1 Re-Os systematics and age of pyrite associated with stratiform Zn-Pb mineralization in the Howards Pass district, Yukon and Northwest Territories, Canada 2 Karen D. Kelley¹, David Selby², Hendrik Falck³, and John F. Slack⁴ 3 4 ¹U.S. Geological Survey, MS 973, Denver, CO 80225 USA; kdkelley@usgs.gov 5 ²Department of Earth Sciences, University of Durham, Durham, DH1 3LE UK ³ NWT Geoscience Office, P.O. Box 1320, Yellowknife, NWT X1A 2L9 Canada 6 7 ⁴U.S. Geological Survey (Emeritus), MS 954, Reston, VA 20192 USA 8 9 Abstract 10 Stratiform Zn-Pb deposits hosted in unmetamorphosed carbonaceous and 11 siliceous mudstones of the Ordovician to Silurian Duo Lake Formation define the 12 Howards Pass district in Yukon Territory and Northwest Territories, western Canada. 13 Collectively, the deposits are among the largest in the world, containing drill-indicated 14 and inferred resources of 423 Mt at 4.84% Zn and 1.59% Pb. Sulphide textures include: 15 (a) fine-scale laminations of sphalerite, galena, and pyrite from <0.05 mm to 1 cm thick, 16 interbedded with carbonaceous sedimentary rock; (b) layers of coarse sulphide that are 17 structurally controlled by microfolds; and (c) veins that cut bedding and sulphide 18 laminations. The finely interlaminated nature of sulphides with mudstone has been used 19 as evidence for syngenetic mineralizing processes, whereas paleomagnetic data 20 determined on coarse layered sulphides suggest a Middle Jurassic age of mineralization. 21 Here, we present new Re-Os isotopic data for 12 pyrite separates obtained from 4 22 laminated sulphide-rich samples from the XY Central (XYC) and Don (DON) deposits, 23 and for 1 unmineralized organic-rich mudstone ~20 m stratigraphically below the 24 sulphide-bearing zone. Pyrite separates that lack mudstone inclusions ("pure") from the 25 XYC deposit contain 2.2 to 4.0 ppb Re, and 93.4 to 123.4 ppt Os; pure pyrite from the 26 DON deposit is significantly more enriched in Re and Os (34–37 ppb Re; 636.8–694.9 ppt

27	Os). The ¹⁸⁷ Re/ ¹⁸⁸ Os values of pure pyrite separates from the XYC and DON deposits
28	range from 137.6 to 197 and 182.1 to 201.4, respectively. Regression of all pure pyrite
29	Re-Os data from both deposits yields an isochron age of 442 ± 14 Ma (MSWD = 7.4) and
30	an initial $^{187}\text{Os}/^{188}\text{Os}$ (Os_i) value of 0.71 \pm 0.07. The Re-Os age indicates that the early
31	phase of pyrite precipitation (and by inference, sphalerite and galena) occurred during the
32	early Silurian, consistent with biostratigraphic ages of the host rocks. The Os_i value of
33	~0.8 for earliest Silurian seawater recorded from organic-rich shale in the basal Silurian
34	Global Stratotype Section and Point (GSSP) at Dobs Linn, Scotland, is very similar to
35	that provided by the Howards Pass pyrite regression, and hence suggests a hydrogenous
36	(seawater) source of Os for the pyrite. Therefore, two possible sources of Os are (1) the
37	Zn- and Pb-bearing hydrothermal fluid that leached Os from footwall sedimentary rocks,
38	which were deposited in seawater; or (2) directly from seawater during precipitation of
39	the pyrite, which suggests that the Os content of the hydrothermal fluid was minor
40	relative to that of seawater.
41 42 43 44	Keywords: Re-Os isotopes, geochronology, Howards Pass, stratabound Zn-Pb, Yukon Territory, Northwest Territories
45	Introduction
46	The Zn-Pb deposits of the Howards Pass district occur in lower Paleozoic strata of
47	the Selwyn Basin in the northern Canadian Cordillera, primarily in eastern Yukon
48	Territory, but extending across the border into Northwest Territories (Fig. 1). Other Zn-
49	Pb districts in the Selwyn Basin include Macmillan Pass or "MacPass" (Tom and Jason
50	deposits), Anvil (Faro, Grum, Swim, Vangorda, and Dy deposits), and Gataga (Cirque
51	and Driftpile deposits).

52	In the Howards Pass district, at least 15 mineralized zones have been identified
53	over a strike length of ~38 km (Fig. 2) (Selwyn Chihong Mining Ltd., 2016). Mineralized
54	zones consist of finely laminated to layered sulphides, or coarse sulphides occurring in
55	veins, foliations, thin fractures, and cleavage planes that cut the laminations and layers.
56	Sulphide minerals include sphalerite, galena, and minor pyrite; chalcopyrite is rare.
57	Collectively, the Zn-Pb deposits are among the largest in the world (Goodfellow 2004;
58	Leach et al. 2005), in total containing 423 Mt of drill-indicated and inferred resources at
59	an average grade of 4.84% Zn and 1.59 % Pb (Kirkham et al. 2012).
60	The deposits in the Howards Pass district are classified as clastic-dominated lead-
61	zinc (CD Zn-Pb) ores, which are typically hosted in shale, sandstone, siltstone, or mixed
62	clastic lithologies, or form replacements of carbonate rocks within a clastic-dominated
63	sedimentary sequence (Leach et al. 2010). CD Zn-Pb deposits are stratabound and mostly
64	stratiform, and commonly display laminated sulphide textures; therefore, they are
65	assumed to have formed synchronously with sedimentation and/or during early burial and
66	diagenesis. However, intricately interlayered sulphides can also be produced by
67	replacement that mimics primary sedimentary features (e.g., Kelley et al. 2004a; Leach et
68	al. 2005). In addition, original textures can be modified by post-mineralization
69	deformation and recrystallization.
70	Textural and paleomagnetic data for the deposit offer contrasting temporal
71	relationships between sedimentation and mineralization in the Howards Pass district.
72	Although not definitive, the finely laminated nature of sulphides intergrown with
73	mudstone has been used as evidence for syngenetic or syndiagenetic mineralizing
74	processes during the early Silurian, given conodont and graptolite biostratigraphic data

75 for the host rocks (Morganti 1979; Norford and Orchard 1985; Goodfellow and Jonasson 76 1986). Crosscutting textures may record recrystallization of primary, fine-grained 77 sulphides by pressure dissolution during synsedimentary deformation (Jonasson and 78 Goodfellow 1986). An alternative explanation is that the laminated sulphides formed 79 concurrently with abundant, secondary, coarse-grained sulphide minerals that occur along 80 cleavage planes and in thin fractures throughout the deposits. The northeast dip of the 81 cleavage planes and their alignment with northwest-trending regional folds (Gordey and 82 Anderson 1993; Martel 2015) suggest that the coarse-grained sulphides formed during 83 tectonism, the onset of which regionally occurred in the Jurassic to Cretaceous (Dusel-84 Bacon et al. 2002; Mair et al. 2006). Furthermore, paleomagnetic dating of coarse-85 grained sulphide veins in the Howards Pass district indicate that they formed during the 86 Middle Jurassic, leading to the further suggestion that the fine-grained sulphides may also 87 have formed at this time (Kawasaki and Symons 2012). Establishing with certainty the 88 age of the laminated sulphide minerals is therefore critical for developing a robust genetic 89 model for the Howards Pass deposits. If the laminated sulphides indeed formed during 90 the Mesozoic, then a tectonically related genesis must be invoked that is distinct from the 91 synsedimentary to syndiagenetic model that is predominant for CD Zn-Pb deposits (see 92 Leach et al. 2010).

Documenting the timing of mineralization for CD Zn-Pb deposits has traditionally
been difficult owing mainly to a lack of datable minerals within the deposits. Commonly,
global Pb-isotope growth curves are used to calculate model Pb ages for CD Zn-Pb
deposits. However, many ages obtained by this approach are much older than their
respective host rocks, and therefore such global growth curves should not be used to

calculate model Pb ages (Leach et al. 2005). A better approach involves the application of
terrane-specific Pb growth curves, as was done for deposits in northern Australia (Large
et al. 2005) and the Selwyn Basin (Godwin and Sinclair 1982). However, the underlying
assumption in building these curves is that mineralization formed by syngenetic
processes. If the deposits to be dated formed after deposition of the host rocks, then such
Pb-isotope growth curves are not relevant for dating mineralization.

