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Abstract: New Ni stable isotope data ($\delta^{60}\text{Ni}$) determined by double-spike MC-ICP-MS for two geologically distinct suites of organic-rich marine sediments from the Sinemurian-Pliensbachian (S-P) Global Stratotype Section and Point (GSSP; Robin Hood's Bay, UK) and the Devonian-Mississippian Exshaw Formation (West Canada Sedimentary Basin) is presented herein. These sediments yield $\delta^{60}\text{Ni}$ values of between 0.2 ‰ and 2.5 ‰, and predominantly have Ni isotopic compositions that are heavier than those of abiotic terrestrial and extraterrestrial samples (extraterrestrial and abiotic terrestrial samples (-0.1 ‰ and 0.4 ‰) (0.15 ‰ and 0.27 ‰), and in some cases present-day seawater (1.44 ‰) and dissolved Ni from riverine input (0.80 ‰). In addition, the observed degree of isotopic fractionation in the marine sediments is far greater than that of these other sample matrices. However, a strong similarity is exhibited between the $\delta^{60}\text{Ni}$ values of the organic-rich sediments studied here and those of ferromanganese crusts (0.9 to 2.5 ‰), suggesting that factors ubiquitous to the marine environment are likely to play a key role in the heightened level of isotopic fractionation in these sample matrices.

A lack of correlation between the Ni stable isotope compositions of the organic-rich sediments and Ni abundance, suggests that isotopic fractionation in these sediments is not controlled by uptake incorporation or enrichment of Ni during sediment accumulation. Further, no relationship is observed between $\delta^{60}\text{Ni}$ and TOC concentrations or bottom-water redox conditions, indicating that the organic carbon reservoir and levels of oxygenation at the sediment-water interface do not exert a primary control on Ni isotope fractionation in marine sediments. Following examination of these relationships, it is therefore more likely that the heavy Ni isotope compositions of marine sediments are controlled by the weathering environment and the dominant sources of dissolved Ni into the global ocean reservoir.

1 **Characterising the nickel isotopic composition of organic-rich marine sediments**

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20 **Abstract**

21 New Ni stable isotope data ($\delta^{60}\text{Ni}$) determined by double-spike MC-ICP-MS for two
22 geologically distinct suites of organic-rich marine sediments from the Sinemurian-

23 Pliensbachian (S-P) Global Stratotype Section and Point (GSSP-~~;~~ Robin Hood's Bay,

24 UK) and the Devonian-Mississippian Exshaw Formation (West Canada Sedimentary

25 Basin) is presented herein. These sediments yield $\delta^{60}\text{Ni}$ values of between 0.2 ‰ and

26 2.5 ‰, and predominantly have Ni isotopic compositions that are heavier than those

27 of abiotic terrestrial and extraterrestrial samples ~~—extraterrestrial and abiotic~~

28 ~~terrestrial samples (-0.1 ‰ and 0.4 ‰)~~(0.15 ‰ and 0.27 ‰), and in some cases

29 present-day seawater (1.44 ‰) and dissolved Ni from riverine input (0.80 ‰). In

30 addition, the observed degree of isotopic fractionation in the marine sediments is far

31 greater than that of these other sample matrices. However, a strong similarity is

32 exhibited between the $\delta^{60}\text{Ni}$ values of the organic-rich sediments studied here and

33 those of ferromanganese crusts (0.9 to 2.5 ‰), suggesting that factors ubiquitous to

34 the marine environment are likely to play a key role in the heightened level of
35 isotopic fractionation in these sample matrices.

36 A lack of correlation between the Ni stable isotope compositions of the organic-rich
37 sediments and Ni abundance, suggests that isotopic fractionation in these sediments
38 is not controlled by ~~uptake-incorporation~~ or enrichment of Ni during sediment
39 accumulation. Further, no relationship is observed between $\delta^{60}\text{Ni}$ and TOC
40 concentrations or bottom-water redox conditions, indicating that the organic carbon
41 reservoir and levels of oxygenation at the sediment-water interface do not exert a
42 primary control on Ni isotope fractionation in marine sediments. Following
43 examination of these relationships, it is therefore more likely that the heavy Ni
44 isotope compositions of marine sediments are controlled by the weathering
45 environment and the dominant sources of dissolved Ni into the global ocean
46 reservoir.

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61 **1. Introduction**

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63 For several decades previous investigations of Ni isotopes have focused
64 predominantly on characterising radiogenic isotopic fractionation in extraterrestrial
65 materials, with a view to enhancing our understanding of planetary processes and
66 the isotopic composition of the early Solar System (eg. Kohman and Robison, 1980;
67 Morand and ~~Allegre~~Allègre, 1983; Shimamura and Lugmair, 1983; Birck and Lugmair,
68 1988; Herzog et al., 1994; Xue et al., 1995; Quitté et al., 2006; Cook et al., 2007;
69 Moynier et al., 2007; Chen et al., 2009). Further, the role of Ni as a bioessential trace
70 metal (eg. Frausto da Silva and Williams, 2001; Cameron et al., 2007; 2009) has led
71 to the recognition that the stable isotopes of Ni may have the potential to be utilised
72 as a powerful biological tool for studies of early life on Earth (Cameron et al., 2009;
73 2012).

74 In addition to its role in cosmochemical and biochemical investigations, the
75 potential of Ni to significantly enhance our understanding of organic-rich
76 sedimentary environments and to provide a powerful geological tracer in the
77 petroleum realm has been recognised, following pioneering work by Lewan and
78 Maynard (1982) and Lewan (1984) (eg. Ellrich et al., 1985; Manning et al., 1991;
79 Alberdi and Lafargue, 1993; López et al., 1995). However, these studies focused on
80 the elemental distribution of Ni rather than on its isotopic characterisation, and as
81 such, no study currently exists that evaluates the behaviour of Ni stable isotopes in

82 organic-rich sediments or indeed within a stratigraphic profile. This can be attributed
83 to Ni being a relatively newly investigated system, together with the difficulty
84 associated with purifying Ni from such complex sample matrices, that has only
85 recently been overcome through advancements in analytical and mass spectrometry
86 techniques (eg. Gall et al., 2012; Cameron and Vance, 2014).

87 Until now, Ni stable isotope systematics in organic-rich sedimentary matrices
88 have not been investigated. Indeed, it is only recently that the Ni isotopic
89 composition of seawater and the sources of Ni to the global oceanic reservoir have
90 been determined (e.g. Cameron and Vance, 2014; Gall et al., 2013). Present-day
91 seawater has an average $\delta^{60}\text{Ni}$ value of 1.44 ± 0.15 ‰, with apparent global isotopic
92 homogeneity (Cameron and Vance, 2014). The oceanic residence time of Ni has been
93 calculated as ~30 kyr (Cameron and Vance, 2014), which is significantly longer than
94 the mixing time of the global oceans (~2,000 yrs; Palmer et al., 1988). This would be
95 sufficient for the ocean to have an isotopically homogenous Ni composition.
96 Cameron et al. (2014) also demonstrate that draw-down of Ni from the surface to
97 deep ocean during trace metal cycling is not accompanied by isotopic fractionation,
98 thus further suggesting that the ~~global~~modern ocean is isotopically homogenous. In
99 the absence of any Ni isotope studies on banded iron formation and shale datasets,
100 it is difficult to speculate on processes occurring in an ancient ocean. However,
101 examination of Ni/Fe data from banded iron formations and extrapolated maximum
102 dissolved Ni concentration values in sea water through time (Konhauser et al., 2009),
103 demonstrates that dissolved nickel concentrations may have reached present day
104 values by ~550 Ma. As such, given the age of the sediments being studied herein
105 (~190-360 Ma), it is appropriate to use what we know regarding modern ocean

106 | circulation and fractionation processes to hypothesise about processes acting in the
107 | ancient oceans.

108 | The predominant input of dissolved Ni to the oceans occurs via riverine
109 | influx, which has been suggested to yield an annual discharge- and concentration-
110 | weighted $\delta^{60}\text{Ni}$ average of +0.80 ‰ (Cameron and Vance, 2014). Significant
111 | variability in the riverine isotopic composition has been observed (+0.29 to +1.34
112 | ‰), which has been attributed to isotopic fractionation of Ni during weathering of
113 | continental crust, resulting in heavier $\delta^{60}\text{Ni}$ values in rivers and seawater. In addition,
114 | mineral dust and volcanic ash also contribute to the oceanic Ni budget (Li and
115 | Schoonmaker, 2003), as well as hydrothermal vent fluids ($\delta^{60}\text{Ni} = 1.5$ ‰; Gall et al.,
116 | 2012).

117 | Herein we present the first attempt at creating a Ni isotope stratigraphic
118 | profile for an organic-rich sedimentary succession. The marine section across the
119 | Sinemurian-Pliensbachian Global Stratotype Section and Point (GSSP), Robin Hood's
120 | Bay, UK, is ideally suited to the present study, as it well understood
121 | biostratigraphically (Hesselbo et al., 2000; Meister et al., 2006) and has been
122 | previously characterised using other isotope stratigraphy techniques, including
123 | strontium ($^{87}\text{Sr}/^{86}\text{Sr}$; Jones et al., 1994; Hesselbo et al., 2000), oxygen ($\delta^{18}\text{O}$), carbon
124 | ($\delta^{13}\text{C}$) (Hesselbo et al., 2000), and Re-Os isotopes (Porter et al., 2013). The section is
125 | also consistently thermally immature (the rocks have not been subjected to enough
126 | heat or pressure to convert any kerogens present to hydrocarbons), thereby
127 | eliminating any potential effects of thermal maturation on the Ni isotope signature.
128 | In addition, to draw comparison between the isotopic composition of samples of
129 | different depositional ages and environments, we present Ni isotope data from a

130 | selection of thermally immature black shale samples from a core of the Exshaw
131 | Formation, Canada.

132 | To accurately assess and interpret any stratigraphic variation of Ni isotopes in
133 | the Robin Hood's Bay section and Exshaw Formation samples, it is critical to
134 | determine whether any fluctuations in paleoredox conditions occur. Nickel primarily
135 | occupies one oxidation state in the natural environment (Ni^{2+}), suggesting that it is
136 | not redox sensitive. However, its preferential association with redox-sensitive
137 | metallo-organic complexes (porphyrins) in organic-rich sediments (Lewan and
138 | Maynard, 1982) indicates that certainly within these sample matrices, redox
139 | conditions at the time of sediment deposition may directly impact the degree of
140 | enrichment or depletion of Ni. Herein, paleoredox conditions have been established
141 | for the Sinemurian-Pliensbachian GSSP section and the Exshaw Formation sample
142 | suite. Although one previous study (Dewaker et al., 2000) provides a preliminary
143 | dataset for the Ni isotope composition of sediments from 3 different basins, our
144 | understanding of the behaviour of Ni isotope systematics within organic-rich
145 | sediments is currently non-existent. Further, advancements in analytical techniques
146 | over the past decade suggest that the methodology employed by Dewaker et al.
147 | (2000) may not have been optimal for Ni separation or Ni stable isotope analysis.

148 | This paper presents the first detailed study of nickel stable isotope
149 | systematics in organic-rich marine sediments. Analysis of marine sediments of
150 | different depositional ages and from two geologically distinct settings, the
151 | Sinemurian-Pliensbachian boundary (UK) and the Devonian-Mississippian Exshaw
152 | Formation (Canada), yields comparable Ni isotope compositional values for both
153 | | sites. These samples provide insight into the incorporation~~uptake~~ of Ni into ocean

154 sediments, and allow evaluation of the contribution of the various dissolved Ni fluxes
155 to the seawater during these time periods.

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157

158 **2. Geological Setting**

159

160 *2.1 The Sinemurian-Pliensbachian boundary GSSP, Robin Hood's Bay, UK*

161 The Sinemurian-Pliensbachian boundary, established from the succession's
162 complete ammonite assemblages (Spath, 1923; Dean et al., 1961; Hesselbo et al.,
163 2000; Meister et al., 2006), occurs in the Pyritous Shales of the Redcar Mudstone
164 Formation within the Lias Group at Robin Hood's Bay (Powell, 1984; Fig. 1). At this
165 point in the Early Jurassic, Robin Hood's Bay was positioned on the margins of a
166 shallow epicontinental sea (eg. Dera et al., 2009) that covered most of Northern
167 Europe, including Britain, during the Mesozoic (Sellwood and Jenkyns, 1975). The
168 facies changes across the boundary, from pale siliceous to finer, more organic-rich
169 mudstones (Fig. 2), indicate an overall relative increase in sea level of at least
170 regional extent (~~eg.~~ Hesselbo et al., 2000; Meister et al., 2006; Porter et al.,
171 2013).

172 The age for the base of the Pliensbachian has been defined by the Geological
173 Time Scale (GTS) 2012 as 189.6 ± 1.5 Ma (Gradstein et al., 2012), derived from cycle-
174 scaled linear Sr trends and ammonite occurrences (as noted above; also includes the
175 lowest occurrence of *Bifericeras donovani*; Gradstein et al., 2012).

176

177 *2.2 Exshaw Formation, West Canada Sedimentary Basin (WCSB)*

178 The West Canada Sedimentary Basin (WCSB) trends approximately NW-SE
179 between the Canadian Shield to the East and the Western Cordillera to the West
180 (Piggott and Lines, 1992). Within the WCSB lies the Exshaw Formation, a thin but
181 laterally continuous unit (2-12 m thick; Leenheer, 1984; Creaney and Allan, 1991).
182 The Exshaw Formation in south-west and western Alberta (Fig. 3) comprises a lower
183 member of organic-rich mudrocks and black shales which rest with minor
184 disconformity upon Upper Devonian carbonate strata (Richards et al., 1999), and are
185 abruptly to gradationally overlain by bioturbated shelf siltstones (Caplan and Bustin,
186 1998, 1999; Creaser et al., 2002). The depositional interval of the lower black shale
187 unit is well constrained biostratigraphically; between the *expansa* and *duplicata*
188 zones of Late Famennian to Early Tournaisian time (over a maximum time period of
189 ~363 – 360 Ma; Caplan and Bustin, 1998). These lower black shales are dark grey,
190 bituminous, relatively thin (consistently between 3-5 m; Meijer et al., 1994) and
191 widespread (Meijer et al., 1994). The Devonian-Mississippian boundary (Exshaw-type
192 section at Jura Creek, ~80 km west of Calgary, Alberta, Canada) represents the
193 boundary between the upper calcareous and lower non-calcareous black shale units
194 (Richards and Higgins, 1988). Selby and Creaser (2005) provide an absolute Model 1
195 Re-Os age for this boundary, and thus the top of the lower black shale unit, of 361.3
196 ± 2.4 Ma. In addition, U-Pb monazite data from a tuff horizon close to the base of the
197 lower black shale member constrains an absolute depositional age for this unit of
198 363.4 ± 0.4 Ma (Richards et al., 2002). Deposition at this time represents part of a
199 continent-wide Famennian-Tournaisian black shale event, and in turn, a possible
200 ocean anoxic event (Piggott and Lines, 1992).

201

202

203 3. Sampling

204

205 A set of 32 samples (SP7-09 to SP39-09) was collected from the Pyritous
206 Shales Member of the Redcar Mudstone Formation, along a 6 m vertical section
207 bracketing the Sinemurian–Pliensbachian boundary (sample SP22-09) at Robin
208 Hood’s Bay (Fig. 2). This marine sequence contains a rich fauna of ammonites both
209 above and below the boundary interval (Hesselbo et al., 2000). Total organic carbon
210 analysis was conducted on all samples, with a consistent sampling interval of ~20 cm
211 for 3 m above and 3 m below the boundary from Beds 69–75 (except within Bed 72,
212 where a smaller sampling interval of ~15 cm was used). Of these samples, 14 were
213 analysed for Ni isotopes at a sampling interval of ~40 cm (Fig. 2).

214 Four samples from the Lower member of the Exshaw Formation were
215 collected from the Alberta Energy and Utilities Board, Core Research Centre, Calgary
216 (Fig. 3). The samples were taken from core 3-19-80-23W5, as detailed in Piggot and
217 Lines (1992) and Creaser et al. (2002). All samples are thermally immature, fine-
218 grained black shales containing very thin parallel and undulating laminations, and
219 showing no evidence of post-depositional disturbance. Drill core samples were
220 obtained to avoid any potential effects of surface weathering, including loss of
221 organic matter (Peucker-Ehrenbrink and Hannigan, 2000). Further, edges of the core
222 were polished and where possible samples were taken from the central part of the
223 core.

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225

226 **4. Analytical Protocol**

227

228 *4.1 Trace element abundance and TOC*

229 The elements V, Cr, Ni and Co were analysed in this study in order to look at
230 relative changes of depositional redox conditions in the sediments of interest.

231 Samples were prepared for trace element analysis at the Durham Geochemistry
232 Group (University of Durham, UK) following the method of Ottley et al., (2003).
233 Sample powders (~100 mg) were digested in a 4:1 solution of 29 N HF and 16 N
234 HNO₃ at ~150 °C for 48 hrs. Samples were then evaporated to near rather than total
235 dryness, to avoid stabilisation of insoluble fluorides (Ottley et al., 2003). This was
236 followed by the addition of 1 ml 16 N HNO₃ and evaporation to near dryness. The
237 previous stage was repeated before the addition of 2.5 ml 16 N HNO₃ and ~10 ml
238 18MΩ water to create a ~4 N HNO₃ solution. Sample beakers were capped and
239 heated on the hotplate overnight at ~100 °C. Once cooled, 1 ml of 1 ppm internal Re
240 and Rh spike was added to the samples (to yield 20 ppb Re and Rh in the final
241 analyte solution) before dilution up to 50 ml with MQ, yielding a ~0.5 N HNO₃
242 solution. Prior to analysis, samples were diluted 10-fold by taking 1 ml from the 50
243 ml solution and diluting it to 10 ml using 0.5 N HNO₃. Samples were then analysed
244 using the Thermo X-Series Quadrupole Inductively Coupled Plasma Mass
245 Spectrometer (ICP-MS).

246 ~~—~~Replicate analyses of USGS International Reference Materials (RMs) AGV-1,
247 BHVO-1 and W-2 ~~and synthetic standards solutions for Mo (10, 20 and 30 ppb~~
248 ~~solutions)~~ were conducted for calibration per sample set.

249 Total organic carbon measurements were performed at Durham University
250 using a Costech Elemental Analyser (ECS 4010) coupled to a ThermoFinnigan Delta V
251 Advantage. Total organic carbon was obtained as part of the isotopic analysis
252 ($\delta^{13}\text{C}_{\text{org}}$) using an internal standard (Glutamic Acid, 40.82 % C). Data accuracy was
253 monitored through routine analyses of in-house standards, which are stringently
254 calibrated against international standards (eg. USGS 40, USGS 24, IAEA 600, IAEA
255 CH6).

