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Phosphorus sources for phosphatic Cambrian carbonates

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1   **P sources for phosphatic Cambrian carbonates**

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13

14   **ABSTRACT**

15   **The fossilization of organic remains and shell material by calcium phosphate**
16   **minerals provides an illuminating, but time-bounded, window into Ediacaran—**
17   **Cambrian animal evolution. For reasons that remain unknown, phosphatic fossil**
18   **preservation declined significantly through Cambrian Series 2. Here we investigate**
19   **the phosphorus (P) sources for phosphatic Cambrian carbonates, presenting**
20   **sedimentological, petrographic, and geochemical data from the Cambrian Series 2–**
21   **3 Thorntonia Limestone, Australia, some of the youngest Cambrian strata to display**
22   **exceptional phosphatic preservation of small shelly fossils. We find that within**
23   **Thorntonia sediments, phosphate was remobilized by organic decay and bacterial**
24   **iron reduction, with subsequent reprecipitation largely as apatite within the**
25   **interiors of small shelly fossils. We discuss the merits of bioclastic-derived, organic**
26   **matter-bound, or iron-bound P as potential sources to these strata. Petrographic**
27   **observations suggest that the dissolution of phosphatic skeletal material did not**
28   **source P for fossil preservation. In contrast, high organic carbon contents imply**
29   **significant organic fluxes of P to Thorntonia sediments. Sedimentology and iron-**
30   **speciation data indicate that phosphorus enrichment occurred during times of**
31   **expanded anoxic, ferruginous conditions in subsurface water masses, suggesting**
32   **that phosphorus adsorption to iron minerals precipitating from the water column**
33   **provided a second significant P source to Thorntonia sediments. Simple**

stoichiometric models suggest that by themselves neither organic carbon burial nor an iron shuttle can account for the observed phosphorus enrichment. Thus, we infer that both processes were necessary for the observed phosphorus enrichment and subsequent fossil preservation in the Thorntonia Limestone.

INTRODUCTION

Phosphorite and phosphatic carbonate define a spectrum of sedimentary lithologies enriched in the authigenic calcium phosphate mineral apatite (Kazakov, 1937; Baturin and Bezrukov, 1979; Riggs, 1986; Cook and Shergold, 1986; Cook et al., 1990; Föllmi, 1996; Trappe, 2001). The punctuated temporal distribution (Cook and McElhinny, 1979; Cook and Shergold, 1984, 1986) and evolving spatial distribution (Brasier and Callow, 2007) of phosphatic lithologies through Earth history suggest that unique and restrictive physical (Filippelli and Delaney, 1992) and/or chemical (e.g., Föllmi, 1996) conditions govern phosphate deposition in time and space.

There are many reasons to want to understand this distribution. Perhaps foremost is the practical concern for understanding how ore-grade sedimentary phosphorites form (e.g., Cook and Shergold, 1986). As with petroleum, phosphate ores are approaching peak production, while global demand continues to rise (Cordell et al., 2009; Filippelli, 2011). At the same time, biogeochemists increasingly invoke perturbations to the ancient phosphorus cycle to explain inferred fluctuations in biological productivity, organic carbon burial and oxidant accumulation over geological time-scales (Tyrrell, 1999; Bjerrum and Canfield, 2002; Saltzman, 2005; Holland et al., 2006; Konhauser et al., 2007; Algeo and Ingall, 2007; Planavsky et al., 2010; Swanson-Hysell et al., 2012). Finally, phosphatic deposits provide a direct window into evolutionary history through

58 the exceptional preservation of fossils (Cook, 1992; Bengtson and Zhao, 1997; Xiao and

59 Knoll, 2000; Butterfield, 2003; Porter, 2004a).

60   A global phosphogenic window coincides with major evolutionary innovation

61 during the Ediacaran and Cambrian periods (Cook and Shergold, 1984; 1986; Cook,

62 1992). Much of our knowledge of early animal diversification derives from

63 biomineralized and soft-bodied metazoans replaced and/or templated by phosphate

64 minerals (Bengtson et al., 1990; Xiao and Knoll, 1999; 2000; Donoghue et al., 2006;

65 Dornbos et al., 2006; Kouchinsky et al., 2012). Phosphatization taphonomy is tied to the

66 biogeochemical cycle of phosphorus and, for reasons that remain unknown, a major

67 decline in the incidence of phosphatic lithologies and phosphatic fossil preservation

68 occurs during Cambrian Series 2 (Cook and McElhinny, 1979; Porter, 2004b; Donoghue

69 et al., 2006). To understand the loss of phosphatic lithologies, and the consequent closure

70 of the Cambrian phosphatization taphonomic window, we must first understand how

71 phosphorus entered the sediment column and how it was subsequently redistributed and

72 concentrated around skeletal elements. In this paper, we ask specifically: what was the

73 source of phosphorus to phosphatic carbonates characterized by exceptional skeletal

74 preservation?

75   Geochemistry provides one avenue to address this question. A common view

76 holds that enhanced delivery of reactive phosphorus (i.e., phosphorus that may undergo

77 biogeochemical transformations within the sediment column) to the sea floor is the

78 primary variable governing the development of phosphatic lithologies (e.g., see Föllmi,

79 1996, and references therein; Papineau, 2010). In modern marine environments, the

80 delivery of reactive phosphorus to the sea floor occurs predominantly in association with

81   two phases (e.g., Delaney, 1998; Benitez-Nelson, 2000): phosphorus bound within

82   organic matter (Redfield, 1958) and/or phosphorus adsorbed to/co-precipitated with

83   particulate iron minerals (herein referred to as the 'Fe-P shuttle') (Berner, 1973; Shaffer,

84   1986; Feely et al., 1991; Feely et al., 1998; Poulton and Canfield, 2006). To examine the

85   extent to which these reactive phosphorus sources contributed to ancient phosphatic

86   deposits, we report high-resolution phosphorus and iron speciation data, stable carbon

87   isotope measurements, and trace element concentrations for the phosphatic Thorntonia

88   Limestone, Georgina Basin, Australia (Cambrian Series 2–3; Southgate, 1988; Southgate

89   and Shergold, 1991), and, for comparison, the overlying non-phosphatic Arthur Creek

90   Formation. We explore the possibility that bioclastic-bound, organic-bound, and iron-

91   bound P sourced the Thorntonia phosphatic carbonates and develop simple mathematical

92   models to assess the relative importance of organic- and iron-bound P. We find that while

93   the high organic carbon content of the Thorntonia Limestone suggests that organic-bound

94   P contributed significantly to authigenic apatite formation, C to P ratios indicate that

95   organic-bound P was insufficient to account entirely for the observed phosphorus

96   enrichment. Sedimentology and iron speciation data indicate that these formations

97   accumulated under anoxic, ferruginous subsurface water masses, allowing for the

98   possibility that P adsorbed to iron minerals precipitating from the water column

99   augmented organic-bound P delivery to the sediment column. Nonetheless, simple

100   mathematical models indicate that, by itself, iron-bound phosphorus delivery is also

101   incapable of accounting for the observed phosphorus enrichment. Thus, we infer that both

102   organic-bound and iron-bound phosphorus sources were necessary for the development

103   of the fossil-bearing phosphatic carbonates of the Thorntonia Limestone.

104

GEOLOGIC BACKGROUND

The Centralian Superbasin is a laterally extensive intracratonic basin that initiated during

Neoproterozoic transcontinental rifting of Rodinia. Regional tectonic events subsequently

dissected the superbasin into a mosaic of discrete, asymmetric, polyphase foreland basins

(Fig. 1a; Walter et al, 1995; Lindsay, 2002; Dunster et al., 2007). Here, we focus on the

phosphatic Cambrian strata of the southern Georgina Basin (Cook and Shergold, 1986;

Southgate, 1988; Southgate and Shergold, 1991), which deposited variably and

diachronously across the basin (Cook and Shergold, 1986; Southgate, 1988; Howard,

1990; Southgate and Shergold, 1991; Dunster et al., 2007).

The Narpa Group encompasses Cambrian Series 2 and Series 3 stratigraphy of the

southern Georgina Basin (Fig. 1b; Ambrose et al., 2001; Dunster et al., 2007). Deposition

of its lowermost member, the phosphatic Thorntonia Limestone, reflects a major

transgression and expansion of the Georgina Basin. For this reason, the basal contact of

the Thorntonia Limestone can unconformably overlie the Shadow Group, conformably

and gradationally overlie the Shadow Group, or overlie and re-work crystalline basement

(Fig. 1b). The rest of the Narpa Group records a basin-wide, shallowing-upward

succession that transitions from outer (lower Arthur Creek Formation), middle (upper

Arthur Creek Formation) and inner ramp (Steamboat Sandstone) depositional

environments into a flat-topped carbonate platform (Arrinthrunga Formation; Ambrose et

al., 2001; Dunster et al., 2007).

Trilobite biostratigraphy assigns Thorntonia rocks to the Ordian and early

Templetonian stages of Australian chronostratigraphy (Laurie, 2004a,b; Dunster et al.,

127 2007), correlative to Cambrian Series 2, Stage 4 and, possibly, lowermost Series 3, Stage

128 5 (Fig. 1b; Babcock and Peng, 2007; Peng and Babcock, 2011). Trilobite biozones within

129 the Arthur Creek Formation are diagnostic for the Australian regional Ordian–

130 Boomerangian stages (Laurie, 2004a, b; Dunster et al., 2007), correlative to uppermost

131 Stage 4 of Cambrian Series 2 through to the Guzhangian Stage of Cambrian Series 3 (Fig.

132 1b; Babcock and Peng, 2007; Peng and Babcock, 2011).

133

134 **METHODS**

135 We examined the sedimentology and lithofacies associations of the Thorntonia and

136 Arthur Creek formations within drill core NTGS 99/1 reposited at the Northern Territory

137 Geological Survey, Alice Springs, Australia. With a water-cooled saw, we cut 534 three-

138 cm-long, quarter-core samples perpendicular to bedding at ~10-25 cm resolution between

139 597.58 and 347.98 meters core depth (mcd). Each sample was again divided

140 (perpendicular to bedding) into two subsamples, one half designated as a hand-sample or

141 thin-section billet, the other half pulverized with a steel ring mill. Each hand-sample

142 billet was micro-drilled along individual laminations for carbonate carbon ($\delta^{13}C_{carb}$) and

143 carbonate oxygen ($\delta^{18}O_{carb}$) isotopic analysis. The evolved CO_2 was measured against an

144 in-house reference gas on a VG Optima dual-inlet mass spectrometer attached to a VG

145 Isocarb preparation system. We report isotopic values in the V-PDB per mil (‰)

146 notation. Standard reproducibility was $1\sigma = < 0.1$‰ and 0.2‰ for $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$,

147 respectively.

148 Sample powders were divided for carbon, phosphorus, iron, and trace element

149 geochemical analyses aimed at diagnosing the sediment- and water-column geochemistry

150   at the time of phosphatic carbonate deposition. To determine carbon mass fractions, we

151   acidified 5-10 g of powdered sample with cold, 2.5 M hydrochloric acid. The resulting

152   insoluble residue (i.e., the non-carbonate fraction, comprised predominately of

153   siliciclastics and organic matter) was isolated by filtration, rinsed thoroughly with de-

154   ionized water, then dried and weighed. The total carbonate fraction was estimated as the

155   weight percent difference between the bulk sample and the insoluble residue. To

156   determine the weight percent of total organic carbon (TOC) and its isotopic composition

157   ($\delta^{13}C_{org}$), aliquots of the insoluble residue were combusted within a Carlo Erba NA 1500

158   Analyzer attached to a Thermo Scientific Delta V Advantage isotope ratio mass

159   spectrometer. Reproducibility of $\delta^{13}C_{org}$ for an acetanilide standard was 0.16‰ (1σ). Of

160   the 100 samples processed, 29 were analyzed in duplicate and yielded an analytical

161   reproducibility of $1\sigma = 0.07$ weight percent (wt.%) TOC. Finally, we estimated the wt.%

162   of silicate phases (either clastic or authigenic) as the wt.% of the insoluble fraction minus

163   the wt.% of the TOC fraction.

164   The speciation of phosphorus (P) was determined with a modified sequential

165   extraction methodology for marine sediment (Ruttenberg, 1992). Here, 150-200 mg of

166   rock powder was sequentially extracted with 10 mL each of (1) 0.3 M sodium-citrate/1 M

167   sodium bicarbonate/0.14 M sodium dithionite (pH = 7.5) for P bound to

168   reducible/reactive ferric iron minerals (P_{Fe}), (2) 1 M sodium acetate (pH = 4.0) for

169   carbonate fluorapatite, biogenic hydroxyapatite, and carbonate-bound P ($P_{auth+carb}$), (3) 1.2

170   M cold HCl for crystalline fluorapatite (P_{xl}), and (4) 1.2 M cold HCl after a 2 hour

171   ignition at 550°C for organic P (P_{org}). To prevent P readsorption during the first two

172   extraction steps, two 5 mL 1 M $MgCl_2$ washes were performed post-extraction.

173   Phosphorus in extracts and wash solutions (except P_{Fe}) was analyzed

174   spectrophotometrically (Thermo Genesys 6) by the molybdate-blue method (Strickland

175   and Parsons, 1972; Ruttenberg, 1992); P_{Fe} was measured by inductively coupled plasma

176   optical emission spectrometry (ICP-OES; Varian Vista-MPX). We note that Ruttenberg

177   (1992) ascribes P-speciation phase (3), P_{xl}, to detrital fluorapatite of igneous and

178   metamorphic origin. We abbreviate this phase as 'xl' for 'crystalline' so as to remove

179   reference to a genetic mechanism (i.e., detrital) for an operationally-defined phase based

180   on a chemical extraction procedure. We hypothesize about the origin of this phase in

181   greater detail in the discussion.

182   To verify the efficiency of the sequential extraction method, total P (P_T) values

183   were determined independently (SGS Mineral Services Group) by inductively coupled

184   plasma atomic emissions spectrometry (ICP-AES) after a standard four acid digestion

185   (HF-$HClO_4$-HCl-HNO_3). These analyses also provide the additional major and trace

186   metal concentrations reported below. To account for variable dilution by siliciclastic

187   influx, we report element concentrations normalized to aluminum (Al) in wt.%/wt.% and

188   ppm/wt.% units for major and trace elements, respectively.

