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# Mineralium Deposita

## Mantle heat drives hydrothermal fluids responsible for carbonate-hosted base metal deposits: Evidence from $^3\text{He}/^4\text{He}$ of ore fluids in the Irish Pb-Zn ore district --Manuscript Draft--

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<b>Abstract:</b>	<p>There is little consensus on whether carbonate-hosted base metal deposits, such as the world-class Irish Zn+Pb ore field, formed in collisional or extensional tectonic settings. Helium isotopes have been analysed in ore fluids trapped in sulphides samples from the major base metal deposits of the Irish Zn-Pb ore field in order to quantify the involvement of mantle-derived volatiles, that require melting to be realised, as well as test prevailing models for the genesis of the ore fields. <math>^3\text{He}/^4\text{He}</math> ratios range up to 0.2 Ra, indicating that a small but clear mantle helium contribution is present in the mineralising fluids trapped in galena and marcasite. Sulfides from ore deposits with the highest fluid inclusion temperatures (<math>\sim 200^\circ\text{C}</math>) also have the highest <math>^3\text{He}/^4\text{He}</math> (<math>&gt; 0.15</math> Ra). Similar <math>^3\text{He}/^4\text{He}</math> are recorded in fluids from modern continental regions that are undergoing active extension. By analogy we consider that the hydrothermal fluids responsible for the carbonate-hosted Irish base metal mineralization circulated in thinned continental crust, undergoing extension, and demonstrates that enhanced mantle heat flow is ultimately responsible for driving fluid convection.</p>
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2           **carbonate-hosted base metal deposits: Evidence from**  
3            **$^3\text{He}/^4\text{He}$  of ore fluids in the Irish Pb-Zn ore district**

4

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## Abstract

There is little consensus on whether carbonate-hosted base metal deposits, such as the world-class Irish Zn+Pb ore field, formed in collisional or extensional tectonic settings. Helium isotopes have been analysed in ore fluids trapped in sulphides samples from the major base metal deposits of the Irish Zn-Pb ore field in order to quantify the involvement of mantle-derived volatiles, that require melting to be realised, as well as test prevailing models for the genesis of the ore fields.  $^3\text{He}/^4\text{He}$  ratios range up to  $0.2 R_a$ , indicating that a small but clear mantle helium contribution is present in the mineralising fluids trapped in galena and marcasite. Sulfides from ore deposits with the highest fluid inclusion temperatures ( $\sim 200^\circ\text{C}$ ) also have the highest  $^3\text{He}/^4\text{He}$  ( $> 0.15 R_a$ ). Similar  $^3\text{He}/^4\text{He}$  are recorded in fluids from modern continental regions that are undergoing active extension. By analogy we consider that the hydrothermal fluids responsible for the carbonate-hosted Irish base metal mineralization circulated in thinned continental crust undergoing extension and demonstrates that enhanced mantle heat flow is ultimately responsible for driving fluid convection.

Keywords: Irish Zn+Pb; Helium isotopes; crustal extension; mantle heat flow

## Introduction

Carbonate-hosted base metal deposits are a major source of the world's Zn, Pb and Ag. The ores hosted in the Carboniferous carbonates in the Irish Midlands constitute the highest concentration of Zn per square kilometre on the planet (Singer 1995), and the province includes the giant Navan deposit (Ashton et al. in press). Despite extensive research, there remains no consensus on the tectonic setting and driving mechanism for their genesis (Russell 1978; Leach et al. 2005; Wilkinson and Hitzman, in press). Difficulty in interpreting the origin of the Irish mineralisation arises partly from the coincidence of both extensional and compressional features within the deposits. For example, extensional features typically appear to have formed early, e.g., syndepositional faulting; submarine debris flow breccias (Boyce et al. 1983a; Taylor 1984; Anderson et al. 1998; Ashton et al. in press), whereas compressional features are common later in the geological history of the deposits, e.g. reverse and thrust faulting; Variscan shortening (Johnston et al. 1996; Hitzman and Beaty 1996; Leach et al. 2010). There are no absolute age determinations for ore deposition, however, controversial paleomagnetic data support ore deposition at 350-269 Ma (Symons et al. 2002; 2007; Pannalal et al. 2008a & b; Johnson et al. 2013).

One view is that the ore deposits developed in compressional tectonic regimes, where crustal thickening was caused by thrust belt loading, leading to extension and the hydrological conditions necessary for topographically driven fluid flow. This is linked to Variscan compression arising from the collision of Gondwana and Laurussia (Fig. 1a; Hitzman 1999; Garven et al. 1999; McCann et al. 2004; Leach et al. 2005; Pannalal et al. 2008a). In this case, mineralisation must be

50 substantially younger (310 Ma) than the age of the host rocks (~350 Ma). In the alternative view  
51 mineralization is intimately related to thinning and extension of the crust and lithosphere during the  
52 Mississippian in response to upwelling of the asthenosphere (fig. 1b Russell 1978). This increased  
53 heat flow in the crust and stimulated convection of surface fluids into basement where interaction  
54 resulted in the generation metal-rich acidic fluids (Russell 1978; LeHuray et al. 1987; Everett et al.  
55 1999, 2003; Walshaw et al. 2006). In this case, the ore deposition occurred during extension around  
56 the time of host rock deposition, and substantially earlier than the age favoured by the  
57 compressional model.

