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Cycling Phosphorus on the Archean Earth: Part I. Continental weathering and riverine
transport of phosphorus

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23 **Abstract:**

24 Phosphorus (P) is the key nutrient thought to limit primary productivity on geological
25 timescales. Phosphate levels in Archean marine sediments are low, but quantification of the P
26 cycle and how it changed through a billion years of recorded Archean history remain a
27 challenge, hindering our understanding of the role played by P in biosphere/geosphere co-
28 evolution on the early Earth.

29 Here, we design kinetic and thermodynamic models to quantitatively assess one key
30 component of the early P cycle – continental weathering – by considering the emergence and
31 elevation of continents, as well as the evolution of climate, the atmosphere, and the absence
32 of macroscopic vegetation during the Archean Eon. Our results suggest that the weathering
33 rate of apatite, the major P-hosting mineral in the rocks, was at least five times higher in the
34 Archean Eon than today, attributable to high levels of $p\text{CO}_{2,g}$. Despite this, the weathering
35 flux of P to the oceans was negligible in the early Archean Eon, increasing to a level
36 comparable to or greater than the modern by the end of eon, a consequence of accelerating
37 continental emergence. Furthermore, our thermodynamic calculations indicate high
38 solubilities of primary and secondary P-hosting minerals in the acidic weathering fluids on
39 land, linking to high Archean $p\text{CO}_{2,g}$. Thus, weathering of P was both kinetically and
40 thermodynamically favorable on the Archean Earth, and river water could transport high
41 levels of dissolved P to the oceans, as also supported by the observed P-depletion in our new
42 compilation of Archean paleosols. Lastly, we evaluated the relative rates of physical erosion
43 and chemical weathering of silicates during the Archean Eon. The results suggest that
44 continental weathering on the early and middle Archean Earth might have been transport-
45 limited due to low erosion rates associated with limited subaerial emergence and low plateau
46 elevations; by the late Archean, however, continental weathering would have transited to
47 kinetically-limited state because of continental emergence, increased plateau elevation, and

48 weakening weathering rates. Overall, our weathering calculations together with paleosol
49 evidence indicate an increasing flux of bioavailable P to the oceans through time, associated
50 with late Archean continental emergence, reaching levels comparable to or higher than
51 modern values by the end of the eon. Increased P fluxes could have fueled increasing rates of
52 primary production, including oxygenic photosynthesis, through time, facilitating the
53 irreversible oxidation of the Earth's atmosphere early in the Proterozoic Eon. (388 words)

54

55

56 **Keywords:** phosphorus; emergence of land; elevation of land; physical erosion; chemical
57 weathering; paleosols (6/6)

58

59 **1. Introduction**

60 Phosphorus (P) is an essential micronutrient. Critical to the genetic material
61 (nucleotides), membranes (phospholipids) and energy transfer (ATP) in cells, its availability
62 is thought to limit primary productivity on geological timescales (Laakso and Schrag, 2018;
63 Ruttenger, 2013; Tyrrell, 1999). Temporal variations in the P content of sedimentary rocks
64 such as iron formation and carbonaceous shale suggest low levels of phosphate in Archean
65 marine sediments (Bjerrum and Canfield, 2002; Planavsky et al., 2010; Reinhard et al., 2017),
66 but quantification of the P cycle and how it changed through a billion years of recorded
67 Archean history remain a challenge, hindering our understanding of the role played by P in
68 biosphere/geosphere co-evolution on the early Earth.

69 The modern P cycle involves two dominant phosphate sources to the sunlit ocean:
70 continental weathering and recycling in the oceans. Continental weathering provides the
71 ultimate source of bio-available P to marine ecosystems, but due to the highly efficient
72 recycling of organic matter in the modern oxidizing ocean, the flux of recycled P exceeds the
73 continental input of P by two to three orders of magnitude (Schlesinger and Bernhardt, 2013).
74 Thus, the high primary productivity of the modern ocean is sustained predominantly by
75 recycled P. P burial on the other hand is determined by P input from continental weathering.
76 On the early Earth, before the oxygenation of the atmosphere and ocean, recycling of
77 organics in anoxic seawater might have been suppressed by a limited supply of oxidants (O₂,
78 sulfate, nitrate, and ferric iron) (Kipp and Stüeken, 2017; Laakso and Schrag, 2018), and P
79 released to subsurface water masses might have been sequestered by reaction with ferrous
80 iron to form vivianite (Derry, 2015). As a consequence, continental weathering might have
81 accounted for a relatively larger proportion of total P supplied to primary producers in
82 Archean oceans.

83 Continental input of P into early oceans, however, is poorly understood, for two major
84 reasons. On the one hand, continental weathering of P might have been limited by less
85 extensive subaerial exposure of land and low elevations (Flament et al., 2013; Korenaga et al.,
86 2017; Rey and Coltice, 2008), as well as a lower P content of early igneous rocks (Cox et al.,
87 2018). On the other hand, high levels of atmospheric CO_{2,g} thought to characterize the early
88 Earth favor weathering and riverine transport of phosphorus (Hao et al., 2017a). In addition,
89 the absence of macroscopic vegetation on Archean continents should also have affected both
90 chemical and physical weathering relative to the modern Earth.

91 Despite these challenges, there have been a few attempts to estimate the continental
92 flux of P into Archean oceans. Hao et al. (2017a) used a thermodynamic model to simulate
93 the maximum solubilities of apatite (Ca₅(PO₄)₃(OH,F,Cl)), the major P-hosted mineral in the
94 crust, in proposed Archean weathering fluids; however, they could not quantify continental
95 fluxes because they lacked terms for weathering kinetics, the growth and elevation of
96 continental land, and the evolution of climate and atmosphere. Recent studies have placed
97 constraints on the parameters that collectively govern these fluxes, including continental
98 emergence *per se* (Flament et al., 2013; Korenaga et al., 2017), atmospheric composition
99 (Krissansen-Totton et al., 2018), and temperature (Krissansen-Totton et al., 2018). Despite
100 uncertainties, these estimates enable us, for the first time, to quantify continental input of
101 bioavailable P to Archean oceans. Here we design kinetic and thermodynamic models to
102 estimate the continental weathering of apatite and riverine transport of P, incorporating the
103 emergence and elevation of continental land, atmospheric composition, climate, and the
104 absence of vegetation.

105

106 **2. Important environmental parameters controlling phosphorus weathering**

107 Continental weathering of phosphorus depends on a number of environmental factors,
108 all of which have evolved through the Earth history.

109

110 *2.1 Emergence of land*

111 Although the volume of continental crust might have increased more or less
112 continually early in Earth history (Hawkesworth and Kemp, 2006; Roberts and Spencer,
113 2015), only limited evidence exists for emergent land before the middle Archean Eon.
114 Various lines of evidence, including stratigraphic observations, geophysical simulations, and
115 geochemical data agree that the early and middle Archean continents had only limited
116 subaerial exposure (Arndt, 1999; Campbell and Davies, 2017; Ernst et al., 2016; Flament et
117 al., 2013, 2008; Korenaga et al., 2017; Kump and Barley, 2007; Molnar, 2018; Trower and
118 Lowe, 2016).

119 For example, the 3.5-3.26 Ga Onverwacht Group, South Africa, contains some ten
120 kilometers of stratigraphy, but nearly all of it is volcanic, and much consists of pillow basalts
121 extruded below sea level (Lowe and Byerly, 1999). With one exception, detrital zircons
122 suggest that such clastic sedimentary rocks as are preserved derive largely from regional
123 volcanics (Drabon et al., 2017). The exception is a three meter sandstone bed near the top of
124 the Onverwacht succession that contains zircons older than 3.8 Ga. These suggest that older
125 differentiated crust existed but was rarely eroded (Byerly et al., 2018). Clastic sedimentary
126 rocks are more abundant in the 3.26-3.22 Ga Fig Tree Group, but the lithic grains that
127 dominate these lithologies again speak to reworking of regional volcanics (Nocita, 1989).
128 Only with deposition of the immediately overlying Moodies Group do we see accumulations
129 of quartz-rich sandstones derived from exposed continental crust. Later Archean basins
130 increase in lateral dimensions, culminating in the latest Archean Transvaal basin, whose
131 spatial scale suggests accumulation along the margin of a large, stable craton (Knoll and

132 Beukes, 2009). Similar features characterize Archean stratigraphy in Western Australia (e.g.,
133 van Kranendonk, 2006).

