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Cobalt and marine redox evolution

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Abstract:

Cobalt (Co) is a bio-essential trace element and limiting nutrient in some regions of the modern oceans. It has been proposed that Co was more abundant in poorly ventilated Precambrian oceans based on the greater utilization of Co by anaerobic microbes relative to plants and animals. However, there are few empirical or theoretical constraints on the history of seawater Co concentrations. Herein, we present a survey of authigenic Co in marine sediments (iron formations, authigenic pyrite and bulk euxinic shales) with the goal of tracking changes in the marine Co reservoir throughout Earth's history. We further provide an overview of the modern marine Co cycle, which we use as a platform to evaluate how changes in the redox state of Earth's surface were likely to have affected marine Co concentrations. Based on sedimentary Co contents and our understanding of marine Co sources and sinks, we propose that from ca. 2.8 to 1.8 Ga the large volume of hydrothermal fluids circulating through abundant submarine ultramafic rocks along with a predominantly anoxic ocean with a low capacity for Co burial resulted in a large dissolved marine Co reservoir. We tentatively propose that there was a decrease in marine Co concentrations after ca. 1.8 Ga resulting from waning hydrothermal Co sources and the expansion of sulfide Co burial flux. Changes in the Co reservoir due to deep-water ventilation in the Neoproterozoic, if they occurred, are not resolvable with the current dataset. Rather, Co enrichments in Phanerozoic euxinic shales deposited during ocean anoxic events (OAE) indicate Co mobilization from expanded anoxic sediments and enhanced hydrothermal sources. A new record of marine Co concentrations provides a platform from which we can reevaluate the role that environmental Co concentrations played in shaping biological Co utilization throughout Earth's history.

Highlights : ► Authigenic iron oxides and pyrite record marine Co concentrations. ► The Precambrian marine Co reservoir was greatest from 2.8–1.84 Ga. ► Sedimentary Co enhancements are linked to anoxia and hydrothermal activity. ► A Neoproterozoic drop in the marine Co reservoir with ventilation is not resolvable. ► The marine Co reservoir broadly corresponds to acquisition of Co-binding proteins.

Keywords: cobal ; trace element proxies ; ocean redox ; shale ; iron formation ; pyrite

Abbreviations : Co, cobalt ; Fe, iron ; Mn, manganese ; IF, iron formation ; OMZ, oxygen minimum zone ; OAE, oceanic anoxic event ; MAR, mass accumulation rate

64 **1. Introduction**

65 The availability of bio-essential trace elements such as Fe, Mo, Zn, Co, Ni, and Cu
66 underpins the emergence, long-term evolution, and activity of life on our planet. The
67 record of trace element utilization imprinted in modern organisms is commonly thought
68 to reflect metal availability in seawater when key metalloproteins evolved (Dupont et al.,
69 2006; Fraústo da Silva and Williams, 2001; Zerkle et al., 2005). The availability and
70 removal of trace elements within aqueous habitats for life reflects the compositional
71 evolution of the Earth's crust, but is also controlled by redox changes driven by
72 metabolic innovation (Anbar, 2008). Temporal patterns in the concentrations and
73 isotopic variations of trace elements in ancient sediments can serve as proxies for major
74 changes in redox conditions in the oceans and atmosphere over geologic timescales
75 (Anbar, 2008; Konhauser et al., 2009; Scott et al., 2008; Scott et al., 2012), and can
76 provide a means to test the idea that environmental availability controlled the
77 evolutionary history of metal utilization. However, empirical records of metal variation
78 through time have only been described for a few trace elements. For some elements
79 (e.g., Mo), the geochemical and biological records roughly converge on and support the
80 interpretation of limited availability and biological utilization for early organisms (David
81 and Alm, 2011; Scott et al., 2008). For other metals, the records do not match so well.
82 For instance, Zn is an especially important yet relatively late adoption in eukaryotic
83 metal-binding protein domains. As such, it was believed that Zn was relatively scarce in
84 seawater until the Neoproterozoic when the oceans became fully oxygenated (Dupont
85 et al., 2006). Yet, surprisingly, Zn abundance in the oceans appears to have been
86 relatively constant throughout much of Earth's history (Scott et al., 2012), and Zn

87 bioavailability may have been limited by the formation of soluble complexes with
88 organics or sulfide (Robbins et al., 2013). Similarly, Ni concentrations were elevated in
89 Archean seawater (Kamber, 2010; Konhauser et al., 2009), yet the proteomic record
90 suggests increasing post-Archean biological Ni utilization (e.g. David and Alm, 2011).
91 Genomic reconstructions support the early biological utilization of Co (David and Alm,
92 2011; Dupont et al., 2006), perhaps reflecting an ancient abundance of dissolved
93 marine Co relative to the modern oceans. However, this model has not yet been tested
94 against the geological record.

95 Cobalt is a bio-essential metal for life, forming amongst others, the central cobalt-
96 corrin complex of cobalamin (vitamin B₁₂). Eukaryotes use Co primarily as cobalamin in,
97 for example, methionine synthesis. Bacteria and archaea additionally use cobalamin in
98 enzymes for anaerobic metabolisms, including fermentation, dehalogenation, and one-
99 carbon compound electron transfers (Banerjee and Ragsdale, 2003). Direct binding of
100 Co also occurs in enzymes such as nitrile hydratase, used in amide metabolism. Cobalt
101 can also substitute for Zn in carbonic anhydrase, an enzyme responsible for
102 interconversion of CO₂ and bicarbonate in some phytoplankton, suggesting that marine
103 Co availability is important in regulating the global carbon cycle (Morel et al., 1994).

104 Cobalt concentrations in modern seawater vary from 3 to 120 pM (Saito and Moffett,
105 2002), with variations dependent on interactions with other metals, biota and organic
106 matter. Cobalt shows nutrient-like behavior with surface minimum concentrations due to
107 biological uptake by phytoplankton (Saito et al., 2010; Saito and Moffett, 2002). Yet
108 strong Co ligands complex nearly all of the dissolved Co in some oligotrophic waters
109 (Noble et al., 2008; Saito, 2004; Saito and Moffett, 2001; Saito et al., 2005), although

110 some portion of this complexed Co pool is likely bioavailable (Saito, 2004; Saito and
111 Moffett, 2001). In coastal and deep waters, Co behaves as a scavenged-type element
112 (Moffett and Ho, 1996; Saito, 2004), becoming oxidized and adsorbed to Mn(III,IV)
113 oxides as they precipitate (Murray and Dillard, 1979). Co scavenging is thought to be
114 catalyzed by Mn(II)-oxidizing bacteria (Moffett and Ho, 1996; Murray et al., 2007).

115 Previous estimates of marine Co concentrations through Earth's history were based
116 on thermodynamic considerations and assumptions regarding evolving marine redox
117 and chemical composition (Saito et al., 2003), and did not consider how some key
118 sources and sinks changed through time. Furthermore, equilibrium mineral precipitation
119 models neglect kinetic control over precipitation. In this study, we use the sedimentary
120 record of Co to track first-order changes in the marine Co reservoir through time, along
121 with estimated magnitudes of the modern sources and sinks to infer the causes for Co
122 reservoir change. We also suggest that the contents of Co of authigenic marine pyrite
123 can be used as a proxy for marine Co concentrations.

124

125 **2. Behavior of Co in marine environments**

126 The formation of authigenic marine phases is subject to thermodynamic control,
127 based on the abundance and speciation of ions, redox, and pH conditions. However,
128 kinetically-driven scavenging reactions also influence the composition of marine
129 precipitates. As a basis for the discussion below, Eh-pH diagrams detailing Co
130 speciation were generated with the Act2 module of Geochemists' Workbench using the
131 Minteq thermodynamic database from 2005. Cobalt(II) was set to 100 nM, Fe(II) and
132 Mn(II) to 50 μ M, bicarbonate to 5 mM, silica to 2.2 mM (saturation with amorphous

133 silica; Konhauser et al., 2007) in seawater ionic strength; physical constraints were
134 25°C and 1 atmosphere ambient pressure. Cobalt does not form carbonate compounds,
135 and Co(OH)_3 precipitates are only possible at very high Eh-pH conditions (**Fig. 1**).
136 Cobalt(II) is oxidized to Co(III) in the same Eh-pH space where Mn(II) oxidation occurs,
137 accounting for the oxidation of Co(II) and adsorption of Co(III) to precipitated Mn(III,IV)
138 oxides (Murray and Dillard, 1979; Takahashi et al., 2007). Iron(II) is oxidized to Fe(III) at
139 a lower redox potential than Co(II) and Mn(II) at marine pH (~8).

