

# **An evaluation of sedimentary molybdenum and iron as proxies for pore fluid paleoredox conditions**

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**ABSTRACT:** Iron speciation and trace metal proxies are commonly applied together in efforts to identify anoxic settings marked by the presence of free sulfide (euxinia) or dissolved iron (ferruginous) in the water column. Here, we use a literature compilation from modern localities to provide a new empirical evaluation of coupled Fe speciation and Mo concentrations as a proxy for pore water sulfide accumulation at non-euxinic localities. We also present new Fe speciation, Mo concentration, and S isotope data from the Friends of Anoxic Mud (FOAM) site in Long Island Sound, which is marked by pore water sulfide accumulation of up to 3 mM beneath oxygen-containing bottom waters. For the operationally defined Fe speciation scheme, ‘highly reactive’ Fe ( $Fe_{HR}$ ) is the sum of pyritized Fe ( $Fe_{py}$ ) and Fe dominantly present in oxide phases that is available to react with pore water sulfide to form pyrite. Observations from FOAM and elsewhere confirm that  $Fe_{py}/Fe_{HR}$  from non-euxinic sites is a generally reliable indicator of pore fluid redox, particularly the presence of pore water sulfide. Molybdenum (Mo) concentration data for anoxic continental margin sediments underlying oxic waters but with sulfidic pore fluids typically show authigenic Mo enrichments (2-25 ppm) that are elevated relative to the upper crust (1-2 ppm). However, compilations of Mo concentrations comparing sediments with and without sulfidic pore fluids underlying

35 oxic and low oxygen (non-euxinic) water columns expose non-unique ranges for each, exposing false  
36 positives and false negatives. False positives are most frequently found in sediments from low oxygen  
37 water columns (for example, Peru Margin), where Mo concentration ranges can also overlap with values  
38 commonly found in modern euxinic settings. FOAM represents an example of a false negative, where,  
39 despite elevated pore water sulfide concentrations and evidence for active Fe and Mn redox cycling in  
40 FOAM sediments, sedimentary Mo concentrations show a homogenous vertical profile across 50 cm  
41 depth at 1-2 ppm. A diagenetic model for Mo provides evidence that muted authigenic enrichments are  
42 derived from elevated sedimentation rates. Consideration of a range of additional parameters, most  
43 prominently pore water Mo concentration, can replicate the ranges of most sedimentary Mo  
44 concentrations observed in modern non-euxinic settings. Together, the modern Mo and Fe data  
45 compilations and diagenetic model provide a framework for identifying paleo-pore water sulfide  
46 accumulation in ancient settings and linked processes regulating seawater Mo and sulfate concentrations  
47 and delivery to sediments. Among other utilities, identifying ancient accumulation of sulfide in pore  
48 waters, particularly beneath oxic bottom waters, constrains the likelihood that those settings could have  
49 hosted organisms and ecosystems with thiotrophy at their foundations.

50

## INTRODUCTION

51 Iron speciation and molybdenum concentrations have been well calibrated in modern settings for  
52 recognizing end-member euxinic (anoxic and H<sub>2</sub>S-containing) and ferruginous (anoxic and iron-rich)  
53 settings in the geologic record (Algeo and Lyons, 2006; Berner, 1970; Canfield and others, 1996;  
54 Canfield and others, 1992; Lyons and Severmann, 2006; Poulton and Canfield, 2005, 2011; Raiswell and  
55 others, 1988; Raiswell and Canfield, 1998; Raiswell and others, 2018). This past research has resulted in  
56 extensive application of these proxies toward an improved understanding of water column redox  
57 evolution and dynamics through time, including Phanerozoic ocean anoxic events (Gill and others, 2011;  
58 März and others, 2008; März and others, 2012), the Proterozoic (Canfield and others, 2007; Johnston and  
59 others, 2012; Li and others, 2010; Planavsky and others, 2011; Poulton and others, 2004; Scott and others,  
60 2008; Sperling and others, 2015), and the Archean (Kendall and others, 2010; Reinhard and others, 2009;  
61 Scott and others, 2011). Beyond the recognition of ancient euxinic and ferruginous water columns, more  
62 recent research has provided a context for using Fe and Mo proxies to infer accumulation of sulfidic pore  
63 waters in ancient sediments, including those deposited beneath water columns lacking dissolved sulfide  
64 and Fe (Scott and Lyons, 2012; Sperling and others, 2015). Refined recognition of these conditions has  
65 important implications for the evolution of the marine sulfate reservoir and for interpretation of the  
66 geochemical impacts of sediment mixing induced by benthic infaunal communities through time

67 (Canfield and Farquhar, 2009; Tarhan and others, 2015). Additionally, pore water sulfide has implications  
68 for bottom water habitability and the evolution of thiotrophy and associated symbiotic relationships  
69 among combined micro-/macrofaunal communities (Sperling and others, 2015; Tarhan and others, 2015).  
70 However, although a broad framework currently exists for understanding the conditions leading to Mo  
71 and Fe fixation in sulfidic sediments (see background), few studies have systematically evaluated proxy  
72 expressions from modern sediments to assess their potential as uniquely pore fluid indicators of  
73 paleoredox in ancient sediments.

74 Here, we specifically assess the paleoredox proxy potential of Fe speciation and Mo concentrations  
75 to recognize the presence or absence of pore water sulfide accumulation during early diagenesis from  
76 modern marine sediments underlying water columns without stable euxinia and a range of ambient  
77 oxygen concentrations. This endeavor is grounded in a broad context provided by compilations of Fe  
78 speciation and Mo concentrations from modern localities where water column and pore water redox  
79 conditions are well characterized. In addition, we present an original case study with Fe-speciation, Mo  
80 concentration, and S concentration and isotope data for sediments from the oxic FOAM (Friends of  
81 Anoxic Mud) site in Long Island Sound (LIS), USA, where sedimentary pore fluids are well-known to  
82 host elevated and persistent pore water sulfide concentrations. Previous studies of LIS, including the  
83 FOAM site, have been fundamental to the initial development of the Fe paleoredox proxies and a range of  
84 other sedimentary geochemical signatures (Aller, 1980a, b; Aller and Cochran, 1976; Benninger and  
85 others, 1979; Benoit and others, 1979; Berner and Westrich, 1985; Canfield, 1989; Canfield and Berner,  
86 1987; Canfield and others, 1992; Canfield and Thamdrup, 1994; Goldhaber and others, 1977;  
87 Krishnaswami and others, 1980; Raiswell and others, 1994; Raiswell and Canfield, 1998; Westrich,  
88 1983). We use a diagenetic model for Mo to provide constraints on the environmental factors that best  
89 explain the observed modern sediment concentration ranges and provide a context for interpreting non-  
90 euxinia related drivers of changes in Mo concentrations from ancient sediments.

## 91 **BACKGROUND AND PROXY FRAMEWORK**

### 92 *The Iron Proxies*

93 The utility of the Fe geochemical proxies is built on a foundation of extensive work on the  
94 reactivity of Fe minerals with dissolved sulfide in sedimentary environments (Berner, 1970; Canfield and  
95 others, 1996; Canfield and others, 1992; Poulton and Canfield, 2005; Raiswell and others, 1988; Raiswell  
96 and others, 1994; Raiswell and Canfield, 1998) and a well-developed understanding of syngenetic (water  
97 column) versus diagenetic pyrite formation (Anderson and Raiswell, 2004; Canfield and others, 1996;

98 Lyons, 1997; Lyons and others, 2003; Raiswell and Anderson, 2005; Wijsman and others, 2001). The  
99 refined sequential extraction scheme of Poulton and Canfield (2005) is designed to target Fe phases,  
100 emphasizing carbonate-bound Fe, oxide Fe (dithionite extractable,  $Fe_{dith}$ ), and magnetite Fe (oxalate  
101 extractable,  $Fe_{mag}$ ), which all react with sulfide to form pyrite ( $Fe_{py}$ ) and Fe monosulfides (acid volatile  
102 sulfur,  $Fe_{AVS}$ ) on time scales relevant to early diagenesis (Canfield, 1989; Canfield and others, 1996;  
103 Canfield and others, 1992). These iron phases, when summed with pyrite, comprise the operationally  
104 defined ‘highly reactive’ Fe ( $Fe_{HR}$ ) pool.

105 Inputs of detrital  $Fe_{HR}$  into sediments permit the production of pyrite when exposed to sulfide, but  
106 typical lithogenic ratios of  $Fe_{HR}/Fe_T < 0.38$  and  $Fe_T/Al$  mass ratios  $\sim 0.5$  are maintained when anoxic  
107 (euxinic or ferruginous) conditions are not present in the water column (Lyons and Severmann, 2006;  
108 Lyons and others, 2003; Raiswell and Canfield, 1998). In contrast, if anoxia develops and persists in the  
109 water column, both  $Fe_{HR}/Fe_T$  and  $Fe_T/Al$  are elevated beyond these crustal baselines, and those  
110 enrichments are often used to infer ancient anoxia. According to one model, soluble Fe(II) generated  
111 during reductive dissolution of Fe-oxides along continental margins diffuses out of sediments, allowing  
112 enhanced delivery of  $Fe_{HR}$  through an ‘Fe shuttle’ to the deep basin where it is captured as syngenetic  
113 pyrite (Anderson and Raiswell, 2004; Canfield and others, 1996; Lyons, 1997; Lyons and Severmann,  
114 2006; Raiswell and Anderson, 2005; Raiswell and Canfield, 1998; Scholz and others, 2014b; Severmann  
115 and others, 2008; Severmann and others, 2010; Wijsman and others, 2001). This ‘extra’ Fe is decoupled  
116 from the local delivery of silicate phases, including unreactive Fe fractions, with the net result of  $Fe_{HR}/Fe_T$   
117  $> 0.38$  (Raiswell and Canfield, 1998) and  $Fe_T/Al > 0.5$ . Under euxinic conditions, near complete reaction  
118 of the  $Fe_{HR}$  to form pyrite leads to  $Fe_{py}/Fe_{HR}$  ratios in excess of 0.7 to 0.8 (März and others, 2008; Poulton  
119 and Canfield, 2011; Poulton and others, 2004).

120 In sulfidic sediments underlying non-euxinic or ferruginous water column conditions, hence  
121  $Fe_{HR}/Fe_T < 0.38$  and  $Fe_T/Al \sim 0.5$ , the  $Fe_{py}/Fe_{HR}$  ratio is anticipated to be  $> 0.7$ . This prediction is based on  
122 work from the Long Island Sound FOAM site (see FOAM background) where it was initially shown that  
123 pore water sulfide accumulation is preceded by the consumption of ‘highly reactive’ Fe minerals via  
124 reaction with sulfide to form pyrite (Canfield, 1989; Canfield and others, 1992). Sequential Fe extractions  
125 and associated  $Fe_{py}/Fe_{HR}$  of ancient shales have been applied previously to interpret pore water redox in  
126 ancient sediments (Sperling and others, 2015), but no study has evaluated the potential of  $Fe_{py}/Fe_{HR}$  from  
127 modern non-euxinic settings to uniquely indicate pore water sulfide accumulation—hence this study.

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### *Molybdenum Geochemistry*

131 Molybdenum is the most abundant transition metal in the modern ocean, with a near uniform  
132 concentration of ~104 nM (Broecker and Peng, 1982; Emerson and Huested, 1991) and a relatively long  
133 residence time of ~450 kyr (Miller and others, 2011). Molybdenum exists almost entirely as molybdate  
134 ( $\text{MoO}_4^{2-}$ ) under oxic conditions, delivered primarily from oxidative weathering of sulfide minerals (Miller  
135 and others, 2011). Molybdate has a strong affinity for sorption to Mn and Fe oxides, which is a significant  
136 pathway of Mo deposition in the modern, dominantly oxic ocean (Barling and Anbar, 2004; Shimmield  
137 and Price, 1986). In the absence of free sulfide in the water column and sediments, Mo buried with oxides  
138 will often diffuse back to the overlying water column following reductive dissolution of the oxides during  
139 sediment diagenesis (Goldberg and others, 2012; Scott and Lyons, 2012; Shimmield and Price, 1986),  
140 with the possibility of little to no authigenic sediment enrichment and thus concentrations near those  
141 characteristic of average continental crust (~1-2 ppm).

