

1 **Lower Wenlock black shales in the northern Holy Cross Mountains, Poland:**
2 **sedimentary and geochemical controls on the Ireviken Event in a deep marine**
3 **setting**

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21
22 **Abstract**

23 The stratigraphic variability and geochemistry of Llandovery/Wenlock (L/W) Series
24 boundary sediments in Poland reveals that hemipelagic sedimentation under an anoxic/euxinic
25 water column was interrupted by low density bottom currents or detached diluted turbid
26 layers that resulted in intermittent seafloor oxygenation. TOC values and inorganic proxies
27 throughout the Wilków 1 borehole section suggest variable redox conditions. U/Mo ratios >1
28 throughout much of the Aeronian and Telychian Stages, together with an absence of pyrite
29 framboids, suggests oxygenated conditions prevailed. However, elevated TOC near the
30 Aeronian/Telychian boundary, together with increased U/Th and V/(V+Ni) ratios and
31 populations of small pyrite framboids are consistent with the development of dysoxic/anoxic
32 conditions at that time. U/Th, V/Cr and V/(V+Ni) ratios, as well as U_{authig} and Mo
33 concentrations suggest that during the Ireviken black shale (IBS) deposition, bottom-water
34 conditions deteriorated from oxic during the Telychian to mostly suboxic/anoxic immediately

35 prior to the L/W boundary, before a brief reoxygenation at the end of the IBS sedimentation
36 in the Sheinwoodian Stage. Rapid fluctuations in U/Mo during the Ireviken Event (IE) are
37 characteristic of fluctuating redox conditions that culminated in an anoxic/euxinic seafloor in
38 the Sheinwoodian. Following IBS deposition, conditions once again became oxygen deficient
39 with the development of a euxinic zone in the water column. The Aeronian to Sheinwoodian
40 deep-water redox history was unstable, and rapid fluctuations of the chemocline across the
41 L/W Series boundary probably contributed to the IE extinctions, which affected mainly
42 pelagic and hemipelagic fauna.

43

44 Keywords: Ireviken Event, redox conditions, inorganic proxies, pyrite framboids, Silurian

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46

47 **1. Introduction**

48

49 The Ireviken Event (IE) records a little-studied, but important Silurian extinction at the
50 Llandovery/Wenlock (L/W) series boundary (Telychian/Sheinwoodian Stage boundary) (e.g.
51 Calner, 2008). Extinction losses began at the base of the Lower *Pseudooneotodus bicornis*
52 conodont Zone and culminated during the Lower *Kockelella ranuliformis* Zone (e.g. Lehnert
53 *et al.*, 2010). The observed carbon and oxygen isotopic excursions began considerably later,
54 but might share their origins with extinctions, through feedbacks in the carbon and oxygen
55 system. Munnecke *et al.*, (2003) suggested that the anoxia responsible for the extinction
56 losses originated in the deep oceans, before invading the shallower shelf seas. The IE scarcely
57 affected shallow-water reefs, while pelagic and hemipelagic organisms such as the graptolites,
58 conodonts and trilobites suffered preferential losses (Calner, 2008).

59 Until now, the reconstruction of palaeoenvironments during the IE has been based on
60 stable carbon and oxygen isotope studies (Munnecke *et al.*, 2003; Cramer & Saltzman, 2005,
61 2007; Noble *et al.*, 2005; Loydell & Fryda, 2007; Lehnert *et al.*, 2010; Vandenbroucke *et al.*,
62 2013), but interpretations have not always been consistent with other sedimentological and
63 geochemical observations (e.g. Page *et al.*, 2007). Some palaeoceanographic models infer
64 permanent anoxia in the pycnocline (Wilde *et al.*, 1991; Bickert *et al.*, 1997), while other
65 authors propose cold, oxic bottom water regimes during deposition of Silurian sediments
66 (Jeppsson, 1990). Major discrepancies exist in proposed sea-level histories (see compilations
67 in Munnecke *et al.*, 2010; Melchin *et al.*, 2012) and in the origins of redox changes (Jeppsson,
68 1990; Bickert *et al.*, 1997; Page *et al.*, 2007).

69 Most knowledge of the IE derives from much better exposed shallow shelf settings
70 (e.g. Munnecke *et al.*, 2003; Lehnert *et al.*, 2010; Racki *et al.*, 2013). Here we investigate
71 palaeoredox conditions from a scarcely studied deep shelf setting using geochemical,
72 petrographical and sedimentological methods. Our palaeoenvironmental proxies have never
73 before (pyrite framboids) or only rarely (inorganic indicators) been applied to the Ireviken
74 extinction event (Emsbo *et al.*, 2010; Racki *et al.*, 2013).

75

76 **2. Geological setting**

77

78 The Holy Cross Mountains (HCM) region of central Poland is traditionally subdivided
79 into the Małopolska Massif (MM) in the south and the Łysogóry Unit (LU) in the north,
80 separated by the Holy Cross Fault (Fig. 1). The MM is considered as a proximal terrane that
81 separated from Baltica but became reattached some time before the late
82 Cambrian/Ordovician. The LU is treated as a part of the passive margin of this
83 palaeocontinent (Dadlez *et al.*, 1994). During the Silurian these units are believed to have
84 occupied a position close to the present SW margin of Baltica which, according to the
85 reconstruction of Torsvik & Rehnström (2001), Hartz & Torsvik (2002) and Cocks & Torsvik
86 (2005), was located between 30°S and 60°S (Cocks, 2002; Nawrocki *et al.*, 2007).

87

88 The Silurian system in the HCM consists of up to 200m of Llandovery – lower
89 Ludlow (Rhuddanian to Sheinwoodian Stages) shale and mudstone deposits which are
90 overlain by a ~2000 m thick succession of greywacke sandstones, mudstones and carbonates
91 (Kozłowski, 2008). These sediments filled a foredeep basin that extended from the HCM to
92 the present SW margin of Baltica (Poprawa *et al.*, 1999; Narkiewicz, 2002) (Fig. 1). The
93 Rhuddanian part of the Silurian shale and mudstone succession is made up of black shales and
94 cherts that accumulated under upwelling conditions (Kremer, 2005) generated by the SE trade
95 winds (Trela & Salwa, 2007). They belong to the Bardo Formation (*op. cit*) and contain a
96 graptolite fauna indicative of the *ascensus/acuminatus*, *vesiculosus* and *cyphus* Zones
97 (Tomczyka & Tomczykowa, 1976; Podhalańska & Trela, 2007). The overlying Aeronian to
98 Gorstian sediments are represented by grey/green shales and mudstones interrupted by a
99 conspicuous black shale intervals of various thickness (up to c.a. 50 cm). In the regional
100 lithostratigraphic subdivision these shales and mudstones are given various informal names
101 (Modliński & Szymański, 2001). The graptolite data indicate that black shale horizons
102 reported in the HCM are coeval with prominent sea-level and palaeoceanographic changes

103 documented by Page *et al.* (2007). A relatively thick black shale interval (10-12 m thick)
104 occurs at the Llandovery/Wenlock Series boundary and straddles the lower Sheinwoodian
105 *murchisoni* graptolite Zone. This bed is correlated with the worldwide Ireviken Event.