58 The current upper mantle is characterised by  $^3\text{He}/^4\text{He}$  of  $6 - 9 R_a$  (where  $R_a$  is the atmospheric  
59 value;  $1.39 \times 10^{-6}$ ) whereas helium in the continental crust is largely derived from the radioactive  
60 decay of U and Th resulting in  $^3\text{He}/^4\text{He} < 0.01 R_a$  (Ozima and Podosek 2002). Waters and gases  
61 sampled from regions of active rifting have  $^3\text{He}/^4\text{He} > 0.04 R_a$  indicating that volatiles are exsolved  
62 from mantle melts and have advected into the shallow crust (Oxburgh et al. 1986). Helium isotopes  
63 of ancient hydrothermal fluids are trapped and preserved in ore minerals and can be used to trace  
64 the contribution of mantle volatiles and heat sources in a variety of ore “deposit-types” (e.g. Stuart  
65 et al. 1995; Burnard and Polya 2004).

66 Here we report the helium isotope composition of ore fluids in sulfides from the main Pb-Zn mines  
67 in Ireland. All contain a small but genetically significant component of mantle-derived He. This  
68 indicates that heat advected from the mantle, most likely during a period of crustal thinning and  
69 extension, was the driver of fluid convection that led to the development of this ore field.

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## 71 **Samples and methods**

72 Helium isotopes are reported from 20 samples of sulfide (galena and marcasite) sourced from the  
73 five main economic Irish-type deposits: Navan, Silvermines, Lisheen, Galmoy and Tynagh. The  
74 samples selected are from areas in or close to putative feeder faults, with the exception of the  
75 Tynagh samples, which are from museum collections, and thus only the general area of origin is  
76 known.

77 Specimens were gently crushed, sieved and 0.5–2 mm sulfide grains were handpicked under a  
78 binocular microscope then washed in analar grade acetone. Helium was extracted from fluid  
79 inclusions by *in vacuo* crushing of approximately ~1 g of each sample in a multi-sample hydraulic  
80 crusher. The gas was purified prior to analysis with a MAP 215-50 mass spectrometer following  
81 procedures similar to those of Stuart et al. (2000). After crushing samples were sieved and the  
82 crushed material (<100  $\mu\text{m}$ ) was weighed to allow determination of He concentrations (Table 1).

83 Sulfur isotopes were measured on 5-10 mg of the powdered sample that remained after crushing for  
84 helium extraction. The sulfides were converted to  $\text{SO}_2$  and analyzed on a VG SIRA 2 mass  
85 spectrometer by standard techniques (Robinson and Kusakabe 1975).

86

## 87 **Results**

88 Atmosphere-corrected  $^3\text{He}/^4\text{He}$  ratios range from 0.03 to 0.21  $R_a$  (Table 1). There is no correlation  
89 between the  $^4\text{He}$  concentration and  $^3\text{He}/^4\text{He}$ , indicating that no significant lattice-hosted radiogenic  
90  $^4\text{He}$  was released by crushing (Stuart et al. 1994; Kendrick et al. 2002). This is consistent with the  
91 extremely low U and Th content of the minerals analysed here (see appendix) and with previous  
92 studies using this apparatus (e.g. Stuart et al. 2003).

93  $^3\text{He}/^4\text{He}$  in excess of  $\sim 0.04 R_a$  in crustal fluids typically requires a contribution of mantle-derived  
94 He (Oxburgh et al. 1986). Before making a similar interpretation for ancient hydrothermal fluids it  
95 is necessary to rule out the generation of nucleogenic  $^3\text{He}$  by bombardment on  $^6\text{Li}$  by thermal  
96 neutrons (Andrews and Kay 1982). Using the neutron flux calculated from the composition of the  
97 ore minerals we calculate that the radiogenic  $^3\text{He}$  produced in the trapped fluids is 5 orders of  
98 magnitude less than measured in these samples (see Appendix). This rules out *in situ* production as  
99 an explanation for the elevated  $^3\text{He}/^4\text{He}$  in the inclusion fluids, and strongly implies that the helium  
100 isotope ratio can be used to faithfully trace the source of volatiles in the ore fluids.

101 Sulfide  $\delta^{34}\text{S}$  values range from +15.9 to -16.1 ‰ (Table 1), which fall well within the range  
102 recorded for each deposit (e.g. Boast et al. 1981; Boyce et al. 1983a; Anderson et al. 1998;  
103 Wilkinson et al. 2005; Barrie et al. 2009).

