Widespread clay authigenesis and highly congruent silicate weathering in the Marinoan aftermath

Yi-Sheng Yin[1], Guang-Yi Wei[1*], Philip A. E. Pogge von Strandmann[2,3], Maxwell A. Lechte[4],

Simon V. Hohl[5], Yi-Bo Lin[1], Da Li[6], Tianyu Chen[1], Tao Yang[1], Feifei Zhang[1], Terry T. Isson[7],

He Zhang[1], Yuanfeng Cai[1], Hong-Fei Ling[1]

[1]*State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and*

Engineering and Frontiers Science Center for Critical Earth Material Cycling, Nanjing

University, 163 Xianlin Avenue, Nanjing 210023, China

2MIGHTY, Institute of Geosciences, Johannes Gutenberg University, 55122 Mainz, Germany

[3]*LOGIC, Department of Earth Sciences, University College London, UK*

[4]*Department of Earth and Planetary Science, McGill University, Montréal, QC, Canada H3A*

0E8

[5]*State Key Laboratory of Marine Geology, School of Ocean and Earth Science, Tongji*

University, 200092 Shanghai, China

[6]*School of Marine Science and Engineering, Nanjing Normal University, Nanjing 210023,*

China

[7]*School of Science, University of Waikato (Tauranga), Tauranga, New Zealand*

*To whom correspondence should be addressed. E-mail: guangyiwei@nju.edu.cn (G.-Y. Wei)

Abstract

The termination of the Cryogenian period marks a transition from an extreme ice- to a greenhouse climate, likely initiated by increased atmospheric CO_2, however uncertainties persist on continental weathering regarding this climate transition. Here we present paired lithium isotope data from carbonate (δ^7Li_{carb}) and carbonate-hosted silicate (δ^7Li_{sili}) components of the Marinoan cap carbonates to constrain C and Si cycles in the deglacial period. We find that the silicate component of cap carbonates is dominated by marine authigenic clays with minor contributions from terrestrial materials and oxides. Built from δ^7Li_{sili} data, large

28 variations of seawater δ^7Li suggest a heterogeneous marine Li reservoir due to a stratified ocean

29 in the deglacial period. Overall, widespread clay authigenesis and low seawater δ^7Li values

30 indicate active carbon-silicon cycling congruent due to warm climate and exposure of fresh

31 rock surface in the Marinoan aftermath, which promotes the deposition of cap carbonates and

32 stabilization of Earth's surface environment.

33 **Keywords:**

34 Snowball Earth; cap carbonate; authigenic clay; continental weathering; Lithium isotope

35

36 **1. Introduction**

37 　　The Cryogenian period (ca. 720–635 Ma) was bookended by two glacial epochs—the

38 Sturtian and Marinoan glaciations—considered to be among the most extreme icehouse

39 climates throughout geological history (Hoffman et al., 1998, 2017). These so-called 'Snowball

40 Earth' events are considered to have featured significant coverage of the global oceans by ice

41 (Kirschvink, 1992). The accumulation of atmospheric CO_2 due to supposed normal volcanic

42 activity and suppressed silicate weathering during these ice ages is suggested to have finally

43 led to deglaciation and a return to warm climate after millions of years (Kirschvink, 1992;

44 Hoffman et al., 1998). The termination of the Cryogenian is marked in the geologic record by

45 the widespread presence of unique carbonate deposits ('cap carbonate') overlying Marinoan

46 glacial deposits, which are considered to represent the sedimentary product of a rapidly

47 warming climate and feature evidence for sequestered atmospheric pCO_2 (Bao et al., 2009;

48 Higgins and Schrag, 2003; Hoffman et al., 2017, 1998). These extreme greenhouse conditions

49 predicted for the post-glacial period are commonly assumed to have resulted in elevated rates

50 of chemical weathering—as part of the silicate weathering feedback—and in turn acting to

51 decrease atmospheric CO_2 levels and regulating climate in the aftermath of the Snowball Earth

52 event (Fabre and Berger, 2012; Higgins and Schrag, 2003; Le Hir et al., 2009). Yet, rates of

53 silicate weathering and climate dynamics remain highly disputed across this event due to the

54 lack of systematic research on paleo-weathering proxies during the interval of Marinoan cap

2

55   carbonate deposition (Huang et al., 2016; Le Hir et al., 2009).

56   Here, we use lithium isotope compositions (δ^7Li) to constrain silicate weathering rate and

57   intensity (i.e., the balance of chemical weathering to physical erosion) in the Marinoan

58   aftermath. Modern global oceans are homogeneous with respect to Li isotopes and their values

59   are strongly regulated by the isotope signature of river waters (Hathorne and James, 2006; Misra

60   and Froelich, 2012). Lithium isotope fractionation during silicate weathering primarily results

61   from the preferential incorporation of ^{6}Li into secondary clays (Hindshaw et al., 2019; Li and

62   Liu, 2020; Vigier et al., 2008; Zhang et al., 2021). Accordingly, the δ^7Li values of river waters

63   reflect a balance of Li sources from primary silicate mineral dissolution and removal via

64   secondary clay formation, and are proposed to reflect the congruency of continental silicate

65   weathering (Dellinger et al., 2015; Pogge von Strandmann et al., 2021). Weathering congruency

66   is also related to silicate weathering intensity (W/D), which is calculated by the ratio of the

67   chemical weathering rate to the total [physical erosion rate (E) + chemical weathering rate (W)]

68   denudation rate (Fig. 1) (Dellinger et al., 2015). Here, based on basic framework from Dellinger

69   et al. (2015) with more recent data on notably intense erosion regions, the modern river systems

70   overall exhibited a negative correlation between dissolved δ^7Li and Li concentration, instead

71   of a typical "boomerang" pattern (Dellinger et al., 2015) (Fig. 1). In this view, significantly

72   high W/D regimes with low δ^7Li and Li concentration would have less direct influence on the

73   mass balance of oceanic Li reservoir, which may have been infrequent through geological time

74   (Pogge von Strandmann et al., 2021). In general, more congruent weathering induces less clay

75   formation (whether high W/D with rapid clay redissolution or low W/D with little clay

76   formation) and leads to largely unfractionated Li isotope signatures (bedrock-like: low δ^7Li)

77   with either low or high dissolved Li concentrations in river waters. On the contrary, incongruent

78   silicate weathering results in significant Li isotope fractionation (high riverine δ^7Li) and

79   relatively low Li fluxes due to substantial secondary clay formation (Dellinger et al., 2015;

80   Pogge von Strandmann et al., 2021). This weathering control on isotopic fractionation permits

81   the use of Li isotopes as a reliable proxy for the intensity and rate of continental silicate

3

82 weathering (Fig. 1).

83   We employ sequential leaching techniques in order to provide a component-selective

84 investigation of the Li isotope composition of carbonate (δ^7Li_{carb}) and carbonate-hosted silicate

85 (δ^7Li_{sili}) components of the Marinoan cap carbonates in South China hosted by the Doushantuo

86 Formation. Here, the carbonate-hosted silicate components refer to the aluminosilicate minerals

87 associated with carbonate minerals, which are normally insoluble residues after carbonate

88 leaching. By comparing these δ^7Li records, we find that the δ^7Li_{carb} records in the cap carbonate

89 successions may have reflected *in situ* diagenetic signals rather than coeval seawater

90 information. Based on XRD and elemental analyses, carbonate-hosted silicate components in

91 the cap carbonate successions comprises predominantly of marine authigenic clays.

92 Accordingly, the δ^7Li_{sili} records are used to trace δ^7Li variations of continental margin seawater

93 in the Marinoan aftermath. Low seawater δ^7Li values estimated from the cap carbonates provide

94 evidence for intense and more congruent silicate weathering in the post-Marinoan period. Such

95 congruent weathering conditions also facilitate the delivery of abundant dissolved Ca, Mg and

96 reactive Si to the ocean, supporting widespread formation of cap carbonates and authigenic

97 clays after the Snowball Earth.

