



# A Basin Redox Transect at the Dawn of Animal Life

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## A basin redox transect at the dawn of animal life

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44 **Multiple eukaryotic clades make their first appearance in the fossil record between**  
45 **~810 and 715 Ma. Molecular clock studies suggest that the origin of animal**  
46 **multicellularity may have been part of this broader eukaryotic radiation. Animals**  
47 **require oxygen to fuel their metabolism, and low oxygen levels have been**  
48 **hypothesized to account for the temporal lag between metazoan origins and the**  
49 **Cambrian radiation of large, ecologically diverse animals. Here, paleoredox**  
50 **conditions were investigated in the Fifteenmile Group, Ogilvie Mountains, Yukon,**  
51 **Canada, which hosts an 811 Ma ash horizon and spans the temporal window that**  
52 **captures the inferred origin and early evolution of animals. Iron-based redox**  
53 **proxies, redox-sensitive trace elements, organic carbon percentages and pyrite**  
54 **sulfur isotopes were analyzed in seven stratigraphic sections along two parallel**  
55 **basin transects. These data suggest that for this basin, oxygenated shelf waters**  
56 **overlay generally anoxic deeper waters. The anoxic water column was dominantly**  
57 **ferruginous, but brief periods of euxinia likely occurred. These oscillations coincide**  
58 **with changes in total organic carbon, suggesting euxinia was primarily driven by**  
59 **increased organic carbon loading. Overall, these data are consistent with proposed**  
60 **quantitative constraints on Proterozoic atmospheric oxygen being greater than 1%**  
61 **of modern levels, but less than present levels. Comparing these oxygen levels against**  
62 **the likely oxygen requirements of the earliest animals, both theoretical**  
63 **considerations and the ecology of modern oxygen-deficient settings suggest that the**  
64 **inferred oxygen levels in the mixed layer would not have been prohibitive to the**  
65 **presence of sponges, eumetazoans or bilaterians. Thus the evolution of the earliest**  
66 **animals was probably not limited by the low absolute oxygen levels that may have**

67 **characterized Neoproterozoic oceans, although these inferred levels would constrain**

68 **animals to very small sizes and low metabolic rates.**

69

70 **1. Introduction**

71 A number of eukaryotic groups first appear in the fossil record between the Bitter  
72 Springs isotope excursion at ~810 Ma and the Sturtian glaciation at ~715 Ma (Macdonald  
73 et al., 2010). This apparent radiation includes the first unequivocal appearances of groups  
74 such as the vase-shaped microfossils, interpreted to be related to lobose, and perhaps  
75 filose, testate amoebae (Porter and Knoll, 2000; Porter et al., 2003), scale microfossils of  
76 uncertain phylogenetic affinity (Cohen et al., 2011; Cohen and Knoll, 2012), and simple  
77 multicellular and coenocytic green algae (Butterfield et al., 1994). Interestingly,  
78 molecular clock studies suggest that the origin of animal multicellularity may have been  
79 part of this broader radiation. Studies utilizing different taxa, genes, calibration points  
80 and clock models have converged on an estimated divergence of ~800 Ma for the last  
81 common ancestor of animals (Berney and Pawlowski, 2006; Lartillot et al., 2009;  
82 Sperling et al., 2010; Erwin et al., 2011; Parfrey et al., 2011). Similar results in these  
83 studies, despite broad methodological differences, suggest this divergence estimate is  
84 approximately correct. This age finds further support in the appearance of presumed  
85 demosponge-specific biomarkers beneath ca. 635 Ma Marinoan glacial deposits (Love et  
86 al., 2009; Kodner et al., 2008); as demosponges represent a derived lineage within  
87 animals, the origin of the animal crown group must be even deeper in time. If the  
88 molecular clock ages and biomarker data are accurate, however, the lack of metazoan  
89 body and trace fossils throughout the Cryogenian and early Ediacaran periods presents a  
90 conundrum (Erwin et al., 2011). It has been hypothesized that animal body size and  
91 diversity may have been limited by relatively low levels of oxygen in the Proterozoic  
92 atmosphere and oceans. In such oceans, it is posited that animals could have been

93 restricted to small and thin body plans that did not fossilize well, with the explosion of  
94 larger and ecologically diverse organisms in the late Ediacaran and Cambrian related in  
95 part to increasing O<sub>2</sub> levels (Cloud, 1968; Rhoads and Morse, 1971; Runnegar, 1982a;  
96 Knoll and Carroll, 1999). Consistent with this hypothesis, different geochemical redox  
97 proxies support a directional change towards more oxygenated conditions in the latest  
98 Proterozoic (reviewed by Och and Shields-Zhou, 2012; Kah and Bartley, 2011).

99         What remains highly uncertain, however, are the atmospheric and oceanic oxygen  
100 concentrations prior to and during earliest animal evolution, specifically during the  
101 Cryogenian period (850-635 Ma). Oxygen levels are generally assumed to have been  
102 relatively low in Cryogenian oceans (e.g. Kump, 2008), but given the lack of widespread  
103 paleoenvironmental documentation, the extent to which early animals were limited by  
104 low oxygen levels remains unknown. Specifically, the physiological requirements of  
105 small animals with low-energy lifestyles that may have characterized the Cryogenian  
106 Period were likely different from the larger, more active and muscular organisms  
107 preserved in Cambrian rocks. This difference needs to be considered when comparing  
108 physiological requirements against the constraints provided by geochemical proxies.

109         Here, we investigate the environmental context of early animal evolution and  
110 compare inferred redox constraints with the likely physiological requirements associated  
111 with different grades of organization in early animal evolution. Previous iron speciation  
112 and sulfur isotope studies of the pre-Sturtian Chuar Group (Canfield et al., 2008; Nagy et  
113 al., 2009; Johnston et al., 2010) provide insight into Cryogenian environments, but are  
114 limited to a single section deposited between ca. 770 and 742 Ma (Karlstrom et al.,  
115 2000). Here we report geochemical redox proxies through seven sections along two

116 parallel platform-to-basin transects in the early Cryogenian Fifteenmile Group in the  
117 Tatonduk and Coal Creek inliers, Ogilvie Mountains, Yukon, Canada (Figs. 1 and 2). The  
118 Fifteenmile Group was deposited in a basin that originated during an episode of  
119 continental extension (Macdonald et al., 2012) prior to  $811.51 \pm 0.25$  Ma, the U-Pb  
120 zircon date on a tuff in the upper portion of the Reefal Assemblage (green line in Mt.  
121 Harper Section, Figs. 3 and 6; Macdonald et al., 2010). Thus the Fifteenmile Group spans  
122 a time period that significantly preceded the earliest macroscopic multicellular forms in  
123 the Ediacaran Period (Narbonne, 2011) but overlaps with molecular-clock estimates for  
124 the divergence of crown-group animals (Erwin et al., 2011, and references above).

125         The paleoredox state of shale samples collected from measured stratigraphic  
126 sections was investigated using a multi-proxy approach. Specifically, iron speciation data  
127 are integrated with major-element and redox-sensitive trace element abundances, total  
128 organic carbon (TOC) percentages, and pyrite sulfur isotope values to obtain an estimate  
129 of overall water-column redox profiles. Together, the geochemical data from these  
130 stratigraphic sections provide the first early Neoproterozoic basin redox transect and give  
131 insight into paleoenvironmental conditions in this basin at the dawn of animal life. These  
132 data can then be placed in the context of other information constraining Mesoproterozoic  
133 and early Neoproterozoic oxygen levels and compared to the likely physiological  
134 requirements of early animals.

135

## 136 **2. Geologic Background**

137         Neoproterozoic strata in the northern Canadian Cordillera are exposed in  
138 erosional windows ('inliers') separated by Phanerozoic cover (Rainbird et al., 1996;

139 Thorkelson et al., 2005) (Fig. 1). In the Coal Creek inlier, the focus of this study,  
140 geological mapping (Fig. 2) and stratigraphic analysis indicate that Neoproterozoic  
141 extension produced a series of NNW-side down normal faults, such that the basin, at least  
142 locally, deepened towards the northwest in present-day coordinates (Macdonald et al.,  
143 2012). The Fifteenmile Group consists of lagoonal, tidal, and supertidal carbonates of the  
144 informal Gibben formation, tidal flat and deltaic deposits of the Chandindu formation,  
145 and mixed carbonates and siliciclastics of the Reefal Assemblage, which is characterized  
146 by km-scale stromatolitic reefs that transition laterally into shale-dominated, deeper water  
147 sub-basins (Macdonald et al., 2012). Shales were sampled from two parallel transects  
148 across the basin (Fig. 2), including a shorter transect passing a short distance from a  
149 stromatolite reef complex into the shale basin (Fig. 4), and a longer transect stepping  
150 further into the basin (Fig. 3). Shales were also investigated from exposures of the Reefal  
151 Assemblage ~75 km to the northwest in the Tatonduk inlier that have yielded distinctive  
152 scale microfossils (Cohen et al., 2011; Cohen and Knoll, 2012). As Fifteenmile Group  
153 strata in the Tatonduk inlier are represented only by shale interbedded with re-deposited  
154 carbonate (and no evidence for shallow-water sedimentation), these exposures are  
155 interpreted to have formed in a deeper, more distal environment than correlative sections  
156 in the Coal Creek inlier (Macdonald et al., 2012); however, displacement along poorly  
157 exposed post-Jurassic faults between the two inliers precludes precise paleogeographic  
158 reconstruction.