134 Geochemical data also support late emergence models. End-Archean increase in the
135 $^{87}\text{Sr}/^{86}\text{Sr}$ of carbonate rocks was originally thought to reflect continental growth (Taylor and
136 McLennan, 1985) or continental igneous rock composition (Bataille et al., 2017), but is
137 equally well explained in terms of late continental emergence (Flament et al., 2013; see also
138 Pons et al., 2013, for a comparable perspective based on Zn isotopes). Indeed, interpretation
139 in terms of emergence helps greatly to reconcile otherwise conflicting stratigraphic and
140 geochemical inferences about continental growth on the Archean Earth. Consistent with this
141 view, Bindeman et al. (2018) and Spencer et al. (2019) have both interpreted the oxygen
142 isotope record in terms of late Archean continental emergence, while Kump and Barley (2007)
143 have argued for an increase in subaerial volcanism near the Archean-Proterozoic boundary.
144 We know of no comparable suite of evidence favoring much earlier emergence of stable
145 continents.

146 Lee et al. (2018) recently proposed a scenario in which pronounced continental
147 emergence developed only near the end of the Proterozoic Eon, catalyzing late
148 Neoproterozoic climatic and redox transformations. This proposal is at odds with several
149 lines of geochemical evidence documenting large continental weathering and erosional fluxes
150 by late Archean times (Bindeman et al., 2018; Satkoski et al., 2016; Viehmann et al., 2018),
151 not to mention thousands of meters of quartzose sandstones in earlier Proterozoic basins
152 around the world. If all land were submerged, there would be no depletion of P during
153 seafloor weathering, which is inconsistent with Archean paleosol records (**Fig. 6**). Moreover,
154 in the warm climate suggested by biogeochemical models for a land-free Archean
155 (Krissansen-Totton et al., 2018), rapid precipitation of vivianite would remove essentially all
156 available P from seawater. Thus, any scenario with essentially no exposed land mass implies

157 minimal global primary production sustained by limited fluxes of P from extraterrestrial
158 sources (Pasek and Lauretta, 2008; Tsukamoto et al., 2018), inconsistent with evidence for
159 substantial biological activity in the Archean ocean. Taken together, sedimentary and
160 geochemical evidence make protracted late Archean continental emergence a more plausible
161 scenario.

162 Quantification of continental emergence depends on a number of parameters, none of
163 them well constrained. These include mantle temperature, crustal composition – and hence
164 buoyancy, seawater volume, modes and rates of tectonic activity, and continental hypsometry
165 (Korenaga et al., 2017). Previous studies of the Archean Earth have rarely incorporated all of
166 these parameters; indeed, parameter selection has commonly seemed arbitrary. For this paper,
167 we chose three models for secular change in continental emergence from two recent studies
168 (**Fig. 1a**) (Flament et al., 2013; Korenaga et al., 2017). Among the available estimates, we
169 suggest that these provide the best understanding of continental emergence available at
170 present. Moreover, because they incorporate multiple models of continental growth and
171 mantle devolatilization/revolatilization, these papers provide a broad range of possible
172 histories.

173 Apart from more limited emergence of the Archean continents, a hotter and more
174 buoyant Archean mantle could not support high plateau elevations (Fig. 1b; Flament et al.,
175 2013; Rey and Coltice, 2008), although the actual elevation should depend on a balance
176 between tectonic uplifting and exhumation/erosion. Based on the classic Culling's model
177 (Culling 1960, 1963), the erosion rates is linearly proportional to topographic slope, which
178 depends on relative elevation. Physical erosion is responsible for the removal of sediment and
179 exposure of fresh rock surface for chemical weathering. We further simplify Culling's model
180 by assuming that physical erosion is proportional to the elevation of land, i.e., $E_r \propto H$, an
181 approach that has previously been applied to macroscale erosion processes (Lee et al., 2015;

182 Jadamec et al., 2007). Thus, physical erosion on the Archean Earth was probably limited by
183 the low elevation of continental land, as well as its limited aerial extent, as investigated below.

184

185 *2.2 P content of rocks*

186 The P content of erodible rocks is another important factor in estimating the
187 weathering flux of P. P content depends on rock composition (Porder and Ramachandran,
188 2013; Ronov, 1982) and exposure through geological time (Cox et al., 2018). On the modern
189 Earth, the exposure area of sedimentary rocks exceeds that of volcanics (Bluth & Kump,
190 1991). Thus, on the modern Earth, the contribution of sedimentary rock weathering to
191 continental P flux can potentially be substantial (Hartmann et al., 2014). On the early
192 Archean, however, this sedimentary reservoir might have been less important. The P content
193 of sedimentary rocks varies widely and can be either higher or lower than that of ultramafic-
194 mafic volcanic rocks (Porder & Ramachandran, 2013; Ronov, 1982), which were the major
195 crustal lithologies in the Archean Eon. Quantification of the contribution of sedimentary rock
196 weathering to P flux needs to consider relative P content, surface exposure, and weathering
197 kinetics of sedimentary vs. volcanic rocks. Collectively, the resultant uncertainty may
198 become too large to yield any useful implications. It is also possible that agpaitic rocks,
199 which are unusually rich in phosphorus, could add complexity to weathering and erosional P
200 fluxes; however, all known examples of agpaitic rocks postdate the Archean (Marks and
201 Markl, 2017). With these unknowns and uncertainties in mind, we instead chose to use
202 relative P content of crust in the Archean and modern Earth. A compilation of more than
203 176,000 igneous rock samples indicates that the P content of the Archean crust was perhaps
204 half that estimated for today, although felsic rocks show no pronounced secular trend (Cox et
205 al., 2018).

206

207 2.3 Archean atmospheric composition

208 Acidity and redox state are two more important controls on the chemical dissolution
209 of phosphorus. Rainwater acidity is controlled by the dissolution of atmospheric CO₂ and
210 deprotonation of H₂CO₃. It has been generally proposed that high levels of CO₂ are required
211 to compensate the weaker young sun (20 to 30 % lower luminosity) (Gough, 1981) and
212 sustain a temperate climate in the Archean. As a result, Archean rainwater is estimated to
213 have been more acidic than modern (Hao et al., 2017a). Log dissolution rate of the major P-
214 hosted minerals, i.e. apatite, has been experimentally shown to increase linearly with
215 decreasing pH (Guidry and Mackenzie, 2003). The solubility limits of P-minerals also
216 depend significantly on pH, as investigated below.

217 The redox state of the Archean atmosphere and surface waters is thought to have been
218 weakly reducing (Hao et al., 2019). Under these conditions, ferrous iron is stable rather than
219 the ferric iron that generally forms in modern oxidizing weathering reactions. Given the
220 much greater solubility of ferrous iron relative to ferric iron, Archean weathering should
221 result in Fe-depletion, as evidenced by the paleosol record (Rye and Holland, 1998) and
222 thermodynamic simulation (Hao et al., 2017b). Today, the largest proportion of the reactive
223 phosphorus pool in riverine transport is Fe-bound phosphorus, because during oxidative
224 weathering Fe(II) is oxidized to Fe(III), leading to the formation of Fe(III)-(hydr)oxide or
225 Fe(III)-coated clay minerals that have a high surface adsorption affinity for phosphate (House,
226 2003; Withers and Jarvie, 2008). This surface retention of P is thought to be a key process
227 limiting dissolved P levels in modern river water. However, we expect there would have been
228 little Fe-bound inorganic phosphate in anoxic Archean river water and, correspondingly, high
229 concentrations of dissolved inorganic phosphate. Below we examine whether or not the
230 acidic and anoxic weathering fluids could transport high concentrations of dissolved
231 phosphate on the Archean Earth.

232

233 *2.4 Absence of vegetation*

234 The presence of land plants affects both chemical weathering and physical erosion.
235 On the one hand, vegetation is thought to facilitate chemical weathering through the secretion
236 of organic ligands that attack primary minerals (Neaman et al., 2005) and/or elevation of soil
237 pCO_{2,g} by means of microbial decomposition of organic debris in the soil (Berner, 2004).
238 Overall, the presence of non-microbial vegetation is proposed to accelerate the chemical
239 dissolution of primary minerals by a factor of 3 to 4, as calculated by cation release from
240 vegetated vs. barren areas (Berner et al., 2004). The enhancing factor of 4 is further supported
241 by attempts to match the COPSE model to multiple Phanerozoic paleo-weathering proxies
242 (Lenton et al., 2018). On the other hand, vegetation can protect substrates from physical
243 erosion and thus hinder the exposure of fresh rock for further weathering, particularly where
244 removal of the soil cover is not efficient (Berner, 2004). It has been shown that vegetation
245 cover (*VC* %) has a negative exponential correlation with soil erosion rate (Gyssels et al.,
246 2005); i.e., $E_r \propto \exp(-b*VC)$, where *b* is an exponential constant. Modern Earth has
247 approximately 60% vegetation cover; whereas, none was present on the Archean Earth.
248 Absence of vegetation on the Archean Earth might compensate partially for the effect of low
249 plateau elevation.