106

107 **3. Materials and Methods**

108

109 The Wilków 1 borehole spans almost all of the Lower Silurian (excluding
110 Rhuddanian) and it records deep shelf facies that are not known from other European
111 sections. Fifty-three samples were collected from the Wilków 1 borehole (Fig. 1), which
112 comprises claystones and black shales (see Deczkowski & Tomczyk, 1969). Due to the
113 relatively high thermal maturation of the sediments (within the “gas window”; conodont
114 alteration index: $CAI > 2$ [Narkiewicz, 2002]; vitrinite-like maceral values calculated to
115 vitrinite reflectance $VR_{equ} = \sim 1.7\%$ [Smolarek *et al.*, 2015]), our research has focused on
116 redox proxies that are not susceptible to alteration by heat, such as pyrite framboid
117 petrography and trace metal concentrations. Sedimentological observations of colour,
118 lithology, sedimentary structures and ichnofabric are supported by thin section petrography of
119 microfacies.

120

121 **3.a. Geochemical signature**

122

123 3.a.1. Total organic carbon (TOC) and total sulphur (TS)

124 Total carbon (TC), total inorganic carbon (TIC) and total sulphur (TS) contents were
125 measured in 53 samples using an Eltra CS-500 IR-analyser with a TIC module. TC were
126 determined using an infrared cell detector on CO_2 gas, which was evolved by combustion
127 under an oxygen atmosphere. TIC contents was derived from reaction with 15% hydrochloric
128 acid and CO_2 was determined by infrared detector. TOC was calculated as the difference
129 between TC and TIC. Calibration was made by means of the Eltra standards. Analytical
130 precision and accuracy were better than $\pm 2\%$ for TC and $\pm 3\%$ for TIC.

131

132 3.a.2. Trace metals analysis

133 34-rock samples from the Wilków 1 borehole were analysed at AcmeLabs,
134 Vancouver, Canada. Samples were chosen based on their position in the section. Major oxides
135 and several minor elements (Ba, Ni, Sr, Zr, Y, Nb, Sc) were measured using ICP-emission
136 spectrometry following a lithium borate fusion and dilute acid digestion of a 0.2g sample

137 pulp. Two separate ICP-MS analyses of trace elements were performed to optimize
138 determination of a 31-element suite (Ba, Be, Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, U, V, W,
139 Zr, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). The reliability of analytical
140 results was monitored by the analyses of international standard reference materials and
141 duplicate analyses of a few samples. Precision and accuracy of the results were better than
142 $\pm 0.05\%$ (mostly $\pm 0.01\%$) for the major elements and generally better than ± 1 ppm for the trace
143 elements.

144

145 3.a.3. Pyrite framboid analysis

146 Pyrite framboid analysis has become a widely used petrographic palaeoredox proxy
147 (e.g. Wignall & Newton, 1998; Bond & Wignall, 2010; Wignall et al., 2010). It is especially
148 valuable for evaluating thermally altered or weathered outcrop samples because, whilst the
149 framboids are sometimes pseudomorphed by iron (oxyhydr)oxides, their distinctive size
150 distributions are retained (Lüning et al., 2003). 28 samples in the form of small chips were
151 polished and examined for pyrite framboid populations using a Philips Environmental
152 Scanning Electron Microscope (ESEM) in back-scattered electron (BSE) mode at the
153 University of Silesia (Sosnowiec, Poland). Framboid diameters (in μm) were measured using
154 the ESEM internal measuring device. Where possible, at least 100 framboids were measured
155 per sample. In samples W 582.3 and W 583.8, fewer than 100 framboids were measured (33
156 and 36 counts respectively) due to their scarcity. The minimum, maximum and mean diameter
157 of framboids in each sample, and their standard deviation were calculated. Framboid size-
158 frequency distributions are depicted in the form of box and whisker plots (see e.g. Wignall &
159 Newton, 1998), and we have generated histograms to better show the size-frequency
160 distribution within a given framboid population.

161

162 **4. Results**

163

164 4.a. Stratigraphy

165 The Silurian of the Wilków 1 borehole includes Middle Llandovery to Lower Ludlow
166 mudstones and shales (601.0 - 417.0 m) overlain by Upper Ludlow fine-grained greywackes,
167 mudstones and shales (Deczkowski & Tomczyk, 1969). The older part of the succession
168 consists largely of grey to dark grey and subordinate black shales that belong to two informal
169 lithostratigraphic units (the Ciekowieckie and Wilkowskie Beds) (Fig. 2).

170 Deczkowski & Tomczyk (1969) reported tectonic contact between the Hirnantian
171 sandy mudstones of the Zalesie Formation (sensu Trela, 2006) and Silurian (uppermost
172 Aeronian Stage) shales of the *sedgwickii* Zone (Table 1), suggesting a hiatus of at least 6
173 million years in the borehole. Deczkowski & Tomczyk (1969) postulate tectonic zones within
174 the Silurian succession, which may have been responsible for the stratigraphic incompleteness
175 of the Wilków section. Nevertheless, the borehole exposes a prominent 9m thick black shale
176 that spans the lower Wenlock *murchisoni* and *riccartonensis* graptolite Zones and extends up
177 to the *flexilis* Zone (Table 1). The black shales are bound at their base by grey shales of the
178 lower Telychian *turriculatus* to *crenulata* Zones (Deczkowski & Tomczyk, 1969), suggesting
179 that the upper Telychian is missing. It cannot be excluded that the 2m thick black shale /
180 greenish grey mudstones below the first appearance of *Cyrtograptus murchisoni* (at a depth of
181 585.0 m) are upper Telychian. The Wenlock (Early Sheinwoodian *murchisoni* -
182 *riccartonensis* – *flexilis* graptolite Zones) black shales grade upwards into grey shales
183 extending up to *leintwardinensis* Zone of the lower Ludfordian stage (Deczkowski &
184 Tomczyk, 1969) (Table 1).