142 Under sulfide-rich conditions, however, Mo is readily converted from  $\text{MoO}_4^{2-}$  to particle reactive  
143 thiomolybdate ( $\text{MoO}_{4-x}\text{S}_x^{2-}$ ; (Erickson and Helz, 2000; Helz and others, 1996; Zheng and others, 2000),  
144 which is buried in association with organic matter and pyrite (Algeo and Lyons, 2006; Chappaz and  
145 others, 2014; Dahl and others, 2017; Wagner and others, 2017). This relationship has particular  
146 importance when considering settings with sulfide restricted to the sediment pore fluids versus euxinic  
147 sites. In either case, if total dissolved sulfide concentrations exceed ~100  $\mu\text{M}$  (with some sensitivity to  
148 ambient pH), quantitative sulfidization of  $\text{MoO}_4^{2-}$  to  $\text{MoS}_4^{2-}$  is expected (Erickson and Helz, 2000; Helz  
149 and others, 1996; Helz and others, 2011; Zheng and others, 2000). Molybdenum enrichments under  
150 euxinic water column conditions typically exceed the average continental crust value of approximately 1-  
151 2 ppm (Taylor and McLennan, 1995) by a significant margin—with sediment concentrations of up to  
152 hundreds of ppm (Scott and Lyons, 2012) and distinct relationships with the abundance of organic carbon  
153 in the sediments (Algeo and Lyons, 2006). In modern sulfidic sediments accumulating beneath an oxic  
154 water column, Mo delivered to the sediments—including that associated with oxide deposition and  
155 subsequent dissolution—is retained upon oxide dissolution via reaction with dissolved sulfide, among  
156 other possibilities (Scholz and others, 2017). Rather than diffusing back to the overlying water column,  
157 this Mo is sequestered with organic matter and/or pyrite in the subsurface layers (Chappaz and others,  
158 2014; Dahl and others, 2017; Erickson and Helz, 2000; Helz and others, 1996; Helz and others, 2011;  
159 Wagner and others, 2017). A recent survey of Mo concentrations from non-euxinic settings with sulfidic

160 pore fluids suggests that authigenic enrichments rarely exceed 25 ppm, with most of these settings having  
161 enrichments below 10 ppm (Scott and Lyons, 2012). A new diagenetic model, the new FOAM data, and  
162 the literature data compilation presented here is intended to extend the proxy potential of Mo  
163 concentrations to differentiate settings with pore fluid sulfide accumulation from those lacking sulfide or  
164 with sulfide also present in the water column.

### 165 *FOAM—The Historical Context*

166 Past studies of FOAM and several nearby locations in Long Island Sound must get credit for  
167 giving rise to the Fe-based paleoredox proxies—specifically, degree of pyritization (DOP),  $Fe_{HR}/Fe_T$ , and  
168  $Fe_{py}/Fe_{HR}$ . The water column is oxygenated at each of these localities (Lee and Lwiza, 2005; Lee and  
169 Lwiza, 2008; Wallace and others, 2014), and sedimentary sulfide concentrations range from 2 to 6 mM at  
170 FOAM and the adjacent study sites characterized by high rates of sulfate reduction (Canfield, 1989;  
171 Canfield and others, 1992; Goldhaber and others, 1977; Westrich, 1983). Studies at FOAM demonstrate  
172 that DOP data from sediments with sulfidic pore waters, but underlying oxic water columns, are clearly  
173 distinguishable from those of euxinic water column settings. Specifically, DOP values from FOAM and  
174 nearby LIS sediments do not exceed  $\sim 0.4$  (Berner, 1970; Canfield and others, 1992; Raiswell and  
175 Canfield, 1998), which are readily distinguished from the values of  $>0.7$  found in sediments underlying  
176 euxinic water columns (Raiswell and others, 1988). Similarly, comparisons of  $Fe_{HR}/Fe_T$  data from FOAM  
177 and other modern oxic localities to sediments in modern euxinic basins established the  $Fe_{HR}/Fe_T$  threshold  
178 of  $\sim 0.38$  now used widely to identify ancient euxinic and ferruginous water columns (Raiswell and  
179 Canfield, 1998). These same studies also demonstrated the reactivity of common Fe minerals—  
180 ferrihydrite, lepidocrocite, goethite, hematite, magnetite—towards sulfide to form pyrite. Concurrently  
181 time, other Fe minerals (for example, sheet silicates) were found instead to react with sulfide on much  
182 longer timescales well beyond those of early diagenesis (Canfield, 1989; Canfield and Berner, 1987;  
183 Canfield and others, 1992; Raiswell and others, 1994).

184 The intermediate DOP values at FOAM, despite high and persistent levels of pore water sulfide,  
185 set the stage of a deeper exploration of reactive iron (reviewed in Lyons and Severmann, 2006) and the  
186 mechanistic underpinnings of the Fe-based paleoredox proxies—leading ultimately to the now widely  
187 used sequential extraction protocol (Poulton and Canfield, 2005). This refined approach targets the  
188 ‘highly reactive’ Fe phases described above. Collectively, data from FOAM and the modern Black Sea  
189 (Canfield and others, 1996) exposed the need for ‘extra’ highly reactive Fe in euxinic settings to explain  
190 observations of elevated DOP and  $Fe_{HR}/Fe_T$  (Anderson and Raiswell, 2004; Canfield and others, 1996;



222 several hours of core retrieval (Seeberg-Elverfeldt and others, 2005). Pore water subsamples for hydrogen  
223 sulfide ( $\Sigma\text{H}_2\text{S}$ ) were fixed with zinc acetate, while subsamples for metal analysis were acidified with trace  
224 metal grade HCl. Residual sediment samples were sealed and frozen immediately, minimizing oxidation.

225 Pore water  $\Sigma\text{H}_2\text{S}$  concentrations were measured using the methylene blue method (Cline, 1969).  
226 Sulfate concentrations were determined by suppressed ion chromatography with conductivity detection  
227 (ICS-2000, AS11 column; Dionex) at the Stable Isotope Geobiology Laboratory at Harvard University.  
228 Pore water concentrations of Mn, Fe, and Mo were measured via inductively coupled plasma-mass  
229 spectrometry (ICP-MS; Agilent 7500ce) at the University of California Riverside. Sample replicates  
230 yielded standard deviations <5% for Mn, Fe, and Mo.

231 Acid volatile sulfur (AVS) and chromium reducible sulfur (CRS) were determined sequentially  
232 using freshly thawed frozen samples and quantified by iodometric titration (Canfield and others, 1986).  
233 Recoveries of sulfur for pure pyrite standards averaged  $86 \pm 9.2\%$  of the expected amount (n=8);  
234 however, duplicate analyses of FOAM samples revealed better reproducibility. To determine the degree  
235 of pyritization (DOP) for FOAM sediments, Fe was extracted using the boiling HCl method of Berner  
236 (1970) and Raiswell and others (1988). Following from previous work (Berner, 1970; Raiswell and  
237 others, 1988), DOP was calculated as  $\text{Fe}_{\text{py}}/(\text{Fe}_{\text{py}} + \text{Fe}_{\text{HCl}})$ .

238 Samples with the bulk of pore water previously extracted but still wet were thawed and weighed  
239 for determination of Fe speciation using a modified version of the sequential Fe extraction of Poulton and  
240 Canfield (2005). An ascorbate step targeting ferrihydrite (Ferdelman, 1988; Kostka and Luther, 1994;  
241 Raiswell and others, 2010), or  $\text{Fe}_{\text{asc}}$ , was added and replaced a sodium acetate extraction that targets  
242 carbonate-bound Fe given the unlikelihood of Fe carbonate precipitation in these sulfide-rich sediments.  
243 To minimize oxidation of Fe sulfide phases during the extraction procedures, the solutions were bubbled  
244 with  $\text{N}_2$  gas prior to extraction, and the headspace extraction vials were filled with  $\text{N}_2$  gas and sealed  
245 throughout the extractions. Replicate samples yielded precisions of <7% for  $\text{Fe}_{\text{asc}}$ ,  $\text{Fe}_{\text{dith}}$ , and  $\text{Fe}_{\text{mag}}$ . All  
246 iron phase values are reported on dry sediment basis corrected for water contents. Combined,  $\text{Fe}_{\text{py}}$ ,  $\text{Fe}_{\text{AVS}}$ ,  
247  $\text{Fe}_{\text{asc}}$ ,  $\text{Fe}_{\text{dith}}$ , and  $\text{Fe}_{\text{mag}}$  represent the total 'highly reactive' Fe pool ( $\text{Fe}_{\text{HR}}$ ).

248 FOAM sediment samples were dried and then homogenized via mortar and pestle after removal  
249 of visible shell material. Total carbon was measured using an Eltra CS-500 carbon-sulfur analyzer. Total  
250 inorganic carbon was determined by measuring  $\text{CO}_2$  liberated after addition of 2.5 N HCl. Total organic  
251 carbon (TOC) was determined as the difference between total carbon and total inorganic carbon.

252 Bulk concentrations of Fe, Mn, Al, and Mo were determined using a total digestion of ashed  
253 samples (450° C) in trace metal grade HF:HNO<sub>3</sub>:HCl. Contents of Fe, Mn, Al, and Mo were measured  
254 using an Agilent 7500ce ICP-MS at the University of California-Riverside. Repeated analyses of USGS  
255 reference material SDO-1 were included to assess accuracy and precision, with all elements analyzed in  
256 this study falling within the reported ranges. The SDO-1 standard contains elevated concentrations of  
257 each of the elements of interest relative to FOAM samples and was therefore diluted during ICP-MS  
258 analysis to mimic the concentration range observed at FOAM. Digestion and analysis of duplicate and  
259 triplicate FOAM sediment samples revealed standard deviations (1σ) of <0.1 wt % for Al, Mn, and Fe  
260 and <0.2 ppm for Mo.

261 For the sake of comparison to past studies, we also include previously unpublished S isotope data  
262 from FOAM. The FOAM-1 core was collected in August 1974 and sectioned in 1-2 cm intervals under N<sub>2</sub>  
263 in a glove bag within ~12 hours of collection. Pore waters were extracted by squeezing and filtered (Kalil  
264 and Goldhaber, 1973). Additional details can be found in Aller (1980a,b).

265 To determine the isotopic composition of pore water sulfate in FOAM-1, pore water samples  
266 were diluted with ~70 mL distilled water, acidified with HCl, and heated. BaSO<sub>4</sub> was precipitated  
267 following addition of BaCl<sub>2</sub> (10% w/v). The acid volatile sulfur was extracted immediately following  
268 sample collection by reaction with cold 12 N HCl and the resulting H<sub>2</sub>S was stripped with N<sub>2</sub> and  
269 precipitated as Ag<sub>2</sub>S in a AgNO<sub>3</sub> trap (Aller, 1980a,b). BaSO<sub>4</sub> and Ag<sub>2</sub>S were combusted to SO<sub>2</sub> (Ag<sub>2</sub>S by  
270 the cupric oxide method), and the sulfur isotope compositions were measured via a Nuclide 6-60 isotope  
271 ratio mass spectrometer at Yale University. For both SO<sub>4</sub><sup>2-</sup> and AVS, the sulfur isotope data are presented  
272 in conventional delta notation (δ<sup>34</sup>S) in permil (‰) relative to the Vienna Canyon Diablo Troilite (VCDT)  
273 standard and Equation 1 below, which also applies to δ<sup>33</sup>S. Park City pyrite, a synthetic ZnS, and a  
274 synthetic PbS were used as secondary standards. Standard deviations (1σ) for the analyses of secondary  
275 standards and duplicate samples were less than 0.1‰.

