galena typically postdating sphalerite. As with B15, this pyritic massive sulphide is generally interpreted as an early mainstage mineralization ore type.

![](_page_23_Figure_1.jpeg)

Figure DR1: Approximate sample locations for Lisheen sample 8S08FW (top) and Silvermines sample B18 (bottom). Modified from Andrew (1986).

![](_page_24_Picture_0.jpeg)

Figure DR2: Lisheen sample 8S08FW (top right figure) and a representative backscattered electron image (top left figure) and reflected light images (bottom figures).

![](_page_24_Picture_2.jpeg)

Figure DR1: Silvermines sample B15 (top left figure) and B18 (top right figure) and representative reflected light images of sample B18 (bottom figures).

## **Appendix DR2: Sample Preparation**

All samples were prepared using a standardized procedure to ensure that a relatively pure pyrite separate was obtained. A bulk sample containing 5-20g of pyrite was crushed and sieved using metal-free equipment to produce 70-200 µm diameter material containing pyrite and several impurity minerals (e.g. sphalerite, galena, calcite, dolomite, and quartz). Heavy liquid separation using methylene iodide ( $\rho = 3.32g/\text{cm}^3$ ) is used separate carbonate and silicates from the sulfides. To separate pyrite from galena and sphalerite a Frantz Isodynamic Separator was used. In the sphalerite-pyrite-galena system we typically observe  $\chi_{\text{sphalerite}} > \chi_{\text{pyrite}} > \chi_{\text{galena}}$  ( $\chi =$  magnetic susceptibility). These differences allow separation of pyrite from sphalerite (eliminated at low induced magnetization) and galena (eliminated at high induced magnetization). The final separate contains ~85-100% pyrite. The remaining impurities are typically found as inclusions or are the result of aggregates of multiple minerals not separated by the crushing process.

# **Analytical Data:**

Sample Name	Re ppb	Os ppt	<sup>187</sup> Re / <sup>188</sup> Os	±2σ	<sup>187</sup> Os / <sup>188</sup> Os	±2σ	Rho	% Re Blank	% <sup>187</sup> Os Blank	% <sup>188</sup> Os Blank
8508FW	3.70	33.24	919.25	9.14	5.588	0.058	0.845	0.19	0.19	4.67
8508FW M1.0	6.18	46.72	1249.60	9.21	7.484	0.056	0.841	0.10	0.10	3.40
8508FW M1.0-2	5.98	47.94	1119.67	7.98	6.735	0.052	0.778	0.10	0.10	3.15
8508FW M1.2	5.78	44.61	1204.48	9.68	7.254	0.067	0.758	0.11	0.11	3.51
8508FW M1.5	3.88	33.29	995.53	9.42	6.034	0.062	0.818	0.16	0.16	4.41
8508FW NM1.5	2.73	31.87	609.76	5.07	3.784	0.031	0.817	0.23	0.22	3.78
8508FW NM1.5-6N	2.44	27.46	643.64	7.13	3.963	0.045	0.820	0.29	0.29	5.09
8508FW NM1.5-10N	2.28	25.53	651.82	14.85	4.077	0.098	0.869	0.50	0.93	9.56
8508FW B	4.31	37.79	952.61	7.54	5.734	0.047	0.815	0.14	0.14	3.66
8508FW B M0.8	8.10	55.94	1501.95	16.05	8.955	0.103	0.861	0.13	0.13	5.15
8508FW B NM1.0	4.14	39.18	837.80	10.33	5.076	0.104	0.561	0.15	0.15	3.36
8508FW B NM1.2	2.52	31.38	556.09	5.01	3.478	0.031	0.797	0.27	0.26	4.08

Table DR1: Lisheen Re-Os data

Table DR2: Silvermines Re-Os data

Sample Name	Re ppb	Total Os ppt	187Re/188 Os	± 2σ	187/188 Os	± 2 <b>σ</b>	rho	% Re Blank	% <sup>187</sup> Os Blank	% <sup>188</sup> Os Blank
B18 A	1.28	156.97	42.106	0.185	0.6743	0.0030	0.396	0.21	0.02	0.08
B18 A M0.7-F	1.37	392.10	17.719	0.085	0.5489	0.0018	0.301	0.32	0.02	0.05
B18 A NM0.7-F	0.63	144.86	22.148	0.200	0.5752	0.0022	0.188	0.79	0.05	0.15
B18 A NM 0.9	0.93	156.82	30.538	0.168	0.6335	0.0030	0.274	0.38	0.03	0.10
B18 A NM 1.0	1.24	178.58	35.616	0.180	0.6519	0.0040	0.599	0.13	0.09	0.30
B18 A NM 1.0-F	1.25	189.07	33.864	0.146	0.6380	0.0019	0.325	0.26	0.02	0.08
B18 A NM 1.2	1.21	159.77	39.011	0.173	0.6675	0.0024	0.342	0.26	0.02	0.09
B18 A NM 1.55	1.59	181.03	45.575	0.231	0.7076	0.0042	0.628	0.12	0.09	0.33
B18 A NM 1.55-F	1.25	90.99	72.681	0.294	0.8589	0.0025	0.370	0.22	0.03	0.14
B18 A NM 2.0-10/5	1.87	108.67	92.002	0.368	0.9701	0.0031	0.384	0.20	0.03	0.16
B18 A NM 2.0-F	1.72	118.02	77.250	0.305	0.8888	0.0031	0.390	0.18	0.02	0.12
B18 A NM 2.0-10/3	2.32	84.80	151.998	0.571	1.2975	0.0045	0.430	0.13	0.02	0.17
B15	0.53	120.22	22.355	0.115	0.5811	0.0021	0.283	0.36	0.02	0.07

Table DR3: Re-Os blank data

Blank	n(Re)	n(Os)	Re (pg)	±2σ	Os (pg)	±2σ	187/188 Os	±2σ
Lisheen	4	4	2.5	1.5	0.34	0.03	0.23	0.05
Silvermines	9	8	1.1	0.6	0.05	0.01	0.18	0.16

n(Re) = number of blank analyses for Re blank determination; n(Os) = number of blank analyses for Os blank determination

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