256

257 *4.2 Nickel stable isotopes*

258 All Ni isotope analyses were conducted at the University of Bristol. Samples
259 (~100 mg) were digested in closed PFA Beakers (Savillex, Minnetonka, MN) in a
260 mixture of concentrated HF and HNO₃ (3:1) at 140 °C for 48 hrs. Dried samples were
261 treated further with 7 N HCl. Chemical separation, purification and analyses of Ni
262 isotopes was carried out as described in detail in Cameron et al. (2009) and Cameron
263 and Vance (2014),—2013). Briefly, sample aliquots were spiked and allowed to
264 equilibrate under heating in closed vials overnight. This was followed by drying down
265 and treatment with 7 N HCl + H₂O₂. The spiked samples were then put through a 3-
266 stage column procedure that in turn removes Fe and Zn, separates Ni from the bulk
267 sample matrix, and final purification to remove any residual Fe and Zn. The first ion-
268 exchange column (AG MP-1M, Bio-Rad) is used to remove Fe and Zn. The dried
269 samples are then taken up in 1M HCl/1 M ammonium citrate, and the pH adjusted to
270 8–9 before loading onto columns filled with Ni resin (Eichrom Technologies). This
271 step separates Ni while removing all other matrix elements in the sample. After
272 oxidation to remove Ni-bound DMG, the samples are finally put through a third

273 [column, which is a repeat of the first anion column, to clean up any residual Fe and](#)
274 [Zn.](#)

275 All analyses were conducted in low resolution mode using a ThermoFinnigan
276 Neptune multi-collector (MC) ICP-MS coupled to an Aridus desolvating nebuliser
277 system (CETAC, Omaha, NE, USA). Samples were introduced in 2% HNO₃ via a CPI
278 PFA nebuliser (50 µl/minute) and spray chamber. Prior to isotopic analysis, the
279 ⁵⁶Fe/⁵⁸Ni ratio was manually checked in high resolution mode in all samples so that
280 any potential isobaric interference from residual sample ⁵⁸Fe could be applied as a
281 correction to Ni mass 58. Relative to the propagated internal uncertainty on δ⁶⁰Ni,
282 the correction was insignificant. Additionally, a small amount of N₂ was introduced
283 to the Aridus sweep gas to reduce a potential interference from ⁴⁰Ar¹⁸O at mass 58.
284 To mitigate inaccuracies in the δ⁶⁰Ni brought on by any instrumental variations,
285 measurements of the pure NIST SRM986 standard were made throughout the
286 analytical session. The reproducibility and accuracy of all isotope ratios were
287 monitored further by measurement of mixtures of the SRM986 standard with the
288 double-spike. All isotopes were measured simultaneously in static mode using a
289 multiple Faraday collector array. All Ni data are reported relative to NIST SRM986, in
290 the standard delta notation ($\delta^{60}\text{Ni} = [({}^{60}\text{Ni}/{}^{58}\text{Ni})_{\text{sample}}/({}^{60}\text{Ni}/{}^{58}\text{Ni})_{\text{NISTSRM986}}]-1] \times 1000$),
291 with all uncertainties reported to the 2σ level.

292

293

294 **5. Results**

295 *5.1 Trace elements and TOC*

296 The trace element ratios Ni/Co, V/Cr and V/(V+Ni) have been utilised by
297 previous studies to evaluate paleoredox conditions at the time of sediment
298 deposition (eg. Hatch and Leventhal, 1992; Jones and Manning, 1994; Schovsbo,
299 2001; Rimmer, 2004). Both Ni and V occur in highly stable tetrapyrrole complexes
300 that are originally derived from chlorophyll and are preferentially preserved under
301 anoxic conditions (Lewan and Maynard, 1982). When organic matter has been
302 extensively exposed to aerobic conditions, preservation of these tetrapyrrole
303 complexes will be low and subsequently the organic matter will have low Ni and V
304 contents. Chromium is not influenced by redox conditions, and thus because of its
305 association with just the detrital fraction and not the organic matter (Dill, 1986), high
306 V/Cr values (>2) are indicative of anoxic conditions. Both Ni and Co are found in
307 pyrite (in addition to the occurrence of Ni in porphyrins), but high Ni/Co values are
308 associated with anoxic conditions (Jones and Manning, 1994). The relationship
309 between these ratios and depositional redox conditions are summarised in Table 1.

310 The abundances of Ni, Co, V, Cr and TOC for all samples from Robin Hood's
311 Bay and the Exshaw Formation, are presented in Table 2. Both the Ni/Co and V/Cr
312 indices for Robin Hood's Bay show that these sediments were deposited under
313 predominantly oxic conditions. ~~Good agreement is observed between both the~~
314 ~~Ni/Co and V/Cr indices for Robin Hood's Bay, which show that the samples were~~
315 ~~deposited under predominantly oxic conditions.~~ However, there is significant
316 disagreement between these ratios and the V/(V+Ni) index. Values for V/(V+Ni)
317 range from ~0.51 – 0.89 and indicate that anoxic conditions prevailed across the
318 Sinemurian-Pliensbachian boundary. Further, six samples suggest that bottom-water

319 circulation ceased and that conditions became euxinic intermittently between ~2.6
320 m above the boundary and ~1.9 m below it (Table 2).

321 The Ni/Co ratio in the Exshaw Formation sediments ranges from 13.8 – 21.4,
322 with all four samples falling within the suboxic-anoxic parameter (Table 2). Similarly,
323 the V/(V+Ni) ratio indicates that three of the samples were deposited under suboxic-
324 anoxic conditions (SP8-10, SP10-10 and SP13-10; values of 0.67, 0.69 and 0.67,
325 respectively). However, whilst V/Cr values of 7.2 and 9.0 suggest a suboxic-anoxic
326 depositional environment for Exshaw Formation samples SP10-10 and SP13-10,
327 respectively, this ratio also yields values that are representative of dysoxic conditions
328 for samples SP8-10 and SP9-10 (2.0 and 2.1, respectively).

329 Total organic carbon content is generally low in the Sinemurian-Pliensbachian
330 sediments, varying from ~0.53 – 2.46 wt. % (Table 2; Fig. 4). The data shows only
331 slight variation prior to the boundary (~0.57 – 0.86 wt. %; Fig. 4), but an overall
332 gradual increase above the boundary (from ~0.58 – 2.46 wt. %; Fig. 4). Total organic
333 carbon values in the Exshaw Formation samples range from 1.2 – 11 wt. %.

334

335 *5.2 Nickel stable isotopes*

336 New Ni stable isotope data for a select suite of the organic-rich sediments at
337 Robin Hood's Bay is presented (see Table 3). From the base of Bed 71 the sampling
338 interval for Ni isotope analysis is ~40 cm (Fig. 2). A profile of $\delta^{60}\text{Ni}$ values for the
339 section is shown alongside Ni concentration and TOC for comparison (Fig. 4).

340 The $\delta^{60}\text{Ni}$ of these samples is extremely variable, ranging from 0.28 ± 0.05 –
341 1.60 ± 0.05 ‰ (Fig. 4; Table 3). Two noticeable peaks in $\delta^{60}\text{Ni}$ values are observed 0.8
342 m above and 2.1 m below the Sinemurian-Pliensbachian boundary (1.26 ± 0.05 ‰

343 and 1.60 ± 0.05 ‰, respectively) that approximately correlate with the tops of beds
344 70 and 74. The greatest range in $\delta^{60}\text{Ni}$ values occurs below the boundary (~ 1.32 ‰),
345 compared to a range of ~ 0.97 ‰ above the boundary (Fig. 4). In this section and
346 dataset there is no apparent relationship between the degree of Ni isotope
347 fractionation and depositional redox conditions, TOC or stratigraphic height (Fig. 4).

348 Nickel stable isotope data for the Exshaw Formation is also presented in
349 Table 3. The $\delta^{60}\text{Ni}$ values in these samples range from 0.46 ± 0.04 to 2.50 ± 0.04 ‰
350 (Table 3). As with the Robin Hood's Bay section, no relationship exists between $\delta^{60}\text{Ni}$
351 and sample depth or between $\delta^{60}\text{Ni}$ and depositional redox conditions, TOC or
352 stratigraphic position (Fig. 4).

353

354

355 **6. Discussion**

356

357 *6.1. Evaluating the suitability of $V/(V+Ni)$ as a redox proxy: How applicable is it?*

358 The Ni/Co and V/Cr redox indices are recommended by a number of workers
359 as the most reliable of the paleo-environmental proxies (eg. Jones and Manning,
360 1994; Rimmer, 2004), and have been used by several studies to provide accurate and
361 consistent evaluations of paleoredox conditions at the time of sediment deposition
362 (eg. Rimmer, 2004; Selby et al., 2009; this study). However, this study finds that
363 there is significant disagreement between these indices and the $V/(V+Ni)$ index. For
364 Robin Hood's Bay, the latter index suggests that the sediments were deposited in
365 predominantly suboxic-anoxic bottom-waters, with intermittent euxinic periods.
366 However, both the V/Cr and Ni/Co ratios indicate that the Robin Hood's Bay samples

367 were deposited under largely oxic condition. Such disparity between the redox
368 indices is also noted by both Rimmer (2004) and Selby et al. (2009), who observe
369 that the V/(V+Ni) index suggests suboxic-anoxic conditions for sediments otherwise
370 indicated to have been deposited under oxic conditions by the V/Cr and Ni/Co ratios.

371 Preliminary work by Lewan and Maynard (1982) and Lewan (1984) suggested
372 that redox potential was a dominant control on the wide range of V/(V+Ni) values
373 observed in petroleum source rocks and oils. Following this, Hatch and Leventhal
374 (1992) were the first to develop and utilise the V/(V+Ni) index as a measure of
375 relative redox potential in organic-rich sediments. Their study focused on applying
376 this index specifically to marine black shales in the Pennsylvanian Stark Shale
377 Member of the Dennis Limestone, Wabaunsee County, Kansas, USA (Hatch and
378 Leventhal, 1992). Therefore, the ranges they defined for the V/(V+Ni) ratio and the
379 associated redox conditions (summarised in Table 1), are applicable to this specific
380 geological basin and are sensitive to localised geochemical variations therein.

381 Hatch and Leventhal (1992) show that for the Stark Shale Member, with the
382 exception of two outliers, low TOC values (<2.5 wt. %) correspond to V/(V+Ni) values
383 <0.75, and samples containing greater TOC (>7.5 wt. %) have corresponding higher
384 V/(V+Ni) values (0.75; Fig. 5). However, this relationship is not observed in the
385 majority of the Sinemurian-Pliensbachian or Exshaw Formation sediments, with
386 samples containing low TOC providing a range in V/(V+Ni) data from ~0.33 – 0.89.

387 This immediately indicates that there are significant geochemical differences
388 between these three geological sites. ~~have differing geochemical frameworks.~~ This
389 may be due to differences in both geological age and stratigraphy, with the Stark
390 Shale Member (Late Carboniferous) being a darker grey, non-sandy shale with higher

391 TOC content (Hatch and Leventhal, 1992). As such, this comparison suggests that the
392 redox index $V/(V+Ni)$, originally developed for a specific geological basin, may not be
393 applicable to other geological sites, particularly those that possess differing
394 geological and geochemical characteristics. Factors that may have a profound effect
395 upon the applicability of such a threshold from one study to another include:
396 differences in the influx of nutrients and trace elements, type and relative amounts
397 of organic matter, and degrees of oceanic mixing (~~eg., eg.~~ Rimmer, 2004). However,
398 these are preliminary findings from a small dataset and further investigation is
399 recommended. In agreement with Rimmer (2004), this study therefore suggests that
400 caution should be taken when applying redox indices established by other studies for
401 ~~specific-single~~ geological sites.

402

403 *6.2. Nickel stable isotope fractionation in marine sediments*

404 Nickel stable isotope data for the Exshaw Formation and the Sinemurian-
405 Pliensbachian GSSP is presented in Table 3 and Figure 6, and is the first to be
406 obtained for a suite of organic-rich marine sediments. The Exshaw Formation shales
407 define a realm of $\delta^{60}Ni$ values of 0.46 ± 0.04 to 2.50 ± 0.04 ‰ (a range of ~ 2.04 ‰;
408 Fig. 6). This range overlaps with, and is comparable to the $\delta^{60}Ni$ data for the
409 Sinemurian-Pliensbachian boundary GSSP (0.28 ± 0.05 to 1.60 ± 0.05 ‰; ~ 1.32 ‰;
410 Fig. 6). Although there are currently no estimations for the Ni isotopic composition
411 of the palaeo-ocean, the present-day global seawater $\delta^{60}Ni$ value has been
412 constrained as 1.44 ± 0.15 ‰ (Cameron and Vance, 2014). This value lies within the
413 $\delta^{60}Ni$ range of the marine sediments (Fig. 6; this study). Draw-down of Ni through
414 the water column does not induce isotopic fractionation, and as such, the Ni stable

415 isotope composition of the ocean is assumed to be homogenous (Cameron and
416 Vance, 2014). However, the Ni stable isotope composition of the organic-rich
417 sediments is far from homogenous, with $\delta^{60}\text{Ni}$ values that are either significantly
418 lighter or heavier than the present-day seawater $\delta^{60}\text{Ni}$ value (Fig. 6). Assuming that
419 global ocean homogeneity has persisted throughout geological time, the
420 fractionation observed in the marine sediments must therefore be recording the
421 substantially variable isotopic compositions of the sources of dissolved Ni into the
422 oceans.

423 This preliminary study presents Ni isotope and Ni concentration data from
424 bulk sample analysis. To assess what fraction of the selected metals may be
425 authigenic versus lithogenic, Table 4 presents Ni concentration data from this study,
426 and from average shale and average upper continental crust. It is clear from this that
427 the authigenic contribution of Ni in these samples is < 50 % (Table 4), suggesting that
428 > 50 % of the sample is represented by the lithogenic fraction.

429 For both sample sets, no correlation is observed between $\delta^{60}\text{Ni}$ and Ni
430 abundance, indicating that the level of Ni isotope fractionation in ~~bulk~~the marine
431 sediments here is not directly controlled by the degree of Ni enrichment. Similarly,
432 no relationship exists between $\delta^{60}\text{Ni}$ and redox for either sample set, suggesting that
433 the level of isotopic fractionation is not solely dictated by the bottom water redox
434 conditions at the time of sediment deposition. However, although it is currently
435 poorly understood, it is interesting to consider whether or not the degree of organic
436 matter preservation could have an effect on the observed isotopic fractionation
437 within the sediments. The samples used for Ni isotope analysis across the
438 Sinemurian-Pliensbachian boundary were deposited in predominantly oxic

439 conditions (using the Ni/Co and V/Cr ratios). The tetrapyrrole complexes known to
440 hold the majority of ~~the~~ Ni in organic matter are poorly preserved under these
441 conditions (Lewan and Maynard, 1982). As such, assuming break down of these
442 complexes is heterogeneous, and that it does not result in the preferential loss of a
443 particular isotope of Ni, this lack of preservation may at least partially contribute to
444 the observed Ni isotope fractionation in these sediments.

445 In addition, no correlation is seen between $\delta^{60}\text{Ni}$ and TOC concentration in
446 these samples, indicating that Ni isotope fractionation is not dependent on the
447 concentration of organic matter in these sediments. However, all samples in this
448 study have TOC contents of <3.0 wt. % (Table 3; apart from Exshaw Fm. sample
449 SP10-10; 11.05 wt. %). As such, to further investigate the relationship between Ni
450 fractionation and the organic carbon reservoir, work should be conducted on
451 samples containing more varied and greater levels of TOC.

452

453 *6.3. Fractionation of nickel stable isotopes in marine organic-rich sediments vs.* 454 *terrestrial samples, extra-terrestrial samples and ferromanganese crusts*

455 Marine sediments from the Exshaw Formation and Sinemurian-Pliensbachian
456 GSSP yield a comparable range in $\delta^{60}\text{Ni}$ values (0.5-2.5 ‰ and 0.3-1.6 ‰,
457 respectively; Fig. 6). Figure 6 compares these Ni isotopic values with that of bulk
458 Earth and extraterrestrial samples (Cameron et al., 2009), including meteorites (0.2
459 ‰ to 0.4 ‰), basalts (0 to 0.3 ‰) and continental sediments (0 to 0.2 ‰). It is clear
460 that these samples are significantly isotopically lighter than the organic-rich
461 sediments (this study). In addition, Ni stable isotope fractionation occurs to a much
462 greater degree in the sedimentary marine environment. Despite this though, there is

463 minimal overlap between the $\delta^{60}\text{Ni}$ values for the organic-rich sediments and those
464 of the abiotic terrestrial and extraterrestrial samples (Fig. 6).

465 The reasons for the heightened isotopic fractionation in marine sediments
466 are currently poorly understood due to an extremely limited sample database.
467 However, the complexity of the marine environment is likely to play a critical role in
468 this. With assumed ocean isotopic homogeneity (Cameron and Vance, 2014), the
469 sources of dissolved Ni into seawater must exert a substantial control on the
470 observed degree of isotopic fractionation. This may be partially attributed to the
471 variability of the Ni isotope composition of the dissolved phase of rivers, which are a
472 dominant source of Ni to the global oceans ($\delta^{60}\text{Ni} = 0.29$ to 1.34 ‰; Cameron and
473 Vance, 2014). The heavier isotope composition of this fraction relative to silicates
474 and continental sediments (0 ‰ to 0.3 ‰; Cameron et al., 2009) likely reflects
475 isotopic fractionation induced by the weathering environment during riverine
476 transport (Cameron and Vance, 2014).

477 However, this study demonstrates that the Ni isotopic composition of
478 organic-rich marine sediments ($\delta^{60}\text{Ni} = 0.28$ to 2.50 ‰; this study) are significantly
479 heavier than that of the riverine source (average $\delta^{60}\text{Ni} = 0.80$ ‰; Cameron and
480 Vance, 2014). This is also the case for the dissolved phase of present-day seawater
481 ($\delta^{60}\text{Ni} = 1.44 \pm 0.15$ ‰; Cameron and Vance, 2014). To reconcile this, there must
482 therefore be either an additional input that is isotopically heavier than the riverine
483 source (Cameron and Vance, 2014).

484 Dissolved trace metals are often removed from the water column via
485 adsorption to mineral surfaces as they are incorporated into the sediment. The
486 adsorption process, in particular to Mn and Fe oxyhydroxides, is known to induce

487 isotopic fraction in a number of stable isotope systems, including Mo and U
488 (Brennecka et al., 2011; Wasylenki et al., 2008; 2011). Sorption to Fe-Mn oxides is
489 the main output of Ni from the oceans (Cameron and Vance, 2014), and more
490 recently, this fractionation effect has also been revealed in the Ni stable isotope
491 system (Wasylenki et al., 2014). In addition, experiments focusing on the adsorption
492 and co-precipitation of Ni with oxyhydroxide phases (Wasylenki et al., 2014) have
493 demonstrated that isotopically light Ni is retained by these phases whilst isotopically
494 heavy Ni is mobilised. This therefore leads to an enrichment of isotopically heavy Ni
495 in the dissolved riverine load (Wasylenki et al., 2014).