250

251 **3. Methods and Materials**

252 *3.1 Chemical weathering model*

253 We modeled the chemical weathering of silicates using the geological carbon cycle
254 model of Krissansen-Totton et al. (2018), with two modifications. First, we used three models
255 for the emergence of land above sea level as introduced above rather than the estimates of
256 continental growth used in Krissansen-Totton et al. (2018). Second, because there was no

257 macroscopic vegetation on the Archean Earth, we set the vegetation compensating factor as
 258 0.25 rather than 0.1 to 1, randomly sampled over the Precambrian in the original model. We
 259 kept all other parameters as in the original code.

260 The dissolution rate of apatite (R) has been proposed (Guidry and Mackenzie, 2000)
 261 to be:

$$262 \quad R = A * \exp\left(-\frac{E_a}{R_g T}\right) * [H^+]^{n_H} \quad (1)$$

263 R : mole/(cm²*s); A : reaction constant, mole/(cm²*s); E_a : activation energy of dissolution
 264 (34.7 kJ/mole) (Guidry and Mackenzie, 2003); R_g : universal gas constant, 0.008 kJ/(mole*K);
 265 T : temperature, K; $[H^+]$: activity of hydrogen ion in the weathering fluid; n_H : reaction order
 266 (0.81 at 2 < pH < 5.5) (Guidry and Mackenzie, 2003).

267 Eqn. 1 has been used to estimate continental inputs of P during the past 600 Ma (Guidry and
 268 Mackenzie, 2000). Guidry and Mackenzie (2000) assumed a constant $[H^+]$ of 10⁻⁵ for soil
 269 waters throughout this interval; however, the log dissolution rate of apatite can decrease
 270 linearly with pH at pH < 6 (Guidry and Mackenzie, 2003). Due to high levels of CO_{2,g} in the
 271 Archean atmosphere, weathering fluids would have been generally acidic (Hao et al., 2017a).

272 Thus,

$$273 \quad \frac{R_{Archean}}{R_{Modern}} = \exp\left[-\frac{E_A}{R_g}\left(\frac{1}{T_{Archean}} - \frac{1}{T_{Modern}}\right)\right] * \left(\frac{H_{Archean}^+}{H_{Modern}^+}\right)^{n_H} \quad (2)$$

274 At acidic pH, $[H^+]$ of rainwater varies approximately with the partial pressure of CO_{2,g}
 275 ($P_{CO_2,g}$):

$$276 \quad [H^+]^2 = K_1 * K_{CO_2} * P_{CO_2,g}$$

$$277 \quad [H^+] = K * \sqrt{P_{CO_2}} \quad (3)$$

278 where $K = \sqrt{K_1 * K_{CO_2}}$; K_1 represents the first deprotonation constant of carbonic acid; K_{CO_2}
 279 represents the solubility constant of CO_{2,g} in water under ambient conditions.

280 It is notable that the pH of weathering fluids would have increased as weathering
 281 progressed due to release of alkalinity from the alteration of silicate and carbonate minerals.
 282 However, as shown in Hao et al. (2017a), the pH increment from rainwater (starting
 283 weathering fluid) to river water (ending weathering fluid) is similar at different levels of
 284 $p\text{CO}_{2,g}$; i.e. $\frac{H_{Archean}^+}{H_{Modern}^+}$ of weathering fluids should depend primarily on $\frac{p\text{CO}_{2,g,Archean}}{p\text{CO}_{2,g,Modern}}$. Apart
 285 from the dissolution of $\text{CO}_{2,g}$, introduction of organic acids as well as SO_x and NO_x gases
 286 may affect the acidity of rainwater, particularly in some local environments or during
 287 particular geologic periods. However, deposition of SO_x and NO_x , which are mostly
 288 anthropogenic today, might have been insignificant for the preindustrial times, let alone for
 289 the Archean Eon. The overall effects of organic acids, which mainly come from macroscopic
 290 vegetation today, were considered in our model as discussed below.

291 Consequently, the relative chemical weathering rate of apatite is

$$292 \quad \frac{R_{Archean}}{R_{Modern}} = \exp \left[-\frac{E_A}{R_g} \left(\frac{1}{T_{Archean}} - \frac{1}{T_{Modern}} \right) \right] * \left(\frac{P_{\text{CO}_{2,Archean}}}{P_{\text{CO}_{2,Modern}}} \right)^{\frac{n_H}{2}} \quad (4)$$

293 Recently, Krissansen-Totton et al. (2018) reconstructed the evolution of Archean surface
 294 environments, including $p\text{CO}_{2,g}$ and temperature, based on a model for the geological carbon
 295 cycle. Here, we incorporate the weathering kinetics of apatite (eqn. 4) into Krissansen-Totton
 296 et al.'s model and use their output of $p\text{CO}_{2,g}$ and temperature of each run to calculate the
 297 weathering kinetics of phosphorus as it changed through the Archean Eon.

298 We developed three versions of our model, reflecting hypotheses for early,
 299 intermediate and late continental emergence (Fig. 1a). All generate results that are similar in
 300 trajectory, albeit different in timing. While the question of when and to what extent
 301 continents emerged above sea level remains a topic for debate, we believe there are
 302 compelling reasons to favor late emergence hypotheses, as proposed in models that relate the
 303 water cycle (Korenaga et al., 2017) and continental hypsometry (Rey and Colitce, 2008) to a

304 secular decline in mantle temperature through the Archean Eon. Based on sedimentary and
305 geochemical evidence (*Sec. 2.1*), we favor large-scale subaerial emergence of continents in
306 the late Archean Eon as the most likely scenario. As we discuss below (**Discussion**),
307 weathering of P on early and middle Archean continents might have also been suppressed by
308 slow physical erosion due to the low elevation of emergent land masses.

309 Lastly, vegetation has been shown to accelerate chemical weathering by a factor of
310 about 4 (Berner, 2004; Lenton et al., 2018); thus, the weathering kinetics of apatite are
311 divided by 4 to compensate for the effect of no vegetation in the Archean.

312 The total flux (p) of P by continental weathering is

$$313 \quad p(t) = SA * R \quad (5)$$

314 SA: global surface area of apatite available for weathering.

315 Therefore,

$$316 \quad \frac{p(Archean)}{p(Modern)} = \frac{SA_{Archean} * R_{Archean} * C(P)_{Archean}}{SA_{Modern} * R_{Modern} * C(P)_{Modern}} \quad (6)$$

317 $C(P)$: content of P in the rock. Here, the ratio of SA * $C(P)$ was used to approximate the
318 relative exposure of apatite minerals for chemical weathering on exposed Archean and
319 modern continents.

320 For simplicity, we assumed an average P content for Archean land equal to half the
321 modern value, i.e. $C(P)_{Archean}/C(P)_{Modern} = 1/2$. This assumption is within the range of values
322 reported in Cox et al.'s compilation (Cox et al., 2018). Regardless of the uncertainties in this
323 estimate, we consider the evolution of crustal P content to be less important for the
324 continental transport of reactive P than weathering rate and continental growth and
325 emergence (Flament et al., 2013; Korenaga et al., 2017). As in Krissansen-Totton et al.
326 (2018), the weathering model was run 10,000 times to build distributions for model outputs.

327 Due to lack of a universal value for the weathering rate of apatite on the modern Earth,
328 we calculated only the relative weathering rate of apatite on the Archean Earth compared to

329 preindustrial time using Eqn. (4) (**Figs. 2-4**). Similarly, we calculated only the relative
330 chemical dissolution flux of P using Eqn. (6), due to the fact that the speciation of P in
331 reducing and acidic Archean river water might have differed substantially from that of
332 preindustrial rivers (*Sec. 4.2* and **Table 2**).

333

334 *3.2 Physical erosion*

335 As mentioned above, elevation and vegetation are two major factors controlling rates
336 of physical erosion:

$$337 \quad \frac{E_{r,Archean}}{E_{r,Modern}} = \frac{H_{Archean}}{H_{Modern}} \times e^{-b(VC_{Archean}-VC_{Modern})} \quad (7)$$

338 Reported b values vary significantly and this variation strongly affects the calculated
339 effectiveness of vegetation on the protection of soil from erosion (Gyssels et al., 2005). Here,
340 we adopt a range of b values from 0.02 to 0.04, representing the range of literature values
341 (Gyssels et al., 2005). With no information of actual Archean plateau elevations, we chose to
342 apply Flament et al.'s (2013) reconstructed maximum plateau, which should approximate an
343 upper limit on actual elevations. The vegetation coverage in the Archean ($VC_{Archean}$) is set to
344 be 0 and modern (VC_{Modern}) to be 60%.