159

### 160 **3. Materials and Methods**



161 234 shale samples from logged stratigraphic sections were crushed to flour and  
162 analyzed for major and minor-element concentrations, iron speciation systematics,  
163 percent carbonate carbon and organic carbon, and pyrite sulfur isotope composition. Iron  
164 sequential extraction followed standard protocols for iron carbonate, iron oxide and  
165 magnetite extractions (Poulton and Canfield, 2005), while pyrite iron content was  
166 quantified using the chromous chloride extraction method (Canfield et al., 1986). Pyrite  
167 sulfur isotopes were determined through combustion via a Costech Elemental Analyzer  
168 linked to a Thermo Scientific Delta V in continuous flow mode (measured as SO-SO<sub>2</sub>)  
169 using Ag<sub>2</sub>S from the chromous chloride extraction. Major- and minor-element  
170 abundances were determined following a standard acid digestion (hydrofluoric,  
171 perchloric, hydrochloric and nitric) and measurement with ICP-AES at SGS Laboratories,  
172 Canada. Percent carbonate carbon was quantified by percent loss on acid dissolution.  
173 Total organic carbon values were determined on acidified samples by combustion within  
174 a Carlo Erba NA 1500 Analyzer attached to a Thermo Scientific Delta V Advantage  
175 isotope ratio mass spectrometer. Complete materials and methods and precision estimates  
176 for each analysis are contained in Supplementary Information.

177

#### 178 **4. Results**

179 All geochemical measurements are reported in Supplemental Information Tables  
180 1 and 2. Iron speciation data are plotted against the sequence stratigraphic framework for  
181 the Coal Creek inlier (Macdonald et al., 2012) in Figs. 3 and 4. Full redox proxy data are  
182 plotted against stratigraphy for the principal investigated sections including the short  
183 transect at Reefer Camp (Fig. 5), the long transect at Mt. Harper (Fig. 6), and the deepest-

184 water section at Mt. Slipper (Fig. 7). Similar plots for sections with more limited data in  
185 the Coal Creek inlier (Mine Camp, East Harper and Mt. Gibben) can be found in  
186 Supplemental Figs. 1-3, respectively.

187

#### 188 4.1 *Multi-proxy estimation of paleo-redox state*

189 An estimate of water-column redox state was determined using a multi-proxy  
190 approach based on iron speciation chemistry, redox-sensitive trace elements (especially  
191 Mo and V) and pyrite sulfur isotope values. In iron speciation chemistry, the highly-  
192 reactive pool (FeHR) consists of iron in pyrite (FeP) plus iron that is reactive to sulfide  
193 on early diagenetic timescales (iron carbonates such as siderite and ankerite, and iron  
194 oxides, including magnetite). The remaining unreactive pool (FeU) consists mainly of  
195 iron in sheet silicates; the sum of the two pools is total iron (FeT). Key to the geological  
196 application of this proxy is the observation that modern sediments deposited under oxic  
197 water columns have a  $\text{FeHR}/\text{FeT} < 0.38$ , while those deposited beneath anoxic water  
198 masses generally have  $\text{FeHR}/\text{FeT} > 0.38$  [Raiswell and Canfield (1998); see also Farrell,  
199 (2011), and Supplementary Information for further discussion]. The proxy can also  
200 distinguish the nature of an anoxic water column based on the proportion of highly  
201 reactive iron that has been sulfidized, with  $\text{FeP}/\text{FeHR}$  ratios  $>0.80$  indicating an euxinic  
202 water column, and lower ratios pointing towards ferruginous conditions (Anderson and  
203 Raiswell, 2004; Poulton and Canfield, 2011).

204 Like all proxies, iron speciation has acknowledged caveats. For instance, dilution  
205 by turbidites or rapid sedimentation can result in low  $\text{FeHR}/\text{FeT}$  ratios, imparting a false  
206 oxic 'signature' to sediments deposited under an anoxic water column (Raiswell and

207 Canfield, 1998; Lyons and Severmann, 2006). Near-shore or estuarine sediments can trap  
208 large amounts of iron oxides, leading to an anoxic FeHR/FeT signature for sediments  
209 deposited under oxic conditions (Poulton and Raiswell, 2002). Weathering can oxidize  
210 Fe<sup>2+</sup> phases to Fe<sup>3+</sup> phases, potentially skewing the interpretation of euxinic versus  
211 ferruginous conditions (see below), although the FeHR term should remain constant  
212 (Canfield et al., 2008). Consistency between independent proxies is the best test of an  
213 inference, and consequently we integrated the iron speciation chemistry with other redox  
214 proxies and sedimentological constraints. Redox-sensitive trace elements such as  
215 vanadium and molybdenum are soluble under oxic conditions but are less soluble under  
216 reducing conditions, and are scavenged by organic and inorganic particles or complex  
217 with sulfide, leading to enrichments compared to average shale values (Tribovillard et al.,  
218 2006). Pyrite sulfur isotope values can further inform paleoenvironmental reconstruction,  
219 because sulfate reduction within a water-column where sulfate is not limiting allows  
220 expression of the biological preference for lighter <sup>32</sup>S, and consequently depleted isotopic  
221 compositions in the resulting pyrite with respect to seawater sulfate. Sulfate reduction  
222 within sediments, on the other hand, where sulfate availability is often diffusion limited,  
223 results in Rayleigh distillation, leading to pyrite values that approach seawater sulfate  
224 (Johnston and Fischer, 2012).

225         In our multi-proxy framework, samples were considered likely to have been  
226 deposited under an oxic water column when they showed FeHR/FeT < 0.38 (Raiswell  
227 and Canfield, 1998), no enrichment in Mo and V with respect to average shales (Gromet  
228 et al., 1984), and relatively enriched  $\delta^{34}\text{S}$  pyrite sulfur isotope values (or not enough  
229 sulfide present in the rock for measurement). Samples were considered to have been

230 deposited under an anoxic, ferruginous water column when they showed FeHR/FeT >  
231 0.38, little to no Mo enrichment but often with V enrichment, and relatively enriched  $\delta^{34}\text{S}$   
232 pyrite sulfur isotope values. Finally, samples were considered to have been likely  
233 deposited under an anoxic, euxinic water column when they showed FeHR/FeT > 0.38,  
234 relatively high FeP/FeHR ratios, Mo and V enrichments, and depleted  $\delta^{34}\text{S}$  pyrite sulfur  
235 isotope values.

236 Euxinic water columns are usually distinguished by FeP/FeHR > 0.80 or 0.70  
237 (Poulton and Canfield, 2011), a ratio which few of these samples surpasses. Samples  
238 interpreted here as euxinic, though, clearly have much higher FeP/FeHR ratios than  
239 samples interpreted as ferruginous (see Figs. 6 and 7), and essentially no iron carbonate  
240 or magnetite. Further, these shales have very depleted  $\delta^{34}\text{S}$  pyrite sulfur isotopes (to -34  
241 ‰) and high molybdenum abundances relative to other Neoproterozoic samples (Scott et  
242 al., 2008). Two likely possibilities exist to explain these patterns: 1) these shales were  
243 deposited beneath an euxinic water column, with subsequent oxidation of pyrite to iron  
244 oxides, or (2) the shales were deposited beneath a ferruginous water column, with the  
245 zone of free sulfide accumulation essentially at the sediment-water interface.

246 Petrographic examination of selected shales did not show widespread evidence for  
247 oxidation of pyrite, although because the samples are from outcrop and surely have  
248 suffered some alteration, it is possible that micron-scale pyrite grains beneath the limits  
249 of routine petrographic detection have been wholly or partially oxidized. In the second  
250 possibility, full access to seawater sulfate and molybdenum pools could explain the  
251 isotopic and abundance patterns for these two elements, while the shorter time interval  
252 exposed to high sulfide levels compared to a fully euxinic water column would result in

253 less sulfidization of highly-reactive iron phases. Recognizing that the development of  
254 truly euxinic conditions is ambiguous and these data may represent sulfide production at  
255 the sediment-water interface, inferences of euxinia in Figs. 5-7 should be treated with  
256 caution.

257

## 258 4.2 *Sedimentary Geochemistry of the Fifteenmile Group*

### 259 4.2.1 *Reefer Camp transect, Coal Creek inlier*

260 Near Reefer Camp, samples from the shallow-water Chandindu formation show  
261 the hallmarks of deposition under an oxic water column (Fig. 5A). Within the  
262 stromatolite reef core of the Reefal Assemblage, thin black shales show high FeHR/FeT,  
263 but because they show no redox-sensitive trace element enrichment, and the FeHR signal  
264 is entirely dominated by iron oxides, this may represent nearshore trapping of oxides, as  
265 occurs in modern settings (Poulton and Raiswell, 2002) rather than a true ocean redox  
266 signal. Samples above the flooding surface atop the stromatolite reef tract have iron  
267 speciation values persistently above 0.38, moderate amounts of iron carbonate, no Mo  
268 enrichment and enriched pyrite sulfur isotope values, pointing to deposition under  
269 ferruginous conditions. Samples from the upper part of the Reefal Assemblage signal an  
270 apparent return to oxic deposition. In Fig. 5B (See Fig. 4 for the stratigraphic relationship  
271 of these sections), the Chandindu formation samples again show evidence for oxic  
272 deposition. Continuing upsection into shale of the Reefal Assemblage, all available  
273 evidence points to deposition under a generally oxic water column.

274

### 275 4.2.2 *Mt. Harper, Coal Creek inlier*

276           Near Mt. Harper, shallow-water sediments of the Chandindu formation also show  
277 evidence for oxic deposition (Fig. 6). The Mt. Harper transect steps much farther  
278 westward into the Reefal Assemblage shale basin than the short transect at Reefer Camp,  
279 and records a thick package of black shale and foreslope carbonate that fill  
280 accommodation space associated with tectonic extension (Macdonald et al., 2012). In  
281 section GO134, the stratigraphically lowest exposed shales of the Reefal Assemblage,  
282 there is evidence for euxinic deposition. Many of these samples do not show  $Fe_{HR}/Fe_T >$   
283 0.38, but as this succession contains many siltstone turbidites and redeposited carbonates  
284 and was likely deposited rapidly during active extension (Macdonald et al., 2012), it is  
285 possible that the highly-reactive iron was diluted by high sedimentation rates. Thus a  
286 threshold for anoxia of 0.22 may be more appropriate (Raiswell and Canfield, 1998; see  
287 also discussion in Supplementary Information). These samples show relatively high  
288  $Fe_P/Fe_{HR}$ , high Mo (~10-32 ppm; high for Neoproterozoic shales—Scott et al., 2008),  
289 and depleted pyrite sulfur isotope values, indicating sulfide production very near to the  
290 sediment-water interface, if not in the water column (see above). The upper half of  
291 section GO134 shows lower Mo and less depleted pyrite sulfur isotope values, potentially  
292 suggesting ferruginous or even oxic conditions. Samples at the base of section S1103  
293 have  $Fe_{HR}/Fe_T < 0.38$ , no redox-sensitive trace element enrichments, and no pyrite,  
294 possibly recording deposition under oxic conditions. This is followed by a second pulse  
295 of euxinic deposition, showing similar characteristics to the samples in GO134, with  
296 elevated  $Fe_P/Fe_{HR}$ , high Mo abundances, and depleted pyrite sulfur isotope values.  
297 There is little evidence for euxinia above this level, with ferruginous conditions dominant  
298 in the upper Reefal Assemblage. In contrast to samples from the lower Reefal

299 Assemblage at Mt. Harper, where the FeHR pool is almost entirely in pyrite and iron  
300 oxides, samples from the upper Reefal Assemblage contain moderate quantities of iron  
301 carbonate. In combination with low Mo, and enriched and variable pyrite sulfur isotope  
302 values, this suggests that the upper half of the Reefal Assemblage accumulated under an  
303 anoxic, ferruginous water column. Brief and fluctuating water column oxygenation may  
304 have occurred, as evidenced by stratigraphically-variable iron speciation signatures.