98

99 **2. Geological background**

100   The southeastern margin of the Yangtze block, South China is considered to have

101 developed a passive continental margin during the late Neoproterozoic, with sedimentary basins

102 recording marine deposition in inner shelf, intra-shelf basins or lagoons, shelf margins and

103 slope/basin environments (Jiang et al., 2003) (Fig. 2A). In this area, the Marinoan glacial

104 succession is represented by glacial diamictites of the Nantuo Formation, overlain by the

105 Doushantuo Formation. The base of the Doushantuo Formation is marked by an approximately

106 5-m-thick cap carbonate succession, which is widely distributed over the Nantuo diamictites on

107 the southeastern Yangtze margin and represents rapid carbonate depositions in the Snowball

108 Earth aftermath (Jiang et al., 2003). The cap carbonate succession mainly contains three units

109 that are transitional to each other and could be lithologically distinguished: the lower part

110 represents a basal disrupted, massive dolostone layer with carbonate breccia and lined cavities

111 filling with cements; the middle part is a middle laminated micritic dolostone layer that contains

112 local tepee-like structures in some specific regions; the upper part is consisted of a thinly

113 laminated limestone and dolostone interval and is transitional to the overlying member II black

114 shales (Jiang et al., 2003; Wang et al., 2016). Based upon the facies relationships of the

115 Ediacaran strata in the South China, the Jiulongwan section in the Three Gorges area (Hubei

116 Province) is interpreted as a cap carbonate succession deposited in a proximal, intra-shelf-basin

117 setting, and the Siduping section southwest of Zhangjiajie (Hunan Province) represents a more

118 distal, upper-slope setting (Wang et al., 2016) (Fig. 2B). A zircon U–Pb age of 635.2 ± 0.6 Ma

119 has been determined for a volcanic ash layer in the upper cap carbonate succession in the Three

120 Gorges area (Condon et al., 2005), which is consistent with the depositional age of cap

121 carbonate in Namibia (Hoffmann et al., 2004).

122

123 **3. Materials and methods**

124 3.1. SEM and XRD analyses

125   A total of 8 carbonate samples were selected for SEM analysis. The cut slabs of studied

126 samples were embedded in epoxy resin, mounted on 1 mm thick quartz slides, and polished

127 into ~100 μm thin sections. The thin sections were then carbon-coated, and their petrographic

128 structures were observed using a Zeiss supra 55 scanning electron microscope (SEM) in

129 backscattered electron (BSE) mode operated at an accelerating voltage of 5 kV at the State Key

130 Laboratory for Mineral Deposits Research, Nanjing University. The SEM is also equipped with

131 energy-dispersive X-ray spectrometers (EDS) for semi-quantitative elemental analysis to aid

132 mineral identification.

133   After leaching with acetic acid and HCl acids to remove carbonate minerals, mineralogy

134 of the silicate component in the studied carbonates was determined using a Bruker D8 Advance

135 X-ray diffractometer at the State Key Laboratory for Mineral Deposits Research, Nanjing

136 University. The diffraction spectral pattern was measured at a 2θ step scan of 0.01° between 20°

137 and 60°. The limit of detection for minerals is 0.1 cps for peak intensity. Determination of

138 different minerals was performed using the XRD data with whole-pattern fitting and Rietveld

139 refinement with DIFFRAC.EVA V4.3.2 software. A semi-quantitative calculation on relative

140 proportions of different minerals was applied with the aid of TOPAS software version 6.0 based

141 on XRD results. A pseudo-Voigt function and an eighth-order Chebyshev polynomial were used

142 to model peak shapes and background, respectively. Zero shifts were taken from refinements

143 of the powder diffraction pattern, and the crystal structural data for the refinement were taken

144 from American Mineralogist Crystal Structure Database (quartz code: 0000789; clinochlore

145 code: 0000119; glauconite code: 0005026; http://rruff.geo.arizona.edu/AMS/amcsd.php). The

146 TOPAS software works by fitting the chosen crystal structural data into the analyzed XRD

147 pattern.

148 3.2. Li isotope analyses

149 In this study, a total of 25 carbonate samples, mainly comprising dolostone or limestone

150 matrices, were collected from the Doushantuo Formation in the Jiulongwan and Siduping

151 sections that can be directly compared to those in previous studies (Jiang et al., 2003; Wang et

152 al., 2016). In addition, 2 diamictite samples were collected within 2 meters under cap carbonate

153 in each section. A sequential leaching method (e.g., Pogge von Strandmann et al., 2019; Wei et

154 al., 2023) was used to extract Li from different components of the bulk carbonate rock samples.

155 For each sample, approximately 400 mg of bulk carbonate powder was first rinsed using 15 mL

156 1 N ammonium acetate to remove exchangeable Li. The residues were then leached using 0.75

157 N acetic acid for 4 hours to preferentially dissolve carbonate components (i.e., dolomite and

158 calcite). The supernatant was extracted at this stage and used to analyze the carbonate Li isotope

159 component (δ^7Li_{carb}). Next, the residues were further reacted with 2 N HCl for 0.5 hour to ensure

160 complete removal of carbonate minerals and Fe-, Mn-oxides. The remaining fraction after

161 carbonate extraction, which host Li bound to silicate minerals (structured/interlayered), was

162 fully digested using concentrated $HF-HNO_3-HCl$ acids and used to analyze the silicate Li

6

163   isotope component ($\delta^7 Li_{sili}$) in the cap carbonates. Besides, the diamictite samples from each

164   section were fully dissolved by HF-HNO$_3$-HCl acids and prepared for the geochemical

165   measurements.

166   Trace and major elemental concentrations were measured for all sample solutions (i.e.,

167   carbonate leachates, carbonate-hosted silicates and diamictite) on an Agilent 7900 Quadrupole

168   ICP-MS with an RSD of <5% at the MOE Key Laboratory of Surficial Geochemistry, Nanjing

169   University, based on repeated analyses of the rock standard BHVO-2 and OSIL Atlantic

170   seawater. An improved single-column method with 5.4 mL AG50W-X12 cation resin was used

171   to purify Li in the different components (Wei et al., 2023). The purified sample solution was

172   then measured on a Thermo Scientific Finnigan Neptune plus MC-ICP-MS at the MOE Key

173   Laboratory of Surficial Geochemistry, Nanjing University. An in-house Li solution (GAGS-Li,

174    $\delta^7 Li$ = 15.1‰ ± 0.5‰, 2σ, n = 11) was used to monitor the long-term reproducibility of Li

175   isotope analyses on the machine. The overall reproducibility and accuracy of the total procedure

176   (sample digestion, Li separation and isotope measurement) were checked by repeated analyses

177   of BHVO-2 ($\delta^7 Li$ = 4.46 ± 0.3‰, 2σ, n=3), GSR-12 (dolomite, [Li]$_{leachate}$ = 1.6 µg/g, $\delta^7 Li$ =

178   13.4 ± 0.5‰, 2σ, n=4) and OSIL seawater ($\delta^7 Li$ = 30.9 ± 0.4‰, 2σ, n = 4), with different

179   aliquots processed through column chemistry (Dellinger et al., 2015; Wei et al., 2020, 2023).

180

181   **4. Results**

182   Component-selective analyses of cap carbonates are conducted in this study to generate

183   elemental and Li isotopic data of carbonate component and carbonate-hosted silicate

184   components, whose results are presented in table S1 and Fig. 2. In the Jiulongwan section,

185    $\delta^7 Li_{carb}$ and $\delta^7 Li_{sili}$ exhibit similar variation trends, ranging from −3.50‰ to 6.58‰ and from −

186   5.43‰ to 5.79‰, respectively. The Li/(Ca+Mg) weight ratios of carbonate components range

187   from 0.88 to 6.31 ($\times 10^6$) and the Li/Th weight ratios of the silicate component range from 5.44

188   to 89.47. In the Siduping section, $\delta^7 Li_{carb}$ values range from 1.97‰ to 6.88‰, and $\delta^7 Li_{sili}$ values

189 range from 1.32‰ to 13.15‰, slightly higher than δ^7Li_{carb} values. The Li/(Ca+Mg) weight

190 ratios of carbonate components range from 0.33 to 13.31 ($\times10^6$) and the Li/Th weight ratios of

191 the silicate component range from 8.19 to 44.28. In both sections, Al/(Ca+Mg) weight ratios of

192 carbonate components are significantly low (0.00022 ± 0.00009 in Jiulongwan samples and

193 0.00021 ± 0.0001 for Siduping samples, 1σ) in comparison with carbonate-hosted silicate

194 components. The four diamictites have similar δ^7Li values ranging from 1.89‰ to 4.02‰ with

195 Li/Th weight ratios from 5.03 to 7.96. Additionally, for carbonate-hosted silicates, the semi-

196 quantitative calculation results show a range from 4.68% to 8.85% of quartz in Jiulongwan

197 samples and from 3.27% to 7.3% of quartz in Siduping samples. Clinochlore takes over from

198 58.89% to 77.56% in Jiulongwan samples and from 81.66% to 84.45% in Siduping samples,

199 respectively. Glauconite ranges from 14.58% to 32.26% in Jiulongwan samples and from 8.87%

200 to 12.85% in Siduping samples. Rp values (used to assess the fitting degree, normally

201 recommended to be lower than 10) shown in TOPAS software after calculation for all samples

202 are from 5.51 to 8.9 which is supportive for our semi-quantitative results.