189   To determine the speciation of iron within our samples, we applied a modified

190   version of the sequential extraction method of Poulton and Canfield (2005). Here, 80-100

191   mg of rock powder was sequentially extracted with 10 mL each of (1) 1 M sodium-

192   acetate, adjusted to pH 4.5 with acetic acid to extract Fe associated with carbonate phases

193   such as siderite and ankerite (Fe_{carb}); (2) 0.28 M sodium dithionite, adjusted to pH 4.8

194   with 0.2 M acetic acid/0.25 M tri-sodium citrate, for iron oxides such as hematite and

195   goethite (Fe_{ox}); and (3) 0.2 M ammonium oxalate/0.17 M oxalic acid for magnetite

196 (Fe_{mag}). The boiling chromium reduction distillation of Canfield et al. (1986) was used to

197 quantify sulfur (S) within pyrite from the insoluble residues derived from carbonate

198 dissolution. We used a pyrite stoichiometry (FeS_2) to relate the extracted S back to iron

199 (Fe_{py}). Total Fe (Fe_T), which comprises the sum of the diagenetically highly reactive

200 phases ($Fe_{HR} = Fe_{carb} + Fe_{ox} + Fe_{mag} + Fe_{py}$), as well as unreactive Fe (Fe_U; predominately

201 silicate-bound Fe), was determined via a boiling HF-HNO_3-$HClO_4$ extraction on an

202 additional aliquot of sample powder. All iron concentrations were measured by atomic

203 absorption spectrometry (AAS). Eight replicates of one sample, 572.64 mcd, yield a RSD

204 of 2%, 13%, and 71% for Fe_{carb}, Fe_{ox}, and Fe_{mag}, respectively. The high RSD of the latter

205 two phases result from measured quantities close to the instrument detection limit; that is,

206 the average wt.% $\pm 1\sigma$ for the eight Fe-speciation replicates is 0.110±0.002, 0.016±0.002,

207 and 0.001±0.001 for Fe_{carb}, Fe_{ox}, and Fe_{mag}, respectively. At higher Fe concentrations for

208 each fraction, the RSD is <5% for each stage, and this is also the case for Fe_{py} and Fe_T

209 (Poulton and Canfield, 2005).

210

211 **RESULTS**

212 **Lithofacies descriptions and paleoenvironmental interpretations for the Thorntonia**

213 **Limestone and Arthur Creek Formation from drill core NTGS 99/1**

214 Markings on drill core NTGS 99/1 assign 598.4–580.1 mcd, 580.1–558.7 mcd, and

215 558.7–554.7 mcd to the informal lower, middle, and upper members, respectively, of the

216 Thorntonia Limestone (previously Hay River Formation), and 554.7–103.2 mcd to the

217 Arthur Creek Formation (previously Marqua Formation; Ambrose et al., 2001; Dunster et

218 al., 2007). In this study, we characterized the sedimentology and geochemistry of the

219   entire Thorntonia Limestone and the lowermost ~200 m of the lower Arthur Creek

220   Formation.

221

222   *Thorntonia Limestone*

223   The Shadow Group is absent from NTGS 99/1. Here, the Thorntonia Limestone directly

224   overlies Paleoproterozoic granite basement. The basal meters of the lower Thorntonia

225   member include lithic fragments and sand grains within dolomudstone, with minor cubic

226   pyrite crystals (Fig. 2a). More generally, the lower Thorntonia consists of dolomudstone

227   and peloidal dolowackestone, with pervasive structural dissolution textures creating a

228   stylolaminated to stylobedded fabric (Fig. 2b). Southgate and Shergold (1991) designated

229   the basal, arkosic, terrigenous unit as a low-stand system tract, and the overlying stylolitic

230   carbonate as a condensed transgressive / high-stand system tract.

231   Below 575.92 mcd (the lower Thorntonia Limestone) and from 580.1 - 575.92

232   mcd (the middle Thorntonia Limestone), the bulk lithology is dolostone. Stratigraphically

233   above this horizon, up to the middle–upper Thorntonia Limestone contact at 558.7 mcd,

234   the bulk lithology is limestone. Nevertheless, petrographic observation of the bulk

235   limestone lithofacies above 575.92 mcd reveals rare euhedral dolomite rhombs within an

236   otherwise calcimudstone or calciwackestone matrix.

237   The middle Thorntonia contains four interbedded and interlaminated lithofacies

238   that occur within generally coarsening-upward meter- to sub-meter-scale packages (Fig.

239   2c). These lithofacies include: (1) black to medium gray carbonate mudstone; (2) dark to

240   medium gray peloidal, bioclastic, and, occasionally, intraclastic wackestone; (3) medium

241   to light gray peloidal and bioclastic packstone; and (4) medium to light gray bioclastic

242   grainstone. Carbonate mudstone or wackestone lithofacies define the base of each

243   package and interlaminate or alternate gradationally on a centimeter to decimeter scale.

244   These carbonate mud-dominated lithologies typically grade upward into, and contact

245   sharply with, laminae and beds of packstone. When present, thin beds of bioclastic

246   grainstone overlie packstone beds. These grainstone beds display basal erosional contacts

247   with millimeter to half-centimeter-scale topography, and an upper contact that is either

248   sharp or erosional and overlain by beds of black to medium-gray carbonate mudstone. In

249   other cases, the upper contact is diffuse and conformable with beds of medium-gray

250   packstone or wackestone (Fig. 2d). There is a broad up-core trend: packages initiate with

251   progressively coarser lithologies and terminate with progressively thicker grainstone

252   beds. The nature of deposition of the Thorntonia Limestone within NTGS 99/1 is

253   consistent with the phosphatic lithofacies model from the northeast Georgina Basin

254   (Cycle mP of Southgate, 1988). Southgate and Shergold (1991) assign these shallowing-

255   upward cycles to the transgressive system tract.

256   We interpret the lithologic association of the middle Thorntonia to reflect

257   deposition within a subtidal to intertidal depositional environment. Mudstone,

258   wackestone, and packstone beds accumulated from suspension sedimentation in calm

259   settings that lacked significant tidal, wave, or storm activity. The coarser grain size and

260   subtle current-generated stratification observed in grainstone beds reflect a higher energy

261   depositional environment. Grainstone beds reveal no internal grading, but do show

262   evidence for amalgamation and winnowing of carbonate mud by currents or waves.

263   Deposition under the influence of waves is also manifest in rosettes of brachiopod and

264   trilobite shell fragments along basal scour surfaces of bioclastic grainstone beds (Fig. 2d).

265   Dunster et al. (2007) interpreted the black, carbonaceous carbonates of the Thorntonia

266   Formation to represent deposition under dysoxic to anoxic conditions.

267   In NTGS 99/1, the upper Thorntonia encompasses a 4 meter-thick vuggy,

268   fossiliferous dolopackstone with laminae, beds, and pockets of bioclastic dolograinstone

269   (Fig. 2e). When present, dolospar crystals form a mosaic around bioclasts (primarily of

270   lingulate brachiopods). In addition to representing a prominent matrix constituent,

271   bioclasts occur as cumulate along dissolution seams.

272   ***Petrography of apatite distribution.*** Apatite displays three predominant modes

273   within the middle and upper Thorntonia Limestone. First, within bioclast-rich carbonate

274   lithologies, apatite occurs primarily as the internal molds (steinkerns) of conical small

275   shelly fossils or, more commonly in the upper Thorntonia Limestone, as lingulate

276   brachiopod skeletal debris (Fig. 3a). Apatite also occludes gaps between, and templates

277   the exterior of, silica-replaced skeletons (Fig. 3a). Second, in rare instances, apatite

278   occurs as cement within bioclastic grainstone lithologies (Fig. 3b), Third, within mud-

279   supported, suspension-deposited carbonate, apatite occurs as sub-angular to sub-rounded

280   coarse-silt to medium-sand-size grains, and as silt- to fine-sand-size, tabular or undulose

281   grains within well-sorted, thin beds (Fig. 3c). Due to the textural maturity and fine grain-

282   size of these lithologies, we cannot say conclusively whether these grains were eroded,

283   transported and winnowed from a site of apatite authigenesis (i.e., allochthonous apatite

284   grains) or whether they were sourced with a detrital siliciclastic influx. We favor the

285   interpretation that these grains represent re-worked authigenic grains (i.e., intraclasts of

286   authigenic cement and steinkern bioclasts) because we observe no comparable-size

287   detrital siliciclastic grains. Below, we discuss the origin of these grains in light of

288   geochemical data.

289

290   ***Arthur Creek Formation***

291   Within NTGS 99/1, the basal 10 m of the lower Arthur Creek encompasses a petroleum-

292   generating, massive black shale (Fig. 2e), or 'hot shale' (e.g., Dunster et al., 2007),

293   succeeded by planar, undulose, and corrugated interlaminae of black to dark gray organic

294   matter- and clay-rich shale and siltstone with medium to light gray calcimudstone and

295   dolomudstone. This shale also contains rare interbeds of very fine-grained bioclastic

296   packstone and grainstone (Fig. 2f). Clay- and iron-oxide-rich laminae include sub-

297   rounded to angular, very well sorted, monocrystalline quartz and authigenic pyrite

298   crystals, the latter of which often occlude pore space. Horizontal alignment of clay

299   minerals indicates that compaction enhanced the physical expression of lamination.

300   Commonly below ~490 mcd, and only rarely above, decimeter-scale light gray limestone

301   nodules displace surrounding laminations and retain faint remnants of lamination,

302   indicating nodular development during compaction, but before lithification (Fig. 2g). We

303   interpret individual laminae to reflect the gravitational settling of fine particles suspended

304   by dilute turbidity currents that wafted sediment towards the basin interior, consistent

305   with an outer-ramp depositional environment (Dunster et al., 2007). The fetid,

306   carbonaceous black shale and black, carbonaceous, laminated dolostone suggest

307   deposition under dysoxic to anoxic conditions (Dunster et al., 2007).

308   In the upper meters of the measured lower Arthur Creek, a second lithofacies

309   interbeds with the laminated facies (Fig. 2h). This facies includes interbeds of light gray

310   calcimudstone and siliciclastic siltstone. Rare truncation of undulatory laminae indicates

311   intermittent deposition under the influence of currents. This facies is a harbinger of the

312   more proximal, oxygenated ramp environment of the overlying upper Arthur Creek

313   Formation (Dunster et al., 2007), which was not measured in this study. Southgate and

314   Shergold (1991) assign the lower Arthur Creek to a transgressive system tract.

315

316   **Geochemistry of the Thorntonia Limestone and Arthur Creek Formation**

317   A generalized stratigraphic column of the Thorntonia and lower Arthur Creek is shown in

318   Figure 4a alongside chemostratigraphic variation in $\delta^{13}C_{carb}$ (Fig. 4b), $\delta^{18}O_{carb}$ (Fig. 4c)

319   and $\delta^{13}C_{org}$ (Fig. 4d). Cross-plots of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ display no statistically

320   significant co-variation (Fig. 4e), thereby suggesting that $\delta^{13}C_{carb}$ values, at least,

321   represent the primary seawater isotopic composition. The $\delta^{13}C_{carb}$ curve generated for

322   NTGS 99/1 displays two positive peaks, the first in the middle Thorntonia (563.92 mcd)

323   and the second in the Arthur Creek (506.51 mcd). Consistent with trilobite

324   biostratigraphy (Laurie, 2004a,b), we correlate the middle Thorntonia excursion to the

325   Ordian–early Templetonian isotopic event and the Arthur Creek excursion to the Late

326   Templetonian–Floran event (Fig. 4b; Lindsay et al., 2005). This assignment corroborates

327   regional isotopic variation in the southern Georgina, Amadeus, and Daly Basins (Lindsay

328   et al., 2005) and, further afield, to the Argentine Precordillera (Gomez et al., 2007), the

329   Great Basin, U.S.A. (Saltzman, 2005), South China (Zhu et al., 2004; Guo et al., 2010),

330   and northwest China (Wang et al., 2011).

331   Small magnitude discontinuities in $\delta^{13}C_{carb}$ chemostratigraphy occur across the

332   informal member boundaries of the Thorntonia Limestone (Fig. 4b). These

333   discontinuities likely represent erosive events or hiatuses in deposition. In support of the

334   former interpretation, an increase in Zr/Al occurs across the middle/upper Thorntonia

335   contact (Supplementary Figure 1). Elevated Zr/Al ratios define erosional surfaces where

336   high-energy currents winnow fine-grained, low-density siliciclastics (characterized by

337   Al) and concentrate high-density minerals (characterized by Zr; Vine and Tourtelot,

338   1970). Unlike carbon isotopes, secondary fluid migration does not affect the Zr/Al ratio.

339   Thus, this proxy confirms sediment winnowing during deposition of the upper

340   Thorntonia. Regionally, the Thorntonia Limestone—Arthur Creek Formation contact

341   represents a sequence boundary, with karstification developed along this surface in the

342   western margin of the basin (Dunster et al., 2007). While the formation boundary within

343   NTGS 99/1 represents a sharp lithologic break, $\delta^{13}C_{carb}$ values display general continuity

344   across this boundary (Fig. 4b), suggesting either relative temporal continuity or fortuitous

345   resumption of deposition with similar carbon isotopic composition. Isopach maps of the

346   Arthur Creek show that the formation thickens to the east-southeast, where the NTGS

347   99/1 drill core intercepted the maximum depocenter of the preserved basin margin

348   (Dunster et al., 2007). Thus, under the former scenario, the Thorntonia Limestone—

349   Arthur Creek Formation boundary within NTGS 99/1 could represent a correlative

350   conformity of the regional sequence boundary, with limited time missing across this

351   lithologic contact.

352   Within NTGS 99/1, $\delta^{13}C_{org}$ displays co-variation with $\delta^{13}C_{carb}$ within the lower

353   Thorntonia Limestone and no co-variation with $\delta^{13}C_{carb}$ within either the middle/upper

354   Thorntonia or the Arthur Creek formations (Fig. 4d,f; lower Thorntonia: $R^2 = 0.75$;

355   middle/upper Thorntonia: $R^2 = 0.04$; Arthur Creek: $R^2 = 0.2$). TOC varies from 0.1-2.9

356   wt.% in the Thorntonia, displaying a generally increasing trend in the lower Thorntonia

357   and high variance in the middle Thorntonia. TOC ranges from 0.1 to 2.5 wt.% in the

358   lower Arthur Creek, with higher values at the base of the formation, decreasing towards a

359   mean of 0.1 wt.% TOC in the upper 100 m of the measured core interval (Fig. 4d).