140 Adsorption of Co(II) and Co(III) to surface sites on Fe(III) (oxyhydr)oxides (Musić et
141 al., 1979) and Mn(III,IV) oxides (Takahashi et al., 2007), respectively, is an important
142 pathway for scavenging of Co under oxic conditions (Koschinsky and Hein, 2003;
143 Stockdale et al., 2010; Takahashi et al., 2007). Soluble Co maxima occur below the O_2 -
144 H_2S chemocline in modern euxinic basins in conjunction with both the soluble Fe and
145 Mn peaks (Dryssen and Kremling, 1990; Öztürk, 1995; Viollier et al., 1995), which
146 indicates that Co is released by reductive dissolution of both Mn(III,IV) oxides and
147 Fe(III) (oxyhydr)oxides. Both poorly crystalline and crystalline Fe(III) (oxyhydr)oxide
148 surfaces efficiently scavenge Co(II) in waters with pH above ~7 (Borggaard, 1987;
149 Gunnarsson et al., 2000; Musić et al., 1979; Dzombak and Morel, 1990), likely as
150 bidentate inner-sphere complexes (Beak et al., 2011), while Co(III) is substituted for Mn
151 in Mn(III/IV) oxides (Manceau et al., 1997). Correlation between Co and Fe in
152 hydrothermal sediments collected from Endeavor Segment, Juan de Fuca (**Fig. 2**; data
153 from Hrishceva and Scott, 2007) implies a common delivery path for both metals and is
154 consistent with an Fe(III) (oxyhydr)oxide Co shuttle.

155 Sorption of Co(II) to ferrihydrite, likely the dominant Co scavenging pathway in

156 Fe(II)-rich seawater (e.g. Konhauser et al., 2009), was investigated with MINTEQ using
157 constants and site densities previously determined for ferrihydrite (Dzombak and Morel,
158 1990). Activities of dissolved components were corrected using the Davies equation,
159 and modeling utilized 100 pM initial Co(II), 0.56M NaCl electrolyte to simulate seawater,
160 and 1 g/L free ferrihydrite mineral (a constant concentration of surface sites during
161 steady-state production of ferrihydrite). We compared Co sorption with and without Co
162 ligands at modern (ca. 40 pM; Saito, 2004; Saito and Moffett, 2001) and high (400 pM)
163 concentrations to investigate whether Co ligands prevent sorption of Co(II) to surface
164 sites of ferrihydrite. The amount of Co(II) sorbed was unaffected at marine pH with 40
165 pM ligands , but Co(II) sorption to ferrihydrite was negligible when ligand concentrations
166 were 400 pM (**Fig. 3**). We note that this model utilizes data for ligands specific to Co(II),
167 but Co(III)-ligand complexes are likely extremely inert (Saito et al., 2005), and should
168 further decrease the pool of Co available for metal sorption. We also did not examine
169 the effects of inorganic species(e.g. Si), which can compete with metals for surface
170 binding sites on ferrihydrite (Konhauser et al., 2007; Konhauser et al., 2009). As
171 illustrated by those studies, the presence of Si should lower the amount of metal bound
172 for any given dissolved Co concentration.

173 In oligotrophic surface waters, Co concentrations are controlled by phytoplankton
174 uptake and binding to organic ligands (Saito and Moffett, 2001, 2002) rather than by the
175 scavenging reactions with Mn that occur in coastal and deep waters (Moffett and Ho,
176 1996). Cobalt concentrations in phytoplankton are similar to abundances of Cd and Cu
177 and enriched by as much as 10x over Mo (Ho et al., 2003). Organic material can also
178 sorb trace elements and transfer them to sediments (Broecker and Peng, 1982;

179 Krauskopf, 1956), although this process is not as quantitatively significant for Co as it is
180 for other metals (e.g., Cd, Zn; Algeo and Maynard, 2004; Yee and Fein, 2003).

181 The formation of sulfide minerals governs the concentrations of Co in anoxic and
182 sulfidic waters. Cobalt sulfide is more soluble than sulfides of some other biologically
183 important elements (e.g. Cu, Zn; Saito et al., 2003), and dissolved Co concentrations
184 below the chemocline of sulfidic waters can exceed average ocean concentrations by
185 several orders of magnitude (Dryssen and Kremling, 1990; Viollier et al., 1995).
186 Previous calculations suggested that the formation of Co-sulfide should scavenge
187 dissolved Co from sulfidic waters (Dryssen and Kremling, 1990; Kremling, 1983), but
188 little evidence exists for this particulate Co phase (Saito et al., 2003). However, field
189 observations show that some Co remains dissolved in sulfidic waters, while less soluble
190 metals (e.g., Cu, Cd) are rapidly removed (Öztürk, 1995; Viollier et al., 1995). The
191 exchange of the bisulfide ion with water molecules hydrating dissolved Co(II) is slower
192 than with those hydrating Fe(II), likely contributing to the persistence of dissolved Co(II)
193 in sulfidic waters (Morse and Luther III, 1999). For most sulfidic marine systems, this
194 means that while FeS is more soluble than CoS (e.g. Saito et al., 2003), FeS formation
195 is kinetically favored, and Co is incorporated into FeS rather than precipitating as CoS
196 (Huerta-Diaz and Morse, 1992; Morse and Arakaki, 1993).

197 The concentration of metals, including Co, in sulfidic waters is also buffered by the
198 formation of soluble metal-sulfide complexes (Daskalakis and Helz, 1992), although this
199 seems to be more important for metals such as Cd, Zn, and Cu that form stronger
200 sulfide complexes. However, above 1 μM total sulfide, soluble Co-sulfide complexes will
201 reduce the dissolved Co(II) pool (Saito et al., 2003). Regardless of the initial phase of

202 aqueous precipitate, Co ultimately substitutes into pyrite during sedimentary diagenesis
203 (Huerta-Diaz and Morse, 1992; Stockdale et al., 2010).

204

205 **3. Marine Co sources and sinks**

206 The concentration of elements in seawater reflects a balance between delivery and
207 removal of elements via precipitation and adsorption processes (e.g. Broecker, 1971;
208 Krauskopf, 1956). To quantitatively interpret changes in the marine Co reservoir, as
209 recorded by sediments deposited under different redox conditions, we detail below
210 estimates of the fluxes of dissolved Co to seawater, and mass accumulation rates
211 (MAR) for sediments deposited under oxic, anoxic and euxinic conditions (**Table 1**).

212

213 *3.1 Marine Co sources*

214 The amount of Co present in the crust ultimately governs the amount of Co delivered
215 to the oceans through fluid-rock interaction. Minerals with higher Fe, Mg, and Cr
216 contents are also enriched in Co (Carr and Turekian, 1961), specifically olivine and
217 pyroxene present in ultramafic rocks (Glassley and Piper, 1978). Dissolved Co is
218 delivered to seawater via rivers and hydrothermal fluids that source Co predominantly
219 from mafic and ultramafic rocks. The estimated riverine flux of Co is 5.5×10^{12} g kyr⁻¹
220 (**Table 1**; Gaillardet et al., 2003). Cobalt fluxes from the continents were likely higher
221 prior to 2.5 Ga due to their more mafic compositions, after which average Co
222 concentrations in the continental crust dropped from 22 to 15 ppm (Condie, 1993). Dust
223 can add dissolved Co to surface waters, but this process is likely to be minor and
224 geographically and seasonally restricted (Shelley et al., 2012).

225 Although recent work has highlighted the role of hydrothermal fluids in supplying
226 scavenged-type elements to the ocean reservoir (e.g. Fe; Saito et al., 2013; Tagliabue
227 et al., 2010), initial measurements have found little evidence for Co fluxes from
228 hydrothermal systems to seawater (Noble et al., 2012; Noble et al., 2008). However,
229 hydrothermal fluids contain Co in concentrations often several orders of magnitude
230 above average seawater (Metz and Trefry, 2000), implying that delivery of hydrothermal
231 Co to open oceans is limited by efficient, near-field scavenging reactions in oxic
232 seawater (German et al., 1991). Using the fluid flow volume through high- and low-
233 temperature hydrothermal systems as estimated from the oceanic Mg budget by
234 Elderfield and Schultz (1996), we calculated Co fluxes out of both types of systems as
235 described by Reinhard et al. (2013). The Co anomaly for high-temperature systems
236 utilized the difference between concentrations within the Plume vent on the Juan de
237 Fuca Ridge (200 nmol kg^{-1} at 246°C) and bottom waters ($0.02 \text{ nmol kg}^{-1}$; Metz and
238 Trefry, 2000). The Co anomaly for low-temperature systems was based on Co data
239 from site 1027 on the Juan de Fuca Ridge (0.7 nmol kg^{-1} at 64°C) relative to bottom
240 waters ($0.03 \text{ nmol kg}^{-1}$; Wheat et al., 2003). We estimate a total hydrothermal Co flux of
241 $1.2 \times 10^{11} \text{ g Co kyr}^{-1}$; 2.4% of total the total Co flux (**Table 1**). We recognize that the net
242 fluxes of most hydrothermally derived metals to the open ocean remain poorly
243 constrained; metals released from hydrothermal vents are readily incorporated into
244 sulfide or oxide precipitates within plumes, thereby diminishing dispersion. However,
245 nanoparticulate sulfides or organic ligands may stabilize and transport trace elements
246 away from vents (Sander and Koschinsky, 2011; Toner et al., 2009; Yucel et al., 2011),
247 increasing trace element, and probably Co, fluxes to the global ocean. We therefore

248 anticipate that global fluxes of Co from hydrothermal systems will be refined in the near
249 future (e.g. GEOTRACES).

