

1 Lithium isotope constraints on the plumeworld hypothesis for the
2 Marinoan Snowball Earth

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24 **ABSTRACT**

25 The Snowball Earth hypothesis predicts that continental chemical weathering was curtailed
26 substantially during but rebounded strongly after the Marinoan ice age some 635 million years ago.
27 Defrosting the planet would result in a plume of fresh glacial meltwater with a different chemical
28 composition than underlying hypersaline seawater, generating an onshore-offshore geochemical gradient.
29 Here we test the plumeworld hypothesis using lithium isotope abundances in the basal Ediacaran

30 Doushantuo cap dolostone that accumulated in the aftermath of the Marinoan snowball Earth along an
31 onshore-offshore transect in South China. Critical to this analysis is whether the cap dolostone formed
32 simultaneously at different water depths, or whether it accumulated sequentially in shallow marine
33 environments as sea level rose in the glacial aftermath. Our data shows an overall decreasing $\delta^7\text{Li}$ trend
34 with distance from the shoreline, which is consistent with either variable mixing of a meltwater plume
35 with high $\delta^7\text{Li}$ and hypersaline seawater with low $\delta^7\text{Li}$ under the isochronous accumulation scenario, or
36 with the progressive dominance of the meltwater plume under the diachronous end member, wherein cap
37 dolostone accumulation accompanied sea level rise. In contrast to the modern oceans with high $\delta^7\text{Li}$, our
38 geochemical model explains the evolution of low $\delta^7\text{Li}$ of syn-glacial silica-rich seawater through
39 enhanced silicate reverse weathering.

40

41 **Keywords:** Cryogenian Period, Marinoan glaciation, Snowball Earth, Plumeworld model, Lithium
42 isotopes.

43

44 INTRODUCTION

45 The Neoproterozoic snowball Earth events [1] represent extreme climate conditions that
46 provide information about the limits of climate change on our planet. One of the best studied of these is
47 the terminal Cryogenian Marinoan glaciation that occurred ca. 650–635 Ma, with its termination marked
48 by the global deposition of fine-grained cap dolostones [1-4]. It has been hypothesized that the
49 hydrological cycle, and hence continental chemical weathering, was greatly reduced during the
50 Marinoan Snowball Earth [1], but that rapid deglaciation resulted in a plumeworld ocean, in which
51 buoyant low-salinity meltwater persistently overlaid denser hypersaline seawater [5]. This plausibly
52 happened in two steps: first, thick sea ice would melt with increasing temperature, which would result
53 in sea level rise due to thermal expansion; second, thick continental glaciers would flow into seawater,
54 and their melting would further raise sea level. Several geochemical studies, utilizing Mg, Sr, and Ca
55 isotopes of basal Ediacaran cap dolostones deposited in the aftermath of the Marinoan Snowball Earth,
56 support the plumeworld hypothesis [6-9]. Boron isotopes are also consistent with rapid changes in the
57 pH of post-glacial seawater [10, 11], possibly associated with variable mixing of fresh and hypersaline
58 marine water masses. A recent box model based on $\delta^{26}\text{Mg}$ balance [7] and an energy model based on
59 turbulent mixing [12] further estimated a timescale of $\sim 10^3$ – 10^4 years for the persistence of the
60 plume [12, 13] before it fully mixed with seawater. Here, we independently test the plumeworld
61 hypothesis through Li isotope analysis of a series of cap dolostones from the basal Ediacaran
62 Doushantuo Formation of South China, coupled with numerical modeling to estimate a timescale for
63 post-glacial mixing of the oceans.

64 The geochemical cycle of lithium in modern oceans is generally well understood [14, 15].
65 Because of their substantial mass difference ($\sim 17\%$), ^6Li and ^7Li fractionate strongly during mineral-
66 fluid interactions [15]. Importantly, the fractionation factors are largely constant, with negligible
67 dependence on temperature, salinity, Li/Ca ratios, biological processes, and redox conditions [16-19].
68 In the modern ocean, the two primary Li sources are riverine flux (1.0×10^{10} mol/yr) derived from

69 continental silicate weathering with an average $\delta^7\text{Li}$ of $\sim 23\text{‰}$ and marine hydrothermal flux (1.3×10^{10}
70 mol/yr) with an average $\delta^7\text{Li}$ of 8.3‰ [20]. The two major sinks are authigenic clay formation associated
71 with silicate reverse weathering and low-temperature basalt alteration [21, 22]. As ^6Li is preferentially
72 partitioned into clays during mineral-fluid interactions (e.g., incongruent silicate weathering and reverse
73 weathering) [19], $\delta^7\text{Li}$ of modern seawater ($\sim 31\text{‰}$) is higher than that of average riverine input.
74 Additionally, since the residence time of lithium in modern oceans is 0.3–1.5 Myr [23], much longer
75 than the oceanic mixing time of $\sim 10^3$ years [20], $\delta^7\text{Li}$ of modern seawater is homogeneous.

