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The Iron Paleoredox Proxies: A Guide to the Pitfalls, Problems and Proper Practice

by

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23 **ABSTRACT. Oceanic anoxia—including euxinic settings defined by the presence of water**
24 **column hydrogen sulfide (H_2S)—is minor in the ocean today. Such conditions, however,**
25 **were common or even dominant in the past, particularly during the Precambrian and**
26 **Phanerozoic oceanic anoxic events. The latter are associated with massive petroleum and**
27 **mineral reserves and many of the major extinction events in the paleontological record.**
28 **Our ability to recognize ancient oxygen deficiencies relies strongly on paleontological data**
29 **viewed in combination with geochemical tracers, and geochemistry is typically our only**
30 **window onto ancient marine redox during the Precambrian when diagnostic skeletal and**
31 **behaviorial traces of oxygen-dependent animals are mostly missing. So far no approach**
32 **has gained wider acceptance than the iron proxies, which rely generally on quantification**
33 **of the extent to which reactive iron (as oxides principally) is converted to pyrite. The**
34 **promise of these approaches lies in part with the relative ease of measurement, but it is this**
35 **ease and the corresponding widespread use that has also led to misuses.**

36 **Much of the recent confidence in the iron paleoredox proxies lies with**
37 **sophisticated deconstruction of the reactive Fe pool via mineral-calibrated wet chemical**
38 **speciation. These validations and calibrations, mostly in the modern ocean, expose the**
39 **challenges, while at the same time opening other doors of opportunity as the catalog of**
40 **controlling factors extends beyond water column redox to include sedimentation rate,**
41 **sedimentary Fe remobilization, signals of oscillatory redox, and hydrothermal versus other**
42 **primary Fe inputs to the ocean, among other factors. Also key is a deep understanding of**
43 **the limitations imposed—or at least the due diligence required—as linked to mineral**
44 **transformations during burial and metamorphism. This review seeks to highlight many of**
45 **the key issues, including appropriate sample choices, as a roadmap for those keen to apply**
46 **Fe proxies in their studies of ancient oceans and their relationships to co-evolving life.**
47 **Among the critical messages to take away is the value of robust Fe-based measures of local**
48 **redox that, when combined with elemental mass balances and isotopic proxies dependent**
49 **on those local conditions, can shed light on the global redox state of the oceans through**
50 **time and related implications for the history of life on Earth.**

51

53 INTRODUCTION

54   Iron geochemistry has arguably become the most widely used approach to assess local

55 oxygen conditions in ancient marine environments. These Fe-based methods have heightened

56 utility because of studies over the past two decades that have explored their mechanistic

57 underpinnings, particularly in modern analog settings, and through increased interest in time

58 periods, particularly in the Precambrian, when paleoredox is otherwise difficult to assess in the

59 absence of unambiguously diagnostic fossils. Added value has also come from coupling of Fe-

60 based paleoredox proxies with other methods, such as trace metal geochemistry and isotope

61 work, that together yield more convincing, and often more nuanced, views of ancient aquatic

62 settings on a range of spatial scales. These iron methods are grounded in careful development of

63 a sequential wet chemical extraction scheme calibrated against pure mineral phases and through

64 extensive analysis of modern marine sediments, wherein direct measures of the oxygen and

65 hydrogen sulfide availability in the water column are possible. In very simple terms, the

66 methods are predicated on the observation that iron-bearing mineral phases (oxides and

67 carbonates in particular) that are reactive toward hydrogen sulfide on short, diagenetic time

68 scales are enriched relative to the total iron pool in sediments deposited beneath anoxic waters

69 that are either ferruginous or sulfidic (see Appendix for definitions). Furthermore the extent to

70 which this iron is converted to pyrite (see Appendix) ties closely to the presence or absence of

71 sulfide. However, since the iron proxies are empirically calibrated they can be misapplied and

72 care must be taken to ensure that the samples being analyzed are equivalent in fundamental ways

73 (for example, lithology) to those against which the proxies were calibrated.

74   A major strength of the iron proxies is the ease with which data can be generated on

75 relatively small samples. Prior to the development of these proxies, different depositional redox

76 environments were recognized by paleoecological or micropaleontological techniques, organic

77 geochemical indicators, carbon-sulfur relationships, or combinations of isotopic data and

78 mineralogy. All of these methods had disadvantages arising from fossil preservation/availability

79 issues, sample size, time-consuming separations, expensive instrumentation, or ambiguities due

80 to compositional effects (Raiswell and others, 1988). With the emergence of the first of the iron

81 proxies, the Degree of Pyritization (see Appendix), many of these difficulties were overcome;

82 sample sizes were small, the analytical methodology was simple and required only basic

83 instrumentation, and the method was supported by earlier studies of Fe mineral diagenesis in

84 modern marine sediments. Despite this important step forward, complications soon emerged,

85 leading to the development of refined proxies (Poulton and Canfield, 2005), but additional steps

86 remain to be taken. As will be seen below, there are many issues that require further

87 consideration, such as the impact of high sedimentation rates, fluctuating redox conditions, iron

88 enrichment mechanisms, diagenetic/metamorphic remobilization, and mineralogical/lithological

89 variations.

90   In recent years, we have observed examples where these wide ranging concerns are

91 not considered adequately. Crucially, we have learned that proxies should be considered in a

92 holistic context to optimize interpretations, a message that will be repeated in the examples that

93 follow. Our goal in this review is to walk through the various iron proxies, provide historical

94 context on their development (for more detail on this see Raiswell and Canfield, 2012), and to

95 illustrate, through a set of case studies, ways in which the proxies can forward our

96 understanding—or lead to ambiguous conclusions. It is not our intent to provide a

97 comprehensive critique of all recent applications of the iron proxies. Rather, our aim is to build a

98 foundation that captures the state of the art while also offering suggestions for best practices as

99 the field moves forward. A glossary in the Appendix provides working definitions of relevant

100 terms used throughout the text.

DEGREE OF PYRITIZATION

102   The Degree of Pyritization (DOP) was originally developed to explore the effects of

103 iron limitation on pyrite formation in modern marine sediments (Berner, 1970) and was only

104 subsequently used to recognize the degree of bottom water oxygenation in organic carbon-

105 bearing marine sediments and ancient rocks (Raiswell and others, 1988). The foundation here is

106 that pyrite formation requires three major components—iron, organic carbon, and sulfate—and

107 each component can limit pyrite formation as a function of the first-order environmental

108 conditions (fig. 1). Specifically, fresh waters and some early Precambrian marine systems may

109 be limited in their supplies of sulfate. Organic carbon content controls pyrite formation in anoxic,

110 non-sulfidic porewaters beneath oxic bottom waters (sometimes termed normal marine,

111 following Raiswell and others, 1988), while iron imitation is indicated when sulfide builds up in

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112 those porewaters. Finally, iron is always limiting within and beneath anoxic/sulfidic (euxinic; see
113 Appendix) bottom waters (Berner, 1984; Raiswell and Berner, 1985). In anoxic bottom waters
114 and porewaters, anaerobic microbes initiate the process of pyrite formation through sulfate
115 reduction—and the more organic C present, the more hydrogen sulfide produced and pyrite
116 formed (until iron becomes limiting). Within this framework, we can imagine that Degrees of
117 Pyritization, and thus extents of Fe limitation, could straightforwardly fingerprint ancient
118 euxinia, and so methods were developed that allow us to quantify different Fe mineral pools.

119   DOP was defined by Berner (1970) as:

120         $$DOP \ = \ \frac{\text{Pyrite Fe}}{\text{Pyrite Fe} \ + \ \text{HCl−soluble Fe}} \hspace{2cm} (1)$$

121 where HCl-soluble Fe is extracted using concentrated HCl (table 1). This method completely
122 dissolves fine-grained iron (oxyhydr)oxides, magnetite, and iron carbonates and partially extracts
123 iron from some iron silicates (micas and clays in particular), such as nontronite, chlorite, and
124 biotite (Raiswell and others, 1994). This HCl-soluble iron was assumed to provide a rough
125 measure of the sediment iron that was reactive towards sulfide. It was hypothesized (Raiswell
126 and others, 1988) that DOP might increase through increased consumption of HCl-soluble Fe in
127 depositional environments where there is increased opportunity for exposure to dissolved sulfide,
128 such as sites marked by euxinia. DOP was subsequently measured in a range of Jurassic,
129 Cretaceous, and Devonian sediments from depositional environments that were grouped into
130 three categories representing a range of decreasing bottom water oxygenation:

131 (1) Aerobic (normal marine): homogeneous bioturbated sediments with trace fossils and an
132 abundant and diverse benthic fauna dominated by epifaunal bivalves. These sediments were
133 deposited from bottom waters that were fully oxygenated.

134 (2) Restricted (normal marine): poorly laminated sediments with sparse bioturbation and
135 bivalves mainly comprising infaunal deposit feeders. Bottom waters were poorly oxygenated or
136 fluctuated between oxic and anoxic.

137 (3) Inhospitable bottom water: finely laminated sediments with little or no bioturbation and a
138 benthic fauna, if present, comprised of epifaunal suspension feeders. Bottom waters were anoxic
139 (contained no dissolved oxygen).

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140   The aerobic normal marine sediments (hereafter termed oxic) had values of DOP
141   <0.45 and were clearly separated from restricted (hereafter dysoxic; see Appendix) samples with
142   DOP values ranging from 0.45-0.80. Samples with inhospitable bottom waters contained only a
143   very limited fauna and must have been mostly anoxic but were not necessarily sulfidic (euxinic).
144   There was some overlap in samples from dysoxic and inhospitable bottom waters (hereafter
145   anoxic, with DOP values of 0.55-0.93), but a boundary at 0.75 separated more than 90% of the
146   samples from these two sets. The overlapping DOP values were attributed to temporal
147   fluctuations between low oxygen and anoxic conditions, suggesting that unambiguous proxy
148   signals can only result from stable depositional environments. Finally, the relatively high DOP
149   values in most anoxic samples were attributed to the presence of sulfide in the bottom waters,
150   which provided an opportunity for detrital iron minerals to react with dissolved sulfide both in
151   the water column and during burial after deposition. In other words, high euxinic DOP values,
152   approaching unity, were thought to result from nearly complete pyritization of all the HCl-
153   extractable iron—thanks to its long exposure to sulfide in the water column, on the seafloor, and
154   during burial.

155   The idea that protracted sulfide exposure alone explains the high DOP values of
156   euxinic sediments turned out to be incorrect. The explanation lies instead with the unique iron
157   properties of such settings. Most pyrite forms from iron (oxyhydr)oxide minerals that are
158   reactive towards sulfide on timescales of less than a year, whereas many other iron minerals
159   react, if at all, on timescales of thousands of years (Canfield, 1989; Canfield and others, 1992,
160   Raiswell and Canfield, 1996). For example, the iron extracted by HCl from nontronite, chlorite,
161   and biotite (see Berner, 1970) is scarcely able to react with H_2S to form pyrite, and thus the
162   measurements of HCl-soluble Fe by Raiswell and others (1988) include minerals that cannot be
163   significantly pyritized. Consistent with this, Canfield and others (1992) found that all the iron
164   (oxyhydr)oxides were sulfidized in the sediments from the Friends of Anoxic Mud (FOAM) site
165   in Long Island Sound, but only intermediate DOP values (~0.40) were reached despite exposure
166   to porewater sulfide concentrations of up to 6 mM for thousands of years (see Case Study 1 and
167   Hardisty and others, in review). These data show that high DOP values in euxinic sediments
168   could not arise as a result of exposure of poorly reactive HCl-soluble Fe minerals to high
169   concentrations of sulfide for long periods of time. Instead, these high DOP values must result

170 from elevated concentrations of the easily pyritized iron (oxyhydr)oxide minerals as compared to

171 oxic sediments.

172   The potential for iron-bearing silicates to react with sulfide was further examined in

173 separate Black Sea studies by Canfield and others (1996) for the deep basinal, euxinic sediments

174 and by Lyons and Berner (1992) for shelf margin sediments and turbidites deposited rapidly

175 under euxinic conditions. Canfield and others (1996) used a dithionite extraction (table 1) to

176 search for iron (oxyhydr)oxide minerals, with negligible effects on the silicates that are partially

177 dissolved in the overly aggressive boiling HCl (see Raiswell and others, 1994). This work,

178 combined with pyrite extractions, showed that the Black Sea sediments contained very little

179 unreacted (oxyhydr)oxide Fe but had 2-3 times more readily pyritized iron compared to typical

180 continental margin sediments. The conclusion was that 'extra' highly reactive iron (see

181 Appendix) was needed to produce high DOP values. Various mechanisms were suggested to

182 explain how additional reactive iron could be derived from the water column.