250

251 *3.2 Oxic sedimentary Co sinks*

252 In sediments where oxygen penetrates at least 1 cm, authigenic Fe(III)
253 (oxyhydr)oxides, Mn(III/IV) oxides and associated Co are permanently buried
254 (Brumsack, 1989; Froelich et al., 1979). Any Fe(II) and Mn(II) released during
255 dissimilatory microbial reduction is reoxidized and immobilized before diffusing out of
256 sediments. Deposition of phytoplankton biomass may also add Co to oxic sediments
257 (Saito, 2004). Regardless of the pathway for authigenic Co delivery to sediments, Co
258 released during early diagenesis is immobilized by scavenging with Fe(III)
259 (oxyhydr)oxides and Mn(III/IV) oxides. Cobalt fluxes to oxic continental margin and
260 hydrothermal sediments are likely higher than those in the deep sea (Douglas and
261 Adeney, 2000; Koschinsky and Hein, 2003), but these fluxes are not well-constrained.
262 Therefore, we use an estimate of $2.3\text{-}5 \mu\text{g Co cm}^{-3} \text{ kyr}^{-1}$ (Krishnaswami, 1976) from
263 deep-sea pelagic sediments for an average authigenic oxic Co MAR.

264

265 *3.3 Euxinic sedimentary Co sinks*

266 Modern sulfidic (sulfide in porewaters) or euxinic (sulfide in bottom waters)
267 environments include basins where authigenic Fe(III) (oxyhydr)oxides and Mn(III/IV)
268 oxides are reductively dissolved below the $\text{O}_2\text{-H}_2\text{S}$ transition zone, releasing associated
269 Co (Dryssen and Kremling, 1990; Öztürk, 1995; Viollier et al., 1995). To estimate an

270 euxinic Co MAR, we subtracted the average terrigenous Co/Al ratio ($198 \mu\text{g g}^{-1}$) from
271 the Co/Al ratio of euxinic sediments ($204 \mu\text{g g}^{-1}$; within errors) from the perennially
272 euxinic Cariaco basin near Venezuela (Piper and Dean, 2002). Utilizing an average
273 sedimentation rate, density, and porosity for euxinic Cariaco sediments (Lyons et al.,
274 2003), our estimated euxinic Co MAR is $5 \mu\text{g Co cm}^{-3} \text{ kyr}^{-1}$ (**Table 1**). We acknowledge
275 that there are large errors in this estimate, and higher euxinic Co MAR are observed in
276 restricted basins (Brumsack, 1989; Hetzel et al., 2009). Although Co is likely enriched
277 above detrital levels in euxinic sediments, there is almost an order of magnitude lower
278 enrichment than metals that form strong sulfide complexes (e.g., Mo), which can be
279 enriched up to 100x above concentrations in oxic sediments (Algeo and Maynard,
280 2004). Cobalt MAR in euxinic sediments below open marine conditions ($5 \mu\text{g Co cm}^{-3}$
281 kyr^{-1}) are similar to Co MAR in oxic marine sediments (2.3 to $5 \mu\text{g Co cm}^{-3} \text{ kyr}^{-1}$), in
282 contrast to Mo (see Scott et al., 2008), demonstrating that expansion of euxinic
283 sediments at the expense of oxic sediments, or vice versa, should not result in major
284 changes to the Co reservoir.

285

286 *3.4 Anoxic sedimentary Co sinks*

287 In anoxic marine sediments lacking dissolved sulfide, Fe(III) (oxyhydr)oxides and
288 Mn(III/IV) oxides are subject to dissimilatory microbial reduction. Fluxes of Co(II) and
289 Mn(II) have been observed out of sediments underlying oxygen- and sulfide-poor
290 bottom water (Brumsack, 1989; Saito, 2004), and plumes of dissolved Co mobilized
291 from anoxic sediments have been observed over oxygen minimum zones (OMZs; Noble
292 et al., 2012), demonstrating the mobility of Co under anoxic conditions. While

293 remobilization under anoxic conditions is an important source of Co in some coastal
294 environment, this process does not represent an exogenous supply of Co, and so we
295 have not included reducing sediments as a source in flux estimates. Because Co is
296 readily mobilized from anoxic sediments, there is no significant flux of Co to anoxic
297 sediments, and Co in anoxic sediments solely reflects what is added with detrital
298 minerals (Brumsack, 1989; van der Weijden et al., 2006). Thus, a decrease in the extent
299 of anoxic sediments at the expense of oxic or euxinic sediments will decrease the size
300 of dissolved Co reservoir, while expansion of anoxic sediments should increase the size
301 of the reservoir.

302 Generally speaking, sediments deposited under an anoxic but non-sulfidic water
303 column, which are often referred to as ferruginous sediments, are also unlikely to
304 permanently remove Co. Rare in the modern but common in the Precambrian,
305 ferruginous sediments are characterized by overlying water column with anoxic
306 conditions with Fe(II) as the main redox buffer (Planavsky et al., 2011). These redox
307 conditions also allowed for the deposition of iron formations (IF), which are likely to be a
308 significant Co sink (**Fig. 4**). However, IFs reflect stabilization of Fe(III) (oxyhydr)oxides
309 under anoxic conditions where there was anomalously high local Fe(III) fluxes.
310 Furthermore, most oxide facies IF are found in deep water settings, and oxides are
311 preserved due to a lack of sufficient organic carbon to drive complete Fe(III) reduction
312 (Konhauser et al., 2005). Therefore, IF likely have higher capacities for Co burial (with
313 authigenic Fe(III) (oxyhydr)oxides) than modern anoxic sediments, although IFs
314 represent a small fraction of overall marine ferruginous settings.

315

316 **4. Archives of Marine Co concentrations**

317 We propose that sedimentary Co concentrations can serve as an archive of marine
318 Co concentrations. We use this premise to evaluate how key sources and sinks for Co
319 have varied through time. This compilation also informs the evolution of marine redox
320 conditions. We focus on two types of sedimentary archives: those in which Co was
321 sequestered by authigenic Fe(III) (oxyhydr)oxides (IF database), or by iron sulfides
322 (sedimentary pyrite and euxinic shale databases).

323

324 *4.1 Iron formations as a Co archive*

325

326 Iron(III) (oxyhydr)oxides, generally thought to be the precursor phases to most IF,
327 have extremely large and reactive surfaces that extensively adsorb cations, including
328 Co(II), at marine pH (Dzombak and Morel, 1990). Therefore, we propose that the record
329 of authigenic Co enrichment in IF can be used to evaluate large-scale changes in
330 marine Co concentrations through time. Similar chemical principles justified using Ni, P,
331 Cr and Zn enrichments in IF to track changes in seawater concentrations of these
332 elements (Konhauser et al., 2011; Konhauser et al., 2009; Planavsky et al., 2010b;
333 Robbins et al., 2013). Precambrian IF are chemical precipitates with minor detrital input.
334 Authigenic, but diagenetically and metamorphically altered, Fe-rich (hematite, magnetite,
335 siderite) and Si-rich (quartz) phases dominate the mineralogy of IF, and so their trace
336 element composition is often inferred to reflect input of these elements from authigenic
337 vs. detrital phases. Post-depositional alteration of the primary trace element seawater
338 signatures is generally minimal unless IF have experienced hydrothermal alteration or
339 near surface weathering (Bau and Moeller, 1993).

340 Historically, Precambrian IF are divided into Algoma-type, which have a spatially
341 limited extent and formed in proximity to volcanic and hydrothermal settings, and
342 Superior-type, which are more extensive and where deposited under marine conditions
343 on a continental shelf or an isolated basin. Both deposits are represented in our dataset
344 and we assign each IF as being Algoma- or Superior-type for simplicity; in reality there
345 is a gradation between these IF types (see Bekker et al., 2010). Large, basin-scale IF
346 deposition experienced a hiatus in the Middle Proterozoic, and a return to IF deposition
347 in the Neoproterozoic was followed by permanent cessation of IF deposition. The lack of
348 IF in intervening intervals is evident in our compilation. We further utilize exhalite
349 deposits and oolitic ironstones to extend the record of Co burial with authigenic Fe oxide
350 facies into the Phanerozoic.