496 ~~Further, Nickel~~ stable isotope data for ferromanganese crusts (0.9-2.5 ‰; Gall et al.,
497 2013) shows that their isotopic composition is comparable to that of the marine
498 organic-rich sediments discussed herein. Following analysis of ferromanganese
499 crusts in proximity to hydrothermal sources, Gall et al. (2013) suggest that
500 hydrothermal fluids may have a Ni stable isotope composition of ~ 1.5 ‰. Thus
501 hydrothermal sources may be contributing to the isotopic composition noted in the
502 marine sediments herein.

503 ~~—~~ However, both marine sediments (this study) and ferromanganese crusts
504 (Gall et al., 2013) are at least in part recording isotopic fractionation from a source
505 that is isotopically heavier than riverine and hydrothermal Ni influxes. As continental
506 weathering is a primary source of Ni to the global oceans, it is likely that weathering-
507 induced isotope fractionation could account for the isotopically heavy Ni
508 composition of organic-rich marine sediments. Further, the heavy Ni isotope
509 signature observed in these sediments may reflect the contribution of heavy
510 dissolved Ni to the oceans following retention of the lighter Ni isotopes during

511 | [weathering of oxyhydroxide phases \(eg. Wasylenki et al., 2014\).](#) In support of this,
512 | analysis of ferromanganese crusts at varying distances from the continental shelf
513 | (Gall et al., 2013) demonstrates that crusts growing in proximity to a continental
514 | shelf contain the heaviest Ni isotope compositions. However, although weathering
515 | does affect the isotopic composition of marine sediments, the effects resulting from
516 | additional factors such as riverine particulates, ~~Mn-oxides~~ and organic compounds
517 | have yet to be constrained (Cameron and Vance, 2014).

518 | In addition, following examination of Ni isotope data from microorganisms
519 | ($\delta^{60}\text{Ni} = \sim 0.0$ to -1.6 ‰; Cameron et al., 2009), it can be noted that the Ni isotope
520 | ratios in the organic-rich sediments herein ($\delta^{60}\text{Ni} = \sim 0.28 - 2.50$ ‰) appear to have
521 | been driven in the opposite direction to those of the microorganisms. Whilst the
522 | causes of Ni isotope fractionation in these sediments are currently poorly
523 | understood, it appears that there is a fractionation effect associated with the Ni
524 | isotope system that may have parallels to the carbon isotope system, with the
525 | microorganisms taking up isotopically lighter Ni, thus potentially leaving behind an
526 | isotopically heavier Ni isotope signature in the sediment. Although it is impossible to
527 | draw a definitive conclusion from the current dataset, this study suggests that
528 | microorganisms and organic matter may play a key role in our understanding of Ni
529 | isotope fractionation [\(in a similar manner to the rhenium-osmium isotope system;](#)
530 | [Cumming et al., 2012; Harris et al., 2013\)](#) in organic-rich marine sediments, and as
531 | such, the importance of further investigation is emphasised.

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538 7. Conclusions

539

540 This first investigation into the Ni stable isotope composition of organic-rich
541 marine sediments from two distinct basins has yielded a number of key
542 observations, outlined below.

543

544 1. This preliminary dataset indicates that organic-rich sediments have a Ni stable
545 isotope composition ($\delta^{60}\text{Ni}$) of 0.28 to 2.50 ‰.

546 2. No relationship is observed between the Ni stable isotope composition of the
547 organic-rich sediments and TOC, suggesting that fractionation is not determined by
548 changes in the organic carbon reservoir.

549 3. Similarly, there is no correlation between $\delta^{60}\text{Ni}$ and Ni abundance or bottom-
550 water redox conditions, suggesting that the process of Ni uptake and enrichment at
551 the sediment-water interface, and the degree of oxygenation in the water-column
552 do not exert primary control on isotopic fractionation.

553 4. The Ni isotope composition of marine sediments is substantially heavier and
554 isotopically distinct to those of abiotic terrestrial and extraterrestrial samples ($\delta^{60}\text{N}$
555 values of -0.1 to 0.3 ‰; Cameron et al., 2009).

556 5. Ni isotopes in marine sediments are isotopically heavier than those in present-
557 day seawater and rivers ($\delta^{60}\text{Ni} = 1.44 \pm 0.15$ ‰ and 0.29 to 1.34~~0.80~~ ‰, respectively;

558 Cameron and Vance, 2014)-, indicating input of an isotopically heavier source of Ni
559 to the ocean.

560 ~~46.~~ The observed range of $\delta^{60}\text{Ni}$ values in marine sediments is comparable to that of
561 ferromanganese crusts (0.9 to 2.5 ‰; Gall et al., 2013). Adsorption of Ni to Fe-Mn
562 oxyhydroxides results in the retention of isotopically light Ni and the mobilisation of
563 isotopically heavier Ni during oxidative weathering (Wasylenki et al., 2014).
564 Subsequently, the dissolved riverine load is enriched in heavier Ni. It is therefore
565 probable that isotopic fractionation driven by the weathering environment plays a
566 key role in yielding the range of $\delta^{60}\text{Ni}$ values that are observed in marine sediments.

567 ~~5. No relationship is observed between the Ni stable isotope composition of the~~
568 ~~organic-rich sediments and TOC, suggesting that fractionation is not determined by~~
569 ~~changes in the organic carbon reservoir.~~

570 ~~6. Similarly, there is no correlation between $\delta^{60}\text{Ni}$ and Ni abundance or bottom-~~
571 ~~water redox conditions, suggesting that the process of Ni uptake and enrichment at~~
572 ~~the sediment-water interface, and the degree of oxygenation in the water column~~
573 ~~do not exert primary control on isotopic fractionation.~~

574 ~~7. Following evidence from Gall et al. (2013), it is probable the continental~~
575 ~~weathering process may induce isotopic fractionation.~~ The relatively heavy Ni stable

576 isotope composition of marine sediments may also in part reflect influxes of
577 dissolved Ni from hydrothermal sources ($\delta^{60}\text{Ni} = 1.5$ ‰; Gall et al., 2013). However,
578 further work is needed to investigate this.

579

580 The complexity of the sediment-seawater system may be the key factor that
581 causes such enhanced levels of Ni isotope fractionation in marine sediments relative

582 | to meteorites, basalts and continental sediments. This preliminary dataset has
583 | produced some new and important data that can be the basis for further research of
584 | Ni in organic-rich marine sediments. As such, it is recommended that the
585 | relationships between Ni isotope fractionation and factors ubiquitous to the marine
586 | depositional system, such as bottom-water redox conditions, the type of organic
587 | matter present, organic matter preservation and TOC, are further explored.

588

589

590 **Figure captions**

591

592 Figure 1: Map and photograph showing the location of the Sinemurian-Pliensbachian
593 GSSP section, Robin Hood's Bay, UK.

594

595 Figure 2: Graphic log showing the Sinemurian-Pliensbachian boundary GSSP and the
596 relative locations of the samples analysed in this study. Samples used for Ni isotope
597 analysis are in bold. Bed number classification taken from Hesselbo and Jenkyns
598 (1995).

599

600 Figure 3: Present-day maturity map of the Exshaw Formation within Alberta, Canada
601 (modified from Creaney and Allan, 1991). Map shows the location of the thermally
602 immature, mature and overmature zones parallel to the Rocky Mountain Front, and
603 the location of the well from which the core samples used in this study originate.

604

605 Figure 4: Nickel isotope ($\delta^{60}\text{Ni}$), Ni abundance, and TOC profiles for the Sinemurian-
606 Pliensbachian section, presented against a corresponding stratigraphic column and
607 graphic log. Black dashed line indicates the position of the Sinemurian-Pliensbachian
608 boundary. ¹Bed numbers are from Hesselbo and Jenkyns (1995).

609

610 Figure 5: Plot showing the relationship between TOC and $V/(V+\text{Ni})$ for the
611 Pennsylvanian Stark Shale Member samples (solid black squares) detailed in Hatch
612 and Leventhal (1992), Robin Hood's Bay sediments (hollow diamonds ~~diamonds~~; this
613 study) and the Exshaw Formation shales (hollow triangles; this study). Black dashed
614 lines mark the parameters discussed in Hatch and Leventhal (1992), whereby values
615 of > 2.5 wt. % TOC correspond to $V/(V+\text{Ni})$ values > 0.75 for the Pennsylvanian Stark
616 Shale Member.

617

618 Figure 6: Nickel stable isotope data for organic-rich marine sediments from Robin
619 Hood's Bay, UK (RHB) and the Exshaw Formation. The grey box represents the
620 average of the Ni isotope data for meteorites, basalts and continental sediments
621 (~ 0.2 ‰ and 1 standard deviation either side of this; Cameron et al., 2009). The
622 white circles show Ni isotope data from ferromanganese crusts (taken from Gall et
623 al., 2013).

624

625 Table 1: Previously established values for the trace element ratios and their
626 corresponding depositional paleoredox conditions.

627

628 Table 2: Summary of trace element and TOC data and the associated ratios used for
629 paleoredox proxies, for the Robin Hood's Bay and Exshaw Formation marine
630 sediments.

631

632 Table 3: New nickel stable isotope data for a selection of Robin Hood's Bay and
633 Exshaw Formation marine sediments.

634

635 Table 4: A summary of elemental data for average shale, average upper continental
636 crust, Robin Hood's Bay and Exshaw Formation marine sediments.

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652 **References**

653

654 Alberdi, M., and Lafargue, E., 1993, Vertical variations of organic matter content in
655 Guayuta Group (upper Cretaceous), Interior Mountain Belt, Eastern
656 Venezuela: *Organic Geochemistry*, v. 20, no. 4, p. 425-436.

657 Birck, J. L., and Lugmair, G. W., 1988, Nickel and chromium isotopes in Allende
658 inclusions: *Earth and Planetary Science Letters*, v. 90, no. 2, p. 131-143.

659 [Brennecka, G. A., Wasylenki, L. E., Bargar, J. R., Weyer, S., and Anbar, A. D., 2011,](#)
660 [Uranium Isotope Fractionation during Adsorption to Mn-Oxyhydroxides:](#)
661 [Environmental Science and Technology, v. 45, no. 4, p. 1370-1375.](#)

662 Cameron, V., Vance, D., Archer, C., and House, C. H., 2007, Nickel stable isotopes as
663 biogeochemical tracers, *Goldschmidt Conference Abstracts*, p. A141.

664 Cameron, V., Vance, D., Archer, C., and House, C. H., 2009, A biomarker based on the
665 stable isotopes of nickel: *Proceedings of the National Academy of Sciences*, v.
666 106, p. 10944-10948.

667 Cameron, V., Vance, D., and Poulton, S., 2011, Nickel isotopes, BIFs and the Archean
668 oceans, *Goldschmidt Conference Abstracts, Mineralogical Magazine*, p. 615.

669 Cameron, V., House, C. H., and Brantley, S. L., 2012, A First Analysis of Metallome
670 Biosignatures of Hyperthermophilic Archea: *Archea*, v. 2012, p. 1-12.

671 Cameron, V., and Vance, D., 2014, Heavy nickel isotope compositions in rivers and
672 the oceans, *Geochimica et Cosmochimica Acta*, v. 128, p. 195-211.

673 Caplan, M. L., and Bustin, R. M., 1998, Sedimentology and sequence stratigraphy of
674 Devonian-Carboniferous strata, southern Alberta: *Bulletin of Canadian*
675 *Petroleum Geology*, v. 46, p. 487-514.

676 Caplan, M. L., and Bustin, R. M., 1999, Palaeoceanographic controls on geochemical
677 characteristics of organic-rich Exshaw mudrocks: role of enhanced primary
678 production: *Organic Geochemistry*, v. 30, no. 2-3, p. 161-188.

679 Chen, J. H., Papanastassiou, D. A., and Wasserburg, G. J., 2009, A search for nickel
680 isotopic anomalies in iron meteorites and chondrites: *Geochimica et*
681 *Cosmochimica Acta*, v. 73, no. 5, p. 1461-1471.

682 Cook, D. L., Wadhwa, M., Clayton, R., Dauphas, N., Janney, P. E., and Davis, A. M.,
683 2007, Mass-dependent fractionation of nickel isotopes in meteoritic metal:
684 *Meteoritics and Planetary Science*, v. 42, no. 12, p. 2067-2077.

685 Creaney, S., and Allan, J., 1991, Hydrocarbon generation and migration in the
686 Western Canada sedimentary basin: Geological Society, London, Special
687 Publications, v. 50, no. 1, p. 189-202.

688 Creaser, R. A., Sannigrahi, P., Chacko, T., and Selby, D., 2002, Further evaluation of
689 the Re-Os geochronometer in organic-rich sedimentary rocks: a test of
690 hydrocarbon maturation effects in the Exshaw Formation, Western Canada
691 Sedimentary Basin: *Geochimica et Cosmochimica Acta*, v. 66, no. 19, p. 3441-
692 3452.

693 [Cumming, V. M., Selby, D., and Lillis, P., 2012, Re-Os geochronology of the lacustrine](#)
694 [Green River Formation: Insights into direct depositional dating of lacustrine](#)
695 [successions, Re-Os systematics and paleocontinental weathering: *Earth and*](#)
696 [*Planetary Science Letters*, v. 359-360, p. 194-205.](#)

697 Dean, W. T., Donovan, D. T., and Howarth, M. K., 1961, The Liassic ammonite Zones
698 and Subzones of the North West European Province: *Bulletin of the Natural*
699 *History Museum*, v. 4, p. 435-505.

700 Dera, G., Pucéat, E., Pellenard, P., Neige, P., Delsate, D., Joachimski, M. M., Reisberg,
701 L., and Martinez, M., 2009, Water mass exchange and variations in seawater
702 temperature in the NW Tethys during the Early Jurassic: Evidence from
703 neodymium and oxygen isotopes of fish teeth and belemnites: Earth and
704 Planetary Science Letters, v. 286, no. 1-2, p. 198-207.

705 Dewaker, K. N., Chandra, K., Arunachalam, J., and Karunasagar, D., 2000, Isotopic
706 fractionation of Ni⁶⁰/Ni⁶¹ in kerogen and bitumen samples: Current Science,
707 v. 79, no. 12, p. 1720-1723.

708 Dill, H., 1986, Metallogeneses of early Paleozoic graptolite shales from the
709 Graefenthal Horst (Northern Bavaria-Federal Republic of Germany):
710 Economic Geology, v. 81, p. 889-903.

711 Ellrich, J., Hirner, A., and Stärk, H., 1985, Distribution of trace elements in crude oils
712 from southern Germany: Chemical Geology, v. 48, no. 1-4, p. 313-323.

713 Frausto da Silva, J.J.R., and Williams, R.J.P., 2001, The Biological Chemistry of the
714 Elements: The Inorganic Chemistry of Life, Oxford University Press, Oxford, p.
715 436-449.

716 Gall, L., Williams, H., Siebert, C., and Halliday, A., 2012, Determination of mass-
717 dependent variations in nickel isotope compositions using double spiking and
718 MC-ICPMS: Journal of Analytical Atomic Spectrometry, v. 27, no. 1, p. 137-
719 145.

720 Gall, L., Williams, H. W., Siebert, C., Halliday, A. N., Herrington, R. J., and Hein, J. R.,
721 2013, Nickel isotopic compositions of ferromanganese crusts and the
722 constancy of deep ocean inputs and continental weathering effects over the
723 Cenozoic: Earth and Planetary Science Letters, v. 375, p. 148-155.

724 Gradstein, F. M., Ogg, J. G., Schmitz, M .D., and Ogg, G. M. 2012. The Geologic Time
725 Scale 2012. Elsevier.

726 [Harris, N. B., Mnich, C. A., Selby, D., and Korn, D., 2013, Minor and trace element and](#)
727 [Re-Os chemistry of the Upper Devonian Woodford Shale, Permian Basin,](#)
728 [west Texas: Insights into metal abundance and basin processes: Chemical](#)
729 [Geology, v. 356, p. 76-93.](#)

730 Hatch, J. R., and Leventhal, J. S., 1992, Relationship between inferred redox potential
731 of the depositional environment and geochemistry of the Upper
732 Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone,
733 Wabaunsee County, Kansas, U.S.A: Chemical Geology, v. 99, no. 1-3, p. 65-82.

734 Herzog, G. F., hall, G. S., and Brownlee, D. E., 1994, Mass fractionation of nickel
735 isotopes in metallic cosmic spheres: Geochimica et Cosmochimica Acta, v. 58,
736 no. 23, p. 5319-5323.

737 Hesselbo, S. P., and Jenkyns, H. C., 1995, A comparison of the Hettangian to Bajocian
738 successions of Dorset and Yorkshire, *in* Taylor, P. D., ed., Field Geology of the
739 British Jurassic, Geological Society, London, p. 105-150.

740 Hesselbo, S. P., Meister, C., and Grocke, D. R., 2000, A potential global stratotype for
741 the Sinemurian-Pliensbachian boundary (Lower Jurassic), Robin Hood's Bay,
742 UK: ammonite faunas and isotope stratigraphy: Geological Magazine, v. 137,
743 no. 6, p. 601-607.

744 Jones, B., and Manning, D. A. C., 1994, Comparison of geochemical indices used for
745 the interpretation of palaeoredox conditions in ancient mudstones: Chemical
746 Geology, v. 111, no. 1-4, p. 111-129.

747 Jones, C. E., Jenkyns, H. C., and Hesselbo, S. P., 1994, Strontium isotopes in Early
748 Jurassic seawater: *Geochimica et Cosmochimica Acta*, v. 58, no. 4, p. 1285-
749 1301.

750 Kohman, T. P., and Robison, M. S., 1980, Iron-60 as a possible heat source and
751 chronometer in the early solar system: *Lunar and Planetary Science*, v. 11, p.
752 564-566.

753 [Konhauser, K. O., Pecoits, E., Lalonde, S. V., Papineau, D., Nisbet, E. G., Barley, M. E.,](#)
754 [Arndt, N. T., Zahnle, K., and Kamber, B. S., 2009, Oceanic nickel depletion and](#)
755 [a methanogen famine before the Great Oxidation Event: *Nature*, v. 458, p.](#)
756 [750-753.](#)

757 Leenheer, M. J., 1984, Mississippian Bakken and other equivalent formations as
758 source rocks in the Western Canada basin: *Organic Geochemistry*, v. 6, p.
759 521-533.

760 Lewan, M. D., 1984, Factors controlling the proportionality of vanadium to nickel in
761 crude oils: *Geochimica et Cosmochimica Acta*, v. 48, no. 11, p. 2231-2238.

762 Lewan, M. D., and Maynard, J. B., 1982, Factors controlling enrichment of vanadium
763 and nickel in the bitumen of organic sedimentary rocks: *Geochimica et*
764 *Cosmochimica Acta*, v. 46, no. 12, p. 2547-2560.

765 Li, H.-Y., Schoonmaker, J., 2003, Chemical composition and mineralogy of marine
766 sediments. In: *Treatise on Geochemistry. Sediments, Diagenesis, and*
767 *Sedimentary Rocks*, v. 7, p. 1-35.