76 In contrast, the lithium geochemical cycle during and immediately after the Marinoan snowball
77 Earth would have been remarkably different from that of the modern ocean. This can be illustrated by
78 considering an end-member scenario of a hard Snowball Earth. During the Marinoan ice age, which
79 lasted between 3.0 and 15.2 Myr [2], riverine Li flux into the ocean would have been attenuated relative
80 to the modern level due to a reduced hydrological cycle and limited continental weathering. In contrast,
81 silicate reverse weathering on the seafloor may have been faster due to generally higher dissolved silica
82 concentrations (lacking known biological sinks for the element during the Neoproterozoic), which
83 would have accelerated clay mineral formation and reduced the magnitude of Li isotopic fractionation
84 [22]. Thus, the attenuated riverine Li flux coupled with reduced isotopic fractionation would
85 hypothetically lead to the preferential distillation of ^7Li from seawater during the glaciation, resulting
86 in lower Li concentrations and $\delta^7\text{Li}$ values preserved in subsequently formed carbonates. Upon the
87 termination of the Marinoan Snowball Earth, thick sea ice would have melted first and mixed with
88 hypersaline deep water. Since sea ice would contain little to no Li, this step would only dilute the
89 hypersaline seawater, but not change its $\delta^7\text{Li}$ composition. Continental glaciers would then melt and
90 deliver ^7Li -rich fluids (presumably with $\delta^7\text{Li}$ similar to modern riverine influx of $\sim 23\text{‰}$) that floated
91 above the aged and ^7Li -depleted hypersaline seawater. The critical question, then, is whether the
92 carbonate precursors to the fine-grained cap dolostones that appear across the platform formed
93 simultaneously under different water depths [24] or whether they formed sequentially in shallow water
94 environments as sea level rose in the glacial aftermath [25].

95 In this study, we evaluate these two contrasting depositional scenarios in light of the known
96 kinetic barriers to dolomite formation, through a detailed evaluation of the sedimentology and multiple
97 isotope records (including previously reported $\delta^{13}\text{C}$ and $\delta^7\text{Li}$, as well as our new $\delta^7\text{Li}$ data) for the
98 Doushantuo cap dolostone in South China. The $\delta^7\text{Li}$ values reveal an onshore-offshore pattern and they
99 are substantially lower than those of Phanerozoic carbonates. To interpret our data, a simple box model
100 was constructed to show that the $\delta^7\text{Li}$ compositions are consistent with an extremely limited riverine Li
101 influx during the Marinoan glaciation and a plumeworld ocean in the aftermath.

102

103 **GEOLOGICAL SETTING AND SAMPLING**

104 The Ediacaran Doushantuo Formation in the Yangtze Block of South China (Fig. 1a–b) consists
105 of carbonate, siltstone, black shale, and phosphorite that overlie glacial diamictites of the Marinoan-age
106 Nantuo Formation and underlie the terminal Ediacaran Dengying Formation or its correlative Liuchapo
107 Formation. The basal Doushantuo Formation is represented by a cap dolostone (Fig. 1c; Supplementary

108 Figures 1a and 2) that is a few meters in thickness, but is widely distributed across the Yangtze platform
109 from shelf to basinal environments [4]. The cap dolostone is laterally persistent and traceable with
110 consistent lithology and internal stratigraphy for at least 350 km in platform-to-basin transects. It consists
111 of thick beds of thinly laminated dolostone accumulated below storm wave base [4]. A distinctive suite
112 of closely associated tepee-like structures, stromatolite-like cavities, layer-parallel sheet cracks, and
113 cemented breccias occurs in the cap dolostone, particularly in the lower interval. While the top of the cap
114 dolostone in slope and basinal facies appear to grade into overlying strata, proximal facies reveal
115 evidence of a locally developed karstic unconformity (Supplementary Figures 1b and 2) [26, 27]. Two
116 indistinguishable zircon U–Pb ages from South China—a 634.6 ± 0.9 Ma age from the uppermost Nantuo
117 Formation [28] and a 635.2 ± 0.6 Ma age from an ash bed immediately above the cap dolostone [29]—
118 constrain the age of the cap dolostone to ~635 Ma.

119 Samples of the Doushantuo cap dolostone were collected from five sections, including the
120 Zhangcunping (ZCP) section (N31°17'34", E111°12'30") and Jiulongwan (JLW) section (N30°48'54",
121 E111°03'20") in Hubei Province, the Daping (DP) section (N28°59'01", E110°27'42") and Siduping
122 (SDP) section (N28°55'05", E110°26'55") in Hunan Province, and the Wuhe (WH) section (N26°45'46",
123 E108°25'7") in Guizhou Province (Fig. 1b). Together with the previously published $\delta^7\text{Li}$ data from the
124 Daotuo (DT) section in Guizhou Province [30], these sections represent a transect from inner shelf to
125 slope facies (Fig. 1b) [31].