276 
$$\delta^{3x}S = \left[ \left( \frac{{}^{3x}S/{}^{32}S}{\text{sample}} / \left( \frac{{}^{3x}S/{}^{32}S}{\text{standard}} \right) - 1 \right] \times 1000 \quad (\text{Equation 1})$$

277 For the 2010 FOAM core, sulfur isotope analyses were performed at the Stable Isotope  
278 Geobiology Laboratory at Harvard University. Minor isotopes were measured via fluorination of Ag<sub>2</sub>S,  
279 as shown below in Equation 2. For sulfate, the samples are first reduced to Ag<sub>2</sub>S with a mixture of  
280 hydriodic acid (HI), hypophosphorous acid (H<sub>3</sub>PO<sub>4</sub>), and hydrochloric acid (HCl) at ~90°C for 3 hours  
281 (Forrest and Newman, 1977; Johnston and others, 2007). Powdered Ag<sub>2</sub>S samples were fluorinated at

282 300°C in an F<sub>2</sub> atmosphere at 10× stoichiometric excess. Product SF<sub>6</sub> was cryogenically and  
283 chromatographically purified and analyzed on a ThermoFinnigan 253 in Dual Inlet mode. Repeated  
284 analyses of standards IAEA-S1, S2, S3 yielded a reproducibility of ±0.2‰ and ±0.006‰ for δ<sup>34</sup>S and  
285 Δ<sup>33</sup>S, respectively. Samples are reported versus VCDT, which is calibrated from the long-term running  
286 average of IAEA-S1 versus the working standard gas at Harvard University.

$$287 \quad \Delta^{33}\text{S} = \delta^{33}\text{S} - [(\delta^{34}\text{S}/1000 + 1)^{0.515} - 1] \times 1000 \quad (\text{Equation 2})$$

## 288 **RESULTS**

289 We compiled literature data (fig. 2 and 3) that includes new data and earlier results from FOAM,  
290 Fe speciation from diverse modern settings (n=1068), and Mo concentrations from modern non-euxinic  
291 settings (n=1421). All citations are given in the respective figure captions. For both Fe speciation and Mo  
292 concentrations, ‘oxic’ is defined as settings with >15 μM O<sub>2</sub>, and low oxygen conditions are defined as  
293 having <15 μM O<sub>2</sub> but without persistent sulfide accumulation in the water column. For Mo, data from  
294 the Namibian Shelf are included in the low oxygen settings. In some cases, these low oxygen settings,  
295 such as the Peru Margin, are reported to have transient water column sulfide plumes (Scholz and others,  
296 2016). We distinguish between data associated with dissolved hydrogen sulfide in the pore waters and  
297 pore waters with either dissolved sulfide below detection or appreciable dissolved Fe, which implies  
298 negligible sulfide. When available, the compiled Fe<sub>py</sub>/Fe<sub>HR</sub> data include iron associated with acid-volatile  
299 sulfide (AVS or ‘FeS’, the iron monosulfide precursors to pyrite formation). In figure 3, intervals with  
300 Mo associated with surface Mn enrichments (>2 wt. % Mn in most cases) are not included.

301 Our pore water sulfide concentrations at FOAM are near 3 mM, which are within the range of  
302 concentrations previously observed (~6 mM; Goldhaber and others, 1977; Canfield and others, 1992),  
303 with measureable sulfide accumulation limited to depths of approximately 8 cm and greater (fig. 4a).  
304 Consistent with the down core increase in sulfide, pore water sulfate concentrations decrease with depth  
305 (fig. 4a). The TOC content ranges from 0.5 to 2.0 wt.% (fig. 4b). Pyrite is observed at all depths (fig. 4c)  
306 and is consistent with previously reported ranges at FOAM (Canfield, 1989; Canfield and others, 1992;  
307 Raiswell and Canfield, 1998). AVS was not detected in this study. Because some AVS has been reported  
308 from past FOAM studies (Aller, 1980b; Canfield, 1989; Canfield and others, 1992; Raiswell and  
309 Canfield, 1998), it may be missing in our samples due to oxidation. Sulfur isotope data (<sup>32</sup>S, <sup>33</sup>S, and <sup>34</sup>S)  
310 for pyrite, acid volatile sulfide, and sulfate are shown for both the FOAM-1 (1974) and FOAM 2010  
311 cores (fig. 4d) and are remarkably similar despite collection separated by nearly 40 years. For the minor

312 sulfur isotopes (fig. 4e), the data mimic previous observations from similar sites (Johnston and others,  
313 2008), with sulfate showing increasing  $\Delta^{33}\text{S}$  in parallel with  $\delta^{34}\text{S}$  increases. Sulfide  $\Delta^{33}\text{S}$  compositions are  
314 also enriched (averaging 0.16‰).

315 Results for individual Fe fractions are shown in Table 1 and figure 5. Dissolved pore water Fe  
316 concentrations peak in the upper 4 cm, rising from 4.24  $\mu\text{M}$  at 0.5 cm to 6.29  $\mu\text{M}$  at 2 cm, before  
317 decreasing to 0.94  $\mu\text{M}$  at 10 cm (fig. 5a). These dissolved Fe values are notably similar to autumn cores  
318 from previous studies at FOAM (Aller, 1980b). Dithionite Fe is the most abundant measured highly  
319 reactive Fe fraction in the upper 10 cm other than pyrite, peaking at 0.14 wt. % (fig. 5b), while other Fe  
320 fractions are negligible (Table 1). Calculated values for DOP are mostly near 0.4,  $\text{Fe}_T/\text{Al}$  ratios are  
321 approximately 0.5, and  $\text{Fe}_{\text{HR}}/\text{Fe}_T$  remains  $<0.38$  (fig. 5c,d). Ratios of  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios decline in the upper  
322 5 cm of the core from 0.86 to 0.55 and are persistently  $>0.8$  starting at 8 cm (fig. 5d). Our values for  
323  $\text{Fe}_T/\text{Al}$ ,  $\text{Fe}_{\text{HR}}/\text{Fe}_T$ ,  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ , and DOP are all similar to those reported or calculated from data published  
324 in previous FOAM studies (Canfield, 1989; Canfield and others, 1992; Krishnaswami and others, 1984;  
325 Raiswell and Canfield, 1998).

326 Solid-phase Mo concentrations at FOAM do not exceed 2 ppm (fig. 6a,b; Table 2). There is a  
327 subsurface pore water Mo maximum of  $\sim 300$  nM at 5-7 cm (fig. 6c). Sedimentary Mn concentrations are  
328 in the same range as previous work (Aller, 1980b), which also show a homogenous distribution in the  
329 upper 10 cm (fig. 6d). The range in pore water Mn (fig. 6e) is similar to that reported for autumn cores in  
330 a previous FOAM study (Aller, 1980b). Pore water Mn accumulation overlies the depth of initial sulfide  
331 accumulation and overlaps with pore water Mo concentrations elevated above those of seawater (fig. 6).

## 332 DISCUSSION

### 333 *Fe speciation as a pore fluid paleoredox indicator*

334 Iron speciation has been widely used to infer water column paleoredox conditions, but only  
335 recently has this application been extended to recognize paleo-pore water sulfide accumulation (Sperling  
336 and others, 2015). Applications toward recognizing ancient pore water sulfide accumulation are well  
337 grounded in work from modern sites, such as FOAM, but no previous study has evaluated the ability of  
338 Fe speciation to uniquely discern pore water sulfide in a diverse range of modern localities. Pore water  
339 sulfide does not accumulate until the most ‘highly reactive’ Fe minerals—for example, ferrihydrite and  
340 hematite—are quantitatively titrated in the sediments to form pyrite or other Fe sulfides (Canfield, 1989;

341 Canfield and others, 1992; Raiswell and others, 1994), thus elevated  $Fe_{py}/Fe_{HR}$  are anticipated for these  
342 settings.

343 In line with expectations, the Fe speciation data compilation in figure 2 provides broad evidence  
344 that  $Fe_{py}/Fe_{HR}$  values are  $<0.7$  in modern sediments where sulfide is independently constrained to be  
345 absent. Data from sulfidic pore water systems are less common but, with few exceptions (discussed next  
346 paragraph), display  $Fe_{py}/Fe_{HR}$  ratios  $>0.7$ . Examples of sites with sulfidic pore waters include the FOAM  
347 site (this study; Canfield, 1989), Peru Margin (Böning and others, 2004; Scholz and others, 2011), Santa  
348 Barbara Basin (Raven and others, 2016), and Argentine Margin (Riedinger and others, 2017). Our FOAM  
349 data reveal up to 3 mM of pore water sulfide (fig. 4) and  $Fe_{py}/Fe_{HR} >0.7$  (fig. 5). Though the collective  
350 data from sites without pore water sulfide have  $Fe_{py}/Fe_{HR} <0.7$ , portions of the FOAM sediment profile  
351 without pore water sulfide do have elevated  $Fe_{py}/Fe_{HR}$  (fig. 5). In the upper 4 cm at FOAM, ratios of  
352  $Fe_{py}/Fe_{HR}$  and DOP are elevated compared to the remainder of the upper ‘sulfide free’ zone in part  
353 because of dissolution of Fe-oxides to produce dissolved Fe in the pore waters—a ‘highly reactive’ Fe  
354 phase, not included in these proxy calculations. Factors leading to the presence of pyrite in the ‘sulfide  
355 free’ zone may result from sediment mixing, terrigenous input, as well as ongoing sulfate reduction  
356 (Canfield and others, 1992; Riedinger and others, 2017). Regardless, the collective data support that  
357 paleo-pore water sulfide accumulation can be recognized in the geologic record via  $Fe_{py}/Fe_{HR}$  values  $>0.7$ ,  
358  $Fe_{HR}/Fe_T$  ratios of  $<0.38$ ,  $DOP < \sim 0.4$ , and  $Fe_T/Al < 0.5$  (Lyons and others, 2003; Raiswell and others,  
359 1988; Raiswell and Canfield, 1998), although threshold values should be applied with caution.

360 The collective data from sites without stable euxinia suggest that  $Fe_{py}/Fe_{HR}$  ratios of  $>0.7$  are  
361 generally a consistent indicator of pore water sulfide accumulation (fig. 2a), but lower values lower do not  
362 necessarily imply a lack of pore water sulfide. Exceptions include sediments from the Santa Barbara  
363 Basin and the Argentine Margin, where pore water sulfide concentrations approach mM levels, yet  
364  $Fe_{py}/Fe_{HR}$  ratios are  $<0.7$ . The trends in the Argentine Margin are likely a combination of high  
365 sedimentation rates and an abundance of magnetite and anomalously high levels of Fe-oxides that react  
366 with sulfide to form pyrite (Riedinger and others, 2017). As was shown in a landmark study at the FOAM  
367 site, dissolved sulfide reacts with ‘reactive’ Fe minerals such as Fe-(oxy)hydroxides and hematite prior to  
368 dissolved sulfide accumulation, but the kinetics of the reaction with magnetite are up to seven orders of  
369 magnitude slower, thus allowing for pore water sulfide accumulation despite the presence of ‘highly  
370 reactive’ Fe as magnetite (Canfield and others, 1992). Sulfur isotope data at FOAM are consistent with  
371 continued pyrite formation from magnetite well below the onset of sulfide accumulation (Canfield and  
372 others, 1992). Along the Argentine Margin, sporadic and rapid sedimentation maintain non-steady state

373 geochemical conditions and decrease the residence time of sediments and ‘reactive’ Fe minerals,  
374 including magnetite, in a thin zone of sulfide accumulation (Riedinger and others, 2017). In this zone, the  
375 rate of sulfate reduction exceeds reaction rates between dissolved sulfide and the abundance of various  
376 ‘highly reactive’ Fe phases (Riedinger and others, 2017).