104 The recent application of the rhenium-osmium (Re-Os) chronometer to Fe- and 105 Cu-bearing sulphide minerals has demonstrated the feasibility of directly dating ore 106 mineralization. However, Red Dog is the only CD Zn-Pb deposit that has been dated 107 successfully by Re-Os methods, due in part to the coarse-grained nature of the sulphide 108 minerals there and to the relatively high Re contents (tens to hundreds of parts per 109 billion) of pyrite within the vein and massive ore (Morelli et al. 2004). Base-metal 110 sulphides in other types of sediment-hosted deposits have also been directly dated using 111 Re-Os geochronology, including the Lince-Estefanía Cu deposit in northern Chile 112 (Tristá-Aguilera et al. 2006), the Kipushi Cu-Co deposit in the Democratic Republic of 113 Congo (Schneider et al. 2007), the Ruby Creek Cu-Co deposit in Alaska (Selby et al. 114 2009), the Tuolugou Co-Au deposit in northwestern China (Feng et al. 2009), the Lisheen 115 and Silvermines Zn-Pb deposits in Ireland (Hnatyshin et al. 2015), and the Caixiashan 116 deposit in northwestern China (Li et al. 2016). 117 This paper presents new Re-Os data for pyrite and black shale from the XY 118 Central (XYC) and DON deposits in the Howards Pass district (Fig. 2). The Re-Os results 119 presented herein (1) further demonstrate the utility of using sulphide minerals for 120 geochronology, (2) deepen our understanding of Re-Os systematics in CD Zn-Pb

deposits, (3) document an age for the layered and laminated stage of mineralization, and(4) provide implications for the origin of the metals.

123

124 Regional and local geology

Stratiform CD Zn-Pb deposits are common in the Selwyn Basin of western
Canada. This basin formed by passive margin sedimentation from the Neoproterozoic to
Devonian. Underlying strata of the Selwyn Basin are Mesoproterozoic and older
crystalline rocks overlain by Mesoproterozoic metasedimentary rocks and mafic sills
related to rift sedimentation and crustal extension that is bracketed between 1.59 and 1.38
Ga (Eisbacher 1985; Snyder et al. 2009).

131 The passive margin sequence within the Selwyn Basin consists of two northwest-132 trending belts of rocks (Gordey and Anderson 1993): (1) in the northeast, the Mackenzie 133 Platform comprises Neoproterozoic to Middle Devonian shallow-water carbonate and 134 sandstone; (2) in the southwest, sedimentary strata include time-equivalent siliciclastic 135 rocks (Neoproterozoic Windermere Supergroup), deep-water limestone (Cambrian 136 Rabbitkettle Formation), and shale and chert of the Ordovician to Silurian Road River 137 Group. Passive margin sedimentation was punctuated by periods of extension and 138 tectonic instability. Mafic igneous rocks occur locally in the Selwyn Basin (Fig. 1) as a 139 result of middle to late Cambrian and Middle Ordovician volcanism (Goodfellow et al. 140 1995).

Devonian-Mississippian black shale, chert, and clastic units of the Earn Group overlie the Road River Group (Fig. 3) (Morganti 1979; Gordey 1980). Deposition of

rocks in the Earn Group reflects regional uplift and erosion followed by subsidence of thecontinental margin.

145	Regionally developed Early to Middle Cretaceous compression and deformation
146	occurred during eastward docking of allochthonous terranes against the North American
147	continent (Gordey and Anderson 1993; Mair et al. 2006). This Cretaceous tectonism in
148	the Howards Pass district resulted in the formation of thin-skinned detachments, folds,
149	imbricate thrusts, and duplex structures (Hodder et al. 2014; Martel 2015); in contrast,
150	large-scale open folds characterize the more competent strata of the Mackenzie Platform
151	to the east (Gordey and Anderson 1993).
152	
153	Stratigraphy of the Howards Pass district
154	Carbonaceous and siliceous mudstones of the Ordovician to Silurian Duo Lake
155	Formation (locally referred to informally as Howards Pass formation) of the Road River
156	Group host most of the Zn-Pb deposits and occurrences (Fig. 3). The stratigraphy in the
157	district is probably more complex than originally defined by Morganti (1979), owing to
158	disruption of the succession by district-scale and local faults as revealed by recent
159	geologic mapping (Hodder et al. 2014; Martel 2015). Specifically, previously reported
160	thicknesses of stratigraphic units in some cases may represent structural repetitions
161	(Hodder et al. 2014).

162 The basal sedimentary unit in the district (Fig. 3) is the Rabbitkettle Formation, 163 consisting of massive and wavy banded limestone, silty limestone, and graded and 164 laminated micrite beds, which together indicate an off-shelf, quiet-water, below wave-165 base depositional setting (Morganti 1979). The Transition zone that overlies the

166 Rabbitkettle Formation was interpreted in early studies as a separate unit, deposited in a 167 similar stratigraphic setting as the Rabbitkettle Formation. However, due to a higher 168 silica/carbonate ratio, Morganti (1979) suggested that the Transition zone was deposited 169 in deeper parts of the basin, below the carbonate compensation depth. In contrast, 170 Hodder et al. (2014) recently demonstrated that structures and textures within the wavy 171 banded limestone represent highly strained to mylonitic features, with strain gradients 172 increasing toward the upper contact with the Duo Lake Formation. Following this recent 173 model, the Transition zone is considered a major detachment surface at the base of the 174 Duo Lake Formation in the Howards Pass district, and therefore is not a separate stratigraphic unit. 175

176 The Duo Lake Formation consists of distinct member subdivisions that have been 177 followed by all subsequent workers; from base to top these consist of: (1) Pyritic 178 mudstone member; (2) Calcareous mudstone and overlying Cherty mudstone (combined 179 as Cherty carbonaceous mudstone on Fig. 3); (3) Active mudstone; and (4) Upper 180 siliceous mudstone (Fig. 3). The Pyritic member ranges from 2 to 10 m in thickness and 181 is dark grey and typically finely laminated (Morganti 1979); pyrite and dolomite are 182 volumetrically minor. This unit is overlain by massive to poorly bedded, dark grey 183 calcareous mudstone at the base, transitioning to siliceous and carbonaceous mudstone at 184 the top. Locally present are microscopic concretions of calcite-pyrite (Morganti 1979). 185 The overlying Active mudstone member hosts nearly all of the Zn-Pb deposits in the 186 district, and ranges in thickness from about 20 to 50 m. It consists of intercalated 187 carbonaceous mudstone, cherty mudstone, and minor chert and limestone. Sulphide 188 lenses within this unit consist of layered, laminated, and massive sphalerite \pm galena,

189	variably deformed by shears and mylonite zones. Pyrite forms thin laminae of fine-
190	grained framboids; apatite is generally present in minor amounts. Overlying the Active
191	member is the Upper siliceous mudstone, which is commonly 20 to 90 m but locally up
192	to 120 m thick in the Howards Pass district and comprises dark grey to black mudstone
193	and minor chert (Morganti 1979) with locally abundant, thin (<1 cm) laminae of fine-
194	grained phosphorite (Goodfellow and Jonasson 1986; Slack et al. 2012). Orange-
195	weathering, silicic, bioturbated mudstone of the Silurian Steel Formation (Flaggy
196	Mudstone Formation in Howards Pass district) overlies the Duo Lake Formation and is
197	an important regional marker unit for stratigraphic correlation (Fig. 3).
198	Contacts between and within units from the upper Rabbitkettle Formation to the
199	lower Earn Group have been locally tectonized such that internal stratigraphy is disrupted
200	by complex thrust imbrication along detachment surfaces (Hodder et al. 2014; Martel
201	2015). As stated above, a prominent flat-lying décollement or zone of ductile and/or
202	brittle deformation occurs at the base of the Duo Lake Formation. Imbricate thrust faults
203	rise stratigraphically upward from this detachment surface and form the floor thrust of the
204	duplex structure that dominates the Howards Pass district (Fig. 3; Hodder et al. 2014).
205	
206	Depositional environment of mudstone host rocks
207	Whole-rock analyses obtained from drill cores in relatively undeformed parts of
208	the deposits show that black mudstones of the Duo Lake Formation contain variable

- $\label{eq:silica} 209 \qquad silica (up to 90 \text{ wt \% SiO}_2) \text{ and carbonaceous or graphitic material (up to 16.5 \text{ wt \% total})}$
- 210 organic carbon, TOC; n = 58) (Slack et al. 2012). Ratios of redox-sensitive trace
- 211 elements, used to determine redox conditions in bottom waters, suggest that sulphidic or

212 anoxic conditions prevailed during deposition of the Cherty calcareous and Active 213 mudstone members, leading up to and continuing during Zn-Pb mineralization (Slack et 214 al. 2012), assuming that deposition of sulphide minerals was concurrent with 215 sedimentation. Iron speciation data, sulphur isotope values of pyrite, and bulk Fe/Al and 216 Mo/TOC ratios generally corroborate this redox interpretation (Johnson et al. 2014). 217 The age of the Duo Lake Formation was initially assigned on the basis of 218 graptolite assemblages to straddle the Ordovician-Silurian boundary (Morganti 1979). 219 Conodonts from the mineralized Active mudstone member further constrain the age to 220 early to middle Llandovery as defined by Norford and Orchard (1985). Coeval Late 221 Ordovician to early Silurian carbonate rocks east of Howards Pass in the Mackenzie 222 Mountains record deposition in primarily shallow subtidal and evaporitic conditions 223 (Pope and Leslie 2013). 224 225 Similar Paleozoic CD Zn-Pb deposits in the region 226 Other Paleozoic CD Zn-Pb deposits in the Selwyn Basin (Goodfellow 2004, 227 2007) are presumed to have formed at different times in the Paleozoic. The Dy, 228 Vangorda, Faro, Grum, and Swim deposits in the Anvil district (Figs. 1 and 3) are hosted 229 in lower Cambrian metasedimentary and minor metavolcanic rocks. Stratigraphically far 230 above the Howards Pass deposits are the Tom and Jason deposits in the Macmillan Pass 231 district (Fig. 1), hosted in Upper Devonian coarse clastic sedimentary rocks of the Earn 232 Group. CD Zn-Pb deposits of the Gataga district, also known as the Kechika Trough of

233 northern British Columbia, are hosted in Upper Devonian carbonaceous shale and chert

of the lower Earn Group.