126

127 RESULTS

128 Lithium isotope compositions of the 36 cap dolostone samples from the five sections were
129 analyzed on a Q-ICP-MS at University of North Carolina at Chapel Hill. The data, along with previously
130 published $\delta^7\text{Li}$ data from the Daotuo section [30], are presented in Fig. 1d–h and Supplementary Table
131 S1. Twenty one of these samples were also analyzed for $\delta^7\text{Li}$ on a MC-ICP-MS at University of Maryland
132 for inter-laboratory comparison, and the results are presented in Supplementary Figure 3 and
133 Supplementary Table S1. The two sets of data agreed excellently, although the UMD dataset has much
134 better analytical uncertainties (approximately $\pm 0.3\text{‰}$, 2σ) than the UNC dataset (approximately $\pm 1.9\text{‰}$,
135 2σ). We choose to use the UNC dataset for discussion because of its better stratigraphic coverage.
136 Consistent with the previously published data [30], the 36 new measurements show that the $\delta^7\text{Li}$ values
137 range from -1.7 to 14.9‰ with an average of 4.4‰ ($n = 36$, $SD = 4.1\text{‰}$), which is significantly lower
138 than those of previously published Precambrian (average = 7.7‰ , $n = 217$, $SD = 5.7\text{‰}$; $p\text{-value} \approx 5.0 \times$
139 10^{-4} , one-tailed T-test), Paleozoic (average = 10.1‰ , $n = 263$, $SD = 4.3\text{‰}$, $p\text{-value} \approx 3.7 \times 10^{-13}$, one-
140 tailed T-test), and Cenozoic-Mesozoic carbonates (average = 23.1‰ , $n = 45$, $SD = 3.8\text{‰}$, $p\text{-value} \approx 1.0$
141 $\times 10^{-34}$, one-tailed T-test) [22].

142 The $\delta^7\text{Li}$ data show a decreasing trend from inner shelf (the ZCP section, average = 14.3‰ , n
143 = 3; Fig. 1e) to upper slope (the DT section, average = 7.4‰ , $n = 30$; and the WH section, average =
144 6.1‰ , $n = 10$; combined average = 7.1‰ ; Fig. 1g) to lower slope facies (the SDP section, average =
145 3.4‰ , $n = 16$; and the DP section, average = -0.3‰ , $n = 4$; combined average = 2.6‰ ; Fig. 1h), with the
146 intrashelf JLW section (average = 0.5‰ , $n = 3$; Fig. 1f) representing an anomaly to this trend. The overall

147 difference in $\delta^7\text{Li}$ between inner shelf and lower slope facies reaches 14.6‰ (Fig. 1d).

148 Although there are notable stratigraphic variations, the DT and WH sections show poorly
149 defined but recognizable stratigraphic trends. At these two sections, $\delta^7\text{Li}$ starts with relatively low values
150 (stage I in Fig. 1g) and then stabilizes at higher values (stage II in Fig. 1g). At DT, $\delta^7\text{Li}$ decreases slightly
151 in the upper cap dolostone (stage III in Fig. 1g). These three stages are not recognized at other studied
152 sections because insufficient stratigraphic coverage and perhaps also slight diachroneity of the cap
153 dolostone at the time scale of 10^3 years [25]. Similar to $\delta^7\text{Li}$ values, $\text{Li}/(\text{Mg}+\text{Ca})$ ratios also show a
154 stratigraphic pattern with an increasing followed by a decreasing trend, best expressed at WH, and SDP
155 (Supplementary Figure 1).

156

157 **DISCUSSION**

158 **Diagenesis and clay mineral contamination**

159 In order to interpret the variable Li isotopic compositions of the Doushantuo cap dolostone
160 across the South China basin in the context of the plumeworld hypothesis, we should have confidence
161 that the $\delta^7\text{Li}$ values in different localities and stratigraphic positions within each unit reflect evolving
162 depositional conditions. Like all geological samples, the Doushantuo cap dolostone undoubtedly
163 experienced diagenesis. The question most relevant to this study is whether diagenetic alteration
164 significantly modified the spatial and stratigraphic patterns of carbonate $\delta^7\text{Li}$, and whether it can account
165 for the observed geochemical patterns.

166 We used petrographic observations and geochemical data to assess the potential for diagenetic
167 alteration of $\delta^7\text{Li}$ [32]. Detailed petrographic observations (Supplementary Figure 4) and diagenetic
168 screening by geochemical proxies—including $\delta^{18}\text{O}$, Rb/Sr , Mn/Sr , $\text{Mn}/(\text{Mg}+\text{Ca})$, and $\text{Sr}/(\text{Mg}+\text{Ca})$
169 (Supplementary Figure 5)—suggest minimal diagenetic alteration of $\delta^7\text{Li}$ values, with the possible
170 exception of the WH section. Importantly, the spatial and stratigraphic patterns of the $\delta^7\text{Li}$ values cannot
171 be explained by diagenetic alteration alone (see SI).

172 To aid the assessment of clay mineral contamination during sample leaching processes, the
173 leachate for $\delta^7\text{Li}$ measurement was also analyzed for elemental concentrations. Because clay and
174 carbonate minerals have different Al and Rb concentrations, these elements were chosen as proxies for
175 clay contamination. The $\text{Rb}/(\text{Mg}+\text{Ca})$ ratios of Doushantuo cap dolostone samples ($n = 36$) range from
176 6.39×10^{-8} to 2.11×10^{-6} ppm/ppm (Supplementary Figure 5a), all below the proposed threshold value of
177 3.0×10^{-5} ppm/ppm [22], suggesting minimal clay mineral contamination. In contrast, $\text{Al}/(\text{Mg}+\text{Ca})$ ratios
178 of Doushantuo cap dolostone samples range from 0.42 to 9.31 ppb/ppm (Supplementary Figure 5b), and
179 many are above the 0.54 ppb/ppm threshold chosen to screen for clay contamination [22]. Nonetheless,
180 no correlation is observed between $\delta^7\text{Li}$ and element ratios of $\text{Rb}/(\text{Mg}+\text{Ca})$, $\text{Al}/(\text{Mg}+\text{Ca})$, and
181 $\text{Li}/(\text{Mg}+\text{Ca})$ (Supplementary Figure 5a–c), indicating that clay mineral contamination is unlikely to be a
182 major driver of the observed $\delta^7\text{Li}$ variations. To further assess clay mineral contamination in samples
183 with elevated $\text{Al}/(\text{Mg}+\text{Ca})$ ratios, Monte Carlo modeling was conducted to quantify the probability of
184 likely clay content in our samples (see SI text). The model suggests that the maximum probability
185 corresponds to a clay mineral content ≤ 0.5 wt.% (Supplementary Figures 6 and 7; see SI text).