360   Despite the lack of covariance between $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ in strata of the middle/upper

361   Thorntonia and the Arthur Creek Formation, one trend emerges: high (> 1.0 wt.%),

362   medium ($0.2 <$ wt.% < 1.0), and low (< 0.2 wt. %) TOC correlate with light,

363   intermediate, and heavy $\delta^{13}C_{org}$ values (Fig. 4d). That is, the lightest $\delta^{13}C_{org}$ values occur

364   in the most organic- and phosphorus-rich lithofacies, the middle Thorntonia Limestone

365   (*cf.*, Bartley et al., 1998, and Guo et al., 2013). The latter two TOC bins generally

366   correspond to samples from the Arthur Creek below and above ~430 mcd, respectively,

367   which is the transition between the laminated facies and the interbedded carbonate

368   mudstone–siliciclastic shale and siltstone facies.

369   Total phosphorus (P_T) within the Thorntonia Limestone ranges up to 3.9 wt.%

370   (Fig. 5a). P_T increases systematically within the lower Thorntonia and the lowermost

371   middle Thorntonia, followed by an additional increase around 575 mcd. We note that the

372   transition from dolostone (stratigraphically below 575.92 mcd) to limestone

373   (stratigraphically above 575.92 mcd) within drill core NTGS 99/1 occurs just below this

374   jump in P content (Figs 5a,b). The overlying meters of the middle and upper Thorntonia

375   display high variance in P_T. In contrast, the maximum value of P_T within the Arthur

376   Creek is 0.4 wt.%, but is typically much lower with a median of 0.03 wt.% and 1st and 3rd

377   quartile values of 0.02 and 0.04 wt.%, respectively (Fig. 5a).

378   We tested the fidelity of the P sequential extraction method by comparing the sum

379   of the operationally-defined pools ($P_T = P_{xl} + P_{auth+carb} + P_{org} + P_{Fe}$) to the total

380   phosphorus content determined by ICP-AES analysis. The consistency between these two

381   measurement techniques (slope of linear regression = 1.1, $R^2 = 0.88$; Fig. 5e) increases

382   confidence in the values of the constituent sequential extraction phases. In both the

383   Thorntonia Limestone and the Arthur Creek Formation, the operationally-defined P_{xl} and

384    $P_{auth+carb}$ phases dominate P_T, while P_{org} and P_{Fe} contribute a negligible fraction (Fig. 5b).

385   The median (1st, 3rd quartile) percent contribution to P_T are: $P_{xl} = 91.5\%$ (77.5, 94.4),

386    $P_{auth+carb} = 7.5\%$ (3.7, 19.5), and $P_{org} = 0.4\%$ (0.2, 1.5). P_{Fe} was measured only on a subset

387   of samples, but this phase contributes minimally to P_T (a median of 0.1% with 1st and 3rd

388   quartiles of 0.0 and 0.4%, respectively).

389   Total iron (Fe_T) varies from 0.06-1.49 wt.% in the Thorntonia Limestone and

390   from 0.32-2.71 wt.% in the Arthur Creek Formation (Fig. 5c). In general, Fe_T is lowest

391   where P_T is highest. Based on the slope of linear regression, 88% of Fe_T resides in Fe_{HR}

392   phases within the Thorntonia ($R^2 = 0.92$; Fig. 6a). In contrast, within the Arthur Creek,

393   ~48% of Fe_T resides in Fe_{HR} ($R^2 = 0.57$; Fig. 6a), consistent with the higher siliciclastic

394   fraction for these lithologies. The lower coefficient of determination for the Arthur Creek

395   Formation reflects a decrease in Fe_{HR}/Fe_T from 0.66 at the base of the formation to ~0.3

396   near the top of the measured core interval. Reduced iron phases, Fe_{py} and Fe_{carb}, dominate

397   Fe_{HR} in both formations, while oxidized and partially oxidized iron phases, Fe_{ox} and

398   Fe_{mag}, contribute a minimal fraction (Fig. 5c). Based on the slope of the linear regression,

399   82% of Fe_{HR} resides as Fe_{carb} within the lower Thorntonia ($R^2 = 0.62$; Fig. 6c) while Fe_{py}

400   accounts for only a minor contribution that has no statistically significant correlation with

401   Fe_{HR} (Fig. 6b). As such, the gradual decrease in Fe_{HR} within the lower Thorntonia reflects

402   a systematic decrease in Fe_{carb} from very high values of 1.3 wt.%, to ~0.3 wt.%. In the

403   middle and upper Thorntonia, 64% of Fe_{HR} resides as Fe_{py} ($R^2 = 0.95$; Fig. 6b) and 31%

404   resides as Fe_{carb} ($R^2 = 0.82$; Fig. 6c). For the lower Arthur Creek, ~73% and 26% of Fe_{HR}

405   reside in Fe_{py} ($R^2 = 0.94$; Fig. 6b) and Fe_{carb} ($R^2 = 0.72$; Fig. 6c), respectively.

406   When we parse the Fe-speciation data of the middle Thorntonia Limestone

407   samples by lithology, we see a similar partitioning of Fe phases as when we group all

408   samples within members (as presented above). Within the dolostone of the middle

409   Thorntonia (580.1 – 575.92 mcd), 98% of Fe_T resides in Fe_{HR} ($R^2 = 0.99$); in contrast,

410   within the limestone of the middle Thorntonia (575.92 mcd – 558.7 mcd), 89% of Fe_T

411   resides in Fe_{HR} ($R^2 = 0.95$). Likewise, within middle Thorntonia dolostone, 67% ($R^2 =$

412   0.94) and 27% ($R^2 = 0.69$) of Fe_{HR} resides in Fe_{py} and Fe_{carb}, respectively; within the

413   middle Thorntonia limestone, 68% ($R^2 = 0.96$) and 30% ($R^2 = 0.86$) of Fe_{HR} resides in

414   Fe_{py} and Fe_{carb}, respectively.

415   Within NTGS 99/1, the median (1st, 3rd quartile) percent acid insoluble fraction

416   (i.e., silicates) within the Thorntonia is 8.3% (5.3, 17.0) as compared to 44.0% (32.8,

417   54.3) for the Arthur Creek (Supplementary Figure 1). TOC/Al ratios are higher and more

418   variable in the Thorntonia than for the Arthur Creek (Supplementary Figure 1). Fe/Al

419   ratios and Mn/Al ratios decline throughout the lower Thorntonia (save for a couple of

420   high values in the upper Thorntonia; Supplementary Figure 1). The detrital-associated

421   trace element ratio Zr/Al is low and variable within the Thorntonia compared to the

422   Arthur Creek Formation and displays an abrupt increase across the middle/upper

423   Thorntonia boundary. (See Supplementary Information for a discussion of aluminum-

424   normalized concentrations of redox-sensitive and bioessential trace metals;

425   Supplementary Figure 2.)

426

427   **DISCUSSION**

428   How do these geochemical data inform our understanding of the source of phosphorus to

429   phosphatic Thorntonia carbonates and, more broadly, the loss of phosphatic lithologies

430   and consequent closure of the phosphatization taphonomic mode during Cambrian Series

431   2? To address these questions, we combine petrographic observations with P-speciation

432   data to quantify authigenic apatite within the Thorntonia Limestone. In turn, we explore

433   the possibility that P bound within bioclasts, organic matter, or iron minerals sourced the

434   observed P within these lithologies. Finally, we present a mathematical framework for

435   which to deconvolve the relative contribution of the two most likely sources—P bound

436   with organic matter or iron minerals—to authigenic apatite nucleation.

437

438   **Source(s) of phosphorus to the Thorntonia Limestone and Arthur Creek Formation**

439   How much of the apatite within the Thorntonia Limestone and Arthur Creek Formation

440   must we account for with P delivery shuttles? Phosphorus speciation provides a

441   (semi)quantitative measure of the partitioning of phosphorus within a sedimentary

442   succession. The majority of P extracted from NTGS 99/1 is operationally classified as

443   fluorapatite of detrital igneous and/or metamorphic origin (P_{xl}; Ruttenberg, 1992) and

444   constitutes a median (1st, 3rd quartile) of 91.5% (77.5, 94.4) of P_T. However, we have

445   three reasons to question this genetic interpretation. First, as described above,

446   petrographic observations reveal that apatite within the Thorntonia Limestone occurs

447   predominantly as the internal molds of small shelly fossils (Fig. 3a) or, occasionally, as

448   cement within bioclastic grainstone (Fig 3b), both indications of an authigenic origin.

449   Given the thermal history of the Georgina Basin, which reached temperatures necessary

450   to develop Type II kerogen (Dunster et al., 2007), burial diagenesis should have increased

451   the crystallinity of authigenic phosphate minerals (Shemesh, 1990). It is thus not

452   surprising that authigenic apatite formed within marine sediment during the Cambrian is

453   now operationally classified as crystalline igneous and metamorphic apatite (*sensu* Föllmi

454   et al., 2005). Second, within mud-supported, suspension-deposited carbonate, apatite

455   occurs as coarse-silt- to medium-sand-size grains. Given that we observe no comparable

456   size detrital siliciclastic grains, we suggest these grains are eroded, transported and

457   winnowed authigenic grains. Third, if the P_{xl} phase comprised fluorapatite sourced to the

458   basin along with a detrital siliciclastic influx, we would predict that it should correlate

459   with the siliciclastic-associated heavy element Zr/Al ratio. We observe no correlation

460   between P_{xl} and Zr/Al (Fig. 5f). Thus, consistent with petrographic observations, we

461   conclude that the P_{xl} pool largely represents authigenic apatite and, therefore, we must

462   account for this phase with a delivery shuttle of P to the sediment column.

463

464   **Bioclastic apatite as a source of phosphorus for authigenic apatite precipitation?**

465   Lingulid brachiopods comprise a fraction of the bioclasts identified in samples analyzed

466   petrographically for carbonate sedimentology and apatite distribution. The presence of

467   these phosphatic bioclasts raises two issues. First, samples that contain apatite bioclasts

468   will have a wt.% P_T that overestimates the quantity of authigenic apatite. Determining the

469   actual wt.% of P within authigenic apatite for these samples would require subtracting the

470   wt.% of bioclastic P from the bulk wt.% P_T determined by phosphorus speciation

471   geochemistry. One method for determining the wt.% of P within primary phosphatic

472   bioclasts would be to use quantitative point-count data to determine the volume of

473   bioclasts, then to multiply this volume by the density of dahllite to determine the mass

474   (wt.%) of P. Given that the percent of primary phosphatic bioclasts visually

475   (qualitatively) rarely exceeds the percent of phosphatic steinkerns and sand-sized

476   authigenic grains (see discussion above), we move forward without quantitative estimates

477   of the wt.% of bioclastic P under the caveat that, for lingulid brachiopod-bearing

478   bioclastic lithologies, P_T overestimates authigenic apatite within a sample.

479   Second, the observation of bioclasts of primary phosphatic shells raises the

480   possibility that *in situ* dissolution of these bioclasts may have contributed to high pore-

481   water phosphate concentration and facilitated subsequent authigenic precipitation.

482   However, petrographic observations show that inarticulate brachiopod and other

483   phosphatic skeletons are not unusually abundant in phosphate-rich Thorntonia horizons,

484   and conversely that authigenic phosphate is not unusually abundant in those samples with

485   the highest abundances of phopshatic skeletons. Nor do these remains show marked

486   evidence of dissolution. Thus, the sedimentation of phosphatic skeletal material does not

487   seem capable of sourcing the phosphate now found in Thorntonia rocks. Further, *in situ*

488   dissolution of phosphatic bioclasts would necessitate pore fluids that promoted the early

489   dissolution of apatite shells without concurrent dissolution of the calcium carbonate

490   shells and sediment molded and/or replaced by the precipitation of authigenic calcium

491   phosphate minerals. For these reasons, we do not invoke phosphatic skeleton-derived P as

492   a significant source for authigenic apatite precipitation. Nevertheless, if phosphatic

493 skeleton dissolution were to have sourced P for authigenic apatite, then the required

494 quantity of organic and iron-bound P (discussed below) would lessen proportionately.

495

496 **Organic-bound phosphorus as a source of phosphorus for authigenic apatite**

497 **precipitation?**

498 Particulate organic carbon represents the main delivery shuttle of phosphorus to the

499 sediment column in the modern ocean (e.g., Delaney, 1998; Benitez-Nelson, 2000), and

500 so we ask whether organic carbon could have sourced the observed amount of P within

501 beds of the Thorntonia Limestone and the Arthur Creek Formation. Perhaps the simplest

502 model for organic-bound P delivery is to assume that organic matter arrived at the sea

503 floor with a Redfield C_{org}:P_{org} molar ratio of ~106:1 (Redfield, 1958). However, C_{org}:P_{org}

504 of organic matter within marine sediment and, therefore, sedimentary rocks, is commonly

505 much higher than the Redfield ratio as a result of the preferential remineralization of P-

506 rich organic compounds within the water-column (Clark et al., 1998) or within the

507 sediment column (Ingall et al., 1993, Ingall and Jahnke, 1997; Van Cappellen and Ingall,

508 1996; Jilbert et al., 2011). C_{org}:P_{org} molar ratios within the Thorntonia Limestone range

509 from 79:1 up to 17,000:1 [median (1st, 3rd quartile) = 1,389:1 (521:1, 3619:1)]. Likewise,

510 C_{org}:P_{org} molar ratios within the Arthur Creek Formation range from 43:1 up to 11,770:1

511 [median (1st, 3rd quartile) = 903:1 (360:1, 3,372:1)]. Thus, C_{org}:P_{org} molar ratios within

512 these lithologies deviate substantially from the Redfield ratio and, at face value, suggest

513 extensive preferential P_{org} loss during organic matter respiration.

