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23 **ABSTRACT.** Oceanic anoxia—including euxinic settings defined by the presence of water  
24 column hydrogen sulfide (H<sub>2</sub>S)—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 behavioral 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.

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## 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.

## 101 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 limitation is indicated when sulfide builds up in

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:

$$120 \quad \text{DOP} = \frac{\text{Pyrite Fe}}{\text{Pyrite Fe} + \text{HCl-soluble Fe}} \quad (1)$$

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).

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<sub>2</sub>S 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 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;

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

206

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



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 ( $0.26 \pm 0.08$ ) are similar to those  
264 from fluctuating/dysoxic sediments ( $0.28 \pm 0.10$ ), but both are clearly separated from the Black  
265 Sea ( $0.70 \pm 0.19$ ) and the Cariaco Basin ( $0.51 \pm 0.03$ ). 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 ( $\text{Fe}_{\text{carb}}$ , sodium acetate-soluble Fe), oxides ( $\text{Fe}_{\text{ox}}$ , dithionite-  
283 soluble crystalline Fe oxides), magnetite ( $\text{Fe}_{\text{mag}}$ , oxalate-soluble Fe) and pyrite ( $\text{Fe}_{\text{py}}$ ):

$$284 \quad \text{Fe}_{\text{HR}} = \text{Fe}_{\text{carb}} + \text{Fe}_{\text{ox}} + \text{Fe}_{\text{mag}} + \text{Fe}_{\text{py}} \quad (3)$$

285 In the case of modern sediments  $\text{Fe}_{\text{HR}}$  would also include the Fe present as AVS ( $\text{Fe}_{\text{AVS}}$ ). This  
286 newer definition demands that we consider whether the threshold value defined earlier — based  
287 on  $\text{Fe}_{\text{HR}}$  data that excluded  $\text{Fe}_{\text{carb}}$  and  $\text{Fe}_{\text{mag}}$ — should be modified. There is no simple answer to  
288 this question. In some cases, the addition of  $\text{Fe}_{\text{mag}}$  may have little impact on  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  for typical  
289 oxic sediments (see Case Study 1; Hardisty and others, in review; Goldberg and others, 2012). In  
290 other cases,  $\text{Fe}_{\text{mag}}$  has been found to represent a significant fraction of  $\text{Fe}_{\text{HR}}$  (for example, in  
291 some glacially derived sediments; März and others, 2012). From hereon all  $\text{Fe}_{\text{HR}}$  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  $\text{Fe}_{\text{HR}}$  as  $\text{Fe}_{\text{ox}} + \text{Fe}_{\text{py}}$  (that is, not including  
298  $\text{Fe}_{\text{carb}}$  and  $\text{Fe}_{\text{mag}}$ ) they found that the mean  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  values for these Cretaceous, Jurassic,  
299 Silurian, Ordovician, and Cambrian sediments ranged from  $0.13 \pm 0.06$  to  $0.17 \pm 0.11$  (average  
300  $0.14 \pm 0.08$ ) —values that are significantly lower (at the  $<0.1\%$  confidence level) than those from  
301 modern sediments ( $0.26 \pm 0.08$ ). Poulton and Raiswell (2002) attributed these low  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$   
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  $\text{Fe}_{\text{HR}}$  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  $\text{Fe}_{\text{HR}}$ . 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  $\text{Fe}_{\text{HR}}$  to pyrite,

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 ( $0.26 \pm 0.08$ ) rather than the lower values ( $0.14 \pm 0.08$ ) 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 ( $0.14 \pm 0.08$ ) 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  $\sim 0.2$  (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.

371 Raiswell and others (2008) found  $Fe_T/Al$  to be  $0.53\pm 0.11$  (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  $0.55\pm 0.11$   
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  $0.47\pm 0.15$  which Cole  
377 and others (2017) suggest should be used in conjunction with a confidence limit of two standard  
378 deviations ( $0.47\pm 0.30$ ) — 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  $Fe_T/Al \sim 0.20$ ; similarly samples from the Windermere Supergroup  
387 (Sperling and others, 2016) had  $Fe_T/Al$  of  $0.32\pm 0.17$  also with variations down to  $\sim 0.2$  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 ( $Fe_T/Al = 3.0\pm 3.8$ ; 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  $0.87\pm 0.04$  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 ( $0.80 \pm 0.06$ ) 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 euxinic conditions 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  $0.88 \pm 0.02$  (with only five  
415 measurements below  $0.80$ ) and  $0.89 \pm 0.02$  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:



- 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

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  $\sim 0.50$  (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

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.