351 We utilize an expanded dataset of Konhauser et al. (2011; 2009), comprising
352 published values as well as new data acquired by bulk analysis and *in situ* LA-ICP-MS.
353 **Supplementary Table 1** reports Co, Al, Ti, Fe, Mn, and S concentrations (where
354 available) for the 1353 Co data points used in this study. The supplementary information
355 also includes references for the published data and the descriptions of iron formations
356 analyzed in this study.

357

358 *4.2 Pyrite as a Co archive*

359 The partitioning of Co into iron sulfide phases is dependent on Co and Fe
360 concentrations, but importantly for our purposes, it appears to be largely independent of
361 the amount of hydrogen sulfide (Morse and Arakaki, 1993). In most sulfidic
362 environments, dissolved Fe^{2+} concentrations are near levels predicted from equilibrium

363 with the amorphous Fe-S phase mackinawite (e.g. Helz et al., 2011). Finally, silicate
364 phases react with sulfide 10^8 X more slowly than Fe(III) (oxyhydr)oxide minerals
365 (Canfield et al., 1992), so Co in detrital minerals should not contribute to Co
366 concentrations in pyrite. Therefore, it is reasonable to assume that the degree of
367 authigenic Co enrichment in sediments deposited below euxinic waters should, to a first
368 order, reflect the dissolved Co concentrations in the water column.

369 In order to use trace element concentrations within pyrite as proxies for seawater
370 concentrations during sediment deposition, it is essential that (1) pyrites formed within
371 the sediments that host them, and (2) the metal inventory of pyrite was not overprinted
372 by secondary alteration processes. In the absence of free oxygen in the Archean
373 atmosphere, detrital pyrite was delivered to marine sediments (Rasmussen and Buick,
374 1999). Therefore, only sulfides with early diagenetic textures (e.g. nodules or
375 disseminated grains) from shales with abundant organic carbon and sulfur and were
376 included in this study (Rouxel et al., 2005), although not all of the sediments included in
377 this study have been definitively demonstrated to have been deposited under euxinic
378 conditions. Post-depositional disturbances to metal content were screened by selecting
379 samples with no obvious sign of alteration (Rouxel et al., 2005; Rouxel et al., 2006)

380 Individual pyrite grains from black shales were digested and trace element data were
381 acquired by Thermo Element2 HR-ICP-MS at Woods Hole Oceanographic Institution as
382 described by Rouxel et al. (2005). A basic description of each sample, as well as the
383 geological setting and age constrains for the host rock, are reported by Rouxel et al.
384 (2005). Previously unreported samples include Devonian-age black shales from the
385 Illinois basin, pyrite nodules from the ca. 1.8 Ga Gunflint Formation of Kakabeca Falls in

386 Ontario, Canada, and pyrite from the ca. 2.7 Ga Manjeri Formation of the Belingwe Belt,
387 Zimbabwe. Cobalt concentrations are reported in **Supplementary Table 2**. Trace
388 element compositions of pyrite from modern anoxic sediments are taken from Huerta-
389 Diaz and Morse (1992) and reference cited therein.

390

391 4.3 *Bulk euxinic shales as a Co archive*

392 Cobalt is enriched in sediments deposited under euxinic conditions (Algeo and
393 Maynard, 2004), and the shales used in this study have Mo contents >25 ppm,
394 consistent with euxinia (Scott and Lyons, 2012). Authigenic Co was distinguished from
395 detrital Co via normalization to a conservative element, in this case Al. This approach is
396 justified as the Co/Al ratio of fine-grained material derived from continents has varied
397 little through time (Condie, 1993), and is similar amongst several compilations (Condie,
398 1993; Kamber et al., 2005; Wedephol, 1971). The Co and Al values for euxinic
399 sediments used in this study have all been previously published (see **Supplementary**
400 **references**). Because it is not always straightforward to distinguish detrital from
401 authigenic trace elements in shales (e.g. Van der Weijden, 2002), we emphasize that
402 the IF and pyrite datasets are likely to be the most robust indicators of the marine
403 reservoir.

404

405 4.4 *Statistical analysis of Co datasets*

406 When grouped by ages that correspond to global events (described below), Co
407 concentrations were log-normally distributed. The statistical differences between
408 average time-binned values were compared using an unpaired t-test of log

409 concentration values. The p values for these comparisons are reported in **Table 2**. The
410 mean and one standard deviation (SD) of log concentration values were then back-
411 transformed to concentration values, and these are reported as mean ($\mu\text{g g}^{-1}$) \cdot / SD in
412 accordance with the multiplicative nature of a log-normal distribution (Limpert et al.,
413 2001).

414

415 **5. Evolution of the marine Co reservoir**

416 *5.1 Reconstructing changes in Co sources and sinks through Earth history*

417 The datasets of Co in IF, pyrite and shale reveal time-resolved patterns in the
418 delivery of Co to marine sediments, and thereby indicate first-order changes to the
419 marine Co reservoir through time (**Fig. 4**). The average Co/Ti ($\mu\text{g g}^{-1}$) of IF ≥ 2.80 Ga
420 (79.85 \cdot / 1.72) are significantly lower than IF deposited between 2.75 to 1.88 Ga (150.57
421 \cdot / 2.67). Average values then significantly drop in IF, exhalite, and oolitic ironstones
422 deposited between 1.72 Ga and modern times (62.25 \cdot / 1.84; **Table 2**), despite that
423 exhalites are prime records of locally derived hydrothermal Co. There is also a
424 significant difference between the average concentrations of Co (ppm) in pyrites from
425 shales deposited between 2.8 and 1.84 Ga (7.34 \cdot / 1.77) and those deposited from 1.8
426 to 0.3 Ga (3.87 \cdot / 1.96; **Table 2**), signifying a concordance of the IF and shale pyrite Co
427 records, and likely global-scale trends in marine Co concentrations.

428 Higher seawater Co concentrations in the interval between 2.8 and 1.84 Ga reflect
429 pervasive anoxia and a higher hydrothermal Co flux to the marine reservoir during the
430 emplacement of oceanic crust, likely due in part to several mantle plume events at this

431 time (Barley et al., 2005; Rasmussen et al., 2012). These events also likely supplied the
432 Fe for major IF deposited from 2.5 to 2.4 Ga, and again between 2.0 and 1.8 Ga (Barley
433 et al., 1997; Rasmussen et al., 2012). In hydrothermal systems, the supply of Co tracks
434 that of Fe (Douville et al., 2002) because the solubility of both elements is enhanced at
435 higher temperature and Cl^- concentrations (Metz and Trefry, 2000). Archean-aged
436 hydrothermal systems are thought to have experienced higher heat flow, enhancing the
437 supply of Fe (Isley, 1995), and likely Co to seawater. Higher Co concentrations from
438 Archean hydrothermal fluids are also more likely due to the prevalence of ultramafic
439 oceanic crust (Arndt, 1983). Compositional control on Co concentrations in
440 hydrothermal fluids is indicated in the ultramafic Rainbow vent field on the Mid-Atlantic
441 Ridge, where Co concentrations reach up to $13 \mu\text{M}$ Co (Douville et al., 2002), an
442 enrichment of at least 10^5 above seawater concentrations. Persistent anoxia would
443 have allowed the dispersion of dissolved Co plumes without trapping near source by
444 oxidative scavenging (Noble et al., 2012). These factors indicate an increased
445 proportion of hydrothermal Co fluxes relative to continental Co fluxes in comparison to
446 modern Co inputs (**Table 1**).

447 The Co concentrations in younger than 1.84 Ga IF are comparable to those prior to
448 2.8 Ga (**Table 2**), potentially indicating that weathering of mafic to ultramafic
449 Neoproterozoic continental crust is not an essential aspect of the large enrichments. This is
450 in contrast to Ni, whose supply to oceans from weathering of emergent oceanic
451 plateaus waned after 2.7-2.6 Ga (Kamber, 2010; Konhauser et al., 2009). Although Co
452 and Ni have generally similar low-temperature geochemical behavior, they are
453 decoupled during high-temperature hydrothermal alteration. Nickel is not as efficiently

454 leached as Co, resulting in low hydrothermal Ni fluxes (Douville et al., 2002).
455 Furthermore, Co-chloride complexes are more stable than Cu-, and, probably, Ni-
456 chloride complexes, resulting in higher Co solubility at low temperatures (Metz and
457 Trefry, 2000). The increase in marine sediment Co concentrations after ca. 2.8 Ga may
458 be driven by changes in the riverine flux of Co from the continents due to increased,
459 permanent, subaerial exposure. Other authors have suggested the emergence of
460 continents between 2.9 and 2.7 Ga (e.g. Pons et al., 2013 and references within).
461 However, the crustal growth rate slows and Co concentrations drop at 2.5 Ga, from 22-
462 25 ppm to 15 ppm (Condie, 1993), in the midst of the highest sedimentary Co
463 concentrations (**Fig. 4 and 5**).