377 To our knowledge, the Fe speciation data compilation in figure 2 is the first to consider both  
378  $Fe_{HR}/Fe_T$  and  $Fe_{py}/Fe_{HR}$  from the full range of modern settings with available data. The original work of  
379 Raiswell and Canfield (1998) did not consider  $Fe_{py}/Fe_{HR}$ , but the data compilation presented here  
380 generally reinforces their conclusions. Specifically, only sediments from the euxinic Black Sea, Cariaco  
381 Basin, and Framvaren Fjord record clear indications of euxinia from the collective Fe speciation data.  
382 Raiswell and Canfield (1998) made the same observation based on their  $Fe_{HR}/Fe_T$  compilation. Other  
383 euxinic sites (for example, Orca Basin and Kau Bay) and low oxygen or ‘nitrogenous’ settings with and  
384 without intermittent euxinia (for example, Peru Margin) have  $Fe_{HR}/Fe_T < 0.38$  and  $Fe_{py}/Fe_{HR}$  values are not  
385 consistently elevated. Other euxinic settings can fall in this group, particularly when marked by very rapid  
386 sedimentation, such as along the Black Sea margin (Lyons and Kashgarian, 2005). For the sample set in  
387 figure 2, the only low oxygen (in this case, seasonally anoxic), non-euxinic site to yield  $Fe_{HR}/Fe_T$  ratios of  
388  $> 0.38$  from multiple samples is the Santa Barbara Basin (Raven and others, 2016), where the Fe  
389 speciation data are in a range typically interpreted as reflect of ferruginous conditions. Redox boundaries,  
390 either temporal or spatial, have been suggested as necessary for elevated Fe-oxide delivery relative to  
391 detrital values, and thus Fe speciation indications of ferruginous conditions (Hardisty and others, 2016a;  
392 Scholz and others, 2014a; Scholz and others, 2014b), but such settings are seemingly rare in the modern  
393 ocean. It is possible, however, that Fe speciation evidence for ferruginous conditions may be more  
394 common than currently known in sediments from modern low oxygen settings lacking persistent water  
395 column sulfide accumulation. To date, each of the modern low oxygen or euxinic localities measured for  
396 Fe speciation only include  $Fe_{py}$  and  $Fe_{dith}$  as part of the ‘highly reactive’ Fe pool (Raiswell and Canfield,  
397 1998; Raven and others, 2016; Scholz and others, 2014b). Consideration of  $Fe_{HR}/Fe_T$  and  $Fe_{py}/Fe_{HR}$   
398 without  $Fe_{mag}$  and  $Fe_{carb}$  specifically makes ferruginous settings more difficult to identify (Raiswell and  
399 others, 2018).

400 Lastly, some oxic localities—specifically nearshore deltaic and fjordic sites characterized by  
401 rapid sediment reworking and high  $Fe_{HR}/Fe_T$  in the source sediments—yield Fe speciation values also  
402 consistent with ferruginous conditions (Aller and others, 2004; März and others, 2012; Poulton and  
403 Raiswell, 2002). Similar trends can be found in  $Fe_T/Al$  for some of these localities, with mass ratios  
404 exceeding the  $\sim 0.5$  typical of sediments underlying oxic waters. Such observations stress the necessity to

405 consider local  $Fe_{HR}/Fe_T$  and  $Fe_T/Al$  detrital baselines, the sedimentary context, and independent  
406 paleoredox proxies when interpreting Fe geochemistry from ancient settings (Cole and others, 2017;  
407 Raiswell and others, 2018).

408

409

#### ***Mo concentrations as a pore fluid paleoredox indicator***

410 Concentrations of Mo and Fe speciation are commonly used to infer the presence of ancient water  
411 column sulfide and some recent studies provide evidence that unique ranges exist for Mo concentrations  
412 beneath modern non-euxinic water columns containing pore water sulfide (Scott and Lyons, 2012). Our  
413 compilation of Mo concentrations from oxic settings with and without pore water sulfide support these  
414 applications and past studies (fig. 3). Specifically, sedimentary Mo concentrations above crustal values  
415 but <40 ppm—but mostly <10 ppm—and with independent constraints of oxic water column conditions  
416 can generally be attributed to the presence of pore water sulfide (fig. 3a). The authigenic Mo enrichments  
417 in oxic settings with sulfidic pore fluids is largely a function of a Mn or Fe oxide shuttle that delivers Mo  
418 to the sediments, and then fixation with sulfide following reductive dissolution of the oxides (Scott and  
419 Lyons, 2012; Zheng and others, 2000). Indeed, the range in Mo concentrations from oxic settings with  
420 sulfidic pore fluids is largely derived from settings with a clear enrichment in Mn and Mo at the surface  
421 (omitted from compilation in fig. 3) and a secondary enrichment in Mo following a decrease in Mn  
422 concentrations below the zone of sulfide accumulation (Scott and Lyons, 2012). For example, this  
423 relationship is observed from sediment at Loch Etive, Scotland (Malcolm, 1985), and an estuary in British  
424 Columbia (Pedersen, 1985). These observations can be clearly contrasted by environments with surficial  
425 Mn enrichments that lack an adjacent subsurface zone of sulfide accumulation, such as some hemipelagic  
426 sediments (Shimmield and Price, 1986). In hemipelagic sediments, large Mo enrichments—in some cases  
427 100s of ppm—can occur in Mn,Fe-crusts in the upper sediment zone, but decrease to near-detrital values  
428 upon Mn and Fe dissolution, and thus elevated concentrations are not preserved in the geologic record.

429 Importantly, we acknowledge that Mo concentrations from low oxygen settings with intermittent  
430 water column and pore water sulfide have concentrations similar to many stable euxinic settings and oxic  
431 settings with pore water sulfide (fig. 3b). This is important for the proxy perspective presented here, as the  
432 current  $Fe_{HR}/Fe_T$  data from low oxygen and intermittently euxinic localities overlap with that of oxic  
433 settings (fig. 2), indicating a need for further proxies for distinction. Additional redox proxies which can  
434 discriminate low oxygen settings from oxic settings include U concentrations (Algeo and Tribovillard,  
435 2009; McManus and others, 2006; Scholz and others, 2011; Sundby and others, 2004), Mo isotopes

436 (Hardisty and others, 2016b; Poulson Brucker and others, 2009; Scholz and others, 2017), nitrogen  
437 isotopes (Scholz and others, 2017), and iodine contents (Owens and others, 2017; Zhou and others, 2017).  
438 In addition, a relationship between TOC and Mo concentrations like that from the Peruvian (Böning and  
439 others, 2004; Scholz and others, 2011; Scholz and others, 2017) and Namibian (Algeo and Lyons, 2006;  
440 Calvert and Price, 1983) oxygen minimum zones (OMZs) is not observed in oxic settings (Algeo and  
441 Lyons, 2006).

442 One possible explanation of the elevated Mo concentrations in these mostly ‘nitrogenous’  
443 localities is the intermittent accumulation of low water column hydrogen sulfide; however,  
444 thermodynamic considerations and observations from weakly sulfidic plumes (<15  $\mu\text{M}$ ) in the Peru OMZ  
445 have been suggested as inconsistent with Mo scavenging in these waters (Scholz and others, 2016; Scholz  
446 and others, 2017). We point out that multiple field and theoretical studies indicate a requirement of  
447 significant dissolved sulfide accumulation (>100  $\mu\text{M}$ ) prior to authigenic Mo accumulation (Chappaz and  
448 others, 2014; Dahl and others, 2017; Erickson and Helz, 2000; Helz and others, 1996; Helz and others,  
449 2011; Wagner and others, 2017; Zheng and others, 2000). In addition, a distinct relationship between Mo  
450 and TOC, like that observed in the Peruvian (Böning and others, 2004; Scholz and others, 2011; Scholz  
451 and others, 2017) and Namibian (Algeo and Lyons, 2006; Calvert and Price, 1983) upwelling zones, is  
452 otherwise uniquely attributed to settings with at least intermittent water column sulfide accumulation  
453 (Algeo and Lyons, 2006). Additional mechanisms of authigenic Mo enrichments from low oxygen  
454 localities include sedimentary delivery via oxides during episodic bottom water oxygenation and Mo  
455 fixation following reaction with pore water sulfide (Algeo and Tribovillard, 2009; Scholz and others,  
456 2011; Scholz and others, 2017). In our data compilation, Mo concentrations from low oxygen settings  
457 with and without pore water sulfide present during sampling are not distinguishable (fig. 3c). This  
458 observation likely stems from intermittent or past pore water and water column sulfide accumulation not  
459 captured or recognized during sampling.

460 Lastly, even with elevated pore water sulfide concentrations, a number of factors in oxic localities  
461 can lead to a lack of Mo enrichments beyond detrital values. This is evident from figure 3, which shows  
462 that there is an overlap in the Mo concentration range from oxic settings with and without pore water  
463 sulfide accumulation. In the next section, we provide a case study from the FOAM site, where we observe  
464 elevated pore water sulfide, but sedimentary Mo concentrations are near detrital values. Ultimately, oxic  
465 settings with and without pore water sulfide accumulation can be discerned via  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  values (fig. 2).  
466 However, as discussed below, the lack of authigenic Mo enrichments from sediments with  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} > 0.8$   
467 may provide additional insights to early diagenetic processes in ancient settings, including sedimentation

468 rates and seasonal oxidative processes. A diagenetic model is used to demonstrate the conditions leading  
469 to the range of authigenic Mo enrichments observed in figure 3.

### 470 *Foam Case Study and Diagenetic Model*

471 Previous studies have not measured Mo at FOAM, but localities with water column redox and  
472 diagenetic regimes similar to FOAM, such as an adjacent site in New Haven Harbor and Boston Harbor,  
473 MA, USA, have reported sedimentary Mo enrichments up to 8 ppm. These Mo concentrations are easily  
474 distinguished from detrital values (1-2 ppm) and are well below Mo concentrations typical of sediments  
475 underlying euxinic water columns (Scott and Lyons, 2012). The up to 3 mM sulfide levels at FOAM are  
476 well above the 100  $\mu$ M ‘action point’ for total dissolved sulfide concentration that favors the  
477 transformation of molybdate to tetrathiomolybdate, which can then be efficiently, often quantitatively,  
478 scavenged (Helz and others, 1996; Zheng and others, 2000). In sulfidic sediments, following Mn and Fe  
479 oxide dissolution, near-complete authigenic Mo removal from pore waters typically occurs at the  
480 transition zone to sulfide accumulation, forming a deeper second solid-phase Mo peak (Scott and Lyons,  
481 2012). Sedimentary Mo peaks are not observed at all at FOAM despite pore water Mo levels greater than  
482 those of the overlying seawater and a clear indication of subsurface Mn and Fe oxide reduction seen in  
483 both pore water and sediment data (figs. 5 and 6). Below we consider sediment mass balance and a  
484 diagenetic model for Mo to determine the factors that influence authigenic Mo enrichments at FOAM and  
485 other non-euxinic localities.