305

#### 306 4.2.3 *Mt. Slipper, Tatonduk inlier*

307 Iron speciation values from the Reefal Assemblage in the Tatonduk inlier (Figure  
308 7), which represent the deepest-water setting studied (Macdonald et al., 2012), generally  
309 show  $\text{FeHR}/\text{FeT} > 0.38$ , indicating persistent deposition under an anoxic water column.  
310 Samples from the base of the section have relatively high  $\text{FeP}/\text{FeHR}$ , high Mo and  
311 depleted pyrite sulfur isotope values, pointing to euxinic deposition (or at least  
312 fluctuating euxinia). At ~90m, these proxy values decrease, indicating a transition to  
313 ferruginous conditions. A possible return to euxinia is seen at the top of the section, from  
314 strata that have yielded scale microfossils (Cohen et al., 2011).

315

#### 316 4.2.4 *Sediment total iron contents*

317 The total iron to aluminum ratio is another informative redox proxy, because  
318 sedimentary iron is authigenically enriched under anoxic water columns (Lyons and  
319 Severmann, 2006). An interesting feature of shale samples from the Fifteenmile Group is  
320 that even samples considered to have been deposited under anoxic conditions have  $\text{Fe}/\text{Al}$   
321 ratios lower than average shale (Gromet et al., 1984). Given the general concordance in

322 these samples of FeHR/FeT, redox-sensitive trace element abundances and pyrite sulfur  
323 isotope data, the inconsistency with Fe/Al likely indicates an intrinsic bias to either total  
324 iron or total aluminum in the Reefal Assemblage, rather than this representing oxic  
325 deposition. Total Al abundances in all shales investigated (average = 7.03 wt %) are  
326 slightly depressed relative to the North American Shale Composite (NASC; Gromet et  
327 al., 1984; 8.94 wt %). In contrast, total Fe (average = 2.43 wt %) is significantly reduced  
328 relative to NASC (4.43 wt %), especially considering that basinal samples interpreted as  
329 anoxic should be enriched in iron. Some Reefal Assemblage shales are exceptionally low  
330 in total iron (<1 weight percent), and have very high FeHR/FeT ratios indicating a near-  
331 absence of detrital iron-silicates. Dilution by carbonate may explain some of the low iron  
332 contents, as some samples are slightly calcareous (to ~30-40%, average 9.45% ± 9.50),  
333 Supplementary Table 1) but low iron contents persist in shale samples that have  
334 essentially no carbonate (e.g. GO134 and S1103 sections). Open-system diagenesis could  
335 have potentially affected these rocks, although even the marls would have had very low  
336 permeability. Further, the main effect of diagenesis in carbonates is to add iron (Brand  
337 and Veizer, 1980), which is unlikely given the low overall amounts of acetate-extractable  
338 iron (average 0.13 weight percent) and the lack of a relationship between percent  
339 carbonate and acetate-extractable iron ( $R^2 = 0.062$ ). Another possibility is that the  
340 provenance was extremely weathered, iron-free material. However, Chemical Index of  
341 Alteration (CIA; Nesbitt and Young, 1982) values average ~70 throughout the dataset,  
342 indicating a fairly unweathered provenance. A few values in the 75-85 range suggest a  
343 weathered source for those samples, but overall there is no obvious correlation between  
344 CIA and total iron. Thus, while several factors may explain some low iron values, none



345 can explain all low values. We note that some other Neoproterozoic sections show  
346 anomalously low FeT/Al (e.g. Sahoo et al., 2012); further study is needed to determine if  
347 these are local, basin-level effects or an as-yet-unexplained aspect of the Neoproterozoic  
348 iron cycle.

349

#### 350 4.2.5 *Redox proxy data and sediment organic carbon contents*

351 Sediment TOC results vary consistently compared to multi-proxy inferences of  
352 redox state (Fig. 8). Sediments likely deposited under an oxic water column have low  
353 organic carbon abundances (average = 0.31% ± 0.49 weight percent; median = 0.19%),  
354 whereas those inferred to have been deposited beneath a ferruginous water column have  
355 higher sediment TOC values (average = 0.66% ± 1.37; median = 0.28%). And sediments  
356 likely deposited beneath euxinic conditions show much greater TOC (average = 2.87% ±  
357 1.49; median = 2.63. Thus, these data are consistent with the hypothesis that the  
358 development of euxinic conditions in Neoproterozoic basins is primarily driven by the  
359 degree of organic carbon loading and the exhaustion of more energetically-favorable  
360 electron acceptors than sulfate (e.g. Fe<sup>3+</sup>) (Johnston et al., 2010).

361

#### 362 4.2.6 *Redox proxy data and water depth*

363 Redox proxy data show a consistent pattern with respect to sedimentological  
364 structures that indicate relative water depth. In particular, all occurrences of hummocky  
365 cross-stratified sandstones encased within shale, which indicate deposition above storm  
366 wave base, show evidence for oxic deposition (Fig. 3-7). In other words, the surface  
367 mixed layer in the basin appears to be oxygenated, at least during storms. While the depth

368 of storm wave base varies among basins (Peters and Loss, 2012), these data indicate that  
369 in this basin, the water column in direct contact with the atmosphere remained oxic.  
370 Oxygenated conditions may extend slightly deeper, as some sediments likely deposited  
371 below storm wave base (such as shales basinward of the stromatolite reef at Reefer  
372 Camp, Fig. 5B) still indicate oxic conditions. A few brief intervals of oxygenated  
373 conditions, or fluctuating anoxia, persist deeper into the Coal Creek inlier shale basin as  
374 recorded in the Mt. Harper (Fig. 6) and Mine Camp (Supplementary Fig. 1) sections, but  
375 the majority of these deeper-water sediments record anoxic conditions. The deepest-water  
376 section at Mt. Slipper in the Tatonduk inlier (Fig. 7), which shows no evidence for wave  
377 activity, is persistently anoxic. Thus, there is a clear redox structure to the basin, with an  
378 oxygenated surface layer where the sediments are in contact with the atmosphere (storm  
379 wave base), and anoxic conditions below this depth.

380

## 381 **5. Discussion**

### 382 5.1 *Fifteenmile Group redox structure in a global context*

383 Quantitative constraints on Proterozoic oxygen levels are notoriously difficult to  
384 obtain (Kump, 2008). O<sub>2</sub> levels must have been above 0.001% present atmospheric levels  
385 (PAL), the limit imposed by the disappearance of mass-independent fractionation of  
386 sulfur isotopes at ~2.45 Ga (Farquhar et al., 2000; Pavlov and Kasting, 2002). Two other  
387 constraints have been proposed for mid-Proterozoic O<sub>2</sub> (Kump, 2008). First, anoxic deep  
388 oceans likely require atmospheric O<sub>2</sub> to be less than 40% PAL (Canfield, 2005). Second,  
389 it has been proposed that iron is only retained in lithified soil horizons, and it has been  
390 since the Paleoproterozoic, when O<sub>2</sub> is greater than 1% PAL (Holland and Beukes, 1990).

391 These limits on Proterozoic O<sub>2</sub> have caveats, and it has even been hypothesized that  
392 levels may not have been dramatically different from the Phanerozoic (Butterfield, 2009).  
393 Nonetheless, it is notable that the basin redox transect of the Fifteenmile Group is  
394 consistent with proposed quantitative limits (Kump, 2008). Indeed, the basin redox  
395 structure of the Fifteenmile Group is similar in many ways to that of the Mesoproterozoic  
396 Roper Group in Australia (Shen et al., 2003), with an oxygenated shelf overlying anoxic  
397 basinal waters. Although there are local drivers for anoxia (Tyson and Pearson, 1991), the  
398 available basin redox transects point to extensive subsurface anoxia in the Proterozoic  
399 oceans, sustained over hundreds of meters of stratigraphic section. This clearly differs  
400 from Phanerozoic ocean anoxic events (Campbell and Squire, 2010), indicating a  
401 different driver and implying lower atmospheric O<sub>2</sub> than the modern. Placing minimum  
402 constraints on global atmospheric pO<sub>2</sub> levels from local iron speciation data is difficult,  
403 but shallow-water facies in the Fifteenmile Group record oxic deposition, as do samples  
404 from the shale basin just off the reef margin at Reefer Camp (Fig. 5), and some samples  
405 from deeper in the shale basin at Mt. Harper (Fig. 6) and Mine Camp (Supplementary  
406 Fig. 1), implying enough atmospheric oxygen to counteract strong benthic reductant  
407 fluxes in a basin otherwise prone to euxinia (cf. Kump et al., 2005).

408         In sum, although there is clear need to study more basins, and develop new global  
409 redox proxies and models, the basin redox transect of the Fifteenmile Group is consistent  
410 with proposed constraints on Proterozoic oxygen levels as being <40% and >1% PAL  
411 (Kump, 2008). We apply these bounds for comparison with the physiological  
412 requirements of early animals.