203

204 **5. Discussion**

205 **5.1 Clay authigenesis in cap carbonate successions during the Marinoan aftermath**

206   The mass ratios of Al/(Ca+Mg) of the carbonate and silicate components in Jiulongwan

207 and Siduping samples are examined to monitor the dissolution of both components in bulk

208 carbonates. The carbonate components of Jiulongwan and Siduping samples have lower

209 average Al/(Ca+Mg) ratios (0.00022 ± 0.00009 in Jiulongwan samples and 0.00021 ± 0.0001

210 for Siduping samples, 1σ) than a conservative filter of 0.00027 in previous research (Kalderon-

211 Asael et al., 2021; Pogge Von Strandmann et al., 2013). Such low Al/(Ca+Mg) ratios suggest

212 little aluminosilicate contamination in the acetic-acid leachate, namely, limited Li contributed

213 from silicates to the carbonate components during leaching procedure of the studied samples.

214 By contrast, the carbonate-hosted silicate components of the Jiulongwan and Siduping samples

215 show much higher average Al/(Ca+Mg) ratios (1.5 ± 0.5 in Jiulongwan samples and 3.2 ± 1.6

8

for Siduping samples, 1σ), closer to those of aluminosilicate rocks (e.g., 2.01 for average upper

continental crust and 4.45 for post-Archean average shale) (Rudnick and Gao, 2014; Taylor and

McLennan, 1985). Such results suggest that aluminosilicates rather than carbonates dominate

the HF-HNO$_3$-HCl leachate. Since lithium contents in silicates are much higher than those in

carbonates, contamination from carbonate leachate should have little influence in carbonate-

hosted silicate components, especially after further removal of carbonate minerals with HCl.

The aluminosilicate component of marine carbonates is traditionally considered to be

derived from terrestrial inputs (Zhao and Zheng, 2014); however, the precipitation of

aluminosilicate clays can also occur in marine environment (a process known as 'reverse

weathering') (Andrews et al., 2020; Isson et al., 2020; Isson and Planavsky, 2018;

Michalopoulos and Aller, 1995; Steiner et al., 2022). Precambrian seawater is interpreted to

have been comparatively Si-rich (due to the lack of widespread biosilicification) and Fe-rich

(due to low marine O$_2$ concentrations) (Isson et al., 2020; Siever, 1992). On this basis, marine

clay authigenesis is proposed to have been more active in Precambrian oceans compared to the

Phanerozoic (Isson and Planavsky, 2018), a view supported by novel isotope work involving

both silicon and lithium (Kalderon-Asael et al., 2021; Trower and Fischer, 2019). The Polarized

Light Microscope (PLM) photographs of thin sections show micritic matrix of the cap

carbonate rock samples with diagenetic veins cutting through as well as recrystallized sparry

calcite (Figs. 3A, C). The Cathodoluminescence (CL) were also used alongside with PLM to

examine diagenesis, and the luminous red areas in CL photographs of the carbonates show

significant diagenetic signatures during their burial (Figs. 3B, D). The Scanning Electron

Microscope (SEM) photographs of thin sections for bulk carbonate samples show amounts of

lamellar clay minerals surrounded by dolomite matrices (Figs. 3E-H). Further, the results of X-

Ray Diffraction (XRD) data and Energy-Dispersive X-ray Spectrometers (SEM-EDS) show

that aluminosilicate minerals in the studied cap carbonates are dominated by Mg-, K-, Fe-

enriched clays (i.e., clinochlore, glauconite) (Figs. 3I, Fig. S4). The SiO$_2$-rich minerals (1~2

μm size) are observed in SEM photographs (Fig. 3F), likely denoting the precipitation of

9

243   authigenic microcrystalline quartz within fine-grained clay matrix, rather than silt-size detrital

244   quartz (Peltonen et al., 2009; Zhao et al., 2017). Clay minerals typically derived from modern

245   continental weathering (e.g., illite, smectite, kaolinite) are rarely observed in the carbonate-

246   hosted silicates. Therefore, It is proposed that the aluminosilicate mineralogy of carbonate-

247   hosted silicate components in the cap carbonates is marine authigenic clay (i.e., direct

248   precipitation of clay minerals from seawater or transformation of a pre-existing cation-poor

249   clay mineral with cation substitution) associated with carbonate deposits (Andrews et al., 2020;

250   Baldermann et al., 2015; Geilert et al., 2023; Isson and Planavsky, 2018). We further examine

251   the origins for carbonate-hosted silicate components by comparing the geochemical

252   compositions of the studied samples to a range of modern and ancient siliciclastic sedimentary

253   rocks including South Pacific marine sediments (Integrated Ocean Drilling Program Expedition

254   Site U1366 drill core) (Dunlea et al., 2015), Cryogenian shales from South China (Datangpo

255   Formation) (Wei et al., 2020), the upper continental crust (UCC) (Rudnick and Gao, 2014),

256   post-Archean average shale (PAAS) (Taylor and McLennan, 1985) and diamictites from the

257   same sections (Fig. 4A). Previous studies have suggested that Th is generally conservative and

258   hosted in resistant minerals during chemical weathering of bedrock (Braun et al., 1993; Ma et

259   al., 2007; Nesbitt, 1979), meaning that Th can be well preserved in the terrestrially weathering

260   products. The authigenic clays in the lower part of the U1366 core show notably low Th

261   contents relative to terrestrial detrital materials given that Th is highly depleted in seawater

262   (Dunlea et al., 2015). Hence, Th can be a useful proxy to fingerprint marine authigenic clays,

263   which typically have significantly higher Li/Th and Al/Th ratios than other siliciclastic

264   sediments and terrestrial detrital materials (Fig. 4A). Diagrams of Li/Th vs. Al/Th for the

265   carbonate-hosted silicate components in the studied cap carbonates are close to those of marine

266   authigenic clays from the U1366 core, and show significant Th depletion relative to terrestrial

267   detrital materials and marine shales (Fig. 4A), indicative of limited Li source from terrestrial

268   detritus. Additionally, appreciable correlations of Fe, Mn vs. Th, Al with higher Fe/Al and

269   Fe/Th relative to terrestrially detrital materials in the carbonate-hosted silicates (Fig. S5)

10

270 suggest the addition of Fe from authigenic clays (e.g, glauconite and clinochlore shown by

271 XRD results in this study) rather than detrital materials or Fe-, Mn-oxides. Taken together, we

272 suggest that marine authigenic clays are a dominant component of carbonate-hosted silicates in

273 bulk cap carbonates, consistent with coupled silica and carbonate precipitation during the

274 Marinoan deglaciation (Fang and Xu, 2022; Penman and Rooney, 2019).

275

276 **5.2 Reliability of δ^7Li_{carb} and δ^7Li_{sili} records in cap carbonates recording coeval seawater**

277 **information**

278 In both the Jiulongwan and Siduping sections, the δ^7Li_{carb} values are similar to the δ^7Li_{sili}

279 values, and these covary within each section (Fig. 2C and Fig. S3). In contrast, absolute values

280 and trends are notably distinct between both sections investigated here. The Jiulongwan

281 samples exhibit a steady rise towards more positive values up section in δ^7Li_{sili} and δ^7Li_{carb} from

282 -5.43‰ to 5.79‰ and -3.54‰ to 6.58‰ respectively. In contrast, the δ^7Li_{sili} values of the

283 Siduping samples show a decreasing trend, ranging between 13.15‰ and 1.32‰, whereas

284 δ^7Li_{carb} values exhibit no significant variations, ranging between 1.97‰ to 6.88‰ (Fig. 2C).

285 Given that the δ^7Li_{carb} values of the studied samples are anomalously low (even reaching

286 negative values in the lowest part of the Jiulongwan section), and are comparable to the δ^7Li_{sili}

287 values obtained for each sample in both sections, we first explore the possible controls on Li

288 isotope compositions of the different components of the Doushantuo cap carbonates. The δ^7Li

289 records in bulk shallow-marine carbonates have been commonly used to track paleo-seawater

290 δ^7Li evolution (Cao et al., 2022; Crockford et al., 2020; Kalderon-Asael et al., 2021; Pogge Von

291 Strandmann et al., 2013), as carbonates formed under strongly fluid-buffered conditions tend

292 to record δ^7Li signals of coeval seawater (Crockford et al., 2020; Dellinger et al., 2020). In this

293 study, δ^7Li_{carb} values of the cap carbonates are significantly lower than those of Phanerozoic

294 shallow-marine carbonates (Kalderon-Asael et al., 2021), but display a remarkable similarity

295 and exhibit consistent variation trends to δ^7Li_{sili} records (Fig. 2C). Moreover, Jiulongwan

296 section documents negative δ^7Li_{carb} values (lowest to −6‰) in the lowest cap carbonate

297 succession and Siduping section exhibits much lower $\delta^7 Li_{carb}$ relative to $\delta^7 Li_{sili}$ values. Although

298 the distinctive Precambrian carbon and silicon cycles can account for the common occurrence

299 of low $\delta^7 Li$ values in the Precambrian carbonates (Kalderon-Asael et al., 2021), it is unlikely