236 Howards Pass deposits

237	Active exploration for lead and zinc in the late 1960s and early 1970s led to the
238	staking of the Howards Pass district in 1972. Throughout many years of exploration, at
239	least 15 mineralized zones have been identified, including the XYC, Anniv, DON, and
240	OP deposits that occur in a ~38-km-long, northwest-trending belt (Fig. 2). In 2010,
241	China's Yunnan Chihong Zinc and Germanium Co. Ltd signed a joint venture agreement
242	with Selwyn Resources Ltd., and in June, 2013, Selwyn Chihong Canada Mining Ltd.
243	became the project's sole owner (Kirby 2014). Collectively, the Howards Pass deposits
244	contain 185.6 Mt of drill-indicated resources at an average grade of 5.20% Zn and 1.79 $\%$
245	Pb, and 237.9 Mt of inferred resources at 4.47% Zn and 1.38% Pb; total resources are 423
246	Mt at 4.84% Zn and 1.59% Pb (Kirkham et al. 2012).
247	Stratigraphic sequences of the Duo Lake Formation are similar in all deposits.
248	Each mineralized zone, averaging about 12 m in thickness, occurs at the same general
249	stratigraphic position (Fig. 4), with high grade zones located preferentially at the base and
250	top of the Active member (Kirkham et al. 2012). On this basis, it is assumed that all
251	deposits formed concurrently. Available Pb isotopic data for sulphides and host rocks
252	indicate that the major deposits (XYC, DON, OP, Anniv) formed from isotopically
253	identical hydrothermal fluids, thus supporting a cogenetic model (Cousens 2007),
254	although multiple mineralizing events in the district cannot be ruled out.
255	The Zn-Pb deposits are situated along the limbs of major synclinal structures that
256	formed during Mesozoic deformation. This deformation also resulted in imbricate thrust
257	faults and the development of several cleavage sets (McClay 1991; Hodder et al. 2014).

258	Low grade, subgreenschist-facies metamorphism affected rocks in the Selwyn Basin at
259	~125-120 Ma (Gabrielse and Yorath 1989), but no metamorphic grade indicator minerals
260	have been identified within the shales or mudstones (McClay 1991). Rather, the key
261	evidence for regional temperature levels derives from reflectance values of graptolites
262	(Riediger et al. 1989), and Conodont Alteration Indices (CAI) that reflect thermal
263	maturity of conodonts and by inference host strata (Epstein et al. 1977). In pre-
264	Cretaceous rocks of the Selwyn Basin, CAI values are 4-5 (Gordey and Anderson 1983;
265	MacNaughton et al. 2008), indicating temperatures of ca. 300° to 400°C during
266	deformation and burial metamorphism. However, despite unquestionable overprinting of
267	textures by low-grade metamorphism and penetrative deformation, many primary
268	depositional and diagenetic features are still preserved within the Howards Pass Zn-Pb
269	sulphides and host strata (Jonasson and Goodfellow 1986; Gadd et al. 2016).
270	
271	Mineralogical and textural characteristics of ore
272	Texturally and mineralogically, all of the Zn-Pb deposits are similar (Morganti
273	1979; Goodfellow 2004). The Anniv, XYC, and DON deposits are the most economically
274	significant within the belt (Mining Yukon 2014). Types of mineral textures include (1)
275	relatively undeformed interlaminations of sulphides and carbonaceous mudstones, having
276	typical grain sizes of less than 250 μ m (Fig. 5b and d); (2) microfolds composed of fine
277	and coarse sulphide laminations and layers (Fig. 5a, c, and f); and (3) sulphide-bearing
278	cleavages, veinlets, and thin fractures that cut bedding and sulphide laminations (Fig. 5g
279	and h). Given that the objective of this study is to determine the age of the laminated
280	sulphides, only the first two of these textural types are discussed. Diverse tectonic

structures that are superimposed on the layered rocks are described in detail by Jonasson
and Goodfellow (1986) and McClay (1991).

283

284 Laminated sulphide zones

285 Individual layers within the laminated sulphide zones range from <0.05 mm to as 286 much as 1 cm thick (Fig. 5a). The fine-scale laminations are represented largely by color 287 variations caused by different proportions of organic matter and quartz intermixed with 288 sulphides (Fig. 6g). Principal minerals in the laminated ore are sphalerite, galena, and 289 pyrite. Chalcopyrite and molybdenite are reported (Goodfellow 2004), but were not 290 observed in samples examined for this study. Barite is absent, although it occurs in 291 overlying Devonian carbonaceous chert and mudstone in the Howards Pass district and 292 regionally (Morganti 1979; Goodfellow 2004, 2007). 293 Pyrite is mainly framboidal to cubic (Fig. 6), comprising irregular masses

294 intergrown with mudstone and other sulphide minerals (Jonasson and Goodfellow 1986;

Gadd et al. 2016). The framboids typically range in size from <5 to at least 50 μ m (Fig.

296 6a, b, e, h), but are locally as large as 200 μm. Thin beds composed of graded framboids

297 occur locally (Jonasson and Goodfellow 1986). Some framboids display well-preserved

298 internal structures, whereas others lack internal features (Fig. 6h). Although discrete

299 framboids are present, pyrite framboids typically coalesce and form irregular masses.

300 Bedding-parallel layers of pyrite are evident in some samples (Fig. 6d, g). Pyrite also

301 forms euhedral cubes 0.1 to 0.4 mm in diameter (Fig. 6c); locally, euhedral pyrite occurs

302 as overgrowths on earlier framboidal pyrite and sphalerite (Fig. 6c, h) or is overgrown by

303 sphalerite (Fig. 6a).

304 Sphalerite grains are concentrated in zones within pyrite-rich layers (Fig. 6d, e), 305 typically in a quartz- or mudstone-rich matrix among pyrite framboids (Fig. 6h, i). The 306 edges of some framboids in the sphalerite-filled matrix are commonly obscured (Fig. 6h, 307 i). Sphalerite also forms inclusions within euhedral pyrite (Fig. 6c), and elongate grains 308 parallel to bedding (Fig. 6g). Individual sphalerite grains are about 5 to 60 µm in 309 diameter. Where present, galena is most common as inclusions in sphalerite, although 310 Gadd et al. (2016) report interlaminations of sphalerite with galena and framboidal pyrite. 311 Mudstone host rocks are locally fossiliferous and in places the sulphide minerals 312 partially replace fossils. An abundance of undeformed microfossils in calcareous lenses 313 and concretions within the Active mudstone include various forms of algae, mazuelloids, 314 and other organic debris (Jonasson and Goodfellow 1986). One sample of unmineralized 315 mudstone from drill core (XYC116-365.8 m), about 4.6 m below the Active member, 316 contains abundant (~20 vol % of the rock) well-preserved radiolarians and sponge 317 spicules (J.A. Dumoulin, U.S. Geological Survey, written communication, 2014). Most of 318 the radiolarians in this sample are $\sim 100-200 \ \mu m$ in diameter, and are similar in 319 appearance to those in calcareous radiolarite layers contained within mudstone in the Red 320 Dog deposit area (Dumoulin et al. 2004). Sponge spicules in unmineralized mudstone 321 from Howards Pass include simple forms with hollow centers (20-40 x 100-950 µm), 322 typically filled with polycrystalline silica or organic matter (J.A. Dumoulin, U.S. 323 Geological Survey, written communication, 2014). Circular features in sulphide samples 324 could either be pyritized radiolarians (Fig. 6j) or cross sections of sponge spicules (Fig. 325 6a, i), suggesting that in some cases pyrite preferentially replaced the rims and/or central 326 cores of spicules; silica or organic matter typically makes up the core, but sphalerite has