464 We propose that the drop in Co concentrations in marine sediments that occurs after
465 1.84 Ga, and reflects a cessation of hydrothermal activity and the emplacement of large
466 igneous provinces (Rasmussen et al., 2012). As supply of hydrothermal Fe and
467 deposition of massive IF waned in the late Paleoproterozoic, so too did the
468 hydrothermal Co flux, shifting towards modern conditions in which continentally-derived
469 Co dominates Co influx (**Table 1**). Hydrothermal supply to the oceans reached modern
470 levels by 0.7-0.8 Ga (Derry and Jacobsen, 1988), with episodic larger mantle inputs re-
471 occurring throughout the Proterozoic and Phanerozoic (Peng et al., 2011; Veizer et al.,
472 1983). Additional Middle Proterozoic samples would be needed to test whether later
473 mantle plume events resulted in a return to globally high marine Co concentrations.

474 The drop in seawater Co concentrations after 1.88 Ga occurs at a time when the
475 extent of euxinic environments in the oceans increased (Poulton et al., 2004) at the
476 expense of ferruginous sediments. Without well-constrained depositional rates for IF, it

477 is impossible to estimate Co MAR from ferruginous settings, although our IF dataset
478 attests to the fact that Co is effectively buried under ferruginous conditions.
479 Nevertheless, given that IFs are rare marine sediments, the contribution of ferruginous
480 sediments to overall Co removal in the oceans was likely low. Further, as stressed
481 above, the Co sink associated with ferruginous settings will be lower than for oxic
482 sediments; although Fe(III) (oxyhydr)oxides sorb Co, Mn(III/IV) oxides, which form at
483 higher Eh, are much more effective at scavenging Co from seawater (Stockdale et al.,
484 2010). Therefore, expansion of euxinic settings to less than 10% of seafloor area in the
485 Middle Proterozoic (Reinhard et al., 2013), are unlikely to explain the drop in the Co
486 reservoir size (cf. Saito et al., 2003) without invoking a waning hydrothermal Co source.
487 Significant areal expansion of oxic *and* euxinic sediments might explain the drop in the
488 Co reservoir, but oxic conditions suitable for Co scavenging were likely confined to
489 Middle Proterozoic surface waters (Planavsky et al., 2010a), and sediments deposited
490 under oxic conditions were of limited extent (Reinhard et al., 2013).

491 The logarithmic range of Co concentrations in sediments, even those from the same
492 formation, is a phenomenon that has been observed for other trace elements (e.g. Zn;
493 Robbins et al., 2013; Scott et al., 2012). This variability is likely primary, based on
494 similar phenomena in modern authigenic sediments (**Fig. 2** and **4**). For Co, this may
495 reflect temporal variability in marine Co concentrations, which is expected because Co
496 is a non-conservative element within the oceans and has an extremely short residence
497 time in seawater, 280 years by our estimate (**Table 1**; 40-120 years; Saito and Moffett,
498 2002). Due to its short residence time, marine Co concentrations respond quickly to
499 perturbations in sources or sinks, such as the development of OMZ that fluctuate on

500 decadal time scales (Noble et al., 2012; Stramma et al., 2008). The highest IF Co/Ti
501 (nearly 160,000 $\mu\text{g g}^{-1}$) and pyrite Co (nearly 2000 ppm) are found in the 2.32 Ga
502 Timeball Hill Formation and the underlying Rooihogte formations. Post-depositional
503 hydrothermal overprint is not likely responsible for elevated Co concentrations because
504 they do not correspond to high Pb or Cu, concentrations (data not shown), which would
505 suggest mineralization. Some of this variation may be primary, and representative of
506 temporally or spatially variable Co concentrations within the basin. However, some
507 variability could be tied to re-distribution between Fe-phases during diagenesis. Despite
508 these variations, the robust statistical differences in time-binned averages (**Table 2**)
509 validate that shifts in sedimentary Co map onto global events, and hence, indicate
510 reservoir changes.

511 Although there are no significant changes in the average Co concentrations from
512 Middle Proterozoic to Phanerozoic in any of the sedimentary records (**Table 2**), there is
513 significant variability in Phanerozoic euxinic shales (**Fig. 5**), many of which were
514 deposited during ocean anoxic events (OAE), which reflect transient rather than
515 pervasive anoxic conditions. The average Co/Al ratios from euxinic black shales
516 deposited during the Cretaceous OAE-2A at Demerera Rise are ~2X larger than euxinic
517 sediments deposited before or after (their Fig. 9; Hetzel et al., 2009). This is
518 dramatically different from other redox-sensitive metals such as Mo and V, whose
519 restricted supply was exhausted during the OAE, leading to depletions of Mo and V
520 during the peak of the OAE relative to sediments deposited before and after. Cobalt is
521 mobilized from anoxic sediments (Noble et al., 2012), and therefore increased Co burial
522 in euxinic sediments might reflect this greater reservoir during anoxic events, and in fact

523 be a proxy for low-oxygen conditions (Saito et al., 2010). OAE Co enrichments may also
524 be linked to, or augmented by a hydrothermal Co pulse (e.g. Brumsack, 2006).
525 Importantly, there is independent evidence for increased hydrothermal input from a
526 sharp shift toward less radiogenic (hydrothermally-derived) initial Os isotope values
527 during the onset of the OAE (Turgeon and Creaser, 2008). Furthermore, other authors
528 have also documented sedimentary Co increases during OAE intervals linked to
529 hydrothermal activity (Orth et al., 1993; Snow et al., 2005). Therefore, the OAE Co
530 records are consistent with the notions developed above that anoxia and hydrothermal
531 activity play a critical role in the global marine Co cycle, and that marine Co
532 concentrations respond on shorter timescales than conservative elements such as Mo.

533 Surprisingly, we find little evidence for a change in the marine Co reservoir with the
534 deep ocean oxygenation, potentially beginning as early as 635 Ma (Sahoo et al., 2012).
535 The average Co/Al ($\mu\text{g g}^{-1}$) for Proterozoic euxinic shales (11.51 \pm 1.73) is not
536 significantly different from Phanerozoic-aged shales (9.33 \pm 1.97), although we
537 emphasize that Phanerozoic shales are dominated by OAE samples, and likely reflect
538 transient anoxia. There is also no statistical support for changes in IF or shale pyrite Co
539 concentrations during similar time intervals (data not shown). We note however, that a
540 paucity of datapoints from the Middle Proterozoic for all three databases hinders
541 interpretation of changes to the Co reservoir with deep ocean oxygenation. The highest
542 Phanerozoic Co concentrations occur in exhalites, which demonstrate that near-source
543 scavenging reactions prevent hydrothermal Co dispersal under oxic conditions, and
544 therefore Phanerozoic exhalites likely reflect only local Co concentrations. Non-OAE
545 euxinic shale pyrites would likely best track changes in the Co reservoir associated with

546 ocean oxygenation. Because expanding oxic sediments at the expense of anoxic should
547 enhance Co removal, and Neoproterozoic hydrothermal activity is likely similar to
548 modern (Derry and Jacobsen, 1988), ocean ventilation should have further decreased
549 the Co reservoir size.

550

551 *5.3 Marine Cobalt reservoir size and biological evolution*

552 Our empirical record of the marine Co reservoir affords an opportunity to discuss
553 hypotheses of Co utilization in biology, and to consider how Co-utilization in aquatic
554 organisms fit to these hypotheses. The biological utilization of metalloproteins may
555 reflect the availability of elements in the environment in which the protein first appeared
556 (e.g. Nisbet and Fowler, 1996). Genomic analyses of all three domains of life indicate
557 that Co-binding proteins originated after 3.3 Ga (David and Alm, 2011). Given the
558 uncertainties in this age stated by the authors (>250 My), it is feasible that origin of
559 many Co-binding proteins coincides with the enhanced marine Co availability we
560 observe after 2.8 Ga, generally supporting the availability hypothesis. However, Co is
561 chemically suited to catalyze reactions involving hydrogen rather than oxygen (Fraústo
562 da Silva and Williams, 2001), and any preferential Co utilization by early organisms may
563 simply reflect the abundance of reduced energy sources such as methane, carbon
564 monoxide, and hydrogen on the early Earth (Zerkle et al., 2005). Because higher Co
565 availability is linked to periods in Earth's history when the oceans were anoxic, had on
566 average lower Co burial rates, higher Co mobility, and probably longer Co residence
567 times, environmental availability and catalytic suitability may both be reflected in the
568 utilization of Co in organisms or proteins that evolved early.