183   The Lyons and Berner (1992) study found that shelf margin sediments and turbidites

184 deposited rapidly under euxinic conditions, in contrast only reached intermediate DOP values

185 (see Case Study 2). This relationship was attributed to their rapid deposition and the associated

186 presence of smaller amounts of readily reactive iron compared to more slowly accumulating

187 euxinic sediments, even though the these sites of rapid deposition experienced long exposure to

188 high levels of sulfide during burial. Conversely, high DOP values in the deep, slowly

189 accumulating Black Sea basin were attained rapidly in the water column and in the uppermost

190 sediment layers. This observation further confirmed that reactive iron enrichments (and not

191 sulfide exposure) were necessary for high DOP values measured using the HCl method, while

192 also asserting the need to consider the sedimentological context and the possible sources and

193 controls for inputs of additional iron. These issues are the focus of discussions below. In

194 conclusion, high values of DOP (>0.75) almost universally reflect euxinic conditions, and low

195 values (<0.45) generally typify oxic depositional conditions. However, it is important to realize

196 that intermediate values can arise both from fluctuating depositional environments and persistent

197 exposure to sulfide-limited porewaters, as well as from rates of sedimentation that are

198 sufficiently high to dilute the additional reactive iron under euxinic conditions (Lyons, 1997;

199 Werne and others, 2002; Cruse and Lyons, 2004; Lyons and Severmann, 2006; Lyons and others,
200 2009).

201   Modern sediments with relatively high concentrations of AVS (Acid Volatile Sulfides;
202 see Appendix) are better characterized by defining a Degree of Sulfidation (DOS; see Appendix),
203 rather than DOP. DOS is derived by the addition of AVS-associated Fe to the numerator and
204 denominator of DOP;

205 $$DOS = \frac{Pyrite\ Fe + AVS\ Fe}{Pyrite\ Fe + AVS\ Fe + HCl-soluble\ Fe} \qquad (2)$$

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207 DOS is preferred over DOP for euxinic systems when AVS is present in appreciable amounts
208 (Boesen and Postma, 1988; Hurtgen and others, 1999; Lyons and Severmann, 2006; Middelburg,
209 1991). However we emphasize that the calibration of DOP is empirical and that the
210 paleoenvironmental boundary values cannot be directly used for DOS. The same is also true
211 where HCl-soluble Fe is replaced by other Fe extractions or by total Fe.

212   Regardless of the above, DOP remains a valid paleoenvironmental proxy subject to the
213 constraints listed below which will, however, be amended in the following discussions. From
214 these collective observations, basic ground rules emerged:

215 (1) Appreciable organic C (>0.5%) should be present. Sediments low in organic C undergo little
216 or no sulfate reduction, and, for example, freshwater (sulfate-limited) and oxic marine sediments
217 can be impossible to distinguish. (Importantly, high amounts of pyrite with very low organic C
218 can, in theory, be a fingerprint of euxinia).

219 (2) Fresh outcrop or drill material should be used to minimize the loss of pyritic sulfur by
220 oxidative weathering. Ahm and others (2017) found that weathering losses of pyrite could be
221 found even in freshly exposed rock and weathering effects were only completely absent in
222 samples taken beneath a drill core surface.

223 (3) Sediments should contain sufficient fine-grained, clastic, iron-containing material. Raiswell
224 and others (1988) suggested that clastics are sufficiently abundant as long as there is less than

225 65% skeletal debris, although recent work suggests that carbonate rocks may offer greater

226 promise than suggested by this earlier work (see later).

227 (4) No additions or losses of sulfur should have occurred as a result of sediment maturation or

228 metamorphism. The formation of metamorphic pyrrhotite will be considered in Case Study 5.

229 (5) Sediments containing late diagenetic, iron-rich concretionary carbonates should be avoided,

230 as iron migration may have added substantial amounts of HCl-soluble Fe.

231 (6) Raiswell and Berner (1986) also suggested that sediments older than the Devonian should be

232 avoided because their associations with more-reactive organic C (in the absence of poorly-

233 metabolizable, terrestrial plant-derived organic C) produce more pyritic sulfur per unit of organic

234 C. However, as will be discussed, there has been an increasing appreciation that the reactive iron

235 flux to the sediment is the predominant control on DOP, and numerous studies have applied

236 these methods to very old, even Precambrian rocks.

237   Constraints 1-5 exclude many common rock types such as coals, evaporites, and

238 sandstones—also cherts and limestones with a low clastic content. The compositional constraints

239 defined by (1) to (5) are re-visited below. Consistent with the idea that the reactive iron flux

240 dominates DOP, Raiswell and Al-Biatty (1989) found the DOP boundary at 0.75 also separates

241 early Paleozoic samples deposited in oxic or dysoxic bottom waters from those deposited under

242 euxinic conditions.

243   THE INDICATOR OF ANOXICITY (Fe_{HR}/Fe_T)

244   The iron extracted by boiling HCl includes iron present in minerals that are too

245 recalcitrant to be pyritized, in turn suggesting the need for a more accurate measure of the iron

246 that was truly highly reactive towards sulfide. The high DOP values observed in modern

247 euxinic sediments (such as the Black Sea; Lyons and Berner, 1992; Canfield and others, 1996;

248 Wisjman and others, 2001) were found to result from a larger pool of iron delivered as

249 (oxyhydr)oxides (larger than that found in oxic sediments) and/or through additional iron

250 supplied in the dissolved ferrous form. Iron as (oxyhydr)oxides (table 1) can be measured by a

251 dithionite extraction (Canfield, 1989), thus allowing highly reactive iron (Fe_{HR}) to be defined as

252 the dithionite-extractable iron (oxyhydr)oxides iron fraction (Fe_{ox}, with high potential to form

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253   pyrite) plus iron already present as pyrite (Fe_{py}). In contrast, the HCl-soluble Fe includes all

254   the Fe minerals soluble in dithionite plus other more recalcitrant Fe minerals that cannot be

255   pyritized – at least on short diagenetic time scales. Importantly, the boiling HCl method should

256   only be used to approximate Fe_{HR} if authigenic iron silicates are present (see Case Study 6),

257   otherwise false signals of reactive iron enrichment can be produced (Wen and others, 2014).

258   Measuring Fe_{HR} as $Fe_{ox} + Fe_{py}$, Raiswell and Canfield (1998) showed that modern oxic

259   continental margin and deep sea sediments exhibit a range of Fe_{HR} contents. Table 2 shows these

260   Fe_{HR}/Fe_T values (which define an Indicator of Anoxicity; see Appendix and Raiswell and others,

261   2001) for oxic, modern continental margin and deep sea sediments along with data from settings

262   with fluctuating/dysoxic conditions and from the euxinic Black Sea and Cariaco Basin. Mean

263   Fe_{HR}/Fe_T ratios from continental margin and deep sea sediments (0.26±0.08) are similar to those

264   from fluctuating/dysoxic sediments (0.28±0.10), but both are clearly separated from the Black

265   Sea (0.70±0.19) and the Cariaco Basin (0.51±0.03). A threshold value of 0.38 was found to

266   separate the highest oxic data from the lowest anoxic/euxinic ratios. However, intense

267   weathering environments (high rainfall and temperatures) can produce higher Fe_{HR}/Fe_T values

268   (ranging up to 0.52; Shi and others, 2011; Raiswell and others, 2016); similarly high values

269   occur through intense physical or biological re-working in marginal marine environments (Aller

270   and others, 1986). As such, there is no a priori reason to regard the 0.38 threshold as a definitive

271   boundary throughout Earth history, and values falling near this boundary should be regarded as

272   ambiguous (as addressed in discussions below). Strongly elevated Fe_{HR}/Fe_T ratios by definition

273   identify anoxic water columns that are either ferruginous or euxinic, and dysoxic regimes (low

274   oxygen but neither euxinic or ferruginous) and those with fluctuating dysoxic conditions are

275   therefore not discernable from oxic environments (Raiswell and Canfield, 1998) and require

276   additional tools to delineate (see table 2).

277   In recent years, Fe_{HR}/Fe_T has been refined in response to an improved understanding

278   of highly reactive iron (Poulton and others, 2004) based on the recognition that rocks often

279   contain highly reactive iron minerals other than pyrite and iron (oxyhydr)oxides—in particular,

280   magnetite, siderite, and ankerite. An analytical scheme was developed (Poulton and Canfield,

281   2005) to measure Fe present in these minerals, leading to a new definition of highly reactive Fe

282   based on Fe present as carbonates (Fe_{carb}, sodium acetate-soluble Fe), oxides (Fe_{ox}, dithionite-

283   soluble crystalline Fe oxides), magnetite (Fe_{mag}, oxalate-soluble Fe) and pyrite (Fe_{py}):

284                          $$Fe_{HR}= Fe_{carb} + Fe_{ox} + Fe_{mag}+ Fe_{py} \qquad (3)$$

285   In the case of modern sediments Fe_{HR} would also include the Fe present as AVS (Fe_{AVS}). This

286   newer definition demands that we consider whether the threshold value defined earlier — based

287   on Fe_{HR} data that excluded Fe_{carb} and Fe_{mag}— should be modified. There is no simple answer to

288   this question. In some cases, the addition of Fe_{mag} may have little impact on Fe_{HR}/Fe_T for typical

289   oxic sediments (see Case Study 1; Hardisty and others, in review; Goldberg and others, 2012). In

290   other cases, Fe_{mag} has been found to represent a significant fraction of Fe_{HR} (for example, in

291   some glacially derived sediments; März and others, 2012). From hereon all Fe_{HR} data in our

292   discussions are derived using the Poulton and Canfield (2005) methodology (unless otherwise

293   specified).

294   This methodological issue may also be relevant to the observations of Poulton and

295   Raiswell (2002), who examined the iron speciation of ancient sediments ranging in age from

296   Ordovician to Jurassic and characterized as oxic (normal marine; Raiswell and Berner, 1986) on

297   the basis of paleoecology and DOP values. Defining Fe_{HR} as $Fe_{ox} + Fe_{py}$ (that is. not including

298   Fe_{carb} and Fe_{mag}) they found that the mean Fe_{HR}/Fe_T values for these Cretaceous, Jurassic,

299   Silurian, Ordovician, and Cambrian sediments ranged from 0.13±0.06 to 0.17±0.11 (average

300   0.14±0.08) —values that are significantly lower (at the <0.1% confidence level) than those from

301   modern sediments (0.26±0.08). Poulton and Raiswell (2002) attributed these low Fe_{HR}/Fe_T

302   values to reductive transformation of residual iron oxides remaining after pyrite formation to

303   poorly reactive silicate Fe during burial. This process has been identified in a number of ancient

304   settings and has been attributed to the transfer of unsulfidized Fe_{HR} to poorly reactive sheet

305   silicate Fe during early-late diagenesis in low-sulfate (and hence low sulfide) marine sediments

306   (for example, Poulton and others, 2010; Cumming and others, 2013).

307   However, Farrell and others (2013) argued that this difference may be due to the

308   inefficiency with which dithionite extracts iron carbonate and magnetite which produces low

309   values of Fe_{HR}. This difficulty, they argued, may be common in Paleozoic rocks because lower

310   sulfate concentrations in the oceans might have resulted in less conversion of Fe_{HR} to pyrite,

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311 leaving residual Fe_{HR} to form iron carbonate and magnetite. Thus, the presence of iron carbonate

312 and magnetite in Paleozoic rocks examined by the sequential methodology of Poulton and

313 Canfield (2005) could potentially produce higher mean Fe_{HR}/Fe_T values, similar to those found in

314 modern sediments (0.26±0.08) rather than the lower values (0.14±0.08) found by summing oxide

315 and pyrite Fe only (see also Farrell and others, 2013). As a consequence, the oxic threshold in

316 Paleozoic rocks should be re-evaluated using the sequential methodology of Poulton and

317 Canfield (2005). In the interim a pragmatic solution to the determination of Fe_{HR} in Paleozoic

318 samples that excludes Fe_{carb} and Fe_{mag} could be a threshold value of <0.22 based on the mean

319 plus one standard deviation (0.14±0.08) for Ordovician-Jurassic sediments (Poulton and

320 Canfield, 2011). However, this value is also not without risk because it assumes that iron

321 carbonate and magnetite are insignificant. In response, Poulton and Canfield (2011) proposed

322 that Fe_{HR}/Fe_T ratios from 0.22-0.38 should be considered equivocal, as they could represent oxic

323 conditions or anoxic conditions when high sedimentation rates have masked water column Fe_{HR}

324 enrichments or when Fe_{HR} has been transferred to poorly reactive silicate Fe during diagenesis.