327	clearly replaced spicule cores in places. Alternatively, these small rounded features may
328	be pyrite framboids with centers composed of algal and mazuelloid fossils, which are
329	locally replaced by sphalerite (Jonasson and Goodfellow 1986).
330	
331	Microfolds
332	Folding of sulphide layers is interpreted to have occurred both during compaction
333	of the sediments and post-sedimentation tectonic deformation. Folded and contorted
334	layers that resulted from compaction (Fig. 5a, c, f) are locally overprinted by
335	recrystallization and the development of pressure-solution cleavages and sulphide-
336	bearing shears and mylonitic features (Fig. 5e, g, h) (McClay 1991). In many folded
337	layers, individual laminae remain predominantly parallel (Fig. 5f) accompanied by some
338	thinning or pinching (Fig. 5c). Within relatively thicker pyritic layers (Fig. 5a),
339	ptygmatic-like folds are present, interpreted as having formed during compaction and
340	final dewatering (Jonasson and Goodfellow 1986). Fold hinges may contain as much as
341	50 vol % sphalerite with grains up to 100 μ m across, a product likely resulting from
342	structural thickening of sphalerite-rich laminae. High-grade galena mineralization
343	preferentially occurs as cleavage-controlled stringers (Gadd et al. 2016) and with
344	sphalerite in the hinge zones of folds (Morganti 1979).
345	

346 Methods

347 Twelve samples of sulphide-rich rock collected from exploration piles and drill
348 cores at the XYC and DON deposits were examined petrographically. Three samples
349 from XYC and one from DON containing layered and laminated sulphides were selected
350 for further study and processing for Re-Os analysis (Table 1; Fig. 5a, c, e, and f). Two of

351 the three XYC sulphide-bearing samples were divided into two or more subsamples in

352 order to obtain multiple pyrite separates from each sample. Additionally, two samples

353 from the XYC deposit (XYC-txt3 and XYC-txt4) were sieved to yield fine (<0.25 mm)

and coarse (~0.25 to 0.5 mm) pyrite separates (indicated by "f" or "c" suffix,

respectively; Table 1). Sample XYC-127-124.5 lacked sufficient pyrite for multiple

356 separates and therefore a single bulk separate was obtained.

357 The DON mineralized sample was collected from drill core (DON-137-303.8).

358 This sample yielded only a fine-grained fraction of pyrite; consequently, the rock was cut

into four sections and pyrite separates were obtained for each.

360 One unmineralized carbonaceous mudstone ~19.6 m stratigraphically below the 361 Zn-Pb-bearing zone (Active mudstone) was collected from drill core at the DON deposit 362 (DON-111-157.8; Table 1). This bulk sample was subsequently processed and ground to 363 a powder.

364 A total of 12 pyrite mineral separates of ~200-400 mg was obtained using 365 traditional isolation methods (crushing, magnetic and/or heavy liquid separation, 366 handpicking). Care was taken to isolate pyrite from the matrix of the mudstone and to 367 ensure that pyrite was free of mudstone fragments adhered to grain surfaces. However, 368 mudstone inclusions within pyrite cannot be visually identified during handpicking. 369 Evidence for the presence of mudstone inclusions was recorded by a white grainy residue 370 that remained after digestion of the separate in inverse *aqua regia* (Table 1), as described 371 below.

372 The Re-Os analyses were conducted at the Source Rock and Sulfide

373 Geochronology and Geochemistry Laboratory at Durham University, Durham, U.K.

374	Pyrite separates were weighed and loaded into a Carius tube with a known quantity of
375	mixed Re-Os tracer solution containing ¹⁸⁵ Re and ¹⁹⁰ Os. Using the Carius tube method,
376	sample and tracer solution were digested and equilibrated using a mixture of 11N HCl (3
377	ml) and 15.5N HNO ₃ (8 ml) (inverse <i>aqua regia</i>) at 220°C for 48 hours (Selby et al.
378	2009). A weighed aliquot of the unmineralized mudstone sample was also digested in a
379	Carius tube containing mixed $^{185}\mbox{Re}$ and $^{190}\mbox{Os}$ tracer solution with 8 ml of 4N H_2SO_4
380	bearing $0.25g/g$ CrO ₃ for 48 hours at 220°C (Selby and Creaser 2003).
381	The acidic medium, aqua regia, digests sulphide minerals and organic matter. The
382	latter is a significant component of unmineralized mudstones in the Howards Pass
383	district. For example, the 10-m-thick mudstone interval from which the unmineralized
384	bulk sample was collected contains 8.6 to 16.0 wt. % TOC ($n = 4$). Organic matter-
385	bearing sedimentary rocks, such as mudstones, are commonly enriched in Re and Os
386	(Selby and Creaser 2003; Selby et al. 2009). Silicate minerals such as quartz, muscovite,
387	and clays present in mudstone of this study are coated with organic matter. These silicate
388	minerals are resistant to digestion in aqua regia. Six of the pyrite separates used in this
389	study contained a silicate residue after dissolution (Table 1). The presence of a silicate
390	residue signifies the strong likelihood that submicroscopic amounts of organic matter
391	from the mudstone had been present (but dissolved with pyrite) in the separate as fine
392	intergrowths with, or contained within, pyrite, or as coatings on grains. Hence, the
393	resulting Re-Os data obtained likely represent a mixture of Re and Os liberated from both
394	pyrite and organic matter. Conversely, the lack of any detectable residue after digestion
395	supports the high purity of these mineral separates, and the absence of any Re and Os
396	incorporated from organic matter.

397 Following Carius tube digestion, osmium was isolated and purified from the 398 acidic digestion medium using solvent extraction (CHCl₃) and micro-distillation methods 399 (Selby and Creaser 2001). Rhenium was then isolated from the resulting Os-extracted 400 acid medium by anion-column and single-bead chromatography methods (Selby and 401 Creaser 2003). The purified Re and Os were loaded onto Ni and Pt filaments, respectively 402 (Selby et al. 2007). Isotopic measurements were conducted using negative thermal 403 ionization mass spectrometry (Creaser et al. 1991) on a Thermo Scientific TRITON mass 404 spectrometer via ion-counting, using a secondary electron multiplier in peak-hopping 405 mode for Os, and static Faraday collection for Re. Total procedural blanks during the 406 course of this study for Re and Os were 3.5 ± 0.4 and 0.7 ± 0.8 pg, respectively, with an average ${}^{187}\text{Os}/{}^{188}\text{Os}$ value of 0.25 \pm 0.05 (1SD, n = 3). All uncertainties are determined 407 408 by error propagation of uncertainties in Re and Os mass spectrometer measurements, 409 blank abundances and isotopic compositions, spike calibrations, and the reproducibility 410 of standard Re and Os isotopic values. In-house solution standards run during the course 411 of the study (in 2010) are 0.16084 ± 0.00013 (1SD, n = 3) for DROsS and 0.5984 ± 0.00013 412 0.0012 (1SD, n = 3) for Re Standard solution, which are in agreement with those reported 413 previously (Nowell et al. 2008; Cumming et al. 2012, and references therein). 414 Regression of the Re-Os data and independent calculation of initial ¹⁸⁷Os/¹⁸⁸Os ratios (Os_i) is carried out using *Isoplot V. 4.15* (Ludwig 2003) and the ¹⁸⁷Re decay 415 constant of 1.666 x 10^{-11} a⁻¹ (Smoliar et al. 1996), respectively. 416 417

418 **Re-Os results**

419	Re-Os analyses were obtained for all 12 pyrite separates and one unmineralized
420	organic-rich mudstone (Table 1). Based on geological and stratigraphic similarities (Fig.
421	4) and textural observations (Figs. 5 and 6) between the Zn-Pb deposits, sulphide
422	mineralization at XYC and DON is considered to be penecontemporaneous. However,
423	given the spatial separation of these two deposits (ca. 12 km), and significant differences
424	in Re and Os abundances of the pyrite separates, Re-Os data for the XYC and DON
425	samples are initially considered separately (Fig. 7).
426	Rhenium and Os concentrations in the eight XYC separates range from 2.2 to
427	21.4 ppb, and 93.4 to 692.3 ppt, respectively (Table 1). The 187 Re/ 188 Os data show a
428	limited range of values (137.6 to 209.7), but the measured ¹⁸⁷ Os/ ¹⁸⁸ Os ratios display more
429	variability (1.723 to 3.128). The Re-Os data as a whole lack a statistical meaningful
430	isochron age (156 \pm 1200 Ma; MSWD = 543; Fig. 7A). Based on the biostratigraphic age
431	of the host rock (Active member, ~442 Ma), Os_i values range from 0.47 to 2.04. Among
432	these eight separates, only three have similar values (Os _i = \sim 0.7; Table 1). These three are
433	the only XYC separates that did not yield a residue after acid digestion. Hence, they are
434	considered to record the Re-Os systematics solely of pyrite and not a mixture derived
435	from pyrite and organic matter contained in mudstone, potentially present as coatings
436	and/or microscopic inclusions in the pyrite. Data for the other separates are interpreted to
437	represent a mixture of Re and Os derived from pyrite and organic matter based on the
438	presence of a silicate residue following digestion. The three separates with similar $\ensuremath{Os_i}$
439	values (~0.7) also possess similar Re-Os isotope values, and as a result, the regression of
440	the Re-Os data yields an imprecise isochron age of 480 ± 570 Ma (MSWD = 6.8; Fig.
441	7a).