186 An effort was made to correct the measured $\delta^7\text{Li}$ for potential clay mineral contamination
187 because even 0.5 wt.% clay mineral contamination could have a notable impact on $\delta^7\text{Li}$ owing to the
188 higher Li content of clay compared to carbonate minerals. As clay minerals typically have lower $\delta^7\text{Li}$
189 values than carbonates [33], corrected carbonate $\delta^7\text{Li}$ values would be higher than measured values if
190 clay contamination had occurred. Using a binary mixing model, we show that the corrected carbonate
191 $\delta^7\text{Li}$ values could be 1‰ to 6‰ higher than the measured values (Supplementary Table S4; see SI text).
192 However, the corrected data do not change the temporal and onshore-offshore patterns of $\delta^7\text{Li}$, and thus
193 we use the measured values for discussion.

194 195 **The dolomite problem**

196 Although most Phanerozoic dolostones are secondary [34], many Precambrian dolostones,
197 particularly fabric-retentive ones, are arguably primary or early diagenetic in origin (e.g., Hood and
198 Wallace [35]). Indeed, it has been experimentally demonstrated that low-temperature precipitation of
199 dolomite or proto-dolomite is feasible in the presence of exopolymeric substances [36-38], dissolved
200 silica [39], and dissolved sulfide [40], which help the dehydration of the Mg^{2+} -water complex and
201 promote dolomite precipitation [39]; incidentally, these conditions were favored in Precambrian oceans
202 because of the abundance of microbial mats, scarcity or absence of Si-biomineralizing organisms, and
203 low oxygen concentrations. The precipitation of the post-Marinoan cap dolostone may have been further
204 facilitated by magnesium sourced from intensive continental weathering [41], as well as the ion released
205 from its hydrophilic tendency in saline solutions through the mixing of the fresh water plume with
206 evolved seawater, first by the addition of melted sea ice, and second by the cap of continental plume
207 water that would mix within a timescale of 10,000 years. Wholesale precipitation of calcium carbonate
208 or calcium sulfate associated with the rise of seawater temperatures and onset of the hydrological cycle
209 would have had the same effect on the Mg/Ca of seawater thereby allowing for dolomite formation,
210 which in some modern environments restricted from the open ocean is mediated by microbial sulfate
211 reducers. Sulfate has previously been indicated as an inhibitor of dolomite formation through
212 complexation with the Mg ion [42] during the replacement of pre-existing calcite or aragonite. In a cold
213 seep environment, the anaerobic oxidation of methane is mediated by anaerobic microbial sulfate
214 reduction (MSR) that results in the production of both sulfide and alkalinity. Hence MSR, which has
215 been associated with the formation of primary dolomite in modern environments [36], would also tend
216 to decrease this potential kinetic barrier. On the other hand, more recent hydrothermal experiments
217 suggest that sulfate primarily protects calcite from dissolution, rather than prevent dolomite from
218 precipitation (e.g., Morrow and Ricketts [43]), and experiments with microbial communities at surface
219 temperatures suggest that sulfate is not a kinetic barrier to biologically-mediated primary dolomite
220 formation [44]. Regardless, it seems that environmental conditions in the aftermath of the Marinoan
221 snowball Earth were conducive to dolomite precipitation, and it is possible that the Doushantuo cap
222 dolostone was primary or early diagenetic in origin.

223 224 **The depositional setting**

225 Sedimentological evidence indicate that the Doushantuo cap dolostone was deposited in a
226 marine environment below the storm wave base, in contrast to Paleozoic and modern dolostones, which
227 are typically found in evaporitic or lagoonal conditions. However, if the kinetic barriers discussed above
228 (increased temperature, freshening of seawater, reduction or dilution of sulfate, and wholesale
229 precipitation of calcium carbonate) were overcome in the post-glacial Plumeworld, cap dolostone could
230 have formed in relatively deep waters across the basin. The lower Doushantuo cap dolostone is
231 characterized by widespread and persistent facies containing ubiquitous teepees and stromatolite-like
232 cavities that have been interpreted as related to methane cold seeps [4]. Similar cavities and cements
233 have been observed in cap dolostones from Australia [45], Namibia [46, 47], eastern California [48], and
234 Norway [49]. If the cold seep environmental interpretation is correct, methanogenic mats must have
235 carpeted the seafloor across the basin, and sulfate reduction would likely have been the dominant
236 recycling metabolism creating alkalinity and primary dolomite [36]. We envision that the sealevel could
237 have risen rapidly during the deglaciation, so this phenomenon could have been isochronous, or it could
238 have happened more slowly if the cap dolostones were diachronous [25, 50]. In the latter model, as sea
239 level progressively rose during the deglaciation, the locus of cap dolostone accumulation would have
240 moved up the continental slope and onto the previously established continental platform. In either case,
241 however, the distal settings would have accumulated Li from the evolved seawater, while more proximal
242 ones would have felt the effects of Li in the freshwater continental plume. Assuming carbon isotope
243 trends in the cap dolostones are temporal markers [25, 50], it would appear that the more distal units are
244 older (preserving the progressive depletion of ^{13}C upwards through the strata: see Siduping and Wuhe)
245 while the proximal ones may be slightly younger insofar as they present either non-variant trends (Daotuo
246 and Jiulongwan) or the enrichment of ^{13}C (Zhangcunping) (Fig. 1).