325 Sperling and others (2016) point out that the lowest values of Fe_{HR}/Fe_T in rapidly sedimented

326 anoxic samples are ~0.2 (Raiswell and Canfield, 1998) and lower values are very likely to be

327 oxic.

328   There are also important compositional constraints on use of the Fe_{HR}/Fe_T ratio for the

329 oxic/anoxic threshold in carbonate-rich sediments. Clarkson and others (2014) used the Poulton

330 and Canfield (2005) methodology on sediments containing 65-80% carbonate, finding that the

331 threshold Fe_{HR}/Fe_T <0.38 was valid as long as Fe_T >0.5%. However, oxic, carbonate-rich

332 sediments with Fe_T <0.5% and organic C <0.5% routinely gave spuriously high Fe_{HR}/Fe_T ratios

333 that would falsely indicate deposition under anoxic conditions. Note also that analytical errors

334 on iron species in carbonate-rich rocks (or any rocks with low values of Fe_{HR} and/or Fe_T) may

335 propagate through to produce values of Fe_{HR}/Fe_T that apparently exceed threshold values (Ahm

336 and others, 2017). Fluid alteration processes in carbonates also result in addition of iron

337 (including the formation of Fe-rich dolomites), and we stress the need for caution in dealing with

338 rocks altered by burial/metamorphic processes (see Case Study 5).

339   Values for Fe_{HR}/Fe_T in dysoxic sediments are essentially similar to those in oxic

340 sediments (<0.38), and, in general, integrated, multi-proxy geochemical approaches are required

341   for recognizing fluctuations in bottom water oxygenation (Raiswell and Canfield, 1998). For

342   example, Boyer and others (2011) examined Devonian black shales with paleontological data

343   (ichnofabric index, species richness) that clearly show short-term fluctuations in bottom water

344   oxygenation that fail to produce distinct shifts in Fe_{HR}/Fe_T. This situation arises because

345   geochemical sampling of rocks inevitably homogenizes the geological record over a significant

346   period of time, limiting our ability to recognize short-term redox variations. However, the

347   paleontological data of Boyer and others (2011) were less useful when a combination of

348   extremely low bottom water oxygenation and/or intermittent anoxia/euxinia precluded clear-cut

349   biological signals. In these cases, finely laminated sediments failed to produce positive signals

350   for anoxia or euxinia based on the threshold of $Fe_{HR}/Fe_T > 0.38$ (or by elevated values of other

351   proxies, including DOP). In all cases threshold values should be applied with caution, with

352   consideration as to depositional environment, sediment composition, and Fe_{HR} extraction

353   methodology.

354   THE Fe_T/Al RATIO

355   Alternative methods for detecting the iron enrichments that are diagnostic for

356   anoxic/euxinic sediments were developed by Werne and others (2002), who used the Fe_T/Ti

357   ratio, and Lyons and others (2003), who used the Fe_T/Al ratio. The Fe_T/Al ratio is more widely

358   used than Fe_T/Ti (see Lyons and Severmann, 2006), and only the Fe_T/Al is considered here—

359   although the same principles apply to both. The Fe_{HR}/Fe_T and Fe_T/Al proxies assume that the

360   enrichment of highly reactive iron is sufficient to produce a measurable and meaningful increase

361   (relative to possible variation in the detrital baseline). Normalization (use of ratios) also allows

362   for corrections for dilution by carbonate or silica-bearing biogenous sediment. The Fe_{HR}/Fe_T and

363   Fe_T/Al indicators both track enrichments that arise from the addition of highly reactive iron, but

364   only the former is sensitive to enrichments that arise from the conversion of an unreactive

365   portion of Fe_T to Fe_{HR}. The use of Fe_T/Al ratios to detect iron enrichments requires a baseline

366   against which enrichment can be assessed. A common threshold for this purpose are the Fe_T/Al

367   ratios in average shale, which range from 0.50 to 0.56 (for example Clarke, 1924; Ronov and

368   Migdisov, 1971; Taylor and McLennan, 1985). Although these averages do not permit the use of

369   statistical tests to assess the probability that an observed enrichment is significant, this problem

370   can be overcome by using a mean and standard deviation for an appropriate Fe_T/Al data set.

13

371   Raiswell and others (2008) found Fe_T/Al to be 0.53 ± 0.11 (confidence limits hereon are

372   for one standard deviation unless otherwise specified) in Paleozoic oxic marine shales. A more

373   recent study (Clarkson and others, 2014) demonstrated that the Fe_T/Al ratio averaged 0.55 ± 0.11

374   in modern marine sediments deposited under oxic conditions and that this value was independent

375   of carbonate content (up to 80%). Cole and others (2017) estimated a Fe_T/Al ratio for 4850 soils

376   collected over a wide area of the continental USA. This data set averaged 0.47 ± 0.15 which Cole

377   and others (2017) suggest should be used in conjunction with a confidence limit of two standard

378   deviations (0.47 ± 0.30) — in effect defining enrichment as $Fe_T/Al > 0.77$. Our preference is to

379   use the sediment data base threshold with a confidence limit of one standard deviation (and thus

380   to define enrichment as $Fe_T/Al > 0.66$) and to require supporting proxy or geological evidence

381   for enrichment.

382   However, the best approach is to define an oxic threshold for any particular geological

383   setting (Lyons and others, 2003; Lyons and Severmann, 2006; Poulton and others, 2010;

384   Sperling and others, 2013; Clarkson and others, 2014). For example, Neoproterozoic samples

385   from the Fifteen Mile Group (Sperling and others, 2013) had a mean Fe_T/Al ratio of 0.34 with

386   variations occurring down to $Fe_T/Al \sim0.20$; similarly samples from the Windermere Supergroup

387   (Sperling and others, 2016) had Fe_T/Al of 0.32 ± 0.17 also with variations down to ~0.2 or less.

388   Clearly it is optimal to consider local detrital Fe_T/Al for a given locality.

389   The level of enrichment reflected in the Fe_T/Al ratio depends on the geologic setting

390   and the mechanism of enrichment, but values rising above 0.66 are conservatively diagnostic of

391   enrichment (whether via chemocline addition, euxinia, or hydrothermal activity; see Case

392   Studies 2 and 3). Large and variable enrichments have been found at hydrothermal sites close to

393   mid-ocean ridges ($Fe_T/Al = 3.0\pm3.8$; Clarkson and others, 2014). Over half these samples had

394    $Fe_T/Al >2.0$ and it seems that Fe_T/Al values above 2.0 most often arise from hydrothermal

395   addition (see Case Study 4). A cautionary note arises because Fe enrichments can be swamped at

396   high siliciclastic sedimentation rates (see Lyons and Severmann, 2006).

397   THE Fe_{py}/Fe_{HR} RATIO

398   The Fe_{py}/Fe_{HR} indicator tracks the extent to which Fe_{HR} is converted to pyrite. Poulton

399   and others (2004) were the first to use Fe_{py}/Fe_{HR}, stating that values 0.87 ± 0.04 were consistent

400 with those found in modern euxinic sediments by Anderson and Raiswell (2004). Canfield and

401 others (2008) concluded that values commonly exceeded 0.8 based on the euxinic data

402 (0.80±0.06) in an unpublished database compiled for Raiswell and Canfield (1998). This ratio

403 reaches values >0.70 to 0.80 in two fundamentally different settings: under euxinic conditions

404 and in the sediments of oxic continental margins where porewaters accumulate sulfide at depth,

405 resulting in near complete conversion of Fe_{HR} to Fe_{py} (see Case Study 1). These two scenarios

406 can be distinguished by considering the Fe_{py}/Fe_{HR} ratio in conjunction with Fe_{HR}/Fe_T and Fe_T/Al;

407 oxic continental margin sediments have Fe_{HR}/Fe_T <0.38 and detrital Fe_T/Al ratios, whereas

408 euxinic sediments have Fe_{HR}/Fe_T >0.38 and elevated Fe_T/Al. Poulton and others (2004) used

409 Fe_{py}/Fe_{HR} (at >0.80) to distinguish euxinicity from ferruginous conditions (indicated by Fe_{py}/Fe_{HR}

410 <0.80 in combination with Fe_{HR}/Fe_T >0.38).

411   As mentioned earlier, this assessment of the Fe_{py}/Fe_{HR} threshold is based on modern

412 sediments for which Fe_{mag} and Fe_{carb} were not determined. Having results for Fe_{carb} and Fe_{mag} in

413 these (or other) euxinic samples would be an important next step. In their absence, the data in

414 table 3 show that the mean Fe_{py}/Fe_{HR} for the Black Sea is 0.88±0.02 (with only five

415 measurements below 0.80) and 0.89±0.02 for the Cariaco Basin. However, addition of as little as

416 0.10% of ($Fe_{mag} + Fe_{carb}$) to the Fe_{HR} values for the Black Sea sediments would be sufficient to

417 decrease the mean Fe_{py}/Fe_{HR} to 0.81 (with 40% of the values below 0.80). A recent study of

418 Phanerozoic euxinic sediments that included $Fe_{mag} + Fe_{carb}$ suggested a slightly lower threshold

419 value of 0.70 for Fe_{py}/Fe_{HR} (see Case Study 4 and Poulton and Canfield, 2011). In this light, we

420 agree that the 0.70 threshold of Poulton and Canfield (2011) may be more appropriate, while

421 sharing their greater confidence in values >0.80. Most importantly, we emphasize that these

422 thresholds should not be held as absolutes and encourage caution during interpretations of data

423 falling on or near the transitions. Many common circumstances, such as fluctuating redox

424 conditions, can yield exceptions to these rules, demanding interpretation in light of other data,

425 including a strong geologic context.

426   PROXIES: THE GROUND RULES

427   The previous sections have drawn attention to important observations that apply to all

428 applications of the iron proxies. These are listed below and then are examined in more detail in

429 the Case Studies that follow:

15

430   • The iron proxies should be interpreted within a broad sedimentological and

431   paleoecological context, taking into account rates of deposition and the extent of

432   reworking by physical or biological processes.

433   • The threshold values defined for Fe_{HR}/Fe_T, Fe_{py}/Fe_{HR}, and Fe_T/Al are not prescriptive, and

434   areas of doubt exist. Specifically, ambiguous signals may occur in environments of

435   marginal or fluctuating redox, settings affected by rapid detrital sedimentation, or due to

436   post-depositional transformation of unsulfidized Fe_{HR} to poorly reactive silicate Fe.

437   • Use of the proxies is particularly risky in cases where measured values of Fe_T or organic

438   C are small (<0.50%).

439   • Samples should be examined petrographically/mineralogically for evidence of Fe_T (and

440   Fe_{HR}) and S secondary mobilization (that is, loss or addition during burial or

441   metamorphism).

442   With these caveats in mind, table 3 and figure 2 present the current best practice threshold values

443   for the iron proxies.

444   CASE STUDY 1: INSIGHTS FROM DETAILED SPECIATION STUDIES.

445   Raiswell and Canfield (1998) originally defined Fe_{HR} as the sum of pyrite Fe and the Fe

446   extracted by dithionite. More recently, however, detailed speciation data from multiple studies

447   have expanded the definition (see eq 2) as operationally defined by Poulton and Canfield (2005).

448   This detailed speciation approach, as presented in the following Case Study, further refines our

449   understanding of the Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} threshold values for distinguishing among oxic,

450   ferruginous, and sulfidic bottom waters and specifically demonstrates the influence of magnetite

451   on Fe_{HR} measurements.

452   The Friends of Anoxic Mud (FOAM) site in Long Island Sound, USA, is an oxic setting

453   with porewater sulfide concentrations as high as 6 mM. Crystalline Fe oxides (Fe_{ox}) in FOAM

454   sediments (fig. 3) are most abundant above the zone of sulfide accumulation and then decrease

455   rapidly down core (Canfield, 1989; Canfield and others, 1992; Hardisty and others, in review).

456   This trend reflects the expected consumption of Fe_{ox} and is similar to other oxic sites with

457   sulfidic porewaters, such as the margin of the Black Sea (Wisjman and others, 2001). FOAM

16

458 sediments, however, have Fe_{HR}/Fe_T ratios <0.38 (Raiswell and Canfield, 1998; Hardisty and

459 others, in review), consistent with their deposition under oxic conditions as is also indicated by

460 Fe_T/Al ratios with values ~0.50 (fig. 3; see also Krishnaswami and others, 1984; Hardisty and

461 others, in review). In contrast, Fe_{py}/Fe_{HR} ratios at FOAM exceed 0.80 and approach 1, consistent

462 with porewater sulfide accumulation and the near complete conversion of Fe_{HR} to pyrite in these

463 relatively organic C-rich sediments (fig. 3). Similar relationships may occur in other continental

464 margin sediments with high porewater sulfide. However these sites can be distinguished from

465 euxinic waters by considering Fe_{py}/Fe_{HR} ratios in conjunction with Fe_{HR}/Fe_T ratios.