514   When organic respiration occurs within the sediment column, liberated P_{org} may

515 'sink-switch' and precipitate as authigenic phosphate minerals (Ruttenberg and Berner,

516   1993), as is likely the case for the development of phosphatic strata within the Thorntonia

517   Limestone. With respect to phosphorus speciation terminology, 'sink-switching' would

518   transfer P from the P_{org} phase to either the authigenic P_{xl} or the $P_{auth+carb}$ phase. In that

519   regard, $C_{org}:P_T$ should provide a better estimate of the retention of organic-bound P to the

520   sedimentary environments of the Thorntonia Limestone and Arthur Creek Formation

521   (Ingall et al., 1993; Ruttenberg and Berner, 1993; Anderson et al., 2001; Algeo and Ingall,

522   2007). $C_{org}:P_T$ ranges from 0.1–16:1 within the Thorntonia Limestone with a median (1st,

523   3rd quartile) value of 2.5:1 (1.2:1, 4.8:1). For the non-phosphatic Arthur Creek Formation,

524    $C_{org}:P_T$ ranges from 5–157:1 with a median (1st, 3rd quartile) value of 17.4:1 (7.6:1,

525   44.5:1). Thus, with the exception of four samples, $C_{org}:P_T$ molar ratios for both the

526   Thorntonia Limestone and the Arthur Creek Formation fall well below the canonical

527   Redfield ratio (Fig. 5d). From this perspective, both the Thorntonia Limestone and the

528   Arthur Creek Formation retain more P than would be expected based on organic matter

529   delivery with a molar $C_{org}:P_{org}$ ratio equal to or greater than the Redfield ratio.

530   Preferential C_{org} remineralization or hydrocarbon migration relative to P retention

531   may have resulted in a molar $C:P_T$ lower than the Redfield ratio. The required > 90% loss

532   of C_{org} (see below) appears to be common in relatively organic-lean sediment deposited

533   on oxic Cenozoic seafloors (Anderson et al., 2001); however, given the organic carbon

534   content of Thorntonia samples, and accepting sedimentological and geochemical

535   arguments for anoxic deposition of the Thorntonia Limestone (see below), such loss

536   would have required massive remineralization under anoxic pore water conditions.

537    $\delta^{13}C_{carb}$ values do not show the distinctly light values that might be expected in this

538   circumstance (Schrag et al., 2013). Assuming that all phosphorus was delivered via

539   organic matter with a Redfield ratio and was subsequently retained within the sediment

540   column, the discrepancy between the Redfield ratio and the measured $C:P_T$ provides a

541   minimum estimate of C_{org} loss (estimated quantitatively in a later section).

542   Organic carbon loss may also occur during low-grade metamorphism (Raiswell

543   and Berner, 1987). Since the lithology of the Thorntonia Limestone precludes a confident

544   application of the suggested metrics to account for this loss (Raiswell and Berner, 1987),

545   we cannot evaluate how much this process may have contributed to the discrepancy

546   between measured $C_{org}:P_T$ values and the Redfield ratio. However, we can explore

547   whether an additional phosphorus delivery shuttle augmented organic-bound P delivery

548   to the sea floor during deposition of the Thorntonia Limestone and Arthur Creek

549   Formation. We discuss this possibility in a later section.

550   Notably, phosphatic strata of the middle Thorntonia Limestone have the highest

551   measured wt. % TOC and the lightest $\delta^{13}C_{org}$ values preserved within this sedimentary

552   succession (Fig. 4c). A similar relationship has been document in Proterozoic basins and

553   attributed to differential recycling of organic matter in benthic mats (e.g., Bartley et al.,

554   1998; Guo et al., 2013). Within the Thorntonia Limestone, this relationship may result

555   from a difference in the primary isotopic composition of organic matter sourcing

556   phosphatic strata, from variable *in situ* remineralization of the sedimentary organic

557   carbon reservoir, or from some combination of these two processes. We do not have an

558   independent line of evidence (e.g., compound specific biomarkers) to distinguish between

559   these possibilities. Instead, we note that acceptance of either of these hypotheses to

560   explain the observed correlation between P content and $\delta^{13}C_{org}$ values makes a prediction

561   for the mechanism of P delivery. For the case of an isotopically distinct organic carbon

562   source to the middle Thorntonia Limestone, the C:P ratio of this source must have been

563   much lower than the canonical Redfield ratio of 106C:1P. For the case of limited C_{org}

564   remineralization within phosphatic strata, an alternative P delivery shuttle to the sediment

565   column must have augmented organic-bound P delivery.

566

567   **Iron-bound phosphorus as a source of phosphorus for authigenic apatite**

568   **precipitation?**

569   If our estimates of organic-bound P delivery fail to account for the phosphate necessary

570   for the observed Thorntonia apatite content, what alternative source could supply this P?

571   A growing body of literature calls upon P adsorbed to the surface or co-precipitated with

572   metal oxides, particularly iron (oxyhydr)oxide particles, as an important shuttle of

573   phosphorus to the sea floor (Berner, 1973; Shaffer, 1986; Feely et al., 1991; Feely et al.,

574   1998; Poulton and Canfield, 2006). Additionally, under anoxic conditions, Fe(II)-

575   phosphates (e.g., vivianite, strengite) may play a more important role for marine P

576   cycling than previously considered (e.g., März et al., 2008; Dellwig et al., 2010; Jilbert

577   and Slomp, 2013). Thus, the release of adsorbed/co-precipitated Fe-bound P to sediment

578   pore waters has previously been invoked as a necessary and significant source of P for

579   sedimentary apatite nucleation (Krom and Berner, 1981; Schuffert et al., 1994, 1998;

580   Slomp et al., 1996; Shen et al., 2000; März et al., 2008; Jilbert and Slomp, 2013).

581   Could the Fe-P shuttle have augmented organic-bound P delivery to Thorntonia

582   and Arthur Creek sediments? In the modern, oxygenated ocean, iron mobility is generally

583   limited to particulate fluxes of insoluble Fe^{3+} phases (Martin and Meybeck, 1979;

584   Poulton and Raiswell, 2002). Under these conditions, we might predict Fe-bound P

585 delivery to these environments to be proportional to the (predominantly siliciclastic)

586 particulate Fe(III) flux. In contrast, under anoxic conditions the reductive dissolution of

587 iron (oxyhydr)oxides by dissimilatory iron reduction or by dissolved sulfide during early

588 diagenesis generates soluble Fe^{2+} that is subsequently redistributed to anoxic slope and

589 basinal environments (Canfield et al., 1996; Severmann et al., 2008; 2010; see review in

590 Lyons and Severmann, 2006). This so-called 'intrabasin iron shuttle' provides a

591 mechanism for decoupling iron delivery to the seafloor from siliciclastic sources and,

592 therefore, we hypothesize that it allows for the delivery of P adsorbed to detrital Fe(III)

593 minerals, Fe(II)-phosphate minerals (e.g., März et al., 2008; Dellwig et al., 2010; Jilbert

594 and Slomp, 2013) and P adsorbed to/co-precipitated with Fe(III)-minerals formed from

595 the oxidation of ferrous iron in the water column (*cf*., Mayer and Jarrell, 2000). In this

596 regard, under either an oxic or an anoxic Cambrian water-column, Thorntonia and Arthur

597 Creek sediments could have received substantial Fe-bound P; however, we note that the P

598 contribution from the Fe-bound P shuttle would have been larger if these sediments

599 accumulated under an anoxic water column.

600   The redox state of the southern Georgina Basin water column during deposition of

601 these middle Cambrian strata can be assessed using data on the speciation and enrichment

602 of sedimentary iron minerals. This geochemical method is most commonly applied to

603 fine-grain siliciclastic lithologies, where the ratios of various mineralogical phases are

604 interpreted to reflect specific and calibrated environmental redox conditions (Canfield et

605 al., 1992; Raiswell and Canfield, 1998; Raiswell et al., 2001; Poulton and Raiswell,

606 2002). On the basis of empirical evidence, Fe_{HR}/Fe_T above 0.38 within fine-grain

607 siliciclastic lithologies indicates sediment accumulation under an anoxic water-column

608   (Raiswell and Canfield, 1998; Raiswell et al., 2001; Poulton and Raiswell, 2002), while

609   Fe_{HR}/Fe_T below a value of ~0.22 is suggestive of oxic conditions (Poulton and Raiswell,

610   2002; Poulton and Canfield, 2011); additionally, in the case of anoxia, Fe_{py}/Fe_{HR}

611   differentiates ferruginous (<0.7-0.8) from euxinic (>0.8) conditions (Anderson and

612   Raiswell, 2004; Poulton et al., 2004; März et al., 2008; Poulton and Canfield, 2011).

613   The Arthur Creek Formation includes a siliciclastic facies (the 'hot shale') that is

614   ideal for iron-based redox proxies (Poulton and Canfield, 2005). Fe_T within the Arthur

615   Creek 'hot shale' ranges up to ~2.7 wt.% (Fig. 6a) and almost all measured highly

616   reactive iron resides in reduced iron minerals (Fig. 6b,c). Fe_{HR}/Fe_T and Fe_{PY}/Fe_{HR}

617   indicate an anoxic, ferruginous redox environment during deposition of the 'hot shale'

618   (Fig. 6a,b). In contrast, strata of the interlaminated siliciclastic shale/siltstone and

619   carbonate calcimudstone facies of the Arthur Creek Formation (directly overlying the

620   'hot shale') contain a lower siliciclastic component, and this requires special attention in

621   interpreting a paleo-redox environment. We note that each iron-speciation sample

622   integrates 3 cm of stratigraphy; therefore, for this lithofacies, our sample preparation

623   method homogenized multiple laminae of pure siliciclastic shale/siltstone and pure

624   carbonate mudstone. Yet, despite the diluting carbonate component, Fe_{HR} is partitioned

625   within this lithofacies in the same proportionality as the 'hot shale' (Fig. 6b,c). In this

626   regard, iron speciation data for this lithofacies of the Arthur Creek Formation are

627   consistent with the anoxic, ferruginous redox environment inferred for the underlying

628   'hot shale'.

629   Strata of the Thorntonia Limestone are composed almost entirely of carbonate,

630   and for this reason we do not to interpret these iron speciation data within the canonical,

631 siliciclastic-derived redox framework. Instead, we emphasize that the black, organic-rich

632 carbonate strata of the middle/upper Thorntonia Limestone (Fig. 2c), biomarker and

633 organic geochemistry of the Thorntonia and Arthur Creek petroleum systems (Boreham

634 and Ambrose, 2005), and trace element data (Supplementary Information) are

635 qualitatively consistent with iron speciation metrics for the Arthur Creek Formation 'hot

636 shale' (Fig. 6) for an anoxic depositional environment during accumulation of the

637 phosphatic middle/upper Thorntonia Limestone. Thus, we conclude that the Fe-oxide

638 bound P shuttle likely augmented organic-bound P delivery to the Thorntonia and Arthur

639 Creek sediment column. Further, if one accepts the sedimentological and geochemical

640 evidence for sediment accumulation under an anoxic, ferruginous water column, this then

641 allows for the possibility that Fe(II)-phosphates provided a second, potentially significant

642 source of P to Thorntonia sediments.

643 Nevertheless, the limited contribution of Fe_{ox} to Fe_{HR} in both the Thorntonia and

644 Arthur Creek (Fig. 5c), the low P_{Fe} values (Fig. 5b), and the present decoupling of P

645 within the Thorntonia from Fe_{HR} phases (Fig. 5g) all suggest that any P delivered to

646 Thorntonia sediments via the Fe-P shuttle must have been subsequently decoupled from

647 iron particles within the sediment column. One way to explain this decoupling is through

648 the reductive dissolution of Fe oxides in anoxic pore-waters. This suggestion is consistent

649 with petrological observations that require wholesale remobilization of P before

650 precipitation within shell interiors (Fig. 3a,b). Thus, the present distribution of P in the

651 Thorntonia Limestone, spatially decoupled from either iron or organic carbon sources,

652 confounds easy attribution to primary source vectors. In the following section we

653 integrate C, Fe, and P geochemical data to explore the relative contribution from organic-

654 bound and iron-bound P delivery sources.

655

656 **Assessing the relative importance of organic-bound versus iron-bound phosphorus**

657 **to authigenic apatite precipitation**

658 To begin, we estimate whether organic matter degradation alone could provide sufficient

659 phosphorus for the observed apatite content in the Thorntonia Limestone. We then

660 quantify how much of this estimated organic carbon must have been lost through

661 remineralization to reconcile the observed wt.% TOC within these strata. To do so, we

662 use a Redfield stoichiometry (Redfield, 1958) to relate the measured sedimentary weight

663 percent phosphorus to the associated flux of organic carbon necessary for this phosphorus

664 delivery. Redfield stoichiometry varies in space and time due to, for instance, taxonomic

665 variability in biomolecular and cellular composition and nutrient availability regulating

666 biosynthetic allocation (e.g., Geider and LaRoche, 2002). Moreover, water-column

667 heterotrophy increases the C:P ratio of particulate organic carbon delivered to the

668 sediment-water interface (Clark et al., 1998). To be conservative, we assume no water-

669 column remineralization and adopt the canonical Redfield ratio (106C:1P) in the

670 calculations below. We also adopt the combined organic-bound and authigenic

671 phosphorus phases determined from the phosphorus speciation extraction as an estimate

672 of the original flux of phosphorus delivered to the sediment via organic matter. This

673 calculation provides a conservative estimate because we neglect iron-adsorbed and

674 carbonate-bound P as potential sources for authigenic apatite (as these can represent

675 primary sources of phosphorus to the sediment column), and we assume no diffusive loss

676 of phosphate from pore-water contemporaneous with sedimentary apatite authigenesis.