247

248 **Low $\delta^7\text{Li}$ values and synglacial distillation**

249 Broadly consistent with a previous compilation of Precambrian carbonate $\delta^7\text{Li}$ values [22], the
250 average $\delta^7\text{Li}$ value of Doushantuo cap dolostone samples (4.4‰) is markedly lower than that of modern
251 carbonates (>20‰) [32, 51], indicating that the $\delta^7\text{Li}$ values of Neoproterozoic seawater were
252 substantially lower than that of modern seawater (31‰). The lower $\delta^7\text{Li}$ values of Precambrian seawater
253 has been interpreted as the result of muted isotopic fractionation in association with clay authigenesis on
254 the seafloor [22]. Because of the scarcity or absence of Si-biomineralizing organisms in Precambrian
255 oceans, the concentration of dissolved silica was high, leading to high rates of reverse weathering, low
256 isotopic fractionation in association with clay authigenesis, reduced removal of the light Li isotope from
257 Precambrian oceans, and consequently low $\delta^7\text{Li}$ values of Precambrian seawater and carbonate proxies
258 [22, 52]. In addition, certain types of clay formation in the Precambrian seawater may have limited Li
259 isotopic fractionation, as We note that the average $\delta^7\text{Li}$ value of the Doushantuo cap dolostone (4.4‰),
260 particularly those from the lower-slope SDP and DP sections (average = 3.4‰ and -0.3‰, respectively),
261 are even lower than the average $\delta^7\text{Li}$ value (7.7‰) of Precambrian carbonates [22], suggesting that
262 additional factors may have affected the seawater $\delta^7\text{Li}_{\text{SW}}$ values during the Marinoan snowball Earth.

263 Inversion of post-Marinoan $\delta^7\text{Li}_{\text{SW}}$ from the $\delta^7\text{Li}_{\text{dolomite}}$ values of the Doushantuo cap dolostone

264 is associated with several sources of uncertainty. These include the poorly constrained isotope
265 fractionation during dolomite precipitation ($\Delta_{\text{dolomite-SW}}$), spatial and chemostratigraphic variations in
266 $\delta^7\text{Li}_{\text{dolomite}}$ of the Doushantuo cap dolostone, potential clay mineral corrections as discussed above, and
267 analytical uncertainty. We have demonstrated that clay contamination and analytical uncertainty are
268 relatively minor, and they do not account for the low values and observed spatial pattern of $\delta^7\text{Li}$.
269 Therefore, in the following discussions we focus on the uncertainty in isotope fractionations and the
270 spatial and chemostratigraphic variations.

271 Some studies have suggested that dolomite formed under fluid-buffered diagenetic conditions
272 in the Great Bahama Bank has $\delta^7\text{Li}_{\text{dolomite}}$ values similar to that of modern seawater [32, 51], indicating
273 a $\Delta_{\text{dolomite-SW}}$ value of $\sim 0\text{‰}$. If so, $\delta^7\text{Li}_{\text{dolomite}}$ values of the Doushantuo cap dolostone would mean a very
274 low $\delta^7\text{Li}_{\text{SW}}$; for example, average $\delta^7\text{Li}_{\text{dolomite}}$ of the SDP section would mean a $\delta^7\text{Li}_{\text{SW}}$ value of $\sim 3.4\text{‰}$.
275 Other studies have shown that the isotopic fractionation associated with calcite/aragonite precipitation
276 ($\Delta_{\text{calcite/aragonite-SW}}$) is around -10‰ [53-55]. If this fractionation is applicable to cap dolomite precipitation,
277 then $\delta^7\text{Li}_{\text{dolomite}}$ values from the SDP section would mean a $\delta^7\text{Li}_{\text{SW}}$ value of $\sim 13.4\text{‰}$.

278 We used a mass balance model to test whether synglacial distillation in an ice-covered ocean
279 during the Marinoan glaciation could drive $\delta^7\text{Li}_{\text{SW}}$ from a modern seawater value of 31‰ to 13‰ as
280 needed to explain the lower slope SDP data (Figs. 2, 3A–B, and Fig. 3; see SI text). For simplicity, we
281 set the pre-Marinoan $\delta^7\text{Li}_{\text{SW}}$ to the modern seawater value of 31‰ and the model tracks $\delta^7\text{Li}_{\text{SW}}$
282 throughout the glaciation to see whether post-Marinoan $\delta^7\text{Li}_{\text{SW}}$ can reach 13‰ . The choice of a post-
283 Marinoan $\delta^7\text{Li}_{\text{SW}}$ of 13‰ is informed by the inferred $\delta^7\text{Li}_{\text{SW}}$ of 13.4‰ based on the average SDP data
284 and an average $\Delta_{\text{dolomite-SW}}$ of -10‰ , which is further explained in Supplementary Information. We
285 emphasize that the model is for illustrative purpose and not meant to reproduce the exact $\delta^7\text{Li}_{\text{SW}}$ values
286 because of the large uncertainty associated with the inversion of $\delta^7\text{Li}_{\text{SW}}$ from $\delta^7\text{Li}_{\text{dolomite}}$.