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  $\sim 0.40$  (Lyons and Berner, 1992; Canfield and  
535 others, 1996; Lyons, 1997; Wijsman and others, 2001; Lyons and Severmann, 2006),  $Fe_{HR}/Fe_T$   
536  $< 0.38$  (Wijsman and others, 2001), and  $Fe_T/Al$  ratios of  $\sim 0.50$  (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  $\sim 0.60$   
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



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.

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.



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

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

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  $\sim 0$  through post-depositional enrichment (Boesen and Postma, 1988). DOS  $\sim 0.4$   
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 Phanerozoic 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  $-20\text{‰}$ ). 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  $+15\text{‰}$ ) than the overlying marine sediments ( $\delta^{34}S$   $-24$  to  $-17\text{‰}$ ). 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 sulfidation front ( $\delta^{34}\text{S} +15$  to  $+34\text{‰}$ ).

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 Shuttles 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  $\text{Fe}_T$ , Al, and inorganic C, with iron speciation carried out by  
778 sequential extractions to quantify  $\text{Fe}_{\text{carb}}$ ,  $\text{Fe}_{\text{ox}}$ ,  $\text{Fe}_{\text{mag}}$ , and  $\text{Fe}_{\text{py}}$ , the sum of which defines  $\text{Fe}_{\text{HR}}$ .  
779 The calcium carbonate ( $\text{CaCO}_3$ ) content is typically ~60% and rarely exceeds 80%,  $\text{Fe}_T$  contents  
780 average ~1% (only one sample contains <0.5%,) and organic C contents are always >2%. These



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)..

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 oxitic (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 oxitic 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 pyrrhotite Fe can be accurately determined.  
905 Asael and others (2013) extracted crystalline pyrrhotite using a hot 6N HCl distillation with  
906 SnCl<sub>2</sub> 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<sub>2</sub>. Provided pyrrhotite 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 pyrrhotite-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<sub>HR</sub> 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<sub>HR</sub>, 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<sub>HR</sub> (Slotznick and others, 2017). Clarkson and others (2014) found that the  
926 ratio Fe<sub>HR</sub>/Fe<sub>T</sub> 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<sub>HR</sub>/Fe<sub>T</sub> 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

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  $Fe_{HR}/Fe_T$  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  $Fe_{HR}/Fe_T < 0.38$ , while anoxic (sulfidic and ferruginous) deposition  
979 was fingerprinted via  $Fe_{HR}/Fe_T$  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 deposition). 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  $Fe_T/Al = 0.55 \pm 0.11$  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



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<sub>2</sub>S 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 
$$\text{DOS} = \frac{\text{Pyrite Fe} + \text{AVS Fe}}{\text{Pyrite Fe} + \text{AVS Fe} + \text{HCl-soluble Fe}}$$

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<sub>2</sub>S 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<sub>2</sub>S. FeS can also react directly with H<sub>2</sub>S 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  $\text{H}_2\text{S}$  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  $\text{H}_2\text{S}$  to produce pyrite.

1420

1421 Fig. 2. Diagnostic fields of  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  and  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ . 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  $\text{Fe}_{\text{ox}}$  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  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} < 0.38$  and  $\text{Fe}_{\text{T}}/\text{Al} \sim 0.55$  (table 3). Sulfidic pore waters commonly  
1427 produce values of  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} > 0.8$ .

1428 Fig. 4. **A)** Compilation of  $\text{Fe}_{\text{HR}}$  versus total Fe for modern oxic marine basins. Red circles  
1429 indicate studies where  $\text{Fe}_{\text{HR}}$  is the sum of pyrite Fe and dithionite Fe (Raiswell and Canfield,  
1430 1998; Wisjman and others, 2001). Green circles represent studies where  $\text{Fe}_{\text{HR}}$  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  $\text{Fe}_{\text{HR}}$  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  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}} < 0.38$  with  $\text{Fe}_{\text{HR}}$  measured as the sum of pyrite Fe  
1436 and dithionite Fe (excluding  $\text{Fe}_{\text{mag}}$  and  $\text{Fe}_{\text{carb}}$  following Raiswell and Canfield, 1998). Green  
1437 circles show the higher  $\text{Fe}_{\text{HR}}$  data obtained for the same samples where  $\text{Fe}_{\text{HR}}$  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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