185

186 4.b. Sedimentary facies: distribution and description

187 Detailed sedimentological study reveals that the apparently monotonous lower
188 Wenlock black shale horizon in the Wilków 1 borehole consists of two distinctive facies, each
189 recording its own depositional conditions. The dominant facies is dark grey to black shales
190 (up to 4.5 m thick), whilst the second facies comprises light grey to greenish-grey clayey
191 mudstones (up to 7 m thick; Fig. 2). The black shales form four horizons interrupted by thin
192 greenish-grey mudstones that sometimes alternate with thin dark shales. Graptolite faunas
193 place the lower black shale horizons within the *murchisoni* Zone, and the upper black shales
194 within the *riccartonensis* – *flexilis* Zones (Table 1). The sandwiched greenish-grey mudstone
195 intervals appears to correlate with the lower *murchisoni*, *rigidus/riccartonensis* boundary and
196 *flexilis* Zone (Table 1; Fig. 3).

197 Dark to black shales reveal conspicuous lamination on a submillimetre to millimetre
198 scale, enhanced by light grey mudstone laminae (Fig. 3A). Black laminae are enriched in fine
199 short fibres of organic matter which in some cases are wrinkled and usually located parallel to
200 the lamina surface (Fig. 3B). The detrital material (silt-size quartz and mica flakes), pyrite
201 framboids and carbonate crystals are trapped between fibres. The mudstone laminae consist of
202 fine silt-sized quartz and are apparently homogenous, however some of them show subtle
203 normal grading and discrete mottling as a result of bioturbation (Fig. 3B). Their contact with

204 the black shale laminae is seen to be variously gradational and sharp. This facies exhibits
205 subordinate erosional surfaces (Fig. 3C) and common, tiny mudstone clasts of submillimetre
206 size that appear as light and rounded spots in the darker matrix (Fig. 3C).

207 The grey and greenish-grey mudstones are present both as thin beds and as intervals of
208 several dozen meters (Fig. 3E). They are largely homogenous with subordinate subtle
209 bioturbation, although some beds reveal flame structures, rip-up clasts, tiny load-casts,
210 inclined microlamination, current ripples and discrete laminae consisting of silt-sized quartz
211 grains (Fig. 3E, F & G). In some cases, mudstone beds are interrupted by dark laminae
212 consisting of submillimetre size mudstone clasts (Fig. 3G).

213

214 4.c. Bulk geochemical data (TOC, TS, CC)

215 Despite being lithologically rather similar, the tested samples are characterized by
216 major variations in TOC, ranging from c.a. 0.2% to 2.7% (Table 3; Fig. 4). TOC values in the
217 Aeronian and Telychian samples do not usually exceed 0.5%. TOC content increases just
218 before the Telychian / Sheinwoodian (Llandovery / Wenlock) boundary, and during the
219 Ireviken black shale sedimentation TOC values fluctuate between 0.6% and 2.7% (Fig. 4).
220 Younger Sheinwoodian samples are characterized by relatively stable and generally higher
221 TOC values in the range of 1.5 % to 2.2%. The total sulphur record follows a similar pattern
222 to that of TOC concentration, excluding a single sample (W 583.0) that is very rich in TS but
223 poor in TOC (possibly due to hydrothermal mineralization by sulphides – see e.g.
224 Rubinowski, 1969). Thus, a good correlation between TOC and TS ($R^2 = 0.7$) is observed,
225 suggesting normal marine deposition (Sageman & Lyons, 2004). Carbonate content (CC)
226 does not exceed 20% by weight, and in most of the samples ranges between 3% and 10%.

227

228 4.d. Trace metal palaeoredox proxies

229

230 Generally, all of our inorganic redox proxies are in accordance, and are indicative of a
231 variety of bottom water redox conditions (Fig. 5). Only the Ni/Co ratio values are out of step
232 with other data (this is not unusual, see Racka et al., 2010), and we have not included Ni/Co
233 in Fig. 5. The lack of correlation between Ni/Co ratio and other trace metal proxies might be
234 attributed to upwelling activity (resulting in Co depletion [Brumsack, 2006]) especially in the
235 upper part of the section, and/or very unstable redox conditions at the Llandovery / Wenlock
236 boundary that lead to partial pyrite oxidation and release of Co and Ni (see Tribovillard et al.,
237 2006; Swanner et al., 2014). The V/(V+Ni), V/Cr, and U/Th ratios, and Mo and U

238 concentrations are low through almost the entire Aeronian and Telychian (excluding some
239 elevated values at the beginning of Aeronian noted for e.g. sample W 601.0). The V/(V+Ni)
240 ratio does not exceed 0.7, U/Th ranges from 0.2 to 0.4, V/Cr ranges from 1 to 2, authigenic
241 uranium (U_{authig}) is below 1 and Mo is about 2 ppm. U/Mo fluctuates between 1.5 and 3.7
242 (Table 4).

243 The uppermost Telychian and the IE in the basal Sheinwoodian records an increase in
244 all inorganic redox proxy ratios, as well as Mo concentrations and U_{authig} content (and also a
245 decrease in U/Mo which subsequently becomes rather unstable). This is consistent with the
246 development of reducing conditions across the Telychian / Sheinwoodian boundary (Fig. 5,
247 Table 4). Following a short phase during which these proxy values decreased, they once again
248 increased and stabilized for the duration of the Sheinwoodian, with values characteristic of
249 anoxic / euxinic conditions (V/(V+Ni) and U/Mo) or of dysoxic (and sporadically oxic)
250 environments (U/Th, U_{authig} and V/Cr) (Table 4). A similar discrepancy whereby V/(V+Ni)
251 exhibits a similar pattern to the other inorganic proxies, but is suggestive of more oxygen-
252 restricted regimes has been recognized in other basins (Rimmer, 2004; Racka *et al.*, 2010).

253

254 4.e. Pyrite framboids

255 Pyrite framboids are common in almost all the Llandovery and Wenlock shales,
256 excluding Telychian samples between 594.3 and 587.1 metres depth, where framboids were
257 absent but euhedral pyrite and other sulphides (e.g. sphalerite) are recorded.