## 104

## 105 Discussion

### 106 *Mantle He in Irish Pb-Zn deposits – extension and deep faulting*

107 Each mine displays a range of  $^3\text{He}/^4\text{He}$  (Table 1) that can most simply be interpreted as a binary  
108 mixture of crustal radiogenic He ( $^3\text{He}/^4\text{He} \sim 0.01 R_a$ ) and mantle-derived He ( $^3\text{He}/^4\text{He} > 6 R_a$ ).  
109 Assuming that the Carboniferous modern sub-continental lithosphere mantle had a  $^3\text{He}/^4\text{He}$  of 10  
110  $R_a$ , the highest  $^3\text{He}/^4\text{He}$  (0.15 to 0.2  $R_a$ ) values are consistent with  $\sim 2\%$  of the He in the ore fluids  
111 being derived from the upper mantle.

112 Previous studies have shown that there is a similar mantle He contribution to crustal fluids in  
113 regions of active extension (e.g. Oxburgh et al. 1986; Ballentine et al. 2002). Mantle helium is  
114 typically absent in aqueous fluids in basins that formed through tectonic loading of the crust during  
115 compression, where crustal radiogenic helium dominates (Oxburgh et al. 1986). Furthermore, the  
116 flux of mantle-derived  $^3\text{He}$  into the continental crust is strongly coupled to mantle heat flow and  
117 both are elevated in extensional settings, even where volcanic activity is not manifest at the surface  
118 (Oxburgh et al. 1986; Marty et al. 1992).

119 Deep faults likely act as conduits for the migration of mantle-derived volatiles into the shallow  
120 crust (e.g. Kennedy et al. 1997). All of the studied deposits are located in areas with evidence of  
121 significant, fault-related subsidence during the Lower Carboniferous (e.g. Boyce et al. 1983a;  
122 Strogen, 1988). Across Ireland the structural grain is strongly influenced by the preceding  
123 Caledonian Orogeny, most manifest in the occurrence of the broad Iapetus Suture Zone (Fig. 1;  
124 Phillips et al. 1976). There is general acceptance that the controlling faults associated with the  
125 deposits are re-activated Caledonian structures (Phillips et al. 1976; Johnston et al. 1996) which

126 have certainly penetrated to the underlying Lower Palaeozoic Caledonian basement (e.g. Dixon et  
127 al. 1990; Everett et al. 2003), and possibly deeper (Mills et al. 1987). It is these faults that  
128 controlled the input of hydrothermal fluids to the deposits, and it is also likely that these  
129 fundamental features also facilitated the tapping of mantle-derived volatiles into the crust. Upon  
130 reaching the crust, the volatiles were diluted by the principal ore fluid of the Irish deposits, which is  
131 considered to be dominated by Mississippian evaporated seawater that had strongly interacted with  
132 the Lower Palaeozoic basement lithologies (Bischoff et al. 1981; Banks et al. 2002; Wilkinson  
133 2010).

134 Fluid inclusion trapping temperatures have not been determined on the samples analysed for He  
135 isotopes, but, there is an abundance of fluid inclusion data (Samson and Russell 1987; Banks and  
136 Russell 1992; Wilkinson et al. 2005; Ashton et al. *in press*) which facilitate comparison of  
137 ‘temperature’ and the concentration of mantle-derived  $^3\text{He}$  in the ore-forming fluids. We note a  
138 tendency for the mineral deposits hosted by Waulsortian Limestone formation in the central  
139 southern part of the orefield (Figure 1) to be generally associated with the highest  $^3\text{He}/^4\text{He}$  and the  
140 highest fluid inclusion temperatures in the metal bearing ore fluid (Figure 2). In contrast, the Navan  
141 deposit is hosted largely by the contemporaneous Navan Group (Andrew 1986), has the lowest  
142 published fluid inclusion temperatures in the metal bearing ore fluid, and consistently displays  
143 lower  $^3\text{He}/^4\text{He}$ .

144 The deposits with highest  $^3\text{He}/^4\text{He}$  and fluid inclusion temperatures (Silvermines, Galmoy, Lisheen)  
145 are located within the central southern part of the Irish Lower Carboniferous in and around the  
146 Shannon Trough. There is abundant evidence that these areas have undergone the greatest  
147 subsidence, with the development of synsedimentary breccias, and cross-fault thickening of  
148 sequences during late Tournaisian (Boyce et al. 1983a; Andrew 1986; Shearley et al. 1995;  
149 Hitzman 1999; Wilkinson et al. 2011; Ashton et al. *in press*). The greatest subsidence at Navan  
150 occurred later, during Chadian times resulting in submarine debris flows, although tectonism is  
151 seen in the upper parts of the Navan Group prior to this. Thus, it appears that the deposits around  
152 the Shannon Trough and southern Ireland, which have a distinct character compared to Navan,  
153 show the highest temperatures of mineralisation as well as the most influence of mantle  $^3\text{He}$ . It is  
154 thus perhaps not surprising new discoveries of Irish-type Zn+Pb ores have been identified,  
155 associated with contemporaneous Carboniferous basaltic diatremes and pyroclastic deposits, in the  
156 Limerick Basin (Figure 1; Redmond 2010; Elliot et al. 2013; McCusker and Reed 2013). This  
157 association between diatremes from low partial melts, extensional faults, and SEDEX deposits has  
158 been documented in the Selwyn Basin, Yukon (Goodfellow et al. 1995).