413

414 5.2 *Physiological requirements of early animals*

415 The consistency of previously proposed constraints on atmospheric oxygen with  
416 the basin redox transect of the Fifteenmile Group prompts the question of whether such  
417 oxygen levels would have prohibited the evolution of animal, eumetazoan or bilaterian  
418 body plans. A common assumption in attempts to link late Precambrian oxygenation and  
419 biospheric evolution is that animals have high respiratory demands. While metazoans do  
420 have a clear and definite requirement for oxygen, they are not a monolithic group, and the  
421 oxygen requirements for any given organism varies widely based on size, metabolism,  
422 and the presence or absence of a circulatory system (Vaquer-Sunyer and Duarte, 2008).  
423 Hypotheses relating geochemical change to early animal evolution must therefore  
424 compare inferred changes against the explicit body plans, ecological strategies and  
425 taxonomic groups presumed to be affected. Determining the physiological requirements  
426 of ancient organisms has obvious uncertainty, but can be accomplished through analogy  
427 with living representatives (Knoll et al., 2007), and thus it is possible to make general  
428 statements about the likely oxygen requirements of Precambrian animals.

429

430 5.2.1 *Diploblastic metazoans*

431 Whether sponges are monophyletic (Philippe et al., 2009) or paraphyletic  
432 (Sperling et al., 2009), they are certainly the sister group or grade of all other animals  
433 (Philippe et al., 2011). Moving up the metazoan phylogenetic tree, the exact relationships  
434 of cnidarians, ctenophores and placozoans to bilaterians are unclear, but all are likely  
435 more closely related to bilaterians than they are to sponges (Philippe et al., 2011).  
436 Importantly, all these animals (diploblasts) are characterized by only two epithelial cell

437 layers, with the space between layers filled largely with metabolically-inert material (e.g.  
438 mesohyl in sponges, mesoglea in cnidarians). From a respiratory point of view, then,  
439 essentially every cell in a diploblastic metazoan is in direct contact with seawater  
440 (Ruppert et al., 2004). Thus, the theoretical oxygen limit for diploblastic animals will not  
441 differ from that of a single-celled eukaryote, barring two minor differences. First, for  
442 unicellular eukaryotes, diffusion of oxygen into the cell can occur across the entirety of  
443 its surface, whereas diffusion into a sheet of cells cannot occur at cell-cell contacts.  
444 Second, animals have a collagenous extracellular matrix, and molecular oxygen is  
445 required for the formation of hydroxyproline in collagen (Fujimoto and Tamiya, 1962;  
446 Prockop et al., 1962). Using the *K<sub>m</sub>* for the proline hydroxylase system of chick embryos,  
447 Towe (1970) suggested oxygen levels of ~3% PAL would be required for collagen  
448 synthesis. However, Rhoads and Morse (1971) cogently noted that collagen-rich  
449 invertebrates are found at oxygen levels beneath this value (see also discussion below on  
450 modern oxygen minimum zones), suggesting that the oxygenase requirements of a  
451 terrestrial vertebrate cannot be applied to marine invertebrates. Further, collagen is now  
452 known to exist in fungi (Celerin et al., 1996; Wang and St. Leger, 2006) and  
453 choanoflagellates (King et al., 2008--although the homology of both to metazoan  
454 collagens remains uncertain), which suggests collagen may have been present in the last  
455 common ancestor of opisthokonts. If so, any oxygen requirement for collagen synthesis  
456 was met far earlier than the origin of animals.

457         In the fossil record, clear eukaryotic organisms are found at ~1800 Ma, and  
458 several lineages of multicellular eukaryotes, which would also have been subject to the  
459 same constraint as early animals of limited diffusion at cell-cell contacts, are found in

460 Mesoproterozoic rocks (Runnegar, 1991; Knoll et al., 2006). The presence of these  
461 organisms long before the Cryogenian implies that any physiological oxygen threshold  
462 for the body plans that characterized the earliest (diploblastic) period of early animal  
463 evolution must have been surpassed far prior to the origin of animals themselves.

464

#### 465 5.2.2 *Bilaterian metazoans- theoretical lower oxygen limits*

466 In contrast to diploblasts, which have sheets of cells separated by inert material,  
467 bilaterian (triploblastic) organisms have metabolically-active cells in three-dimensions  
468 (Knoll, 2011). Body size (and the ability of the organism to exist at a given oxygen  
469 concentration) is consequently limited by the ability to maintain functional internal  
470 oxygen levels, either through pure diffusion or through a blood vascular system (BVS).  
471 The implications of this constraint under hypothetical Precambrian oxygen levels have  
472 been extensively discussed (e.g. Raff and Raff, 1970; Runnegar, 1982a,b; 1991; Catling  
473 et al., 2005; Payne et al., 2010). Using a theoretical framework for the diffusion of  
474 oxygen into an idealized animal (Alexander, 1971), these studies have demonstrated that  
475 low oxygen levels will restrict bilaterians to small, thin body plans. What has not been  
476 asked in these theoretical calculations is what oxygen levels will prohibit the existence of  
477 bilaterian body plans.

478 Superficially, this question would seem to hinge on the nature of the last common  
479 ancestor of bilaterians (consider Carroll et al., 2001, versus Erwin and Davidson, 2002),  
480 specifically whether this ancestor was a complex, coelomate organism with a heart and  
481 BVS, or a much simpler organism that transported oxygen through pure diffusion.  
482 However, as noted by Budd and Jensen (2000), due to structural size requirements,

483 notably the physical space required to fit a functional BVS, this transport system is not  
484 present in modern organisms less than ~3mm in size. Following the framework of  
485 Alexander (1971; see Supplementary Information for details), we estimate that the most  
486 likely minimal oxygen requirement for a 3 mm-long x 67  $\mu\text{m}$ -wide worm with a  
487 circulatory system, such as an annelid, is ~0.14% PAL (Fig. 9). The most likely minimal  
488 oxygen requirements for a 600 x 25  $\mu\text{m}$  diameter worm limited by pure diffusion, such as  
489 a nematode, is ~0.36% PAL (Fig. 9)—note that these values are with respect to ambient  
490 dissolved oxygen concentrations and do not consider temperature or salinity effects on  
491 the dissolution of oxygen in water. The estimated oxygen requirements for these two  
492 hypothetical ancestors differ slightly, but their broad similarity and the overlap in  
493 sensitivity analyses (Fig. 9) suggests that pure diffusion and a BVS likely represent  
494 optimal designs below and above this size threshold.

495         Although there are uncertainties in the optimal values for the parameters in the  
496 equations governing oxygen requirements (see Supplementary Information), three facts  
497 suggest the values described above represent conservative estimates for the minimum  
498 oxygen concentrations necessary to sustain bilaterians. First, for the bilaterian limited by  
499 pure diffusion, a sensitivity analysis (Fig. 9 and Supplementary Table 7) demonstrates  
500 that one of the most important terms at very low oxygen levels is the minimum cellular  
501 oxygen concentration. This will be a small, but non-zero, number (Raff and Raff, 1970).  
502 Raff and Raff (1970) used a value of  $1/10^{\text{th}}$  the shared  $K_m$  of yeast and mammalian  
503 cytochrome oxidase. Here, rather than adopting an arbitrary but likely more accurate  
504 fractional value, we use the shared yeast-mammal  $K_m$  (Chance, 1957) as our ‘most  
505 likely’ value for this parameter (note that investigated invertebrate cytochrome oxidases

506 have a similar value (e.g. Gnaiger et al., 2000)). This ensures that the most important  
507 parameter in the model is an over-estimate. Second, for the hypothetical ancestor with a  
508 circulatory system, we assumed the organism did not have respiratory pigments.  
509 Although the homology of metazoan respiratory pigments is unclear (Terwilliger, 1998),  
510 their presence in this hypothetical last common bilaterian ancestor would greatly increase  
511 diffusion rates. Thus, our assumption that respiratory pigments were absent again results  
512 in a conservative estimate. Finally, and most importantly, these theoretical calculations  
513 assume a perfectly tubular organism (Alexander, 1971). Such an organism does not exist,  
514 as real animals have body wall rugosities, gills, and other structures that dramatically  
515 increase diffusive surface area with respect to volume; even the gut is a gas-exchange  
516 organ. Consequently, these ‘most likely’ values and the sensitivity analyses are not  
517 intended to yield a precise number. Rather, these models provide an indication of the  
518 lower bound of oxygen levels necessary to preclude the bilaterian body plan from  
519 Proterozoic oceans. No matter the complexity of the last common ancestor of bilaterians,  
520 theoretical modeling suggests the bilaterian body plan was unlikely to have been  
521 prohibited unless O<sub>2</sub> levels were < 0.4% PAL.

522

### 523 5.2.3 *Bilaterian metazoans- empirical lower oxygen limits*

524 These theoretical calculations can be tested with empirical observations of the  
525 oxygen limits of bilaterians in modern oxygen-minimum zones (OMZs). Unlike the biota  
526 on shelves or in regions of anthropogenic eutrophication that show deleterious oxygen  
527 responses at relatively minor oxygen depletions (Diaz and Rosenberg, 1995; Levin et al.,  
528 2009), OMZs have experienced geologically long-lasting dysoxic- to anoxic conditions,



529 allowing the fauna to adapt to these levels and providing an excellent analogue for  
530 Precambrian oceans with persistently low oxygen levels. It should be noted that  
531 organisms in modern OMZs have likely secondarily adapted to these environments rather  
532 than originating in them. Thus, the type of adaptations allowing organisms to inhabit  
533 these environment must be considered. For example, organisms with extreme metabolic  
534 adaptations, such as amitochondriate loriciferans living in an euxinic Mediterranean basin  
535 (Danovaro et al., 2010), cannot inform us about Precambrian animal evolution, as the  
536 transformation of the mitochondria into a hydrogenosome was certainly not a primitive  
537 feature. Most of the adaptations allowing bilaterians to inhabit modern low-oxygen  
538 environments, though, appear to lie in their very small, thin body plans (with high  
539 surface-area to volume ratios for increased diffusion) and enlarged respiratory organs  
540 (Levin, 2003; Gooday et al., 2010; Jeffreys et al., 2012; Lamont and Gage, 2000; Neira et  
541 al., 2001)—that is, with morphological adaptations that would have been possible, and  
542 perhaps likely, in early bilaterians. Consequently these animals can provide a useful  
543 analogue for Precambrian animal life in low-oxygen conditions.