258 The Rhuddanian and Aeronian samples contain abundant small framboids (mean
259 diameters around 5 μm), with low standard deviations (Table 2). The beginning of Telychian
260 is marked by the disappearance of framboids, which remained absent through most of the
261 stage. Small framboids reappear at the end of the Telychian, at a depth of 586.0m in the
262 borehole. The samples from the IE interval are characterized by very rapid fluctuations in
263 pyrite framboid size distributions and in their standard deviations (Table 2, Fig. 4). For
264 example, in the laminated shale at depth 585.0m, pyrite framboids occur along individual
265 laminae. Analyses of framboids from individual laminae (negating time-averaging effects, see
266 Wignall *et al.*, 2010) yield different framboid size frequencies, suggesting rapidly changing
267 conditions (in this case from anoxic / euxinic to upper dysoxic (Fig. 6a & b). In sample W
268 598.2 the contact between lighter and darker sediments separates very different framboid
269 populations (in the lighter layer framboids suggest dysoxic conditions, while the darker layer
270 contains a framboid population characteristic of anoxia/euxinia (Fig. 6c & d). Above the

271 Telychian / Sheinwoodian boundary framboid diameters have a very narrow range (mean c.
272 4.0 μm , SD c. 1.0), typical of restricted, oxygen-free conditions.

273 **5. Discussion**

274
275 5.a. Facies evolution on the basis of sedimentological record

276 The Lower Wenlock (Sheinwoodian) benthic oxygenation history and associated sea-
277 level changes recorded in the Wilków 1 borehole were likely driven by major early
278 Sheinwoodian climatic changes (compare Page *et al.*, 2007). Thus, sedimentological and
279 stratigraphic data from South America indicates that the Llandovery and Early Wenlock saw
280 the expansion of glaciation on Gondwana (Diaz-Marinez & Grahn, 2007) driving third-order
281 eustatic sea-level changes and consequently impacting on palaeoceanographic conditions
282 (Loydell, 2007; Lehnart *et al.*, 2010). In sequence stratigraphic terms, black shales record
283 either the basal part of the transgressive systems tract, or the maximum flooding surface
284 (Wignall, 1991; Wignall & Maynard, 1993). In the early Sheinwoodian shale and mudstone
285 succession of the LU the black shales derived from sediment starvation and oxygen deficient
286 conditions during deglacial transgressive periods that favoured the development of benthic
287 microbial mats and biofilms that are preserved as organic matter fibres. However, the fine silt
288 material in the lighter coloured laminae indicate periodic deposition from diluted low density
289 bottom currents, or dust clouds of aeolian origin interrupting accumulation of hemipelagic
290 organic-rich clays (see O'Brien, 1996). Tiny mudstone micro-clasts within the dark laminae
291 probably originated from the intermittent erosion of a partially consolidated mudstone
292 substrate and subsequent transport by bottom currents. A similar fabric has been interpreted
293 elsewhere as the result of accumulation of faecal pellets or burrow fills modified by
294 compaction (see Schieber *et al.*, 2010). The activity of bottom currents contributed to short-
295 lived oxygenation events in the LU sedimentary basin and to periodic water column mixing
296 (compare with Schieber, 1994).

297 The Sheinwoodian greenish-grey mudstones record periods of long-lived benthic
298 oxygenation that promoted bioturbation and subsequent homogenization of the muddy
299 sediment. The occurrence of discrete erosional (rip-up clasts, cut and fill, and flame
300 structures) and sedimentary structures within this facies suggests that bottom currents
301 influenced sedimentary conditions. According to Page *et al.* (2007) this type of shale and
302 mudstone facies can result from water-column ventilation in response to increased
303 thermohaline circulation during the glacial maxima and regressions.

304 Graptolite faunas clearly correlate the Lower Wenlock black shale horizons in the LU
305 with the *murchisoni* and late *riccartonensis* Zone sea-level highs postulated by Loydell (1998)
306 and Loydell & Frýda (2007). The black shales are interrupted by a relatively short interval of
307 increased greenish-grey mudstone intercalations which may reflect sea-level fall from the late
308 *murchisoni* to early *riccartonensis* graptolite Zones (*op. cit.*). Thin green mudstones above the
309 upper *riccartonensis* black shales appear to be coeval with Loydell's (1998) short-term
310 regressive-transgressive event during the *flexilis* Zone (Table 1). As is the case in the eastern
311 Baltic area (Loydell, 1998; Kaljo & Martma, 2006), there is a stratigraphic gap in the Wilków
312 section that spans the upper Telychian and appears to be related to sea-level fall during this
313 time interval. The base of the black shale interval may be of uppermost Telychian age, but a
314 lack of precise biostratigraphic data hampers any sequence stratigraphic correlations and sea-
315 level reconstructions.

316

317 5b. Reconstruction of depositional environments based on integrated geochemical proxies

318 There is general correspondence between total organic carbon (TOC) and our
319 inorganic redox proxies, which reveal repeated changes in benthic oxygenation. Two peaks in
320 TOC occur near the Aeronian / Telychian boundary and during the lower Telychian. The later
321 phase of enhanced TOC continued across the Telychian / Sheinwoodian boundary and (with
322 some fluctuations) well into the Sheinwoodian (Figs. 4 & 5). The TOC increase associated
323 with the Aeronian / Telychian boundary is probably the local manifestation of the so called
324 "Sandvika event" (Calner, 2008), but there is lack of comparable data from other worldwide
325 sections. Similar TOC values from the Sheinwoodian (basal Wenlock) were reported by
326 Loydell & Fryda, (2007) from the Banwy River section, Wales and by Racki *et al.*, (2013)
327 from the Podolia, Ukraine and patterns are similar to those presented here. In both cases
328 authors reported noticeable increase of TOC concentration in the lower Wenlock deposits, but
329 in those relatively shallow facies absolute values are two to three times lower than those
330 observed in the Holy Cross Mountains. Vandenbroucke *et al.* (2013) inferred that primary
331 productivity increased just before the IE on the basis of sections in Gotland. Further afield,
332 Noble *et al.*, (2005), noted a sharp increase in TOC to 3% precisely at the Telychian /
333 Sheinwoodian boundary in the deep water Cape Phillips Formation, Arctic Canada, followed
334 by a similarly sharp decrease to < 1% during the *centrifugus – insectus* Zone (Table 1). The
335 above data suggests that in deeper shelf settings TOC enrichment began prior to the L/W
336 boundary while in shallow water sections this did not begin until after L/W boundary. This
337 implies that oxygen depleted waters expanded from the deeper parts of the basin (compare to

338 the model of Hammarlund *et al.*, 2012 proposed for the Ordovician/Silurian boundary) and
339 reached the deep shelf during the early Wenlock.