768 López, L., Lo Mónaco, S., Galarraga, F., Lira, A., and Cruz, C., 1995, VNi ratio in
769 maltene and asphaltene fractions of crude oils from the west Venezuelan
770 basin: correlation studies: *Chemical Geology*, v. 119, no. 1-4, p. 255-262.

771 Manning, L. K., Frost, C. D., and Branthaver, J. F., 1991, A neodymium isotopic study
772 of crude oils and source rocks: potential applications for petroleum
773 exploration: *Chemical Geology*, v. 91, no. 2, p. 125-138.

774 Meijer, N. C., Johnston, D. I., and Fullmer, E. G., 1994, Devonian stratigraphy and
775 depositional history across Peace River Highland, west central Alberta and
776 nearby British Columbia: *Geological Survey of Canada Open File 2851*, p. 40
777 pp.

778 Meister, C., Aberhan, M., Blau, J., Dommergues, J.-L., Feist-Burkhardt, S., Hailwood,
779 E. A., Hart, M., Hesselbo, S. P., Hounslow, M. W., Hylton, M., Morton, N.,
780 Page, K., and Price, G. D., 2006, The Global Boundary Stratotype Section and
781 Point (GSSP) for the base of the Pliensbachian Stage (Lower Jurassic), Wine
782 Haven, Yorkshire, UK: *Episodes*, v. 29, no. 2, p. 93-114.

783 Morand, P., and Allègre, C. J., 1983, Nickel isotopic studies in meteorites: *Earth and*
784 *Planetary Science Letters*, v. 63, no. 2, p. 167-176.

785 Moynier, F., Blichert-Toft, J., Telouk, P., Luck, J.-M., and Albarède, F., 2007,
786 Comparative stable isotope geochemistry of Ni, Cu, Zn, and Fe in chondrites
787 and iron meteorites: *Geochimica et Cosmochimica Acta*, v. 71, no. 17, p.
788 4365-4379.

789 Ottley, C. J., Pearson, D. G., and Irvine, G. J., 2003, A routine method for the
790 dissolution of geological samples for the analysis of REE and trace elements
791 via ICP-MS, *in* Holland, G., and Tanner, S. D., eds., *Plasma source mass*
792 *spectrometry: applications and emerging technologies*, p. 221-230.

793 Palmer, M. R., Kenison Falkner, K., Turekian, K. K., and Calvert, S. E., 1988, Sources of
794 osmium isotopes in manganese nodules: *Geochimica et Cosmochimica Acta*,
795 v. 52, no. 5, p. 1197-1202.

796 Peucker-Ehrenbrink, B., and Hannigan, R. E., 2000, Effects of black shale weathering
797 on the mobility of rhenium and platinum group elements: *Geology*, v. 28, no.
798 5, p. 475-478.

799 Piggott, N., and Lines, M. D., 1992, A case study of migration from the West Canada
800 Basin, *in* England, W. A., and Fleet, A. J., eds., *Petroleum Migration*, Volume
801 59, Geological Society Special Publication, p. 207-225.

802 Powell, J. H., 1984, Lithostratigraphical nomenclature of the Lias Group in the
803 Yorkshire Basin: *Proceedings of the Yorkshire Geological Society*, v. 45, p. 51-
804 57.

805 Quitté, G., Meier, M., Latkoczy, C., Halliday, A.N., and Günther, D., 2006, Nickel
806 isotopes in iron meteorites—nucleosynthetic anomalies in sulphides with no
807 effects in metals and no trace of ^{60}Fe : *Earth and Planetary Science Letters*, v.
808 242, p. 16-25.

809 Quitté, G., and Oberli, F., 2006, Quantitative extraction and high precision isotope
810 measurements of nickel by MC-ICPMS: *Journal of Analytical Atomic*
811 *Spectrometry*, v. 21, p. 1249-1255.

812 Richards, B. C., and Higgins, A. C., 1988, Devonian-Carboniferous beds of the Palliser
813 and Exshaw formations at Jura Creekm Rocky Mountains, southwestern
814 Alberta, *in* McMillan, N. J., ed., *Devonian of the world*, Canadian Society of
815 *Petroleum Geologists Memoir*, Volume 14, p. 399-412.

816 Richards, B. C., Mamet, B. L., and Bamber, E. W., 1999, Uppermost Devonian and
817 Carboniferous sequence stratigraphy, biostratigraphy and basin
818 development, Banff region, southwestern Alberta, XIV International Congress
819 on the Carboniferous and Permian, Field Trip, 4-7 and 4-17 Guidebook:
820 Calgary, Alberta.

821 Richards, C., Ross, G. M., and Utting, J., 2002, U-Pb geochronology, lithostratigraphy
822 and biostratigraphy of tuff in the Upper Famennian to Tournaisian Exshaw
823 Formation: Evidence for a mid-Paleozoic magmatic arc on the northwestern
824 margin of North America, *in* Hills, L. V., Henderson, C. M., and Bamber, E. W.,
825 eds., Carboniferous and Permian of the World: XIV ICCP Proceedings, Volume
826 19, Can Soc Petrol Geol Mem, p. 158-207.

827 Rimmer, S. M., 2004, Geochemical paleoredox indicators in Devonian-Mississippian
828 black shales, Central Appalachian Basin (USA), *Chemical Geology*, v. 206, no.
829 3-4, p. 373-391.

830 [Rudnick, R. L., and Gao, S., 2003, 3.01 Composition of the Continental Crust: Treatise](#)
831 [on Geochemistry, v. 3, p. 1-64.](#)

832 Schovsbo, N. H., 2001, Why barren intervals? A taphonomic case study of the
833 Scandinavian Alum Shale and its faunas: *Lethaia*, v. 34, no. 4, p. 271-285.

834 Sclater, F., Boyle, E., Edmond, J., 1976, On the marine geochemistry of nickel: *Earth*
835 *and Planetary Science Letters*, v. 31, p. 119-128.

836 Selby, D., and Creaser, R. A., 2005, Direct radiometric dating of the Devonian-
837 Mississippian time-scale boundary using the Re-Os black shale
838 geochronometer: *Geology*, v. 33, p. 545-548.

839 Selby, D., Mutterlose, J., and Condon, D. J., 2009, U-Pb and Re-Os geochronology of
840 the Aptian/Albian and Cenomanian/Turonian stage boundaries: Implications
841 for timescale calibration, osmium isotope seawater composition and Re-Os
842 systematics in organic-rich sediments: *Chemical Geology*, v. 265, no. 3-4, p.
843 394-409.

844 Sellwood, B. W., and Jenkyns, H. C., 1975, Basins and swells and the evolution of an
845 epeiric sea (Pliensbachian-Bajocian of Great Britain): *Journal of the Geological*
846 *Society*, v. 131, no. 4, p. 373-388.

847 Shimamura, T., and Lugmair, G. W., 1983, Ni isotopic compositions in Allende and
848 other meteorites: *Earth and Planetary Science Letters*, v. 63, no. 2, p. 177-
849 188.

850 Spath, L. F., 1923, Correlation of the Ibex and Jamesoni Zones of the Lower Lias:
851 *Geological Magazine*, v. 60, p. 6-11.

852 [Wasylenki, L., Spivak-Birndorf, L., Howe, H., and Wells, R., 2014, Experiments reveal](#)
853 [the mechanism by which Ni isotopes fractionate in the weathering](#)
854 [environment: *Goldschmidt Abstracts*, 2661.](#)

855 [Wasylenki, L. E., Rolfe, B. A., Weeks, C. L., Spiro, T. G., and Anbar, A. D., 2008,](#)
856 [Experimental investigation of the effects of temperature and ionic strength](#)
857 [on Mo isotope fractionation during adsorption to manganese oxides:](#)
858 [Geochimica et Cosmochimica Acta, v. 72, p. 5997-6005.](#)

859 [Wasylenki, L. E., Weeks, C. L., Bargar, J. R., Spiro, T. G., Hein, J. R., and Anbar, A. D.,](#)
860 [2011, The molecular mechanism of Mo isotope fractionation during](#)
861 [adsorption to birnessite: *Geochimica et Cosmochimica Acta*, v. 75, no. 17, p.](#)
862 [5019-5031.](#)

863 | [Wedepohl, K. H., 1971, Environmental influences on the chemical composition of](#)
864 | [shales and clays: Physics and Chemistry of the Earth, v. 8, p. 305-333.](#)
865 | Xue, S., Herzog, G. F., Hall, G. S., Klein, J., Middleton, R., and Juenemann, D., 1995,
866 | Stable nickel isotopes and cosmogenic beryllium-10 and aluminum-26 in
867 | metallic spheroids from Meteor Crater, Arizona: Meteoritics, v. 30, p. 303-
868 | 310.

Characterising the nickel isotopic composition of organic-rich marine sediments

Highlights

- New Ni stable isotope data for two suites of organic-rich marine sediments (ORMS)
- The Ni isotope compositions (Ni IC) of both suites are comparable
- The Ni IC of ORMS are heavier than bulk Earth samples and present-day seawater
- The Ni IC of ORMS are comparable to that of ferromanganese crusts
- Factors ubiquitous to the marine realm are likely to drive fractionation in ORMS

1 **Characterising the nickel isotopic composition of organic-rich marine sediments**

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3

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15 Keywords: Nickel isotope fractionation, Ni isotopes, $\delta^{60}\text{Ni}$, organic-rich marine
16 sediments, Sinemurian-Pliensbachian GSSP, Exshaw Formation, redox

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20 **Abstract**

21 New Ni stable isotope data ($\delta^{60}\text{Ni}$) determined by double-spike MC-ICP-MS for two

22 geologically distinct suites of organic-rich marine sediments from the Sinemurian-

23 Pliensbachian (S-P) Global Stratotype Section and Point (GSSP; Robin Hood's Bay, UK)

24 and the Devonian-Mississippian Exshaw Formation (West Canada Sedimentary Basin)

25 is presented herein. These sediments yield $\delta^{60}\text{Ni}$ values of between 0.2 ‰ and 2.5

26 ‰, and predominantly have Ni isotopic compositions that are heavier than those of

27 abiotic terrestrial and extraterrestrial samples (0.15 ‰ and 0.27 ‰), and in some

28 cases present-day seawater (1.44 ‰) and dissolved Ni from riverine input (0.80 ‰).

29 In addition, the observed degree of isotopic fractionation in the marine sediments is

30 far greater than that of these other sample matrices. However, a strong similarity is

31 exhibited between the $\delta^{60}\text{Ni}$ values of the organic-rich sediments studied here and

32 those of ferromanganese crusts (0.9 to 2.5 ‰), suggesting that factors ubiquitous to

33 the marine environment are likely to play a key role in the heightened level of
34 isotopic fractionation in these sample matrices.

35 A lack of correlation between the Ni stable isotope compositions of the organic-rich
36 sediments and Ni abundance, suggests that isotopic fractionation in these sediments
37 is not controlled by incorporation or enrichment of Ni during sediment
38 accumulation. Further, no relationship is observed between $\delta^{60}\text{Ni}$ and TOC
39 concentrations or bottom-water redox conditions, indicating that the organic carbon
40 reservoir and levels of oxygenation at the sediment-water interface do not exert a
41 primary control on Ni isotope fractionation in marine sediments. Following
42 examination of these relationships, it is therefore more likely that the heavy Ni
43 isotope compositions of marine sediments are controlled by the weathering
44 environment and the dominant sources of dissolved Ni into the global ocean
45 reservoir.

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58 **1. Introduction**

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60 For several decades previous investigations of Ni isotopes have focused
61 predominantly on characterising radiogenic isotopic fractionation in extraterrestrial
62 materials, with a view to enhancing our understanding of planetary processes and
63 the isotopic composition of the early Solar System (eg. Kohman and Robison, 1980;
64 Morand and Allègre, 1983; Shimamura and Lugmair, 1983; Birck and Lugmair, 1988;
65 Herzog et al., 1994; Xue et al., 1995; Quitté et al., 2006; Cook et al., 2007; Moynier et
66 al., 2007; Chen et al., 2009). Further, the role of Ni as a bioessential trace metal (eg.
67 Frausto da Silva and Williams, 2001; Cameron et al., 2007; 2009) has led to the
68 recognition that the stable isotopes of Ni may have the potential to be utilised as a
69 powerful biological tool for studies of early life on Earth (Cameron et al., 2009;
70 2012).

71 In addition to its role in cosmochemical and biochemical investigations, the
72 potential of Ni to significantly enhance our understanding of organic-rich
73 sedimentary environments and to provide a powerful geological tracer in the
74 petroleum realm has been recognised, following pioneering work by Lewan and
75 Maynard (1982) and Lewan (1984) (eg. Ellrich et al., 1985; Manning et al., 1991;
76 Alberdi and Lafargue, 1993; López et al., 1995). However, these studies focused on
77 the elemental distribution of Ni rather than on its isotopic characterisation, and as
78 such, no study currently exists that evaluates the behaviour of Ni stable isotopes in
79 organic-rich sediments or indeed within a stratigraphic profile. This can be attributed
80 to Ni being a relatively newly investigated system, together with the difficulty

81 associated with purifying Ni from such complex sample matrices, that has only
82 recently been overcome through advancements in analytical and mass spectrometry
83 techniques (eg. Gall et al., 2012; Cameron and Vance, 2014).

84 Until now, Ni stable isotope systematics in organic-rich sedimentary matrices
85 have not been investigated. Indeed, it is only recently that the Ni isotopic
86 composition of seawater and the sources of Ni to the global oceanic reservoir have
87 been determined (e.g. Cameron and Vance, 2014; Gall et al., 2013). Present-day
88 seawater has an average $\delta^{60}\text{Ni}$ value of 1.44 ± 0.15 ‰, with apparent global isotopic
89 homogeneity (Cameron and Vance, 2014). The oceanic residence time of Ni has been
90 calculated as ~30 kyr (Cameron and Vance, 2014), which is significantly longer than
91 the mixing time of the global oceans (~2,000 yrs; Palmer et al., 1988). This would be
92 sufficient for the ocean to have an isotopically homogenous Ni composition.
93 Cameron et al. (2014) also demonstrate that draw-down of Ni from the surface to
94 deep ocean during trace metal cycling is not accompanied by isotopic fractionation,
95 thus further suggesting that the modern ocean is isotopically homogenous. In the
96 absence of any Ni isotope studies on banded iron formation and shale datasets, it is
97 difficult to speculate on processes occurring in an ancient ocean. However,
98 examination of Ni/Fe data from banded iron formations and extrapolated maximum
99 dissolved Ni concentration values in sea water through time (Konhauser et al., 2009),
100 demonstrates that dissolved nickel concentrations may have reached present day
101 values by ~550 Ma. As such, given the age of the sediments being studied herein
102 (~190-360 Ma), it is appropriate to use what we know regarding modern ocean
103 circulation and fractionation processes to hypothesise about processes acting in the
104 ancient oceans. The predominant input of dissolved Ni to the oceans occurs via

105 riverine influx, which has been suggested to yield an annual discharge- and
106 concentration-weighted $\delta^{60}\text{Ni}$ average of +0.80 ‰ (Cameron and Vance, 2014).
107 Significant variability in the riverine isotopic composition has been observed (+0.29
108 to +1.34 ‰), which has been attributed to isotopic fractionation of Ni during
109 weathering of continental crust, resulting in heavier $\delta^{60}\text{Ni}$ values in rivers and
110 seawater. In addition, mineral dust and volcanic ash also contribute to the oceanic Ni
111 budget (Li and Schoonmaker, 2003), as well as hydrothermal vent fluids ($\delta^{60}\text{Ni} = 1.5$
112 ‰; Gall et al., 2012).

113 Herein we present the first attempt at creating a Ni isotope stratigraphic
114 profile for an organic-rich sedimentary succession. The marine section across the
115 Sinemurian-Pliensbachian Global Stratotype Section and Point (GSSP), Robin Hood's
116 Bay, UK, is ideally suited to the present study, as it well understood
117 biostratigraphically (Hesselbo et al., 2000; Meister et al., 2006) and has been
118 previously characterised using other isotope stratigraphy techniques, including
119 strontium ($^{87}\text{Sr}/^{86}\text{Sr}$; Jones et al., 1994; Hesselbo et al., 2000), oxygen ($\delta^{18}\text{O}$), carbon
120 ($\delta^{13}\text{C}$) (Hesselbo et al., 2000), and Re-Os isotopes (Porter et al., 2013). The section is
121 also consistently thermally immature (the rocks have not been subjected to enough
122 heat or pressure to convert any kerogens present to hydrocarbons), thereby
123 eliminating any potential effects of thermal maturation on the Ni isotope signature.
124 In addition, to draw comparison between the isotopic composition of samples of
125 different depositional ages and environments, we present Ni isotope data from a
126 selection of thermally immature black shale samples from a core of the Exshaw
127 Formation, Canada.

128 To accurately assess and interpret any stratigraphic variation of Ni isotopes in
129 the Robin Hood's Bay section and Exshaw Formation samples, it is critical to
130 determine whether any fluctuations in paleoredox conditions occur. Nickel primarily
131 occupies one oxidation state in the natural environment (Ni^{2+}), suggesting that it is
132 not redox sensitive. However, its preferential association with redox-sensitive
133 metallo-organic complexes (porphyrins) in organic-rich sediments (Lewan and
134 Maynard, 1982) indicates that certainly within these sample matrices, redox
135 conditions at the time of sediment deposition may directly impact the degree of
136 enrichment or depletion of Ni. Herein, paleoredox conditions have been established
137 for the Sinemurian-Pliensbachian GSSP section and the Exshaw Formation sample
138 suite. Although one previous study (Dewaker et al., 2000) provides a preliminary
139 dataset for the Ni isotope composition of sediments from 3 different basins, our
140 understanding of the behaviour of Ni isotope systematics within organic-rich
141 sediments is currently non-existent. Further, advancements in analytical techniques
142 over the past decade suggest that the methodology employed by Dewaker et al.
143 (2000) may not have been optimal for Ni separation or Ni stable isotope analysis.

144 This paper presents the first detailed study of nickel stable isotope
145 systematics in organic-rich marine sediments. Analysis of marine sediments of
146 different depositional ages and from two geologically distinct settings, the
147 Sinemurian-Pliensbachian boundary (UK) and the Devonian-Mississippian Exshaw
148 Formation (Canada), yields comparable Ni isotope compositional values for both
149 sites. These samples provide insight into the incorporation of Ni into ocean
150 sediments, and allow evaluation of the contribution of the various dissolved Ni fluxes
151 to the seawater during these time periods.

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155 **2. Geological Setting**

156

157 *2.1 The Sinemurian-Pliensbachian boundary GSSP, Robin Hood's Bay, UK*

158 The Sinemurian-Pliensbachian boundary, established from the succession's
159 complete ammonite assemblages (Spath, 1923; Dean et al., 1961; Hesselbo et al.,
160 2000; Meister et al., 2006), occurs in the Pyritous Shales of the Redcar Mudstone
161 Formation within the Lias Group at Robin Hood's Bay (Powell, 1984; Fig. 1). At this
162 point in the Early Jurassic, Robin Hood's Bay was positioned on the margins of a
163 shallow epicontinental sea (eg. Dera et al., 2009) that covered most of Northern
164 Europe, including Britain, during the Mesozoic (Sellwood and Jenkyns, 1975). The
165 facies changes across the boundary, from pale siliceous to finer, more organic-rich
166 mudstones (Fig. 2), indicate an overall relative increase in sea level of at least
167 regional extent (eg. Hesselbo et al., 2000; Meister et al., 2006; Porter et al., 2013).