442	Only one of four pyrite separates from the DON deposit sample yielded a silicate
443	residue after digestion (Table 1). Collectively, the four separates have Re and Os
444	abundances of 33.6 to 37.0 ppb and 599.8 to 694.9 ppt, respectively. With the exception
445	of the Re-Os data for DON-137(1), the Re-Os isotope compositions are similar, and do
446	not yield a geologically meaningful isochron age (2075 \pm 1700 Ma; MSWD = 85; Fig.
447	7B). Furthermore, the DON separates (excluding DON-137(1)) yield Os _i values similar to
448	those of three of the XYC separates (~0.7; Table 1). The DON separates possessing
449	similar Os _i values have very similar Re-Os isotope values, which yield a highly imprecise
450	isochron age of 457 ± 1500 Ma (MSWD = 19; Fig. 7B). Nominally, this age is very
451	similar to that obtained for the XYC separates.
452	As stated above, separates that did not yield a significant silicate residue
453	following acid digestion provide the best record of the Re-Os isotope systematics of
454	pyrite, and contain limited to no evidence of Re and Os derived from organic matter that
455	occurred as coatings on grains or intergrowths with pyrite. Data for these six separates
456	produce a Re-Os isochron age of 442 \pm 14 Ma (MSWD =7.4) and an Os_i value of 0.71 \pm
457	0.07 (Fig. 8).
458	The unmineralized black calcareous and carbonaceous mudstone sample (DON-
459	111-157.8) that was collected ca. 20 m below the Active member in the footwall of the

460 Zn-Pb mineralized zone consists of organic matter, calcite, quartz, muscovite, pyrite, and

dolomite (Morganti 1979). The sample contains 51 ppb Re and 1.6 ppb Os (1632 ppt Os),

462 and 187 Re/ 188 Os and 187 Os/ 188 Os values of ~197 and 2.505, respectively (Table 1). The

463 Re-Os data yield an Os_i value (calculated at 442 Ma) of 1.05 ± 0.01 . Because the sampled

464 interval is ca. 20 m below the mineralized Active member, it was likely deposited

thousands or millions of years earlier. However, even a few million years will not

466 appreciably affect the calculated Os_i value. For example, at 445 Ma, the calculated Os_i is

467 1.04.

468

469 **Discussion**

470 Temporal relationships between pyrite and sphalerite

471 The laminated nature of the Zn-Pb sulphide zones in the Howards Pass district has 472 been attributed to predominantly exhalative processes of mineralization (Jonasson and 473 Goodfellow 1986; Goodfellow 2007). In contrast, a Middle Jurassic paleomagnetic age 474 was obtained on coarse-grained sulphide-rich rock (Kawasaki and Symons (2012). These 475 authors suggest that the laminated sulphides also possibly, but less likely, formed during 476 the Mesozoic. The aim of the present study is to use the Re-Os chronometer on pyrite 477 from Howards Pass to determine an absolute age of Zn-Pb mineralization for the layered 478 and laminated sulphides. In order to do so, documentation of a linked paragenesis of 479 pyrite and sphalerite is necessary. Such documentation is not straightforward, because the 480 Howards Pass deposits have been affected by post-ore deformation and metamorphism. 481 Pyrite in the Howards Pass laminated sulphide zones occurs as framboids <5 to 482 200 µm in diameter, euhedral overgrowths on framboids, and as concentrations of 483 subhedral and euhedral grains within relatively thick layers (Figs. 5 and 6). Abundant 484 framboidal pyrite is typical of some other CD Zn-Pb deposits such as Citronen Fjord in 485 North Greenland (Kragh et al. 1997) and HYC in northern Australia (Williams 1978). On 486 the other hand, many large CD Zn-Pb ores lack abundant framboidal pyrite (e.g., Red 487 Dog; Kelley et al. 2004b). The presence of framboidal pyrite does not necessarily

488 indicate formation during sedimentation because it may form tens to hundreds of millions 489 of years after deposition of the host rocks, during late diagenesis, low-grade 490 metamorphism, and/or hydrothermal alteration (Scott et al. 2009). However, based on 491 analogy with modern marine environments (Canfield et al. 1992; Wilkin and Barnes 492 1997; Wilkin et al. 1997) and textural studies of other unmetamorphosed CD Zn-Pb 493 deposits (e.g., Williams 1978; Kragh et al. 1997), framboidal pyrite in the Howards Pass 494 sulphide deposits most likely formed in anoxic or sulphidic pore fluids within centimeters 495 of the sediment-water interface, or in some cases in sulphidic bottom waters. The 496 overgrowths of euhedral pyrite on framboidal pyrite also probably formed early, during 497 diagenesis as suggested by similarities in trace and minor element contents and spatial 498 associations between this type of pyrite and the framboidal pyrite (Gadd et al. 2016). 499 Sphalerite in the laminated sulphide zones typically forms the matrix between 500 framboidal pyrite grains (Fig. 6a, c, f), and although not observed in this study, some 501 framboidal pyrite grains have reported cores of sphalerite (Goodfellow and Jonasson 502 1986), suggesting that in places sphalerite predated or was concurrent with early pyrite 503 formation. In some laminae, sphalerite is intergrown with or encased by euhedral pyrite 504 (Fig. 6b, d, h). If the euhedral pyrite formed during sedimentation and diagenesis as 505 suggested by Gadd et al. (2016), then by inference the sphalerite inclusions within 506 euhedral pyrite also formed at this time, or earlier. Some sphalerite and pyrite show 507 evidence of selective replacement of fossils (Fig. 6a, h, i), which argues for subseafloor 508 precipitation of these sulphides. However, such textures do not conclusively determine 509 the timing between pyrite and sphalerite deposition. Although numerous examples exist 510 of intergrowths between sphalerite and pyrite (Fig. 6b, h), observed textures do not

511	preclude the formation of sphalerite after framboidal pyrite. Primary textural features
512	assumed to represent synsedimentary exhalative (SEDEX) co-precipitation of sulphide
513	minerals may also result from the subseafloor replacement by sulphide of carbonate
514	layers within mudstone during sedimentation and early diagenesis (e.g., Anarraaq
515	deposit, northern Alaska; Kelley et al. 2004a), or by replacement many millions of years
516	after sedimentation (Leach et al. 2005). Therefore, carbonate cement in the Howards Pass
517	mudstones, preserved long after pyrite formation, could have been later replaced by
518	sphalerite. However, without compelling textural evidence to support such a late
519	paragenesis for sphalerite (e.g., overgrowths on euhedral pyrite or crosscutting
520	relationships), the simplest model is one in which pyrite and sphalerite within the
521	laminated sulphides formed concurrently, during sedimentation and/or diagenesis.
522	
523	Purity of pyrite separates
524	Based on the fine-grained nature (typically $<250 \ \mu m$) and intergrowths of pyrite
525	and sphalerite at Howards Pass, much of the pyrite likely contains sphalerite fragments or
526	inclusions (e.g., Fig. 6b; Gadd et al. 2016). However, because sphalerite typically
527	contains less Re and Os (e.g., orders of magnitude lower concentrations in sphalerite

528 compared to pyrite in massive ore from Red Dog; Morelli et al. 2004), the Re-Os

529 systematics of pyrite are likely unaffected by sphalerite inclusions.

The finely intergrown nature of pyrite and mudstone in our samples presented the greatest challenge to obtaining pure pyrite separates. Impure separates can yield Re-Os data that do not record the age of the pyrite, but rather a mixed age that reflects Re-Os systematics of both the pyrite and the organic component of mudstone, the latter

potentially having high Re and Os contents (Selby and Creaser 2003; Selby et al. 2009).

Therefore, it is critical to document the purity of the pyrite separates in order to provide arobust interpretation of the age data.

537 Most pyrite separates were hand-picked after heavy liquid and magnetic 538 separations. Pyrite grains having visible mudstone intergrowths were excluded, but 539 mudstone inclusions within pyrite or coatings of organic matter on grains cannot be 540 identified visually during hand picking. Six of the 12 pyrite separates contained residual 541 minerals (quartz, muscovite, clays hosted in mudstone) following digestion with aqua 542 regia at 220°C (Table 1). Given that organic matter coats grains and/or occurs as 543 submicron inclusions in pyrite, occurrence of the residue signifies that organic matter was 544 likely present and dissolved with the pyrite. As a result, the Re and Os budget will 545 include both that of dissolved pyrite and organic matter. The six separates that produced a 546 silicate residue have widely varying calculated Os_i values (-0.77 to 2.04) that are distinct 547 from the ~ 0.7 value of other pyrite separates that are considered to be pure and lack 548 mudstone inclusions or coatings. The wide variation in the Os_i values is consistent with 549 studies that have shown heterogeneity of Re and Os contents in organic matter, especially 550 in <10 g samples. In cases where Re and Os covary inconsistently, the resulting Os_i value 551 will be highly variable (Kendall et al. 2009).