466   The original data from FOAM used only Fe_{py} and Fe_{ox} to define the highly reactive pool

467 and yielded a Fe_{HR}/Fe_T ratio of 0.20-0.30 and Fe_{py}/Fe_{HR} values >0.90 (and approaching 1) within

468 the zone of sulfide accumulation (Raiswell and Canfield, 1998; Hardisty and others, in review).

469 In the case of FOAM, more detailed speciation based on recent measurements of Fe_{py}, Fe_{ox}, and

470 Fe_{mag} produces little change in the ratios, with the new values of Fe_{HR}/Fe_T = 0.20-0.30 and

471 Fe_{py}/Fe_{HR} = 0.80 to 1.0, suggesting that the contributions of Fe_{mag} to Fe_{HR} are insignificant.

472 However, in other continental margin sediments, with fundamentally different sediment sources,

473 the inclusion of magnetite in Fe_{HR} might produce a significant decrease in ratios for Fe_{py}/Fe_{HR},

474 which could be particularly important for values are near the ferruginous threshold.

475   For example, application of an adapted Poulton and Canfield (2005) sequential extraction

476 scheme to glacially derived non-sulfidic sediments (März and others, 2012), sulfide-limited

477 continental margin sediments (Goldberg and others, 2012), and Baltic Sea sediments with

478 fluctuating redox states (Hardisty and others, 2016) show Fe_{mag} representing a significant

479 fraction of the highly reactive Fe pool. In the case of the glacially derived sediments, Fe_{mag}

480 comprises 0.10-0.52% of the dry sediment weight in a highly reactive iron pool of 1-3% (März

481 and others, 2012). From this, we acknowledge the potential for Fe_{mag} to be an important fraction

482 of the highly reactive Fe pool that can potentially affect Fe_{py}/Fe_{HR} and Fe_{HR}/Fe_T.

483   The addition of Fe_{mag} and Fe_{carb} is expected to be most important for the recognition of

484 ferruginous environments. Examinations of modern ferruginous marine settings (for example the

485 Orca Basin chemocline) via Fe paleoredox proxies are few in number because of the rarity of this

486 condition in the modern ocean (Hurtgen and others, 1999; Lyons and Severmann, 2006; Scholz

487 and others, 2014a,b), but common ferruginous settings have been inferred from detailed Fe

17

488 speciation in the geologic past (for example, Poulton and Canfield, 2011; Planavsky and others,
489 2011; Sperling and others, 2015). Sperling and others (2015) presented a literature compilation
490 of detailed Fe speciation spanning 2300 to 360 million years ago, in which ~3270 data points
491 each include Fe_{py}, Fe_{ox} and Fe_{carb}. A filtering of a subset of these data for $Fe_{HR}<0.40$ (as defined
492 by $Fe_{py} + Fe_{ox}$) reveals the potential for major differences for the same data set when highly
493 reactive Fe is defined by the sum of pyrite, dithionite, oxalate, and sodium acetate Fe (compare
494 fig. 4A and 4B). The implication of this comparison is that some sediments require measurement
495 of the larger highly reactive Fe suite in order to indicate deposition beneath anoxic bottom
496 waters. The lack of Fe_{ox} and Fe_{carb} measurements may give falsely low Fe_{HR}/Fe_T values
497 (indicating an absence of anoxicity), specifically for sediments deposited beneath ferruginous
498 bottom waters — where there is greater capacity for magnetite (including later overprints), and
499 Fe-carbonates to form and be preserved.

500   In conclusion, we stress that these threshold values, though proven as useful redox
501 indicators, should be viewed as guidelines and that the full suite of speciation data can be
502 essential. Applications of the updated sequential extraction scheme to modern marine sediments
503 are scarce, with data still lacking for sediments from modern dysoxic, euxinic, fluctuating anoxic
504 or euxinic, and deep sea settings. Considering the small number of modern settings with full
505 sequential Fe data and the importance of factors such as sedimentation rate, threshold values for
506 Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} should be interpreted cautiously alongside complementary geochemical
507 and paleontological data.

508   CASE STUDY 2: RECOGNIZING DEPOSITIONAL IRON ENRICHMENTS
509   Recognition of iron enrichment underpins the Fe_{HR}/Fe_T and Fe_T/Al threshold values that
510 distinguish between oxic and anoxic depositional environments. Correct interpretation of the
511 threshold values requires an understanding of the mechanisms of iron enrichment, which vary
512 among different depositional environments. Enrichment may occur at the time of deposition via
513 the transport of iron from the shelf to a euxinic deep basin, by diagenetic iron mobilization at
514 sedimentological/geochemical boundaries, by detrital sediment delivery, or by upwelling of deep
515 water Fe(II) sourced from hydrothermal vents or porewaters. These examples are discussed
516 below.

18

518   The Black Sea is the world's largest euxinic basin, with a pycnocline facilitating redox

519   stratification characterized by an oxic shelf and euxinic conditions from the shelf margin to the

520   deep basin. Rapidly deposited sediments occur along the upper slope, where deposition rates

521   range from 0.77 cm/yr or are even instantaneous in the case of turbidites (Crusius and Anderson,

522   1991; Anderson and others, 1994), and enhanced siliciclastic inputs mute the flux of water

523   column-derived iron — in contrast to the deep basin abyssal plain where sedimentation rates are

524   0.02 cm/yr (Rozanov and others, 1974; reviewed in Lyons and Berner, 1992). According to

525   current models, iron enrichments in the deep basinal euxinic sediments reflect microbial Fe

526   reduction on the oxic shelf, diffusion of reduced iron into the overlying waters, followed by

527   transport of a proportion of the resulting iron to the deep basin, where it is captured by the

528   sulfidic water column and precipitated as pyrite. The operation of this 'iron shuttle' (see

529   Appendix) allows the accumulation of Fe_{HR} in euxinic settings (Wijsman and others, 2001;

530   Raiswell and Anderson, 2005; Lyons and Severmann, 2006; Severmann and others, 2008,

531   2010)..

532   Important details have emerged from careful consideration of DOP values in different

533   Black Sea depositional environments. Rapidly depositing muds beneath a sulfidic water column

534   along the basin margin reveal DOP values of ~0.40 (Lyons and Berner, 1992; Canfield and

535   others, 1996; Lyons, 1997; Wijsman and others, 2001; Lyons and Severmann, 2006), Fe_{HR}/Fe_T

536   <0.38 (Wisjman and others, 2001), and Fe_T/Al ratios of ~ 0.50 (Lyons and Severmann, 2006) —

537   similar to the Black Sea shelf where bottom waters are well-oxygenated (Wijsman and others,

538   2001) and to other oxic sites like FOAM in Long Island Sound (Goldhaber and others, 1977;

539   Canfield and others, 1992; Raiswell and Canfield, 1998; Hardisty and others, in review). By

540   contrast, the deep euxinic basin of the Black Sea displays DOP values frequently >0.70 (Lyons

541   and Berner, 1992; Canfield and others, 1996; Lyons, 1997; Wijsman and others, 2001; Lyons

542   and Severmann, 2006), Fe_{HR}/Fe_T >0.38 (Wijsman and others, 2001), and Fe_T/Al ratios of ~0.60

543   (Lyons and Severmann, 2006), which together with Fe_{py}/Fe_{HR} > 0.80, are a euxinic fingerprint.

544   The contrasting dampening of DOP and Fe_{HR}/Fe_T, and Fe_T/Al ratios in turbidites and slope

545   settings of rapid deposition is tied to the balance of siliciclastic versus Fe_{HR} input, where

546   relatively high rates of siliciclastic deposition mute the Fe_{HR} enrichment from the shuttle and are

547 thus unfavorable for expression of a anoxic fingerprint, regardless of the redox conditions during

548 deposition. Pyritization of the remaining detrital iron only produces spurious proxy values that

549 are comparable to continental margin sediments, like FOAM (see above). The importance of

550 considering the depositional influences on proxies emerges powerfully from figure 5, where

551 there is a clear inverse relationship between Fe_T/Al and siliciclastic accumulation rates (Lyons

552 and Severmann, 2006).

553   The non-detrital Fe_{HR} input to anoxic settings is regulated by a shelf-to-basin shuttle and

554 has been studied in detail in the Black Sea (Canfield and others, 1996; Lyons and Severmann,

555 2006; Severmann and others, 2008). Most of the iron diffusing into the overlying waters on the

556 oxic shelf is rapidly oxidized and re-deposited to surface sediments on the shelf but eventually

557 escapes from the shelf despite many reduction-oxidation cycles (Lyons and Severmann, 2006).

558 Escape creates a deficit of highly reactive iron on the shelf (Wijsman and others, 2001; Lyons

559 and Severmann, 2006; Severmann and others, 2010) that is also revealed by depletions in the

560 lighter Fe isotope on the oxic shelf compared to the input from detrital weathering and the

561 sediments in the deep euxinic basin (Severmann and others, 2008). The implication is that some

562 isotopically light iron produced during microbial iron reduction on the shelf has been exported

563 from that location and accumulates in the deep basin.

564   The Black Sea shows us that iron enrichment in euxinic sediments depends on the

565 amount of Fe_{HR} added to the sediments versus the amount of siliciclastic material. Enhanced

566 delivery of Fe produces an enrichment that can be observed in high Fe_T/Al and Fe_{HR}/Fe_T ratios,

567 in parallel with the high DOP and Fe_{py}/Fe_{HR} values that reflect the ubiquity of sulfide in the

568 euxinic system.

<div align="center">The Orca Basin</div>

569

570   The Orca Basin is a 400 km^2 depression, on the continental slope of the northwest Gulf of

571 Mexico, produced by salt tectonics. Water depths at the basin rim are ~1800 m, increasing to

572 more than 2400 m within the basin. A brine pool occupies the bottom 200 m of the basin, and the

573 strong density gradient limits physical exchange between the brine and overlying seawater.

574 Dissolved oxygen is rapidly depleted at 2200 m depth, and the brine below that depth is

575 permanently anoxic, with ferruginous conditions at the pycnocline and euxinia in the deepest

20

576 waters. A large fraction of the particulates settling into the basin are trapped along a sharp

577 density interface, producing a dramatic rise in particulate Fe at the brine/redox interface (Trefry

578 and others, 1984; Van Cappellen and others, 1998).

579 Lyons and Severmann (2006) studied sites on the oxic margin and within the adjacent

580 anoxic basin, as well as in the intermediate, chemocline portion of the water column. They

581 reported data for HCl-soluble iron, sulfidic iron (both pyrite and AVS), Fe_T, and Al. Sediments

582 on the oxic margin consist of homogenous, bioturbated olive-brown to light gray muds with Fe

583 sulfide levels falling below the detection limit. By contrast, sediments within the anoxic basin are

584 soupy, black laminated muds containing ~1% AVS and ~0.1% pyrite S.

585 DOS values in the Orca Basin sediments below the chemocline range from 0.40 to 1.0

586 (Lyons and Severmann, 2006). Sediments within the chemocline at 2240 m are brick red with

587 gray mottling, and the sulfide contents here are also below detection limits, resulting in near-zero

588 DOS values. Iron enrichment in the chemocline is clearly not the result of sulfide precipitation

589 but instead is produced by the deposition of iron (oxyhydr)oxides where the particulate iron

590 maximum impinges on the seafloor. This particulate iron (oxyhydr)oxide maximum is sourced

591 by the oxidation of reduced iron supplied from the underlying anoxic waters to the oxic-anoxic

592 boundary at the chemocline. Lyons and Severmann (2006) noted that the iron enrichments in the

593 chemocline are not expressed in elevated DOS values. No dithionite data were reported, but the

594 absence of sulfides requires Fe_{py}/Fe_{HR} to be near-zero. Total iron extraction does, however,

595 produce elevated Fe_T/Al values (fig. 6). Together, the low DOS and enriched Fe_T/Al (and

596 presumably high Fe_{HR}/Fe_T and low Fe_{py}/Fe_{HR}) specifically identify a ferruginous setting at the

597 pycnocline, consistent with water column observations of redox zonation within the Orca Basin

598 (Van Cappellen and others, 1998).

599 The Peruvian Oxygen Minimum Zone (OMZ)

600 Similar to the Orca Basin chemocline, enriched values of Fe_T/Al have been noted along

601 the oxic-anoxic boundary of the Peruvian OMZ (Scholz and others, 2014a,b), where dissolved Fe

602 accumulates in the waters but dissolved sulfide is absent (Chever and others, 2015). In this case,

603 however, it was specifically observed that Fe_T/Al and Fe isotopes within the core of the Peruvian

604 OMZ, where conditions are most reducing, did not reflect an anoxic setting. Instead, these values

605   were similar to those of the oxic shelf of the Black Sea, indicating that the sediments and water

606   column in the low oxygen setting similarly remobilize and transport Fe_{HR} to environments more

607   favorable for deposition — in this case the anoxic-oxic boundary (Scholz and others, 2014a,b).