168 The age for the base of the Pliensbachian has been defined by the Geological
169 Time Scale (GTS) 2012 as 189.6 ± 1.5 Ma (Gradstein et al., 2012), derived from cycle-
170 scaled linear Sr trends and ammonite occurrences (as noted above; also includes the
171 lowest occurrence of *Bifericeras donovani*; Gradstein et al., 2012).

172

173 *2.2 Exshaw Formation, West Canada Sedimentary Basin (WCSB)*

174 The West Canada Sedimentary Basin (WCSB) trends approximately NW-SE
175 between the Canadian Shield to the East and the Western Cordillera to the West

176 (Piggott and Lines, 1992). Within the WCSB lies the Exshaw Formation, a thin but
177 laterally continuous unit (2-12 m thick; Leenheer, 1984; Creaney and Allan, 1991).
178 The Exshaw Formation in south-west and western Alberta (Fig. 3) comprises a lower
179 member of organic-rich mudrocks and black shales which rest with minor
180 disconformity upon Upper Devonian carbonate strata (Richards et al., 1999), and are
181 abruptly to gradationally overlain by bioturbated shelf siltstones (Caplan and Bustin,
182 1998, 1999; Creaser et al., 2002). The depositional interval of the lower black shale
183 unit is well constrained biostratigraphically; between the *expansa* and *duplicata*
184 zones of Late Famennian to Early Tournaisian time (over a maximum time period of
185 ~363 – 360 Ma; Caplan and Bustin, 1998). These lower black shales are dark grey,
186 bituminous, relatively thin (consistently between 3-5 m; Meijer et al., 1994) and
187 widespread (Meijer et al., 1994). The Devonian-Mississippian boundary (Exshaw-type
188 section at Jura Creek, ~80 km west of Calgary, Alberta, Canada) represents the
189 boundary between the upper calcareous and lower non-calcareous black shale units
190 (Richards and Higgins, 1988). Selby and Creaser (2005) provide an absolute Model 1
191 Re-Os age for this boundary, and thus the top of the lower black shale unit, of 361.3
192 \pm 2.4 Ma. In addition, U-Pb monazite data from a tuff horizon close to the base of the
193 lower black shale member constrains an absolute depositional age for this unit of
194 363.4 \pm 0.4 Ma (Richards et al., 2002). Deposition at this time represents part of a
195 continent-wide Famennian-Tournaisian black shale event, and in turn, a possible
196 ocean anoxic event (Piggott and Lines, 1992).

197

198

199 **3. Sampling**

200

201 A set of 32 samples (SP7-09 to SP39-09) was collected from the Pyritous
202 Shales Member of the Redcar Mudstone Formation, along a 6 m vertical section
203 bracketing the Sinemurian–Pliensbachian boundary (sample SP22-09) at Robin
204 Hood’s Bay (Fig. 2). This marine sequence contains a rich fauna of ammonites both
205 above and below the boundary interval (Hesselbo et al., 2000). Total organic carbon
206 analysis was conducted on all samples, with a consistent sampling interval of ~20 cm
207 for 3 m above and 3 m below the boundary from Beds 69–75 (except within Bed 72,
208 where a smaller sampling interval of ~15 cm was used). Of these samples, 14 were
209 analysed for Ni isotopes at a sampling interval of ~40 cm (Fig. 2).

210 Four samples from the Lower member of the Exshaw Formation were
211 collected from the Alberta Energy and Utilities Board, Core Research Centre, Calgary
212 (Fig. 3). The samples were taken from core 3-19-80-23W5, as detailed in Piggot and
213 Lines (1992) and Creaser et al. (2002). All samples are thermally immature, fine-
214 grained black shales containing very thin parallel and undulating laminations, and
215 showing no evidence of post-depositional disturbance. Drill core samples were
216 obtained to avoid any potential effects of surface weathering, including loss of
217 organic matter (PeuckerEhrenbrink and Hannigan, 2000). Further, edges of the core
218 were polished and where possible samples were taken from the central part of the
219 core.

220

221

222 **4. Analytical Protocol**

223

224 *4.1 Trace element abundance and TOC*

225 The elements V, Cr, Ni and Co were analysed in this study in order to look at relative
226 changes of depositional redox conditions in the sediments of interest. Samples were
227 prepared for trace element analysis at the Durham Geochemistry Group (University
228 of Durham, UK) following the method of Ottley et al., (2003). Sample powders (~100
229 mg) were digested in a 4:1 solution of 29 N HF and 16 N HNO₃ at ~150 °C for 48 hrs.
230 Samples were then evaporated to near rather than total dryness, to avoid
231 stabilisation of insoluble fluorides (Ottley et al., 2003). This was followed by the
232 addition of 1 ml 16 N HNO₃ and evaporation to near dryness. The previous stage was
233 repeated before the addition of 2.5 ml 16 N HNO₃ and ~10 ml 18MΩ water to create
234 a ~4 N HNO₃ solution. Sample beakers were capped and heated on the hotplate
235 overnight at ~100 °C. Once cooled, 1 ml of 1 ppm internal Re and Rh spike was
236 added to the samples (to yield 20 ppb Re and Rh in the final analyte solution) before
237 dilution up to 50 ml with MQ, yielding a ~0.5 N HNO₃ solution. Prior to analysis,
238 samples were diluted 10-fold by taking 1 ml from the 50 ml solution and diluting it to
239 10 ml using 0.5 N HNO₃. Samples were then analysed using the Thermo X-Series
240 Quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-MS). Replicate
241 analyses of USGS International Reference Materials (RMs) AGV-1, BHVO-1 and W-2
242 were conducted for calibration per sample set.

243 Total organic carbon measurements were performed at Durham University
244 using a Costech Elemental Analyser (ECS 4010) coupled to a ThermoFinnigan Delta V
245 Advantage. Total organic carbon was obtained as part of the isotopic analysis
246 ($\delta^{13}\text{C}_{\text{org}}$) using an internal standard (Glutamic Acid, 40.82 % C). Data accuracy was
247 monitored through routine analyses of in-house standards, which are stringently

248 calibrated against international standards (eg. USGS 40, USGS 24, IAEA 600, IAEA
249 CH6).

250

251 *4.2 Nickel stable isotopes*

252 All Ni isotope analyses were conducted at the University of Bristol. Samples
253 (~100 mg) were digested in closed PFA Beakers (Savillex, Minnetonka, MN) in a
254 mixture of concentrated HF and HNO₃ (3:1) at 140 °C for 48 hrs. Dried samples were
255 treated further with 7 N HCl. Chemical separation, purification and analyses of Ni
256 isotopes was carried out as described in detail in Cameron et al. (2009) and Cameron
257 and Vance (2014). Briefly, sample aliquots were spiked and allowed to equilibrate
258 under heating in closed vials overnight. This was followed by drying down and
259 treatment with 7 N HCl + H₂O₂. The spiked samples were then put through a 3-stage
260 column procedure that in turn removes Fe and Zn, separates Ni from the bulk
261 sample matrix, and final purification to remove any residual Fe and Zn. The first ion-
262 exchange column (AG MP-1M, Bio-Rad) is used to remove Fe and Zn. The dried
263 samples are then taken up in 1M HCl/1 M ammonium citrate, and the pH adjusted to
264 8–9 before loading onto columns filled with Ni resin (Eichrom Technologies). This
265 step separates Ni while removing all other matrix elements in the sample. After
266 oxidation to remove Ni-bound DMG, the samples are finally put through a third
267 column, which is a repeat of the first anion column, to clean up any residual Fe and
268 Zn.

269 All analyses were conducted in low resolution mode using a ThermoFinnigan
270 Neptune multi-collector (MC) ICP-MS coupled to an Aridus desolvating nebuliser
271 system (CETAC, Omaha, NE, USA). Samples were introduced in 2% HNO₃ via a CPI

272 PFA nebuliser (50 $\mu\text{l}/\text{minute}$) and spray chamber. Prior to isotopic analysis, the
273 $^{56}\text{Fe}/^{58}\text{Ni}$ ratio was manually checked in high resolution mode in all samples so that
274 any potential isobaric interference from residual sample ^{58}Fe could be applied as a
275 correction to Ni mass 58. Relative to the propagated internal uncertainty on $\delta^{60}\text{Ni}$,
276 the correction was insignificant. Additionally, a small amount of N_2 was introduced
277 to the Aridus sweep gas to reduce a potential interference from $^{40}\text{Ar}^{18}\text{O}$ at mass 58.
278 To mitigate inaccuracies in the $\delta^{60}\text{Ni}$ brought on by any instrumental variations,
279 measurements of the pure NIST SRM986 standard were made throughout the
280 analytical session. The reproducibility and accuracy of all isotope ratios were
281 monitored further by measurement of mixtures of the SRM986 standard with the
282 double-spike. All isotopes were measured simultaneously in static mode using a
283 multiple Faraday collector array. All Ni data are reported relative to NIST SRM986, in
284 the standard delta notation ($\delta^{60}\text{Ni} = [({}^{60}\text{Ni}/{}^{58}\text{Ni})_{\text{sample}}/({}^{60}\text{Ni}/{}^{58}\text{Ni})_{\text{NISTSRM986}}]-1] \times 1000$),
285 with all uncertainties reported to the 2σ level.

286

287

288 **5. Results**

289 *5.1 Trace elements and TOC*

290 The trace element ratios Ni/Co, V/Cr and V/(V+Ni) have been utilised by
291 previous studies to evaluate paleoredox conditions at the time of sediment
292 deposition (eg. Hatch and Leventhal, 1992; Jones and Manning, 1994; Schovsbo,
293 2001; Rimmer, 2004). Both Ni and V occur in highly stable tetrapyrrole complexes
294 that are originally derived from chlorophyll and are preferentially preserved under
295 anoxic conditions (Lewan and Maynard, 1982). When organic matter has been

296 extensively exposed to aerobic conditions, preservation of these tetrapyrrole
297 complexes will be low and subsequently the organic matter will have low Ni and V
298 contents. Chromium is not influenced by redox conditions, and thus because of its
299 association with just the detrital fraction and not the organic matter (Dill, 1986), high
300 V/Cr values (>2) are indicative of anoxic conditions. Both Ni and Co are found in
301 pyrite (in addition to the occurrence of Ni in porphyrins), but high Ni/Co values are
302 associated with anoxic conditions (Jones and Manning, 1994). The relationship
303 between these ratios and depositional redox conditions are summarised in Table 1.

304 The abundances of Ni, Co, V, Cr and TOC for all samples from Robin Hood's
305 Bay and the Exshaw Formation, are presented in Table 2. Both the Ni/Co and V/Cr
306 indices for Robin Hood's Bay show that these sediments were deposited under
307 predominantly oxic conditions. However, there is significant disagreement between
308 these ratios and the $V/(V+Ni)$ index. Values for $V/(V+Ni)$ range from $\sim 0.51 - 0.89$ and
309 indicate that anoxic conditions prevailed across the Sinemurian-Pliensbachian
310 boundary. Further, six samples suggest that bottom-water circulation ceased and
311 that conditions became euxinic intermittently between ~ 2.6 m above the boundary
312 and ~ 1.9 m below it (Table 2).

313 The Ni/Co ratio in the Exshaw Formation sediments ranges from 13.8 – 21.4,
314 with all four samples falling within the suboxic-anoxic parameter (Table 2). Similarly,
315 the $V/(V+Ni)$ ratio indicates that three of the samples were deposited under suboxic-
316 anoxic conditions (SP8-10, SP10-10 and SP13-10; values of 0.67, 0.69 and 0.67,
317 respectively). However, whilst V/Cr values of 7.2 and 9.0 suggest a suboxic-anoxic
318 depositional environment for Exshaw Formation samples SP10-10 and SP13-10,

319 respectively, this ratio also yields values that are representative of dysoxic conditions
320 for samples SP8-10 and SP9-10 (2.0 and 2.1, respectively).

321 Total organic carbon content is generally low in the Sinemurian-Pliensbachian
322 sediments, varying from ~0.53 – 2.46 wt. % (Table 2; Fig. 4). The data shows only
323 slight variation prior to the boundary (~0.57 – 0.86 wt. %; Fig. 4), but an overall
324 gradual increase above the boundary (from ~0.58 – 2.46 wt. %; Fig. 4). Total organic
325 carbon values in the Exshaw Formation samples range from 1.2 – 11 wt. %.

326

327 *5.2 Nickel stable isotopes*

328 New Ni stable isotope data for a select suite of the organic-rich sediments at
329 Robin Hood's Bay is presented (see Table 3). From the base of Bed 71 the sampling
330 interval for Ni isotope analysis is ~40 cm (Fig. 2). A profile of $\delta^{60}\text{Ni}$ values for the
331 section is shown alongside Ni concentration and TOC for comparison (Fig. 4).

332 The $\delta^{60}\text{Ni}$ of these samples is extremely variable, ranging from 0.28 ± 0.05 –
333 1.60 ± 0.05 ‰ (Fig. 4; Table 3). Two noticeable peaks in $\delta^{60}\text{Ni}$ values are observed 0.8
334 m above and 2.1 m below the Sinemurian-Pliensbachian boundary (1.26 ± 0.05 ‰
335 and 1.60 ± 0.05 ‰, respectively) that approximately correlate with the tops of beds
336 70 and 74. The greatest range in $\delta^{60}\text{Ni}$ values occurs below the boundary (~1.32 ‰),
337 compared to a range of ~0.97 ‰ above the boundary (Fig. 4). In this section and
338 dataset there is no apparent relationship between the degree of Ni isotope
339 fractionation and depositional redox conditions, TOC or stratigraphic height (Fig. 4).

340 Nickel stable isotope data for the Exshaw Formation is also presented in
341 Table 3. The $\delta^{60}\text{Ni}$ values in these samples range from 0.46 ± 0.04 to 2.50 ± 0.04 ‰
342 (Table 3). As with the Robin Hood's Bay section, no relationship exists between $\delta^{60}\text{Ni}$

343 and sample depth or between $\delta^{60}\text{Ni}$ and depositional redox conditions, TOC or
344 stratigraphic position (Fig. 4).

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347

348 **6. Discussion**

349

350 *6.1. Evaluating the suitability of V/(V+Ni) as a redox proxy: How applicable is it?*

351 The Ni/Co and V/Cr redox indices are recommended by a number of workers
352 as the most reliable of the paleo-environmental proxies (eg. Jones and Manning,
353 1994; Rimmer, 2004), and have been used by several studies to provide accurate and
354 consistent evaluations of paleoredox conditions at the time of sediment deposition
355 (eg. Rimmer, 2004; Selby et al., 2009; this study). However, this study finds that
356 there is significant disagreement between these indices and the V/(V+Ni) index. For
357 Robin Hood's Bay, the latter index suggests that the sediments were deposited in
358 predominantly suboxic-anoxic bottom-waters, with intermittent euxinic periods.
359 However, both the V/Cr and Ni/Co ratios indicate that the Robin Hood's Bay samples
360 were deposited under largely oxic condition. Such disparity between the redox
361 indices is also noted by both Rimmer (2004) and Selby et al. (2009), who observe
362 that the V/(V+Ni) index suggests suboxic-anoxic conditions for sediments otherwise
363 indicated to have been deposited under oxic conditions by the V/Cr and Ni/Co ratios.

364 Preliminary work by Lewan and Maynard (1982) and Lewan (1984) suggested
365 that redox potential was a dominant control on the wide range of V/(V+Ni) values
366 observed in petroleum source rocks and oils. Following this, Hatch and Leventhal

367 (1992) were the first to develop and utilise the $V/(V+Ni)$ index as a measure of
368 relative redox potential in organic-rich sediments. Their study focused on applying
369 this index specifically to marine black shales in the Pennsylvanian Stark Shale
370 Member of the Dennis Limestone, Wabaunsee County, Kansas, USA (Hatch and
371 Leventhal, 1992). Therefore, the ranges they defined for the $V/(V+Ni)$ ratio and the
372 associated redox conditions (summarised in Table 1), are applicable to this specific
373 geological basin and are sensitive to localised geochemical variations therein.

374 Hatch and Leventhal (1992) show that for the Stark Shale Member, with the
375 exception of two outliers, low TOC values (<2.5 wt. %) correspond to $V/(V+Ni)$ values
376 <0.75, and samples containing greater TOC (>7.5 wt. %) have corresponding higher
377 $V/(V+Ni)$ values (0.75; Fig. 5). However, this relationship is not observed in the
378 majority of the Sinemurian-Pliensbachian or Exshaw Formation sediments, with
379 samples containing low TOC providing a range in $V/(V+Ni)$ data from ~0.33 – 0.89.
380 This immediately indicates that there are significant geochemical differences
381 between these three geological sites. This may be due to differences in both
382 geological age and stratigraphy, with the Stark Shale Member (Late Carboniferous)
383 being a darker grey, non-sandy shale with higher TOC content (Hatch and Leventhal,
384 1992). As such, this comparison suggests that the redox index $V/(V+Ni)$, originally
385 developed for a specific geological basin, may not be applicable to other geological
386 sites, particularly those that possess differing geological and geochemical
387 characteristics. Factors that may have a profound effect upon the applicability of
388 such a threshold from one study to another include: differences in the influx of
389 nutrients and trace elements, type and relative amounts of organic matter, and
390 degrees of oceanic mixing (eg. Rimmer, 2004). However, these are preliminary

391 findings from a small dataset and further investigation is recommended. In
392 agreement with Rimmer (2004), this study therefore suggests that caution should be
393 taken when applying redox indices established by other studies for single geological
394 sites.

395

396

397 *6.2. Nickel stable isotope fractionation in marine sediments*

398 Nickel stable isotope data for the Exshaw Formation and the Sinemurian-
399 Pliensbachian GSSP is presented in Table 3 and Figure 6, and is the first to be
400 obtained for a suite of organic-rich marine sediments. The Exshaw Formation shales
401 define a realm of $\delta^{60}\text{Ni}$ values of 0.46 ± 0.04 to 2.50 ± 0.04 ‰ (a range of ~ 2.04 ‰;
402 Fig. 6). This range overlaps with, and is comparable to the $\delta^{60}\text{Ni}$ data for the
403 Sinemurian-Pliensbachian boundary GSSP (0.28 ± 0.05 to 1.60 ± 0.05 ‰; ~ 1.32 ‰;
404 Fig. 6). Although there are currently no estimations for the Ni isotopic composition
405 of the palaeo-ocean, the present-day global seawater $\delta^{60}\text{Ni}$ value has been
406 constrained as 1.44 ± 0.15 ‰ (Cameron and Vance, 2014). This value lies within the
407 $\delta^{60}\text{Ni}$ range of the marine sediments (Fig. 6; this study). Draw-down of Ni through
408 the water column does not induce isotopic fractionation, and as such, the Ni stable
409 isotope composition of the ocean is assumed to be homogenous (Cameron and
410 Vance, 2014). However, the Ni stable isotope composition of the organic-rich
411 sediments is far from homogenous, with $\delta^{60}\text{Ni}$ values that are either significantly
412 lighter or heavier than the present-day seawater $\delta^{60}\text{Ni}$ value (Fig. 6). Assuming that
413 global ocean homogeneity has persisted throughout geological time, the
414 fractionation observed in the marine sediments must therefore be recording the

415 substantially variable isotopic compositions of the sources of dissolved Ni into the
416 oceans.