345

346 *3.3 Thermodynamic calculations of P-minerals' solubilities*

347 Solubility limits for primary and secondary phosphate minerals in Archean river water
348 and seawater were calculated using the equilibrium constants of their dissolution reactions
349 under ambient conditions (25 °C and 1 atm) (**Table 1**). Based on previous studies, we made
350 various assumptions about concentrations for ions other than phosphate.

351 For our reconstruction of Archean river water, F^- concentration was assumed to be
352 equal to that of modern river water; i.e., 1.3×10^{-8} mole/L (Deshmukh et al., 1995) although
353 the actual level is unknown. This simple consideration might over- or under-estimate the

354 solubility limits of F-bearing phosphates. However, our calculations suggest that the F-
355 bearing phosphates are highly soluble in the Archean weathering fluids (**Fig. 5a** and **b**) and
356 the results are still valid even with orders of magnitude higher or lower levels of fluorine.
357 Due to high levels of CO_{2,g}, Archean river water is expected to have been more acidic than at
358 present (Hao et al., 2017b). Acidity of the weathering fluid also depends on the extent of
359 reactions with silicate and carbonate minerals, increasing at high reaction extent due to the
360 release of alkalinity by rock alteration. Here, we investigated a wide range of Archean pCO_{2,g}
361 values (1 to 10^{-2.5} bar) from Krissansen-Totton et al. (2018) and modeled the corresponding
362 chemistry of Archean river water using a previously reported late Archean weathering model
363 (Hao et al., 2017b). The outputs, particularly pH and aqueous activity of Ca²⁺, Fe²⁺, Cl⁻, and
364 SiO_{2, aq} (**Table S1**), were used to calculate the solubilities of primary and secondary P-
365 minerals, based on the reported thermodynamics of these minerals (**Table 1**). As for the
366 solubilities of variscite (AlPO₄·2H₂O) and strengite (FePO₄·2H₂O), Al(III) and Fe(III) levels
367 were assumed to be limited by the solubility of their corresponding amorphous hydroxides.
368 However, Fe(OH)₃ is not believed to have precipitated widely during Archean weathering, as
369 supported by observations of Fe-depletion in Archean paleosols (Rye and Holland, 1998).
370 Therefore, the solubility of strengite, although calculated in this study, should serve only as a
371 lower limit on Archean river water.

372

373 *3.4 P-weathering in paleosol record*

374 Paleosol selection for our analysis is based mainly on standards proposed by Rye and
375 Holland (1998), augmented by more recent additions. **Table S2** lists all data sources.

376 The enrichment index of P is defined as:

$$377 \Delta\left(\frac{P}{Ti}\right) = \frac{\left(\frac{P}{Ti}\right)_{Paleosol} - \left(\frac{P}{Ti}\right)_{Bedrock}}{\left(\frac{P}{Ti}\right)_{Bedrock}} \quad (8)$$

378 $\Delta(P/Ti) > 0$ indicates enrichment of P during weathering whereas $\Delta(P/Ti) < 0$ indicates
379 depletion of P. Since positive values of $\Delta(P/Ti)$ reflect the addition of P to the paleosols, most
380 likely by mineral aerosols, we decided to use only negative $\Delta(P/Ti)$ values for Student's t-test
381 (**Fig. 6**). **Fig. S4** presents all $\Delta(P/Ti)$ values and the corresponding statistical results.

382

383 **4. Results**

384 *4.1 Continental weathering of phosphorus*

385 As noted above, we have applied three cases of land emergence to simulate ratios of
386 apatite dissolution rate (rate per unit area, e.g. mole/cm²*s in this study; Figs. 2a-4a) and P
387 weathering flux (Figs. 2b-4b) through the Archean Eon relative to modern.

388 In the case of slow late Archean emergence of land (Flament et al., 2013), the relative
389 weathering rate of apatite decreases slowly but monotonically through the Archean Eon (**Fig.**
390 **2a**), largely due to the secular decline of pCO_{2,g} (**Fig. S1**). When we compensate for a lack of
391 vegetation, the apatite dissolution rate is always greater than five times the modern,
392 indicating that dissolution of apatite was kinetically favorable under the acidic conditions of
393 the Archean land surface. However, the relative weathering flux of P remains negligible until
394 3.5 Ga, when land starts to emerge and then increases rapidly (**Fig. 2b**), reaching a value
395 ranging from 0.25 to 1 by the end of the Eon. The increase in weathering flux is largely
396 ascribed to the late Archean emergence of land, which more than compensates for the
397 declining weathering rate of apatite. However, continental weathering flux of silicates
398 simulated by Krissansen-Totton et al. (2018) decreased slightly through the Archean Eon (Fig.
399 3E in Krissansen-Totton et al., 2018). This lack of synchronization is due to the different
400 settings of land fraction (relative to the modern land area). In their simulations, Krissansen-
401 Totton et al. (2018) assumed 0-75% land fraction emergence above sealevel and no change
402 with time during the Archean Eon. Under these circumstances, decreasing pCO_{2,g} and

403 temperature (Fig. 3B & D in Krissansen-Totten et al., 2018) would inevitably result in a
404 decreasing continental flux of silicate weathering. As argued by Krissansen-Totten et al.
405 (2018), the degree of land emergence has only a minor influence on the evolutionary history
406 of seawater pH and climate, the foci of their study. However, the geologic history of land
407 emergence as discussed in Sec. 2.1 is highly relevant to the estimation of continental
408 weathering flux. For this reason, we used reconstructed histories of Archean land emergence
409 (Fig. 1a) as inputs into our weathering model, which shows an increasing continental flux of
410 P through time. In **Fig. S1-3**, we also displayed our reconstructed evolution of continental
411 silicate weathering, which shows increasing flux as well, consistent with other geochemical
412 studies. These increasing fluxes of continental weathering are mainly driven by the land
413 emergence.

414 In the second case, where land emerged rapidly from the middle Archean (Korenaga
415 et al., 2017), the trends of relative weathering rate and flux are similar to the case described
416 above (**Fig. 3**). That said, the relative weathering rate of apatite decreases to even lower
417 levels toward the end of the Archean (**Fig. 3a**) compared with the slow emergence case. This
418 difference lies in the lower levels of $p\text{CO}_{2,g}$ and temperature, a consequence of stronger
419 continental weathering on a larger land surface in the late Archean Eon (**Fig. S2**). Similar to
420 the first case, the relative chemical weathering flux of P increases from the middle Archean
421 and reaches a value close to or higher than 1 by the end of the Archean, representing a flux
422 comparable to or higher than the modern value (**Fig. 3b**), again because of continental
423 emergence.

424 In the last case, where land started emerging early in the Archean Eon (Korenaga et
425 al., 2017), the relative weathering rate of apatite once again declines monotonically with time
426 (**Fig. 4a**). The relative weathering flux of P, however, increases rapidly from the early
427 Archean, reaching a plateau value of 0.5 to 4 in the middle Archean (3.5 Ga) before

428 decreasing slightly into the late Archean (**Fig. 4b**). This trend differs from two cases
429 discussed above, mainly due to the rapid emergence of land in the early Archean. The
430 declining weathering flux is largely ascribed to the declining weathering rate of apatite. In
431 this case, the weathering flux of P is comparable to or higher than the modern level since the
432 middle Archean. However, as mentioned earlier, we believe this case of early land emergence
433 is not well supported by sedimentary and geochemical evidence. Additionally, on the early-
434 middle Archean Earth, continental weathering, although chemically favorable, might have
435 been severely limited by low rates of physical erosion, reflecting the low mean elevation of
436 continental land (**Fig. 1b**), as elaborated in **Discussion**.

437 In summary, given three different cases of land emergence, Archean chemical
438 weathering of apatite is always kinetically more favorable than today, and the weathering
439 flux of P is predicted to have reached levels comparable to today at least by the end of the
440 Archean Eon.