300 that the seawater Li reservoir could have been characterized by such negative $\delta^7 Li$ values,

301 considering the Li sources and sinks of the oceans and their attendant Li isotope fractionations

302 (Li and West, 2014). By comparing $\delta^7 Li_{carb}$ and $\delta^7 Li_{sili}$ of the studied cap carbonate samples, we

303 propose that the low $\delta^7 Li_{carb}$ values of cap carbonates are likely induced by isotopic exchange

304 with authigenic clays contained in the carbonate during early diagenesis. Dolostones generally

305 have significantly higher Li contents relative to primary calcite or aragonite (Dellinger et al.,

306 2020), suggesting that more Li is incorporated in dolostones during the dolomitization of

307 primary aragonite or calcite minerals. Due to the presence of reactive biogenic silica, clay

308 authigenesis in recent carbonate-rich sediments has been demonstrated to prominently shift the

309 $\delta^7 Li$ values of bulk carbonates away from its initial values during early diagenesis (Andrews et

310 al., 2020). Syn-sedimentary to early diagenetic dolomitization is considered to have been an

311 essential process in the formation of Precambrian dolostones (Fabre et al., 2013; Font et al.,

312 2006; Hood and Wallace, 2012), consistent with the petrographic observation of pervasive

313 diagenetic carbonate minerals (in luminous red colour distributed in Figs. 3A-D). We suggest

314 that the release of Li from clays within sediments under relatively acidified conditions may

315 have supplied more isotopically light Li to local seawater or sedimentary pore water (Zhang et

316 al., 2021), giving rise to the low $\delta^7 Li$ of dolostones following syn-sedimentary dolomitization.

317 This hypothesis is supported by the correlation between $\delta^7 Li_{carb}$ and $\delta^7 Li_{sili}$ of the studied

318 dolostones (Fig. S3), which suggests a silicate influence on the Li isotope composition of the

319 carbonate component during the early carbonate diagenesis. Although we do not imply that all

320 carbonate Li isotope records are predominantly controlled by the exchange between carbonate

321 and silicate components, indistinguishable $\delta^7 Li_{sili}$ and $\delta^7 Li_{carb}$ signatures in cap carbonates

322 highlight that the aluminosilicate components may have regulated the Li isotope compositions

323 of Precambrian carbonates, reinforcing the importance of component-selective geochemical

12

324 analyses of ancient carbonate rocks for paleo-environmental reconstruction (Isson et al., 2020;

325 Isson and Planavsky, 2018).

326 Given the large uncertainties associated with δ^7Li_{carb} signatures in cap carbonates, we

327 choose to instead focus our remaining discussion on the aluminosilicate components and their

328 isotopic compositions. According to the geochemical signatures of these marine authigenic

329 clays, we first use Li/Th ratios of the studied samples to estimate Li isotope compositions of

330 the purely authigenic component (δ^7Li_{auth}) hosted by cap carbonates (Fig. 4B). Diamictites from

331 both sections represent mixture of different terrestrially weathering and eroded products (i.e.,

332 detrital clay and other residual mineral) that were delivered to continental shelf after mineral

333 sorting. Thus, we use compositions of diamictites to denote the average source of terrestrially

334 detrital endmembers in each section (see Supplementary materials). Overall, the carbonate-

335 hosted silicates have significantly high Li/Th ratios relative to diamictites, resulting in relatively

336 consistent variations of δ^7Li_{auth} δ^7Li_{sili} in both sections (Fig. S1). This observation further

337 supports the inference that marine authigenic clays dominate the carbonate-hosted silicate

338 components in cap carbonates. Authigenic clays (e.g., clays directly precipitating from seawater

339 or neomorphic clays interacted with seawater) can document the geochemical information of

340 coeval water mass by fully considering the isotopic fractionations between clay mineral and

341 ambient water. Thus, the δ^7Li_{auth} records in cap carbonates are adopted to reconstruct of post-

342 Marinoan seawater δ^7Li evolution. Different from the modern ocean system, the overall Li

343 isotope fractionation between Precambrian seawater and authigenic clays is postulated to have

344 been lower, associated with more rapid and efficient Li uptake in marine sediments (Clark and

345 Johnson, 2008; Kalderon-Asael et al., 2021; Li et al., 2021), when dissolved silica and clay

346 mineral saturation would have been elevated, prior to the evolution of silicifying organisms

347 (Isson and Planavsky, 2018). In this framework, more extensive and rapid formation of

348 authigenic clays and thus higher Li uptake rates in marine sediments would result in muted Li

349 isotope fractionation in Precambrian oceans (e.g., Δ^7Li_{auth} = ~ −5‰, defined as $\delta^7Li_{authigenic\ clay}$ −

350 $\delta^7Li_{seawater}$) (Kalderon-Asael et al., 2021) compared to that for the modern ocean characterized

13

351   by sluggish rates of reverse weathering ($\Delta^7\text{Li}_{auth}$ = ~ –20‰) (Hindshaw et al., 2019; Li and

352   West, 2014; Zhang et al., 2021). Thus, we calculate the past seawater Li isotope compositions

353   at $\Delta^7\text{Li}_{auth}$ = ~ –5‰ (Precambrian ocean) and ~ –20‰ (modern ocean) in a depth profile (Fig.

354   4B). Temperature can also influence Li isotope fractionation during clay formation from

355   seawater (Li and West, 2014). A temperature change from 0℃ to 40–60℃, which is considered

356   as the estimated temperature gradients predicted for the deglaciation interval (Higgins and

357   Schrag, 2003; Le Hir et al., 2009; Yang et al., 2017), would result in a 6–8‰ decrease in $\Delta^7\text{Li}_{auth}$.

358   Given that the difference in $\delta^7\text{Li}_{auth}$ between the lowest parts of the Jiulongwan and Siduping

359   sections is around ~20‰, a temperature change cannot entirely explain this full difference.

360   Further, temperature-controlled variations in Li isotope fractionation between authigenic clays

361   and seawater cannot induce the opposing trends of $\delta^7\text{Li}_{auth}$ in the Jiulongwan and Siduping

362   sections. Despite these arguments, the formation of cap carbonates is suggested as resulting

363   from synsedimentary or very early diagenesis (Fabre et al., 2013; Font et al., 2006; Gammon,

364   2012; Wei et al., 2019), occurring immediately below the sediment-water interface (Hood and

365   Wallace, 2012). Given relatively thin cap carbonate successions in the studied sections, we

366   suggest that the carbonate-hosted silicate components more likely precipitated in step with

367   carbonate formation (or at least prior to dolomitization), rather than in the deep sedimentary

368   column (e.g., 500 m depth Site U1338A through the late Cenozoic) (Andrews et al., 2020). In

369   this view, variations in $\delta^7\text{Li}_{auth}$ values of the Jiulongwan and Siduping cap carbonates are likely

370   driven by changes in $\delta^7\text{Li}$ values of bottom seawater or upper porewaters near the sediment-

371   water interface, which can be used to trace evolution of the silicate weathering in the Marinoan

372   aftermath.

373

374   **5.3 Post-Marinoan seawater Li isotope compositions and active carbon-silicon cycle**

375   Given possibly muted isotopic fractionations between authigenic clays and seawater in the

376   Precambrian oceans, we propose a $\Delta^7\text{Li}_{auth}$ value of –5‰ to –20‰ (from possible Precambrian

377   ocean Li cycle to modern ocean Li cycle) to estimate post-Marinoan $\delta^7\text{Li}_{seawater}$ values via

14

378   carbonate-hosted clays (Fig. 4B) (Kalderon-Asael et al., 2021). Reconstruction of $\delta^7\text{Li}_{seawater}$

379   values during cap carbonate deposition suggests a highly dynamic marine Li cycle in the post-

380   Marinoan glacial oceans. In the lowest interval of cap carbonate succession, the Jiulongwan

381   and Siduping sections reveal the opposite trend of $\delta^7\text{Li}_{seawater}$, suggesting spatial and temporal

382   heterogeneity in the Li reservoir of continental shelf seawater in the earliest post-glacial period.

383   The more proximal Jiulongwan section documents low $\delta^7\text{Li}_{seawater}$ signals, potentially due to

384   preferential record of riverine Li inputs during the climate transition, with the depositional

385   environment being within an estuarine plume (Wei et al., 2019). By contrast, the more distal

386   Siduping section records high $\delta^7\text{Li}_{seawater}$ signals in its bottom part, likely inheriting the Li

387   isotope composition of the open ocean. The offset between $\delta^7\text{Li}_{seawater}$ values recorded in the

388   lower interval of these two sections also suggests the persistence of stratified, and hence

389   isotopically heterogeneous, seawater on continental margins, also known as "plumeworld", due

390   to large amounts of freshwater released from icesheet melting (Fig. 5) (Giddings and Wallace,

391   2009; Shields, 2005; Wei et al., 2019; Yang et al., 2017). The heterogeneous $\delta^7\text{Li}_{seawater}$ on

392   continental margins only exists in the earliest post-glacial period. Following the transgression,

393   the stratified waters gradually become more mixed, resulting in convergent $\delta^7\text{Li}_{seawater}$ records

394   of the Jiulongwan and Siduping sections in the middle and upper interval of cap carbonates.