486 We use estimates of the lithogenic Mo ( $Mo_{lith}$ ) input relative to the observed bulk Mo  
487 concentrations ( $Mo_{bulk}$ ) to determine the contribution, if any, from authigenic Mo ( $Mo_{auth}$ ):

$$488 \quad Mo_{bulk} = Mo_{lith} + Mo_{auth} \quad \text{(Equation 3)}$$

489 Although constraints on the lithogenic input of Mo to sediments in Long Island Sound are  
490 lacking, we can estimate this component using a bulk average value of Mo/Al for granite- and sandstone-  
491 derived lithogenic material of  $8-18 \times 10^{-6}$  (McLennan, 2001; Poulson Brucker and others, 2009; Turekian  
492 and Wedepohl, 1961). Both rock types are common regionally near FOAM. This lithogenic Mo range  
493 also overlaps with baseline Mo concentrations found in Buzzards Bay and Boston Harbor, MA (Morford  
494 and others, 2009; Morford and others, 2007), which have similar weathering source rocks. Considering an  
495 average sedimentary Al concentration of 6.0 wt.% at FOAM (Table 1), we calculate a lithogenic Mo input  
496 of 0.36-1.4 ppm. This contribution is negligible for sediments with large authigenic Mo enrichments, but  
497 considering an average Mo concentration for FOAM sediments of 1.02 ppm,  $Mo_{lith}$  has the potential to

498 make up anywhere from 35-100% of the bulk Mo concentrations. If authigenic Mo is accumulating at  
499 FOAM, it is clearly at very low concentrations.

500 The total authigenic consumption flux of dissolved Mo within marine sediments can be  
501 quantitatively estimated using an early diagenetic model (Equ. 4). The model tracks solid (organic matter  
502 accumulation and authigenic tetrathiomolybdate formation) and dissolved phases (Mo, H<sub>2</sub>S, O<sub>2</sub>) in  
503 diffusional exchange with seawater, within the upper 200 cm of the sediment column.

$$504 \quad \frac{\partial[X]}{\partial t} = D \frac{\partial^2[X]}{\partial z^2} - \omega \frac{\partial[X]}{\partial z} - \text{rxn} \quad (\text{Equation 4})$$

505 Parameters and associated citations are given in Table 5. The sum reaction of the time rate of  
506 change of dissolved species in pore waters can be described as the sum of the diffusion term ( $D \frac{\partial^2[X]}{\partial z^2}$ ), the  
507 advection term ( $\omega \frac{\partial[\text{Mo}]}{\partial z}$ ), and the reaction term (rxn). The variable  $D$  is the diffusion coefficient,  $\omega$  is the  
508 sedimentation rate, and  $z$  the depth away from the sediment-water interface (Boudreau, 1997). The  
509 consumption of oxygen through aerobic respiration of organic matter was parameterized as  
510  $k_{org} [\text{org}] \frac{[\text{O}_2]}{[\text{O}_2] + k_{o_2}}$ , where  $k_{org}$  is the reaction rate constant and  $k_{o_2}$  the limiting concentration for O<sub>2</sub>. The  
511 term  $\frac{\partial[\text{Mo}]}{\partial z}$  considers the gradient in pore water Mo concentrations from the depth of O<sub>2</sub> consumption—  
512 and hence the onset of oxide dissolution and associated release of sorbed Mo—to the depth where Mo  
513 concentrations decrease to stable values within the zone of pore water sulfide accumulation. The reaction  
514 term for tetrathiomolybdate is expressed as  $k_{th} [\text{H}_2\text{S}] [\text{Mo}]$ , where  $k_{th}$  is the reaction rate constant. The  $k_{org}$   
515 and  $k_{th}$  were determined by calibrating the model to pore water Mo and sulfide data derived from the  
516 FOAM site (Table 5). Dissolved sulfide levels were set at a constant value under conditions where  
517 oxygen has been quantitatively consumed through respiration. Further, if [O<sub>2</sub>] is greater than zero, [H<sub>2</sub>S]  
518 is assumed to be zero.

519 Next, we explore the sensitivity of authigenic Mo enrichments within marine sediments over a  
520 wide range of parameter space considered in figure 3 and the associated discussions—but using FOAM  
521 site values as a baseline (fig. 7; Table 5). At the most basic level, the delivery of organic carbon and the  
522 associated accumulation of pore water sulfide through sulfate reduction is a requirement from the model  
523 in order to achieve even muted authigenic Mo enrichments (fig. 7d,e). The model is sensitive to pore  
524 water Mo concentrations at the depth of O<sub>2</sub> consumption (fig. 7a), which implies that higher delivery of  
525 Mo to the sediments via oxides and burial and diffusion of seawater will increase authigenic enrichments  
526 upon reaction of the dissolved Mo with appreciable pore water sulfide. As in similar previous models

527 (Morford and others, 2009), we find authigenic Mo enrichment to be most highly sensitive to  
528 sedimentation rates (fig. 7a,c). For example, sedimentation of  $>0.2 \text{ cm yr}^{-1}$  can severely mute authigenic  
529 enrichments in marginal settings such as FOAM, explaining the observed sediment Mo concentration  
530 values (fig. 6). Muted Mo concentrations have even been observed from euxinic portions of the Black Sea  
531 where sedimentation rates are elevated (Lyons and Kashgarian, 2005). Conversely, particularly low  
532 sedimentation rates in combination with elevated pore water Mo at the depth of  $\text{O}_2$  consumption can  
533 allow for relatively elevated authigenic Mo concentrations (fig. 7a,c). These conditions replicate the  
534 ranges of Mo concentrations observed from other oxic sites with pore water sulfide and elevated  
535 authigenic enrichments (fig. 3). In addition, if we consider a sensitivity analysis that integrates the most  
536 extreme  $\frac{\partial[\text{Mo}]}{\partial z}$  and  $\omega$  from Peru Margin Sites with available data ( $\sim 350 \text{ nM}$  and  $\sim 0.025 \text{ cm yr}^{-1}$ ,  
537 respectively; Scholz and others, 2011), the model provides evidence that sedimentary Mo concentration  
538 of up to  $\sim 70 \text{ ppm}$  are possible (fig. 7a,c)—a range which explains the bulk of the existing sedimentary Mo  
539 data from low oxygen environments (fig. 3). However, under no relevant conditions can the model  
540 replicate the  $>100 \text{ ppm}$  Mo found in some of these low oxygen environments (Böning and others, 2004;  
541 Brongersma-Sanders and others, 1980; Calvert and Price, 1983; Scholz and others, 2011; Scholz and  
542 others, 2017). Such a result provides evidence that water column sulfide accumulation, or additional  
543 sedimentary Mo delivery parameters not considered in our model are likely necessary to explain the  
544 extreme elevated Mo enrichments from these low oxygen settings (fig. 3; Scholz and others, 2017).

545        Lastly, though sedimentation rates and sedimentary Mo delivery can explain the ranges of authigenic  
546 Mo accumulation from oxic settings, seasonal variations in sediment chemistry not considered in our  
547 model are all likely to contribute to muted authigenic Mo formation. Previous studies have shown that  
548 sediments with seasonal variations in redox state, metabolic rates, or biogenic mixing of particles between  
549 redox zones of the sediments, like FOAM (Aller, 1980a, b; Goldhaber and others, 1977), minimize  
550 retention of authigenic Mo phases (Morford and others, 2009; Wang and others, 2011). At FOAM, a  
551 range of previous work provides evidence that bioturbation, pore water redox, and organic matter  
552 remineralization rates all vary seasonally within the upper few cm of the sediment pile (Aller, 1980a, b;  
553 Goldhaber and others, 1977). Specifically, lower temperatures during the winter months decrease infaunal  
554 activity and metabolic rates. Together, these processes result in relatively more oxidizing conditions near  
555 the sediment water interface during the winter relative to summer through decreased upward mixing of  
556 reduced sediments and decreased rates of sulfate reduction, with the consequence of net oxidation of  
557 reduced sedimentary phases such as pyrite (Aller, 1980a, b; Goldhaber and others, 1977; Green and Aller,  
558 1998, 2001; Westrich and Berner, 1988). However, despite these known dynamics, data generated for this

559 study that overlap with that of previous FOAM works (S isotopes (fig. 4d); dissolved Fe and Mn, and  
560 sulfide; sedimentary Fe speciation, Mn, and S concentrations) are remarkably comparable despite, in  
561 some cases, nearly 40 years difference in the time of our sampling (see Results section for details).  
562 Indeed, despite temperature, metabolic, and faunal seasonal dynamics which induce non-steady state  
563 sedimentary and geochemical conditions in the upper ~10 cm, previous seasonal observations have also  
564 proven a consistency of dissolved and sedimentary geochemical characteristics for a given season from  
565 year to year (Aller, 1980a,b). Considerations of non-steady state factors should be considered in future  
566 models, but previous studies and ours provide evidence that FOAM may be best characterized as a  
567 ‘dynamic steady state’.

568

569

## CONCLUSIONS

570 Based on observations from modern settings, we provide constraints on the use of sedimentary Fe  
571 speciation and Mo concentrations as paleoredox proxies to uniquely identify the presence/absence of pore  
572 water sulfide accumulation during early diagenesis in ancient non-euxinic water column settings. To this  
573 end, we compare ratios of pyrite-to-‘highly reactive’ Fe ( $Fe_{py}/Fe_{HR}$ ) and Mo concentrations from modern  
574 non-euxinic settings with and without observations of sedimentary pore water sulfide accumulation. We  
575 also provide original Fe speciation, sedimentary Mo, and S isotope data from the FOAM site in Long  
576 Island Sound, where pore water sulfide concentrations are in excess of 3 mM. The FOAM site has played  
577 an essential role in our understanding of Fe reactivity toward sulfide and the development of a commonly  
578 applied Fe speciation scheme (Berner and Canfield, 1989; Canfield and Berner, 1987; Canfield and  
579 others, 1992; Raiswell and Canfield, 1998) and the earlier DOP approach (Berner, 1970; Canfield and  
580 others, 1992; Raiswell and others, 1988)—in large part through proximity to Yale University and the  
581 research group of Bob Berner. Given previous observations at FOAM and other similar localities with  
582 pore water sulfide, we expected  $Fe_{HR}/Fe_T$  values of  $<0.38$  (Raiswell and Canfield, 1998),  $Fe_T/Al$  ratios of  
583  $\sim 0.5$ , (Krishnaswami and others, 1984),  $Fe_{py}/Fe_{HR} > 0.8$ , and Mo concentrations 2-25 ppm (Scott and  
584 Lyons, 2012). Deviations from these predictions are explored in the context of the broader data  
585 compilation and sensitivity analyses of an authigenic Mo model.

586 Iron speciation data from the literature and our new FOAM results fit the predicted ranges, with  
587 most of the ‘highly reactive’ Fe pool reacted with  $\Sigma H_2S$  to form pyrite and resulting, with few exceptions,  
588 in  $Fe_{py}/Fe_{HR}$  values as a generally confident indicator of the presence/absence of pore water sulfide  
589 accumulation during early diagenesis. Molybdenum concentrations at FOAM, by contrast, did not fall

590 within the typical range for sulfidic pore fluids (Scott and Lyons, 2012). Oxidic settings with pore water  
591 sulfide accumulation, including FOAM, commonly display Mo concentrations similar to detrital values,  
592 hence overlapping with that observed in oxidic settings lacking pore water sulfide. A diagenetic model that  
593 considers pore water dissolved Mo, bottom water O<sub>2</sub>, pore water sulfide, sedimentation rate, and organic  
594 rain rates provides evidence that there is indeed an authigenic Mo flux to the sediments at FOAM, but that  
595 episodic and generally high sedimentation rates likely prevent expression beyond typical lithologic  
596 values. In addition, low oxygen (but non-euxinic) water column environments—most prominently the  
597 Peru Margin—have the potential for a large range of Mo concentrations, regardless of pore water redox,  
598 overlapping with both euxinic settings and oxidic environments with pore water sulfide. The additional  
599 application of Fe speciation differentiates euxinic and low oxygen (non-euxinic) settings, but other  
600 paleoredox proxies (for example, U concentrations, N isotopes, Mo isotopes, iodine contents) are  
601 necessary to discern low oxygen environments from oxidic settings. If paleoredox indicators beyond Fe  
602 speciation and Mo concentrations provide independent constraints on oxidic water column conditions, Mo  
603 concentrations are a generally reliable indicator of the presence pore water sulfide accumulation.