340 Such a scenario is confirmed by our inorganic proxies. U/Th ratios suggest that during
341 the IE, bottom-water conditions changed from being initially oxic at the end of Telychian to
342 suboxic / anoxic, before returning to oxic for a short time at the end of the event (Fig. 5). A
343 similar history can be inferred from V/Cr values, U_{authig} and Mo concentrations (Table 4). The
344 values of $V/(V+Ni)$ are suggestive of more oxygen-restricted conditions, from dysoxic/anoxic
345 (0.5 - 0.8, see Table 4) in the basal and middle parts of the section to euxinic (> 0.84) by the
346 upper Sheinwoodian (Fig. 5). We observe general similarities between patterns in the above
347 mentioned redox proxies with the U/Mo ratio, defined recently by Zhou *et al.*, (2012) as a
348 depositional environment indicator that distinguishes anoxic/euxinic from dysoxic conditions
349 (Table 4). The U/Mo proxy (Zhou *et al.*, 2012) as applied to the Wilków 1 section reveals
350 $U/Mo > 1$ in the Aeronian and Telychian, suggesting oxygenated conditions. Fluctuating
351 values during the IE include those < 1 in the Sheinwoodian that are characteristic of an
352 anoxic/euxinic redox environment (Zhou *et al.*, 2012).

353 Elevated TOC near the Aeronian / Telychian boundary, together with increased U/Th
354 and $V/(V+Ni)$ ratios (Fig. 5) and the occurrence of small pyrite framboids (see below)
355 suggests that more oxygen-restricted conditions prevailed during the lesser known Sandvika
356 event. However, other inorganic proxies shows no significant changes.

357 Based on these results, Aeronian sedimentation records dysoxic to anoxic/euxinic
358 conditions, and almost the entire Telychian was oxic. The L/W boundary interval was
359 distinguished by rapidly changing conditions from dysoxic to anoxic/euxinic, even down to
360 the millimetre scale within the studied sediments (Fig. 6). The youngest investigated
361 sediments of the Sheinwoodian Stage yield relatively stable values for all inorganic proxies,
362 indicative of dysoxic to anoxic sedimentary conditions.

363

364 5c. Correlation of pyrite framboid and inorganic redox proxies

365 Pyrite framboid analysis is routinely used as palaeoredox proxy and has been applied
366 to marine basins dating back to the Ediacaran (e.g. Wignall & Newton, 1998; Zhou & Jiang,
367 2009; Bond & Wignall, 2010; Wignall *et al.*, 2010; Algeo *et al.*, 2011; Hammarlund *et al.*,
368 2012; Marynowski *et al.*, 2012; Wang *et al.*, 2012). Framboids form in waters that are
369 supersaturated with respect to both Fe monosulphides and pyrite in which reaction kinetics
370 favour the formation of the framboidal varieties of the former (Wilkin *et al.*, 1996). In euxinic
371 basins the locus of framboid and euhedral pyrite formation is separated by the thickness of the

372 sulphidic water column and often Fe limitation within the sediments ensures that sediments
373 have very high proportions of syngenetic framboids (e.g. Ross and Degens, 1974; Wilkin and
374 Arthur, 2001). Syngenetic framboids, such as those in the modern Black Sea, rarely reach 6-7
375 μm diameter before the dense particles sink to the sea bed and accumulate as small-sized
376 populations with a narrow size distribution (Wilkin et al., 1996). This resulting size-frequency
377 distribution is useful for identifying ancient euxinia because it contrasts with framboid
378 populations from more oxygenated settings (Wilkin et al., 1996; Wilkin and Arthur, 2001).
379 Thus, in dysoxic settings (bottom-water oxygen levels between 0.2 – 2.0 ml $\text{O}_2/\text{l H}_2\text{O}$),
380 framboids form within the sediment as populations with a broader size distribution and
381 consequently have a larger standard deviation (Wilkin et al., 1996). In dysoxic sediments
382 formed in the oxygen-minimum zones offshore of Oman and Angola, framboid populations
383 range up to 20 μm diameter (Schallreuter, 1984; Lallier-Verges et al., 1993). Shallower-water
384 dysoxic sediments, such as those encountered in Baltic lagoons have similar-sized populations
385 (Neumann et al., 2005) as do those of the Mississippi shelf where framboids average 9 – 13
386 μm diameter, with a total size range of 4 – 20 μm diameter (Brunner et al., 2006).

387 Pyrite populations of euxinic and dysoxic settings are clearly distinguishable, however
388 the distinction between euxinic and suboxic sediments (forming in bottom waters of 0.0 – 0.2
389 ml $\text{O}_2/\text{l H}_2\text{O}$) is less clear-cut. Recent suboxic sediments from the Santa Barbara Basin have
390 very small framboid populations at some levels that are typical of those encountered in
391 euxinic basins (Schieber and Schimmelmann, 2006, 2007). It may be that the smaller
392 framboid populations settled from the water column during transient euxinia – brief phases
393 that would be impossible to distinguish in the geological record, due to the time-averaging
394 effect of analysing a rock chip typically of 1 – 2 cm thickness. This effect is particularly
395 notable in environments subject to high amplitude redox changes. The Salton Sea, a
396 hypereutrophic lake in southern California, experiences summer euxinia and winter oxic. Its
397 sediments contain abundant framboids showing a narrow size-frequency distribution around 5
398 μm that record the euxinic phases (De Koff et al., 2008), but not the oxic phases. However,
399 redox fluctuations in the HCM are likely to have been less dynamic at the yearly-to-decadal
400 scale due to the large water masses involved.

401 Comparing TOC and inorganic palaeoredox indicators with pyrite framboid size
402 distributions in the Wilków borehole (Figs. 4 & 5) yields a good correlation between all (in
403 particular there is strong agreement in redox inferred from pyrite framboids and the $\text{V}/(\text{V}+\text{Ni})$
404 ratio). Pyrite framboids are absent from almost all of the Llandovery section (10 m thick)

405 which also records very low TOC, and low inorganic proxy values. During the Telychian /
406 Sheinwoodian boundary interval, all proxies display sharp fluctuations (on the cm scale) that
407 indicate a full range of conditions from oxic/dysoxic to euxinic. Above the 6 m thick
408 Telychian / Sheinwoodian boundary interval, most of our redox proxies stabilized. Thus,
409 Wenlock sedimentary rocks contain exclusively small pyrite framboid diameters, and
410 relatively high concentrations of redox sensitive trace metals, typical of anoxic/euxinic
411 conditions.