159 The occurrence of the mantle He component demands a high heat flow in the crust during  
160 mineralisation, and also provides a strong genetic link to crustal extension. This extension is  
161 reflected in differential subsidence across Ireland during the Lower Carboniferous, linked to  
162 reactivation of deep-lying, inherited fault systems. These faults facilitated the movement of mantle  
163 volatiles into the crust where they mixed with and were diluted by the hydrothermal fluids which  
164 carried the ore metals.

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### *Significance for carbonate-hosted mineralisation*

Despite the evident relationship between mantle He, tectonism, heat and ore-bearing hydrothermal fluids, the greatest concentration of base metals, at Navan, does not correlate with the most intense heat flow and strongest mantle He isotope signature. Indeed, Navan is 4 to 5 times larger than any of the central, southern deposits but has the lowest contribution of mantle  $^3\text{He}$  in our study. Thus, whilst the mantle influence is felt, and is genetically significant in terms of its association with extension, the influence of mantle volatiles, and fluid heat, was not the major influence on ore deposit size. It appears rather to be the efficiency of precipitation of ore metals that is key to ability to develop economic levels of accumulation; in particular the dominance of bacteriogenic sulfide (Fallick et al. 2001).

This importance of bacteriogenic sulfide is echoed in the absence of correlation between helium and sulfur isotope data. Sulfide ore deposition in all economic Irish-type Pb-Zn deposits was a result of mixing of a hot, hydrothermal fluid with a cool, surface fluid. In practice, the hydrothermal metal-bearing fluid had a limited reduced sulfide component, that was likely derived from the underlying Lower Palaeozoic basement (Blakeman et al. 2002)  $\delta^{34}\text{S}$  range from 0 to +15‰. In contrast, the surface fluid was essentially seawater containing bacteriogenic sulfide, with a typical ore-stage  $\delta^{34}\text{S} = -15 \pm 10$  ‰. Thus, it might be anticipated that sulfides with a dominantly hydrothermal  $\delta^{34}\text{S}$  signature would have higher  $^3\text{He}/^4\text{He}$  than those dominated by seawater-derived sulfur. The absence of such a correlation between S and He isotopes between or within the deposits (Figure 3) highlights the importance of mixing with surface/shallow crustal fluids in the genesis of these deposits, but underlines that ore forming processes are not reliant simply on heat. The seawater-derived fluid, with its associated bacteriogenic sulfide, overwhelms the sulfur budget in all producing Irish-type deposits (e.g. Boyce et al. 1983b; Anderson et al. 1998; Blakeman et al. 2002; Fallick et al. 2001).

### **Conclusions**

Helium isotopes have been measured in sulfides from every producing Irish mine. All contain a component of mantle-derived He indicating that at least some heat from the mantle during a period of crustal attenuation was involved in the fluid convection which led to the development of this ore field (Figure 4). The mantle heat may be important in initiating or driving localized hydrothermal cells but its existence is an indication of the tectonic setting and thermal regime of Irish ore field genesis.

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207

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343

344 **Figure captions**

345 Figure .1 Simplified geological map of Ireland, showing location of those Mississippian carbonate-  
346 hosted Irish-type deposits that have produced substantial ore; all have been analysed in this study  
347 (adapted from hand out map Minerals Ireland Exploration & Mining Division). The approximate  
348 trace of the inferred Iapetus Suture is shown in purple after Phillips et al. (1976).

349 Figure 2. Maximum fluid inclusion temperatures of sphalerite for all ore Irish deposits shown  
350 against  $^3\text{He}/^4\text{He}$  values of ore fluids. All deposits are dominated  $^3\text{He}/^4\text{He}$  ratios that are above  
351 crustal radiogenic values, demanding a contribution of mantle-derived volatiles. The mines with  
352 the highest maximum fluid temperatures have the largest contribution of mantle-derived He in  
353 fluids. Inset figure shows measured  $^3\text{He}/^4\text{He}$  relative to modern mantle values. Fluid inclusion  
354 temperature data from Wilkinson (2010).