604 Overall, our results confirm that Fe speciation applications to identify ancient pore water sulfide  
605 accumulation are reasonable, similar to applications of Sperling and others (2015), but point to the  
606 requirement of more nuanced considerations for similar applications of Mo concentrations. When Fe  
607 speciation and Mo concentrations are applied together to ancient sediments, the modern framework and  
608 authigenic Mo model combined here may be used to constrain trends in pore water sulfide accumulation  
609 and modes and ranges of Mo delivery to non-euxinic sediments. These constraints provide a context for  
610 tracking evolutionary trends in benthic habitation as well as controls on seawater sulfate and Mo  
611 concentrations through time.

612

613

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615 preceding work at the site fundamental to our understanding of early diagenesis and commonly applied  
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627

628 **Table captions**

629 **Table 1.** Results for Fe speciation, degree of pyritization (DOP), and bulk sedimentary Fe and Al  
630 concentrations. The data are presented in figure 5.

631 **Table 2.** Sedimentary and pore water Mo and Mn concentrations. These data are presented in figure 6.

632 **Table 3.** Sulfur isotope values for pore water sulfate and AVS for samples from FOAM. The data are  
633 presented in figure 4.

634 **Table 4.** Multiple sulfur isotope data from the 2010 FOAM core. The data are presented in figure 4.

635 **Table 5.** Variables and values used for model calibration and sensitivity tests in figure 7.

636 **Figure Captions**

637 **Figure 1.** Map showing FOAM location. Image is taken from Google Earth.

638 **Figure 2.** Compilation of Fe speciation data from modern sediments. **(A)** non-euxinic water columns with  
639 (Canfield, 1989; Raven and others, 2016; Riedinger and others, 2017; Scholz and others, 2014b) and  
640 without (Aller and others, 2004; Canfield, 1989; Goldberg and others, 2012; Henkel and others, 2016;  
641 Riedinger and others, 2017; Scholz and others, 2014b; Wehrmann and others, 2014; Wijsman and others,  
642 2001) pore water sulfide in the host sediments. **(B)** Euxinic (Lyons and others, 2003; Raiswell and  
643 Canfield, 1998; Wijsman and others, 2001), low oxygen (Raiswell and Canfield, 1998; Raven and others,  
644 2016; Scholz and others, 2014b), and oxic water columns (Aller and others, 2004; Aquilina and others,  
645 2014; Canfield, 1989; Goldberg and others, 2012; Henkel and others, 2016; März and others, 2012; Peketi  
646 and others, 2015; Raiswell and Canfield, 1998; Riedinger and others, 2017; Scholz and others, 2014b;  
647 Wehrmann and others, 2014; Zhu and others, 2012; Zhu and others, 2015). Low oxygen is defined as <15  
648  $\mu\text{M O}_2$  but lacking detected sulfide. Notably, the ‘highly reactive’ Fe is determined differently between  
649 the publications, including the sequential extraction of Poulton and Canfield (2005), its predecessors (for  
650 example, Raiswell and Canfield, 1998; Aller and others, 2004), and other modifications (for example,  
651 Raven and others, 2016). When available,  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  includes iron from the acid volatile S extraction in  
652 the numerator. The horizontal line represents the suggested boundary for oxic water column conditions  
653 for modern sediments, 0.38 (Canfield and Raiswell, 1998). The vertical line represents the  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$   
654 boundary for indication of sulfide accumulation of 0.7, which is discussed in the main text. The solid bars  
655 represent  $\pm 1\sigma$  of the respective data.

656 **Figure 3.** Box and whisker plots comparing sedimentary Mo concentrations from: **(A)** Oxic water column  
657 settings with (Malcolm, 1985; Morford and others, 2007; Pedersen, 1985; Poulson Brucker and others,  
658 2009) and without (Böning and others, 2004; Goldberg and others, 2012; Morford and others, 2009;  
659 Poulson Brucker and others, 2009; Scholz and others, 2011; Zheng and others, 2000) appreciable pore  
660 water sulfide concentrations. Intervals where Mo is associated with Mn enrichments (>2 wt. % Mn in  
661 most cases) are not included. Note the difference in scale in part A relative to B and C. **(B)** Oxic (Böning  
662 and others, 2004; Goldberg and others, 2012; Malcolm, 1985; McManus and others, 2006; Morford and  
663 Emerson, 1999; Morford and others, 2009; Morford and others, 2007; Pedersen, 1985; Poulson Brucker  
664 and others, 2009; Poulson and others, 2006; Scholz and others, 2011; Shimmield and Price, 1986; Sundby  
665 and others, 2004; Zheng and others, 2000) and low oxygen water columns (Böning and others, 2004;  
666 Brongersma-Sanders and others, 1980; Calvert and Price, 1983; McManus and others, 2006; Morford and

667 Emerson, 1999; Nameroff and others, 2002; Poulson Brucker and others, 2009; Poulson and others, 2006;  
668 Scholz and others, 2011; Zheng and others, 2000)—defined as  $<15 \mu\text{M O}_2$  but lacking dissolved sulfide.  
669 (C) Low oxygen water column sites with (Böning and others, 2004; Poulson Brucker and others, 2009;  
670 Scholz and others, 2011; Zheng and others, 2000) and without (Nameroff and others, 2002; Scholz and  
671 others, 2011; Zheng and others, 2000) appreciable sulfide concentrations in the pore waters. A lack of  
672 appreciable sulfide is defined by sulfide measured but  $<100 \mu\text{M}$ , sulfide measured but below detection, or  
673 sulfide not measured but with elevated dissolved Fe concentrations.

674

675 **Figure 4.** FOAM concentration profiles for (A) pore water sulfate and hydrogen sulfide, (B) total organic  
676 carbon (TOC), and (C) weight percent sulfur in pyrite. Also included are isotope compositions of (D)  $^{34}\text{S}$   
677 ( $\delta^{34}\text{S}$ ) of sulfate and dissolved sulfide and (E)  $^{33}\text{S}$  ( $\Delta^{33}\text{S}$ ) for sulfate and dissolved sulfide. In part D, data  
678 are shown from both the cores utilized for measurement in A, B, C, E of this figure (2010 core) and  
679 previously unpublished data from core FOAM-1 (Aller 1980a, b).

680

681 **Figure 5.** (A) Dissolved pore water Fe concentrations, (B) dithionite Fe to total Fe ratios ( $\text{Fe}_{\text{dith}}/\text{Fe}_{\text{T}}$ ), (C)  
682 degree of pyritization (DOP), and (D) ratios of highly reactive Fe to total Fe concentrations ( $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ),  
683 total Fe to Al ratios ( $\text{Fe}_{\text{T}}/\text{Al}_{\text{T}}$ ), and pyritized Fe over highly reactive Fe ( $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ ). The vertical bar  
684 represents the range of DOP previously measured at FOAM from Canfield and others (1992).

685 **Figure 6.** Sedimentary (A) Mo concentrations, (B) Mo/Al mass ratios, (C) pore water Mo concentrations,  
686 (D) sedimentary Mn concentrations, and (E) pore water Mn concentrations. Horizontal dashed lines  
687 represent the depth of significant sulfide accumulation. Shaded areas represent Mo/Al average shale  
688 values from Turekian and Wedepohl (1961).

689

690 **Figure 7.** Diagenetic model results. Baseline values (red dot) are parameters determined from the FOAM  
691 site and are presented in Table 5. Unless otherwise indicated, the model sensitivity analyses use the  
692 FOAM values for relevant parameters. We explore the sensitivity of marine authigenic Mo enrichments to  
693 dissolved seawater Mo and  $\text{O}_2$ , sedimentation rates, organic matter rain flux and porewater  $\text{H}_2\text{S}$  levels  
694 over a wide range of parameter space relevant to that considered in figure 3.

**Figure 1**



Figure 2.