412

413 5.d. Causes and consequences of sea level changes

414 Three major episodes of L/W boundary sedimentation can be reconstructed, based on
415 new data:

416 i) pre-IE times (Telychian Stage) record a sea level lowstand, intensive water
417 circulation and low productivity. Such conditions might have resulted from sea level fall
418 (Ross & Ross, 1998; Brett *et al.*, 2009 but see also Loydell, 1998; Johnson, 2006; 2010;
419 Spengler & Read, 2010; review in: Munnecke *et al.*, 2010; Melchin *et al.*, 2012) that may be
420 connected with icehouse pulses (Page *et al.*, 2007);

421 ii) during the IE the basin saw intensive chemocline fluctuations during a marine
422 transgression, and moderate productivity. The late Telychian sea level rise and transgression
423 was probably associated with deglaciation, during which sedimentary conditions on the deep
424 shelf became oxygen-restricted. Very intense anoxic/euxinic zone oscillations are recorded by
425 both inorganic proxies and pyrite framboids (Figs. 4 & 5). Typically, rapid chemocline
426 fluctuations result in time-averaged geochemical and petrographic redox proxies that might be
427 interpreted as a signal of dysoxia, but might actually derive from short-lived, repeated oxic to
428 anoxic-euxinic transitions. Rapid fluctuations of the chemocline in the water column, reported
429 also by McLaughlin *et al.*, (2012) represent a potent kill mechanism in the Ireviken mass
430 extinction scenario. Redox changes in the deeper water masses would likely preferentially
431 affect pelagic and hemipelagic organisms (e.g. Jeppson, 1990; Munnecke *et al.*, 2003). These
432 observations are compatible with reconstructions of depositional conditions based on
433 sedimentological data and stable isotope records through the Ireviken black shale deposition
434 by Page *et al.*, (2007) and McLaughlin *et al.*, (2012). The one discrepancy in each of those
435 studies is the interpretation of the transgression / regression pulse, which stems from the use
436 of different sea-level curves (Ross & Ross, 1998; Johnson, 2010) that record local conditions
437 (see e.g. Brett *et al.*, 2009).

438 Two phases of deposition in our environmental model (Fig. 7a & 7b) generally
439 correspond to humid (H) and arid (A) periods described by Bickert *et al.*, (1997). During A
440 conditions at low latitudes, better ventilated episodes frequently occurred due to evaporation
441 and downwelling of warm, saline and well oxygenated surface water. During H periods
442 anoxic deep waters invade deep shelf areas due to estuarine water circulation, leading to
443 deposition of black shales. However, Page *et al.*, (2007) presented a different interpretation of
444 Silurian sea level fluctuations closely connected with glacial events, which correlate well with
445 our geochemical results. A third model (Fig 7c) is proposed for intervals during which
446 inorganic proxies suggests oxic to dysoxic bottom water conditions, but the predominance of
447 tiny pyrite framboids is typical for occurrence of a euxinic water column (e.g. Bond &
448 Wignall, 2008). Our data confirms the occurrence of euxinia in the Silurian ocean (see
449 Munnecke *et al.*, 2003) but the application of multiple proxies adds to the possible water-
450 column structure before and during the IE.

451 iii) following the IE stable conditions developed with a euxinic zone in the water
452 column and dysoxic to sporadically anoxic bottom water and moderate productivity (Fig. 7).

453 Following the Ireviken black shale sedimentation, redox conditions became more
454 stable for a time, reflected in all of our redox proxies (Figs. 4 & 5). An anoxic/euxinic zone
455 occurred in the water column (very small pyrite framboids) while the seafloor experienced
456 oxygen-deficient conditions interspersed with episodes of anoxia/euxinia (inorganic redox
457 proxies; Tables 2 & 4; Fig. 7).

458

459 5e. Comparison of the model with other Palaeozoic events

460 A very similar redox history to that presented here for the Ireviken Event has been
461 described by Hammarlund *et al.*, (2012) and Harper *et al.*, (2013) for the end Ordovician mass
462 extinction event (see also Armstrong & Harper, 2014). Similarities between the end
463 Ordovician and IE have been postulated by Noble *et al.* (2005, and references therein)
464 because of the coincidence of a positive $\delta^{13}\text{C}$ excursion, biotic extinction, widespread eustatic
465 low stands and sedimentary hiatuses in shallow waters, sediments that are poor in organic
466 carbon, and the short duration of events. Our data supports the assertion that the sedimentary
467 redox record for the Ireviken black shale is analogous to that described from end Ordovician
468 event.

469 In parallel scenarios, fluctuating photic zone euxinia in the water column has been
470 proposed for the much better-known Permian–Triassic Panthalassic Ocean successions
471 (Algeo *et al.*, 2011) and Famennian (Late Devonian) black shales (Marynowski *et al.*, 2011;

472 2012). In both scenarios bottom water conditions were at least periodically oxic / dysoxic
473 during black shale deposition despite evidence for euxinia in the water column. In the case of
474 Devonian black shales, the existence of a euxinic water column was confirmed by pyrite
475 framboids and biomarkers from green sulphur bacteria (Marynowski et al., 2011, 2012; Racka
476 et al., 2010). Such palaeoenvironmental scenarios took place with some frequency during the
477 Phanerozoic.

478

479 **6. Conclusions**

480

- 481 • Inorganic trace metal redox proxies suggest that during the Ireviken bio-crisis, bottom-
482 water conditions ranged from oxic (Telychian) to mostly suboxic/anoxic (the first
483 phase of IE) and back to oxic again (the last phase of IE). Oxygen-depleted waters
484 expanded from the deeper parts of the basin and reached the deep shelf during the first
485 phase of Ireviken black shale deposition. Post-IE conditions stabilized and became
486 anoxic/suboxic on the sea-floor with a euxinic zone in the water column.
- 487 • General similarities are observed in the patterns of all our redox proxies and in the
488 U/Mo ratio. Large variations in these values during the Ireviken black shale
489 sedimentation are suggestive of rapid redox fluctuations. Such fluctuations can be
490 connected with deglaciation, in a similar scenario as has been proposed for the O/S
491 extinction event.
- 492 • Rapid fluctuations of the chemocline in the water column during the Ireviken Event
493 was likely a major trigger of the Ireviken mass extinction, which affected mainly
494 pelagic and hemipelagic organisms. Shallow water dwellers, such as reef ecosystems,
495 were relatively unaffected during the IE.

496

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504

505 **7. References**

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719

720 **Figure captions**

721

722 **Fig. 1.** Schematic geological map of the Holy Cross Mountains showing the location of the
723 Wilków 1 borehole ($50^{\circ}54'44.5''N$, $20^{\circ}50'59.4''E$).