441

442 *4.2 Riverine transport of phosphorus*

443 Today, continental weathering of P-hosting minerals generates various forms of
444 phosphorus. Among these, detrital particulate phosphorus is the largest component but is not
445 biologically available to the marine ecosystem. Bioavailable phosphorus, also known as
446 ‘reactive’ phosphorus, is composed of dissolved inorganic phosphorus (DIP), dissolved
447 organic phosphorus (DOP), particulate organic phosphorus (POP), Fe-bound inorganic
448 phosphorus (PIP, Fe-bound), and about 20% aeolian phosphorus (desorption from aeolian
449 dusts) (Compton et al., 2000). The largest proportion of the reactive phosphorus pool is Fe-
450 bound phosphorus, because during oxidative weathering Fe(II) is oxidized to Fe(III), leading
451 to the formation of Fe(III)-(hydr)oxide or Fe(III)-coated clay minerals that have a high
452 surface adsorption affinity for phosphate (House, 2003; Withers and Jarvie, 2008). This

453 surface retention of P is thought to be a key process limiting dissolved P levels in modern
454 river water. However, in the Archean, when the atmosphere was anoxic and weakly reducing,
455 weathering is thought to have leached Fe(II) without oxidation, as supported by the
456 previously noted Fe-depletion in Archean paleosols (Rye and Holland, 1998). Therefore, we
457 expect that there would have been little Fe-bound inorganic phosphate in Archean river water
458 and, correspondingly, a higher concentration of dissolved inorganic phosphate (**Table 2**).
459 Moreover, due to higher levels of atmospheric CO₂, Archean weathering fluids, including
460 rainwater and river water, are thought to have been more acidic than today (Hao et al., 2017a).
461 As presented in **Fig. 5a and b**, acidic and reducing Archean weathering fluids allow much
462 higher solubilities of primary and secondary P-bearing minerals than dissolved P levels in
463 modern river water at a wide range of pH values (4.5 – 7.5) (Gaillardet et al., 2014). Indeed,
464 the dissolution of P-minerals in Archean acidic waters is both kinetically and
465 thermodynamically more favorable than today. High solubility of phosphate in Archean river
466 water would enable riverine transport of rapidly weathered phosphate to the sea(s).

467 Based on **Fig. 2b-4b**, the continental weathering flux of phosphorus in the late
468 Archean was 0.3 to 3.5 times the modern value. In this study, we assumed that the total
469 dissolved inorganic phosphate in Archean river water was the sum of modern DIP and Fe-
470 bound PIP multiplied by the ratio of chemical weathering flux (p) between the Archean and
471 modern (**Table 2**). Similarly, we assumed that chemical weathering of organic P from
472 sedimentary rock (DOP and POP) and the physical weathering of phosphate (detrital and
473 aeolian P) are influenced primarily by the relative weathering area (**Table 2**). However, this
474 simple consideration might over- or under-estimate the contribution of these components. For
475 example, physical weathering is dependent on many environmental factors, including
476 elevation, climate, and vegetation (Drever, 1994; Edmond et al., 1995; Zhou et al., 2008). In
477 the Archean, these all differed from today (see **Discussion**), complicating estimates of detrital

478 and aeolian P fluxes on the early Earth. Similarly, the weathering of organic P depends on a
479 number of environmental factors, including the redox state of weathering fluids, the content
480 of organic-P in sedimentary rock, and the presence of life. For example, organic matter
481 should have had a longer retention time in anoxic Archean environments compared to today.
482 Thus, organic P, once weathered, might have been stably transported in reducing Archean
483 waters. Empirical analyses, however, show that the P content of Archean shales is lower than
484 that of their modern counterparts (Reinhard et al., 2017). Regardless of these uncertainties,
485 the contributions of organic and aeolian components to overall riverine fluxes would have
486 been relatively small compared with the combined fluxes of dissolved inorganic and Fe-
487 bound P. We note again that detrital P, although representing the largest proportion of
488 continental P, is not biologically available. Therefore, we believe that our calculations
489 provide a reasonable estimate of the continental input of bioavailable P to the Archean ocean.

490 Direct evidence of P-behaviors during Archean weathering comes from the paleosol
491 record. The mobility of P in paleosols was assessed as the ratio of P to the immobile element
492 Ti (relative to underlying bedrock) (**Methods and Materials**). To minimize the effect of
493 post-depositional processes, we focused on long term trends in the mean level of P/Ti, a
494 method applied widely in interpretations of ancient sediments (Cox et al., 2018; Planavsky et
495 al., 2010; Stüeken et al., 2012). The result (**Fig. 6 & S4**) shows stronger depletion of P in
496 Archean paleosols compared with younger examples. In addition, a Student's t-test of P/Ti in
497 Archean and post-Archean paleosols confirms that Archean paleosols are significantly more
498 depleted in P than their post-Archean counterparts ($p < 10^{-4}$) (**Fig. 6b & S4b**). These results
499 are qualitatively coherent with the outputs of our weathering models, which indicate more
500 pronounced weathering of P in the Archean relative to the modern Earth.

501

502 **5. Discussion**

503 Continental weathering is generally classified as either kinetically- or transport-
504 limited, depending on relative rates of chemical weathering and physical erosion (West et al.,
505 2005). For kinetically-limited weathering, the rate of physical erosion exceeds the rate of
506 chemical weathering; total weathering flux is then limited by the chemical weathering supply.
507 In the case of transport-limited weathering, the rate of chemical weathering depends on
508 exposure of fresh rock by physical erosion; total weathering flux is limited by the removal of
509 regolith by physical erosion. Climate and tectonics are two major factors controlling these
510 weathering scenarios.

511 Considering the high atmospheric $p\text{CO}_{2,g}$ of Archean Earth (Hart, 1978; Kasting et al.,
512 1989; Krissansen-Totton et al., 2018; Owen et al., 1979), chemical weathering of silicates
513 should have been more rapid than in the modern environment (Berner, 2004). In contrast,
514 physical erosion of Archean continents might have been limited by the restricted area and
515 low elevation of mountainous areas. Geophysical models indicate that hot Archean
516 continental lithosphere could not support mountains with high elevations (Flament et al.,
517 2013; Rey and Coltice, 2008). Specifically, the maximum elevation of continental plateaus
518 might have increased from around 1000 to 3900 m (**Fig. 1b**) as the mantle cooled through
519 Archean time, in contrast to 5500 m for present-day Tibet (Flament et al., 2013). The
520 elevation of mountainous areas has long been proposed to control maximum erosion fluxes
521 (Edmond et al., 1995). Vegetation cover is another important factor that strongly affects
522 erosion (Gyssels et al., 2005). In order to decipher whether Archean weathering was
523 kinetically or transport limited, we adopted models from the literature to quantify the relative
524 rates of silicate weathering and physical erosion (**Methods and Materials**).

525 The result (**Fig. 7**) shows an increasing rate of physical erosion but decreasing rate of
526 chemical weathering from the early to late Archean Eon. During the Archean, the maximum
527 elevation of mountainous areas increased through time, as did the total area of emergent crust

528 (Flament et al., 2013; Korenaga et al., 2017), resulting in enhanced physical erosion. At the
529 same time, declining $p\text{CO}_{2,g}$ and temperature would have led to decreasing rate of chemical
530 weathering. The absence of vegetation in the Archean could have strengthened physical
531 erosion because of the lack of sediment protection (Drever, 1994); on the other hand,
532 weakened chemical weathering (Berner, 2004) would have had the opposite effect. The no-
533 vegetation effect, however, remained constant throughout the Archean and, hence, makes no
534 contribution to rate changes within the Eon.

535 In all three scenarios, the system begins in a predominantly transport-limited regime
536 and transitions to one of largely kinetic limitation, with the time of cross-over depending on
537 the model for continental emergence. Thus, in our preferred scenario, high rates of chemical
538 weathering were favored by early and middle Archean conditions (**Fig. 2-4**), but continental
539 flux of P to the oceans would have been limited by slow physical erosion and the limited
540 exposure of fresh rock. It is notable that our model input of elevation represents the
541 maximum elevation of Archean plateaus reconstructed by Flament et al. (2013). The actual
542 elevation might have been much lower, indicating even slower erosion rates. As relative rates
543 of physical erosion increased, they came to exceed the relative rate of chemical weathering in
544 the late Archean (3.0 to 2.5 Ga) (**Fig. 7**). From then on, continental flux of P was dominated
545 by the flux of chemical weathering (**Fig. 2b-4b**). On the modern Earth silicate weathering is
546 transport-limited in catchments such as continental cratons while kinetically limited in alpine
547 and submontane catchments (West et al., 2005). On the global scale, Hartmann et al. (2014)
548 estimated the effect of soil on chemical weathering flux and suggested a 40 % reduction by
549 soil shielding compared to an Earth surface covered by young rocks. Nevertheless, our
550 calculated relative rate of physical erosion could exceed that of chemical weathering by
551 several-fold on the late Archean Earth (**Fig. 7**), marking a notable transition from large-scale
552 transport-limited weathering in the early and middle Archean to kinetically-limited

553 weathering in the late Archean Eon. This result confirms our flux calculations, which indicate
554 that continental weathering could have contributed comparable or higher amounts of
555 bioavailable phosphorus to the late Archean ocean ecosystem than occurs today.