287 In this model, the seawater lithium reservoir (M) depends on the influxes from riverine input
288 (F_{riv}) and high temperature alteration at the mid-ocean ridges (F_{HT}), as well as outfluxes through
289 authigenic clay mineral formation (F_{a}) and low-temperature alteration (F_{LT}). The isotopic composition of
290 seawater ($\delta^7\text{Li}_{\text{SW}}$) depends on the size of the lithium reservoir, influxes, outfluxes, and their isotopic
291 compositions ($\delta^7\text{Li}_{\text{riv}}$ and $\delta^7\text{Li}_{\text{HT}}$) or fractionation factors ($\Delta^7\text{Li}_{\text{a}} = \delta^7\text{Li}_{\text{a}} - \delta^7\text{Li}_{\text{SW}}$ and $\Delta^7\text{Li}_{\text{LT}} = \delta^7\text{Li}_{\text{LT}} -$
292 $\delta^7\text{Li}_{\text{SW}}$). We set the model time to 10 Myr in light of the estimated duration of the Marinoan glaciation
293 of <15 Myr and most likely ~ 12 Myr [2, 56]. The high temperature input (F_{HT} and $\delta^7\text{Li}_{\text{HT}}$) was set the
294 same as modern values since geophysical models estimate hydrothermal heat flux to be near-modern and
295 to have stayed constant during our studied time interval [57, 58]. A series of sensitivity tests were
296 performed to explore a wide range of possible values for F_{riv} (0%, 10%, and 20% of modern values; Fig.
297 2), $\Delta^7\text{Li}_{\text{a}}$ (-20‰ to 0‰ ; Fig. 2), $\Delta^7\text{Li}_{\text{LT}}$ (-18‰ , -10‰ , and -8‰ ; Fig. 2), and $\delta^7\text{Li}_{\text{riv}}$ ($= 10\text{‰}$ to the
298 modern value of 23‰ ; Fig. 3). Additional parameter details for the model are provided in Supplementary
299 Table S5.

300 The model results show that within the parameter space explored and under the conditions of
301 low or no riverine fluxes ($F_{\text{riv}} \approx 0\text{‰}$; Fig. 2g and Fig. 3) and minimal fractionation ($\Delta^7\text{Li}_{\text{a}} \approx 0\text{‰}$; $\Delta^7\text{Li}_{\text{LT}}$
302 -8‰), $\delta^7\text{Li}_{\text{SW}}$ can evolve from a modern seawater value of 31‰ to $<13\text{‰}$ on a timescale of $\sim 7-8$ Myr

303 (Fig. 2g). These conditions would be favored in a snowball Earth scenario, particularly with the
304 exceedingly limited riverine flux towards the peak of glaciation [1, 59]. Additionally, elevated reverse
305 weathering, driven by the high concentrations of dissolved silica in Precambrian oceans prior to the
306 ecological rise of Si-biomineralizing organisms [52], may have effectively limited Li isotopic
307 fractionation during rapid formation of authigenic clay minerals [22]. Thus, it is plausible that evolved
308 seawater at the end of the Marinoan snowball Earth could have a $\delta^7\text{Li}_{\text{SW}}$ value of $\sim 13\text{‰}$ (Fig. 4b), much
309 lower than that of the modern seawater (31‰) and even lower than that of the modern riverine input
310 (23‰). If so, upon the termination of the snowball Earth when riverine input resumes, the Li isotopic
311 gradient between seawater and freshwater plume would be reversed (Fig. 4c) relative to the modern ocean
312 (Fig. 4a).

313

314 **Li isotope evidence for a post-Marinoan plumeworld ocean**

315 A reversed $\delta^7\text{Li}$ gradient between evolved seawater and riverine input is consistent with the
316 observed spatial trend in $\delta^7\text{Li}$ of the Doushantuo cap dolostone, and lends support to the plumeworld
317 hypothesis. This hypothesis predicts that the meltwater plume and hence the spatial gradient in $\delta^7\text{Li}$
318 would be sustained for $\sim 10^3$ – 10^4 years [5, 12, 13]. Insofar as the cap dolostone may represent a similar
319 timescale of $\sim 10^4$ years [2], the spatial and temporal dynamics of the plumeworld ocean should be
320 recorded in the cap dolostone. Indeed, the overall spatial gradient in $\delta^7\text{Li}$ of the Doushantuo cap
321 dolostone, from $\sim 14.3\text{‰}$ in inner shelf facies to 7.4‰ and 6.1‰ in upper slope facies and to 3.4‰ and
322 -0.3‰ in lower slope facies, is broadly consistent with a plumeworld ocean and can be explained by
323 variable degree of isotopic mixing between riverine input from glacial meltwater and evolved hypersaline
324 seawater [5]. Thus, cap dolostone deposited in the inner-shelf environment would have been more
325 strongly influenced by the meltwater plume and have higher $\delta^7\text{Li}$ values than those in slope settings
326 where aged hypersaline seawater asserted greater influence.