608   Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} were further evaluated as part of the study (using $Fe_{HR} = Fe_{ox} + Fe_{py}$),

609   revealing elevated values near or at the previously discussed 'thresholds' for euxinic water

610   column at the OMZ anoxic-oxic boundary. Water column sulfide accumulation was not noted.

611   These indications of euxinia may be a function of missing Fe_{HR} fractions, which would otherwise

612   yield the appropriate ferruginous signal (see Case Study 1). Large concentrations of glauconite

613   (up to 15 wt. %) are being produced from Fe_{HR} fractions due to the oscillatory nature of the

614   fringes of the OMZ. Glauconite (with both ferric and ferrous Fe) is essentially insoluble in

615   dithionite (Raiswell and others, 1994), and failure to account for this source of Fe_{HR} produces a

616   falsely high Fe_{py}/Fe_{HR} signal for euxinia. Alternatively, similar to the diagenetic remobilization

617   scenarios discussed as part of Case Study 3, exposure of the 'highly reactive' Fe to porewater

618   sulfide at the fringes of the OMZ may promote diagenetic pyritization of the Fe_{HR} pool, leading

619   to a false euxinic signal. Regardless, these scenarios have the potential to produce false euxinic

620   signals for the oxic-anoxic (ferruginous) transition if Fe proxies are used alone. We stress that

621   such settings can be distinguished in the geologic record, as they lack the Mo enrichments typical

622   of euxinia.

623   Quaternary Glacial Sediments

624   Depositional iron enrichments have also been documented in sediments from glacial-

625   interglacial cycles in the Quaternary Arctic (März and others, 2012). The Central Arctic Ocean

626   contains prominent, basin-wide brown layers enriched in Mn and Fe (oxyhydr)oxides that occur

627   during interglacial intervals. These horizons show high values of Fe_T/Al (up to 0.68) that are

628   typical of euxinic or ferruginous conditions. However, the mean values of Fe_T/Al are 0.59 in

629   both the glacial and interglacial intervals, which suggest a high local baseline. There is a near-

630   complete lack of pyrite in these organic-poor sediments (Fe_{py}/Fe_{HR} is <0.05), and thus DOP is

631   low, and euxinia would not be predicted. The Fe_{HR}/Fe_T ratio in the interglacial intervals (0.45-

632   0.60) lies above the oxic/anoxic threshold, but the Fe_T/Al data are <0.66. The Fe_{HR}/Fe_T data

633   suggest a ferruginous depositional environment that requires further investigation via the

634   geochemical, sedimentological, and paleoceanographic context.

22

635   The interglacial intervals correspond to decreases in Al and Fe_T, which suggest an
636   important sedimentological/provenance control (März and others, 2012). High baseline Fe_T/Al
637   may be partially responsible for the apparently ferruginous Fe_T/Al values, but März and others
638   (2012) also suggest that the peaks have been blurred by post-depositional migration of Fe from
639   anoxic porewaters up to the sediment surface where Fe (oxyhydr)oxides are precipitated. This
640   mechanism requires oxic bottom waters. The proxy data in this sequence suggest anoxic bottom
641   waters, but crucially, there is no paleoceanographic evidence for widespread ferruginous bottom
642   waters in the Arctic during the last 13,000 yr. Thus, März and others (2012) show that the
643   interglacial periods produced enhanced transport of Fe_{HR} from the Arctic rivers and into the deep
644   basin, coupled with early diagenetic enrichment of Fe and Mn at the sediment/water interface.
645   Here, resolution of ambiguous proxy signals has ultimately been possible only because an
646   oceanographic context is available for recent sediments.

647   CASE STUDY 3: RECOGNIZING DIAGENETIC IRON ENRICHMENTS

648   Cases of diagenetic remobilization and enrichment may also be difficult to recognize
649   from proxy data alone but should be considered wherever there is a juxtaposition of sediments
650   with compositions that have different potentials for diagenetic reactions involving organic C,
651   sulfur, and iron. Berner (1969) designed experiments to study the diagenetic behavior of organic
652   C-rich layers enclosed by organic C-poor sediment. Three different cases were recognized based
653   on the relative amounts of reactive Fe and dissolved sulfide — described as having high, low, or
654   intermediate Fe contents, which determined whether sulfide or iron diffused into the organic C-
655   rich sediments. The addition of sulfide or iron from the surrounding sediments potentially
656   confounds the use of iron proxy data to determine the depositional environments of the organic
657   C-rich horizon and the surrounding organic C-poor sediments.

658   The high Fe_{HR} model was arbitrarily defined by Berner (1969) as applying to organic C-
659   rich sediments generating sulfide but with a high enough Fe_{HR} content to maintain sulfide at low
660   levels. Dissolved iron in the organic C-poor sediments below (or from the water column above)
661   can then diffuse to the base of, or into, the organic C-rich layer to form pyrite. The addition of Fe
662   (which is fixed by sulfide) may be sufficient to produce signatures of euxinia in the organic C-
663   rich layer.

23

664   The low reactive Fe model of Berner (1969) occurs where sulfate reduction produces

665   sufficient sulfide to consume all the Fe_{HR} within the organic C-rich layer. Sulfide then diffuses

666   downwards into the organic C-poor sediment, where it forms pyrite at the edges of the

667   lithological transition using Fe_{HR} contained within the sediment and porewater Fe along the

668   migration pathway. Sulfide migration alone is the key signature for this model. In the absence of

669   iron enrichment within the organic-rich layer, the original oxic sediment signatures of the

670   organic C-poor sediments would remain unaltered, but Fe_{py}/Fe_{HR} may approach euxinic levels.

671   The association of oxic Fe_{HR}/Fe_T values with high Fe_{py}/Fe_{HR} is inconsistent with euxinia and

672   indicates that porewaters were Fe-limited during diagenetic pyrite formation. In this case, the

673   influence of migration can be recognized because the high Fe_{py}/Fe_{HR} values cross a prominent

674   lithological boundary and because oxic values are still recorded by Fe_{HR}/Fe_T, Fe_T/Al, and DOP

675   (see also Owens and others, 2012).

676   The Mediterranean Sapropels

677   At intermediate reactive iron contents, dissolved sulfide migrates downwards from an

678   organic C-rich layer into an organic C-poor layer where it meets upward diffusing Fe (Berner,

679   1969). The depth of pyrite formation then depends on the relative rates of supply of sulfide and

680   dissolved Fe. This model has been used to explain the migration (and enrichment) of both Fe and

681   sulfide in the Mediterranean sapropels, where deposition of organic C-rich sapropels occurs

682   within a thick sequence of organic C-poor sediments. Unfortunately, there are no Fe_{HR} data for

683   the sapropels, but Passier and others (1996) show that the organic C-rich sapropel layer (S_1 in

684   core GC17) is enriched in organic C (2-3%), pyrite sulfur (~1%), and Fe (the Fe_T/Al ratio is

685   ~0.70), which is consistent with a euxinic origin (fig. 7). The sediments about 5 cm below the

686   sapropel have essentially the same compositions, but the sediments 15 cm below have lower

687   organic C contents (<0.3%), lower S contents (~0.1%), and Fe_T/Al ~0.50, consistent with

688   deposition under oxic conditions.

689   Passier and others (1996) interpret the sapropel to have either been deposited under

690   sulfidic bottom waters or to have produced sufficient sulfide to consume all the Fe_{HR} and

691   generate sulfidic porewaters. Sulfide then diffused downwards into the organic C-poor sediment

692   immediately below to produce enrichment in pyrite sulfur (fig. 7). However the sediment below

693   the sapropel (depths ~0.25 to 0.30 mbsf) is also enriched in Fe_T thus producing Fe_T/Al ratios

24

694 comparable to those in the sapropel and much higher than in the sulfide-poor sediments below

695 0.3 mbsf. Hence, pyrite has formed using Fe_{HR} contained within the sediment plus dissolved iron

696 diffusing upwards that is liberated from Fe_{HR} in sediments lower in the sequence. Migration of

697 Fe upwards to this horizon has to occur to produce the observed elevated Fe_T/Al values in the

698 organic-poor sediments that were deposited beneath oxic bottom waters. This migration of Fe

699 confounds the use of the Fe proxies, as the horizon below the sapropel now contains proxy

700 signals that have been altered by the addition of Fe_{HR} to yield $Fe_T/Al >0.55$ (and likely Fe_{HR}/Fe_T

701 >0.38, and Fe_{py}/Fe_{HR} ratios of 0.80-1.0). These signals are consistent with euxinia, in clear

702 contradiction with the depositional environment, but the influence of migration can be

703 recognized in this case because the high proxy values persist across the prominent lithological

704 boundary between the organic C-rich and organic C-poor sediments. The sedimentological

705 context provides key insight.

706   The Baltic Sea

707   The Baltic Sea represents a unique depositional setting where, ~8-8.5 kyr ago, rising sea

708 level transitioned the Baltic basin from a freshwater lake to the modern brackish conditions. This

709 transition is recognized throughout the basin by changes in faunal communities and

710 sedimentology, as well as a change from low to high organic C contents (Andrén and others,

711 2011). Directly following this salinity transition, the ensuing silled basin formed a halocline,

712 resulting in an anoxic period lasting ~4 kyr and recognized in multiple sub-basins in the Baltic

713 Sea by lamination records (Zillén and others, 2008). In line with these relationships, multiple

714 geochemical records show elevated DOP (and DOS), Fe_T/Al, Fe_{HR}/Fe_T, Fe_{py}/Fe_T, and trace

715 metals indicative of a euxinic water column in some sub-basins, all coincident with increases in

716 organic C >4 wt.% (Boesen and Postma, 1988; Fehr and others, 2008; Jilbert and Slomp, 2013;

717 Lepland and Stevens, 1998; Sohlenius and others, 1996, 2001; Hardisty and others, 2016). The

718 Baltic sediments have a particularly high abundance of AVS that requires the use of the Degree

719 of Sulfidation (DOS) and $(Fe_{py} + Fe_{AVS})/Fe_{HR}$, which is preferred (see earlier) over DOP and

720 Fe_{py}/Fe_{HR} for euxinic systems when AVS is present in appreciable amounts.

721   In the lacustrine, organic C-poor clay sediments directly underlying the brackish muds,

722 multiple studies have observed the mobilization of sulfate and sulfide downwards from the

723 overlying brackish sediments, as in Berner's low Fe model. In this case, unlike the intermediate

25

724   Fe model, upward fluxes of porewater Fe from the lacustrine sediments constrain downward

725   dissolved sulfide migration, and hence post-depositional Fe_{HR} and Fe_{py} enrichments occur directly

726   along the margins of the sediment transition. As a result, Fe enrichment produces elevated

727   Fe_T/Al and DOS as well as Fe_{HR}/Fe_T. Multiple studies have noted enrichments of pyrite, Fe

728   monosulfides, greigite, and elemental S in the lacustrine sediments directly underlying the

729   brackish sapropel (for example Boesen and Postma, 1988; Holmkvist and others, 2014).

730   Reported DOS values in these lacustrine sediments are typically near 0.4, elevated from a

731   baseline of DOS ~0 through post-depositional enrichment (Boesen and Postma, 1988). DOS ~0.4

732   is consistent with an oxic setting and indicates that sulfidation of the in situ Fe_{HR} pool is more

733   important than addition from upward diffusing dissolved Fe, thus preventing false anoxic signals

734   in these cases.

735   Sulfur Isotope Signals of Fe Enrichment

736   Iron enrichments in the Mediterranean sapropels and the Baltic Sea are recognized by

737   multiple, elevated proxy values that occur across prominent sedimentological boundaries. These

738   circumstances in the Recent and Phanerozic record can often be identified by sulfur isotope data

739   even with limited other proxy data. The early stages of sulfate reduction are characterized by the

740   production of isotopically light sulfide (typically $\delta^{34}S$ <-40 to -20‰). Continued sulfate

741   reduction produces heavier dissolved sulfide, which can diffuse away to form pyrite with

742   relatively heavy isotopic values in adjacent sediments. Middelburg (1991) demonstrated iron

743   enrichment across a marine-freshwater boundary in Kau Bay (Indonesia) using sulfur isotope

744   data. Here, marine sediments are being deposited from bottom waters that are commonly low in

745   oxygen and non-sulfidic but intermittently euxinic. In the past, the basin became isolated from

746   the ocean and brackish/freshwater sediments were deposited. There are only two samples from

747   the brackish/freshwater sediments, and proxy data are limited. Nevertheless, Middelburg (1991)

748   showed that the marine, brackish and freshwater sediments have rather similar organic C

749   contents (3-5%), but the freshwater sediments are enriched in sulfide sulfur, which is isotopically

750   heavier ($\delta^{34}S$ up to +15‰) than the overlying marine sediments ($\delta^{34}S$ -24 to -17‰). Isotopically

751   heavy sulfides also occur across lithological boundaries in the Cariaco Basin (Lyons and others,

752   2003) as well as in the freshwater sediments of the Black Sea (Jorgensen and others, 2004),

753 where methane diffuses upward into iron-rich sediments and drives sulfate reduction to produce

754 an isotopically heavy sulfidiation front ($\delta^{34}S$ +15 to +34‰).