677   Following the above arguments, our estimate for the weight percent organic

678 carbon delivered to the sediment column ($\hat{C}_{org}^*$) that can account for the measured

679 phosphorus content is given by:

680 $$\hat{C}_{org}^* = (P_{xl} + P_{org}) \times R \times \left(\frac{\alpha_c}{\alpha_p}\right) \tag{1}$$

681 where R is the adopted Redfield ratio and α_C and α_P represent the molar weights of

682 carbon and phosphorus, respectively (Slomp et al., 2004). We estimate the percentage of

683 organic carbon remineralization necessary to reconcile the difference between the

684 delivery estimate, $\hat{C}_{org}^*$, and the measured wt.% total organic carbon (C_{org}) within

685 Thorntonia and Arthur Creek rocks (Slomp et al., 2004) as:

686 $$\% \; loss \; of \; \hat{C}_{org}^* = \left(\frac{\hat{C}_{org}^* - C_{org}}{\hat{C}_{org}^*}\right) \times 100 \; . \tag{2}$$

687 This value represents an estimate of organic carbon remineralization in the time between

688 delivery to the sediment-water interface and lithification. Applying these equations to

689 samples within the phosphorus-enriched middle and upper Thorntonia yields a median

690 $\hat{C}_{org}^*$ of 18.6 wt.% and a median loss of 97.8% of this estimated delivery flux (Fig. 7). For

691 comparison, applying these equations to samples from the Arthur Creek indicates a

692 median organic carbon loss estimate of 74.0% from a median organic carbon delivery

693 estimate, $\hat{C}_{org}^*$, of only 1.1 wt.% (Fig. 7). If, instead, we consider more typical ratios of

694 $C_{org}:P_{org}$ delivered to the sediment column, that is, C:P >> 106:1 (Ingall et al., 1993; Van

695 Cappellen and Ingall, 1996; Clark et al., 1998; Algeo and Ingall, 2007), then the required

696 C_{org} delivery ($\hat{C}^*_{org}$) and the estimated % $\hat{C}^*_{org}$ loss increase proportionally. Likewise, any

697 diffusive/advective loss of phosphate from the sediment column prior to lithification

698 (Ingall et al., 1993; Slomp et al. 2002; 2004) would increase the requisite $\hat{C}^*_{org}$ and, thus,

699 the inferred % $\hat{C}^*_{org}$ loss.

700   If organic carbon represented the sole delivery source of phosphorus to the

701 sediment column, what would have been the oxidant demand for the organic carbon

702 remineralization estimated above? Dissimilatory microbial metabolisms couple the

703 remineralization of sedimentary organic carbon to the reduction of an oxidant (primarily

704 O_2, NO_3^-, SO_4^{2-}, and Fe^{3+}; Konhauser, 2007). Thus, a portion of the estimated organic

705 carbon loss can be accounted for in the early diagenetic minerals pyrite and siderite,

706 which form from microbial dissimilatory sulfate and ferric iron respiration, respectively.

707 In the following calculations, we assume the stoichiometry of Fe-(oxyhydr)oxide

708 reduction, where one mole of organic carbon is remineralized per four moles of siderite

709 produced:

710         $CH_2O + 8H^+ + 4Fe(OH)_3 \Rightarrow 4Fe^{2+}_{(aq)} + CO_2 + 11H_2O$ (3)

711         $4Fe^{2+}_{(aq)} + 4CO_2 + 4H_2O \Rightarrow 4FeCO_3 + 8H^+,$ (4)
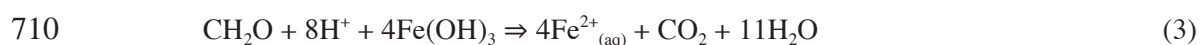
712 and sulfate reduction, where four moles of organic carbon are remineralized per mole of

713 pyrite produced:

714         $4CH_2O + 2SO_4^{2-} \Rightarrow 2H_2S + 4HCO_3^-$ (5)

715         $Fe^{2+}_{(aq)} + 2H_2S \Rightarrow FeS_2 + 4H^+ .$ (6)

716 We note that if Fe^{2+} for pyrite formation were also reduced locally it would require

717 additional C_{org} consumption, akin to Eqn. (3).

718   To correct for the presence of siderite within samples, we relate the measured

719   molar quantity of siderite to the Fe^{3+} respiration stoichiometries of Eqns. 3 and 4 to

720   estimate the necessary weight percent of organic carbon consumed to produce this

721   siderite ($C_{siderite}$):

722    $$C_{siderite} = \left(\frac{\left[measured\ siderite(mol) \times \left(\frac{1\ mol\ C_{org}}{4\ mol\ siderite} \right) \right] \times \gamma}{sample\ weight\ (g)} \right) \times 100 \qquad (7)$$

723   where γ converts measured values in moles to wt.%. Likewise, to correct for the presence

724   of pyrite, we relate the measured molar quantity of pyrite within each sample to the

725   stoichiometry of SO_4^{2-} respiration (Eqns. 5 and 6) in order to estimate the weight percent

726   of organic carbon remineralized to produce this pyrite (C_{pyrite}):

727    $$C_{pyrite} = \left(\frac{\left[measured\ pyrite\ (mol) \times \left(\frac{4\ mol\ C_{org}}{1\ mol\ pyrite} \right) \right] \times \gamma}{sample\ weight\ (g)} \right) \times 100 \quad . \qquad (8)$$

728   Equation (8) does not account for any C_{org} consumed to reduce iron for pyrite (e.g., Eqn.

729   3). In this regard, Eqns. 8 and 9 conservatively underestimate the weight percent of

730   organic carbon remineralized to form pyrite for the case that iron was reduced locally,

731   rather than sourced as Fe^{2+}.

732   With these estimates, we augment Eqn. (2) as:

733    $$\left(\frac{\hat{C}_{org}^* - \left(C_{org} + C_{pyrite} + C_{siderite} \right)}{\hat{C}_{org}^*} \right) \times 100 \quad . \qquad (9)$$

734   This exercise yields a corrected median % $\hat{C}_{org}^*$ loss for the middle and upper Thorntonia

735   members of 96.2%, not significantly different than the estimate from Eqn. 2 (Fig. 7). In

736   contrast, and with the exception of phosphorus-enriched samples in the uppermost

737   measured meters, the corrected median loss for the Arthur Creek indicates that there is an

738 excess wt.% of organic carbon to account for the observed wt.% phosphorus (Fig. 7).

739 However, the observed quantity of siderite within Thorntonia and Arthur Creek samples

740 may represent a late diagenetic addition to the sediment column and, thus, may not have

741 formed through local iron respiration consuming C_{org}. If this were the case, the % C_{org}

742 loss would be less than the value estimated by Eqn. (9), and closer to the value

743 determined by Eqn. (2).

744   With sulfate and ferric iron accounted for, the only quantitatively important

745 remaining oxidant is molecular oxygen (Konhauser, 2007). In this regard, and if the

746 above assumptions hold, the implication is that the majority of the hypothesized organic

747 carbon loss was through respiration using molecular oxygen. We define a ratio of the

748 estimate of organic matter consumed through anoxic respiration (that is, with Fe^{3+} and

749 SO_4^{2-}: $C_{siderite}$ and C_{pyrite}, respectively) to the estimate of C_{org} loss not accounted for by

750 this estimated anoxic remineralization. We calculate the ratio of anoxic to oxic

751 respiration as:

752 $$\frac{anoxic}{oxic}\ respiration = \frac{C_{pyrite}+C_{siderite}}{\hat{C}^*_{org} -(C_{org}+ C_{pyrite}+C_{siderite})} \ . \qquad (10)$$

753 In solving Eqn. (10), we obtain a median (1st, 3rd quartile) value of 0.02 (0.1, 0.4) for the

754 middle and upper Thorntonia members. This is to say that a median 2% of the estimated

755 organic carbon delivery required to source the observed phosphorus content was

756 remineralized through anoxic pathways—98% must have been remineralized with

757 molecular oxygen to explain the absence of this organic carbon from measured samples.

758 If, however, one assumes a diffusive loss of either sulfide or ferrous iron from the

759 sediment column (i.e., the numerator underestimates the organic carbon consumed by

760 anoxic remineralization), the estimated percent of anoxic remineralization becomes a

761   minimum. If such diffusive loss occurred, then the proportion of C_{org} remineralized

762   through oxic respiration would be less than 98% and approach 0% as the sedimentary

763   production of sulfide and/or Fe^{2+} through microbial dissimilatory redox reactions

764   quantitatively consumed $\hat{C}^*_{org}$. While we cannot determine the diffusive flux of

765   reductants from Thorntonia or Arthur Creek sediments based on preserved geochemical

766   signals, we note that such a diffusive loss would be possible if the redox boundary

767   resided within the water column.

768   The calculated weight percent organic carbon required to deliver the observed

769   phosphorus is notable; the median value, 18.6 wt.%, exceeds organic carbon export to the

770   sea floor in most modern marine environments (Hedges and Keil, 1995). While such low

771   organic carbon preservation efficiencies (or, as we describe, high % $\hat{C}^*_{org}$ loss estimates)

772   commonly occur within modern marine environments, they typify depositional

773   environments with low sediment accumulation rates (< ~0.02 cm/yr) or oxygenated shelf

774   settings (> 20 μM bottom-water O_2; Canfield, 1994; Hedges and Keil, 1995). While we

775   cannot provide unequivocal evidence that substantial aerobic carbon respiration did not

776   consume most of the C_{org} originally delivered to the Thorntonia sediment column, we

777   find it difficult to reconcile how such substantial aerobic respiration could have

778   proceeded without concurrently driving the sediment column anoxic, providing a

779   negative feedback on the efficiency of organic carbon respiration. Moreover, we note that

780   the oxidant demand to remineralize this magnitude of organic carbon is difficult to

781   reconcile with Cambrian oxygen levels, perhaps 15 – 50% present atmospheric

782   concentrations (Dahl et al., 2010; Bergman et al., 2004; for alternative views, see Berner,

783   2006; Garrels and Lerman, 1984). Nevertheless, it remains a possibility that episodes of

784 intense aerobic respiration—and efficient capture of released P within authigenic

785 phases—account for Thorntonia Limestone phosphatic carbonate precipitation (although

786 see Föllmi et al. (2005) for discussion of a Miocene phosphogenic episode in which P

787 sourced from aerobic respiration was ruled out). If, however, one accepts the conclusion

788 that organic burial alone does not provide an adequate source of phosphorus to the

789 sediment column, then an additional source of P must have been present during

790 Thorntonia deposition.

791   Phosphorus adsorbed onto and/or co-precipitated with metal oxide particles

792 provides a second potential source of P to the sediment column whose importance

793 depends, in part, on the magnitude of the flux of metal oxides to the sediment column

794 (Shaffer, 1986; Feely et al., 1990; Feely et al., 1998; Poulton and Canfield, 2006).

795 Accordingly, we estimate phosphorus delivery under the assumption of an appreciable

796 iron-bound P flux, for simplicity based entirely on P adsorbed to iron (oxyhydr)oxides.

797 This assumption is consistent with the order-of-magnitude calculations presented above;

798 nonetheless, we acknowledge that other metal oxides, particularly manganese, play an

799 important role in the cycling of phosphorus (e.g., Dellwig et al., 2010).

800   Ideally, iron-speciation measurements could provide the basis for a quantitative

801 estimate of Fe-bound P delivered to the sediment column. But before we can perform

802 such a calculation, we ask whether the Fe_{ox}, Fe_{mag}, Fe_{carb}, and Fe_{py} pools as determined by

803 iron speciation in carbonate-rich strata of the Thorntonia Limestone and Arthur Creek

804 Formation reflect primary depositional reservoirs, or if post-depositional diagenesis could

805 have converted iron into, out of, or between these phases of the highly reactive iron pool?

806 Specifically, if these lithologies experienced closed system (with respect to mass)

807   diagenetic remobilization of Fe, then it is likely that appreciable amounts of Fe were

808   transferred between highly reactive iron phases (e.g., the formation of Fe_{carb} and Fe_{py}

809   through the reduction of an Fe_{ox} precursor phase). In this regard, the value for Fe_{HR} would

810   still accurately represent the primary iron pool—and could thus be used in calculations of

811   Fe-bound P delivery—however calculations involving any individual Fe_{HR} phase (e.g.,

812   Fe_{ox}, Fe_{carb}) would not provide robust estimates of Fe-bound P. Alternatively, if these

813   lithologies underwent open system diagenesis, the resulting addition or loss of Fe from

814   the Fe_{HR} pool (from any and/or all constituent phases) would render *any* calculation based

815   on the iron speciation data suspect. While we cannot eliminate the possibility of Fe

816   addition during open system diagenesis, we note that Fe-speciation data for the

817   Thorntonia Limestone and Arthur Creek Formation are consistent with other redox

818   proxies (see above) favoring the view that the highly reactive iron species to these rocks

819   record a substantial depositional flux.

820   In the following discussion we provide a methodology to address the potential

821   contribution of the Fe-P shuttle to Thorntonia and Arthur Creek sediments under the

822   assumption of limited or closed system iron diagenesis. To this end, we employ iron

823   speciation data from these lithologies for illustrative calculations. These calculations

824   provide a consistency argument given that organic-bound P was likely insufficient to

825   account for the measured P content. Throughout this discussion, we introduce and

826   emphasize the caveats inherent to the use of a diagenetically mobile element in these

827   calculations.

828   The molar ratio of the co-precipitation of phosphorus onto iron (oxyhydr)oxide

829   particles conforms to a distribution coefficient (K_D) model that scales linearly to the

830   ambient seawater phosphate concentration ([P_{sw}]) (Feely et al., 1991; 1998; Konhauser et

831   al., 2007):

832   $$\left(\frac{P}{Fe}\right)_{molar} = K_D \times [P_{SW}].$$ (11)

833   Thus, to estimate the delivery of iron-bound phosphorus, $\hat{P}_{Fe}^*$, we multiply an estimate of

834   iron oxide delivery ($\hat{F}e_{ox}^*$) by the adsorption coefficient of phosphorus to iron oxides

835   (K_D) for a given estimate of seawater phosphate concentration ([P_{sw}]):

836   $$\hat{P}_{Fe}^* = \gamma \hat{F}e_{ox}^* \times K_D \times [P_{SW}]$$ (12)

837   where γ converts measured values (in wt.%) to moles as required in the definition of the

838   adsorption coefficient. Within anoxic pore-waters, a fraction of the iron oxides delivered

839   to the sediment column will be reduced by dissimilatory iron reduction and converted to

840   ferrous iron, and these ions will either precipitate as pyrite or iron carbonate, or

841   advect/diffuse to the overlying water column. Accordingly, a full accounting of $\hat{F}e_{ox}^*$

842   would include all of these conservation and loss terms. The estimate would become a

843   lower bound on $\hat{P}_{Fe}^*$ if we ignored the ferrous iron loss flux, which in any event is

844   unconstrained, and included only the measured iron oxide (Fe_{ox}), pyrite (Fe_{py}) and iron-

845   carbonate phases (Fe_{carb}). We note, however, that at least some of the measured Fe (most

846   obviously the Fe_{carb} phase) may have originated from diagenetic remobilization of iron to

847   these carbonates. (For the lower Thorntonia Limestone, Fe_{carb} comprises a median (1st, 3rd

848   quartile) of 76.8 % (71.3, 81.8) of the total iron pool; in contrast, for the phosphatic

849   middle/upper Thorntonia and for the Arthur Creek Formation, Fe_{carb} accounts for only

850 28.7 % (22.3, 33,2) and 20 % (15.15, 23.5) of Fe_T, respectively.) In this regard, this

851 calculation may overestimate $\hat{P}_{Fe}^*$.