417 This preliminary study presents Ni isotope and Ni concentration data from
418 bulk sample analysis. To assess what fraction of the selected metals may be
419 authigenic versus lithogenic, Table 4 presents Ni concentration data from this study,
420 and from average shale and average upper continental crust. It is clear from this that
421 the authigenic contribution of Ni in these samples is < 50 % (Table 4), suggesting that
422 > 50 % of the sample is represented by the lithogenic fraction.

423 For both sample sets, no correlation is observed between $\delta^{60}\text{Ni}$ and Ni
424 abundance, indicating that the level of Ni isotope fractionation in bulk marine
425 sediments here is not directly controlled by the degree of Ni enrichment. Similarly,
426 no relationship exists between $\delta^{60}\text{Ni}$ and redox for either sample set, suggesting that
427 the level of isotopic fractionation is not solely dictated by the bottom water redox
428 conditions at the time of sediment deposition. However, although it is currently
429 poorly understood, it is interesting to consider whether or not the degree of organic
430 matter preservation could have an effect on the observed isotopic fractionation
431 within the sediments. The samples used for Ni isotope analysis across the
432 Sinemurian-Pliensbachian boundary were deposited in predominantly oxic
433 conditions (using the Ni/Co and V/Cr ratios). The tetrapyrrole complexes known to
434 hold the majority of Ni in organic matter are poorly preserved under these
435 conditions (Lewan and Maynard, 1982). As such, assuming break down of these
436 complexes is heterogeneous, and that it does not result in the preferential loss of a
437 particular isotope of Ni, this lack of preservation may at least partially contribute to
438 the observed Ni isotope fractionation in these sediments.

439 In addition, no correlation is seen between $\delta^{60}\text{Ni}$ and TOC concentration in
440 these samples, indicating that Ni isotope fractionation is not dependent on the
441 concentration of organic matter in these sediments. However, all samples in this
442 study have TOC contents of <3.0 wt. % (Table 3; apart from Exshaw Fm. sample
443 SP10-10; 11.05 wt. %). As such, to further investigate the relationship between Ni
444 fractionation and the organic carbon reservoir, work should be conducted on
445 samples containing more varied and greater levels of TOC.

446

447 *6.3. Fractionation of nickel stable isotopes in marine organic-rich sediments vs.*
448 *terrestrial samples, extra-terrestrial samples and ferromanganese crusts*

449 Marine sediments from the Exshaw Formation and Sinemurian-Pliensbachian
450 GSSP yield a comparable range in $\delta^{60}\text{Ni}$ values (0.5-2.5 ‰ and 0.3-1.6 ‰,
451 respectively; Fig. 6). Figure 6 compares these Ni isotopic values with that of bulk
452 Earth and extraterrestrial samples (Cameron et al., 2009), including meteorites (0.2
453 ‰ to 0.4 ‰), basalts (0 to 0.3 ‰) and continental sediments (0 to 0.2 ‰). It is clear
454 that these samples are significantly isotopically lighter than the organic-rich
455 sediments (this study). In addition, Ni stable isotope fractionation occurs to a much
456 greater degree in the sedimentary marine environment. Despite this though, there is
457 minimal overlap between the $\delta^{60}\text{Ni}$ values for the organic-rich sediments and those
458 of the abiotic terrestrial and extraterrestrial samples (Fig. 6).

459 The reasons for the heightened isotopic fractionation in marine sediments
460 are currently poorly understood due to an extremely limited sample database.
461 However, the complexity of the marine environment is likely to play a critical role in
462 this. With assumed ocean isotopic homogeneity (Cameron and Vance, 2014), the

463 sources of dissolved Ni into seawater must exert a substantial control on the
464 observed degree of isotopic fractionation. This may be partially attributed to the
465 variability of the Ni isotope composition of the dissolved phase of rivers, which are a
466 dominant source of Ni to the global oceans ($\delta^{60}\text{Ni} = 0.29$ to 1.34 ‰; Cameron and
467 Vance, 2014). The heavier isotope composition of this fraction relative to silicates
468 and continental sediments (0 ‰ to 0.3 ‰; Cameron et al., 2009) likely reflects
469 isotopic fractionation induced by the weathering environment during riverine
470 transport (Cameron and Vance, 2014).

471 However, this study demonstrates that the Ni isotopic composition of
472 organic-rich marine sediments ($\delta^{60}\text{Ni} = 0.28$ to 2.50 ‰; this study) are significantly
473 heavier than that of the riverine source (average $\delta^{60}\text{Ni} = 0.80$ ‰; Cameron and
474 Vance, 2014). This is also the case for the dissolved phase of present-day seawater
475 ($\delta^{60}\text{Ni} = 1.44 \pm 0.15$ ‰; Cameron and Vance, 2014). To reconcile this, there must
476 therefore be either an additional input that is isotopically heavier than the riverine
477 source (Cameron and Vance, 2014).

478 Dissolved trace metals are often removed from the water column via
479 adsorption to mineral surfaces as they are incorporated into the sediment. The
480 adsorption process, in particular to Mn and Fe oxyhydroxides, is known to induce
481 isotopic fraction in a number of stable isotope systems, including Mo and U
482 (Brennecke et al., 2011; Wasylenki et al., 2008; 2011). Sorption to Fe-Mn oxides is
483 the main output of Ni from the oceans (Cameron and Vance, 2014), and more
484 recently, this fractionation effect has also been revealed in the Ni stable isotope
485 system (Wasylenki et al., 2014). In addition, experiments focusing on the adsorption
486 and co-precipitation of Ni with oxyhydroxide phases (Wasylenki et al., 2014) have

487 demonstrated that isotopically light Ni is retained by these phases whilst isotopically
488 heavy Ni is mobilised. This therefore leads to an enrichment of isotopically heavy Ni
489 in the dissolved riverine load (Wasylenki et al., 2014).

490 Nickel stable isotope data for ferromanganese crusts (0.9-2.5 ‰; Gall et al.,
491 2013) shows that their isotopic composition is comparable to that of the marine
492 organic-rich sediments discussed herein. Following analysis of ferromanganese
493 crusts in proximity to hydrothermal sources, Gall et al. (2013) suggest that
494 hydrothermal fluids may have a Ni stable isotope composition of ~ 1.5 ‰. Thus
495 hydrothermal sources may be contributing to the isotopic composition noted in the
496 marine sediments herein.

497 However, both marine sediments (this study) and ferromanganese crusts
498 (Gall et al., 2013) are at least in part recording isotopic fractionation from a source
499 that is isotopically heavier than riverine and hydrothermal Ni influxes. As continental
500 weathering is a primary source of Ni to the global oceans, it is likely that weathering-
501 induced isotope fractionation could account for the isotopically heavy Ni
502 composition of organic-rich marine sediments. Further, the heavy Ni isotope
503 signature observed in these sediments may reflect the contribution of heavy
504 dissolved Ni to the oceans following retention of the lighter Ni isotopes during
505 weathering of oxyhydroxide phases (eg. Wasylenki et al., 2014). In support of this,
506 analysis of ferromanganese crusts at varying distances from the continental shelf
507 (Gall et al., 2013) demonstrates that crusts growing in proximity to a continental
508 shelf contain the heaviest Ni isotope compositions. However, although weathering
509 does affect the isotopic composition of marine sediments, the effects resulting from

510 additional factors such as riverine particulates and organic compounds have yet to
511 be constrained (Cameron and Vance, 2014).

512 In addition, following examination of Ni isotope data from microorganisms
513 ($\delta^{60}\text{Ni} = \sim 0.0$ to -1.6 ‰; Cameron et al., 2009), it can be noted that the Ni isotope
514 ratios in the organic-rich sediments herein ($\delta^{60}\text{Ni} = \sim 0.28 - 2.50$ ‰) appear to have
515 been driven in the opposite direction to those of the microorganisms. Whilst the
516 causes of Ni isotope fractionation in these sediments are currently poorly
517 understood, it appears that there is a fractionation effect associated with the Ni
518 isotope system that may have parallels to the carbon isotope system, with the
519 microorganisms taking up isotopically lighter Ni, thus potentially leaving behind an
520 isotopically heavier Ni isotope signature in the sediment. Although it is impossible to
521 draw a definitive conclusion from the current dataset, this study suggests that
522 microorganisms and organic matter may play a key role in our understanding of Ni
523 isotope fractionation (in a similar manner to the rhenium-osmium isotope system;
524 Cumming et al., 2012; Harris et al., 2013) in organic-rich marine sediments, and as
525 such, the importance of further investigation is emphasised.

526

527 **7. Conclusions**

528

529 This first investigation into the Ni stable isotope composition of organic-rich
530 marine sediments from two distinct basins has yielded a number of key
531 observations, outlined below.

532

533 1. This preliminary dataset indicates that organic-rich sediments have a Ni stable
534 isotope composition ($\delta^{60}\text{Ni}$) of 0.28 to 2.50 ‰.

535 2. No relationship is observed between the Ni stable isotope composition of the
536 organic-rich sediments and TOC, suggesting that fractionation is not determined by
537 changes in the organic carbon reservoir.

538 3. Similarly, there is no correlation between $\delta^{60}\text{Ni}$ and Ni abundance or bottom-
539 water redox conditions, suggesting that the process of Ni uptake and enrichment at
540 the sediment-water interface, and the degree of oxygenation in the water-column
541 do not exert primary control on isotopic fractionation.

542 4. The Ni isotope composition of marine sediments is substantially heavier and
543 isotopically distinct to those of abiotic terrestrial and extraterrestrial samples ($\delta^{60}\text{N}$
544 values of -0.1 to 0.3 ‰; Cameron et al., 2009).

545 5. Ni isotopes in marine sediments are isotopically heavier than those in present-day
546 seawater and rivers ($\delta^{60}\text{Ni} = 1.44 \pm 0.15$ ‰ and 0.29 to 1.340 ‰, respectively;
547 Cameron and Vance, 2014), indicating input of an isotopically heavier source of Ni to
548 the ocean.

549 6. The observed range of $\delta^{60}\text{N}$ values in marine sediments is comparable to that of
550 ferromanganese crusts (0.9 to 2.5 ‰; Gall et al., 2013). Adsorption of Ni to Fe-Mn
551 oxyhydroxides results in the retention of isotopically light Ni and the mobilisation of
552 isotopically heavier Ni during oxidative weathering (Wasylenki et al., 2014).
553 Subsequently, the dissolved riverine load is enriched in heavier Ni. It is therefore
554 probable that isotopic fractionation driven by the weathering environment plays a
555 key role in yielding the range of $\delta^{60}\text{N}$ values that are observed in marine sediments.

556 7. The relatively heavy Ni stable isotope composition of marine sediments may also
557 in part reflect influxes of dissolved Ni from hydrothermal sources ($\delta^{60}\text{Ni} = 1.5 \text{ ‰}$; Gall
558 et al., 2013). However, further work is needed to investigate this.

559

560 The complexity of the sediment-seawater system may be the key factor that
561 causes such enhanced levels of Ni isotope fractionation in marine sediments relative
562 to meteorites, basalts and continental sediments. This preliminary dataset has
563 produced some new and important data that can be the basis for further research of
564 Ni in organic-rich marine sediments. As such, it is recommended that the
565 relationships between Ni isotope fractionation and factors ubiquitous to the marine
566 depositional system, such as bottom-water redox conditions, the type of organic
567 matter present, organic matter preservation and TOC, are further explored.

568

569

570 **Figure captions**

571

572 Figure 1: Map and photograph showing the location of the Sinemurian-Pliensbachian
573 GSSP section, Robin Hood's Bay, UK.

574

575 Figure 2: Graphic log showing the Sinemurian-Pliensbachian boundary GSSP and the
576 relative locations of the samples analysed in this study. Samples used for Ni isotope
577 analysis are in bold. Bed number classification taken from Hesselbo and Jenkyns
578 (1995).

579

580 Figure 3: Present-day maturity map of the Exshaw Formation within Alberta, Canada
581 (modified from Creaney and Allan, 1991). Map shows the location of the thermally
582 immature, mature and overmature zones parallel to the Rocky Mountain Front, and
583 the location of the well from which the core samples used in this study originate.

584

585 Figure 4: Nickel isotope ($\delta^{60}\text{Ni}$), Ni abundance, and TOC profiles for the Sinemurian-
586 Pliensbachian section, presented against a corresponding stratigraphic column and
587 graphic log. Black dashed line indicates the position of the Sinemurian-Pliensbachian
588 boundary. ¹Bed numbers are from Hesselbo and Jenkyns (1995).

589

590 Figure 5: Plot showing the relationship between TOC and $V/(V+\text{Ni})$ for the
591 Pennsylvanian Stark Shale Member samples (solid black squares) detailed in Hatch
592 and Leventhal (1992), Robin Hood's Bay sediments (hollow diamonds; this study)
593 and the Exshaw Formation shales (hollow triangles; this study). Black dashed lines
594 mark the parameters discussed in Hatch and Leventhal (1992), whereby values of >
595 2.5 wt. % TOC correspond to $V/(V+\text{Ni})$ values > 0.75 for the Pennsylvanian Stark
596 Shale Member.

597

598 Figure 6: Nickel stable isotope data for organic-rich marine sediments from Robin
599 Hood's Bay, UK (RHB) and the Exshaw Formation. The grey box represents the
600 average of the Ni isotope data for meteorites, basalts and continental sediments
601 ($\sim 0.2\text{‰}$ and 1 standard deviation either side of this; Cameron et al., 2009). The
602 white circles show Ni isotope data from ferromanganese crusts (taken from Gall et
603 al., 2013).

604

605 Table 1: Previously established values for the trace element ratios and their
606 corresponding depositional paleoredox conditions.

607

608 Table 2: Summary of trace element and TOC data and the associated ratios used for
609 paleoredox proxies, for the Robin Hood's Bay and Exshaw Formation marine
610 sediments.

611

612 Table 3: New nickel stable isotope data for a selection of Robin Hood's Bay and
613 Exshaw Formation marine sediments.

614

615 Table 4: A summary of elemental data for average shale, average upper continental
616 crust, Robin Hood's Bay and Exshaw Formation marine sediments.

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636 **References**

637

638 Alberdi, M., and Lafargue, E., 1993, Vertical variations of organic matter content in
639 Guayuta Group (upper Cretaceous), Interior Mountain Belt, Eastern
640 Venezuela: *Organic Geochemistry*, v. 20, no. 4, p. 425-436.

641 Birck, J. L., and Lugmair, G. W., 1988, Nickel and chromium isotopes in Allende
642 inclusions: *Earth and Planetary Science Letters*, v. 90, no. 2, p. 131-143.

643 Brennecka, G. A., Wasylenki, L. E., Bargar, J. R., Weyer, S., and Anbar, A. D., 2011,
644 Uranium Isotope Fractionation during Adsorption to Mn-Oxyhydroxides:
645 *Environmental Science and Technology*, v. 45, no. 4, p. 1370-1375.

646 Cameron, V., Vance, D., Archer, C., and House, C. H., 2007, Nickel stable isotopes as
647 biogeochemical tracers, *Goldschmidt Conference Abstracts*, p. A141.

648 Cameron, V., Vance, D., Archer, C., and House, C. H., 2009, A biomarker based on the
649 stable isotopes of nickel: *Proceedings of the National Academy of Sciences*, v.
650 106, p. 10944-10948.

651 Cameron, V., Vance, D., and Poulton, S., 2011, Nickel isotopes, BIFs and the Archean
652 oceans, Goldschmidt Conference Abstracts, Mineralogical Magazine, p. 615.

653 Cameron, V., House, C. H., and Brantley, S. L., 2012, A First Analysis of Metallome
654 Biosignatures of Hyperthermophilic Archea: *Archea*, v. 2012, p. 1-12.

655 Cameron, V., and Vance, D., 2014, Heavy nickel isotope compositions in rivers and
656 the oceans, *Geochimica et Cosmochimica Acta*, v. 128, p. 195-211.

657 Caplan, M. L., and Bustin, R. M., 1998, Sedimentology and sequence stratigraphy of
658 Devonian-Carboniferous strata, southern Alberta: *Bulletin of Canadian
659 Petroleum Geology*, v. 46, p. 487-514.

660 Caplan, M. L., and Bustin, R. M., 1999, Palaeoceanographic controls on geochemical
661 characteristics of organic-rich Exshaw mudrocks: role of enhanced primary
662 production: *Organic Geochemistry*, v. 30, no. 2-3, p. 161-188.

663 Chen, J. H., Papanastassiou, D. A., and Wasserburg, G. J., 2009, A search for nickel
664 isotopic anomalies in iron meteorites and chondrites: *Geochimica et
665 Cosmochimica Acta*, v. 73, no. 5, p. 1461-1471.

666 Cook, D. L., Wadhwa, M., Clayton, R., Dauphas, N., Janney, P. E., and Davis, A. M.,
667 2007, Mass-dependent fractionation of nickel isotopes in meteoritic metal:
668 *Meteoritics and Planetary Science*, v. 42, no. 12, p. 2067-2077.

669 Creaney, S., and Allan, J., 1991, Hydrocarbon generation and migration in the
670 Western Canada sedimentary basin: Geological Society, London, Special
671 Publications, v. 50, no. 1, p. 189-202.

672 Creaser, R. A., Sannigrahi, P., Chacko, T., and Selby, D., 2002, Further evaluation of
673 the Re-Os geochronometer in organic-rich sedimentary rocks: a test of
674 hydrocarbon maturation effects in the Exshaw Formation, Western Canada

675 Sedimentary Basin: *Geochimica et Cosmochimica Acta*, v. 66, no. 19, p. 3441-
676 3452.

677 Cumming, V. M., Selby, D., and Lillis, P., 2012, Re-Os geochronology of the lacustrine
678 Green River Formation: Insights into direct depositional dating of lacustrine
679 successions, Re-Os systematics and paleocontinental weathering: *Earth and*
680 *Planetary Science Letters*, v. 359-360, p. 194-205.

681 Dean, W. T., Donovan, D. T., and Howarth, M. K., 1961, The Liassic ammonite Zones
682 and Subzones of the North West European Province: *Bulletin of the Natural*
683 *History Museum*, v. 4, p. 435-505.