544         In using OMZs as Precambrian analogues, it has long been recognized that the  
545 faunas are characterized by such small, thin, body plans (Rhoads and Morse, 1971). What  
546 has emerged in the four decades of oceanographic research since Rhoads and Morse's  
547 seminal paper is just how little oxygen is actually required by bilaterian animals. It is now  
548 clear that non-chemosymbiotic benthic macrofaunal (retained on 0.3 mm sieves)  
549 bilaterians can and do live in Rhoads and Morse's 'azoic' zone of <0.10 mL/L oxygen<sup>1</sup>

---

<sup>1</sup> A difficulty in interdisciplinary research on the biological effects of differing oxygen levels is the use of different units by different research communities (Hofmann et al.,

550 (Levin, 2003; Gooday et al., 2010; Levin et al., 2000; Palma et al., 2005; Zettler et al.,  
551 2009; Levin et al., 1991; Levin et al., 2002; Ingole et al., 2010), often with densities of  
552 hundreds to thousands of animals per square meter. Bilaterian faunas can even be found  
553 as low as 0.02 ml/L O<sub>2</sub>, equivalent to ~0.3% of modern surface ocean levels (assuming a  
554 normal surface ocean concentration of ~6 mL/L) in the OMZ off Chile (Palma et al.,  
555 2005), Peru (Levin et al., 2002) and the Bay of Bengal (R. Akkur, pers. comm.). The  
556 exact oxygen concentrations actually required to exclude bilaterians are likely even  
557 lower, these oxygen measurements are determined from O<sub>2</sub> sensors or seawater samples  
558 from CTD casts collected several meters (~5 m) above the seafloor. The oxygen levels at  
559 which bilaterians are recorded (namely 0.02 mL/L) approach the detection limit of the  
560 Winkler titration technique (Paulmier et al., 2006), and CTD cast values generally over-  
561 estimate in-situ benthic conditions (Breur et al., 2009). Thus, both theoretical calculations  
562 and empirical observations in modern OMZs suggest the presence of bilaterians would  
563 not have been limited unless atmospheric O<sub>2</sub> was considerably less than 1% PAL, and  
564 likely less than 0.4% PAL.

565

## 566 7. Conclusions

567 Geochemical transects of the ~800 Ma Fifteenmile Group in the Ogilvie  
568 Mountains document shallow-water facies characterized by low FeHR/FeT, a lack of  
569 enrichment in redox-sensitive trace elements, and relatively heavy and variable pyrite  
570 sulfur isotope values. Deeper-water facies (those deposited below storm wave base) are  
571 characterized by FeHR/FeT > 0.38, enrichment in redox-sensitive trace elements, and

---

2011). For consistency here we report oxygen levels as in the benthic ecology literature (mL/L). For reference 0.01 mL/L  $\approx$  0.44  $\mu$ mol/kg  $\approx$  0.014 mg/L  $\approx$  0.4 atm.

572 more depleted pyrite sulfur isotope values. Overall, this points towards an oxygenated  
573 surface layer, down to storm wave base, overlying a generally anoxic deep basin.  
574 Fluctuations between euxinic and ferruginous conditions sub-storm wave base appear to  
575 have been controlled by variations in organic carbon loading. As proxies like iron  
576 speciation and redox-sensitive trace elements provide evidence of local environments,  
577 more geochemical studies from other basins are necessary to begin building the global  
578 picture of redox heterogeneity. Further, the development of quantitative global redox  
579 tracers and better modeling are needed to place tighter constraints on the history of  
580 oxygen on Earth. Nonetheless, the Fifteenmile Group redox structure is comparable to  
581 that of a well-characterized Mesoproterozoic basin (Shen et al., 2003)—albeit with more  
582 evidence for ferruginous conditions-- and both basins are consistent with broad estimates  
583 for atmospheric oxygen levels between 1 and 40% PAL (Kump, 2008).

584         Comparing these likely O<sub>2</sub> levels with the estimated physiological requirements of  
585 early animals suggests that sufficient atmospheric oxygen, even for mobile bilaterians,  
586 was present well in advance of the origin of animals. Unless early Neoproterozoic oxygen  
587 levels were substantially < 1% PAL, and likely < 0.4% PAL, atmospheric oxygen levels  
588 would not have prohibited the sponge, eumetazoan and bilaterian body plans. This  
589 conclusion does not imply that animals necessarily lived in the Fifteenmile basin, but  
590 rather that global O<sub>2</sub> levels were likely adequate for the presence of animals. Notably, this  
591 does not negate the possibility of an oxygenation event around the Sturtian glaciation  
592 (Planavsky et al., 2010; Frei et al., 2009), or the use of oxygenated ‘oases’ beneath  
593 photosynthetic mats by the earliest trace makers in the geological record (Gingras et al.,

594 2011), but it does suggest that such conditions were not necessary for the origin of either  
595 animals or bilaterians.

596         It is important to remember, though, that while low Precambrian oxygen levels  
597 would not have prohibited animals, including bilaterians, the environmental milieu would  
598 still have exerted a strong effect on life. Most importantly, low oxygen certainly would  
599 have constrained these organisms to very small and thin body plans with little metabolic  
600 scope (Raff and Raff, 1970; Runnegar, 1982a, b; Payne et al., 2010). Faunas in modern  
601 low-O<sub>2</sub> OMZ analogues have very small body sizes, reduced diversity, and simple food  
602 webs (Levin, 2003; Gooday et al., 2009; Sperling et al., in review). In other words,  
603 although all available data suggests bilaterians *can* live down to 1% PAL or less, the  
604 fauna would be limited to a select few—those organisms that were a couple millimeters  
605 in length and had low-energy lifestyles. Thus, while no oxygenation event need be  
606 invoked to explain the origin of animals or bilaterians themselves, the hypothesized end-  
607 Neoproterozoic oxygenation event (the timing and magnitude of which remains  
608 debated—Kah and Bartley, 2011; Och and Shields-Zhou, 2012) may still have played a  
609 role in the later Ediacaran diversification of macroscopic animals and the Cambrian  
610 ‘Explosion’ (e.g. Runnegar, 1982a; Rhoads and Morse, 1971; Knoll and Carroll, 1999).  
611 Although Cambrian diversification was certainly multifaceted (Erwin et al., 2011), a  
612 latest Proterozoic increase in oxygen levels could have allowed for an increase in both  
613 size and metabolic scope, including potentially the advent of predation, a metabolically-  
614 costly feeding strategy.

615

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628

## 629 **FIGURE CAPTIONS**

630 **Fig. 1-** Location map of the Coal Creek and Tatonduk inliers, Yukon Territory, Canada,  
631 with stars marking the location of the inliers.

632

633 **Fig. 2-** Geological map of the Coal Creek inlier, Ogilvie Mountains, Yukon Territory,  
634 showing sections (in red) studied in this paper. The stratigraphic framework for basin  
635 transects A – A' and B – B' are found in Fig. 3 and 4. The units studied as part of this  
636 paper are the informal Gibben formation, Chandindu formation and Reefal Assemblage  
637 of the Fifteenmile Group. Geological mapping by Macdonald et al. (2012).

638

639 **Fig. 3-** Stratigraphic framework and iron speciation chemistry for transect A – A' at Mine  
640 Camp, Mt. Harper and Mt. Gibben, Coal Creek inlier. Iron speciation chemistry  
641 (specifically the ratio of highly reactive iron (FeHR) to total iron (FeT)) from fine-  
642 grained siliciclastic rocks is plotted against the stratigraphic columns. Vertical line on  
643 iron speciation plots denotes a ratio of 0.38, with samples having higher ratios considered  
644 to have been deposited under an anoxic water column, and samples with lower ratios  
645 likely to have been deposited under an oxic water column. Complete redox proxy data for  
646 individual sections is found in Fig. 6 (Mt. Harper), Supplemental Fig. 1 (Mine Camp),  
647 Supplemental Fig. 2 (East Harper) and Supplemental Fig. 3 (Mt. Gibben). *m-* mud; *si-*  
648 silt; *ms-* medium sand; *cs-* coarse sand; *cg-* conglomerate. *Gib.* = Gibben formation.

649

650 **Fig. 4-** Stratigraphic framework and iron speciation chemistry for transect B – B' at  
651 Reefer Camp, Coal Creek inlier. Sections are located 5 km apart and record a transition in  
652 the Reefal Assemblage from a stromatolite reef complex into a deeper-water shale basin.  
653 Iron speciation chemistry (specifically the ratio of highly reactive iron (FeHR) to total  
654 iron (FeT)) from fine-grained siliciclastic rocks is plotted against the stratigraphic  
655 columns. Vertical line on iron speciation plots denotes a ratio of 0.38, with samples  
656 having higher ratios considered to have been deposited under an anoxic water column,  
657 and samples with lower ratios likely to have been deposited under an oxic water column.  
658 Complete redox proxy data for individual sections at Reefer Camp is found in Fig. 5.  
659 Legend for stratigraphic columns and sediment type abbreviations as in Fig. 3.  
660 Abbreviations: *W.* = Wernecke Supergroup, *Gib.* = Gibben formation, *Cha.* = Chandindu  
661 formation.

662

663 **Fig. 5-** Redox proxy data from sections B' (Fig. 5A) and B (Fig. 5B) at Reefer Camp,  
664 Coal Creek inlier. From left to right, proxy data plotted and their respective relevant  
665 baseline data denoted by vertical red lines are: highly reactive to total iron ( $\text{FeHR}/\text{FeT}$ ;  
666 0.38), pyrite iron to highly reactive iron ( $\text{FeP}/\text{FeHR}$ ; 0.80), total iron to total aluminum  
667 ( $\text{FeT}/\text{Al}$ ; 0.50), molybdenum (2.6 ppm), vanadium (130 ppm), pyrite sulfur isotope  
668 values (0 ‰), and weight percent total organic carbon. Relative base level curve from  
669 sequence stratigraphic study of Macdonald et al. (2012). The far right column is a  
670 subjective estimate of water column redox state based on the multi-proxy data, and is  
671 meant to represent general trends rather than an estimate for every point. Euxinia(?)  
672 denotes uncertainty regarding whether these samples represent deposition under a truly  
673 euxinic water column or a ferruginous water column with sulfide production at or near  
674 the sediment-water interface (see text). Legend for stratigraphic column and formation  
675 name abbreviations as in Fig. 3 and 4.