569 Consistent with a greater utilization of Co by early organisms, bacteria and archaea
570 have a greater number of genes that encode for Co-binding proteins (Zhang and
571 Gladyshev, 2010), and their genomes encode a larger proportion of Co-binding proteins
572 than eukarya (Dupont et al., 2006). In contrast, a lack of encoded Co-binding proteins in
573 eukarya should indicate evolution predominantly after 1.8 Ga. This is broadly consistent
574 with initial diversification of eukaryotes in the middle to late Proterozoic (Knoll et al.,
575 2007). The persistence of the cobalamin-requiring gene *metH* in eukaryotic
576 phytoplankton, involved in biosynthesis of the essential amino acid methionine,
577 suggests that lower marine Co concentrations were not a sufficient selection pressure to
578 drive loss of the *metH* gene in favor of a cobalamin-independent but less efficient gene
579 (Bertrand et al., 2013), or that key Co-binding proteins were maintained and few new
580 Co-binding proteins were acquired during genome expansion. Alternately, the
581 persistence of *metH* in eukaryotic phytoplankton may reflect a later acquisition (Croft et
582 al., 2005), and it often occurs in eukaryotic phytoplankton that already contained the
583 cobalamin-independent gene (Helliwell et al., 2011). Thus, eukaryotic *metH* persistence
584 may be related to its efficiency rather than Co availability.

585 Enzymes that directly bind Co rather than cobalamin also offer insight into how metal
586 availability regulates enzyme utilization. Both diatoms and eukaryotic algae can
587 substitute Co (or Cd) for Zn in the carbonic anhydrase enzyme that interconverts CO₂
588 and bicarbonate when Zn concentrations are limiting (Morel et al., 1994; Saito and
589 Goepfert, 2008). Such substitution may be a strategy for coastal algae to deal with
590 intense metal drawdown during algal blooms (Saito and Goepfert, 2008), but also
591 indicates that expression of metal-binding proteins encoded at the genomic level are

592 affected by temporally and spatially variable metal concentrations. The trends in Co
593 sedimentary records presented here reflect geological control over element delivery and
594 burial; short-term and spatial variability will therefore not be resolvable with our dataset.
595 Furthermore, the amount of metal-binding protein expressed (i.e. the metallome) should
596 fluctuate with physical and chemical conditions and the physiological state of the cell
597 (Bertrand et al., 2013; Saito et al., 2011). Proteomic records are therefore an important
598 complement to the genome in understanding why utilization of metal-binding proteins
599 persist, are lost or acquired as metal concentrations change.

600 Finally, although genomic utilization may reflect availability of metals during
601 evolution, it can also indicate later adaptations to changing metal abundances. For
602 instance marine cyanobacteria have an absolute requirement for Co that cannot be met
603 by other metals (Saito et al., 2002; Sunda and Huntsman, 1995), which again may
604 reflect evolution in largely anoxic or sulfidic oceans with greater Co availability (Saito et
605 al., 2003), yet thrive in the oxic oceans where Co concentrations are often less than 40
606 pM. Cobalt utilization may have persisted in cyanobacteria as Co availability declined
607 due to the acquisition of Co-binding ligands (Saito and Moffett, 2001; Saito et al., 2005).
608 The hypothesis that availability dictates utilization implies that the earliest life lacked
609 strategies for acquisition of metals (Nisbet and Fowler, 1996). However, it is clear that
610 modern organisms possess strategies to deal with limitation. Thus, the evolutionary
611 history of metal-acquisition genes may be an important consideration when comparing
612 metal availability to biological utilization, and many of these proteins are still being
613 identified (Zhang and Gladyshev, 2010).

614

615 **6. Conclusions**

616 Trace elements are proxies for tracking marine redox evolution, but most studies
617 have focused on metals that partition strongly into anoxic or sulfidic sediments (e.g.,
618 Mo). For Co, and Fe and Mn, which have short residence times in the modern ocean,
619 marine concentrations respond dynamically to changes in delivery and removal. High
620 seawater Co concentrations from ~2.8-1.84 Ga, recorded by IF and authigenic pyrites,
621 resulted from widespread anoxia and enhanced hydrothermal activity and are probably
622 linked to Fe fluxes that resulted in the deposition of IF. The marine Co reservoir
623 decreased after ~1.84 Ga due to waning hydrothermal Co delivery. The expansion of
624 euxinic sediments at the expense of anoxic sediments, which are a negligible sink for
625 Co, may have also contributed to the Middle Proterozoic Co reservoir decrease.
626 Variability of Phanerozoic IF and euxinic shale Co concentrations are linked to localized
627 hydrothermal activity and/or transient anoxic conditions, and as such obscure any global
628 changes in the marine Co reservoir associated with deep-water oxidation. Our study of
629 the concentrations of Co in marine sediments through time reveals a more nuanced
630 view of the marine Co reservoir through Earth's history than is possible with theoretical
631 models based on thermodynamic equilibrium (e.g. Saito et al., 2003). This emerging
632 view of the evolution of the marine Co reservoir through time provides a framework for
633 interpreting Co availability influenced the acquisition and utilization of Co in biology.

634

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646

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961 **Figures and Tables**

962 **Fig. 1. a.** Speciation diagram of Co (white) and Fe in varying Eh-pH conditions. Co^{2+} is
963 stable under marine Eh and pH conditions (i.e. 7-8) inferred for the Precambrian ocean.
964 In the absence of carbonate, Fe^{2+} is soluble. **b.** Speciation diagram of Co (white) and
965 Mn, showing the similar redox potential for Mn(II) and Co(II) oxidation, which are both
966 higher than that of Fe(II) oxidation.

967 **Fig. 2.** Co-precipitation of Co with Fe (oxyhydr)oxides can be inferred based on a
968 correlation coefficient of 0.763 from previously published data from hydrothermal
969 sediments at the Endeavor Segment, Juan de Fuca Ridge (Hrshceva and Scott, 2007).

970 **Fig. 3.** Sorption of Co^{2+} to strong >(s) and weak >(w) surface sites on ferrihydrite in
971 seawater when **a.** no organic Co-ligands are present, **b.** modern (40 pM) concentrations
972 of organic ligands (dashed line) are present, and **c.** for an extreme case of 400 pM of
973 organic ligands.

974 **Fig. 4.** The Co/Ti of IF (symbols) and of evolving continental crust (black line; Condie,
975 1993). Data points are from bulk (squares) and laser-ablation (circles) analyses of
976 Precambrian Superior-type IF (red) and Algoma-type IF (black). Also included are
977 Phanerozoic shallow-marine ironstones (blue) and hydrothermal and exhalative
978 deposits (green). Data points with >0.5 wt% Mn have been excluded from this
979 compilation.

980 **Fig. 5.** Cobalt concentrations in pyrite (circles) from modern (open) and ancient (filled)
981 euxinic shales, and bulk euxinic shales (squares). For reference, the crustal evolution
982 trend (solid line) is included, based on the Restoration Model of Condie (1993). Modern

983 pyrite Co concentrations from coastal sediments reflect high concentrations of trace
984 metals delivered from rivers and petroleum reservoirs (Huerta-Diaz and Morse, 1992).

985

Table 1. Modern Cobalt Budget

<i>Sources</i>		
Riverine Flux	5.5×10^{12}	g kyr^{-1}
Hydrothermal Flux	1.3×10^{11}	g kyr^{-1}
Oceanic Reservoir Mass	1.6×10^{12}	g
Residence Time	0.28	kyr
<i>Sinks</i>		
Oxic MAR	2.3-5	$\mu\text{g Co cm}^{-2} \text{ kyr}^{-1}$
Euxinic MAR	5	$\mu\text{g Co cm}^{-2} \text{ kyr}^{-1}$

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Table 2. Statistical differences between Cobalt concentrations in sediments by age bin.

Iron Formations

Age Bin	Mean Co/Al ($\mu\text{g g}^{-1}$)	*/ SD	<i>p-value</i> *
≥ 2.80 Ga	79.85	1.72	
2.75 to 1.88 Ga	150.57	2.67	<0.0001
≤ 1.72 Ga	62.25	1.84	<0.0001

Euxinic Shale Pyrite

Age Bin	Mean Co (ppm)	*/ SD	<i>p-value</i> *
2.80 to 1.84 Ga	7.34	1.77	
1.80 to 0.30 Ga	3.87	1.96	<0.0001

Euxinic Shale

Age Bin	Mean Co/Ti ($\mu\text{g g}^{-1}$)	*/ SD	<i>p-value</i> *
≥ 0.695 Ga	11.51	1.73	
≤ 0.531 Ga	9.33	1.97	0.0842

**p-values* refer to comparison between the age bin indicated and the preceding age bin.

996

997 **Supplementary Figures and Tables**

998 **Supplementary Table 1.** Co, Ti, Fe, and Mn concentrations and the source of the data
 999 for the iron-formation samples used in this study.

1000 **Supplementary Table 2.** Co concentrations and the source of the data for pyrite and
 1001 bulk shale analyses used in this study.