684 Dera, G., Pucéat, E., Pellenard, P., Neige, P., Delsate, D., Joachimski, M. M., Reisberg,
685 L., and Martinez, M., 2009, Water mass exchange and variations in seawater
686 temperature in the NW Tethys during the Early Jurassic: Evidence from
687 neodymium and oxygen isotopes of fish teeth and belemnites: *Earth and*
688 *Planetary Science Letters*, v. 286, no. 1-2, p. 198-207.

689 Dewaker, K. N., Chandra, K., Arunachalam, J., and Karunasagar, D., 2000, Isotopic
690 fractionation of Ni⁶⁰/Ni⁶¹ in kerogen and bitumen samples: *Current Science*,
691 v. 79, no. 12, p. 1720-1723.

692 Dill, H., 1986, Metallogenesis of early Paleozoic graptolite shales from the
693 Graefenthal Horst (Northern Bavaria-Federal Republic of Germany):
694 *Economic Geology*, v. 81, p. 889-903.

695 Ellrich, J., Hirner, A., and Stärk, H., 1985, Distribution of trace elements in crude oils
696 from southern Germany: *Chemical Geology*, v. 48, no. 1-4, p. 313-323.

697 Frausto da Silva, J.J.R., and Williams, R.J.P., 2001, The Biological Chemistry of the
698 Elements: The Inorganic Chemistry of Life, Oxford University Press, Oxford, p.
699 436-449.

700 Gall, L., Williams, H., Siebert, C., and Halliday, A., 2012, Determination of mass-
701 dependent variations in nickel isotope compositions using double spiking and
702 MC-ICPMS: Journal of Analytical Atomic Spectrometry, v. 27, no. 1, p. 137-
703 145.

704 Gall, L., Williams, H. W., Siebert, C., Halliday, A. N., Herrington, R. J., and Hein, J. R.,
705 2013, Nickel isotopic compositions of ferromanganese crusts and the
706 constancy of deep ocean inputs and continental weathering effects over the
707 Cenozoic: Earth and Planetary Science Letters, v. 375, p. 148-155.

708 Gradstein, F. M., Ogg, J. G., Schmitz, M .D., and Ogg, G. M. 2012. The Geologic Time
709 Scale 2012. Elsevier.

710 Harris, N. B., Mnich, C. A., Selby, D., and Korn, D., 2013, Minor and trace element and
711 Re-Os chemistry of the Upper Devonian Woodford Shale, Permian Basin,
712 west Texas: Insights into metal abundance and basin processes: Chemical
713 Geology, v. 356, p. 76-93.

714 Hatch, J. R., and Leventhal, J. S., 1992, Relationship between inferred redox potential
715 of the depositional environment and geochemistry of the Upper
716 Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone,
717 Wabaunsee County, Kansas, U.S.A: Chemical Geology, v. 99, no. 1-3, p. 65-82.

718 Herzog, G. F., hall, G. S., and Brownlee, D. E., 1994, Mass fractionation of nickel
719 isotopes in metallic cosmic spheres: Geochimica et Cosmochimica Acta, v. 58,
720 no. 23, p. 5319-5323.

721 Hesselbo, S. P., and Jenkyns, H. C., 1995, A comparison of the Hettangian to Bajocian
722 successions of Dorset and Yorkshire, *in* Taylor, P. D., ed., *Field Geology of the*
723 *British Jurassic*, Geological Society, London, p. 105-150.

724 Hesselbo, S. P., Meister, C., and Grocke, D. R., 2000, A potential global stratotype for
725 the Sinemurian-Pliensbachian boundary (Lower Jurassic), Robin Hood's Bay,
726 UK: ammonite faunas and isotope stratigraphy: *Geological Magazine*, v. 137,
727 no. 6, p. 601-607.

728 Jones, B., and Manning, D. A. C., 1994, Comparison of geochemical indices used for
729 the interpretation of palaeoredox conditions in ancient mudstones: *Chemical*
730 *Geology*, v. 111, no. 1-4, p. 111-129.

731 Jones, C. E., Jenkyns, H. C., and Hesselbo, S. P., 1994, Strontium isotopes in Early
732 Jurassic seawater: *Geochimica et Cosmochimica Acta*, v. 58, no. 4, p. 1285-
733 1301.

734 Kohman, T. P., and Robison, M. S., 1980, Iron-60 as a possible heat source and
735 chronometer in the early solar system: *Lunar and Planetary Science*, v. 11, p.
736 564-566.

737 Konhauser, K. O., Pecoits, E., Lalonde, S. V., Papineau, D., Nisbet, E. G., Barley, M. E.,
738 Arndt, N. T., Zahnle, K., and Kamber, B. S., 2009, Oceanic nickel depletion and
739 a methanogen famine before the Great Oxidation Event: *Nature*, v. 458, p.
740 750-753.

741 Leenheer, M. J., 1984, Mississippian Bakken and other equivalent formations as
742 source rocks in the Western Canada basin: *Organic Geochemistry*, v. 6, p.
743 521-533.

744 Lewan, M. D., 1984, Factors controlling the proportionality of vanadium to nickel in
745 crude oils: *Geochimica et Cosmochimica Acta*, v. 48, no. 11, p. 2231-2238.

746 Lewan, M. D., and Maynard, J. B., 1982, Factors controlling enrichment of vanadium
747 and nickel in the bitumen of organic sedimentary rocks: *Geochimica et*
748 *Cosmochimica Acta*, v. 46, no. 12, p. 2547-2560.

749 Li, H.-Y., Schoonmaker, J., 2003, Chemical composition and mineralogy of marine
750 sediments. In: *Treatise on Geochemistry. Sediments, Diagenesis, and*
751 *Sedimentary Rocks*, v. 7, p. 1-35.

752 López, L., Lo Mónaco, S., Galarraga, F., Lira, A., and Cruz, C., 1995, VNi ratio in
753 maltene and asphaltene fractions of crude oils from the west Venezuelan
754 basin: correlation studies: *Chemical Geology*, v. 119, no. 1-4, p. 255-262.

755 Manning, L. K., Frost, C. D., and Branthaver, J. F., 1991, A neodymium isotopic study
756 of crude oils and source rocks: potential applications for petroleum
757 exploration: *Chemical Geology*, v. 91, no. 2, p. 125-138.

758 Meijer, N. C., Johnston, D. I., and Fullmer, E. G., 1994, Devonian stratigraphy and
759 depositional history across Peace River Highland, west central Alberta and
760 nearby British Columbia: *Geological Survey of Canada Open File 2851*, p. 40
761 pp.

762 Meister, C., Aberhan, M., Blau, J., Dommergues, J.-L., Feist-Burkhardt, S., Hailwood,
763 E. A., Hart, M., Hesselbo, S. P., Hounslow, M. W., Hylton, M., Morton, N.,
764 Page, K., and Price, G. D., 2006, The Global Boundary Stratotype Section and
765 Point (GSSP) for the base of the Pliensbachian Stage (Lower Jurassic), Wine
766 Haven, Yorkshire, UK: *Episodes*, v. 29, no. 2, p. 93-114.

767 Morand, P., and Allègre, C. J., 1983, Nickel isotopic studies in meteorites: Earth and
768 Planetary Science Letters, v. 63, no. 2, p. 167-176.

769 Moynier, F., Blichert-Toft, J., Telouk, P., Luck, J.-M., and Albarède, F., 2007,
770 Comparative stable isotope geochemistry of Ni, Cu, Zn, and Fe in chondrites
771 and iron meteorites: *Geochimica et Cosmochimica Acta*, v. 71, no. 17, p.
772 4365-4379.

773 Ottley, C. J., Pearson, D. G., and Irvine, G. J., 2003, A routine method for the
774 dissolution of geological samples for the analysis of REE and trace elements
775 via ICP-MS, *in* Holland, G., and Tanner, S. D., eds., *Plasma source mass
776 spectrometry: applications and emerging technologies*, p. 221-230.

777 Palmer, M. R., Kenison Falkner, K., Turekian, K. K., and Calvert, S. E., 1988, Sources of
778 osmium isotopes in manganese nodules: *Geochimica et Cosmochimica Acta*,
779 v. 52, no. 5, p. 1197-1202.

780 Peucker-Ehrenbrink, B., and Hannigan, R. E., 2000, Effects of black shale weathering
781 on the mobility of rhenium and platinum group elements: *Geology*, v. 28, no.
782 5, p. 475-478.

783 Piggott, N., and Lines, M. D., 1992, A case study of migration from the West Canada
784 Basin, *in* England, W. A., and Fleet, A. J., eds., *Petroleum Migration, Volume
785 59, Geological Society Special Publication*, p. 207-225.

786 Powell, J. H., 1984, Lithostratigraphical nomenclature of the Lias Group in the
787 Yorkshire Basin: *Proceedings of the Yorkshire Geological Society*, v. 45, p. 51-
788 57.

789 Quitté, G., Meier, M., Latkoczy, C., Halliday, A.N., and Günther, D., 2006, Nickel
790 isotopes in iron meteorites—nucleosynthetic anomalies in sulphides with no

791 effects in metals and no trace of ^{60}Fe : *Earth and Planetary Science Letters*, v.
792 242, p. 16-25.

793 Quitté, G., and Oberli, F., 2006, Quantitative extraction and high precision isotope
794 measurements of nickel by MC-ICPMS: *Journal of Analytical Atomic*
795 *Spectrometry*, v. 21, p. 1249-1255.

796 Richards, B. C., and Higgins, A. C., 1988, Devonian-Carboniferous beds of the Palliser
797 and Exshaw formations at Jura Creekm Rocky Mountains, southwestern
798 Alberta, *in* McMillan, N. J., ed., *Devonian of the world*, Canadian Society of
799 *Petroleum Geologists Memoir*, Volume 14, p. 399-412.

800 Richards, B. C., Mamet, B. L., and Bamber, E. W., 1999, Uppermost Devonian and
801 Carboniferous sequence stratigraphy, biostratigraphy and basin
802 development, Banff region, southwestern Alberta, XIV International Congress
803 on the Carboniferous and Permian, Field Trip, 4-7 and 4-17 Guidebook:
804 Calgary, Alberta.

805 Richards, C., Ross, G. M., and Utting, J., 2002, U-Pb geochronology, lithostratigraphy
806 and biostratigraphy of tuff in the Upper Famennian to Tournaisian Exshaw
807 Formation: Evidence for a mid-Paleozoic magmatic arc on the northwestern
808 margin of North America, *in* Hills, L. V., Henderson, C. M., and Bamber, E. W.,
809 eds., *Carboniferous and Permian of the World: XIV ICCP Proceedings*, Volume
810 19, *Can Soc Petrol Geol Mem*, p. 158-207.

811 Rimmer, S. M., 2004, Geochemical paleoredox indicators in Devonian-Mississippian
812 black shales, Central Appalachian Basin (USA), *Chemical Geology*, v. 206, no.
813 3-4, p. 373-391.

814 Rudnick, R. L., and Gao, S., 2003, 3.01 Composition of the Continental Crust: Treatise
815 on Geochemistry, v. 3, p. 1-64.

816 Schovsbo, N. H., 2001, Why barren intervals? A taphonomic case study of the
817 Scandinavian Alum Shale and its faunas: *Lethaia*, v. 34, no. 4, p. 271-285.

818 Sclater, F., Boyle, E., Edmond, J., 1976, On the marine geochemistry of nickel: *Earth*
819 and Planetary Science Letters, v. 31, p. 119-128.

820 Selby, D., and Creaser, R. A., 2005, Direct radiometric dating of the Devonian-
821 Mississippian time-scale boundary using the Re-Os black shale
822 geochronometer: *Geology*, v. 33, p. 545-548.

823 Selby, D., Mutterlose, J., and Condon, D. J., 2009, U-Pb and Re-Os geochronology of
824 the Aptian/Albian and Cenomanian/Turonian stage boundaries: Implications
825 for timescale calibration, osmium isotope seawater composition and Re-Os
826 systematics in organic-rich sediments: *Chemical Geology*, v. 265, no. 3-4, p.
827 394-409.

828 Sellwood, B. W., and Jenkyns, H. C., 1975, Basins and swells and the evolution of an
829 epeiric sea (Pliensbachian-Bajocian of Great Britain): *Journal of the Geological*
830 *Society*, v. 131, no. 4, p. 373-388.

831 Shimamura, T., and Lugmair, G. W., 1983, Ni isotopic compositions in Allende and
832 other meteorites: *Earth and Planetary Science Letters*, v. 63, no. 2, p. 177-
833 188.

834 Spath, L. F., 1923, Correlation of the Ibex and Jamesoni Zones of the Lower Lias:
835 *Geological Magazine*, v. 60, p. 6-11.

836 Wasylenki, L., Spivak-Birndorf, L., Howe, H., and Wells, R., 2014, Experiments reveal
837 the mechanism by which Ni isotopes fractionate in the weathering
838 environment: *Goldschmidt Abstracts*, 2661.

839 Wasylenki, L. E., Rolfe, B. A., Weeks, C. L., Spiro, T. G., and Anbar, A. D., 2008,
840 Experimental investigation of the effects of temperature and ionic strength
841 on Mo isotope fractionation during adsorption to manganese oxides:
842 *Geochimica et Cosmochimica Acta*, v. 72, p. 5997-6005.

843 Wasylenki, L. E., Weeks, C. L., Bargar, J. R., Spiro, T. G., Hein, J. R., and Anbar, A. D.,
844 2011, The molecular mechanism of Mo isotope fractionation during
845 adsorption to birnessite: *Geochimica et Cosmochimica Acta*, v. 75, no. 17, p.
846 5019-5031.

847 Wedepohl, K. H., 1971, Environmental influences on the chemical composition of
848 shales and clays: *Physics and Chemistry of the Earth*, v. 8, p. 305-333.

849 Xue, S., Herzog, G. F., Hall, G. S., Klein, J., Middleton, R., and Juenemann, D., 1995,
850 Stable nickel isotopes and cosmogenic beryllium-10 and aluminum-26 in
851 metallic spheroids from Meteor Crater, Arizona: *Meteoritics*, v. 30, p. 303-
852 310.