676

677 **Fig. 6-** Redox proxy data from the Mt. Harper section, Coal Creek inlier. This figure is a  
678 composite section from the Mt. Harper area (Fig. 2). Redox proxy data and their relevant  
679 baseline values (marked by vertical red lines) as in Figure 5. Relative base level curve  
680 from sequence stratigraphic study of Macdonald et al. (2012). The far right column is a  
681 subjective estimate of water column redox state based on the multi-proxy data, and is  
682 meant to represent general trends rather than an estimate for every point. Euxinia(?)  
683 denotes uncertainty regarding whether these samples represent deposition under a truly  
684 euxinic water column or a ferruginous water column with sulfide production at or near

685 the sediment-water interface (see text). Legend for stratigraphic column and formation  
686 name abbreviations as in Fig. 3 and 4.

687

688 **Fig. 7-** Redox proxy data from the Mt. Slipper section, Tatonduk inlier. Redox proxy data  
689 and their relevant baseline values (marked by vertical red lines) as in Figure 5. Relative  
690 base level curve from sequence stratigraphic study of Macdonald et al. (2012). The far  
691 right column is a subjective estimate of water column redox state based on the multi-  
692 proxy data, and is meant to represent general trends rather than an estimate for every  
693 point. Euxinia(?) denotes uncertainty regarding whether these samples represent  
694 deposition under a truly euxinic water column or a ferruginous water column with sulfide  
695 production at or near the sediment-water interface (see text). Legend for stratigraphic  
696 column and formation name abbreviations as in Fig. 3 and 4. Scale microfossils described  
697 by Cohen et al. (2011) are found at the top of the Reefal Assemblage at this locality.

698

699 **Fig. 8-** Boxplot analysis of total organic carbon weight percentages for samples  
700 determined likely to have been deposited under a ferruginous and euxinic water column.  
701 Bottom-water redox state for each sample was estimated using a multi-proxy framework  
702 including iron speciation data, redox-sensitive trace elements and pyrite sulfur isotope  
703 values (see text for details). Samples designated as euxinic may represent sulfide  
704 accumulation at the sediment-water interface rather than true water-column euxinia (see  
705 text). The box represents the 25<sup>th</sup> and 75<sup>th</sup> percentiles, the thick horizontal line represents  
706 the median, and the whiskers represent minimum and maximum values. An extreme



707 outlier in the ferruginous set (E1002- 470.4; 9.87 wt %) was included in the boxplot  
708 calculations but not graphed.

709

710 **Fig. 9-** Theoretical minimum oxygen requirements for the last common ancestor (LCA)  
711 of bilaterians, following the equations governing the diffusion of oxygen into an  
712 organism from Alexander (1971) and modified by Payne et al. (2010). Estimates were  
713 made for two potential body plans characterizing the bilaterian LCA, a 600  $\mu\text{m}$  long  
714 worm limited by pure diffusion, and a 3-mm long worm with a circulatory system. ‘Most  
715 likely’ values represent values estimated from optimal values for all parameters (see  
716 Supplemental Information). Minimum and maximum values were derived from the  
717 literature for each parameter and global minimum and maximum values were estimated.  
718 A sensitivity analysis was then conducted for each parameter by varying that parameter  
719 between minimum and maximum values while keeping all other parameters at their ‘most  
720 likely’ values. All estimates for oxygen requirements are far less than the 1% of Present  
721 Atmospheric Levels indicated by canonical views of atmospheric oxygen levels in the  
722 Proterozoic (Kump, 2008). Lowest row for extant mobile bilaterians shows the current  
723 lower oxygen limit at which bilaterians are found in the modern ocean ( $0.02 \text{ mL/L O}_2 \approx$   
724  $0.33\%$  of modern surface ocean levels assuming a normal surface ocean level of  $6 \text{ mL/L}$ ).  
725 Bilaterians are found at these levels off the coasts of Peru, Chile, and in the Bay of  
726 Bengal. This oxygen level may represent an overestimate due to the methodology used to  
727 measure oxygen in most benthic ecology studies (Breur et al., 2009 and see text).

728

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Highlights for Sperling *et al.*

- 1) We present the first early Neoproterozoic basin redox transect
- 2) Redox proxy data are consistent with quantitative constraints on Proterozoic O<sub>2</sub>
- 3) Inferred Proterozoic oxygen levels would not prohibit the presence of animals

**Figure 1**

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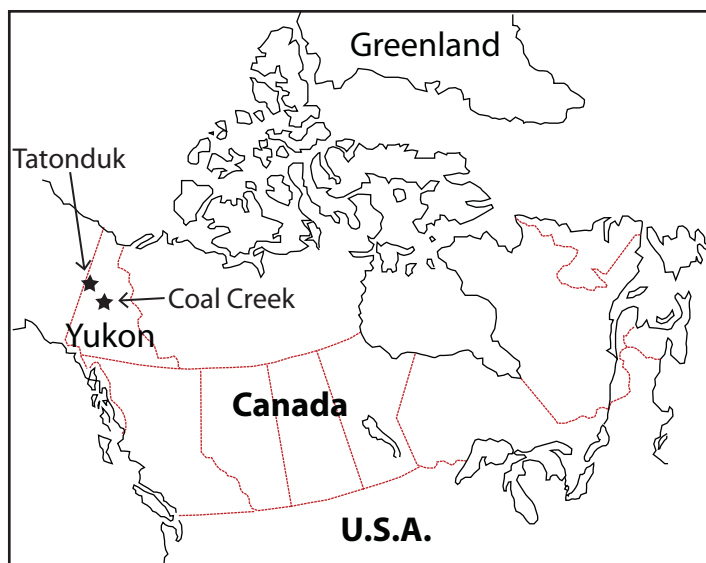




Figure 2  
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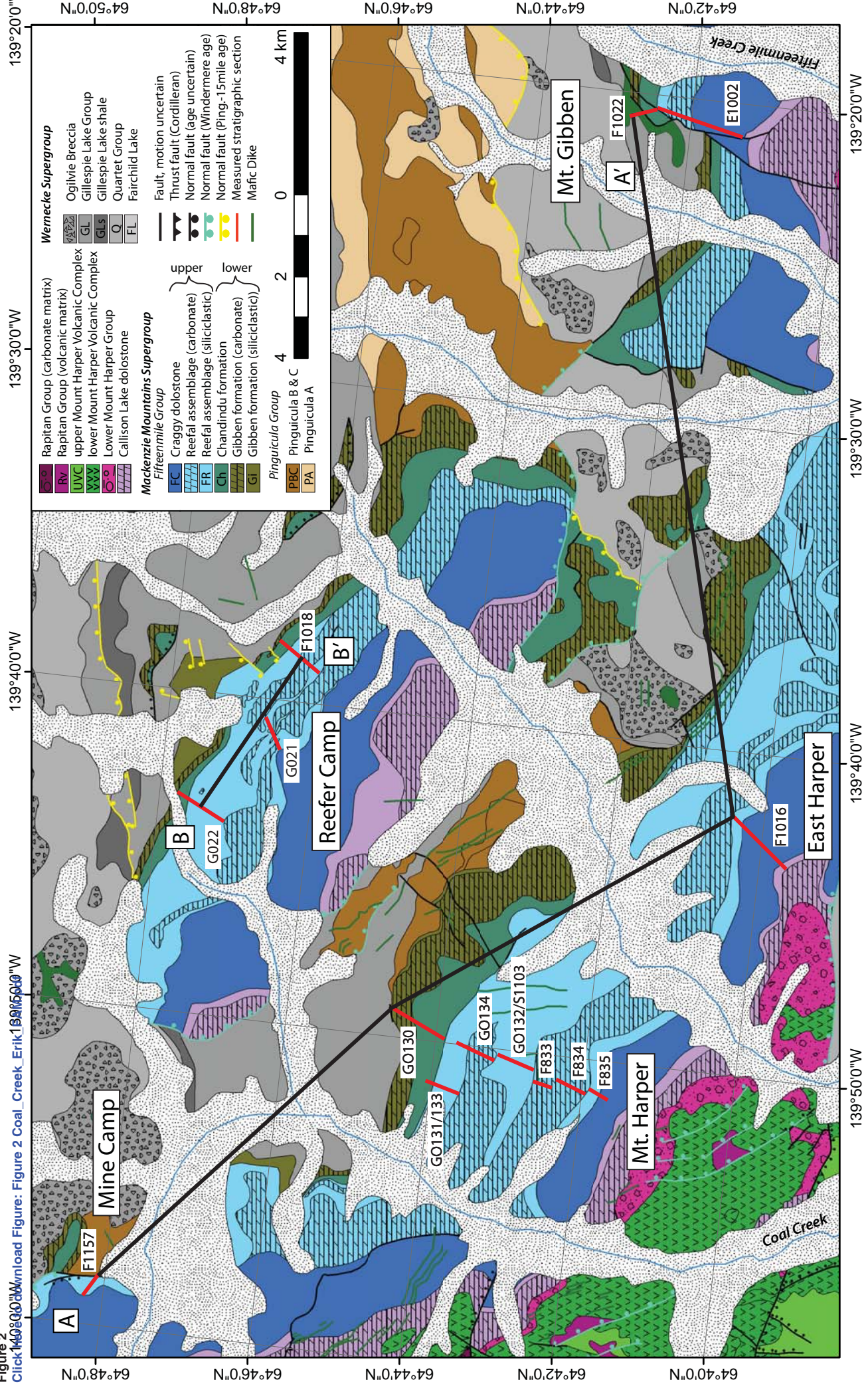
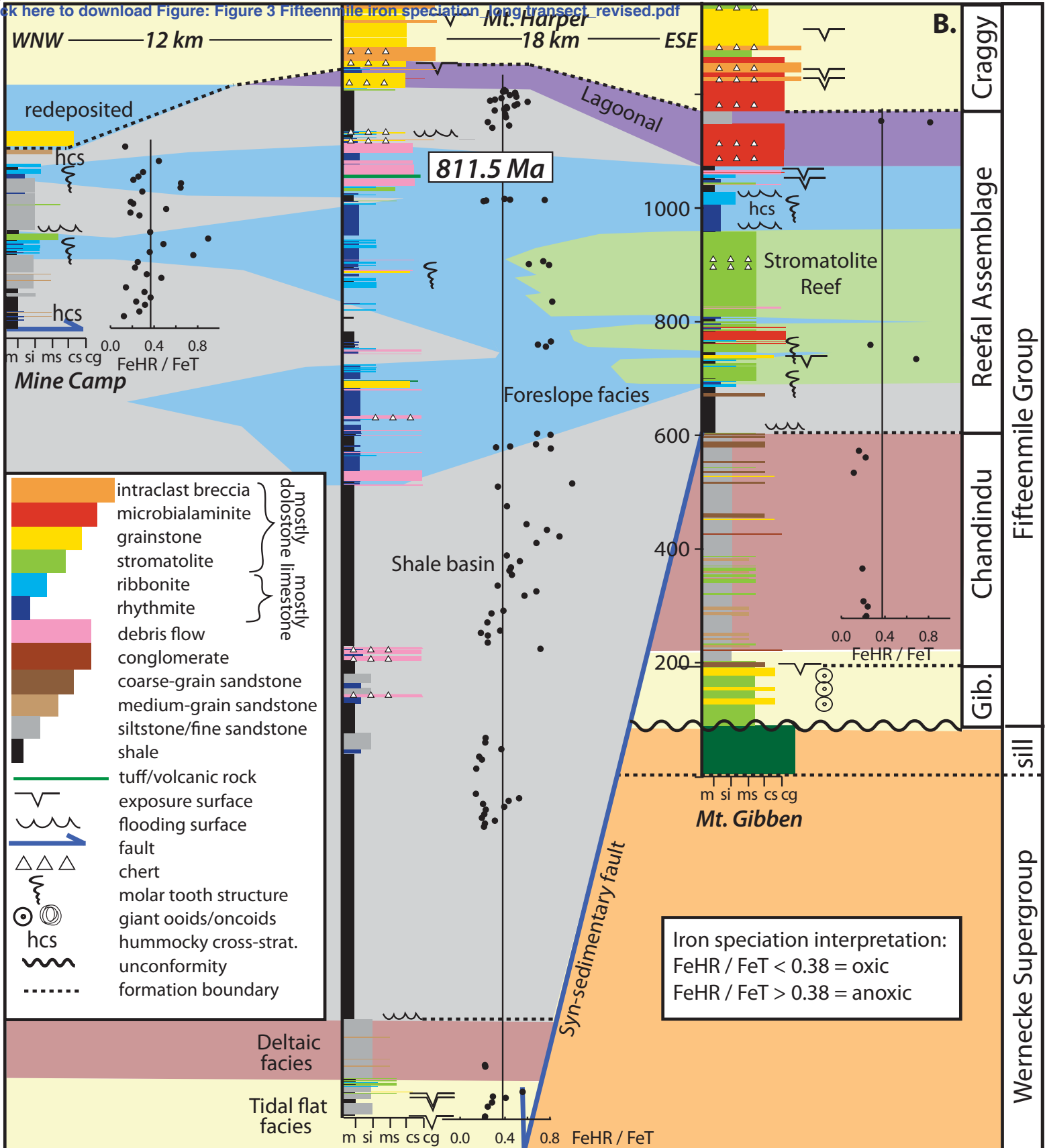