Based on the above discussion, only pyrite separates that did not yield silicate residues after digestion are considered to record the Re-Os systematics solely of pyrite and not a mixture between those of pyrite and organic matter contained in mudstone. The purity with respect to mudstone or organic matter inclusions within these pyrite separates is assumed to be 90% or greater (referred to as pure pyrite).

557	The Re and Os concentrations of pure pyrite separates from the DON deposit
558	(34.0–37.0 ppb and 636.8–694.9 ppm, respectively; Figs. 4f and 5g-i) are distinct
559	compared with those of pure pyrite from the XYC deposit (2.2-4.0 ppb and 93.4 to 123.4
560	ppb; Figs. 4a, e and 5). Even if small amounts of mudstone still remained in the separates,
561	a comparison of pyrite compositions suggests that this is not the cause of the large
562	differences in Re contents (~30 ppb) between the DON and XYC separates. The Re
563	content of unmineralized mudstone from the DON deposit is only 50.85 ppb (Table 1),
564	and therefore an unrealistically large component of mudstone would be necessary to
565	increase Re contents of the pyrite sample by 30 ppb. Hence, contamination by mudstone
566	is considered quantitatively unimportant and thus unlikely to account for the differences
567	in pyrite Re and Os isotope values determined for the XYC and DON deposits.
568	Because the objective of this study is to determine the age of the early stage of
569	mineralization that produced the laminated sulphides and not the later coarse-grained
570	veins, the separates also require purity with respect to pyrite type or stage. Most hand
571	samples chosen for processing are finely laminated and free of any apparent coarse-
572	grained veins (Fig. 5). However, one hand sample (XYC-txt3) has obvious later veining
573	(Fig. 5e) and although the late veins were avoided during processing, it is possible that
574	late coarse pyrite was incorporated in the mineral separates. Fine-grained (<0.25 mm) and
575	coarse-grained (~0.25 to 0.5 mm) fractions of pyrite from this sample lack significant
576	variation in Re and Os concentrations or isotope ratios (Table 1). Interestingly, most
577	separates that were excluded based on the presence of residues are fractions from the
578	XYC-txt3 sample, and two of these are coarse-grained (Table 1). If late pyrite is present
579	in these separates, it may explain why the Re-Os data from all XYC separates lack a

statistically meaningful isochron age (Fig. 7a). Regardless, these samples were not usedin the final age calculation.

582

583 Age of host rocks and mineralized zones

584 Biostratigraphic data for the Howards Pass region include graptolite and conodont 585 ages (Fig. 9). Notably, many uncertainties in the biostratigraphic ages arise from poor 586 preservation and/or undiagnostic character (Norford and Orchard 1985). Graptolites are 587 rare and poorly preserved, and within the Howards Pass district all known occurrences in 588 the Active mudstone are sheared (Norford and Orchard 1985). However, units 589 stratigraphically above and below contain graptolites in zones at least 0.2 m thick. 590 Graptolites at the top of the Upper siliceous mudstone member and in the footwall 591 Calcareous mudstone unit bracket the mineralization age to Late Ordovician or early 592 Silurian (Morganti 1979). Two samples of black mudstone from a stratigraphic section about 20 km southwest of Howards Pass yielded graptolites of early Llandovery and 593 594 middle Llandovery age as interpreted by Norford and Orchard (1985), but this mudstone 595 is not mineralized and therefore its direct correlation with the Active member is 596 conjectural (Fig. 9).

597 Seven conodont samples collected from the Duo Lake Formation northwest of the 598 Howards Pass district were determined to be of Late Ordovician to early Silurian age 599 (McCracken 2014). Within the district, biostratigraphic ages for the Active mudstone 600 member and overlying units are based on conodonts that were obtained not only from 601 outcrop but also drill cores (Norford and Orchard 1985). Pyritized fragments of 602 radiolarians recovered from the Active mudstone are not diagnostic (F. Cordey,

University of Lyon, written communication, 2014), but conodonts from the ore zone are
diagnostic, although relatively small (<1.5 mm). Most conodont species in the Active
member were reported by Norford and Orchard (1985) to represent the *kentuckyensis*zone; these resemble representative species that may have coexisted in the *Distomodus kentuckyensis* zone (Norford and Orchard 1985), which equates to absolute ages ranging
from ~443.8 to 441 Ma (Fig. 9) based on the geologic time scale of Gradstein et al.
(2012).

Ambiguities and uncertainties in biostratigraphic ages and correlation with regional units in the district illustrate the need to directly date mineralizing events. Assuming that Fe and Zn-Pb sulphide minerals formed contemporaneously, the Re-Os age of pyrite may be used to indirectly date the base-metal event. Textures of sulphide samples from the Howards Pass deposits are suggestive of coeval deposition of pyrite and sphalerite. If this assumption is incorrect, an age determination for pyrite at least provides a maximum age of sphalerite mineralization.

617 An important observation regarding the Re-Os systematics in pyrite from the 618 Howards Pass district is that although samples from different deposits (DON and XYC) have highly variable Re and Os abundances, as well as ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os ratios 619 620 (Table 1), the data collectively yield a well-defined regression with a Re-Os isochron age of 442 ± 14 Ma (Fig. 8). This age is consistent with the early Llandovery biostratigraphic 621 622 age of the host rocks (Fig. 9), and suggests that mineralization occurred during the early 623 Silurian, concurrent with sedimentation or early diagenesis. Formation of the stratiform 624 Zn-Pb deposits during the Jurassic-Cretaceous (Kawasaki and Symons 2012) is ruled out

by this isochron age, excluding the remobilization of coarse sulphides into late fracturesthat likely occurred in the Mesozoic.

627

628 *Re-Os isotope compositions and source implications*

629 The 15 sites of known Zn-Pb mineralization that occur ca. 38 km along strike in 630 the Howards Pass district (Fig. 2) are similar with respect to stratigraphic, textural, 631 geochemical, and mineralogical characteristics (Figs. 4-6). These similarities suggest that 632 the individual deposits and occurrences are part of the same hydrothermal system, 633 supported by Pb isotope data for sphalerite and galena from several of the deposits that 634 indicate mineralization formed from isotopically homogeneous fluids (Cousins 2007). 635 Although it has been proposed that the northwest-trending belt of deposits resulted from 636 deposition in separate local sub-basins (Morganti 1979; Goodfellow 2004, 2007), the 637 recent work of Hodder et al. (2014) suggests that the northwest trend instead is a 638 structural artifact of the surface traces of parallel, southwest-dipping thrust faults. 639 If the assumption is correct that mudstone inclusions in pyrite are not the cause of 640 the variability in Re and Os abundances, and that the deposits formed from the same or 641 similar hydrothermal fluids, alternative explanations are needed for the observed 642 differences in Re and Os systematics between the XYC and DON deposits. Notably, it is 643 not uncommon for pyrite within a single sulphide deposit to possess highly variable Re 644 and Os abundances. For example, the Re and Os abundances of pyrite separates from 645 massive sulphide ores at Red Dog (~351–383 ppb Re, 3353–3637 ppt Os) are greatly 646 different from those of pyrite in vein ore (~14–31 ppb Re, 98–235 ppt Os) from a different part of the deposit (Morelli et al. 2004), and those of pyrite from silicified wall 647

648	rocks at Red Dog (~2.7–34 ppb Re, 85–789 ppb Os; Slack et al. 2015). Furthermore,
649	pyrite and other associated sulphides composing modern deep-sea massive sulfide
650	deposits show highly variable Re and Os abundances (0.1–74 ppb Re, 2–54 ppt Os; Zeng
651	et al. 2014). The variations in Re and Os isotopic composition of pyrite from the DON
652	deposit compared with those from the XYC deposit may reflect differences in Re and Os
653	concentrations in the mineralizing fluids. Such differences may be due to changing fluid
654	chemistry or redox conditions (e.g., Re is highly mobile under oxidized conditions and
655	precipitates under reduced conditions) with time, deposition in different portions of the
656	deposit, or derivation of Re and Os from different sources as observed for massive sulfide
657	deposits in modern seafloor-hydrothermal systems (Zeng et al. 2014).
658	The Os _i values of sulphides and host rock provide additional information about
659	the sources of metals. The Os_i value calculated from the pyrite Re-Os isochron is 0.71 \pm
660	0.07 (Fig. 8). The single sample of unmineralized mudstone collected ~ 20 m
661	stratigraphically below the Active mudstone has an Os_i value of 1.05 (calculated at 442
662	Ma; Table 1), which is nearly identical to that of modern seawater (e.g., Peucker-
663	Ehrenbrink and Ravizza 2000). It could be argued that this sample may not record the Os_i
664	of coeval seawater during sulphide deposition, for two reasons: (1) because the sampled
665	interval is 20 m below the mineralized Active mudstone, and could represent thousands
666	or millions of years of intervening sedimentation, and (2) because the residence time of
667	Os in seawater is short (~10 to 20 ka; Steele et al. 2009). However, even if we consider
668	the unmineralized mudstone to be 3 m.y. older than the active mudstone unit (Late
669	Ordovician, Late Hirnantian), the calculated Os_i value does not appreciably change (Os_i
670	at 445 Ma = 1.04). Of interest is that the Os_i value of 1.04 to 1.05 for mudstone in the

671 footwall to mineralization coincides with the highly radiogenic Os_i signature recorded

672 from the Global Stratotype Section and Point (GSSP) at Dobs Linn, Scotland, during the

673 deglacial phase of the Late Ordovician Hirnantian glaciation (Finlay et al., 2010).