Figure 1

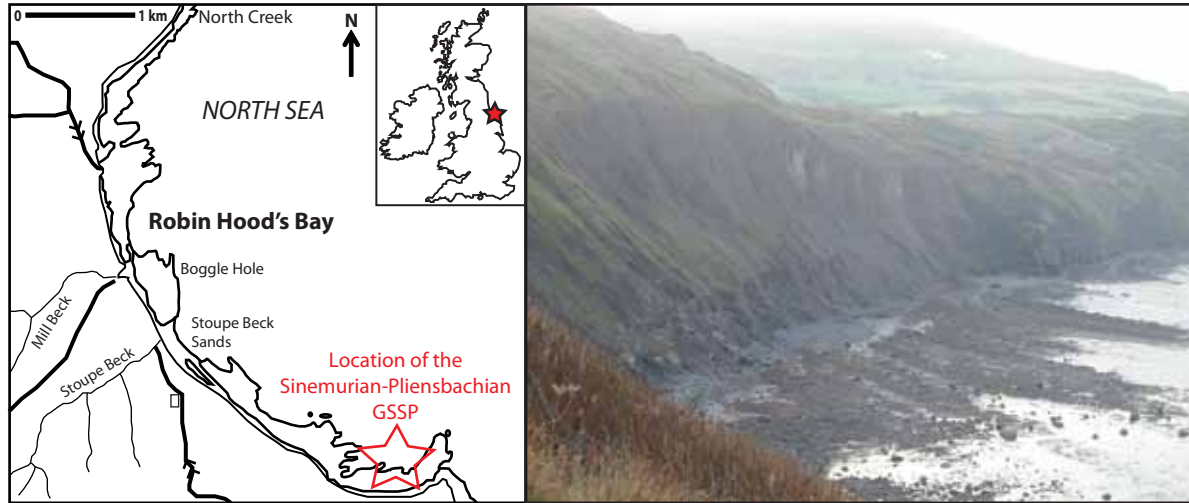


Figure 2

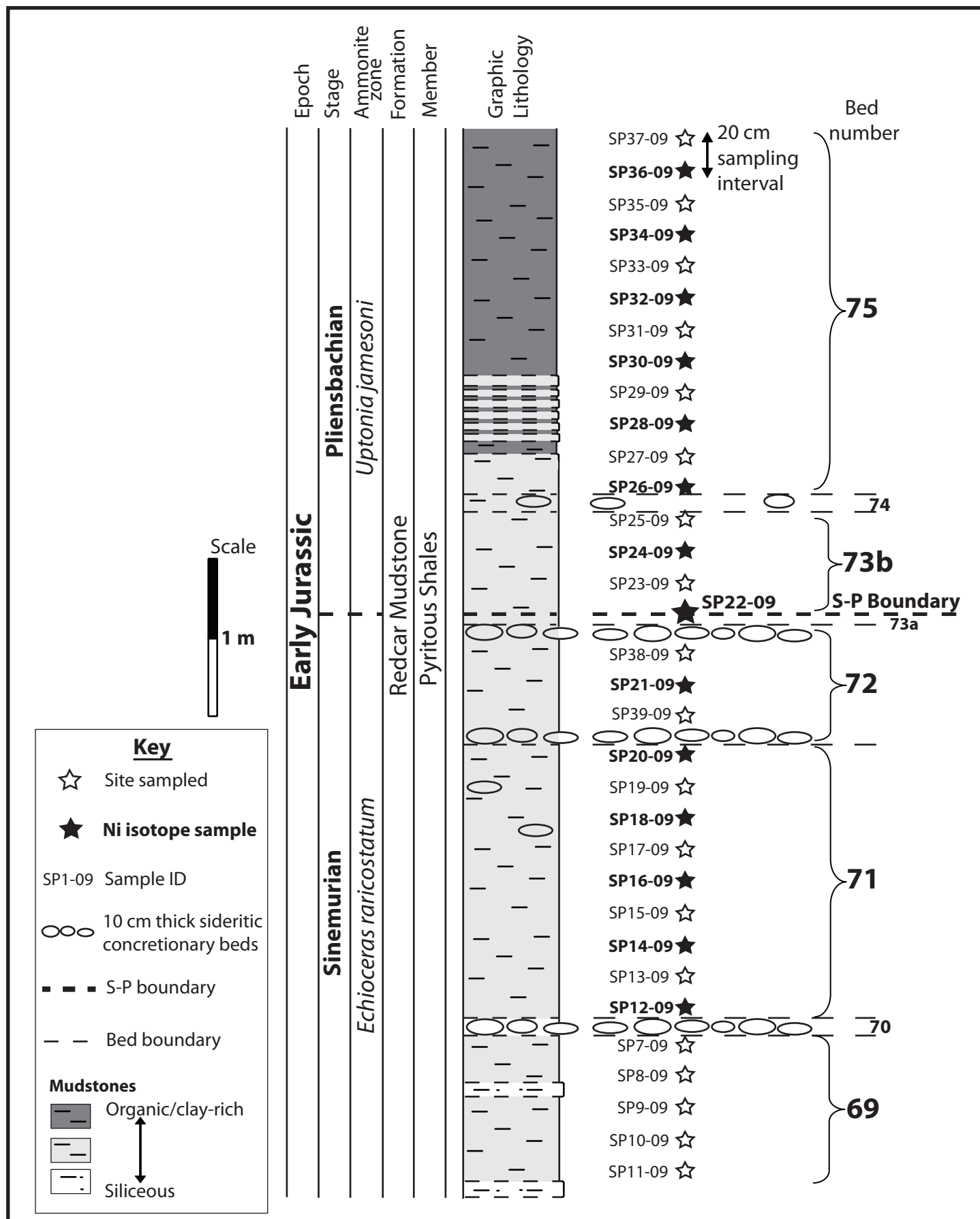


Figure 3

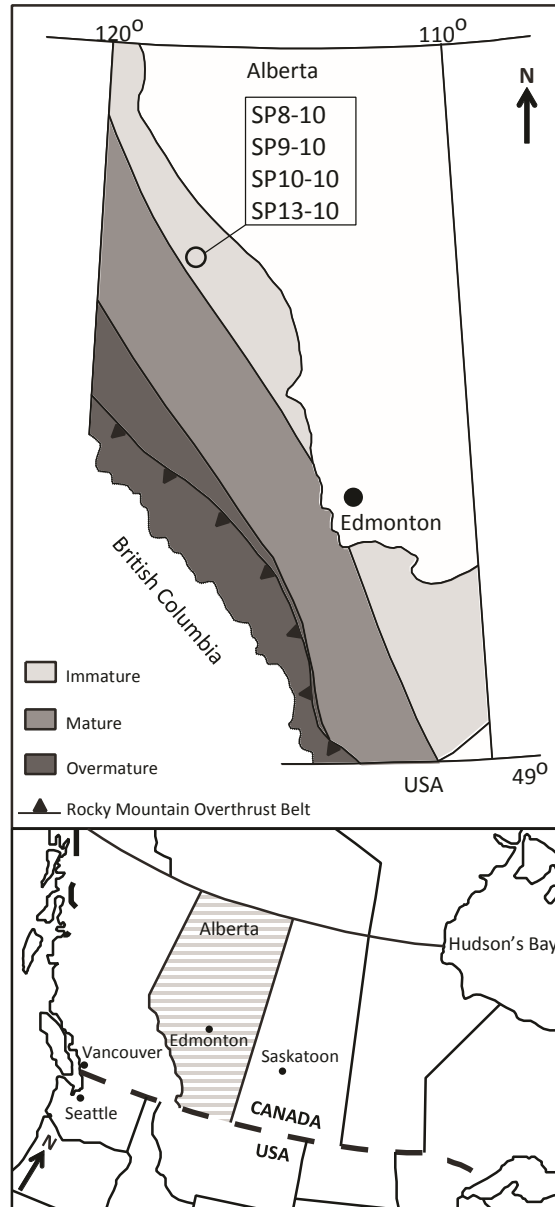


Figure 4

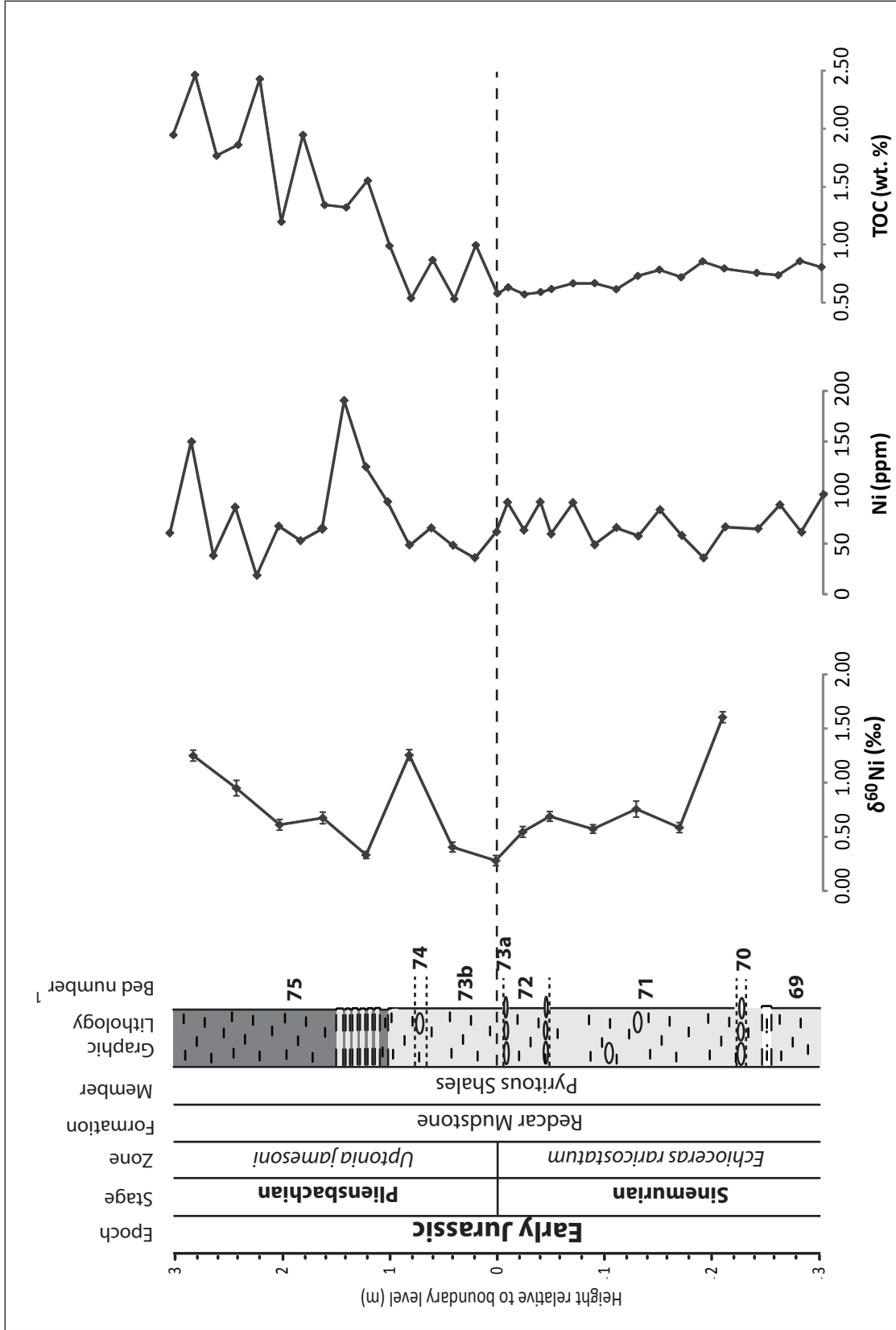


Figure 5

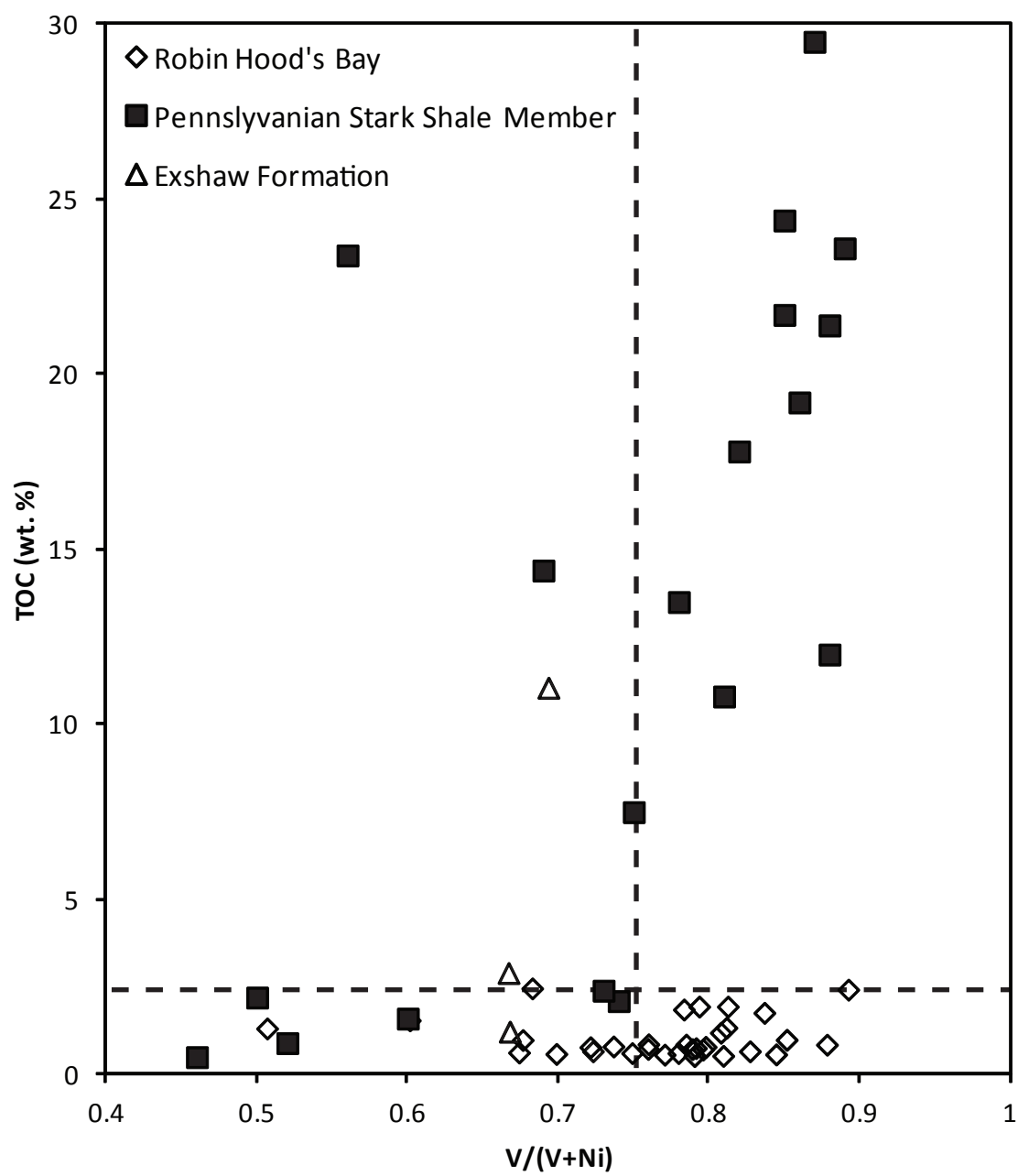


Figure 6

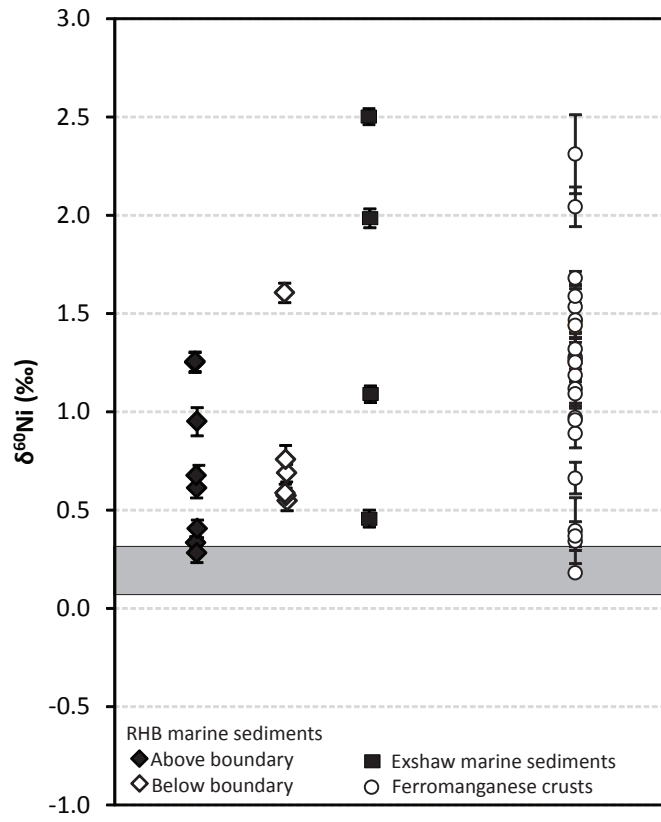


Table 1[Click here to download Table: Table 1 Redox parameters.pdf](#)

	Oxic	Dysoxic	Suboxic-anoxic	Euxinic
V/Cr ^a	<2.00	2.00-4.25	>4.25	
Ni/Co ^a	<5.00	5.00-7.00	>7.00	
V/(V+Ni) ^b		0.46-0.60	0.54-0.82	>0.84

^a Jones and Manning (1994)^b Hatch and Leventhal (1992); Schovsbo (2001)

Table 2

[Click here to download Table: Table 2 Trace element data.pdf](#)

Sample	Distance from S-P boundary (m) ^a	Depth (m) ^b	Trace elements (ppm)				Redox ratios			TOC (wt. %)
			V	Cr	Ni	Co	V/Cr	Ni/Co	V/(V+Ni)	
Robin Hood's Bay, UK										
SP37-09	3.0		230.9	130.6	60.11	26.87	1.77	2.24	0.79	1.94
SP36-09	2.8		322.4	148.2	149.9	24.70	2.18	6.07	0.68	2.46
SP35-09	2.6		194.0	107.6	37.86	18.95	1.80	2.00	0.84	1.76
SP34-09	2.4		309.3	134.5	85.57	19.82	2.30	4.32	0.78	1.86
SP33-09	2.2		152.9	107.5	18.43	12.88	1.42	1.43	0.89	2.43
SP32-09	2.0		280.8	147.3	66.81	16.21	1.91	4.12	0.81	1.20
SP31-09	1.8		227.3	130.9	52.47	20.46	1.74	2.56	0.81	1.94
SP30-09	1.6		277.7	146.9	64.49	16.37	1.89	3.94	0.81	1.34
SP29-09	1.4		195.6	158.7	190.5	20.61	1.23	9.24	0.51	1.32
SP28-09	1.2		188.8	120.2	125.2	34.40	1.57	3.64	0.60	1.55
SP27-09	1.0		189.8	148.2	90.83	21.69	1.28	4.19	0.68	0.99
SP26-09	0.8		204.9	133.4	48.25	16.55	1.54	2.92	0.81	0.54
SP25-09	0.6		205.8	130.1	65.09	22.05	1.58	2.95	0.76	0.87
SP24-09	0.4		181.1	142.6	48.06	17.63	1.27	2.73	0.79	0.53
SP23-09	0.2		204.8	120.1	35.70	19.10	1.71	1.87	0.85	0.99
SP22-09	0.0		332.6	276.8	61.23	18.45	1.20	3.32	0.84	0.58
SP38-09	-0.1		186.7	165.8	90.33	20.09	1.13	4.50	0.67	0.63
SP21-09	-0.3		211.1	122.5	62.86	20.41	1.72	3.08	0.77	0.57
SP39-09	-0.4		210.1	154.5	90.66	20.83	1.36	4.35	0.70	0.59
SP20-09	-0.5		209.2	135.9	59.13	15.35	1.54	3.85	0.78	0.62
SP19-09	-0.7		234.8	164.9	90.00	25.73	1.42	3.50	0.72	0.67
SP18-09	-0.9		231.6	142.8	48.40	18.42	1.62	2.63	0.83	0.67
SP17-09	-1.1		195.1	133.8	65.42	25.03	1.46	2.61	0.75	0.61
SP16-09	-1.3		213.1	132.0	57.04	20.22	1.62	2.82	0.79	0.73
SP15-09	-1.5		214.8	129.9	83.02	25.72	1.65	3.23	0.72	0.78
SP14-09	-1.7		225.0	133.1	57.69	17.88	1.69	3.23	0.80	0.72
SP13-09	-1.9		256.4	127.2	35.53	15.94	2.02	2.23	0.88	0.86
SP12-09	-2.1		261.0	142.8	66.18	23.19	1.83	2.85	0.80	0.79
SP8-09	-2.3		244.2	136.2	64.39	22.01	1.79	2.93	0.79	0.76
SP9-09	-2.6		277.4	140.3	87.84	21.88	1.98	4.01	0.76	0.74
SP10-09	-2.8		222.0	146.7	60.89	21.79	1.51	2.79	0.78	0.86
SP11-09	-3.0		273.9	139.0	97.97	18.88	1.97	5.19	0.74	0.81
Exshaw Formation, Canada^c										
SP8-10		1753	108.7	53.5	3.75	54.08	2.03	14.42	0.67	1.23
SP9-10		1754	40.3	19.5	3.75	80.14	2.07	21.37	0.33	1.99
SP10-10		1756.2	350.2	38.9	11.25	154.88	9.00	13.77	0.69	11.05
SP13-10		1756.5	132.8	18.5	4.11	66.33	7.17	16.15	0.67	2.90

^a Parameter only applicable to Robin Hood's Bay samples

^b Parameter only applicable to Exshaw Formation samples

^c All samples are thermally immature and from core 3-19-80-23W5

Table 3

[Click here to download Table: Table 3 Ni isotope data.pdf](#)

Sample ID	Distance from S-P boundary (m) ^a	Depth (m) ^b	$\delta^{60}\text{Ni}$ (‰)	2σ	Ni (ppm)
<i>Robin Hood's Bay, UK</i>					
SP36-09	2.8		1.25 ± 0.05		149.92
SP34-09	2.4		0.95 ± 0.07		85.57
SP32-09	2		0.61 ± 0.05		66.81
SP30-09	1.6		0.67 ± 0.05		64.49
SP28-09	1.2		0.33 ± 0.03		125.18
SP26-09	0.8		1.26 ± 0.05		48.25
SP24-09	0.4		0.40 ± 0.05		48.06
SP22-09	0		0.28 ± 0.05		61.23
SP21-09	-0.25		0.55 ± 0.05		62.86
SP20-09	-0.5		0.69 ± 0.04		59.13
SP18-09	-0.9		0.57 ± 0.04		48.40
SP16-09	-1.3		0.76 ± 0.07		57.04
SP14-09	-1.7		0.58 ± 0.05		57.69
SP12-09	-2.1		1.60 ± 0.05		66.18
<i>Exshaw Formation, Canada^c</i>					
SP8-10		1753	1.09 ± 0.04		54.1
SP9-10		1754	1.98 ± 0.05		80.1
SP10-10		1756.2	0.46 ± 0.04		154.9
SP13-10		1756.5	2.50 ± 0.04		66.3

^a Parameter only applicable to Robin Hood's Bay samples^b Parameter only applicable to Exshaw Formation samples^c All samples are thermally immature and from core 3-19-80-23W5

Table 4

[Click here to download Table: Table 4 Elemental summary.pdf](#)

Element (ppm)	Average shale ^a	Average		
		Upper Crust ^b	This Study ^c	This study ^d
Ni	68	47	18-190	54-154
Co	19	17	3-11	12-34
V	130	97	152-332	40-350
Cr	90	92	107-268	18-53

^a Average shale values from Wedepohl (1971)

^b Average upper continental crust values from Rudnick and Gao (2003)

^c Samples from Robin Hood's Bay, UK

^d Samples from the Exshaw Formation, Canada