355 Figure 3.  $\delta^{34}\text{S}$  vs.  $^3\text{He}/^4\text{He}$  for samples from the Irish Pb-Zn province. There is no statistically  
356 significant correlation between  $\delta^{34}\text{S}$  and  $^3\text{He}/^4\text{He}$ . It should also be noted that even in isotopically  
357 light sulfides, generated from bacteriogenic sulfide, there is still a clear mantle signature implying  
358 that even further mixing with a fluid containing bacteriogenic sulfur at the site of deposition did not  
359 mask the mantle  $^3\text{He}/^4\text{He}$  signature.

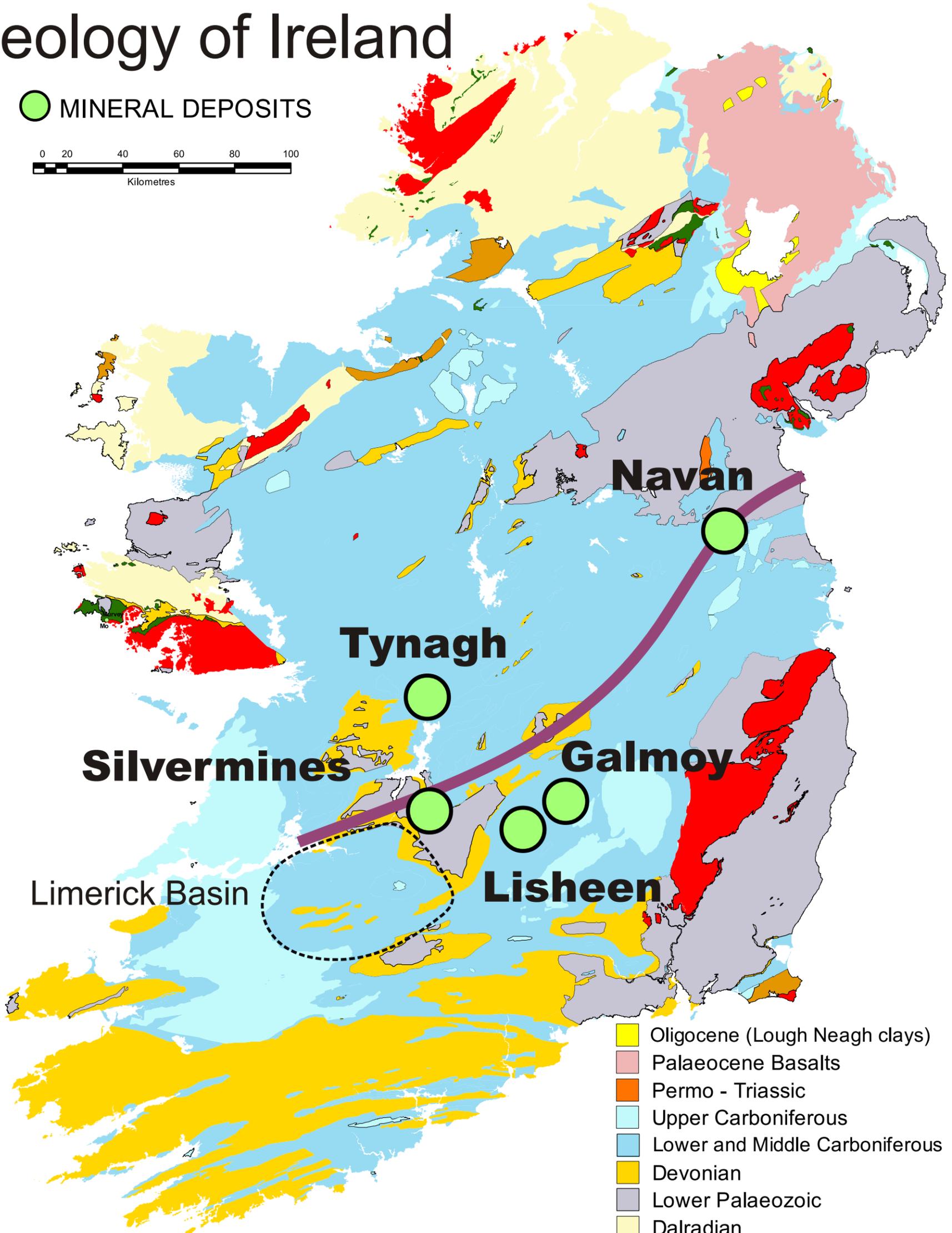
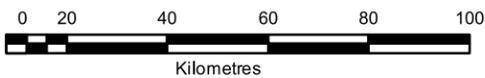
360 Figure 4. Schematic section of the rifting crust with some degree of mantle melting (modified  
361 from Latin et al., 1990). The red arrow indicates release of mantle helium from a location of partial  
362 melting under the extended crust. This volatile helium then mixes with and is diluted by the ore  
363 fluids in the basement beneath the deposits. Mines with the largest mantle  $^3\text{He}$  component have  
364 been diluted the least by crustal fluids and are therefore potentially closer to rift axis, and areas of  
365 mantle melting.  
366