852   Magnetite may form through the reductive dissolution of mixed ferrous–ferric

853 oxide phases (e.g., Zegeye et al., 2012), and, as such, could be considered in the

854 summation of primary iron oxide minerals ($\hat{Fe}_{ox}^*$); however, magnetite may also form

855 during prograde metamorphism, in which case inclusion of this phase would over-

856 estimate the primary ferric iron flux to the sediment column. We include Fe_{mag} within our

857 calculation because the authigenic pathway likely exceeds weathering and metamorphic

858 overprints for this depositional environment. (Regardless, within NTGS 99/1 magnetite

859 represents a negligible component of Fe_T, therefore this assumption does not alter the

860 illustrative estimate for $\hat{P}_{Fe}^*$.) Therefore, we rewrite Eqn (12) in the approximate form:

861
$$\hat{P}_{Fe}^* = \gamma\left(Fe_{ox} + Fe_{py} + Fe_{carb} + Fe_{mag}\right) \times K_D \times [P_{SW}] . \qquad (13)$$

862   A host of seawater ions—notably silica, trace metals and rare earth elements—

863 compete with phosphorus for adsorption sites on the surface of iron oxide particles (e.g.,

864 Berner, 1973; Trocine and Trefry, 1988; Olivarez and Owen, 1989; Trefry and Metz,

865 1989; Feely et al., 1991; Feely et al., 1998; German et al., 1990; Konhauser et al., 2007).

866 Thus, the choice of K_D depends on the assumption of the seawater composition of

867 Cambrian oceans. As these element concentrations are broadly unknown for the

868 Paleozoic Era, we focus here only on the role of the major seawater constituent dissolved

869 silica in competition for iron-surface anion sites. Following Siever's (1992) inference of

870 cristobalite saturation for early Phanerozoic seawater ($[Si_{SW}] = 0.67$ mM), Konhauser et

871 al. (2007) determined experimentally a $K_D = 0.0108$ for ferrihydrite at this silica

872 saturation state. Notably, the linear range of the K_D model depends on the phosphorus

873   concentration of ambient seawater. At cristobalite saturation, the linearity of the K_D

874   model saturates above ~5 μM [P_{sw}]. This is to say that the co-precipitation and delivery of

875   phosphorus bound to iron oxides remains constant at and above this ambient seawater

876   phosphate concentration.

877   Hence, we adopt [P_{sw}] = 5 μM to calculate a maximum estimate for $\hat{P}^*_{Fe}$ at the

878   adopted [Si_{SW}]. We emphasize that the chosen value of 5 μM is a simplistic assumption

879   and that water column phosphorus concentrations are affected by variable environmental

880   factors that are difficult to generalize, even under well-constrained modern conditions.

881   Nevertheless, this adopted phosphate concentration is consistent with modern anoxic

882   environments, including the Black Sea and Cariaco Basin (Shaffer, 1986; Scranton et al.,

883   2006). For example, in the Black Sea, higher phosphate concentrations in the ferruginous

884   chemocline than in the underlying sulfidic waters result from the dissolution of settling

885   Fe-oxides and the release of adsorbed phosphate (Brewer and Murray, 1973). Similar

886   processes are suggested to explain the phosphate concentrations (up to 9 μM dissolved P)

887   in the ferruginous Lake Matano (Crowe et al., 2008) where the release of Fe(III)-bound P

888   at the chemocline is balanced by the precipitation of Fe(II)-phosphates below the

889   chemocline.

890   Applying Eqn. (13) to samples from the middle and upper Thorntonia members

891   yields a median estimate for iron-bound P of 0.1 wt.% as compared to a median estimate

892   of 0.2 wt.% for the Arthur Creek (Fig. 7). In this formulation, phosphorus delivery by

893   iron oxides is proportional to the highly reactive iron phases (Fe_{HR}) determined from iron

894   speciation geochemistry. While Fe_{HR}/Fe_T decreases between the P-enriched middle /

895   upper Thorntonia members and the Arthur Creek, the observed increase in Fe_T within the

896　Arthur Creek compensates such that the molar estimate of $\hat{Fe}_{ox}^{*}$, and, thus, $\hat{P}_{Fe}^{*}$ remains

897　roughly constant between the two formations. As such, and if the above assumptions

898　hold, this implies that the relative contribution of the Fe-P shuttle to the observed weight

899　percent sedimentary P was much greater during deposition of the Arthur Creek Formation

900　because of the lower wt.% P_T measured throughout this formation. Indeed, the median

901　estimate of $\hat{P}_{Fe}^{*}$ = 0.2 wt.% for the Arthur Creek greatly exceeds the median measured P_T

902　(0.03 wt.%; Fig. 7). In contrast, the median estimate of $\hat{P}_{Fe}^{*}$ = 0.1 wt.% for the middle and

903　upper Thorntonia members provides only ~10% of the median measured P_T (0.98 wt.%;

904　Fig. 7), and proportionally less for samples with the highest measured P_T approaching 4

905　wt.%. Likewise, any diffusive loss of P from the sediment column prior to lithification

906　would increase the requisite $\hat{P}_{Fe}^{*}$ and, in the case of the Thorntonia, increase the

907　deficiency between the observed P_T and P hypothesized to have been delivered associated

908　with Fe_{ox} ($\hat{P}_{Fe}^{*}$).

909　　　The formulation of our equations may significantly overestimate Fe-bound P

910　delivery for two reasons. First, our calculations adopt a K_D value based on an estimate of

911　contemporaneous seawater silica concentrations. Second, our calculations adopt a

912　seawater phosphate concentration that maximizes the potential for phosphorus delivery

913　by the iron shuttle. If we presumed a higher seawater silica concentration (that is,

914　decreased K_D), or if, for an assumed [Si_{SW}], we also assumed a lower [P_{SW}], then we

915　would calculate a lower P delivery flux per unit Fe_{ox}. Thus, both of these changes would

916　yield a lower estimate of $\hat{P}_{Fe}^{*}$ for a given iron flux to the sediment column.

917   Some iron minerals are more effective P delivery shuttles than others. The

918   capacity for iron minerals to scavenge and deliver phosphorus to the sea floor depends on

919   a number of factors, including the surface density of adsorption sites, which in part is

920   related to mineral surface area. In this regard, amorphous to poorly crystalline phases will

921   scavenge more phosphate than highly crystalline phases. (We note, however, that

922   progressive crystallization may result in the subsequent desorption of P from adsorption

923   sites. If this desorption occurs within the sediment column, outside the length-scales of

924   advection/diffusion with the overlying water-column, Fe-bound P could provide a

925   significant source of P to the sediment column.) Here we assumed ferrihydrite as the

926   carrier phase (Konhauser et al., 2007), however, a range of other iron minerals form

927   during anaerobic Fe^{2+} oxidation (e.g., Kappler and Newman, 2004; Zegeye et al., 2012).

928   For instance, in the only detailed study of Fe mineralogy in a ferruginous water column

929   (Lake Matano, Indonesia), Zegeye et al. (2012) found that ferrihydrite was quantitatively

930   transformed to carbonated green rust ('fougerite') during settling through the water

931   column, with more minor formation of magnetite. Unfortunately, no experimental data

932   currently exist for P adsorption to green rust under the chemical conditions likely

933   encountered in Cambrian oceans (e.g., Lake Matano has relatively low [Si]). However,

934   adsorption of oxyanions to green rust tends to be far higher than for ferrihydrite (Randall

935   et al., 2001), and thus such a finding highlights the need to consider multiple and varied

936   carrier phases for the ancient Fe-P shuttle. An iron carrier phase with an adsorption

937   coefficient (K_D) with respect to P greater than ferrihydrite could have delivered more P to

938   Thorntonia sediments for a given iron flux to the sea floor.

939   Are there other scenarios in which the delivery of Fe-bound P could have been

940   greater than that inferred from the formulations of equations 11 through 13? To answer

941   this question it is necessary to address whether the measured Fe_{HR} is an accurate proxy

942   for the contribution of Fe_{ox} to the sediment column, or whether it could underestimate the

943   original Fe_{ox} flux ($\hat{F}e_{ox}^{*}$), and, thus, $\hat{P}_{Fe}^{*}$ to the sediment column. Next, we explore

944   hypothetical redox scenarios in which Fe-bound P could contribute more substantially to

945   authigenic apatite. Without an independent line of evidence that the constituent phases of

946   the highly reactive iron pool represent the primary fluxes of iron to the sediment column,

947   we choose not to advocate for this possibility for the Thorntonia Limestone.

948   Nevertheless, with regard to the broader question of the mechanism for phosphatic

949   carbonate deposition, we find it informative to evaluate the circumstances in which the

950   Fe-bound delivery shuttle could contribute substantially to phosphogenesis and

951   phosphatic carbonate deposition.

952   One can envision a spectrum of scenarios for the relative magnitudes of Fe_{ox}

953   delivery to and Fe^{2+} loss from the sediment column. These scenarios fall within three

954   generalized categories: Fe_{ox} delivery (1) greater than, (2) nearly equal to, or (3) less than

955   Fe^{2+} diffusive/advective loss. In the following discussion we discount scenario (3)

956   because such an imbalance defines an unsustainable Fe cycle. To begin, we consider the

957   scenario that (1) Fe_{ox} delivery exceeds Fe^{2+} loss. This can result from two opposing redox

958   regimes. (1a) If the majority of Fe_{ox} delivered to the sediment column were stabilized

959   within oxygenated pore-water then this would preclude widespread iron reduction. In this

960   instance, only a small amount P would be liberated from the Fe_{ox} delivery shuttle, and

961   Fe_{ox} would dominate Fe_{HR}. (1b) Alternatively, if sedimentary electron donors (e.g., C_{org})

962   contributed to pore-water anoxia, some fraction of the delivered Fe_{ox} would be reduced to

963   Fe^{2+}, and any P bound to these Fe_{ox} particles would be released to pore-waters. To

964   maintain the low Fe^{2+} loss fraction defining this scenario, any Fe^{2+} ions produced must be

965   captured quantitatively within authigenic ferrous iron minerals. In this instance,

966   sedimentary Fe would be partitioned amongst Fe_{ox}, Fe_{carb}, and Fe_{py} phases, and the

967   dominance of the latter two minerals would imply that much of the original Fe_{ox} flux was

968   reduced. Notably, with regard to P delivery, either scenario for high Fe_{ox} delivery relative

969   to Fe^{2+} loss predicts that the measurement of sedimentary Fe_{HR} represents a close

970   approximation of the magnitude of P delivery associated with the Fe-P shuttle ($\hat{P}_{Fe}^{*}$). If,

971   for example, the Fe cycle were operating in this manner at the time of deposition of the

972   middle and upper Thorntonia members then, under the above assumptions, the Fe-shuttle

973   would be constrained to have contributed a median of ~10% P_T (as determined from Eqn.

974   13) and, therefore, could not represent a dominant source of P for the observed

975   enrichment.

976   If scenarios 1a and 1b cannot source significant amounts of Fe-bound P to

977   phosphatic lithologies, can scenario 2? Like scenario (1b) above, scenario (2) necessitates

978   a redox environment that facilitates the reductive dissolution of the majority of Fe_{ox}

979   delivered to the sediment column, regardless of the size of this flux. In contrast, scenario

980   (2) is distinguished from scenario (1) by the condition that the majority of the

981   sedimentary Fe^{2+} produced must escape to the overlying water column, resulting in less

982   capture of Fe^{2+} ions in authigenic minerals. Such diffusive loss requires anoxia within the

983   water-mass overlying the sediment column. As above, Fe retained within the sediment

984   can reside in any combination of Fe_{ox}, Fe_{carb}, and/or Fe_{py} phases. Notably, Scenario (2)

985   allows for the measured Fe$_{HR}$ value to significantly underestimate iron oxide delivery to

986   the sea floor ($\hat{Fe}^*_{ox}$) and, therefore, to underestimate the Fe-P shuttle ($\hat{P}^*_{Fe}$). If, for

987   example, the Fe cycle were operating with an extensive benthic flux of Fe^{2+} to the water

988   column during deposition of the middle Thorntonia Limestone, and if a mechanism

989   existed to preferentially retain the delivered P, then the Fe-P shuttle could have provided

990   a significant proportion of the observed P to these phosphatic strata, that is, greater than

991   the ~10% estimated from Eqn. (13).

992   In summary, simple models of Fe-bound P delivery estimates ($\hat{P}^*_{Fe}$), as determined

993   from Eqn. (13), indicate that this delivery shuttle could have sourced the measured P

994   content of the Arthur Creek Formation. In contrast, our estimates of Fe-bound P can only

995   account for a median of 10% of the P content the Thorntonia Limestone. (This estimate

996   assumes that Fe$_{HR}$ in Thorntonia rocks reflects deposition from the water column. To the

997   extent that Thorntonia iron minerals reflect open-system diagenesis, this estimate would

998   be even lower.) Only by invoking a major diffusive loss of iron from the Thorntonia

999   sediment column with subsequent capture of delivered P within authigenic phases—a

1000   scenario for which we do not advocate, yet do not find inconsistent with the assumption

1001   of limited diagenesis—could Fe-bound P have provided a more substantial contribution

1002   to phosphatic carbonates of the Thorntonia Limestone.

1003

1004   **CONCLUSIONS**

1005   Within drill core NTGS 99/1, phosphorus enrichment is confined to the middle

1006   and upper members of the Thorntonia Limestone, and petrographic observations reveal

1007   that this enrichment reflects authigenic apatite mineral nucleation primarily associated

1008   with the interior of bioclasts and, more rarely, as cement in bioclastic grainstone. Under

1009   the canonical model that phosphorus bound within organic matter represents the only

1010   significant delivery flux of phosphorus to the sediment column, molar $C_{org}:P_T$ well below

1011   the Redfield ratio requires significant C_{org} loss or a second delivery source of phosphorus

1012   to Thorntonia sediments.