1002 **Supplementary references**

Figure 1

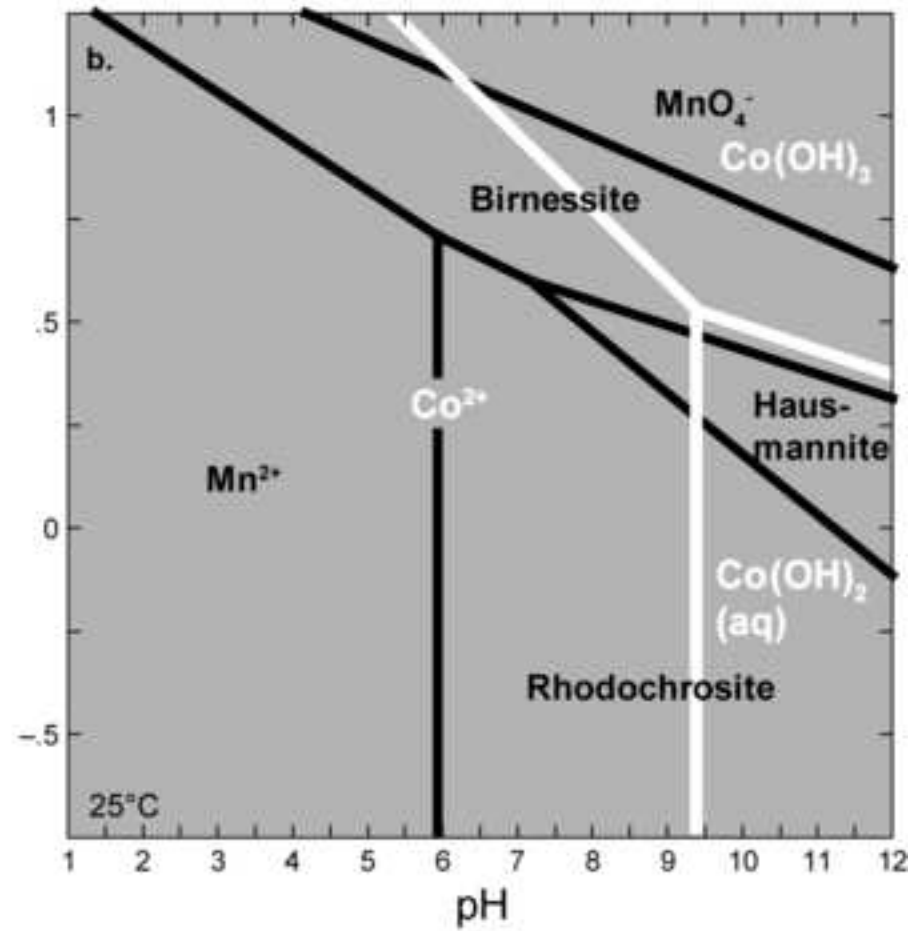
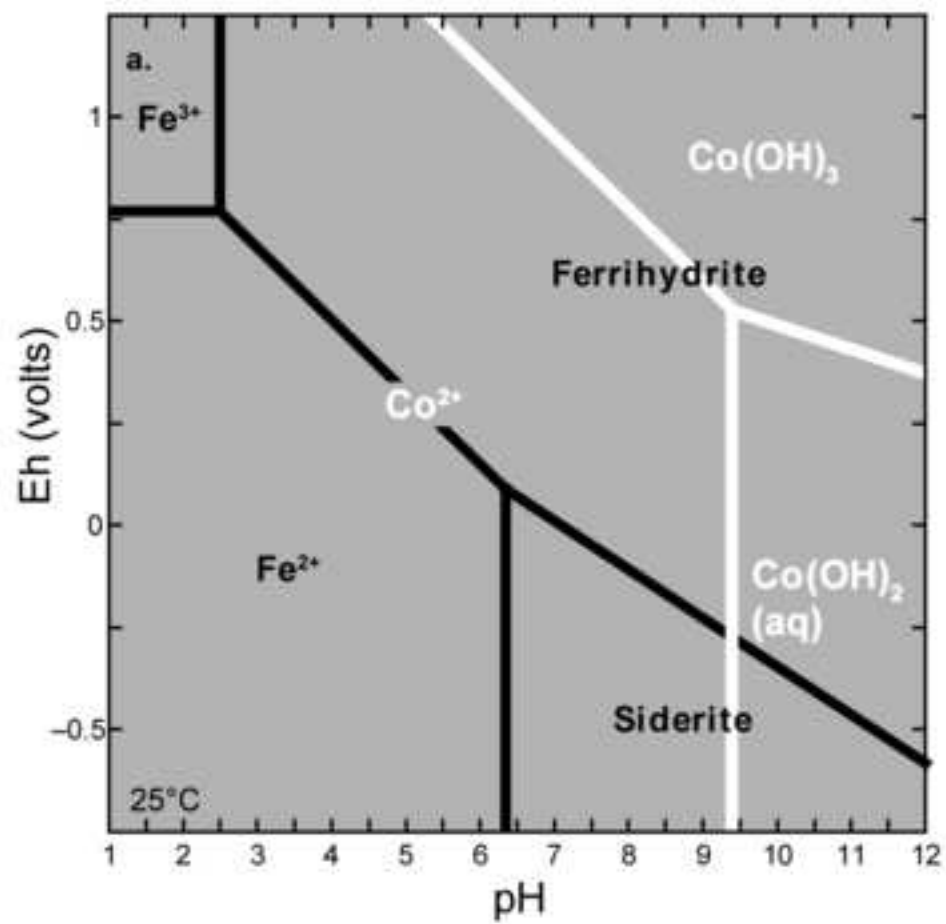


Figure 2.