395   Two important inferences about Cryogenian surface environments can be made from these

396   contrasting proximal and distal marine Li records. Firstly, assuming a constant hydrothermal Li

397   flux during this time (Kalderon-Asael et al., 2021), the notably low $\delta^7\text{Li}_{seawater}$ records ($< 12‰$)

398   from the lower Jiulongwan section (i.e., proximal facies) require a much lower riverine $\delta^7\text{Li}$

399   relative to modern times (modern average $\delta^7\text{Li}_{river} = 23‰$) (Huh et al., 1998). This may be

400   indicative of highly congruent silicate weathering in the earliest post-glacial period, possibly

401   due to widespread glacial till (Fabre and Berger, 2012). Secondly, the estimated high $\delta^7\text{Li}_{seawater}$

402   of glacial oceans (as inferred from the $\delta^7\text{Li}_{auth}$ values from the distal facies of the lowest

403   Siduping section) could have resulted from gradual light ^6Li removal in the preceding glacial

404   period ocean due to inhibited continental silicate weathering, ongoing marine clay authigenesis

15

405   and continued oceanic crust alteration (Gernon et al., 2016). Following the post-glacial

406   transgression, the stratified waters gradually become more mixed, resulting in convergent

407    $\delta^7Li_{seawater}$ records of the Jiulongwan and Siduping sections in the middle and upper interval of

408   cap carbonates (Fig. 4B), which may reflect the Li isotope compositions of the earliest

409   Ediacaran seawater. Further, in the middle and upper cap carbonate successions, the Jiulongwan

410   and Siduping sections document uniform $\delta^7Li_{seawater}$ signatures ($< 25‰$), which are much lower

411   than that of the modern ocean (Misra and Froelich, 2012). These signatures suggest that more

412   congruent silicate weathering may have persisted throughout the cap carbonate deposition (Fig.

413   4B), consistent with warm climate high run-off and abundant finely ground glacial material

414   undergoing weathering.

415   For modern rivers, there is a clear relationship between δ^7Li and the Li concentration,

416   demonstrating that low δ^7Li values correspond to either high or low Li concentrations of river

417   waters (Fig. 1), due to either abundant primary rock dissolution or redissolution of previously

418   formed clays under the different weathering intensities (W/D) (Dellinger et al., 2015). Based

419   on new data compilation from modern rivers, we use a Li isotope mass balance model to

420   evaluate changes in silicate weathering in the Marinoan glacial aftermath by constraining the

421   average δ^7Li and Li concentration of post-Marinoan river waters (see Supplementary materials

422   for model and parameter descriptions). Due to potentially different marine Li cycles in

423   Precambrian and modern oceans (Kalderon-Asael et al., 2021), we consider a much lower Li

424   isotope fractionation between authigenic clay and seawater assumed for Precambrian oceans

425   (Fig. 6A), superimposed with cross-plots of δ^7Li vs. Li concentration based upon modern river

426   waters. With these assumptions for the Precambrian style of Li cycling during cap carbonate

427   deposition (Kalderon-Asael et al., 2021), the δ^7Li_{auth} records of cap carbonates would indicate

428   a value of ~11‰ for post-Marinoan global seawater at steady states. Such low $\delta^7Li_{seawater}$ values

429   in the post-glacial ocean would require high Li concentrations (~8 μmol/L) and low δ^7Li values

430   (~ 4‰) of river waters when considering a Precambrian oceanic Li cycle (Fig. 6A). This low

431   *W/D* scenario with high dissolved Li concentration and low δ^7Li indicates much higher physical

432 erosion than chemical weathering rates in the deglacial period, which is similar to ancient or

433 modern systems with high uplift rate and humid climate (i.e., Paleocene-Eocene Thermal

434 Maximum, modern Taiwan and New Zealand) (Herman et al., 2013; Huang et al., 2016; Pogge

435 Von Strandmann et al., 2021; Pogge von Strandmann and Henderson, 2015). This δ^7Li value

436 evaluated for post-glacial river waters is consistent with the $\delta^7Li_{seawater}$ recorded in the lowest

437 part of the proximal Jiulongwan section (Fig. 6A), further supporting the interpretation that the

438 lowest part of the Jiulongwan section documents more riverine, rather than open seawater

439 signals in the earliest post-glacial period with a large estuarine plume (Wei et al., 2019). We

440 also test the model by assuming modern Li isotopic fractionations between authigenic clays

441 and seawater to reconstruct coeval seawater δ^7Li values, and accordingly marine Li cycles (Fig.

442 6B). Despite the different Li isotopic fractionations, modeling results consistently demonstrate

443 the similar weathering regimes that require high Li concentration and low δ^7Li value for the

444 post-Marinoan river waters (Fig. 6B). Although a high W/D regime may also result in low

445 seawater δ^7Li value under a modern style of oceanic Li cycle, notably low dissolved Li

446 concentration in this condition should cause global oceanic Li reservoir buffered by

447 hydrothermal fluids and induce more stable seawater δ^7Li, which is opposite to large and rapid

448 δ^7Li changes in the deglacial period (Fig. 4B). Additionally, based on new data compilations of

449 modern river systems, extremely high chemical weathering intensity with consistently low δ^7Li

450 and Li concentration generally corresponds to tropical rainforest regions with notably low

451 physical erosion rate that may not be common in modern continental weathering system (Fig.

452 1). Taken together, for oceanic Li isotope mass balance, a negative correlation between δ^7Li

453 and Li is expected to be most relevant.

454 The evaluation of average riverine δ^7Li and Li concentration suggest an increase in total

455 denudation rates and decrease in silicate weathering intensity (i.e., a lower *W/D*) in the earliest

456 Ediacaran, whereby primary rock dissolution is much more rapid than clay formation. This

457 weathering regime (i.e., a greater increase in physical erosion rates relative to chemical

458 weathering rates) is consistent with the case that the post-Marinoan glacial interval is

17

459 characterized by warming climate, high terrestrial run-off, and more exposure of fresh rock

460 surfaces (Fabre and Berger, 2012; Higgins and Schrag, 2003; Le Hir et al., 2009; Yang et al.,

461 2017). All of the above processes cause physical erosion rates to increase more rapidly than

462 chemical weathering rates (Gaillardet et al., 1999) , leading to more dissolution of primary

463 rocks than formation of secondary clays (i.e., congruent weathering) (Pogge von Strandmann

464 et al., 2021; Zhang et al., 2022). Active physical erosion and high run-off would also maintain

465 high chemical weathering rates (Fabre and Berger, 2012; Gaillardet et al., 1999) and ultimately

466 export abundant dissolved Ca, Mg and reactive Si, Al to the continental shelf (Baldermann et

467 al., 2015; Dunlea et al., 2015; Geilert et al., 2023). Such abundant Si and Al inputs in the

468 deglacial period may have facilitated the deposition of silicate materials in deeper basins (e.g.,

469 West Africa, Mongolia) (Penman and Rooney, 2019), and preservation of authigenic clays in

470 carbonates without dilution of detrital materials in shallow-water environment that is away from

471 terrestrial inputs.

472

6. Conclusions

474   This study reported first δ^7Li along with major and trace elemental data of carbonate and

475 carbonate-hosted silicate components in the Marinoan cap carbonates, in order to better

476 constrain continental weathering evolution in the aftermath of Snowball Earth. The

477 petrographic and elemental analyses of the studied samples suggest the marine authigenic clays,

478 instead of terrestrial detrital clays, dominating the carbonate-hosted silicate components, which

479 could be used to reconstruct the coeval seawater compositions. By contrast, the carbonate

480 components of cap carbonate samples are highly altered during the early diagenesis, and cannot

481 document pristine seawater information. Built from the carbonate-hosted silicate components,

482 we further evaluate Li isotope compositions of post-glacial seawater and track the silicate

483 weathering in the Marinoan aftermath. The estimated seawater δ^7Li records highlight the spatial

484 and temporal heterogeneity in the Li reservoir of continental shelf seawater in the earliest post-

485 glacial period. Moreover, persistence of significantly lower seawater δ^7Li relative to modern

486 ocean indicates high silicate weathering rate but low weathering intensity, which is consistent

487 with warming climate, high terrestrial run-off, and more exposure of fresh rock surfaces in the

488 deglacial period.

489

496 **Data and materials availability**

497 All geochemical data needed to evaluate the conclusion in the paper available in the main text

498 and Supplementary materials.