724 **Fig. 2.** Schematic cross-section showing stratigraphy and facies pattern of the Llandovery and
725 Wenlock in the Holy Cross Mountains (after Malec, 2006, modified)

726 **Fig. 3.** Sedimentological features of the lower Sheinwoodian rocks from the Wilków 1
727 borehole. **A.** Distinct light laminae with subtle normal grading interrupting dark shales. Note
728 discrete mottling bioturbation within light laminae and erosional surface (es) at its base
729 cutting the underlying dark shale. **B.** Photomicrograph showing details of Fig. 2A (plane
730 polarised light); black laminae enriched in short fibres of organic matter and pyrite framboids
731 intercalated with mudstone laminae. Note scattered silt-sized quartz grains and forming
732 discrete laminae. **C.** Laminated dark shales with light mudstone laminae, erosional surface
733 (es) cutting laminated sediment. Note numerous tiny subrounded mudstone clasts (mc) in dark
734 sedimentary background. **D.** Wispy and discontinuous mudstone laminae interrupting
735 organic-rich background. **E.** Grey/green clayey mudstone interbeds with alternating black
736 shale layers showing mottling bioturbation (mb) in the lower part and parallel lamination in
737 its upper portion, discrete normal grading within the light laminae, current ripple (cr), and
738 load-cast structures (Ls). **F.** Photomicrograph showing discontinuous laminae consisting of
739 silt-sized quartz grains within mudstone beds (PPL). Note dark organic and pyrite rich
740 laminae in the upper part of photomicrograph. **G.** Mudstone with flame structure (fs), rip-up
741 clasts (rc) and tiny mudstone clasts (mc) occurring as light and subrounded spots in dark
742 sedimentary background.

743 **Fig. 4.** Composite plot of the Wilków 1 borehole showing total organic carbon content -TOC
744 (%), carbonate content - CC (%), total sulphur - TS (%) and pyrite framboid diameters [μm]
745 (see Table 2).

746 **Fig. 5.** Stratigraphic distribution of the trace metal redox indicators across the Wilków 1
747 borehole (see Table 3).

748 **Fig. 6.** Histograms showing the distribution of pyrite framboids within two adjacent layers in
749 sample W 585.0 (a and b) and two layers in sample W 598.2 (c: light coloured layer; and d:
750 dark colour layer). Black bars = framboid diameters below 5 μm , Grey bars = framboid
751 diameters above 5 μm . Mean = mean diameter, SD = standard deviation, N = number of
752 measurements, FD = framboid diameter.

753 **Fig. 7.** Three conceptual models showing sedimentary conditions detected before, during and
754 after Ireviken Event: a) before - oxic to sporadically dysoxic sedimentary conditions during a
755 lowstand, with intensive water circulation and low productivity, b) during – very intensive
756 chemocline fluctuations caused by transgressive seas with moderate productivity, c) after –
757 relatively stable conditions with a euxinic zone in the water column and dysoxic to
758 sporadically anoxic bottom waters and moderate productivity.

759

760 **Table captions**

761

762 **Table 1.** Graptolite biozones recognized by Deczkowski & Tomczyk (1969) in grey and black
763 shales.

764 **Table 2.** Pyrite framboid data from Wilków 1 borehole (N = number in sample, SD =
765 standard deviation, FD = framboid diameter).

766 **Table 3.** Percentage content of total organic carbon – TOC (%), carbonate content - CC (%)
767 and total sulphur – TS (%) in samples from the Wilków 1 borehole.

768 **Table 4.** Evolving palaeoredox conditions interpreted for the Wilków 1 borehole as indicated
769 by different trace metals ratios. Threshold values: 1) Hatch & Leventhal (1992); 2) Jones &
770 Manning (1994); 3) Wignall (1994); and 4) Zhou *et al.*, (2012).

771

Stratigraphy		Graptolite biozones	Characteristic species	
Silurian	Wenlock	Sheinwoodian	<i>Cyrtograptus rigidus</i> and <i>C. perneri</i> Zones	<i>Monograptus flemingi primus</i> , <i>Monoclimacis flumendosae</i> , <i>Streptograptus retroflexus</i> , <i>Monograptus latus</i> , <i>Pristiograptus pseudodubius</i> , <i>Monograptus flemingi</i> .
			<i>Monograptus antennularius</i>	<i>M. flexilis</i>
			<i>Cyrtograptus purchisoni</i> and <i>Monograptus riccartonensis</i> Zones	<i>Monograptus priodon</i> , <i>Monoclimacis vomerina</i> , <i>Cyrtograptus purchisoni bohemicus</i> , <i>Pristiograptus cf. dubius</i>
	Llandovery	Aeronian to Telychian	<i>Stimulograptus sedgwickii</i> to <i>Monoclimacis crenulata</i> Zones	<i>Spirograptus cf. turriculatus</i> , <i>M. cf. griestoniensis</i> , <i>Pristiograptus nudus</i> , <i>Monograptus marii</i> , <i>M. vale</i>

Table. 2.

Sample	Min FD [μm]	Max FD [μm]	Mean [μm]	SD	N
W 561.0	1.8	9.4	4.72	1.26	100
W 569.0	1.9	12.3	4.95	1.64	100
W 571.0	2.8	13.0	5.39	1.83	100
W 573.0	1.8	9.6	3.92	1.37	100
W 574.5	2.0	10.8	4.08	1.34	100
W 576.0	1.6	7.9	4.21	1.23	100
W 577.5	2.4	8.2	3.93	0.99	100
W 579.3	2.2	11.9	5.37	1.52	100
W 579.8	2.2	11.2	4.65	1.38	100
W 580.5	3.1	11.2	5.81	1.38	100
W 581.1	1.8	9.2	3.91	1.25	100
W 581.6	3.2	14.5	6.74	2.20	100
W 582.3	3.1	8.3	5.62	1.18	33
W 583.0	2.3	13.0	5.53	1.90	100
W 583.8	4.8	18.2	8.17	2.72	36
W 585.0	2.5	10.9	5.35	1.69	100
W 585.5	2.8	9.3	4.55	1.19	100
W 586.0	2.3	7.9	5.19	1.04	100
W 596.5	3.5	13.3	6.09	1.91	100
W 597.5	2.6	10.8	5.42	1.60	100
W 598.2	2.6	11.6	5.40	1.57	100
W 600.9	2.5	19.0	7.24	2.19	100