755   In conclusion we note that diagenetic iron enrichments are driven by depositional and

756 associated geochemical discontinuities (non-steady state conditions), and all these cases require

757 careful consideration of proxy data in relation to their geochemical and sedimentological context

758 and the depositional environment more generally. Interpreting ratio changes at facies/lithological

759 boundaries requires extreme caution.

760   CASE STUDY 4: RECOGNIZING ENRICHMENT PROCESSES WITH Mo ABUNDANCES

761   AND Fe ISOTOPES

762   Case Studies 2 and 3 explored mechanisms of localized iron enrichment in marginal

763 basins and epicontinental seas, as these have been the focus of many previous studies using the

764 iron proxies. However, multiple enrichment processes may operate on an ocean-wide scale

765 where signals from localized processes may occur together with basin-wide processes.

766 Resolving complex, mixed signals, requires additional evidence from other geochemical proxies,

767 as well as careful consideration of the geological context.

768   Cretaceous Black Shales with Shuttle and Hydrothermal Fe Sources

769   This example considers the geochemical signatures of ferruginous or sulfidic bottom

770 waters in an oceanic depositional environment where there is potential for hydrothermal activity.

771 This case study (from März and others, 2008) is based on a core retrieved during ODP Leg 207

772 at site 1261 on the Demerara Rise in the equatorial Atlantic. The sediments consist of a finely

773 laminated black claystone that spans the Cretaceous Oceanic Anoxic Event (OAE 3). OAE 3

774 corresponds with a period of enhanced hydrothermal activity (Jones and Jenkyns, 2001) and

775 thus, the possibility that hydrothermal fluxes would have reached the Demerara Rise at this time

776 cannot be ignored.

777   The core was analyzed for Fe_T, Al, and inorganic C, with iron speciation carried out by

778 sequential extractions to quantify Fe_{carb}, Fe_{ox}, Fe_{mag}, and Fe_{py}, the sum of which defines Fe_{HR}.

779 The calcium carbonate ($CaCO_3$) content is typically ~60% and rarely exceeds 80%, Fe_T contents

780 average ~1% (only one sample contains <0.5%,) and organic C contents are always >2%. These

27

781 compositions allow use of the iron proxies (see table 3). The Fe_{HR}/Fe_T ratios mostly lie between

782 0.40 and 0.65 except for a few intervals where $Fe_{HR}/Fe_T > 0.80$, and thus iron enrichment is

783 clearly indicated (fig. 8). Further detail emerges by considering the Fe_{py}/Fe_{HR} data, which vary

784 between approximately 0.60 and 0.90, with many values lying above 0.70 (in the range of

785 possible euxinia), but only five samples have $Fe_{py}/Fe_{HR} > 0.80$ (and give clear euxinic signals).

786 None of these five has a Fe_T/Al ratio >0.60, but figure 8 shows that Fe_T/Al frequently lies below

787 0.50, which suggests that the local threshold for Fe_T/Al enrichment is significantly below 0.55.

788 These subdued Fe_T/Al signals are inconclusive evidence for euxinia but the $Fe_{HR}/Fe_T > 0.40$

789 suggests the sequence is generally Fe-enriched and possibly euxinic (when $Fe_{HR}/Fe_T > 0.70$).

790   However, Mo abundance provides crucial diagnostic evidence (März and others, 2008).

791 The behavior of Mo has been discussed in detail in Scott and others (2008) and Scott and Lyons

792 (2012), among many other papers, and only brief details are supplied here. Molybdenum

793 enrichments exceeding 100 ppm are strong evidence for the presence of hydrogen sulfide and

794 abundant dissolved Mo in the water column. However, enrichments above the crustal average (1-

795 2 ppm) and below 25 ppm indicate that dissolved sulfide was present but only in the porewaters.

796 Concentrations between 25 and 100 ppm are characteristic of oscillatory or seasonal euxinia or

797 restricted systems with persistent euxinia that draw down the Mo reservoir (Scott and Lyons,

798 2012). März and others (2008) show that the sediments at site 1261 never show Mo <50 ppm,

799 and there are prolonged periods with Mo >100 ppm. These high Mo samples have a mean

800 Fe_{py}/Fe_{HR} of 0.68±0.06, close to the lower limit of 0.70 for euxinicity (table 3). The Mo signals

801 of euxinia clarify the iron proxy signals and support the interpretation of März and others (2008)

802 that persistent euxinia was punctuated by brief periods of anoxic, non-sulfidic bottom waters —

803 that latter being recorded in the transitional Fe data. The Fe_T/Al values at this site are <<2.0 and

804 are more likely to result from euxinicity than a hydrothermal source (see fig. 9 and earlier). We

805 caution, however, that these Mo relationships can be compromised at time of widespread euxinia

806 when the global marine inventory is drawn down and sediment enrichments in individual euxinic

807 settings are correspondingly muted (for example Scott and others, 2008).

808

809   Cretaceous Black Shales with Multiple Iron Sources

28

810   In this Case Study, we discuss Deep Sea Drilling Project (DSDP) Sites 105, 367, and 144

811   using data from Owens and others (2012), who explore the causes of iron enrichment in a basin-

812   wide context. In this case several contemporaneous enrichment processes occur to varying

813   degrees, and their relative contributions can only be deciphered by using iron proxy data

814   supported by Mo abundance and iron isotopes. These sediments deposited during OAE 2 record

815   the pervasive deposition of black shales on the continental shelves extending to deep waters.

816   Deposition at Site 105 is marked by alternating organic-poor, bioturbated green claystone

817   (with organic C ~1%) and black shales (organic C up to 25%) that clearly record fluctuating

818   redox conditions. Site 367 is the deepest and is located near the ancestral mid-ocean ridge. Prior

819   to, and during the OAE, deposition at this site consisted of laminated, organic C-rich sediments

820   (up to 40% organic C) with biomarker evidence that suggests euxinic conditions extended into

821   the photic zone. Site 144 sediments consist of interlayered, laminated carbonaceous limestone

822   and calcareous clays (organic C up to 30%) that were deposited at shallow depths on the mid-

823   ocean ridge. The origin of OAE 2 has been postulated to reflect an expansion of hydrothermal

824   activity that generated iron-rich conditions in the photic zone which stimulated enhanced primary

825   production, even prior to the OAE. However, iron-enriched sediments can also be produced by

826   shuttle delivery and diagenetic remobilization, and Owens and others (2012) sought to

827   distinguish these, and the hydrothermal, signals using Fe_T/Al data supported by Mo abundance

828   and iron isotopes.

829   Iron isotopes provide additional perspective because specific enrichment mechanisms can

830   have diagnostic isotopic signatures. Hydrothermal iron shows relatively little deviation in $\delta^{56}Fe$

831   from average igneous rocks (~0.0 to -0.5‰). However, operation of an iron shuttle requires that

832   high concentrations of porewater Fe are formed by iron reduction, which produces isotopically

833   light dissolved iron that diffuses into the overlying seawater and is transported to basinal areas.

834   Transported iron encountering sulfidic conditions is precipitated, often quantitatively, and the

835   resulting pyrite is isotopically light. Isotopically light pyrite also forms when porewater iron is

836   mobilized and precipitated as pyrite during diagenesis, usually where sediments with very

837   different organic C contents are interlayered (see Case Study 3).

838   Sediments at Site 144 show high values of Fe_T/Al even before the OAE (fig. 10) but with

839   considerable variability from <0.50 to >1.5. All the Fe isotope data are uniform, with $\delta^{56}Fe$

840 averaging ~0.0 ‰ both before and during the OAE. High values of Fe_T/Al with iron isotope

841 data that inversely track the level of enrichment would result from shuttle delivery (Severmann

842 and others, 2008), while the absence of co-variation is more consistent with a hydrothermal

843 source (Owens and others, 2012). The location of Site 367 is an area of pervasive euxinicity

844 (indicated by Mo values >100 ppm and consistent with Fe_T/Al values ~2.0). A hydrothermal

845 contribution is likely at this location but there are weak shifts in $\delta^{56}Fe$ towards negative values

846 that suggest a minor shuttle contribution. However there is no correlation between the shifts in

847 $\delta^{56}Fe$ and Fe_T/Al, which should occur if shuttle sources predominated. These contributions must

848 have been minor compared to hydrothermal inputs (Owens and others, 2012). Site 105 shows

849 complex, fluctuating patterns wherein high Fe_T/Al values correspond with very negative $\delta^{56}Fe$

850 (fig. 10), which would indicate substantial shuttle contributions. However Mo concentrations are

851 mostly <16 ppm, and thus persistent euxinia is unlikely. Instead, the interlayering of organic C-

852 rich and organic C-poor sediments indicates that the variability in Fe enrichments and isotope

853 composition most likely result from diagenetic remobilization (see Case Study 3). These

854 examples from Owens and others (2012) show the value of coupling Mo concentrations with iron

855 isotope and speciation data.

856 CASE STUDY 5: RECOGNIZING THE INFLUENCE OF BURIAL AND METAMORPHISM

857   The iron proxies have often been applied to ancient sediments, although there is

858 potential for the abundances of Fe and S species to be significantly modified by deep burial or

859 metamorphic fluid processes that add or remove Fe and S or alter their speciation. There are

860 numerous potential reactions that can involve the addition or removal of iron as carbonates,

861 oxides, sulfides, and silicates during burial or metamorphism and special care is therefore

862 needed to avoid false signals in deeply buried and highly metamorphosed sediments (Raiswell

863 and others, 2011; Asael and others, 2013; Reinhard and others, 2013; Slotznick and others,

864 2017). An important first step is to examine the petrography of samples representative of the

865 major lithologies for any evidence that the sediments were open or closed to fluids that added or

866 removed Fe and S. Addition may be recognized by late overgrowths on diagenetic phases or by

867 the occurrence of new, late-stage minerals. In some cases, it may be possible to use petrographic,

868 trace element or isotopic data to quantify the extent of addition or loss, and the speciation data

869 can then be corrected back to their pre-alteration values (or the samples can be avoided)..

30

870   The simplest cases will be those where iron is conserved (recognized by uniform

871   Fe_T/Al) but transferred among different carbonate or oxide species that contribute to Fe_{HR}. A plot

872   of Fe_T/Al may provide a preliminary indication of open versus closed system behavior for iron

873   during metamorphism, but caution is needed as secondary overprints might also reflect Fe

874   migration at lithological boundaries or a varying depositional environment. There is also

875   potential for proxy data to be altered where systems are open to the transfer of C-O-S-H species

876   that may alter speciation (Asael and others, 2013; Reinhard and others, 2013; Slotznick and

877   others , 2017). Further, it is also imperative, where possible, to use a local threshold to define

878   iron conservation—as the following example will show. Figure 11 includes Fe_T/Al data from Jia

879   (2006) from the Paleozoic Cooma metamorphic complex (SE Australia). At this location,

880   metapelites of uniform age and composition occur across a continuous metamorphic grade from

881   subgreenschist (~ 150 °C) to upper amphibolite (760 °C) facies. The mean Fe_T/Al ratio of the

882   subgreenschist facies sediments is 0.39, which is used as a threshold for local oxic (non-Fe

883   enriched) conditions. Thus, we define $\Delta Fe_T/Al$ as $(Fe_T/Al)_t$ - $(Fe_T/Al)_l$, where the subscripts t

884   and l, denote respectively the Fe_T/Al ratio for any temperature t and for the local Fe_T/Al ratio

885   threshold l. A set of Fe_T and Al data are also available in Yui and others (2009) over a smaller

886   temperature range (100-435 °C) for pelites of Tertiary age with essentially the same mineral

887   composition and the mean Fe_T/Al ratio of the zeolite facies (0.47) is used as a local threshold..

888   Figure 11 reveals little variation in $\Delta Fe_T/Al$ for both sets of data as a function of temperature,

889   and iron has clearly been conserved in both cases across substantial temperature gradients.