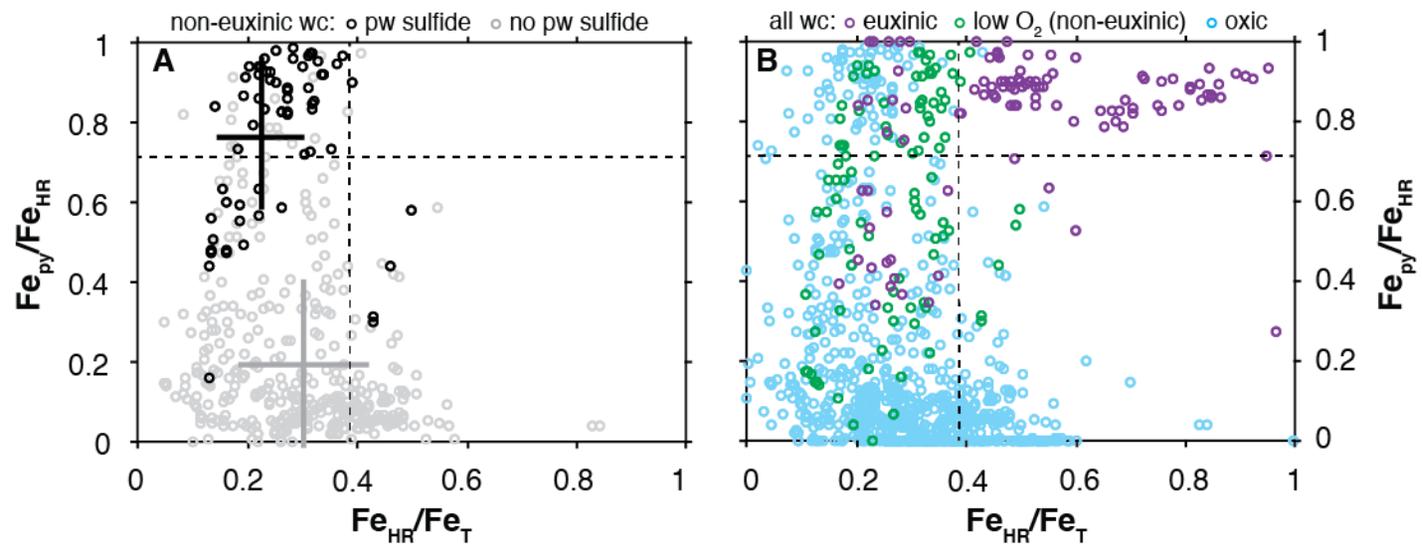


Figure 3

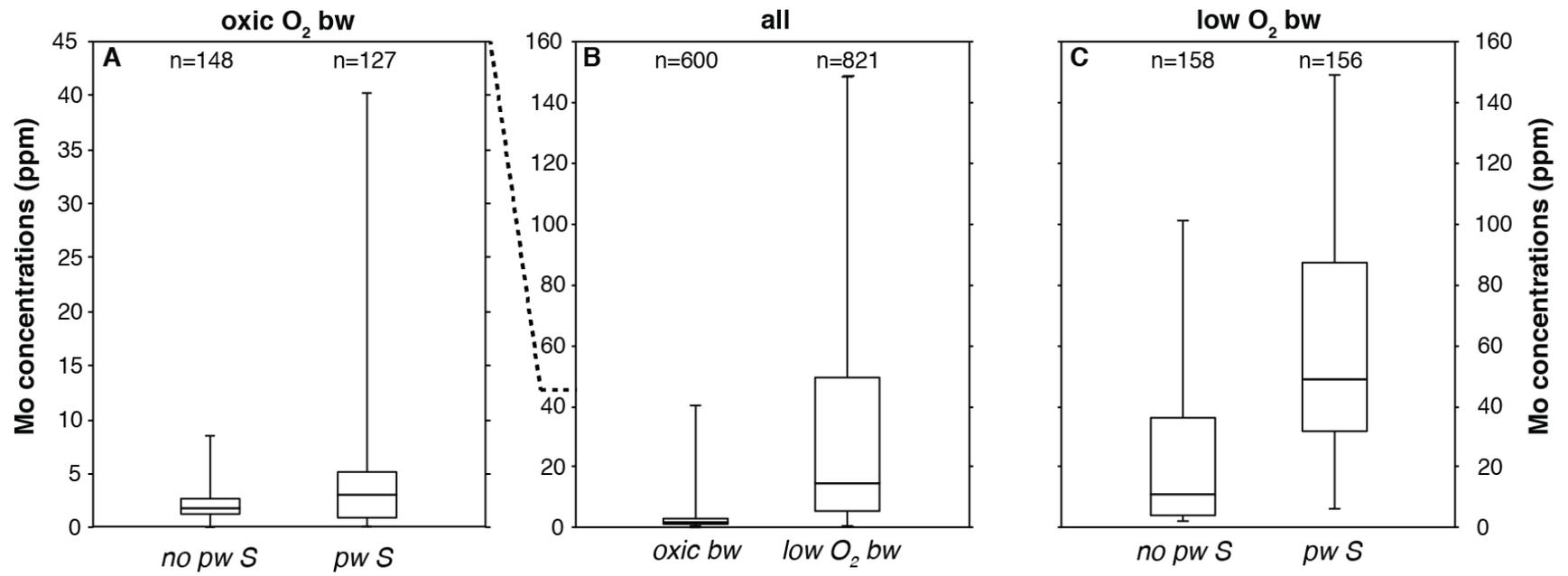


Figure 4

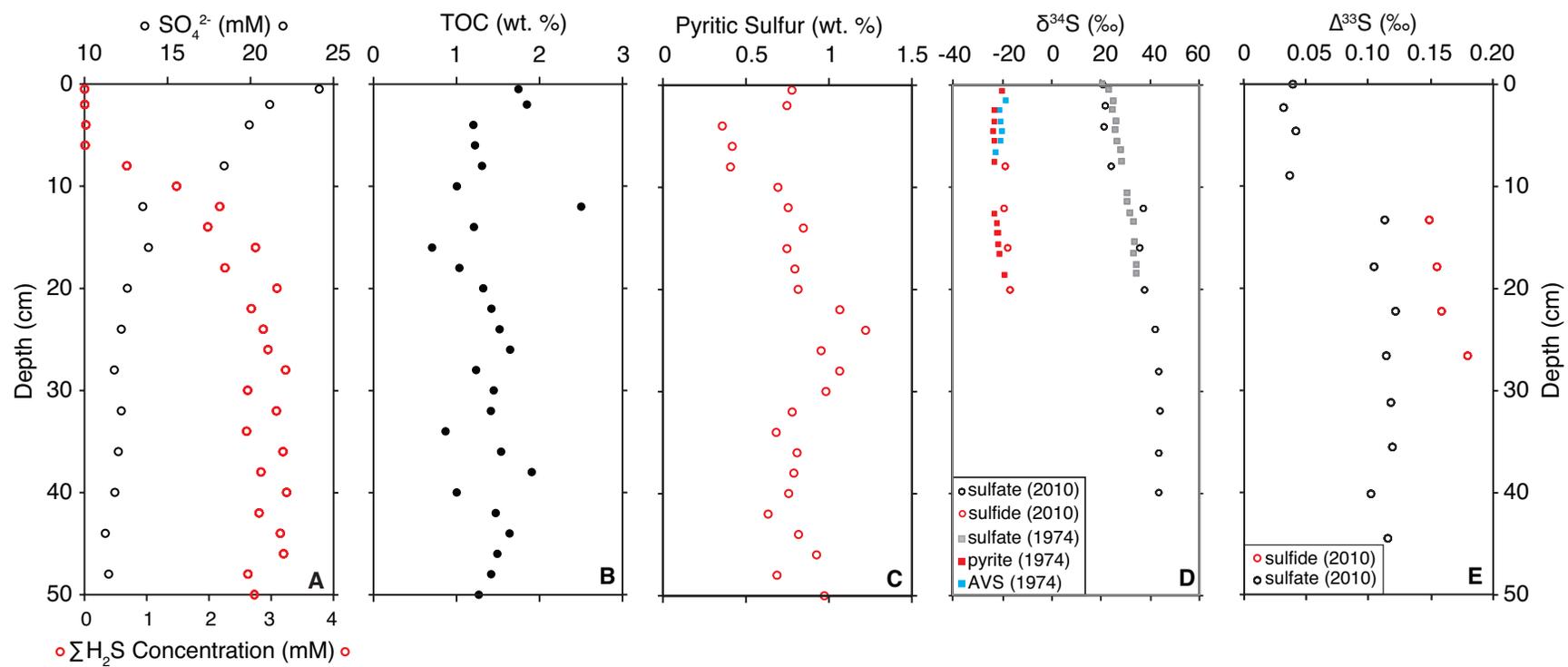


Figure 5

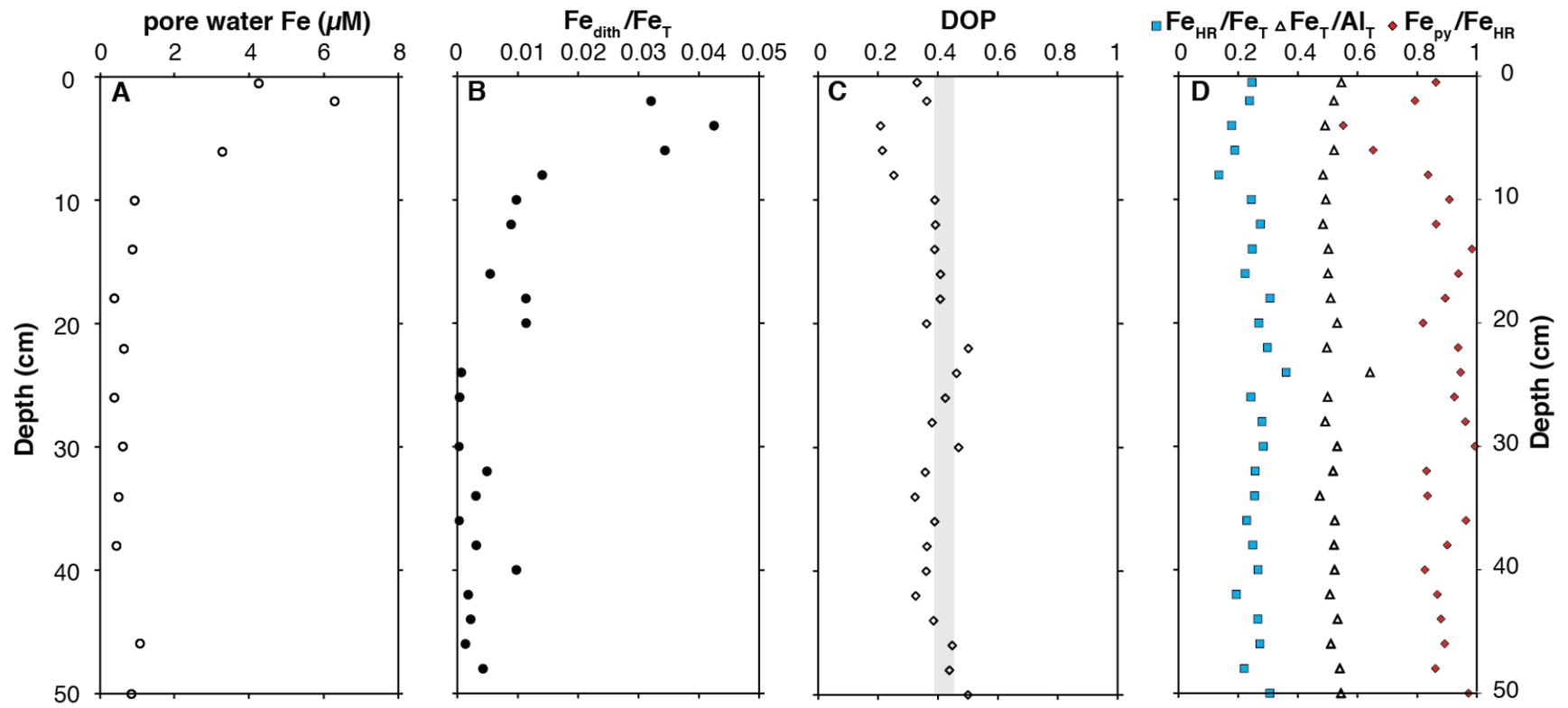


Figure 6

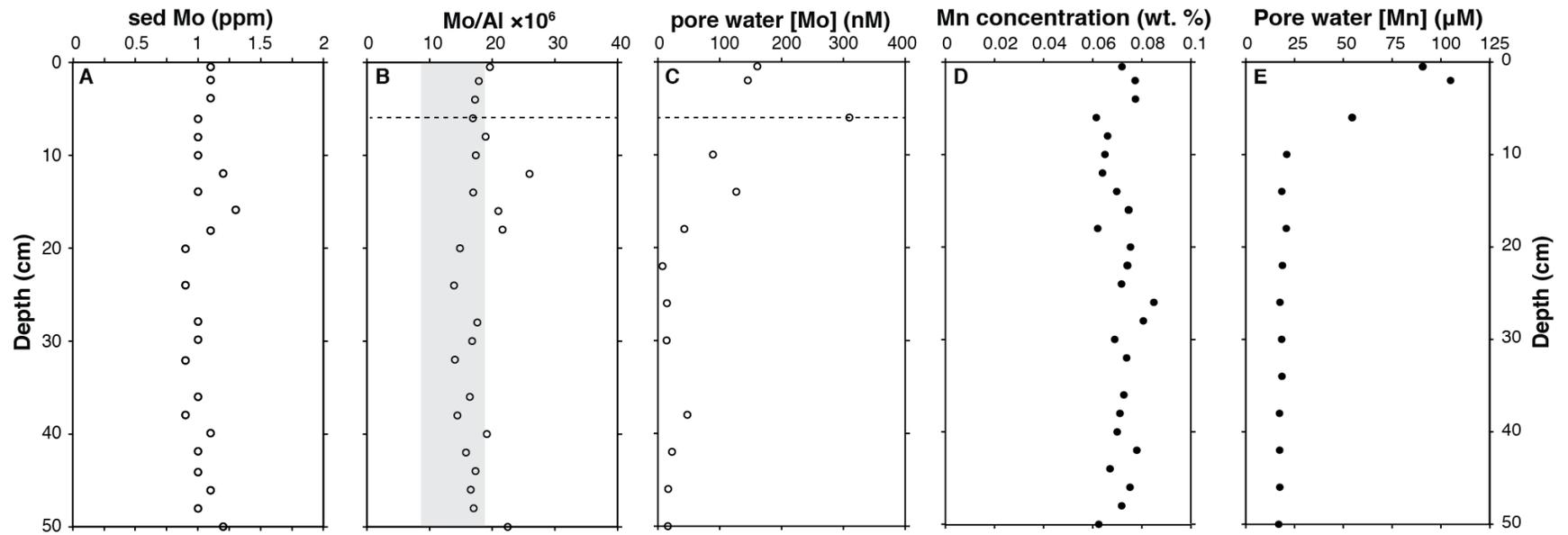


Figure 7.