499 **Author contributions:**

500 G.-Y.W. and H.-F.L. conceived and supervised the project. Y.-S.Y., S.V.H., Y.-B.L., D.L.

501 collected the samples. Y.-S.Y., H.Z., Y.C. carried out data analyses. G.-Y.W., P.A.E.P.vS.,

502 M.A.L, T.T.I. conducted data interpretation. Y.-S.Y. and G.-Y.W. writing the draft with

503 substantial inputs from P.A.E.P.vS., M.A.L., T.C., T.Y., F.Z., H.-F.L., T.T.I.

504

505 **References**

506 Andrews, E., Pogge von Strandmann, P.A.E., Fantle, M.S., 2020. Exploring the importance of

507   authigenic clay formation in the global Li cycle. Geochim. Cosmochim. Acta 289, 47–

508   68. https://doi.org/10.1016/j.gca.2020.08.018

509 Baldermann, A., Warr, L.N., Letofsky-Papst, I., Mavromatis, V., 2015. Substantial iron

510   sequestration during green-clay authigenesis in modern deep-sea sediments. Nat.

511   Geosci. 8, 885–889. https://doi.org/10.1038/ngeo2542

512 Bao, H., Fairchild, I.J., Wynn, P.M., Spötl, C., 2009. Stretching the Envelope of Past Surface

513   Environments: Neoproterozoic Glacial Lakes from Svalbard. Science (80-.). 323, 119–

514   122.

515 Braun, J.J., Pagel, M., Herbilln, A., Rosin, C., 1993. Mobilization and redistribution of REEs

516   and thorium in a syenitic lateritic profile: A mass balance study. Geochim. Cosmochim.

517   Acta 57, 4419–4434. https://doi.org/10.1016/0016-7037(93)90492-F

518 Cao, C., Bataille, C.P., Song, H., Saltzman, M.R., Cramer, K.T., Wu, H., Korte, C., Zhang,

519   Z., Liu, X., 2022. Persistent late Permian to Early Triassic warmth linked to enhanced

520   reverse weathering. Nat. Geosci. 15, 832–838. https://doi.org/10.1038/s41561-022-

521   01009-x

522 Clark, S.K., Johnson, T.M., 2008. Effective isotopic fractionation factors for solute removal

523   by reactive sediments: A laboratory microcosm and slurry study. Environ. Sci. Technol.

524   42, 7850–7855. https://doi.org/10.1021/es801814v

525 Condon, D., Zhu, M., Bowring, S., Wang, W., Yang, A., Jin, Y., 2005. U-Pb ages from the

526   neoproterozoic Doushantuo Formation, China. Science (80-.). 308, 95–98.

527   https://doi.org/10.1126/science.1107765

528 Crockford, P.W., Kunzmann, M., Blättler, C.L., Kalderon-Asael, B., Murphy, J.G., Ahm,

529   A.S., Sharoni, S., Halverson, G.P., Planavsky, N.J., Halevy, I., Higgins, J.A., 2020.

530   Reconstructing Neoproterozoic seawater chemistry from early diagenetic dolomite.

531   Geology 49, 442–446. https://doi.org/10.1130/G48213.1

20

532   Dellinger, M., Gaillardet, J., Bouchez, J., Calmels, D., Louvat, P., Dosseto, A., Gorge, C.,

533   Alanoca, L., Maurice, L., 2015. Riverine Li isotope fractionation in the Amazon River

534   basin controlled by the weathering regimes. Geochim. Cosmochim. Acta 164, 71–93.

535   https://doi.org/10.1016/j.gca.2015.04.042

536   Dellinger, M., Hardisty, D.S., Planavsky, N.J., Gill, B.C., Kalderon-Asael, B., Asael, D.,

537   Croissant, T., Swart, P.K., West, A.J., 2020. The effects of diagenesis on lithium isotope

538   ratios of shallow marine carbonates. Am. J. Sci. 320, 150–184.

539   https://doi.org/10.2475/02.2020.03

540   Dunlea, A.G., Murray, R.W., Sauvage, J., Spivack, A.J., Harris, R.N., D'Hondt, S., 2015.

541   Dust, volcanic ash, and the evolution of the South Pacific Gyre through the Cenozoic

542   Ann. Paleoceanography 30, 1078–1099. https://doi.org/10.1002/2015PA002829

543   Fabre, S., Berger, G., 2012. How tillite weathering during the snowball Earth aftermath

544   induced cap carbonate deposition. Geology 40, 1027–1030.

545   https://doi.org/10.1130/G33340.1

546   Fabre, S., Berger, G., Chavagnac, V., Besson, P., 2013. Origin of cap carbonates: An

547   experimental approach. Palaeogeogr. Palaeoclimatol. Palaeoecol. 392, 524–533.

548   https://doi.org/10.1016/j.palaeo.2013.10.006

549   Fang, Y., Xu, H., 2022. Coupled dolomite and silica precipitation from continental

550   weathering during deglaciation of the Marinoan Snowball Earth. Precambrian Res. 380,

551   106824. https://doi.org/10.1016/J.PRECAMRES.2022.106824

552   Font, E., Nédélec, A., Trindade, R.I.F., Macouin, M., Charrière, A., 2006. Chemostratigraphy

553   of the Neoproterozoic Mirassol d'Oeste cap dolostones (Mato Grosso, Brazil): An

554   alternative model for Marinoan cap dolostone formation. Earth Planet. Sci. Lett. 250,

555   89–103. https://doi.org/10.1016/j.epsl.2006.06.047

556 Gaillardet, J., Dupre, B., Louvat, P., Allegre, C.J., 1999. Global silicate weathering and CO2

557   consumption rates deduced from the chemistry of large rivers. Chem. Geol. 159, 3–30.

558 Gammon, P.R., 2012. An organodiagenetic model for Marinoan-age cap carbonates.

559   Sediment. Geol. 243–244, 17–32. https://doi.org/10.1016/j.sedgeo.2011.12.004

560 Geilert, S., Frick, D.A., Garbe-Schönberg, D., Scholz, F., Sommer, S., Grasse, P., Vogt, C.,

561   Dale, A.W., 2023. Coastal El Niño triggers rapid marine silicate alteration on the

562   seafloor. Nat. Commun. 14, 10–17. https://doi.org/10.1038/s41467-023-37186-5

563 Gernon, T.M., Hincks, T.K., Tyrrell, T., Rohling, E.J., Palmer, M.R., 2016. Snowball Earth

564   ocean chemistry driven by extensive ridge volcanism during Rodinia breakup. Nat.

565   Geosci. 9, 242–248. https://doi.org/10.1038/ngeo2632

566 Giddings, J.A., Wallace, M.W., 2009. Sedimentology and C-isotope geochemistry of the

567   "Sturtian" cap carbonate, South Australia. Sediment. Geol. 216, 1–14.

568   https://doi.org/10.1016/j.sedgeo.2009.01.007

569 Hathorne, E.C., James, R.H., 2006. Temporal record of lithium in seawater: A tracer for

570   silicate weathering? Earth Planet. Sci. Lett. 246, 393–406.

571   https://doi.org/10.1016/j.epsl.2006.04.020

572 Herman, F., Seward, D., Valla, P.G., Carter, A., Kohn, B., Willett, S.D., Ehlers, T.A., 2013.

573   Worldwide acceleration of mountain erosion under a cooling climate. Nature 504, 423–

574   426. https://doi.org/10.1038/nature12877

575 Higgins, J.A., Schrag, D.P., 2003. Aftermath of a snowball Earth. Geochemistry, Geophys.

576   Geosystems 4, 1–20. https://doi.org/10.1029/2002GC000403

577   Hindshaw, R.S., Tosca, R., Goût, T.L., Farnan, I., Tosca, N.J., Tipper, E.T., 2019.

578   Experimental constraints on Li isotope fractionation during clay formation. Geochim.

579   Cosmochim. Acta 250, 219–237. https://doi.org/10.1016/j.gca.2019.02.015

580   Hoffman, P.F., Abbot, D.S., Ashkenazy, Y., Benn, D.I., Brocks, J.J., Cohen, P.A., Cox, G.M.,

581   Creveling, J.R., Donnadieu, Y., Erwin, D.H., Fairchild, I.J., Ferreira, D., Goodman, J.C.,

582   Halverson, G.P., Jansen, M.F., Le Hir, G., Love, G.D., Macdonald, F.A., Maloof, A.C.,

583   Partin, C.A., Ramstein, G., Rose, B.E.J., Rose, C. V., Sadler, P.M., Tziperman, E.,

584   Voigt, A., Warren, S.G., 2017. Snowball Earth climate dynamics and Cryogenian

585   geology-geobiology. Sci. Adv. 3. https://doi.org/10.1126/sciadv.1600983

586   Hoffman, P.F., Kaufman, A.J., Halverson, G.P., Schrag, D.P., 1998. A neoproterozoic

587   snowball earth. Science (80-.). 281, 1342–1346.