890   Slotznick and others (2017) also found near-conservation of Fe_T across metamorphic grade and

891   hence proxy data from DOP, Fe_{py}/Fe_{HR}, Fe_{HR}/Fe_T, and Fe_T/Al will all remain valid provided

892   there are no speciation changes resulting from the additions of C-O-S-H-bearing fluids.

893   A more complex case arises where changes in Fe_T/Al can be identified. Such changes

894   may occur where the depositional environment changes between oxic and euxinic or where

895   boundary effects produce iron migration (see Case Study 3). These cases may be recognized by

896   lithological discontinuities and by changes in DOP and careful interpretation of samples in their

897   lithological context may avoid false signals. However the addition or removal of iron by during

898   metamorphism may add or remove Fe from Fe_{HR} and/or Fe_{py} and will produce false signals

899   unless such changes are identified by petrographic or isotopic data.

900   Changes in both iron and sulfur speciation can arise as a consequence of metamorphic

901   reactions by which pyrite is altered to pyrrhotite (Reinhard and others, 2013; Slotznick and

902   others, 2016). Slotznick and others (2017) found pyrrhotite formation that was a major influence

903   on iron speciation data. In theory, however, proxy data can be corrected by apportioning

904   pyrrhotite into different iron pools, assuming that pyrrohotite Fe can be accurately determined.

905   Asael and others (2013) extracted crystalline pyrrhotite using a hot 6N HCl distillation with

906    $SnCl_2$ acting as a reductant. This method is too aggressive for the complete separation of pyrite

907   from pyrrhotite in modern sediments but in ancient metamorphosed sediments, where pyrite is

908   more crystalline, the relative yields of pyrrhotite and pyrite can be quantified as the difference

909   between chromium reducible sulfur (which extracts both pyrite and pyrrhotite; Canfield and

910   others, 1986) and the sulfur extracted by $HCl/SnCl_2$. Provided pyrrohotite concentrations are

911   low, the cautious interpretation of all chromous chloride-extracted S as pyrite will not introduce

912   major errors.

913   Large concentrations of pyrrhotite present intractable problems because different

914   pyrrohotite-forming reactions derive iron from different iron pools and thus have different

915   consequences for the iron proxies. Pyrite can be altered to pyrrhotite using Fe_{HR} or Fe from

916   silicates, can be converted to pyrrhotite by the introduction of Fe-bearing fluids, and can be

917   formed by the thermal decomposition of pyrite. These reactions all have different consequences

918   for total sulfur, total iron, $Fe_{HR,}$ and sulfide species and thus for the iron proxies. In theory,

919   determination of pyrrhotite sulfur would allow the pre-alteration rock composition to be derived,

920   provided the correct reaction can be identified and assuming only one process is involved. The

921   overarching message is that rocks with significant concentrations of pyrrhotite are best avoided

922   unless Fe speciation can be constrained by petrographic or field observations (Slotznick and

923   others, 2017).

924   The presence of diagenetic carbonates may also exert a significant effect on the

925   determination of Fe_{HR} (Slotznick and others, 2017). Clarkson and others (2014) found that the

926   ratio Fe_{HR}/Fe_T in modern carbonates with minimal diagenetic over-printing behaves essentially

927   the same as siliciclastic rocks. However deep burial dolomitization using an external source of

928   iron severely compromises proxy data and Clarkson and others (2014) suggested that ankerite-

929   rich samples are best avoided. Slotznick and others (2017) also found that Fe_{HR}/Fe_T signals were

930   potentially compromised by trace amounts of Fe in carbonates that produced false signals for a

931   ferruginous water column. It was concluded that samples with proportionately high Fe_{carb} should

932   be investigated petrographically to determine whether the carbonates are primary or reflect

933   diagenetic/metamorphic processes. The problem essentially relates to the source of iron which

934   may not necessarily be derived from other in situ Fe_{HR} phases, and may be derived instead from

935   an external source. Iron from an external source may produce high Fe_T/Al values and such

936   samples with high concentrations of Fe_{carb} should be subjected to further detailed petrographic,

937   microprobe and/or isotopic analysis. We are in full agreement with Slotznick and others (2017)

938   that mineralogical and petrographic approaches should be combined with iron speciation data to

939   disentangle the effects of post-depositional processes on metamorphic rocks – ultimately to

940   provide an accurate picture of paleoenvironmental redox conditions. In sum, proxy data must be

941   used with extreme caution when metamorphic overprints are substantial (Slotznick and others,

942   2017).

943   CASE STUDY 6: PRECAMBRIAN SEDIMENTS: BRINGING IT ALL TOGETHER

944   Our Case Studies have illuminated a range of potential problems that we now revisit in

945   relation to applications in Precambrian sediments where unique challenges exist for several

946   reasons. First, the absence of fossils makes it impossible to calibrate the thresholds against

947   paleoecological observations, and caution must be exercised in extrapolating threshold values

948   derived from younger rocks. Second, complications may arise from metamorphic and

949   compositional effects that make it difficult to define the original depositional Fe_{HR} contents of

950   these rocks. Third, the Proterozoic oceans displayed considerable spatial and depth variability in

951   composition, with weakly oxygenated surface waters overlying predominantly ferruginous water

952   columns with mid-depth, near-shore euxinia (for example Poulton and others, 2004, 2010; and

953   reviewed in Lyons and others, 2014). Multiple, basin-wide variations may require that all

954   available proxy data are considered in a holistic context. This section begins by discussing how

955   these challenges may be addressed for each of the different proxies.

956   We have seen that DOP values are robust and can be unaffected by burial/metamorphic

957   alteration. Specifically, DOP values are calculated from Fe data derived from boiling HCl,

958   which includes much iron present in minerals formed post-depositionally (whether syngenetic,

959   diagenetic, or metamorphic) from phases that would have originally been reactive towards

33

960   dissolved sulfide, carbonate, or silica in Precambrian sediments. Thus boiling HCl quantitatively

961   removes all the iron present in the post-depositional silicates greenalite, stilpnomelane, and

962   minesotaite but only 26% of the total iron in iron chlorite (chamosite). The failure to extract Fe

963   as chamosite could potentially lead to an overestimate of DOP and threshold values need to be

964   interpreted cautiously in this context.

965   The Fe_T/Al ratio is clearly sensitive to iron enrichment (provided a baseline can be

966   established). Ideally, the threshold is defined using oxic sediments in the particular

967   geological/basinal setting. However, suitable oxic sediments may be difficult to identify in the

968   Precambrian record, in part because oxic conditions were far less common. Enrichment may

969   arise from the addition of Fe by a shelf-to-basin shuttle or by hydrothermal activity. Iron inputs

970   in marginal marine basins and oceanic areas remote from hydrothermal activity can reasonably

971   be interpreted as due to the operation of a shuttle. Nevertheless, it may still be difficult to

972   recognize shuttle activity in oceanic settings where contemporaneous hydrothermal activity is

973   occurring—because the influence of hydrothermal inputs into a ferruginous ocean can be

974   widespread, in contrast to more localized impacts in a mostly oxic ocean.

975   As discussed earlier, critical issues with the Fe_{HR}/FeT ratio relate to the methodology

976   used to measure Fe_{HR} and with the definitions of the oxic and anoxic thresholds. The thresholds

977   were originally defined based on Fe_{HR} as the sum of Fe_{py} and Fe_{ox}, and oxic deposition was then

978   proposed for settings with Fe_{HR}/FeT <0.38, while anoxic (sulfidic and ferruginous) deposition

979   was fingerprinted via Fe_{HR}/FeT ratios >0.38. This approach assumes that the contributions from

980   iron carbonate and magnetite are minimal. However phases poorly soluble in dithionite

981   (magnetite and some iron carbonates) are common in Precambrian sediments (and possibly also

982   in Paleozoic sediments; see earlier). In these circumstances, a better measure of Fe_{HR} is obtained

983   as the sum of Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{py}. In such cases, the original value of the oxic threshold

984   at <0.38 should be used with caution (bearing in mind that there have been no such measures of

985    $Fe_{HR}$for Precambrian sediments that have been independently verified as reflecting oxic

986   depositon). A more conservative approach, based on observations of Fe_{HR}/Fe_T in Paleozoic

987   sediments, places the threshold for oxic deposition in ancient rocks at 0.22.

988   Euxinia is expressed in Fe_{py}/Fe_{HR} ratios by near-complete consumption of Fe_{HR} via pyrite

989   formation. The original threshold, based on Fe_{ox}, defined euxinia by values >0.80, but Fe_{HR}

990 measured as the sum of $Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{py}$ will be larger than Fe_{ox} (significantly so if

991 Fe_{carb} and Fe_{mag} are high). In these cases, a lower threshold (>0.70) is best used to recognize

992 euxinia, with some uncertainty for values falling between 0.70 and 0.80 (Poulton and Canfield,

993 2011). We can explore these Precambrian complications below in a specific example.

994   The Mount McRae Shale

995   The importance of considering multiple proxy indicators has been emphasized in recent

996 studies of the McRae Shale, which consists of two pyritic, organic C-rich shales (the Lower and

997 Upper Shale Units) interbedded with a sideritic banded iron formation and occasional carbonates

998 (Kaufmann and others, 2007; Anbar and others, 2007). Iron speciation data (Reinhard and

999 others, 2009) provided evidence for an anoxic water column that was mainly ferruginous but

1000 with euxinic intervals where oxidative weathering on the continents supplied sulfate for sulfate

1001 reduction, forming pyrite on the continental shelf. The following examples show how single

1002 proxy data are vulnerable to misinterpretation and how complementary data are needed to

1003 illuminate ambiguous signals in Precambrian rocks.

1004   (i) Reinhard and others (2009) measured Fe_{HR} content as the sum of $Fe_{carb} + Fe_{ox} + Fe_{mag}$

1005 $+ Fe_{py}$. Depth variations in Fe_{HR}/Fe_T (fig. 12) show most samples lying close to the oxic/anoxic

1006 boundary at 0.38 except in the Upper Shale Interval (USI), where euxinia is indicated by DOP

1007 >0.75 and Fe_{py}/Fe_{HR} >0.70. The Lower Shale Interval (LSI) has values of Fe_{HR}/Fe_T close to the

1008 0.38 threshold, but Fe_T/Al ratios are >1.0 in this unit which Reinhard and others (2009)

1009 considered to provide unequivocal evidence for iron addition and thus a ferruginous water

1010 column. The consideration of complementary Fe_T/Al data by Reinhard and others (2009)

1011 avoided a potential pitfall.

1012   The low Fe_{HR}/Fe_T values in the LSI arose because carbonate Fe (ankerite and siderite)

1013 was only partially extracted by acetate and by oxalate. Thus, the estimates of Fe_{HR} were too low,

1014 and Fe_{HR}/Fe_T appeared close to the oxic threshold (fig. 12). The McRae carbonates can, however,

1015 be quantitatively extracted by cold 10% HCl (Raiswell and others, 2011), and the higher values

1016 of Fe_{HR} then result in high Fe_{HR}/Fe_T values that are unequivocally anoxic (fig. 12) and consistent

1017 with the Fe_T/Al data. Methodologies should always be cross-checked to ensure that completion

1018 extraction has occurred.

1019   (ii) The USI samples from approximately 140-150 m show consistently high values of

1020   DOP and Fe_{py}/Fe_{HR} that Reinhard and others (2009) interpreted as euxinic based also on the

1021   abundance of Mo. High values of DOP and Fe_{py}/Fe_{HR} on their own are not unambiguous

1022   evidence for euxinia because such results are also produced where ferruginous bottom waters

1023   occur over sulfidic porewaters. Molybdenum abundance in this case provided the crucial

1024   diagnostic evidence for euxinia, as it does in Case Study 4.

1025

1026   SUMMARY AND RECOMMENDED APPROACH

1027   A flowpath for decision making is illustrated in figure 13 and should be used in

1028   conjunction with the summary table for the proxy values (table 3).The text provides essential

1029   further details. Specifically, we encourage users of the Fe approach to:

1030   1. Record the main geological features of the sequence to be studied—for example, depth of

1031   burial, basinal history, thermal maturity, and/or metamorphic grade. Collect thin sections of

1032   representative lithologies and determine mineralogy, grain size, et cetera.

1033   2. Produce a stratigraphic section (see for example Sperling and others, 2016) that records grain

1034   size, color, bed characteristics, et cetera. The scale of the log should distinguish the sampled bed

1035   (or beds) and the presence of fossil material, veins, concretionary or coarse iron minerals, or any

1036   other conspicuous heterogeneities (see 3 below).