556

557 **6. Conclusions**

558 Chemical weathering depends on several factors that have changed through time,
559 including temperature, pH, vegetation cover, and the chemical composition, exposed area,
560 and elevation of land masses. Given high but decreasing $p\text{CO}_2$ in the Archean atmosphere,
561 rates of apatite weathering should have been high early in the Archean and then decreasing
562 through the duration of the eon. Despite the high apatite weathering rates dictated by
563 relatively acidic rainwater, P fluxes from the continents to the oceans were probably very low
564 in the early Archean because of limitations in the exposed surface area and elevation of
565 continents. As continents emerged through time, P fluxes to the oceans would have increased,
566 reaching values comparable to the modern by the end of the eon.

567 We have modeled secular changes in P fluxes in relation to three distinct models for
568 continental emergence. Not surprisingly, they give results that differ in timing but agree in
569 overall trend. Increasingly, stratigraphic, geophysical, and geochemical data support strong
570 continental emergence in the late Archean Eon (Bindeman et al., 2018; Flament et al., 2013,
571 2008; Spencer et al., 2019), favoring a variant on the model results shown in **Figure 1**.
572 Depending on the exact time scale of continental emergence, the major increase in P flux to
573 the ocean could have occurred close to the Archean-Proterozoic boundary.

574 Such a history has a number of implications for primary production early in Earth
575 history. Among other things, the inferred time trajectory of P flux to the oceans lessens the
576 need for models that posit the evolution of oxygenic photosynthesis just before the Great
577 Oxidation Event at ca. 2.4 Ga. Even if oxygenic phototrophs (cyanobacteria) existed in early

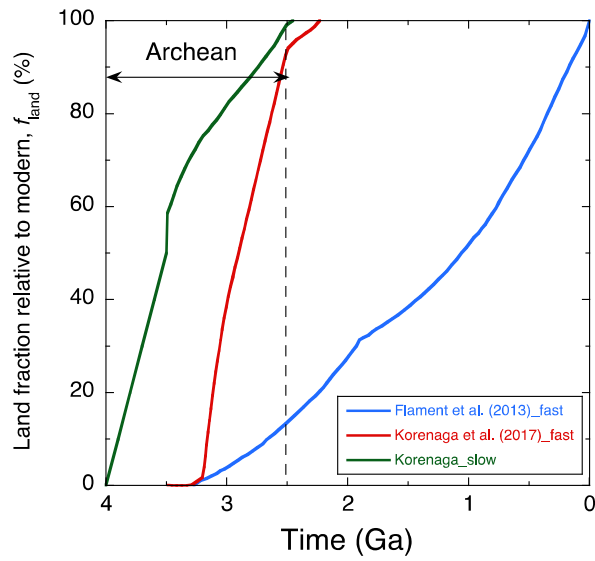
578 Archean oceans, rates of primary production might have been too low to affect atmospheric
579 oxygenation. Also, above a critical level of Fe/P in the oceans, anoxygenic photoautotrophs
580 would have been favored ecologically over oxygenic photoautotrophs in most parts of the
581 Archean biosphere (Jones et al., 2015), which could account for the carbon mass balance
582 inferred from carbon isotopes (Krissansen-Totton et al., 2015) without producing O₂.
583 Transiently high oxygen production – and consequently, “oxygen oases” – would have been
584 possible locally where P availability was high and/or the availability of alternate electron
585 acceptors for photosynthesis was low. Molecular phylogenies that place the origin of
586 oxygenic photosynthesis in freshwater (Blank and Sanchez-Baracaldo, 2010) are consistent
587 with this reasoning and our model results. And, as others have argued (e.g., Flament et al.,
588 2008; Campbell and Davies, 2017), increased P fluxes associated with late Archean
589 continental emergence could have fueled the relatively high rates of oxygenic photosynthesis
590 needed to nudge Earth’s surface into a permanently oxic state.

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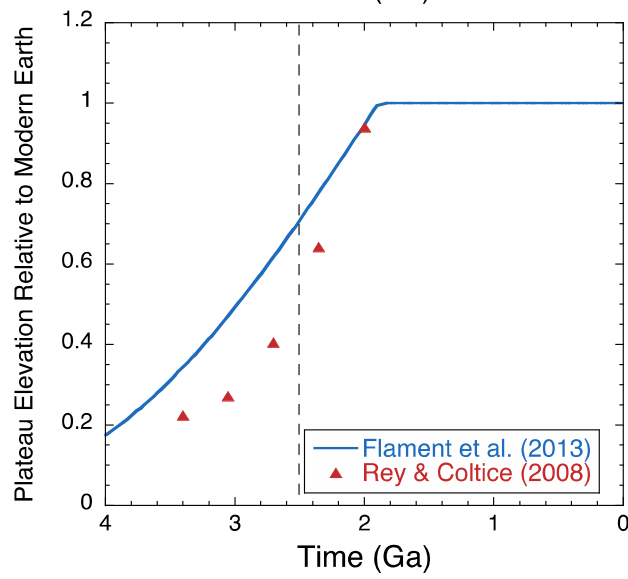
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597 **Author contributions** JHH and AHK conceived of the project. JHH compiled and FH
598 analyzed the paleosol data. JHH and FH performed the simulations; JHH and AHK analyzed
599 the results. All authors discussed the results and wrote the manuscript.

600



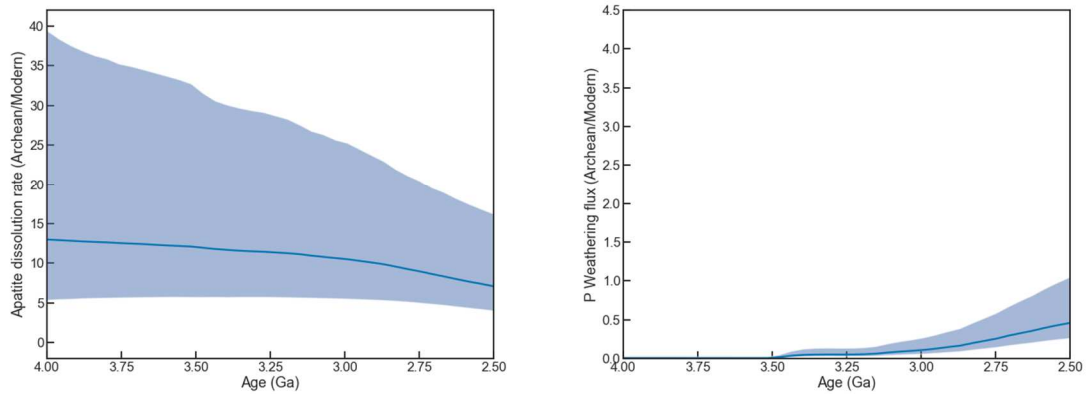
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602

603 Figure 1. The timing of continental emergence: (a) emergence of continental land above sea
 604 level according to Flament et al. (2013) and Korenaga et al. (2017) and (b) ratio of maximum
 605 plateau elevation on the Archean Earth relative to today (5520 m).

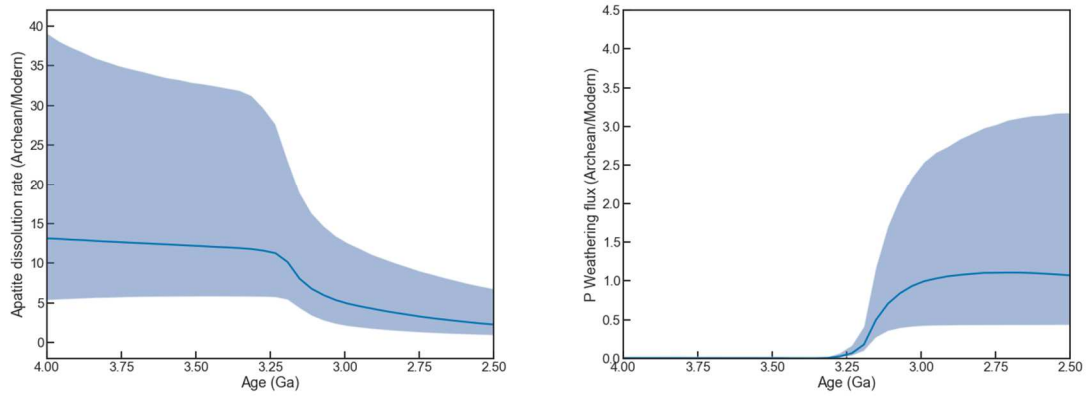
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609 Figure 2. Continental weathering of phosphorus in the case of slow continental emergence in
610 the late Archean Eon (Flament et al., 2013, in Figure 1): (a) ratio of acidic dissolution rates of
611 apatite (rate per unit area) in the Archean relative to today; (b) ratio of weathering flux of
612 phosphorus in the Archean relative to today. Solid lines show median outputs, and shaded
613 regions show 95% confidence intervals.