367 **Table 1.**  $^3\text{He}/^4\text{He}$  and  $\delta^{34}\text{S}$  of sulphides from the Irish Pb-Zn ore field.  
368

Figure 1

# Geology of Ireland

● MINERAL DEPOSITS



**Navan**

**Tynagh**

**Silvermines**

**Galmoy**

**Lisheen**

Limerick Basin

- Oligocene (Lough Neagh clays)
- Palaeocene Basalts
- Permo - Triassic
- Upper Carboniferous
- Lower and Middle Carboniferous
- Devonian
- Lower Palaeozoic
- Dalradian
- Pre - Dalradian
- Granite
- Intermediate to Basic Intrusives

■ Iapetus Suture

Figure 2

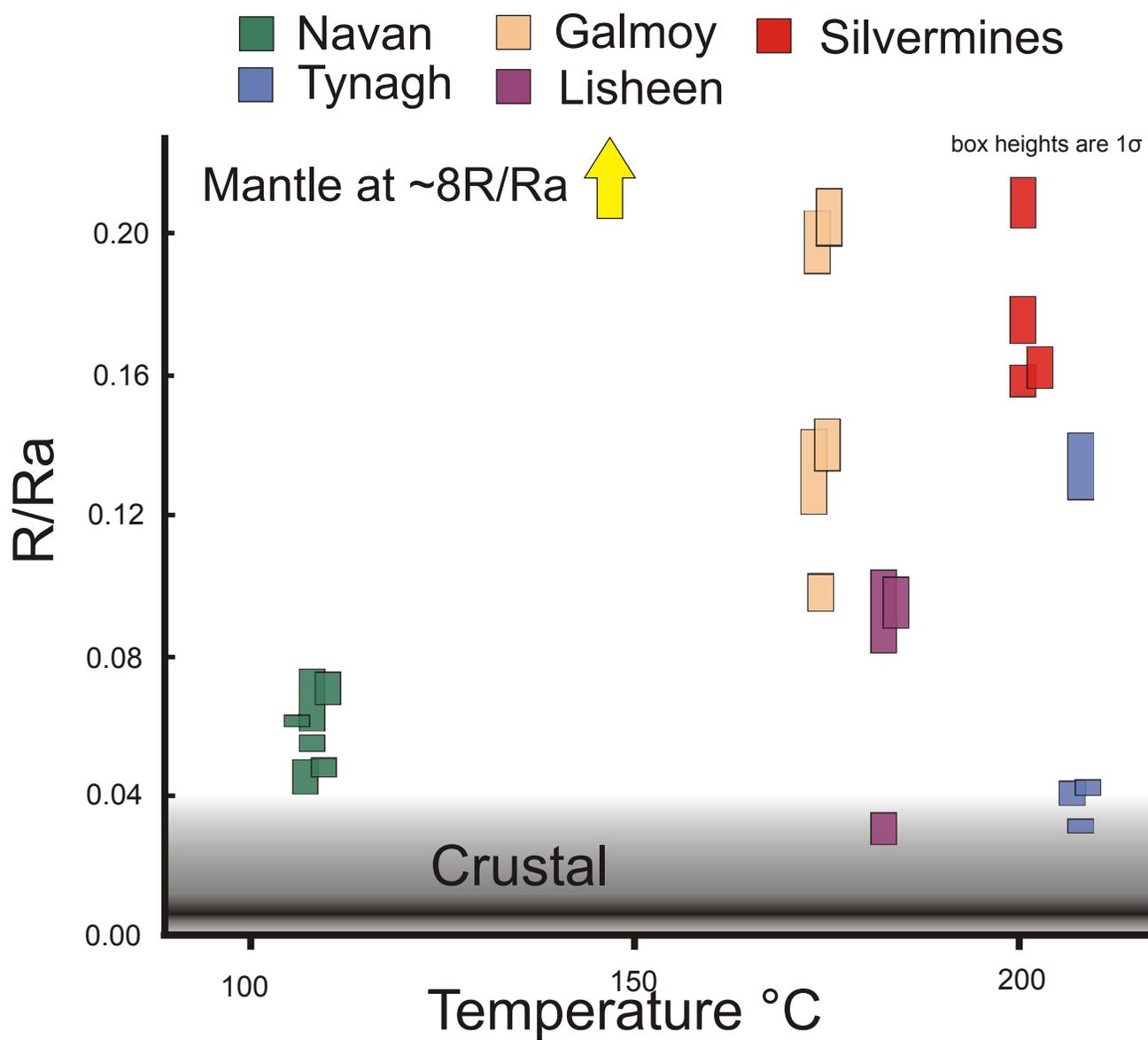


Figure 3

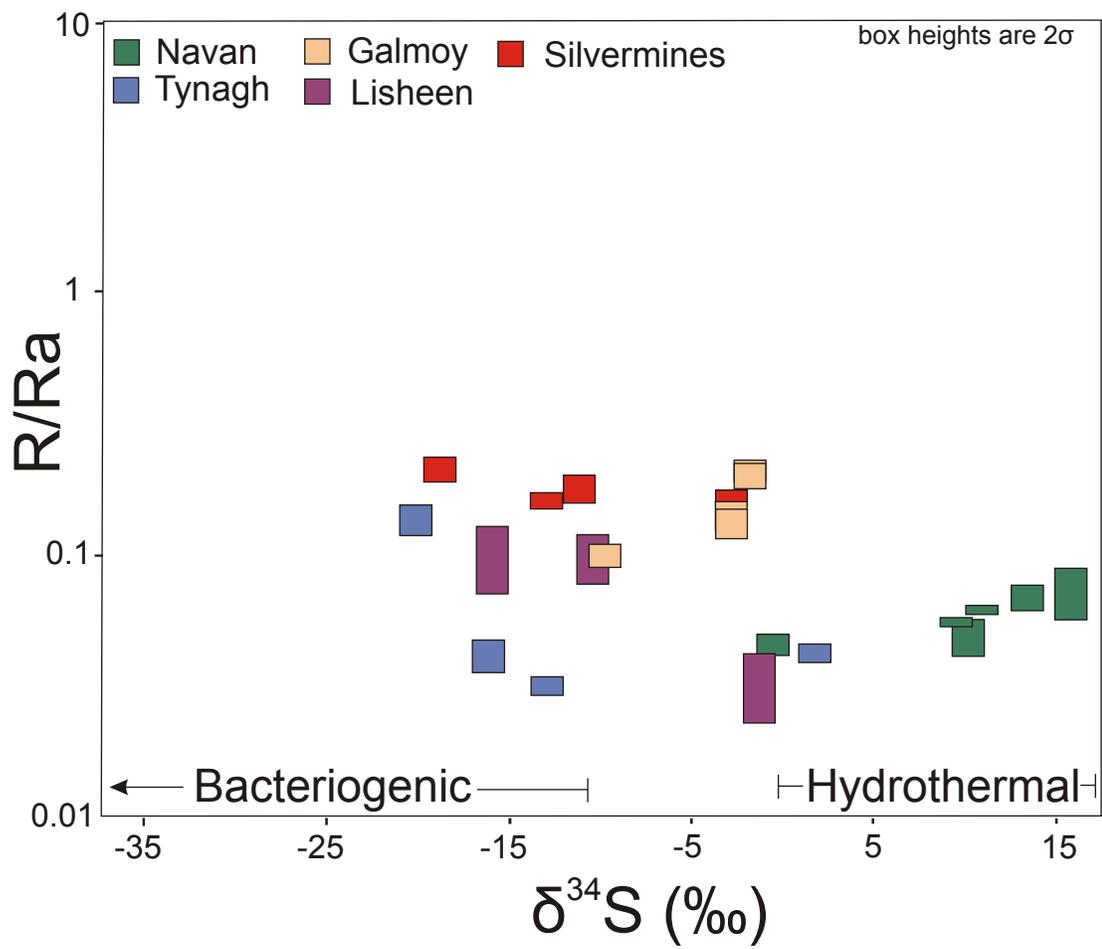
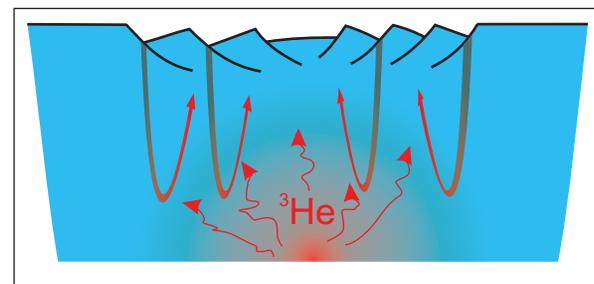
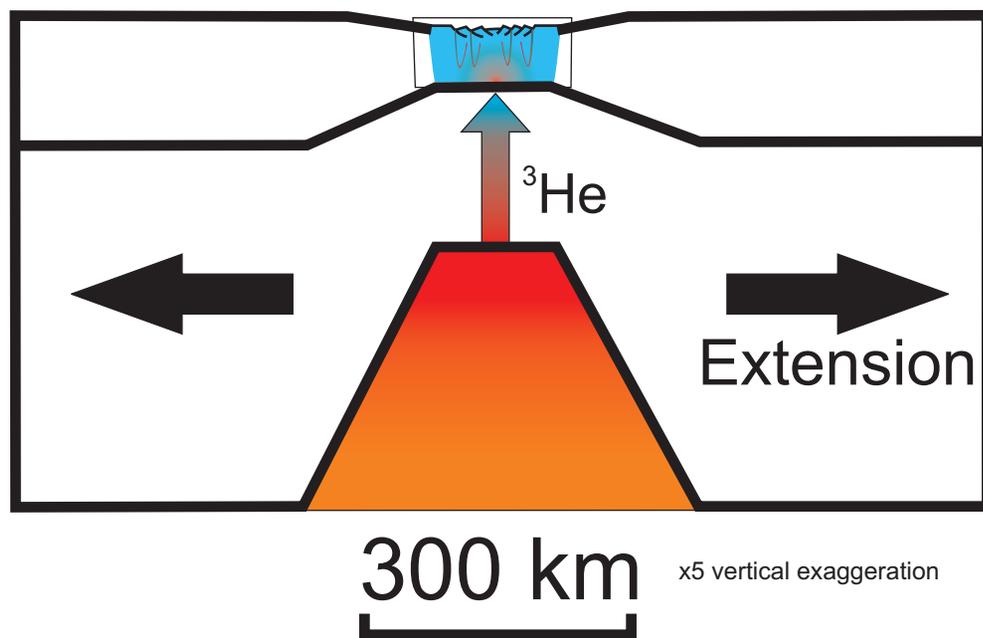