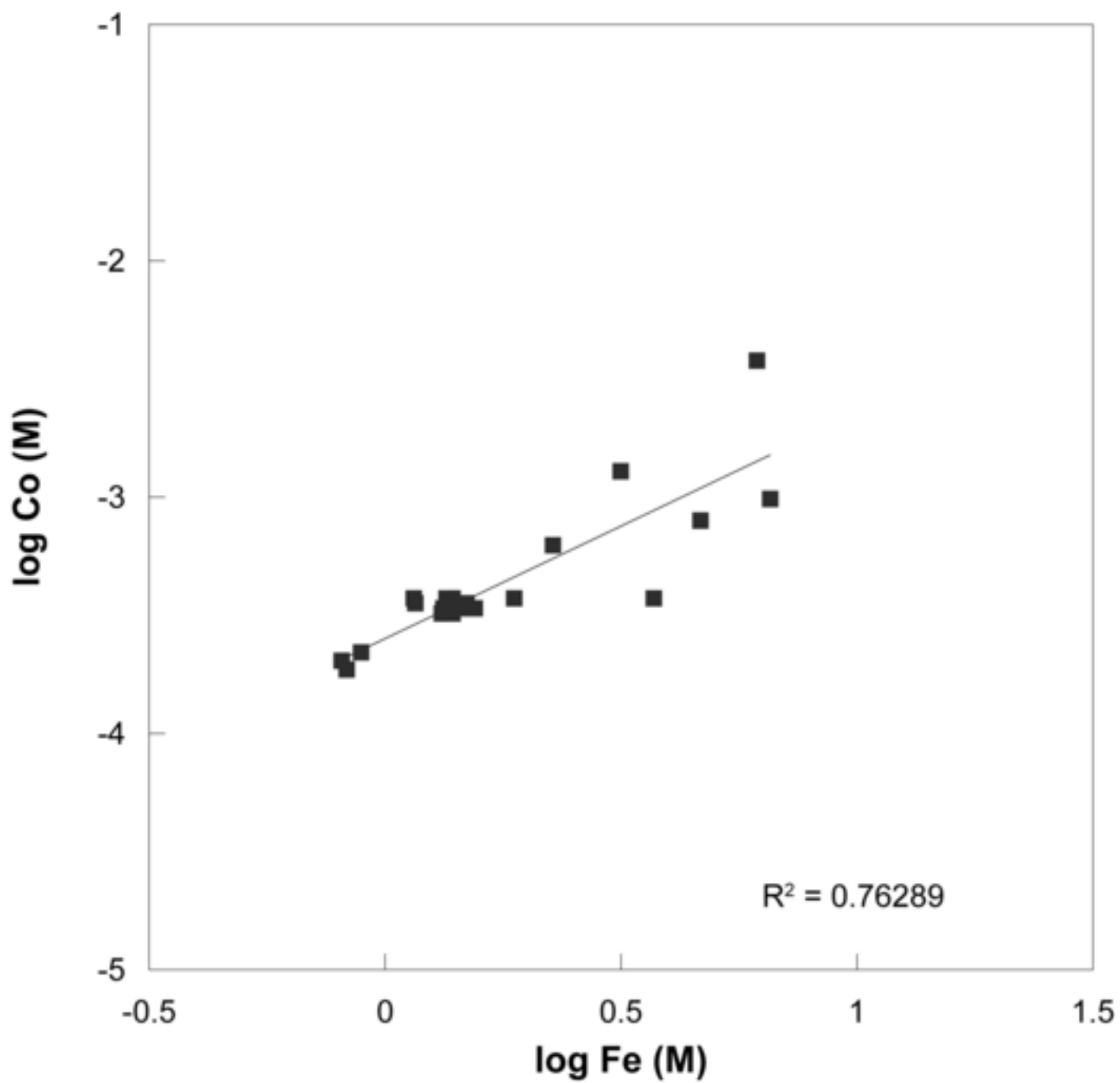


Figure 3

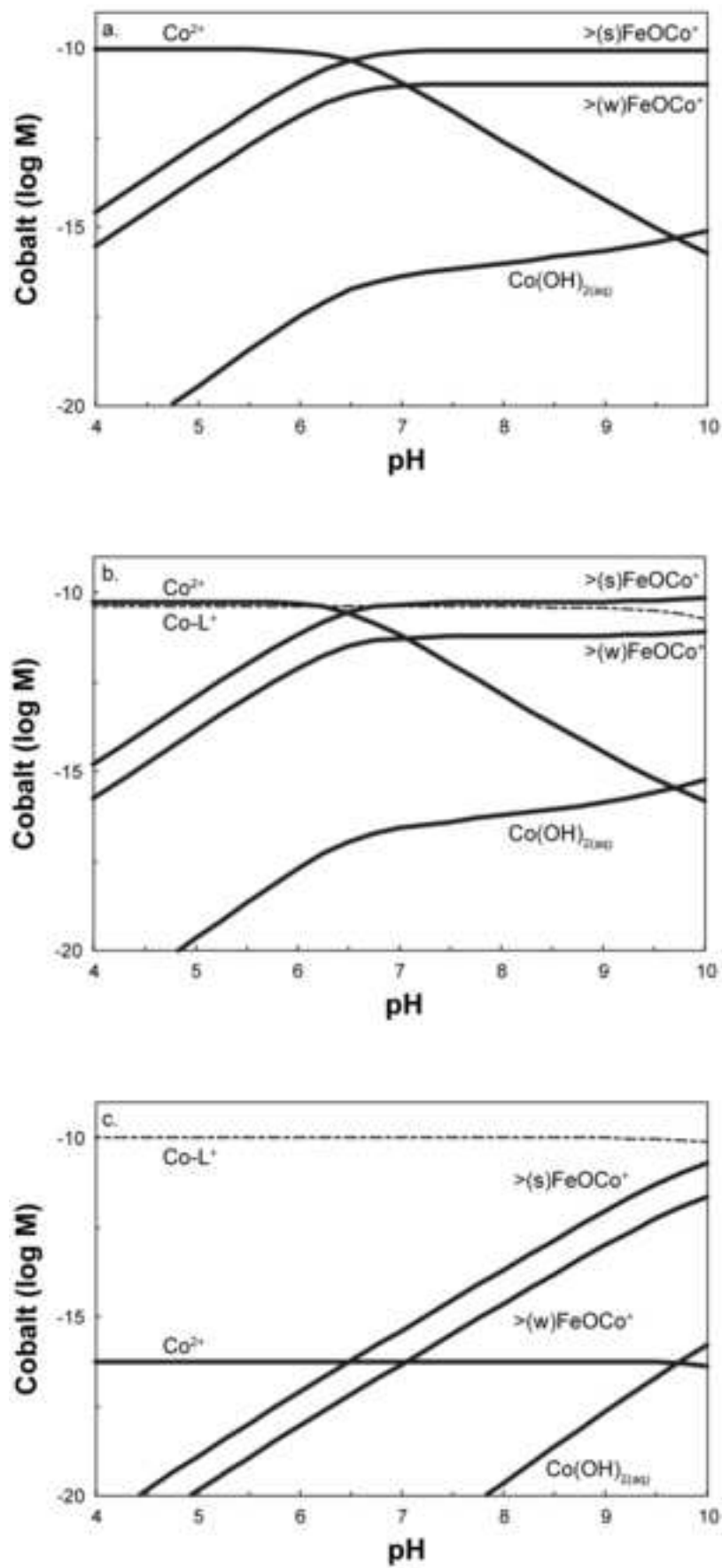


Figure 4.

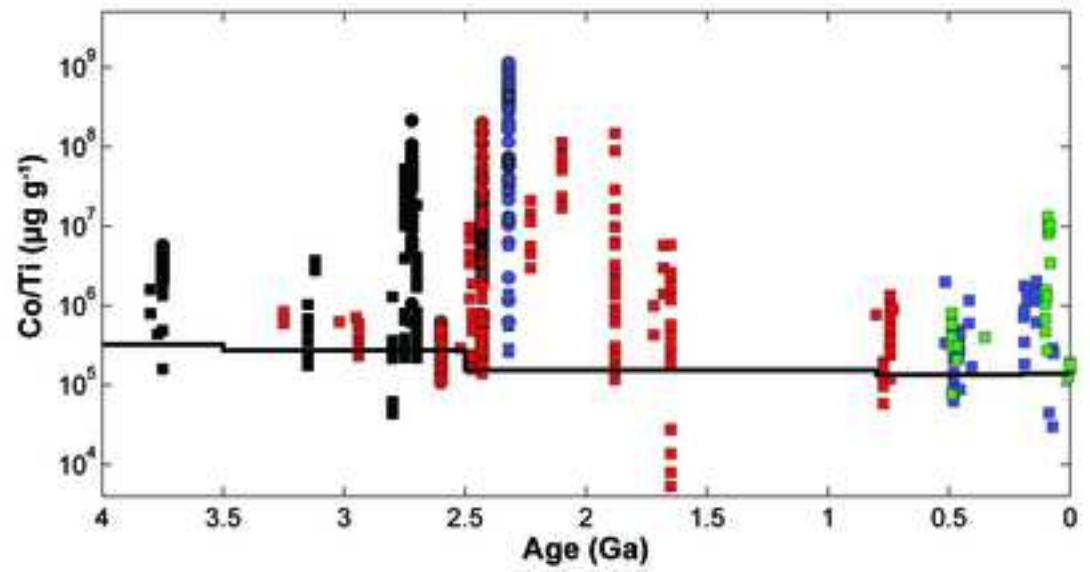


Figure 5.

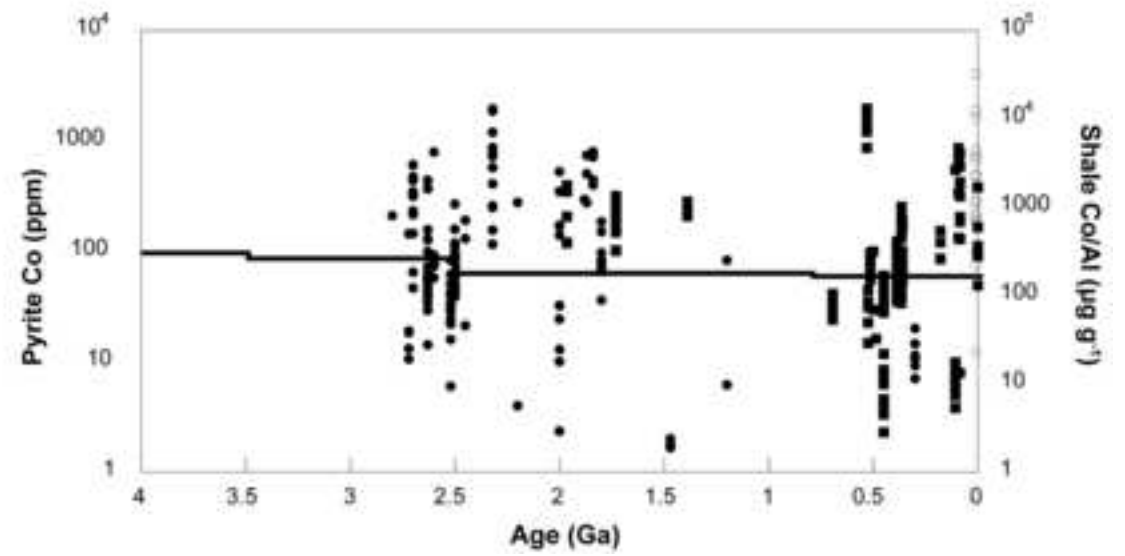


Table 1. Modern Cobalt Budget

*Sources*Riverine Flux 5.5×10^{12} g kyr⁻¹Hydrothermal Flux 1.3×10^{11} g kyr⁻¹Oceanic Reservoir Mass 1.6×10^{12} g
Residence Time 0.28 kyr*Sinks*Oxic MAR 2.3-5 $\mu\text{g Co cm}^{-2} \text{ kyr}^{-1}$ Euxinic MAR 5 $\mu\text{g Co cm}^{-2} \text{ kyr}^{-1}$

Supplementary references

[Click here to download Supplementary material for on-line publication only: Supplementary_Table1_references.doc](#)