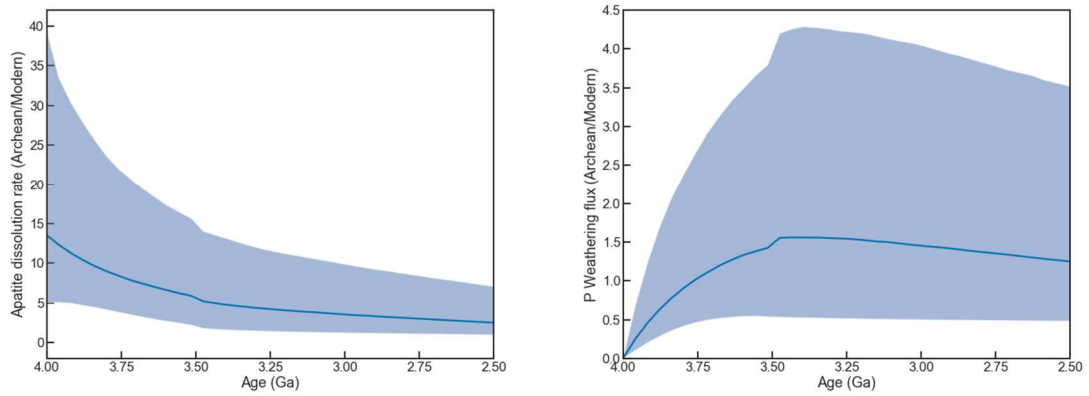
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616 Figure 3. Continental weathering of phosphorus in the case of rapid continental emergence in
 617 the late Archean (Korenaga et al., fast in Figure 1): (a) acidic dissolution rates of apatite
 618 relative to today;(b) weathering flux of phosphorus relative to today. Solid lines show median
 619 outputs, and shaded regions show 95% confidence intervals.

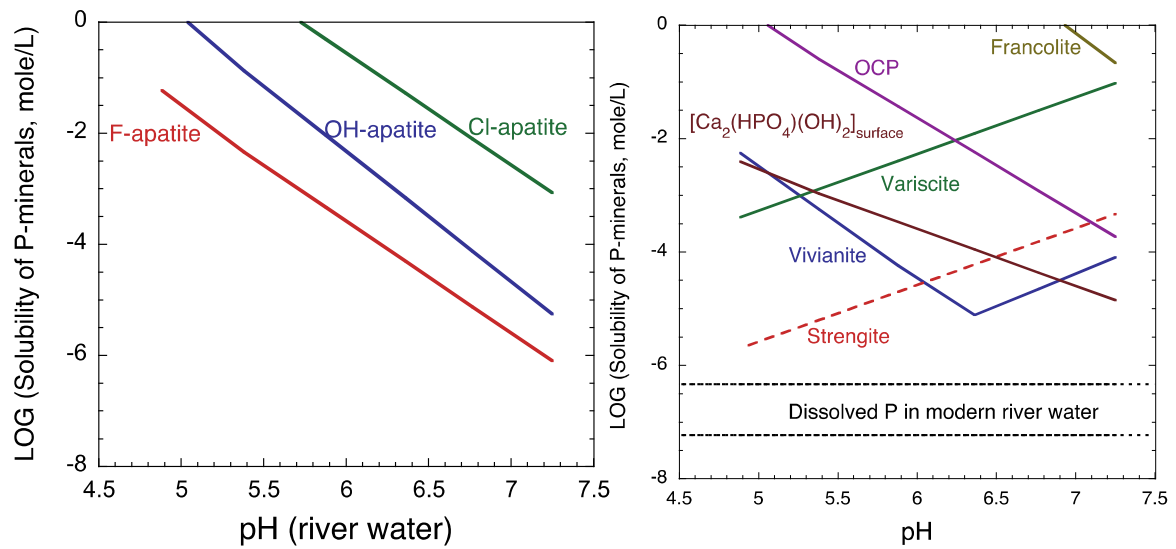
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621

622 Figure 4. Continental weathering of phosphorus in the case of rapid continental emergence of
 623 in the early Archean Eon (Korenaga_slow in Figure 1): (a) acidic dissolution rates of apatite;
 624 (b) weathering flux of phosphorus. Solid lines show median outputs, and shaded regions
 625 show 95% confidence intervals.

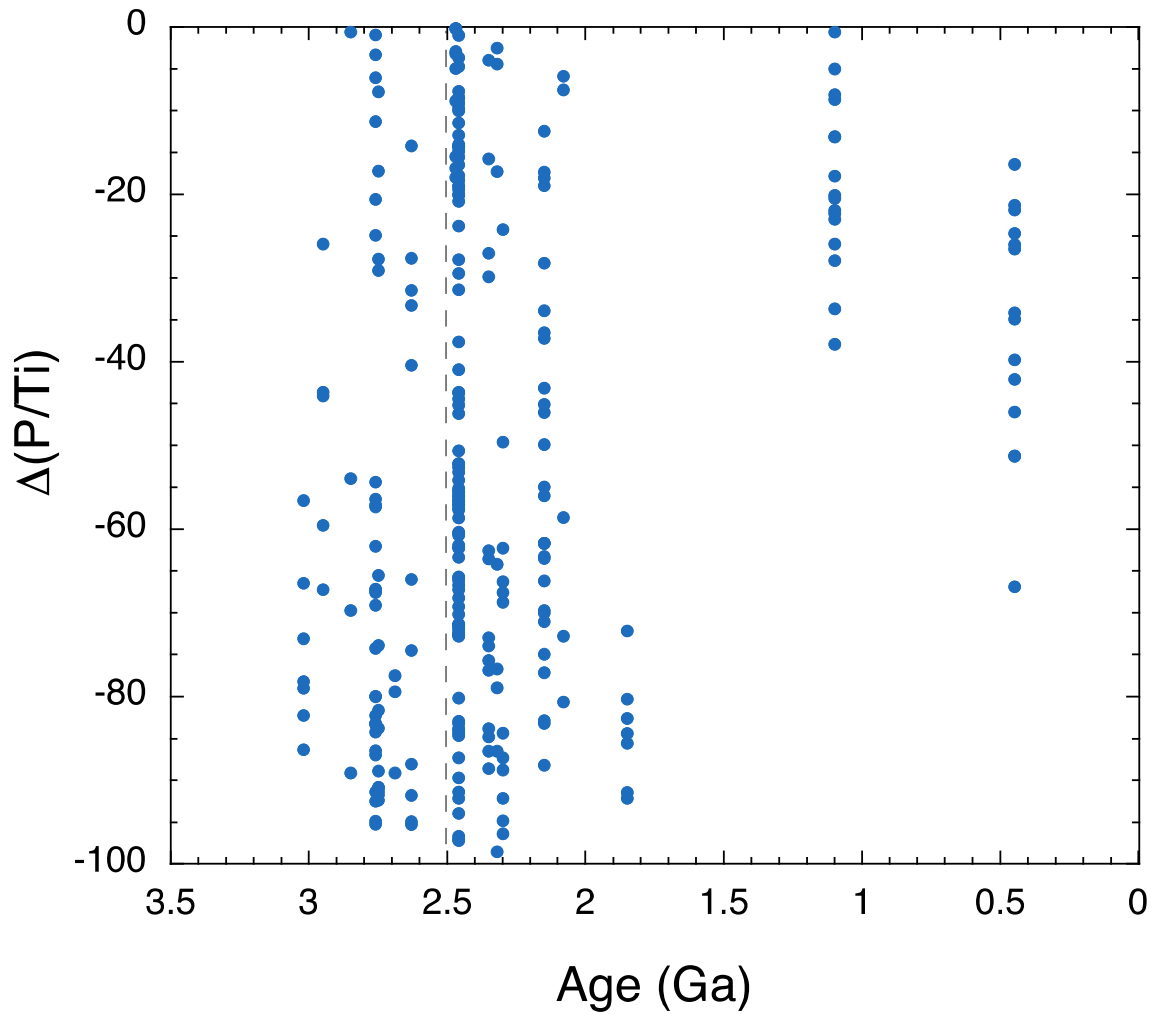
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627

628 Figure 5. Leaching weathering of phosphorus on the Archean continents. (a) Solubility limits
 629 of apatite in the Archean rainwater as a function of pH. (b) Solubility limits of various
 630 secondary P-bearing minerals in Archean river water as a function of pH. See **Methods &**
 631 **Materials** and **Table S1** for assumptions on the concentrations of other ions and **Table 1** for
 632 thermodynamic data.