1037   3. Aim to sample unweathered shales, siltstones, or carbonates (ideally core material) that are

1038   fine-grained and relatively dark in color, consistent with the presence of at least some organic

1039   matter and clays/silicates. Coarse sands and sandstones should be avoided. The analyses require

1040   ~0.5 g of sediment (approximately equivalent to a cube with edges of ~ 5mm). Grind away any

1041   weathered surfaces.

1042   4. Study the samples for the presence of heterogeneities that may now be apparent on the freshly

1043   exposed faces. Crush the samples gently to produce grains very roughly around 1 mm in

1044   diameter and scan the fragments again for the presence of coarse iron minerals. Cut or handpick

1045   out any coarse minerals, such as macroscopic pyrite or veins. The aim is to collect representative

1046   samples rather than large, anomalous heterogeneities (nugget effects) that can skew the data.

1047   Crush samples to a powder.

1048   5. Analyze samples for inorganic C and organic C, and total Fe and Al, pyrite sulfur, HCl-soluble

1049   Fe and dithionite-soluble Fe for Fe_{ox} (as a minimum, extractions specific to Fe_{carb} and Fe_{mag} may

1050   also be necessary; see text). Samples with Fe_T >0.5% and organic C <0.5% should be treated

1051   with caution.

1052   6. Examine sediment texture and mineralogy for evidence of S addition or loss. Regional

1053   remobilization may be indicated by pyrite grain-size and texture and is most likely in thermally

1054   mature or metamorphosed sediments.

1055   7. Examine sediment iron mineralogy for evidence of local Fe remobilization and the formation

1056   of late diagenetic and metamorphic Fe minerals (for example, magnetite, siderite, and iron

1057   silicates). Magnetite and siderite require the use of the Poulton and Canfield (2005) protocol.

1058   Local remobilization of Fe into iron silicates will invalidate all proxy data except DOP and

1059 Fe_T/Al, assuming that the secondary silicates are soluble in boiling HCl for DOP measurement.

1060   8. Examine sediment sulfide mineralogy. The presence of iron monosulfides (AVS, pyrrhotite)

1061   require that Fe_{HR} is calculated using the appropriate mineral stoichiometry. The presence of other

1062   sulfides related to secondary mineralization should be avoided (or removed by handpicking, if

1063   possible) during sampling and should be ignored during the derivation of Fe_{HR} and Fe_{py}.

1064   9. Examine proxy data. Table 3 provides a simple (not prescriptive) entry-point guide to proxy

1065   values, which should not be interpreted in isolation of the detailed discussions in the text. DOP

1066   values of <0.45 suggest an oxic or dysoxic environment and data >0.75 suggest a euxinic

1067   depositional environment. Oxic/dysoxic environments may be further confirmed by Fe_{HR}/Fe_T

1068   <0.22 (ancient) or <0.38 (modern), although we caution that false positive signals for

1069   oxic/dysoxic conditions in the ancient record are possible, for example, under high rates of

1070   sedimentation. Values of Fe_T/Al = 0.55±0.11 can confirm oxic/dysoxic deposition provided the

1071   local source has similar values and there are no dilution effects from high sedimentation rate.

1072   Values of Fe_T/Al >0.66 indicate anoxic deposition but require supporting proxy and/or

1073   geological evidence. Samples with Fe_T/Al = 0.66-2.0 should be examined for their Fe_{HR}/Fe_T and

1074 Fe_{py}/Fe_{HR} properties to demonstrate a ferruginous or euxinic depositional environment. Samples

1075 with $Fe_T/Al >2.0$ require supporting geological evidence for/against local hydrothermal addition.

1076 Intermediate values of DOP require careful consideration of Fe_T/Al, Fe_{HR}/Fe_T, and Fe_{py}/Fe_{HR},

1077 along with other proxy data, for an unambiguous interpretation—as they can reflect sulfidic pore

1078 fluids beneath oxic/dysoxic waters.

1079   Despite the many caveats and considerations offered in this report, we end on an

1080 optimistic note. Many factors can control the distributions of reactive iron in marine sediments

1081 and sedimentary rocks, but we can minimize the risk of ambiguous interpretations when the

1082 diverse controlling factors are viewed within a multi-proxy context. Such an approach offers

1083 unique perspectives on, for example, rates of sedimentation and Fe source-sink relationships, and

1084 corresponding Fe capture pathways. At the same time, Fe-based constraints on local paleoredox

1085 allow us to interpret independent trace metal records in terms of seawater inventories modulated

1086 by local basinal restriction or the global redox landscape of the oceans and atmosphere. These

1087 and other opportunities explain why the Fe proxies have been and will continue to be at the

1088 center of studies aimed at the co-evolution of the oceans and their life.

1089 ACKNOWLEDGEMENTS

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1097

1098 APPENDIX

1099 This appendix present simple explanations for the terms commonly used in discussing the iron

1100 proxies. It is intended to make the text accessible to scientists without a formal background in

1101 sediment geochemistry and it should be used as only an entry point into the relevant literature.

1102   Acid Volatile Sulfide (AVS): The operationally defined acid volatile sulfides consist of metastable

1103   iron sulfide minerals and dissolved sulfide species that emit H_2S when treated with strong acids.

1104   AVS is largely transformed to pyrite during diagenesis.

1105   Anoxic: Waters that contain no dissolved oxygen and may either contain dissolved iron

1106   (ferruginous) or dissolved sulfide (euxinic).

1107   Degree of Pyritization (DOP): Defined as the ratio between pyrite Fe and the sum of pyrite Fe

1108   plus the iron soluble in concentrated boiling HCl. It was envisaged that all the iron minerals

1109   dissolved by HCl could react with dissolved sulfide (and thus a first attempt to estimate Highly

1110   Reactive Iron; see below). However this aggressive extraction dissolves a wide range of iron

1111   minerals some of which have little or no capacity to react to form pyrite.

1112   Degree of Sulfidation (DOS): DOS is derived by the addition of Fe present as AVS (see above)

1113   to the numerator and denominator of DOP

1114
$$\mathrm{DOS} \; = \frac{\text{Pyrite Fe+AVS Fe}}{\text{Pyrite Fe+AVS Fe+HCl−soluble Fe}}$$

1115

1116   DOS is often preferred over DOP for systems when AVS is present in appreciable amounts.

1117   Dysoxic: Waters that contain low levels of dissolved oxygen (less than saturation levels) but are

1118   neither ferruginous nor sulfidic.

1119   Euxinic: Anoxic waters that contain dissolved sulfide and negligible concentrations of dissolved

1120   iron.

1121   Ferruginous: Anoxic waters that contain dissolved iron and negligible concentrations of

1122   dissolved sulfide.

1123   Highly Reactive Iron: The iron present as sediment minerals that are capable of reacting with

1124   dissolved sulfide to form pyrite or AVS. Estimated as the sum of pyrite iron (which has formed

1125   from iron minerals that have already reacted with dissolved sulfide) plus the iron present as the

1126   (oxyhydr)oxide minerals soluble in dithionite. It is now accepted, however, that highly reactive

1127 iron also includes the minerals siderite, magnetite and ankerite, in addition to iron

1128 (oxyhydr)oxides.

1129 Indicator of Anoxicity: Defined as the ratio between (Highly Reactive Iron)/Total Fe, where

1130 highly reactive iron is measured as pyrite Fe plus the Fe soluble in dithionite. This term is now

1131 largely obsolete as Highly Reactive Iron is more correctly defined to include siderite, magnetite

1132 and ankerite (see Highly Reactive Iron).

1133 Iron Shuttle: Iron enrichments in the deep basinal euxinic sediments are sourced by microbial Fe

1134 reduction in oxic shelf sediments, diffusion of reduced iron into the overlying waters, followed

1135 by transport of a proportion of the resulting iron (now oxidized to Fe (oxyhydr)oxides or still

1136 dissolved) to the deep basin, where it is captured by the sulfidic water column and precipitated as

1137 pyrite.

1138 Pyrite Iron: The iron present as pyrite, excluding AVS. The H_2S produced by sulfate reduction

1139 reacts with Fe minerals to form FeS (measured as AVS), which then reacts with partially

1140 oxidised sulfide species or H_2S. FeS can also react directly with H_2S to produce pyrite.

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1416   Figure Captions.

1417   Fig. 1. Schematic model of pyrite formation (after Berner, 1984 and Hurtgen and others, 1999).

1418 H_2S produced by sulfate reduction reacts with Fe minerals to form FeS, which then reacts with

1419   partially oxidised sulfide species. FeS can also react directly with H_2S to produce pyrite.

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1421   Fig. 2. Diagnostic fields of Fe_{py}/Fe_{HR} and Fe_{HR}/Fe_T. Solid lines are recommended values and

1422   dashed line is a suggested boundary for ancient sediments only

1423   Fig. 3. FOAM porewater and sediment variations with depth (Hardisty and others, in review).

1424 Fe_{ox} represents dithionite-soluble Fe. DOP values are similar to those previously reported at

1425   FOAM (Canfield and others, 1992). DOP values below the grey boundary define oxic conditions

1426   as do values of Fe_{HR}/Fe_T <0.38 and Fe_T/Al ~0.55 (table 3). Sulfidic pore waters commonly

1427   produce values of Fe_{py}/Fe_{HR} >0.8.

1428   Fig. 4. **A**) Compilation of Fe_{HR} versus total Fe for modern oxic marine basins. Red circles

1429   indicate studies where Fe_{HR} is the sum of pyrite Fe and dithionite Fe (Raiswell and Canfield,

1430   1998; Wisjman and others, 2001). Green circles represent studies where Fe_{HR} is the sum of pyrite

1431   Fe, dithionite Fe and oxalate Fe (Goldberg and others, 2012; Hardisty and others, in review). The

1432   dashed line has a slope of 0.38 which is that found to constrain oxic modern marine basins in

1433   previous studies (Raiswell and Canfield, 1998). **B**) Compilation of Fe_{HR} versus total Fe for a

1434   literature compilation spanning from 2300 to 360 million years ago (Sperling and others, 2015).

1435   Red circles represent samples with Fe_{HR}/Fe_T <0.38 with Fe_{HR} measured as the sum of pyrite Fe

1436   and dithionite Fe (excluding Fe_{mag} and Fe_{carb} following Raiswell and Canfield, 1998). Green

1437   circles show the higher Fe_{HR} data obtained for the same samples where Fe_{HR} is the sum of pyrite

1438   Fe, dithionite Fe and oxalate Fe (as proposed by Poulton and Canfield, 2005). The differences

1439   between the red and green circles shows how the differences in speciation methodology affect

1440   interpretation of the Fe_{HR}/Fe_T threshold.

1441   Fig. 5. Dilution effect of siliciclastic accumulation rates on Fe_T/Al (from Lyons and Severmann,

1442   2006).

1443   Fig. 6. Fe_T/Al ratios for Orca Basin sediments (from Lyons and Severmann, 2006). Dashed line

1444   represents mean ratio in modern sediments (see table 3).

1445   Fig. 7. Depth variations in organic C, total S and Fe_T/Al for sapropel S1 in core GC17 (from

1446   Passier and others, 1996). Enrichments in pyrite S and Fe_T/Al are found within the sapropel and

1447   in the sediments below.

1448   Fig. 8. Variations in the iron proxies (Fe_T/Al, Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR}) through core at site 1261

1449   (from März and others, 2008). Fe_{HR}/Fe_T values >0.38 indicate Fe-enrichment, values of

1450 Fe_{py}/Fe_{HR}>0.70 are possibly euxinic.

1451   Fig. 9. Maximum Fe_T/Al values in modern (blue) and ancient (red) euxinic sediments (from

1452   Raiswell and others, 2011).The two values above 2.0 are from Precambrian sediments (see text).

1453   Fig. 10. Stratigraphic variations in Fe_T/Al, $\delta^{56}Fe$ and Mo abundance at DSDP sites 367, 144 and

1454   603B (from Owens and others, 2012). Error bars represent precision of 0.08‰. The grey bar

1455   shows the location of OAE 2. Fe_T/Al values of 1-2 are Fe-enriched with Mo >100 ppm indicating

1456   euxinicity.

1457   Fig. 11. $\Delta Fe_T/Al$ variations with temperature (blue squares data from Jia, 2006; red circles data

1458   from Yui and others, 2009)

1459   Fig. 12. Depth variations in Fe_{HR}/Fe_T and Mo content in the Upper (USI) and Lower Shale

1460   intervals (LSI) of the McRae Shale. Red circles use Fe_{HR} data from Reinhard and others (2009)

1461   and black crosses are Fe_{HR} data from Raiswell and others (2011). The dashed line represents the

1462   anoxic threshold (Fe_{HR}/Fe_T = 0.38).

1463   Fig. 13. Decision schematic for valid proxy interpretation

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