1013   Interpreted together, sedimentological observations and iron speciation data

1014   suggest that sediment within the southern Georgina Basin accumulated under anoxic,

1015   ferruginous conditions. This redox diagnosis is consistent with previous research

1016   documenting the propensity for anoxic, ferruginous conditions in subsurface water

1017   masses of late Neoproterozoic and Cambrian oceans (Canfield et al., 2008) driven by the

1018   relative fluxes of electron donors (organic carbon) and electron acceptors (reactive Fe,

1019   sulfate) into a basin (Johnston et al., 2010). If correct, the conclusion of an active iron

1020   redox cycle contemporaneous with the deposition of the Thorntonia Limestone and

1021   Arthur Creek Formation provides a second mechanism for augmented sedimentary

1022   phosphorus delivery—phosphorus adsorbed to particulate iron minerals.

1023   The stoichiometries of delivery estimates and remineralization reactions indicate

1024   that the phosphorus content of the Arthur Creek Formation is easily accounted for by any

1025   combination of phosphorus associated with organic matter and/or iron oxide fluxes.

1026   However, the observed phosphorus content of the Thorntonia is difficult to reconcile with

1027   reasonable fluxes of either organic-bound or iron-bound phosphorus alone. Thus, we

1028   suggest that both sources were necessary to account for Thorntonia Limestone phosphatic

1029   carbonate deposition.

1030   The discontinuous nature of phosphorite and phosphatic carbonate through Earth

1031   history speaks to discontinuous mechanisms of formation. We hypothesize that redox-

1032   mediated phosphorus delivery via the Fe-P shuttle, rather than a discontinuous organic

1033   carbon flux, provides the more intermittent mechanism for phosphorus delivery to the

1034   sediment column. That said, ferruginous bottom waters appear to have been widespread

1035   in Proterozoic oceans, whereas phosphatic carbonates are not. Thus, the episodic nature

1036   of phosphate deposition must additionally depend on the fate of phosphate after it enters

1037   the sediment column. Where the oxic-anoxic interface lies well within the water column,

1038   microbial reduction of ferric iron within the sediments will remobilize P, with a high

1039   probability of escape back to the water column. Where phosphate in solution is trapped

1040   by skeletons, however, or bound to decay-resistant materials such as chitinous

1041   exoskeletons, mineral phosphate may be reprecipitated in sediments. With this in mind,

1042   it would appear that delivery mechanisms, post-delivery fate within sediments, and

1043   evolution all contributed to the observed geological record of Cambrian phosphate

1044   accumulation.

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1517 **Figure captions:**

1518 **Figure 1: (A)** Areal extent of the constituent basins of the Neoproterozoic Centralian

1519 Superbasin. The black dot marks the drill locality for core NTGS 99/1 in the southern

1520 Georgina Basin. **(B)** Chronostratigraphy and lithostratigraphic nomenclature for the

1521 Northern Territory outcroppings of Cambrian strata within the southern Georgina Basin

1522 (modified from Dunster et al., 2007). The symbol "(?)" reflects uncertainties in

1523 correlating regional Australian trilobite Zones with International Cambrian System

1524 designations.

1525

1526 **Figure 2:** Lithofacies of the Thorntonia Limestone and Arthur Creek Formation in NTGS

1527 99/1. **(A)** Sandy dolostone of the lower Thorntonia Limestone, just above the contact

1528 with the underlying Paleoproterozoic granite basement (~595.8 – 595.6 mcd). **(B)**

1529 General character of the mottled-to-stylonodular, dolomitic lower Thorntonia Limestone

1530 (584 – 580.5 mcd). **(C)** Characteristic meter to sub-meter scale lithologic alternations and

1531 color variation within limestone of the middle Thorntonia Limestone (577.7 – 571.4

1532 mcd). (1) Denotes black and dark gray calcimudstone; (2) denotes lighter gray

1533 calcimudstone, wackestone and packstone; and (3) denotes limestone grainstone. Note

1534 the general up-package coarsening and lightening, often without cyclic or predictable

1535 variation. **(D)** Bioclastic grainstone to mudstone transition from 570.15 – 570.05 mcd

1536 (middle Thorntonia Limestone; all limestone). **(E)** Appearance of the vuggy, bioclastic

1537 dolomitic grainstone of the upper Thorntonia Limestone (left) and the overlying basal

1538 'hot shale' of the lower Arthur Creek Formation (right). Contact at 554.7 mcd. **(F)** The

1539 laminated siliciclastic shale/siltstone and calcimudstone facies of the lower Arthur Creek

1540 Formation. **(G)** Light-gray early diagenetic nodule (calcimudstone) displacing dark-gray

1541 laminations within the lower Arthur Creek Formation at 532.8 – 532.65 mcd (arrows

1542 mark the exterior of the nodule). **(H)** General appearance of the interbedded siliciclastic

1543 mudstone/siltstone and calcimudstone (neomorphosed to microspar) facies of the lower

1544 Arthur Creek Formation above ~430 mcd.

1545

1546 **Figure 3:** Photomicrographs under plane-polarized light of authigenic apatite distribution

1547 within the middle Thorntonia Limestone. **(A)** A limestone packstone with apatite

replacement specifically targeting the interior of conical small shelly fossil elements at 570.35 mcd. **(B)** Wholesale matrix and grain phosphatization at of a limestone at 575.17 mcd. **(C)** Dispersed, allochthonous grains of authigenic apatite within a limestone at 560.69 mcd (see text for discussion of origin).

Figure 4: Lithology and stable isotope chemostratigraphy of the Thorntonia Limestone and lower Arthur Creek Formation within drill core NTGS 99/1. For all panels, data for the lower and middle/upper Thorntonia Limestone are plotted in open and solid blue circles, respectively, while data for the Arthur Creek Formation are plotted in solid red circles. **(A)** Generalized stratigraphic column depicting the lithology of the lower, middle, and upper Thorntonia Limestone and the lower Arthur Creek Formation. Lithologic abbreviations: Siliciclastics: slts = siltstone; Carbonates: mds = mudstone; wks = wackestone; pks = packstone; grn = grainstone. Vertical axis reflects meters core depth from the surface. **(B)** Carbonate carbon isotopic composition (relative to V-PDB). **(C)** Carbonate oxygen isotopic composition (relative to V-PDB). **(D)** Total organic carbon isotopic composition (symbol size scaled to wt.% total organic carbon (TOC)). **(E)** Cross-plot of carbonate carbon and carbonate oxygen isotopic composition. **(F)** Cross-plot of organic carbon and carbonate carbon isotopic composition.

Figure 5: Phosphorus and iron speciation geochemistry, molar C:P ratios, and correlations between P and other geochemical metrics within the Thorntonia Limestone and Arthur Creek Formation. **(A)** The weight percent of total phosphorus (filled green circles) and subtotal phosphorus (open green circles) for those samples whose P_{Fe} concentrations were not determined from P-speciation geochemistry. Weight percent total Fe (open red circles) from Fe-speciation geochemistry. Note the logarithmic scale to emphasize, in particular, the P content of the middle and upper Thorntonia Limestone. **(B)** The weight percents of operationally-defined phosphorus phases as determined by phosphorus-speciation geochemistry. Note the logarithmic scale. See text for discussion of the operationally-defined P phases. **(C)** The weight percents of iron phases as determined by iron-speciation geochemistry. Note the logarithmic scale. **(D)** The molar ratio of organic carbon to total phosphorus. Grey line intersects the axis at C:P = 106:1,

1579   the canonical Redfield ratio. **(E)** Correlation between the weight percent phosphorus

1580   within individual samples as determined from ICP-AES versus that determined by the

1581   sequential extraction method (see Methods section). Slope of linear regression = 1.1; R^2 =

1582   0.88. **(F)** Correlation between the zirconium to aluminum ratio (ppm/%) and the

1583   operationally-defined P_{xl} phase (see text for discussion) determined from phosphorus

1584   speciation geochemistry. **(G)** Cross-plot of the weight percent of highly reactive iron

1585   species (Fe_{HR}; oxides, magnetite, pyrite, and iron carbonates) determined from iron-

1586   speciation geochemistry versus the weight percent of total phosphorus determined from

1587   phosphorous-speciation geochemistry.

1588

1589   **Figure 6:** Iron-speciation geochemistry. For all panels, data for the lower and

1590   middle/upper Thorntonia Limestone are plotted in open and solid blue circles,

1591   respectively, while data for the laminated facies and interbedded siliciclastic/carbonate

1592   mudstone facies of the Arthur Creek Formation are plotted in solid and open red circles,

1593   respectively. Data from the Arthur Creek 'hot shale' appear as solid red circles with a

1594   black outline. **(A)** A cross-plot of the weight percent total iron (Fe_T) versus the weight

1595   percent iron within highly reactive phases (Fe_{HR}; oxides, magnetite, pyrite, and iron

1596   carbonates). We plot slopes of 1 and 0.38 as a reference for comparing these carbonate

1597   data to previously published iron-speciation data, but we do not advocate interpreting

1598   carbonate data (blue circles) within the canonical siliciclastic framework. Slope of

1599   regressions (not plotted) reflect the percentage of the total iron residing in highly reactive

1600   phases (lower Thorntonia = 57%, R^2: 0.53; middle/upper Thorntonia = 89%, R^2: 0.95;

1601   laminated facies of the Arthur Creek = 53%, R^2: 0.44; interbedded siliciclastic shale /

1602   siltstone and carbonate mudstone facies of the Arthur Creek = 26%, R^2: 0.90). **(B)** A

1603   cross-plot of the weight percent highly reactive iron (Fe_{HR}) versus the weight percent iron

1604   within pyrite (Fe_{py}). We plot slopes of 1 and 0.8 for reference (see (a)). Slope of

1605   regressions (not plotted) reflect the percentage of the highly reactive iron residing within

1606   pyrite (lower Thorntonia = 17%, R^2: 0.07; middle/upper Thorntonia = 64%, R^2: 0.95;

1607   laminated facies of the Arthur Creek = 75%, R^2: 0.95; interbedded siliciclastic shale /

1608   siltstone and carbonate mudstone facies of the Arthur Creek = 30%, R^2: 0.50). We note

1609   that the linear regression for the 'hot shale' ($Fe_{py} = 0.8*(Fe_{HR})-0.2$) is the same for the

1610   lower Arthur Creek laminated facies exclusive of the 'hot shale' data. **(C)** A cross-plot of

1611   the weight percent highly reactive iron (Fe_{HR}) versus iron carbonate (Fe_{carb}). Slope of

1612   regressions (not plotted) reflect the percentage of the highly reactive iron residing within

1613   iron carbonate (lower Thorntonia = 82%, R^2: 0.62; middle/upper Thorntonia = 31%, R^2:

1614   0.82; laminated facies of the Arthur Creek = 25%, R^2: 0.68; interbedded siliciclastic shale

1615   / siltstone and carbonate mudstone facies of the Arthur Creek = 52%, R^2: 0.73). We note

1616   that the linear regression for the 'hot shale' ($Fe_{carb} = 0.25*(Fe_{HR})+0.15$) is similar for the

1617   lower Arthur Creek laminated facies exclusive of the 'hot shale' data ($Fe_{carb} =$

1618 $0.20*(Fe_{HR})+0.15$).

1619

1620   **Figure 7:** Assessing the potential contribution of organic-bound and iron-bound

1621   phosphorus (P) to authigenic apatite precipitation. For the case of organic-bound P

1622   delivery (left), the dashed boxes depict the median estimated weight percent organic

1623   matter (wt.% $\hat{C}_{org}^*$) necessary to account for the measured wt.% sedimentary P based on

1624   equation (1) with a Redfield ratio of 106C:1P. Dark grey boxes represent the median

1625   wt.% total organic carbon (TOC) measured within samples. Light gray boxes represent

1626   the corrected wt.% $\hat{C}_{org}^*$ (see discussion leading to equation (9)). All values plotted to

1627   scale. Organic carbon delivery can account for all of the P within the Arthur Creek

1628   Formation. In contrast, the blank area within the dashed Thorntonia Limestone box

1629   represents the amount of $\hat{C}_{org}^*$ that would have to have been remineralized to account for

1630   the observed sedimentary P content if it were sourced by organic-bound P alone.

1631   For the case of iron-bound P delivery (right), the dashed boxes depict the median

1632   measured wt.% P_T within samples while the dark grey boxes represent the estimated

1633   delivery of iron-bound P ($\hat{P}_{Fe}^*$) as determined from equation (13) assuming a partition

1634   coefficient for ferrihydrite and a seawater phosphate concentration of 5 μm (see text for

1635   discussion). All values plotted to scale. In this regard, and under these assumptions, the

1636   Fe-P delivery shuttle can account for all of the P within the Arthur Creek Formation. In

1637   contrast, only by invoking Fe^{2+} loss from the sediment column and preferential capture of

1638   Fe-bound P within authigenic phases, could the Fe-P shuttle have contributed more

1639   substantially (> ~10%) to the phosphatic carbonate of the Thorntonia Limestone.

a

Georgina

NTGS 99/1

Ngalia

Amadeus

Officer

b

Arrinthrunga Formation	Series 3, Guzhangian – Furongian, Paibian
Steamboat Sandstone	
Arthur Creek Formation	Series 3, Stage 5 (?) – Series 3, Guzhangian
Thorntonia Limestone	Series 2, Stage 4 – Series 3, Stage 5 (?)
Red Heart Dolostone	Terreneuvian – Series 2, Stage 3 (?)
Mount Baldwin Formation	
Adam Shale	

Narpa Group — Shadow Grp.