588   https://doi.org/10.1126/science.281.5381.1342

589   Hoffman, P.F., Macdonald, F.A., Halverson, G.P., 2011. Chapter 5: Chemical sediments

590   associated with Neoproterozoic glaciation: Iron formation, cap carbonate, barite and

591   phosphorite. Geol. Soc. Mem. 36, 67–80. https://doi.org/10.1144/M36.5

592   Hoffmann, K.H., Condon, D.J., Bowring, S.A., Crowley, J.L., 2004. U-Pb zircon date from

593   the Neoproterozoic Ghaub Formation Namibia: Constraints on Marinoan glaciation.

594   Geology 32, 817–820. https://doi.org/10.1130/G20519.1

595   Hood, A. van S., Wallace, M.W., 2012. Synsedimentary diagenesis in a Cryogenian reef

596   complex: Ubiquitous marine dolomite precipitation. Sediment. Geol. 255–256, 56–71.

597   https://doi.org/10.1016/j.sedgeo.2012.02.004

598   Huang, K.J., Teng, F.Z., Shen, B., Xiao, S., Lang, X., Ma, H.R., Fu, Y., Peng, Y., 2016.

599   Episode of intense chemical weathering during the termination of the 635 Ma Marinoan

600   glaciation. Proc. Natl. Acad. Sci. U. S. A. 113, 14904–14909.

601   https://doi.org/10.1073/pnas.1607712113

602   Huang K F, Liu Y H, Wang R M, et al. Riverine Li isotope fractionation in small

603   mountainous rivers of Taiwan[C]//AGU Fall Meeting Abstracts. 2016, 2016:

604   V51A3038.

605   Huh, Y., Chan, L.H., Zhang, L., Edmond, J.M., 1998. Lithium and its isotopes in major world

606   rivers: implications for weathering and the oceanic budget. Geochim. Cosmochim. Acta

607   62, 2039–2051. https://doi.org/10.1016/S0016-7037(98)00126-4

608   Isson, T.T., Planavsky, N.J., 2018. Reverse weathering as a long-term stabilizer of marine pH

609   and planetary climate. Nature 560, 471–475. https://doi.org/10.1038/s41586-018-0408-4

610   Isson, T.T., Planavsky, N.J., Coogan, L.A., Stewart, E.M., Ague, J.J., Bolton, E.W., Zhang,

611   S., McKenzie, N.R., Kump, L.R., 2020. Evolution of the Global Carbon Cycle and

612   Climate Regulation on Earth. Global Biogeochem. Cycles 34, 1–28.

613   https://doi.org/10.1029/2018GB006061

614   Isson, T.T., Zhang, S., Lau, K. V., Rauzi, S., Tosca, N.J., Penman, D.E., Planavsky, N.J.,

615   2022. Marine siliceous ecosystem decline led to sustained anomalous Early Triassic

616   warmth. Nat. Commun. 13. https://doi.org/10.1038/s41467-022-31128-3

617   Jiang, G., Kennedy, M.J., Christie-Blick, N., 2003. Stable isotopic evidence for methane

618   seeps in Neoproterozoic postglacial cap carbonates. Nature 426, 822–826.

619   https://doi.org/10.1038/nature02201

24

620   Jiang, G., Shi, X., Zhang, S., Wang, Y., Xiao, S., 2011. Stratigraphy and paleogeography of

621   the Ediacaran Doushantuo Formation (ca. 635-551Ma) in South China. Gondwana Res.

622   19, 831–849. https://doi.org/10.1016/j.gr.2011.01.006

623   Kalderon-Asael, B., Katchinoff, J.A.R., Planavsky, N.J., Hood, A. v. S., Dellinger, M.,

624   Bellefroid, E.J., Jones, D.S., Hofmann, A., Ossa, F.O., Macdonald, F.A., Wang, C.,

625   Isson, T.T., Murphy, J.G., Higgins, J.A., West, A.J., Wallace, M.W., Asael, D., Pogge

626   von Strandmann, P.A.E., 2021. A lithium-isotope perspective on the evolution of carbon

627   and silicon cycles. Nature 595, 394–398. https://doi.org/10.1038/s41586-021-03612-1

628   Kirschvink, J.L., 1992. Late Proterozoic low-latitude global glaciation: the snowball Earth.

629   Proterozoic Biosph. 52, 51–52.

630   Le Hir, G., Donnadieu, Y., Goddéris, Y., Pierrehumbert, R.T., Halverson, G.P., Macouin, M.,

631   Nédélec, A., Ramstein, G., 2009. The snowball Earth aftermath: Exploring the limits of

632   continental weathering processes. Earth Planet. Sci. Lett. 277, 453–463.

633   https://doi.org/10.1016/j.epsl.2008.11.010

634   Li, F., Penman, D., Planavsky, N., Knudsen, A., Zhao, M., Wang, X., Isson, T., Huang, K.,

635   Wei, G., Zhang, S., Shen, J., Zhu, X., Shen, B., 2021. Reverse weathering may amplify

636   post-Snowball atmospheric carbon dioxide levels. Precambrian Res. 364, 106279.

637   https://doi.org/10.1016/j.precamres.2021.106279

638   Li, G., West, A.J., 2014. Evolution of Cenozoic seawater lithium isotopes: Coupling of global

639   denudation regime and shifting seawater sinks. Earth Planet. Sci. Lett. 401, 284–293.

640   https://doi.org/10.1016/j.epsl.2014.06.011

641   Li, W., Liu, X.M., 2020. Experimental investigation of lithium isotope fractionation during

642   kaolinite adsorption: Implications for chemical weathering. Geochim. Cosmochim. Acta

643   284, 156–172. https://doi.org/10.1016/j.gca.2020.06.025

644 Ma, J.L., Wei, G.J., Xu, Y.G., Long, W.G., Sun, W.D., 2007. Mobilization and re-distribution

645   of major and trace elements during extreme weathering of basalt in Hainan Island, South

646   China. Geochim. Cosmochim. Acta 71, 3223–3237.

647   https://doi.org/10.1016/j.gca.2007.03.035

648 Michalopoulos, P., Aller, R.C., 1995. Rapid clay mineral formation in Amazon delta

649   sediments: Reverse weathering and oceanic elemental cycles. Science (80-.). 270, 614–

650   617. https://doi.org/10.1126/science.270.5236.614

651 Misra, S., Froelich, P.N., 2012. Lithium isotope history of cenozoic seawater: Changes in

652   silicate weathering and reverse weathering. Science (80-.). 335, 818–823.

653   https://doi.org/10.1126/science.1214697

654 Nesbitt, H.W., 1979. Mobility and fractionation of rare earth elements during weathering of a

655   granodiorite. Nature 279, 206–210. https://doi.org/10.1038/279206a0

656 Peltonen, C., Marcussen, Ø., Bjørlykke, K., Jahren, J., 2009. Clay mineral diagenesis and

657   quartz cementation in mudstones: The effects of smectite to illite reaction on rock

658   properties. Mar. Pet. Geol. 26, 887–898.

659   https://doi.org/10.1016/j.marpetgeo.2008.01.021

660 Penman, D.E., Rooney, A.D., 2019. Coupled carbon and silica cycle perturbations during the

661   Marinoan snowball Earth deglaciation. Geology 47, 317–320.

662   https://doi.org/10.1130/G45812.1

663 Pogge von Strandmann, P.A.E., Dellinger, M., West, A.J., 2021. Lithium Isotopes.

26

664   Cambridge University Press, Cambridge.

665   Pogge von Strandmann, P.A.E., Henderson, G.M., 2015. The Li isotope response to mountain

666   uplift. Geology 43, 67–70. https://doi.org/10.1130/G36162.1

667   Pogge Von Strandmann, P.A.E., Jenkyns, H.C., Woodfine, R.G., 2013. Lithium isotope

668   evidence for enhanced weathering during Oceanic Anoxic Event 2. Nat. Geosci. 6, 668–

669   672. https://doi.org/10.1038/ngeo1875

670   Pogge Von Strandmann, P.A.E., Jones, M.T., Joshua West, A., Murphy, M.J., Stokke, E.W.,

671   Tarbuck, G., Wilson, D.J., Pearce, C.R., Schmidt, D.N., 2021. Lithium isotope evidence

672   for enhanced weathering and erosion during the Paleocene-Eocene Thermal Maximum.