633



634

Group 1: (P/Ti)_Archean
 Group 2: (P/Ti)_post-Archean

	Group 1	Group 2
Count	75	212
Mean	-63.9824	-48.2789
Variance	779.282	822.446
Std. Dev.	27.9156	28.6783
Std. Err	3.22342	1.96963

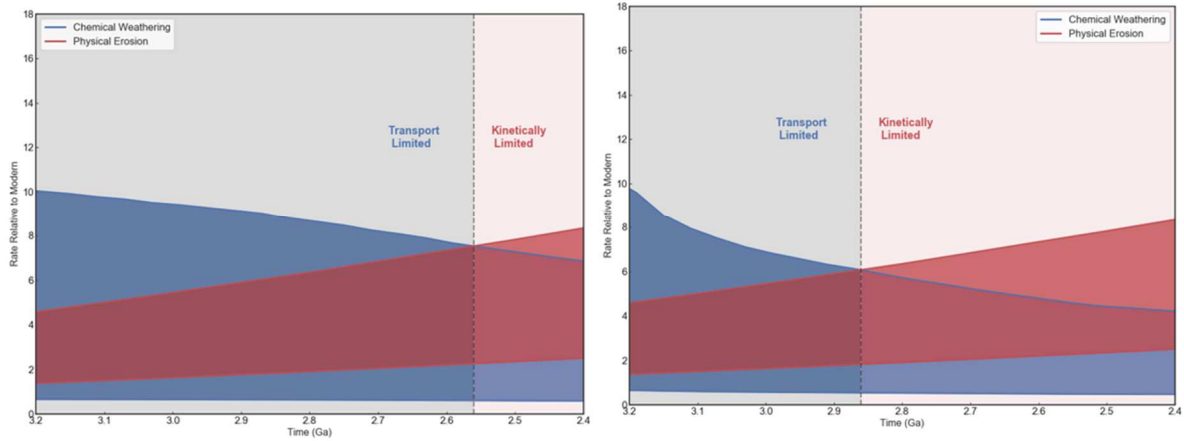
Mean Difference	-15.7035
Degrees of Freedom	133
t Value	-4.1571
t Probability	< .0001

635

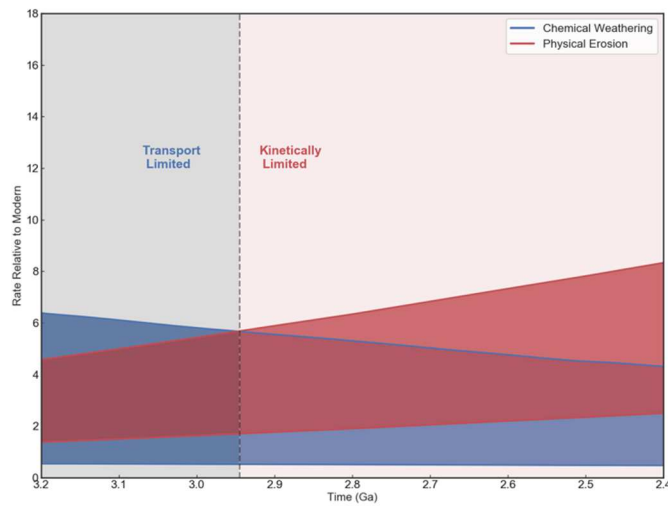
636 Figure 6. Leaching weathering of P recorded in paleosols. (a) P depletion ($\Delta P/Ti < 0$) relative
 637 to bedrock in paleosols; (b) Student's t-test results of Archean and post-Archean paleosols'
 638 $\Delta P/Ti$.

639

640



641



642

643 Figure 7. Relative intensity of chemical and physical weathering on the Archean Earth
644 compared with today in the three cases of continental emergence: (a) slow emergence in the
645 late Archean; (b) rapid emergence in the late Archean; (c) rapid emergence in the early
646 Archean. Blue shaded regions display 95% confidence intervals of the Archean silicate
647 weathering rate relative to today.

648

649 Table 1. Solubility reactions of primary and secondary P-bearing minerals in Archean river water.

Solubility in river water	Combined reaction ^a	Log K
OH-apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH}) + 7\text{H}^+ \rightarrow 5\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4^- + \text{H}_2\text{O}$	16.5 ^a
Cl-apatite	$\text{Ca}_5(\text{PO}_4)_3\text{Cl} + 6\text{H}^+ \rightarrow 5\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4^- + \text{Cl}^-$	12.0 ^a
F-apatite	$\text{Ca}_5(\text{PO}_4)_3\text{F} + 6\text{H}^+ \rightarrow 5\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4^- + \text{F}^-$	-1.15 ^a
Vivianite	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} + 4\text{H}^+ \rightarrow 3\text{Fe}^{2+} + 2\text{H}_2\text{PO}_4^- + 8\text{H}_2\text{O}$	3.31 ^b
Variscite	$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}_{\text{s}} + \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_{3,\text{am}} + \text{H}_2\text{PO}_4^- + \text{H}^+$	-8.27 ^c
Strengite	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}_{\text{s}} + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_{3,\text{am}} + \text{H}_2\text{PO}_4^- + \text{H}^+$	-10.6 ^d
$[\text{Ca}_2(\text{HPO}_4)(\text{OH})_2]_{\text{surface}}$	$\text{Ca}_5(\text{PO}_4)_3(\text{OH}) + 3\text{H}_2\text{O} + \text{H}^+ \rightarrow 2\text{Ca}_2(\text{HPO}_4)(\text{OH})_2 + \text{Ca}^{2+} + \text{H}_2\text{PO}_4^-$	-2.59 ^e
Octacalcium phosphate (OCP)	$\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O} + 5\text{H}^+ \rightarrow 4\text{Ca}^{2+} + 3\text{H}_2\text{PO}_4^- + 2.5\text{H}_2\text{O}$	10.3 ^f
Francolite	$\text{Ca}_{10}(\text{PO}_4)_{5.5}(\text{CO}_3)_{0.5}\text{F}_{2.5} + 12\text{H}^+ \rightarrow 10\text{Ca}^{2+} + 5.5\text{H}_2\text{PO}_4^- + 0.5\text{CO}_2\text{g} + 2.5\text{F}^- + 0.5\text{H}_2\text{O}$	38.0 ^g

650 ^aCalculated with SUPCRT92b (Johnson et al., 1992); ^bCalculated with SUPCRT92 and the reported log $K_{\text{sp,Vivianite}}$ (Al-Borno and Tomson,
651 1994); ^cCalculated with SUPCRT92b and the reported log $K_{\text{sp,Variscite}}$ (Stumm and Morgan, 1996); ^dCalculated with SUPCRT92b, log $K_{\text{s,Fe}(\text{OH})_3}$
652 (Liu and Millero, 1999), and the reported log $K_{\text{sp,Strengite}}$ (Stumm and Morgan, 1996); ^eCalculated with SUPCRT92b and data from (Fox et al.,
653 1985); ^fCalculated with SUPCRT92b and data from log $K_{\text{sp,OCP}}$ (Tung et al., 1988); ^gCalculated with SUPCRT92b and data from log $K_{\text{sp,Francolite}}$
654 (Vieillard, 1978).

655 Table 2. The continental flux of biologically available P (= DIP + DOP + POP + PIP Fe-
 656 bound + 20% Aeolian) (Compton et al., 2000) in the late Archean compared with
 657 preindustrial time (in 10^{10} moles P/yr).

Riverine Phosphorus	Preindustrial	Late Archean	Bioavailability
DIP (dissolved inorganic P)	0.97-1.6	1.5-30 ^a	Y
DOP (dissolved organic P)	0.65	0.1-0.65 ^b	Y
POP (particulate organic P)	2.9	0.3-2.9 ^c	Y
PIP (particulate inorganic P), Fe-bound	4.8-9.7	0	Y
PIP, detrital	22-39	2.2-39 ^d	N
Aeolian phosphorus	3.2	0.3-3.2 ^e	20% ^f
Total (bioavailable P)	10-15.5	4-34	

658 ^a(DIP(modern) + PIP,Fe-bound (modern)) * p(Archean)/p(Modern); ^bDOP(modern) *
 659 SA(Archean)/SA(Modern); ^cPOP(modern) * SA(Archean)/SA(Modern);
 660 ^dPIP,detrital(Modern) * SA(Archean)/SA(Modern); ^eAeolian(modern) *
 661 SA(Archean)/SA(Modern); ^fAssume same percentage on the Archean Earth.

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