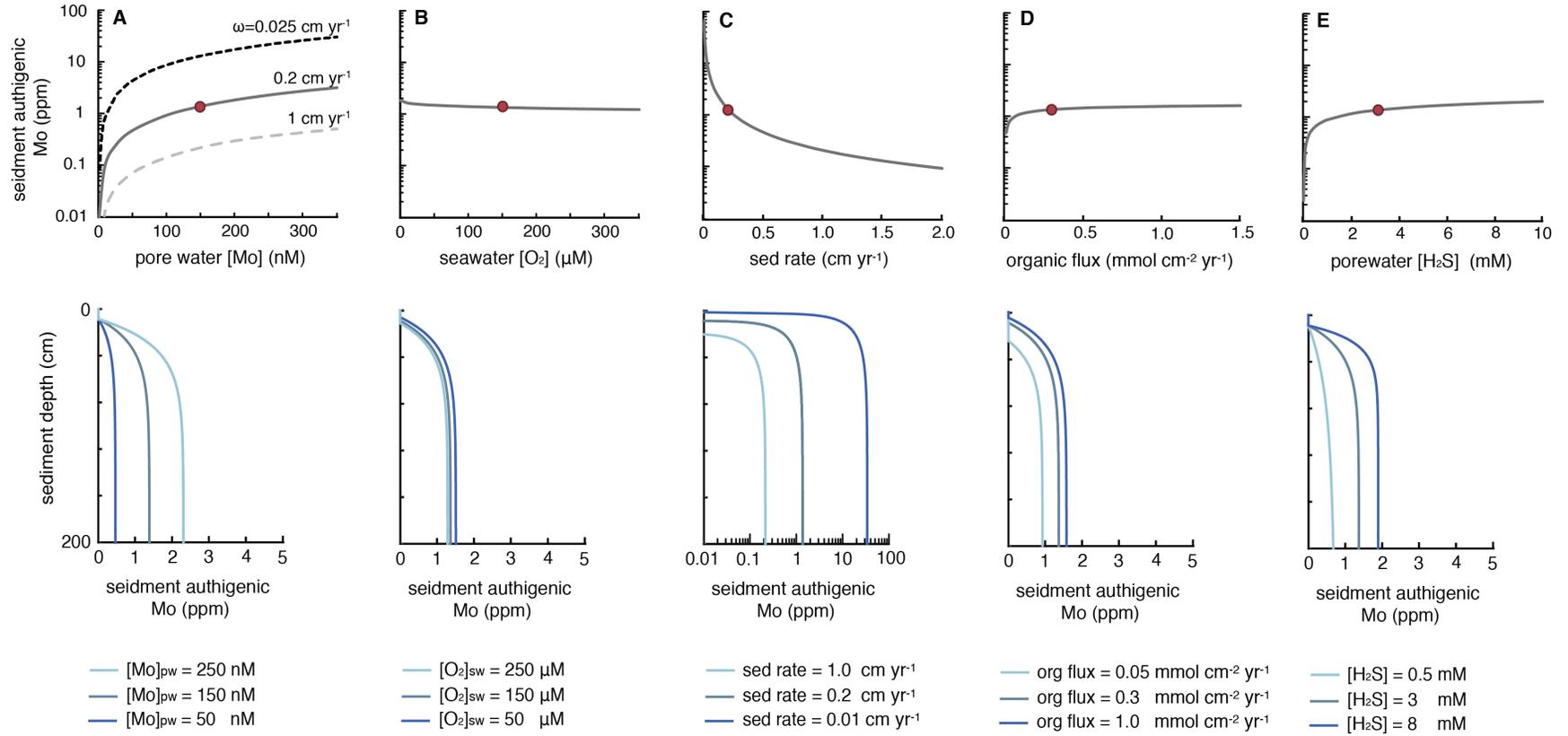


Table 1.

Depth (cm)	Fe <sub>asc</sub> (wt %)	Fe <sub>dith</sub> (wt %)	Fe <sub>mag</sub> (wt %)	Fe <sub>py</sub> (wt %)	Fe <sub>HCl</sub> (wt %)	Fe <sub>T</sub> (wt %)	Al <sub>T</sub> (wt %)	Fe <sub>HR</sub> /Fe <sub>T</sub>	Fe <sub>py</sub> /Fe <sub>HR</sub>	Fe <sub>T</sub> /Al	DOP	TOC (wt %)
0.5	0.02	< D.L.	0.09	0.68	1.37	3.18	5.82	0.25	0.86	0.55	0.33	1.75
2	<D.L.	0.11	0.06	0.65	1.14	3.44	6.61	0.24	0.79	0.52	0.36	1.85
4	0.06	0.13	0.05	0.31	1.18	3.16	6.43	0.18	0.55	0.49	0.21	1.20
6	0.03	0.10	0.06	0.36	1.33	2.96	5.67	0.19	0.65	0.52	0.22	1.22
8	0.01	0.04	0.02	0.35	1.05	3.13	6.45	0.14	0.84	0.48	0.25	1.31
10	0.01	0.03	0.02	0.60	0.94	2.72	5.51	0.24	0.91	0.49	0.39	1.01
12	0.01	0.02	0.06	0.66	1.02	2.77	5.71	0.27	0.86	0.48	0.39	2.50
14	< D.L.	< D.L.	0.01	0.74	1.16	3.03	6.03	0.25	0.98	0.50	0.39	1.21
16	0.01	0.02	0.01	0.65	0.94	3.11	6.19	0.22	0.94	0.50	0.41	0.71
18	0.02	0.03	0.03	0.69	1.00	2.53	4.95	0.31	0.89	0.51	0.41	1.04
20	0.05	0.04	0.07	0.71	1.25	3.21	6.04	0.27	0.82	0.53	0.36	1.32
22	< D.L.	< D.L.	0.06	0.93	0.92	3.32	6.67	0.30	0.94	0.50	0.50	1.42
24	0.01	< D.L.	0.05	1.06	1.24	3.12	4.85	0.36	0.95	0.64	0.46	1.52
26	< D.L.	< D.L.	0.07	0.83	1.12	3.69	7.38	0.24	0.93	0.50	0.43	1.65
28	< D.L.	< D.L.	0.04	0.93	1.51	3.45	7.01	0.28	0.96	0.49	0.38	1.24
30	< D.L.	< D.L.	0.02	0.86	0.97	3.03	5.69	0.28	0.99	0.53	0.47	1.45
32	0.04	0.02	0.08	0.68	1.21	3.17	6.12	0.26	0.83	0.52	0.36	1.41
34	0.03	0.01	0.08	0.59	1.24	2.79	5.89	0.26	0.83	0.47	0.32	0.87
36	< D.L.	< D.L.	0.03	0.70	1.10	3.19	6.09	0.23	0.96	0.52	0.39	1.54
38	< D.L.	0.01	0.07	0.69	1.20	3.06	5.87	0.25	0.90	0.52	0.36	1.91
40	0.03	0.03	0.08	0.66	1.17	3.00	5.73	0.27	0.83	0.52	0.36	1.00
42	0.02	0.01	0.06	0.55	1.14	3.28	6.47	0.19	0.87	0.51	0.33	1.47
44	0.02	0.01	0.07	0.71	1.13	3.04	5.70	0.27	0.88	0.53	0.39	1.64
46	0.01	< D.L.	0.09	0.81	0.99	3.31	6.48	0.27	0.89	0.51	0.45	1.49
48	0.02	0.01	0.06	0.60	0.77	3.16	5.84	0.22	0.86	0.54	0.44	1.42
50	< D.L.	< D.L.	0.02	0.85	0.84	2.84	5.22	0.31	0.97	0.54	0.50	1.27

D.L. = Detection limit

**Table 2.**

<b>Depth (cm)</b>	<b>Pore water Mo (nM)</b>	<b>Bulk Mo (ppm)</b>
0.5	157.4	1.1
2	139.8	1.1
4		1.1
6	296.5	1.0
8		1.0
10	79.9	1.0
12		1.2
14	115.1	1.0
16		1.3
18	35.9	1.1
20		0.9
22	3.0	
24		0.9
26	4.5	
28		1.0
30	13.9	1.0
32		0.9
34		
36		1.0
38	34.2	0.9
40		1.1
42	14.4	1.0
44		1.0
46	14.8	1.1
48		1.0
50	8.4	1.2

**Table 3**

Core	Depth (cm)	$\delta^{34}\text{S}$ sulfate (‰)	$\delta^{34}\text{S}$ AVS (‰)	$\delta^{34}\text{S}$ pyrite (‰)
FOAM-1	0	20.5		
FOAM-1	0.5	23.4		-20.1
FOAM-1	1.5	25.1	-18.4	
FOAM-1	2.5	24.7	-21.1	-23.0
FOAM-1	3.5	26.2	-20.3	-23.2
FOAM-1	4.5	25.8	-19.9	-23.4
FOAM-1	5.5	26.8	-20.7	-22.9
FOAM-1	6.5	28.2	-22.7	
FOAM-1	7.5	28.6		-23.1
FOAM-1	10.5	30.9		
FOAM-1	11.5	30.9		
FOAM-1	12.5	32		-23.2
FOAM-1	13.5	33.3		-22.1
FOAM-1	14.5			-21.8
FOAM-1	14.5			-21.7
FOAM-1	15.5	33.8		-21.6
FOAM-1	16.5	33.5		-21.1
FOAM-1	17.5	34.3		
FOAM-1	18.5	34.6		-19.1

**Table 4**

<b>Depth</b>	<i>sulfate</i>		<i>sulfide</i>	
	$\delta^{34}\text{S}$ (‰)	$\Delta^{33}\text{S}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\Delta^{33}\text{S}$ (‰)
0 (bw)	20.85	0.040		
2	21.87	0.032		
4	21.44	0.041		
8	23.98	0.036		
12	37.35	0.113	-18.95	0.149
16	36.00	0.104	-19.48	0.155
20	37.97	0.122	-17.80	0.159
24	42.16	0.115	-17.07	0.179
28	43.63	0.117		
32	44.28	0.119		
36	43.65	0.102		
40	43.80	0.116		

**Table 5**

Parameters	Values	Units	Sources
Dissolved seawater [Mo]	150	nM	(this study – FOAM)
Dissolved seawater [O <sub>2</sub> ]	150	μM	
Mo Diffusion coefficient ( $D_{Mo}$ )	391	cm <sup>2</sup> yr <sup>-1</sup>	(Malinovsky and others, 2007)
O <sub>2</sub> Diffusion coefficient ( $D_{O_2}$ )	621	cm <sup>2</sup> yr <sup>-1</sup>	(Ferrell and Himmelblau, 1967; Hayduk and Laudie, 1974)
Sedimentation rate ( $w$ )	0.2	cm yr <sup>-1</sup>	(Goldhaber and others, 1977; Krishnaswami and others, 1984)
Sediment porosity ( $\phi$ )	0.8	-	(Boudreau, 1997)
Organic rate constant ( $k_{org}$ )	$4.0 \times 10^{-3}$	yr <sup>-1</sup>	(Arndt and others, 2009) (this study – FOAM)
Thiomolybdate rate constant ( $k_{th}$ )	$1 \times 10^3$	mmol cm <sup>-2</sup> yr <sup>-1</sup>	(this study – FOAM)
Limiting concentration for O <sub>2</sub> ( $K_{O_2}$ )	$20 \times 10^{-6}$	mmol cm <sup>-3</sup>	(Reed and others, 2011)
Organic rain flux ( $F_{org}$ )	0.3	mmol cm <sup>-2</sup> yr <sup>-1</sup>	(this study – FOAM)

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