CAMBRIAN

Figure 2
Click here to download Figure: NTGS Fig 2.pdf

Figure 3
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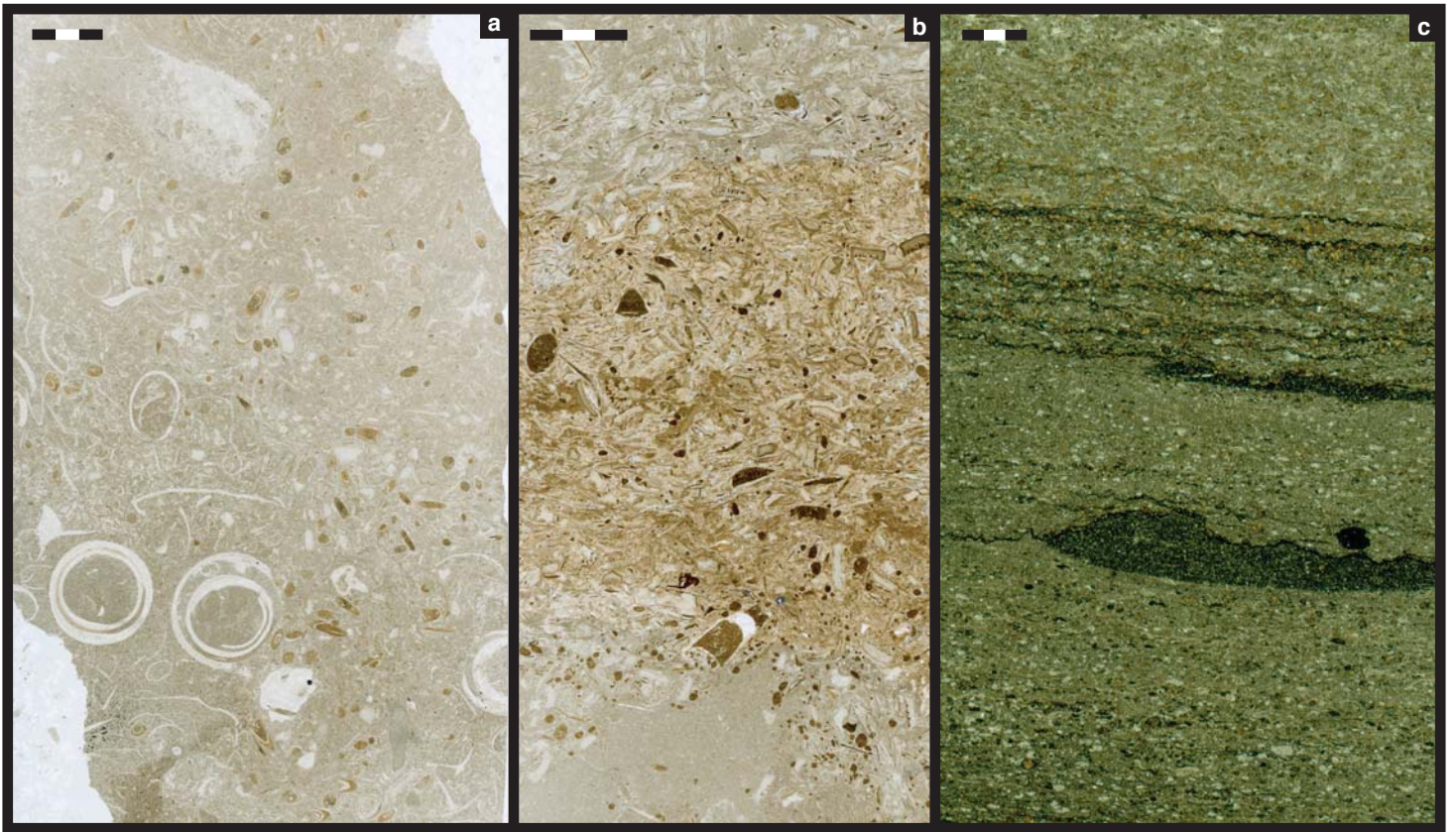
Figure 4
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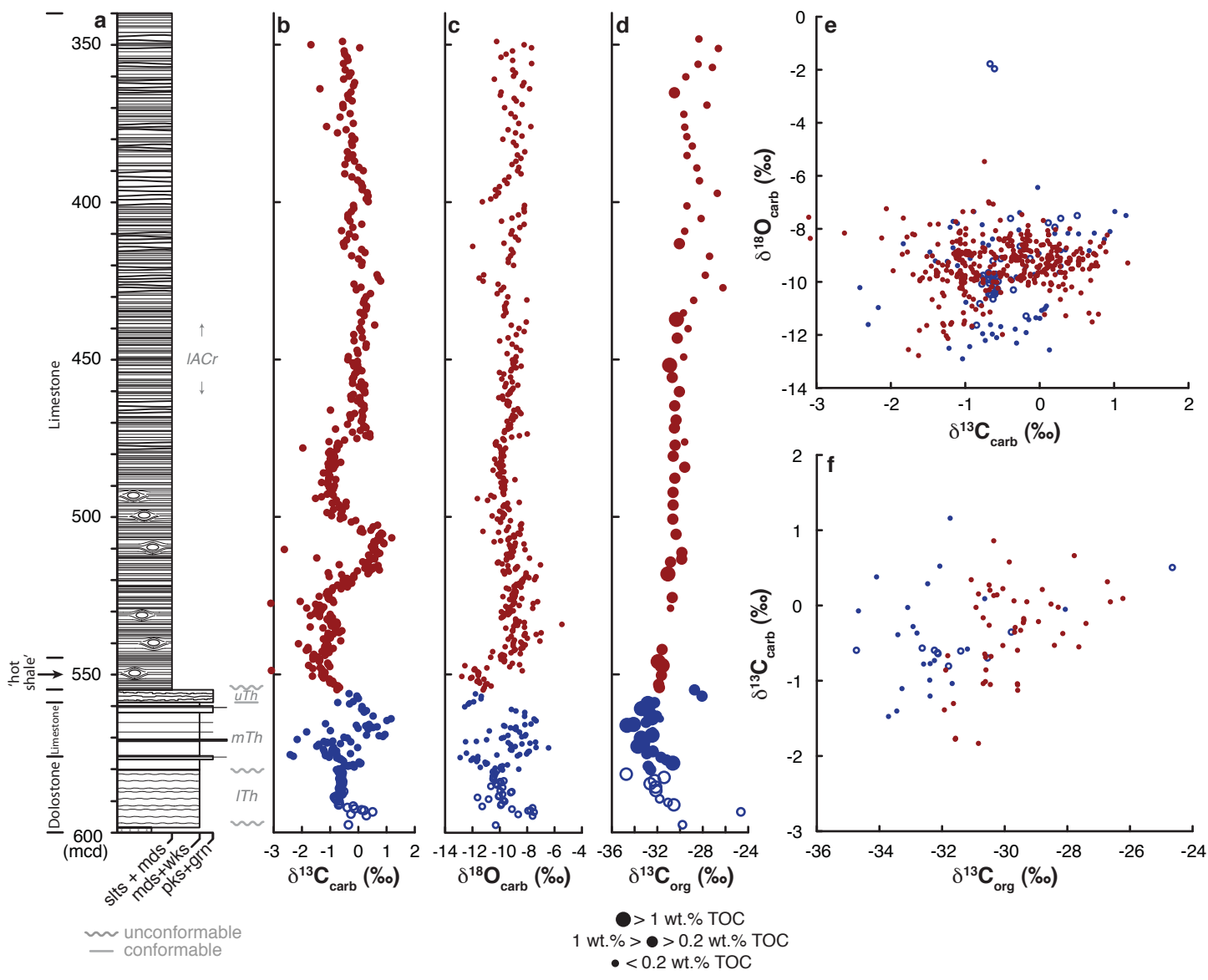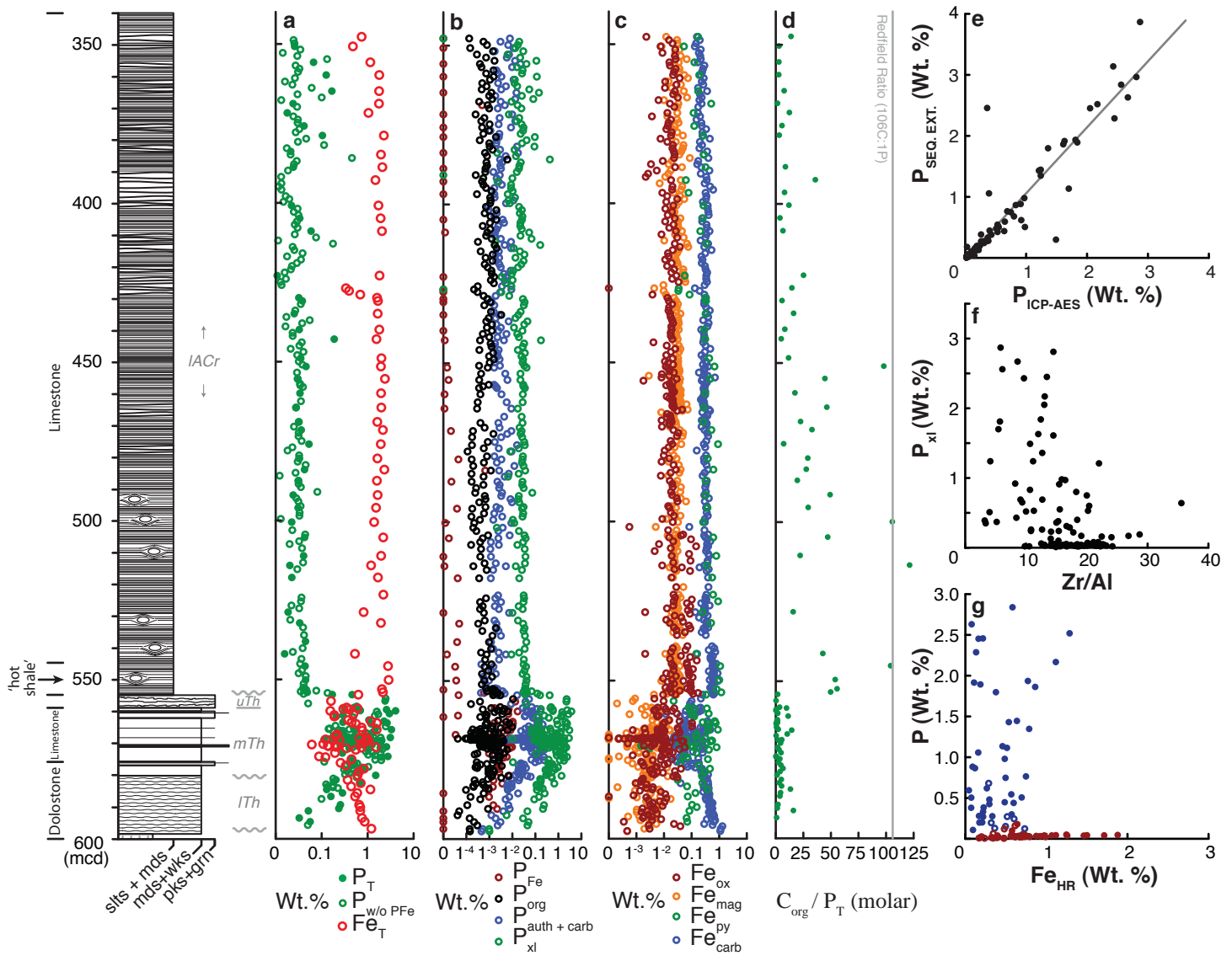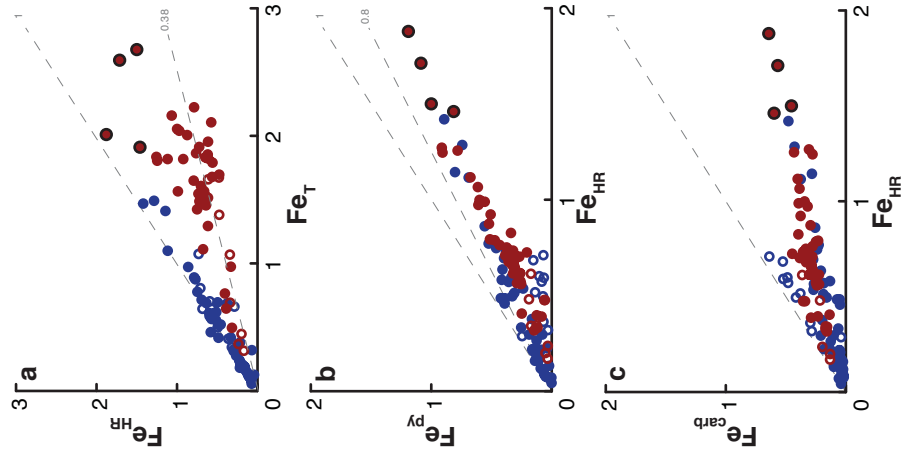> 1 wt.% TOC
1 wt.% > ● > 0.2 wt.% TOC
● < 0.2 wt.% TOC

Figure 5
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Organic-bound P delivery

middle/upper Thorntonia Limestone   Arthur Creek Formation

C_{org} remineralization

18.6 wt.% $\hat{C}_{org}^{*}$ 1.1 wt.% $\hat{C}_{org}^{*}$

Iron-bound P delivery

middle/upper Thorntonia Limestone   Arthur Creek Formation

Fe^{2+} loss, P capture

0.98 wt.% P_T 0.03 wt.% P_T
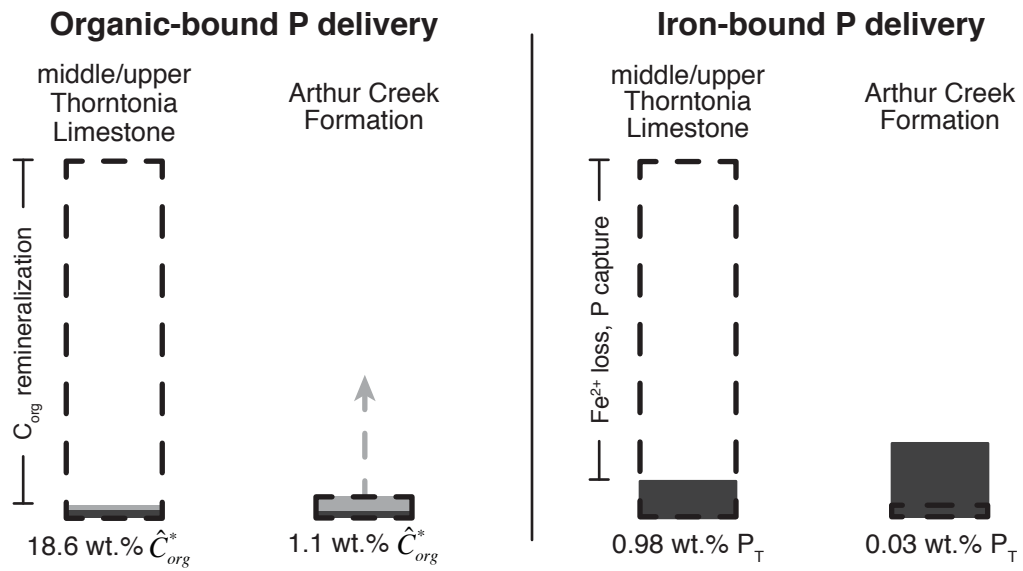
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