776

777

Sample	TOC [%]	CC [%]	TS [%]	Sample	TOC [%]
W 561.0	1.46	12.32	1.21	W 581.6	0.21
W 569.0	1.64	9.75	1.17	W 582.5	0.72
W 571.0	1.50	7.87	1.14	W 583.6	0.94
W 573.0	1.81	20.09	1.28	W 584.5	2.01
W 574.5	1.80	17.62	1.39	W 585.5	1.91
W 576.0	2.19	7.91	1.47	W 586.5	0.98
W 577.5	2.18	6.35	1.50	W 587.4	0.12
W 579.3	2.08	7.15	1.51	W 588.4	0.28
W 579.8	2.20	6.72	1.38	W 589.0	0.05
W 580.5	1.58	4.09	0.58	W 589.8	0.14
W 581.1	2.72	6.40	1.27	W 590.5	0.11
W 581.6	1.30	3.47	0.35	W 591.8	0.10
W 582.3	0.62	4.34	0.10	W 592.8	0.27
W 583.0	2.02	3.24	2.38	W 593.3	0.12
W 583.8	1.19	3.54	0.15	W 594.5	0.12
W 585.5	1.34	0.90	0.08	W 595.5	0.12
W 586.0	0.73	5.22	0.28	W 596.5	0.82
W 587.1	0.33	2.94	0.02	W 597.2	0.51
W 588.0	0.31	4.40	0.01	W 598.5	0.96
W 590.7	0.34	2.58	0.00	W 599.0	0.05
W 591.1	0.40	1.15	0.01	W 599.4	0.05
W 591.8	0.47	3.91	0.00	W 600.0	0.05
W 592.0	0.29	8.13	0.00	W 600.5	0.10
W 594.3	0.23	0.17	0.04	W 601.0	0.05
W 594.5	0.28	1.56	0.01	W 602.4	1.66
W 596.3	0.76	0.45	0.03		
W 596.5	1.39	0.17	1.30		
W 600.9	0.48	0.22	0.22		

Sample	V ppm	Ni ppm	Cr ppm	U ppm	Th ppm	Mo ppm	$U_{\text{authig.}}^*$	U/Mo	V/(V+Ni)	V/Cr	U/Th
W 561.0	199.0	71.6	82.1	7.6	10.0	17.2	4.3	0.44	0.74	2.42	0.76
W 569.0	380.0	71.3	82.1	6.5	9.1	17.0	3.5	0.38	0.84	4.63	0.71
W 571.0	402.0	69.2	88.9	7.2	9.5	14.7	4.0	0.49	0.85	4.52	0.76
W 574.5	94.0	39.4	75.3	5.0	10.0	5.1	1.7	0.98	0.70	1.25	0.50
W 576.0	97.0	45.7	68.4	4.5	9.0	4.4	1.5	1.02	0.68	1.42	0.50
W 577.5	300.0	75.1	88.9	10.5	9.3	21.3	7.4	0.49	0.80	3.37	1.13
W 579.8	298.0	89.4	82.1	10.4	8.9	35.4	7.4	0.29	0.77	3.63	1.17
W 581.1	227.0	52.1	109.5	4.5	13.7	0.9	-0.1	5.00	0.81	2.07	0.33
W 581.6	99.0	63.0	66.0	3.0	14.0	1.9	-1.7	1.58	0.61	1.50	0.21
W 582.5	130.0	38.0	68.0	5.0	14.0	1.9	0.3	2.63	0.77	1.91	0.36
W 583.0	251.0	57.4	95.8	6.6	12.8	4.5	2.3	1.47	0.81	2.62	0.52
W 583.6	165.0	42.0	52.0	8.0	16.0	1.9	2.7	4.21	0.80	3.17	0.50
W 584.5	249.0	105.0	55.0	9.0	12.0	60.0	5.0	0.15	0.70	4.53	0.75
W 585.5	332.0	77.0	46.0	9.0	11.0	18.0	5.3	0.50	0.81	7.22	0.82
W 586.0	151.0	37.3	95.8	4.4	13.6	1.5	-0.1	2.93	0.80	1.58	0.32
W 586.5	143.0	61.0	65.0	5.0	14.0	1.9	0.3	2.63	0.70	2.20	0.36
W 587.4	105.0	57.0	63.0	4.0	14.0	1.9	-0.7	2.11	0.65	1.67	0.29
W 588.4	92.0	68.0	69.0	4.0	13.0	1.9	-0.3	2.11	0.58	1.33	0.31
W 589.0	99.0	60.0	80.0	2.4	13.4	2.0	-2.1	1.18	0.62	1.24	0.18
W 589.8	99.0	75.0	71.0	4.0	15.0	1.9	-1.0	2.11	0.57	1.39	0.27
W 590.5	96.0	66.0	76.0	4.0	15.0	1.9	-1.0	2.11	0.59	1.26	0.27
W 591.8	89.0	63.0	67.0	4.0	14.0	1.9	-0.7	2.11	0.59	1.33	0.29
W 592.8	96.0	68.0	76.0	3.0	15.0	1.9	-2.0	1.58	0.59	1.26	0.20
W 593.3	79.0	62.0	58.0	4.0	12.0	1.9	0.0	2.11	0.56	1.36	0.33
W 594.5	95.0	67.0	72.0	3.0	16.0	1.9	-2.3	1.58	0.59	1.32	0.19
W 595.5	113.0	65.0	84.0	4.0	14.0	1.9	-0.7	2.11	0.63	1.35	0.29
W 596.5	157.0	80.0	91.0	6.0	13.0	1.9	1.7	3.16	0.66	1.73	0.46
W 597.2	140.0	64.0	97.0	5.0	14.0	1.9	0.3	2.63	0.69	1.44	0.36
W 598.5	180.0	89.0	94.0	7.0	16.0	1.9	1.7	3.68	0.67	1.91	0.44
W 599.0	123.0	50.0	100.0	3.1	13.0	2.0	-1.2	1.57	0.71	1.23	0.24
W 599.4	164.0	60.0	100.0	5.7	14.1	2.0	1.0	2.84	0.73	1.64	0.40
W 600.0	135.0	50.0	100.0	4.9	13.2	2.0	0.5	2.46	0.73	1.35	0.37
W 600.5	101.0	77.0	95.0	4.0	14.0	1.9	-0.7	2.11	0.57	1.06	0.29
W 601.0	196.0	110.0	90.0	6.0	11.6	21.0	2.1	0.29	0.64	2.18	0.52
W 602.4	86.0	82.0	93.0	3.0	11.0	1.9	-0.7	1.58	0.51	0.92	0.27

$$* U_{\text{authig.}} = U_{\text{total}} - \text{Th}_{\text{total}}/3$$

Bottom water redox conditions

	$U_{\text{authig.}}$	V/(V+Ni)	V/Cr	U/Th
Oxic	<2	<0.46	<2	<0.75
Dysoxic	2.0-10.0	0.46-0.60	2-4.25	0.75-1.25
Anoxic	10.0-15.0	0.54-0.82	>4.25	>1.25

Euxinic	>15.0	≥0.84-0.89		
<i>Source of data</i>	3)	1)	2)	2)

784