674 The Os_i value of ~0.71 determined from the pyrite Re-Os isochron is similar to 675 that of earliest Silurian seawater recorded in mudstone from the basal Silurian section at 676 Dobs Linn after rapid deglaciation (Finlay et al. 2010). The nominal temporal agreement 677 of the pyrite Os_i value with the Dobs Linn mudrock value suggests a hydrogenous 678 (seawater) source for the Os. Based on the ~442 Ma age that indicates synsedimentary to 679 diagenetic sulphide precipitation at Howards Pass, two sources of Os are possible: (1) the 680 Zn- and Pb-bearing hydrothermal fluid, which leached Os from footwall sedimentary 681 rocks that were deposited in seawater; or (2) directly from seawater during precipitation 682 of the pyrite, which suggests that the Os content of the hydrothermal fluid was minor 683 relative to that of seawater. The latter scenario is consistent with recent studies that show 684 a predominant seawater-derived source of Os in modern seafloor massive sulphide 685 deposits (Zeng et al. 2014).

686 Based on regional geologic constraints and the textural, isotopic, and 687 geochronological data obtained from this study, a genetic model is proposed for the 688 Howards Pass deposits that is consistent with that proposed for CD Zn-Pb deposits 689 worldwide (Leach et al. 2005; 2010): (1) ore fluids originated as evolved, oxidized, 690 brines in shallow evaporative basins; silicified evaporate casts and the abundance and 691 diversity of macrofauna in shallow platform carbonate rocks in the Mackenzie Mountains 692 east of Howards Pass are evidence that warm-water, arid conditions prevailed in Late 693 Ordovician and early Silurian time (Pope and Leslie 2013); (2) the brines infiltrated and

circulated through underlying oxidized clastic rocks or fractured basement to depths of 3
to 5 km; (3) Pb and Zn were extracted and the metalliferous brines ascended into organicrich rocks that facilitated reduction of seawater or porewater sulphate to H₂S; and (4)
pyrite, sphalerite, and galena were deposited at or near the seafloor during sedimentation
and early diagenesis. The Zn- and Pb-bearing hydrothermal fluid may have leached Os
from seawater-deposited footwall sedimentary rocks, or Os was sourced directly from
seawater and incorporated in pyrite.

701

702 Conclusions

703 Pure (<10 vol % mudstone inclusions) pyrite separates obtained from laminated 704 sulphide zones in two different deposits (XYC and DON) have highly variable Re and Os abundances, as well as ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os ratios, and collectively vield a well-705 706 defined regression with a Re-Os isochron age of 442 ± 14 Ma. Similarity in stratigraphic, 707 textural, geochemical, and mineralogical characteristics among deposits in the district, 708 and previous Pb isotope compositions for galena and sphalerite from different deposits, 709 together argue for a single hydrothermal system, although individual mineralized centers 710 may represent deposition in separate local sub-basins. Observed variations in Re and Os 711 isotopic composition of pyrite between the two studied deposits may reflect differences in 712 Re and Os concentrations in the ore-forming fluids, perhaps due to changing fluid 713 chemistry (e.g., redox conditions) with time or space, including differences in relative 714 timing of sulphide deposition and/or depositional sites within the basin. 715 The initial Os isotope composition of mudstone in the footwall to mineralization 716 coincides with the highly radiogenic Os_i signature recorded from Dobs Linn during the

deglacial phase of the Late Ordovician Hirnantian glaciation and pyrite from mineralized
rocks at Howards Pass is similar to that of earliest Silurian seawater following rapid
deglaciation (Finlay et al. 2010), suggesting that (1) the Zn- and Pb-bearing hydrothermal
fluid leached Os from footwall sedimentary rocks that were deposited in seawater; or (2)
Os was derived directly from seawater during precipitation of the pyrite, which suggests
that the Os content of the hydrothermal fluid was minor relative to that of seawater.

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1005	Figures
1007 1008 1009 1010 1011 1012	Fig. 1 Map showing the Mackenzie Platform and time-equivalent shale and chert facies of Selwyn Basin (modified from Goodfellow 2004). Clastic-dominated Zn-Pb (CD Zn-Pb) deposits of Howards Pass district are immediately west of carbonate platform. Other significant Zn-Pb districts of Paleozoic age include Macmillan Pass (Tom and Jason deposits), Anvil (Dy, Faro, Grum, Swim, and Vangorda deposits), and Gataga (Cirque and Driftpile deposits).
1013 1014 1015	Fig. 2 Map showing location of Howards Pass district on border between Yukon and Northwest Territories. At least 15 mineralized centers lie along a northwest-trending belt

1016 termed the "zinc corridor." Samples used for this study were collected from the DON

- and XY Central (XYC) deposits. SCML, Selwyn Chihong Mining Ltd. Modified fromKirkham et al. (2012).
- 1019

1020 Fig. 3 Stratigraphic column of Selwyn Basin in Howards Pass district (modified from 1021 Morganti 1979; Goodfellow 2004). Howards Pass formation is an informal local name 1022 for a ~230-m-thick sequence of mudstone rocks that are stratigraphically equivalent to 1023 the Duo Lake Formation of the Road River Group (Morganti 1979). Active member 1024 contains all major mineralized zones in Howards Pass district. Deposits in MacMillan 1025 Pass and Gataga districts occur in the Devonian Earn Group, whereas those in Anvil 1026 district are in lower Cambrian strata (Goodfellow 2004, 2007). Recent mapping by 1027 Hodder et al. (2014) reveals complexity of deformation that includes a major flat-lying 1028 décollement (red wavy lines) at top of Rabbitkettle Formation, and imbricate thrust faults 1029 (grey wavy lines) occurring throughout Duo Lake Formation. Note that Gull Lake and 1030 Narchilla Formations are represented, respectively, by Sekwi and Vampire Formations in 1031 region (Gordey and Anderson 1993). See text for discussion.

1032

Fig. 4 a Cross section of XYC deposit showing inferred large syncline and relatively
 uniform thickness of sulphide-bearing zone (active mudstone unit). b Cross section of
 DON deposit illustrating structural disruption, but overall similar stratigraphic sequence
 compared to other deposits in Howards Pass district (Selwyn Resources, written
 communication, 2010). Note different scales in a compared to b.

1038

Fig. 5 Photographs showing textures of pyrite and other sulphides in laminated and 1039 1040 layered ore from Howards Pass. a Mineralized ore pile sample from the XYC deposit 1041 (XYC-txt4; Table 1) consisting primarily of thin (0.05 to 1.5 mm) laminae of sulphides alternating with carbonaceous mudstone, and one relatively thick, crenulated pyrite-rich 1042 1043 layer (microscopic textures shown in Fig. 6a, b, and c). Samples used for Re-Os analysis 1044 (shown by red arrows) were taken from thick pyrite-rich layer (XYC-txt4(1) and from 1045 thinner layer in lower left of photo (XYC-txt4(2); Table 1). b Undeformed layered 1046 sulphide ore from drill core (sample XYC 116-329; photomicrographs shown in Fig. 6c, 1047 d, and e). c Pyritic layers in carbonaceous mudstone, contorted and folded (XYC 127-1048 124.5; Table 1); sample for Re-Os is bulk pyrite separate that was not processed into 1049 different size fractions. d Undeformed interlayered mudstone and sulphides (light layers 1050 are sphalerite) showing minor offset (DON 22-68). e Pyrite interlayered with mudstone 1051 and cut by pressure-solution features (XYC-txt3; Table 1; microscopic textures shown in 1052 Fig. 6f). Three portions of rock were processed for Re-Os analysis (shown by red 1053 arrows): XYC-txt3(1) from upper right of photograph and XYC-txt3(2) and XYC-txt3(3) 1054 from middle and lower portions, respectively; samples were also separated into size fractions (<0.25 mm and 0.25 to 0.5 mm). f strongly folded interlayered sulphides and 1055 1056 mudstone (DON 137-303.8; photomicrographs shown in Fig. 6g, h, i, j). Core was cut into four equally thick sections and processed for Re-Os analysis; samples were not 1057 separated into size fractions. g Layered ore (tan layers are sphalerite-rich) from DON 1058 1059 deposit, cut by later sulphide-filled cleavages and fractures. h Early layered sulphide cut 1060 by sulphide-rich shears and mylonitic features.