327 The Jiulongwan (JLW) data stand as an outlier from the overall spatial trend of decreasing $\delta^7\text{Li}$
328 values from shelf to slope environments. It is possible that the Jiulongwan section breaks the trend
329 because it was located in a semi-restricted intrashelf lagoon where hypersaline seawater was more
330 intensively distilled during the glaciation. Although it is thought that the intrashelf lagoon developed
331 after the deposition of the Doushantuo cap dolostone [31], it is possible that glacial scouring during the
332 Marinoan ice age may have already created an intrashelf depression that was protected from the open
333 ocean by a thick pile of glacial diamictite [27].

334 The plumeworld model may also help to explain the $\delta^7\text{Li}$ chemostratigraphic trend observed in
335 the Doushantuo cap dolostone (Fig. 5). The most complete chemostratigraphic profiles show that the
336 basal cap dolostone (stage I) has the lowest $\delta^7\text{Li}$ values and lowest Li/(Mg+Ca) ratios (Fig. 1g and
337 Supplementary Figure 1d, e, j). These low values are consistent with the predicted low $\delta^7\text{Li}$ values and
338 Li concentrations in evolved hypersaline seawater (Fig. 5b). We hypothesize that stage I cap dolostone
339 was deposited during early deglaciation but prior to the development of the plumeworld ocean, and was
340 thus strongly influenced by hypersaline seawater (Fig. 5c). During this stage, the melting of sea ice may
341 have diluted the Li concentrations of seawater, but it would not have influenced the $\delta^7\text{Li}_{\text{SW}}$ because sea

342 ice contains little Li.

343 In stage II, a meltwater plume formed, an onshore-offshore $\delta^7\text{Li}$ gradient developed, and stage
344 II cap dolostone at different localities was variously influenced by the mixing of meltwater plume and
345 hypersaline seawater (Fig. 5d). Because of intense post-glacial chemical weathering [24], terrestrial
346 meltwater was replenished with alkalinity and characterized by high $\delta^7\text{Li}$ values. Thus, despite the spatial
347 patterns discussed above, there is an overall increase in $\delta^7\text{Li}$ from stage I to stage II (Fig. 1g and
348 Supplementary Figure 1d–e and 1j), reflecting the arrival of a meltwater plume from the terrestrial realm,
349 although the stratigraphic trend is not observed at all sections, likely because of poor stratigraphic
350 coverage (e.g., ZCP, JLW, and DP) and the maximum extent of the meltwater plume not reaching lower
351 slope sections (e.g., DP). Finally, stage III cap dolostone may have witnessed the collapse of the
352 plumeworld and the mixing of meltwater and seawater (Fig. 5e), as evidenced by the return of $\delta^7\text{Li}$ to
353 lower values (Fig. 1g and Supplementary Figure 1d, j).

354 We note that the stratigraphic trend is not as robust as the spatial pattern, partly because of
355 variable stratigraphic coverage, and also because the exact shape of the chemostratigraphic profile is
356 dependent on the paleobathymetric location (hence the mixing ratio of the meltwater and seawater) and
357 is further complicated by the possible diachroneity of cap dolostone deposition at the time scale of 10^3
358 years [25]. However, the chemostratigraphic trend is bolstered by other geochemical proxies. For
359 example, the three stages of cap dolostone deposition can also be recognized on the basis of $\delta^{44}\text{Ca}$,
360 $^{87}\text{Sr}/^{86}\text{Sr}$, $^{88}\text{Sr}/^{86}\text{Sr}$, and $\delta^{26}\text{Mg}$ [6–9] (Fig. 6). Stage II cap dolostone is characterized by geochemical
361 signatures of a terrestrial meltwater plume, with lower $\delta^{44}\text{Ca}$, higher $^{87}\text{Sr}/^{86}\text{Sr}$, and lower $\delta^{26}\text{Mg}$ values
362 than stage I and stage III cap dolostone. Together, multiple lines of geochemical evidence offers support
363 to the plumeworld hypothesis and point to a physically and chemically dynamic ocean system at the end
364 of the Marinoan snowball Earth.

365

366 SUMMARY

367 Lithium isotope data from the basal Ediacaran Doushantuo cap dolostone in South China are
368 consistent with enhanced reverse silicate weathering during the Marinoan snowball Earth and a
369 plumeworld ocean in the aftermath. The $\delta^7\text{Li}$ values are lower than those of Phanerozoic carbonates, and
370 they show a decreasing trend from inner shelf facies to slope facies. We hypothesize that the spatial
371 trend reflects differential mixing between meltwater with a relatively high $\delta^7\text{Li}_{\text{riv}}$ value and evolved
372 hypersaline seawater with a low $\delta^7\text{Li}_{\text{sw}}$ value, irrespective of whether the caps were isochronous or
373 diachronous, the latter of which is our preferred interpretation. The Li isotope contrast between proximal
374 and distal cap dolostones is thus consistent with a post-glacial plumeworld ocean, where a persistent,
375 terrestrially derived meltwater plume occurred on top of evolved hypersaline seawater. The Doushantuo
376 cap dolostone also exhibits a recognizable stratigraphic trend, beginning with low $\delta^7\text{Li}$ and $\text{Li}/(\text{Mg}+\text{Ca})$
377 values followed by an increasing and then a decreasing trend. Although this chemostratigraphic trend
378 remains to be confirmed, it is also consistent with the development of a post-glacial meltwater plume,
379 reflecting the influence of evolved seawater in the beginning of cap dolostone deposition, followed by
380 increasing impact of terrestrial meltwater, and then mixing of meltwater and seawater. Additionally, the

The manuscript is a non-peer-reviewed preprint on EarthArXiv.