Figure 3

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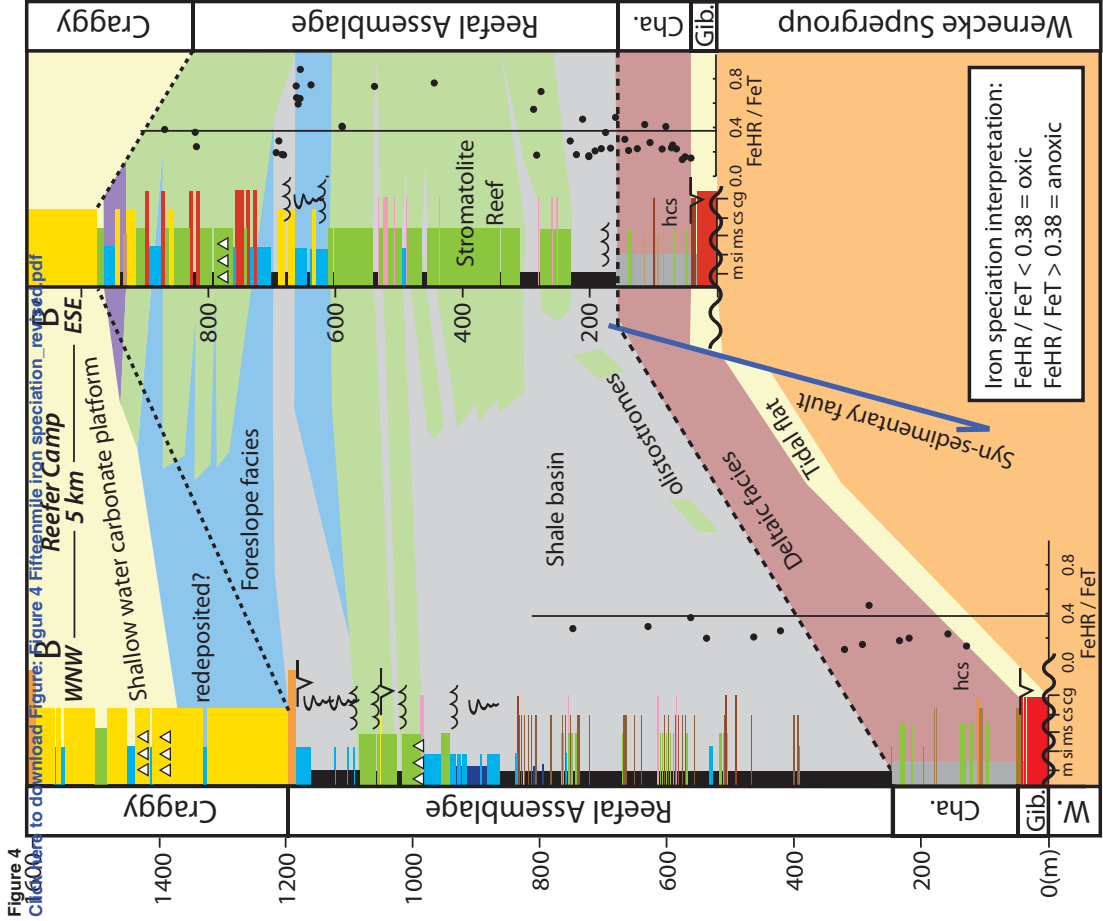


Figure 5

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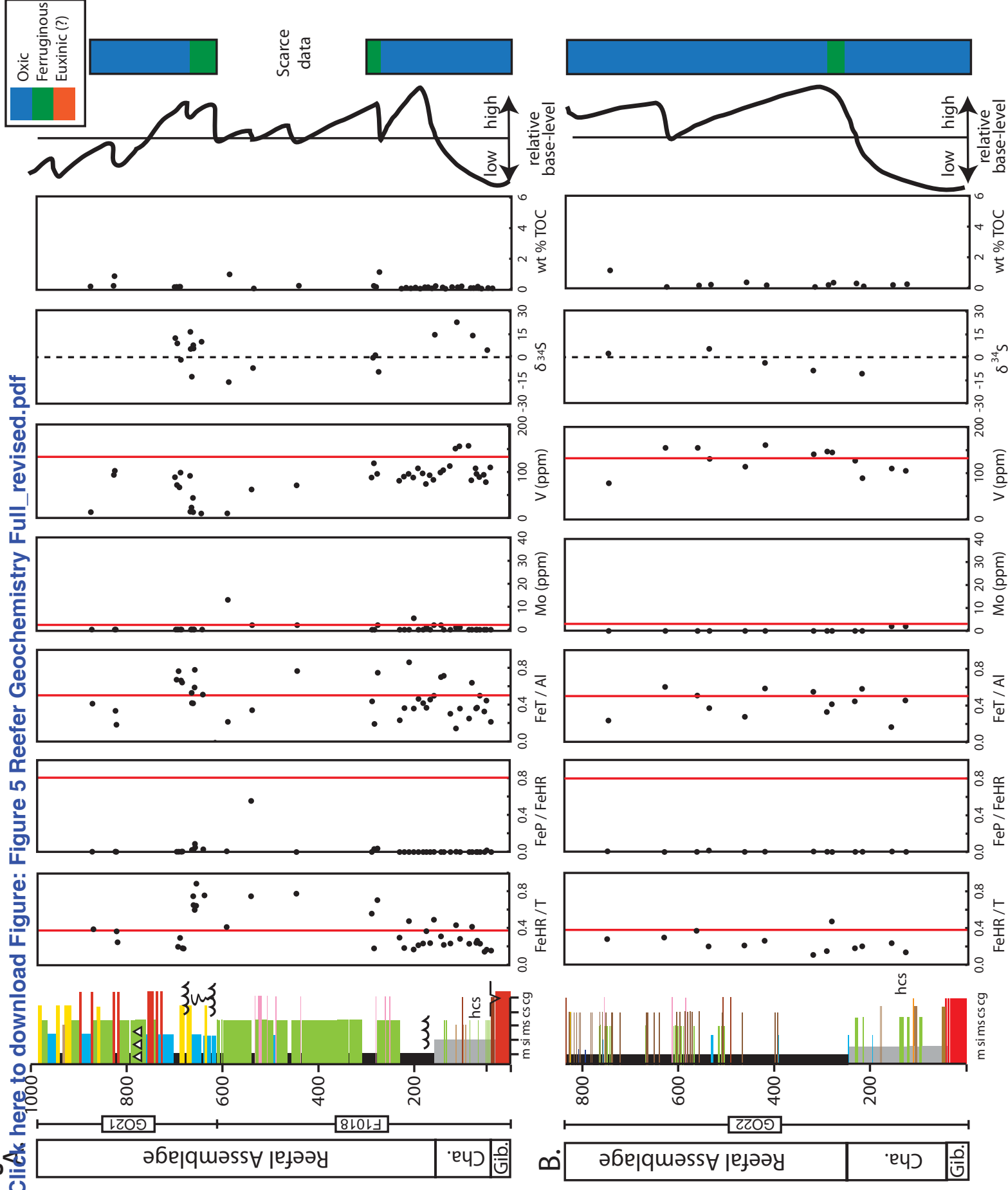