1062 Fig. 6 Images of pyrite and other sulphides from rocks shown in Figure 5. a 1063 Photomicrograph in reflected light (rock shown in Fig. 5a) of pyrite framboids in 1064 carbonaceous mudstone; note size range of framboids from <10 to 50 µm in diameter. 1065 Minor euhedral pyrite grains are also present as overgrowths on framboids or as separate 1066 grains. Cross sections of probable pyritized sponge spicules occur in upper portion of 1067 photograph. Sphalerite forms subhedral grains in quartz or mudstone matrix among 1068 framboids. **b** Backscattered electron (BSE) image of framboidal pyrite (same sample as 1069 shown in Fig. 6a); c Photomicrograph in reflected light of relatively thick layer of pyrite 1070 (Fig. 5a) showing euhedral pyrite in mudstone/quartz matrix. Minor sphalerite and galena 1071 (latter not shown) are enclosed in euhedral pyrite. **d** Photomicrograph in reflected light of 1072 framboidal pyrite in mudstone with sphalerite; note accumulations of framboidal pyrite 1073 form crude layers (dashed lines, rock shown in Fig. 5b). e BSE image of sphalerite-rich 1074 layer (rock shown in Fig. 5b); sphalerite encloses framboidal and euhedral pyrite and 1075 minor galena, within quartz and mudstone matrix. f Photomicrograph in reflected light of 1076 alternating coarse- and fine-grained layers of pyritic mudstone and minor sphalerite 1077 (dashed white lines); solid white lines are direction of superimposed cleavage (rock 1078 shown in Fig. 5e). g Sphalerite and pyrite in layered ore from the DON deposit (rock shown in Fig. 5f). Darker bands reflect greater proportions of organic matter, but contain 1079 1080 pyrite and sphalerite. h BSE image showing sphalerite and pyrite from DON deposit 1081 (same sample as shown in g), illustrating size range of framboidal pyrite (~ 2 to 20 μ m). i 1082 Primarily euhedral pyrite intergrown with sphalerite in layered ore from DON deposit 1083 (rock shown in Fig. 5f). **j** Photomicrograph in reflected light of pyritized radiolarians 1084 with sphalerite from DON deposit. Abbreviations: sp = spicule; sph = sphalerite; gn =1085 galena; py = pyrite.

1086

Fig. 7 ¹⁸⁷Re/¹⁸⁸Os vs. ¹⁸⁷Os/¹⁸⁸Os plots for pyrite separates from DON and XYC deposits. 1087 a Pyrite from XYC deposit shows limited range in ¹⁸⁷Re/¹⁸⁸Os ratios and more variable 1088 1089 ¹⁸⁷Os/¹⁸⁸Os ratios. All Re-Os data lack a geologically or statistically meaningful isochron 1090 age. Three separates (open symbols) that did not yield any residue following sample 1091 digestion and thus are considered to reflect solely the Re-Os systematics of pyrite, yield 1092 an age, although imprecise, which is broadly in agreement with the biostratigraphic age 1093 of the host rock (see text). **b** All pyrite separates from the DON deposit lack a 1094 geologically meaningful age. However, similar to that shown in (a) for XYC deposit, 1095 three separates that did not exhibit residue following digestion (open symbols) yield an 1096 age, although highly imprecise, which coincides with that of the host rock (see text for 1097 discussion).

1098

1099Fig. 8 187 Re/ 188 Os vs. 187 Os/ 188 Os plot showing Re-Os data for all pyrite separates from1100XYC and DON deposits. Linear regression of Re-Os data for pyrite yielding no residue1101following sample digestion, and therefore having little to no contamination by host rocks1102(bold red type – open symbols) yields an isochron age of 442 ± 14 Ma (MWSD = 7.4)1103and initial 187 Os/ 188 Os value of 0.71 ± 0.07. See text for discussion.

1104

Fig. 9 Approximate biostratigraphic fossil ages for units in Howards Pass district (from
 Norford and Orchard 1985; McCracken 2014) compared to Re-Os isochron age of pyrite

1107 obtained in this study. Biostratigraphic ages from district are shown as black boxes (ruled

- 1108 or solid for graptolites and conodonts, respectively). Range of ages approximate. Two
- regional graptolite samples (blue ruled boxes) collected 20 km southwest of Howards
- 1110 Pass (Norford and Orchard 1985), and seven conodont samples (blue solid bars) collected
- 1111 northwest of Howards Pass (blue solid bars) from McCracken (2014) are also shown. See
- 1112 text for discussion.
- 1113
- 1114 Table 1. Re-Os data for sulphides from Zn-Pb deposits in the Howards Pass district.



Figure 1.



Figure 2.





Figure 4.



Figure 5.





Figure 7.



Figure 8.





Sample number	Sample Type ^a	size fraction	Post digestion residue ^b	Re (ppb)	±c	Os (ppt)	±c	¹⁹² Os (ppt)	±c	¹⁸⁷ Re/ ¹⁸⁸ Os	±c	¹⁸⁷ Os/ ¹⁸⁸ Os	±c	rho ^d	Osi @ 442'
XYC deposit															
Sample 1 - 5 sub s	samples														
XYC-txt3 (1c)	pyrite+HR	~0.25 to 0.5 mm	yes - minor	5.36	0.03	177.1	0.8	59.3	0.5	179.7	1.9	1.908	0.020	0.780	0.58
XYC-txt3 (1f)	pyrite+HR	<0.25 mm	yes	5.39	0.02	164.1	0.6	51.1	0.4	209.7	1.8	2.619	0.020	0.847	1.07
XYC-txt3 (2c)	pyrite+HR	~0.25 to 0.5 mm	yes	3.70	0.02	169.0	1.8	50.1	0.9	146.9	2.8	3.128	0.078	0.693	2.04
XYC-txt3 (2f)	pyrite+HR	<0.25 mm	yes	3.86	0.02	129.0	0.4	40.6	0.3	188.8	1.6	2.508	0.018	0.832	1.11
XYC-txt3 (3f)	pyrite ^f	<0.25 mm	no	3.97	0.02	123.4	1.4	40.1	0.9	197.0	4.4	2.205	0.071	0.644	0.75
Sample 2															
XYC-txt4 (1f)	pyrite ^f	<0.25 mm	no	2.21	0.01	93.4	0.4	31.9	0.3	137.6	1.6	1.723	0.019	0.782	0.71
XYC-txt4 (2f)	pyrite ^f	<0.25 mm	no	3.34	0.02	122.6	0.4	41.2	0.3	161.3	1.5	1.883	0.015	0.815	0.69
Sample 3															
XYC127-124.5	pyrite+HR	<0.5 mm	yes - minor	21.38	0.08	692.3	1.0	234.3	0.8	181.6	0.9	1.813	0.007	0.580	0.47
DON deposit															
Sample 4 - 4 subs	amples (same core	interval separated in	nto 4 equal parts)												
DON137(1)	pyrite+HR	<0.5 mm	yes	33.65	0.13	599.8	1.9	207.3	1.2	322.9	2.3	1.618	0.018	0.441	-0.77
DON137(3)	pyrite ^f	<0.5 mm	no	34.94	0.13	636.8	1.4	182.1	0.7	381.7	2.0	3.530	0.016	0.566	0.71
DON137(4)	pyrite ^f	<0.5 mm	no	36.99	0.14	694.9	1.1	201.4	0.6	365.4	1.7	3.382	0.011	0.546	0.68
DON137(2)	pyrite ^f	<0.5 mm	no	34.04	0.13	644.8	1.4	186.5	0.7	363.1	1.9	3.403	0.015	0.580	0.72
DON111-157.8	fresh mudstone	powdered		50.85	0.17	1632.2	5.3	514.4	0.9	196.7	0.7	2.505	0.005	0.345	1.05

^aHR = host rock (Active mudstone member, Howards Pass formation)

^bMineral separates of 6 samples contained a significant residue (silicate minerals including quartz, muscovite, clays) after dissolution of the sample in *aqua regia* acid, interpreted to be the un portion of the host rock. However, organic matter present as fine intergrowths with, or contained within pyrite, or as coatings on grains is dissolved in *aqua regia*; hence, the resulting Re-Os d represents a mix of Re and Os liberated from both pyrite and organic matter. ^cUncertainties reported at the 2 sigma level. ¹⁸⁷Os/¹⁸⁸Os uncertainites reported at 2s.d.