381 inferred $\delta^7\text{Li}$ of the evolved seawater (~13‰) requires isotopic distillation of the ocean during the
382 Marinoan snowball Earth, with little riverine influx and muted isotopic fractionation associated with
383 enhanced reverse weathering of the seafloor in a silica-rich ocean. The lithium isotope data presented
384 here may ultimately allow us to test the severity of the Marinoan glaciation, and extreme biogeochemical
385 reorganization associated with its aftermath.

386 **METHODS**

387 **Lithium isotopic analyses and elemental analyses**

388 Lithium isotope compositions and elemental concentrations of all 38 samples were analyzed
389 using quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS, Agilent™ 7900) at the
390 University of North Carolina, Chapel Hill. Lithium isotope ratios were measured using the standard-
391 sample bracketing method [60]. After lithium chromatographic purification [60, 61], samples and lithium
392 standard IRMM-016 were diluted to 0.5 ng/g in 2% nitric acid to match matrix. Lithium was then
393 introduced through a PFA nebulizer and analyzed under the hot plasma (1550 W) condition. The
394 integration time for ⁷Li and ⁶Li are 1s and 12s respectively. Each analysis consisted of 1000 integrations
395 and was repeated 7 times, followed by a long washing time (180 seconds) to decrease memory effects.
396 Li isotope compositions were expressed relative to the IRMM-016 Li standard, defined as $\delta^7\text{Li}(\text{‰}) =$
397 $[(^7\text{Li}/^6\text{Li})_{\text{sample}} / (^7\text{Li}/^6\text{Li})_{\text{IRMM-016}}] - 1 \times 1000$. The long-term external precision is 1.1‰ [60].

398 Twenty one sample solutions were selected for $\delta^7\text{Li}$ analysis on a Thermo Scientific Neptune
399 Plus MC-ICP-MS with an Apex-IR inlet system in Department of Geology at University of Maryland,
400 College Park, for inter-laboratory comparison. Lithium isotopes were measured with a 50 $\mu\text{L}/\text{min}$ PFA
401 nebulizer at low resolution using X skimmer and Jet sampler cones. A typical ⁷Li signal intensity was 2–
402 3 V for 5 ppb Li solution. Samples and the international lithium standard LSVEC were diluted to 2 ng/g
403 in 2% nitric acid to match matrix, and $\delta^7\text{Li}$ values were analyzed using a standard-sample bracketing
404 method relative to the LSVEC standard. Each sample was measured three separate times to report
405 standard deviation (2SD), and each individual measurement consists of 40 cycles in one block with 4.194
406 second integration time for each cycle. Nitric acid (2%) was measured before each sample and standard
407 for background subtraction. Accuracy and precision were also assessed from repeated measurements of
408 a 2 ppb in-house standard (UMD-1), reporting $\delta^7\text{Li}$ 55.3‰ \pm 0.4 (2SD, n = 22), in a good agreement with
409 the published values of $\delta^7\text{Li}$ 54.7 \pm 1.0‰ (2SD, n = 31)[62].

410 Elemental concentrations were analyzed in Agilent ultra-high matrix introduction (UHMI)
411 mode. Samples were calibrated against matrix-matched multi-element standards before being analyzed
412 under UHMI mode, in which helium gas was used to reduce potential isobaric interferences. Background
413 intensities were monitored periodically by aspirating 2% v/v HNO₃ blank, and an internal standard
414 solution containing Be, Ge, In, and Bi was used to correct for the instrumental drift. A limestone standard,
415 NIST-1d, obtained from the National Institute of Standards and Technology (NIST), was measured
416 routinely, yielding long-term accuracy of <10% for major elements [63].

417

418 **DATA AVAILABILITY**

419 All geochemical data generated here are included in Supplementary Table S1. A description of the Li
420 mass-balance model and quantifying clay contamination through Monte Carlo sampling are available in
421 Supplementary Information. Additional code (in Python) has been posted on GitHub
422 (<https://github.com/eart0381/BoxModel>).

423

424 **SUPPLEMENTARYDATA**

425 Supplementary data are available at *NSR* online

426

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436

437 **AUTHOR CONTRIBUTIONS**

438 T.G., M.T., and S.X. designed research; T.G., M.T., X.W., and S.X. performed research; T.G., M.T.,
439 X.W., S.W., X.L, G.J., B.G., M.N., A.J.K., T.L., and S.X. contributed new reagents/analytic tools; T.G.,
440 M.T., X.W., X.L., and S.X. performed data analysis; and T.G., M.T., X.W., X.L, G.J., A.J.K., and S.X.
441 wrote the paper, with input from other co-authors.

442

443 *Conflict of interest statement.* Nondeclared

444

445

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