Figure 4



-  Asthenospheric upwelling
-  High  $^3\text{He}/^4\text{He}$  (mantle derived)
-  Low  $^3\text{He}/^4\text{He}$  (crustal)
-  Seawater derived brine

Table 1

Sample	Mineral	Source	Location and or sample number	$\delta^{34}\text{S}$	$4\text{He}$ (10 <sup>-6</sup> cc/g)†
<b>Navan</b>					
IRHe-1	gal	H	2-1 Lens	10.9	10.4
IRHe-2	gal	H	2-2 Lens box 2.1 3 w245	9.5	7.2
IRHe-3	gal	H	2-5 Lens box 2.1 17	-0.5	2.2
IRHe-6	mar	I	3-1 lens	15.9	0.57
IRHe-25	mar	I	N01358, D19313 Blakeman	10.2	0.8
IRHe-26	mar	I	DDH U24309	13.4	0.7
<b>Lisheen</b>					
IRHe-7	gal	P	loc MN17054	-15.9	0.1
IRHe-8	gal	P	loc MW 50D02	-10.3	0.1
IRHe-9	gal	P	loc MN 2X60	-1.2	0.2
<b>Galmoy</b>					
IRHe-10	gal	R	RE1a - R Orebody G Fault	-1.7	1.7
IRHe-10*	gal	R	"	-1.7	0.9
IRHe-11	gal	R	RB2a - R Orebody NW	-2.8	0.2
IRHe-11*	gal	R	"	-2.8	0.2
IRHe-12	gal	R	GNE - G Orebody NW Feeder	-9.71	0.1
<b>Tynagh</b>					
IRHe-13	gal	GSI	box 1780	-20	7.4
IRHe-14	gal	GSI	box 1781	-12.8	2.3
IRHe-15	gal	GSI	box 1777	1.8	2.3
IRHe-21	gal	GSI	box 1776	-16.1	2.3
<b>Silvermines</b>					
IRHe-4	gal	GSI	452-2 Mogul	-12.9	6.1
IRHe-5	gal	GSI	B45-2 Mogal Silvermine	-18.7	1.8
IRHe-19	gal	GSI	B zone feeder 4500	-11	9.1
IRHe-23	gal	I		-2.7	5.2

*gal = galena, mar = marcasite, \* recrushed of same sample, †uncertainty in measured <sup>4</sup>He is governed*  
H = Hunterian Museum, I = Internal SUERC samples, P = Paul Mc Dermott from Galmoy  
R = Roy Coates from Lisheen, GSI = Geological Survey of Ireland

$^3\text{He}/^4\text{He}$ (R/Ra)	$\sigma\text{R/Ra}$	$^4\text{He}/^{20}\text{Ne}$	20Ne
0.062	0.001	11194	0.001
0.055	0.001	7964	0.001
0.045	0.002	11467	0.000
0.071	0.008	n.d.	n.d.
0.048	0.004	34	0.025
0.068	0.004	759	0.001
0.095	0.014	n.d.	n.d.
0.096	0.007	n.d.	n.d.
0.031	0.005	n.d.	n.d.
0.199	0.008	170496	0.000
0.206	0.008	4532	0.000
0.140	0.007	355	0.001
0.133	0.011	266	0.001
0.099	0.004	n.d.	n.d.
0.135	0.008	64406	0.000
0.032	0.001	n.d.	n.d.
0.042	0.002	n.d.	n.d.
0.041	0.003	45	0.052
0.159	0.004	n.d.	n.d.
0.210	0.006	4745	0.000
0.177	0.006	603	0.015
0.163	0.005	2289	0.002

*d by reproducibility of standard  $^4\text{He}$  ( $\pm 1\%$ )*

Appendix

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Appendix table

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