Figure 6

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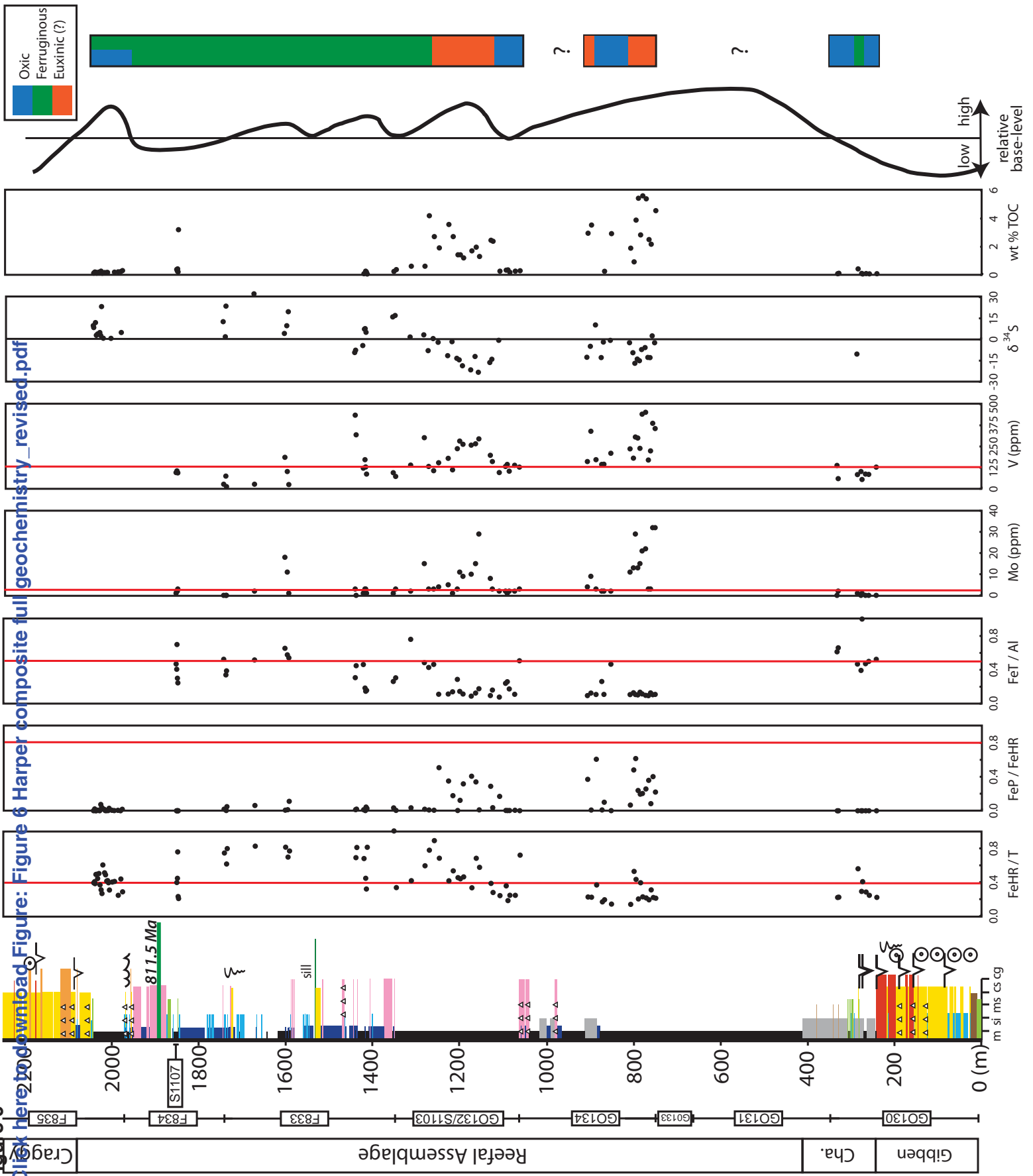


Figure 7

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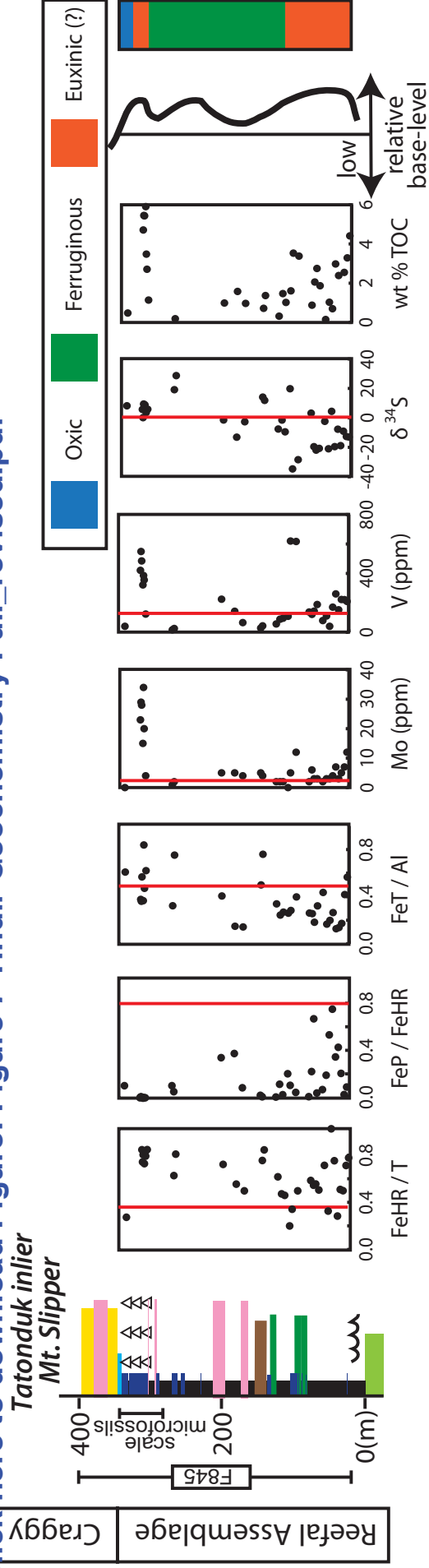




Figure 8  
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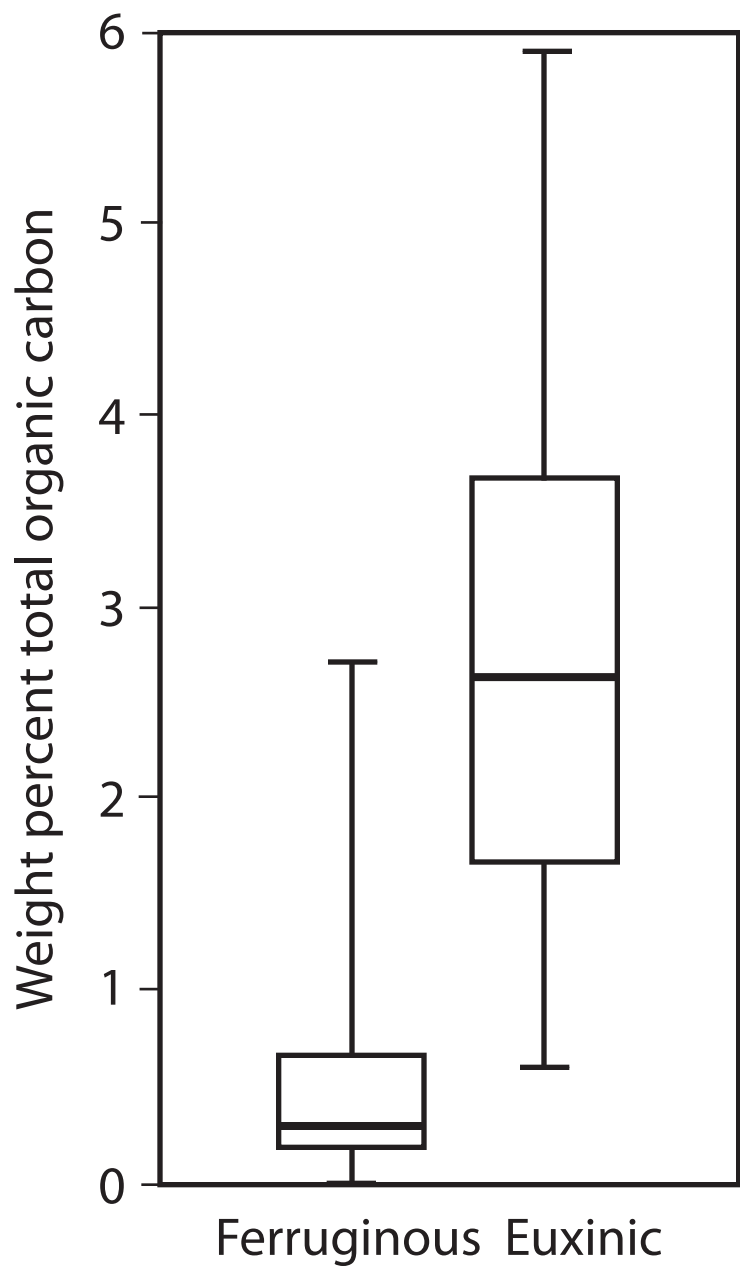


Figure 9

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