673   Sci. Adv. 7, 1–12. https://doi.org/10.1126/sciadv.abh4224

674   Pogge von Strandmann, P.A.E., Schmidt, D.N., Planavsky, N.J., Wei, G., Todd, C.L.,

675   Baumann, K.H., 2019. Assessing bulk carbonates as archives for seawater Li isotope

676   ratios. Chem. Geol. 530, 119338. https://doi.org/10.1016/j.chemgeo.2019.119338

677   Rudnick, R.L., Gao, S., 2014. Composition of the Continental Crust, in: Treatise on

678   Geochemistry: Second Edition. Elsevier, pp. 1–51. https://doi.org/10.1016/B978-0-08-

679   095975-7.00301-6

680   Shields, G.A., 2005. Neoproterozoic cap carbonates: A critical appraisal of existing models

681   and the plumeworld hypothesis. Terra Nov. 17, 299–310. https://doi.org/10.1111/j.1365-

682   3121.2005.00638.x

683   Siever, R., 1992. The silica cycle in the Precambrian. Geochim. Cosmochim. Acta 56, 3265–

684   3272. https://doi.org/10.1109/LSP.2004.830109

685   Steiner, Z., Rae, J.W.B., Berelson, W.M., Adkins, J.F., Hou, Y., Dong, S., Lampronti, G.I.,

686   Liu, X., Achterberg, E.P., Subhas, A. V, 2022. Authigenic Formation of Clay Minerals

687   in the Abyssal North Pacific Global Biogeochemical Cycles. Global Biogeochem.

688   Cycles. https://doi.org/10.1029/2021GB007270

689 Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: Its Composition and Evolution,

690   The Journal of Geology. The University Of Chicago Press.

691 Trower, E.J., Fischer, W.W., 2019. Precambrian Si isotope mass balance, weathering, and the

692   significance of the authigenic clay silica sink. Sediment. Geol. 384, 1–11.

693   https://doi.org/10.1016/j.sedgeo.2019.02.008

694 Vigier, N., Decarreau, A., Millot, R., Carignan, J., Petit, S., France-Lanord, C., 2008.

695   Quantifying Li isotope fractionation during smectite formation and implications for the

696   Li cycle. Geochim. Cosmochim. Acta 72, 780–792.

697   https://doi.org/10.1016/j.gca.2007.11.011

698 Wang, X., Jiang, G., Shi, X., Xiao, S., 2016. Paired carbonate and organic carbon isotope

699   variations of the Ediacaran Doushantuo Formation from an upper slope section at

700   Siduping, South China. Precambrian Res. 273, 53–66.

701   https://doi.org/10.1016/j.precamres.2015.12.010

702 Wei, G.Y., Hood, A. v. S., Chen, X., Li, D., Wei, W., Wen, B., Gong, Z., Yang, T., Zhang,

703   Z.F., Ling, H.F., 2019. Ca and Sr isotope constraints on the formation of the Marinoan

704   cap dolostones. Earth Planet. Sci. Lett. 511, 202–212.

705   https://doi.org/10.1016/j.epsl.2019.01.024

706 Wei, G.Y., Wei, W., Wang, D., Li, T., Yang, X., Shields, G.A., Zhang, F., Li, G., Chen, T.,

707   Yang, T., Ling, H.F., 2020. Enhanced chemical weathering triggered an expansion of

708   euxinic seawater in the aftermath of the Sturtian glaciation. Earth Planet. Sci. Lett. 539,

709   116244. https://doi.org/10.1016/j.epsl.2020.116244

710   Wei, G.Y., Zhang, F., Yin, Y.S., Lin, Y.B., Pogge von Strandmann, P.A.E., Cao, M., Li, N.,

711   Xiong, G., Chen, X., Fan, C., Xu, C., Tan, F., Zhang, X., Yang, H., Ling, H.F., Shen,

712   S.Z., 2023. A 13 million-year record of Li isotope compositions in island carbonates:

713   Constraints on bulk inorganic carbonate as a global seawater Li isotope archive.

714   Geochim. Cosmochim. Acta 344, 59–72. https://doi.org/10.1016/j.gca.2023.01.013

715   Yang, J., Jansen, M.F., Macdonald, F.A., Abbot, D.S., 2017. Persistence of a freshwater

716   surface ocean after a snowball Earth. Geology 45, 615–618.

717   https://doi.org/10.1130/G38920.1

718   Zhang, F., Dellinger, M., Hilton, R.G., Yu, J., Allen, M.B., Densmore, A.L., Sun, H., Jin, Z.,

719   2022. Hydrological control of river and seawater lithium isotopes. Nat. Commun. 13,

720   3359. https://doi.org/10.1038/s41467-022-31076-y

721   Zhang, X. (Yvon), Saldi, G.D., Schott, J., Bouchez, J., Kuessner, M., Montouillout, V.,

722   Henehan, M., Gaillardet, J., 2021. Experimental constraints on Li isotope fractionation

723   during the interaction between kaolinite and seawater. Geochim. Cosmochim. Acta 292,

724   333–347. https://doi.org/10.1016/j.gca.2020.09.029

725   Zhao, J., Jin, Zhenkui, Jin, Zhijun, Wen, X., Geng, Y., 2017. Origin of authigenic quartz in

726   organic-rich shales of the Wufeng and Longmaxi Formations in the Sichuan Basin,

727   South China: Implications for pore evolution. J. Nat. Gas Sci. Eng. 38, 21–38.

728   https://doi.org/10.1016/j.jngse.2016.11.037

729   Zhao, M.Y., Zheng, Y.F., 2014. Marine carbonate records of terrigenous input into

29

730   Paleotethyan seawater: Geochemical constraints from Carboniferous limestones.

731   Geochim. Cosmochim. Acta 141, 508–531. https://doi.org/10.1016/j.gca.2014.07.001

732

733 **Figures**

734 **Fig. 1.** Relationships of δ^7Li values and Li concentrations for modern river waters (see

735 Supplementary materials for data source). The weathering intensity (*W/D*) is defined as ratios

736 of chemical weathering rates to total denudation rates (Dellinger et al., 2015). The colourful

737 circles represent data from low to moderate W/D regions and triangles represent data from

738 moderate-high W/D regions.

739

740 **Fig. 2.** Stratigraphic and geochemical profiles of the cap dolostones from the Jiulongwan and

741 Siduping sections. (A) paleogeographic map of South China (Jiang et al., 2011); (B)

742 reconstruction of the shelf-to-basin paleogeographic transect in the Yangtze Block (Jiang et al.,

743 2011); (C) and (D) δ^7Li and Li/Th for the silicate component, and δ^7Li and Li/(Ca+Mg) for the

744 carbonate component of the cap carbonates from the Jiulongwan and Siduping sections. The

745 circles represent the silicate component and the triangles represent the carbonate component in

746 bulk cap carbonate samples. The small numbers in the plot are values exceeding the x-axis

747 range.

748

749 **Fig. 3.** Polarized light microscope (PLM), cathodoluminescence (CL) and scanning electron

750 microscope (SEM) photographs of thin sections for bulk carbonate samples (JLW-9 and SDP-

751 21). The sample JLW-9 is shown in (A) (B) (E) (F). The sample SDP-21 is shown in (C) (D)

752 (G) (H) (CL and SEM photographs of more samples can be found in the Supplementary

753 materials). In which, (A) and (C) are PLM photographs, (B) and (D) are CL photographs, (E)

754 (F) (G) (H) are SEM photographs. The distributions of luminous red in (B) and (D) represent

755 the diagenetic carbonate minerals. (I) presents the results of XRD chromatograms of the silicate

756 component hosted in carbonates (JLW-7,8,9 and SDP-6,15,21). In the XRD pattern, quartz

757 always shows the highest peaks with clay minerals show smooth and low peaks which seem to

758 be suppressed by quartz peaks. Counterintuitively, this may not represent a dominant

759 occupation of quartz in mineralogy because quartz has higher diffraction efficiency and better

31

760 crystal form in comparison with phyllosilicate minerals. The semi-quantitative calculation

761 results show little contribution of quartz in comparison with marine authigenic clays.

762

763 **Fig. 4.** (A) Cross-plots of Li/Th vs. Al/Th for the silicate component of cap carbonates and

764 diamictites from the Jiulongwan and Siduping sections and their comparisons with other

765 modern and ancient sediment records, including site U1366 drill core (Dunlea et al., 2015),

766 Cryogenian Datangpo shales(Wei et al., 2020), upper continental crust (UCC) (Rudnick and

767 Gao, 2014), post-Archean average shale (PAAS) (Taylor and McLennan, 1985) and diamictite

768 from Siduping section. (B) Calculation of δ^7Li for authigenic clays with Monte Carlo estimated

769 uncertainties (2σ) in carbonate-associated silicate component of cap carbonates, and evaluation

770 of coeval seawater δ^7Li (blue and orange curves).

771

772 **Fig. 5.** Schematic diagram of marine Li cycle on continental margin in the aftermath of the

773 Marinoan glaciation.

774

775 **Fig. 6.** Modeling seawater δ^7Li variations as functions of average Li concentrations and δ^7Li

776 values of river waters at steady state. In (A), Precambrian ocean Li cycle is assumed with 20%

777 Li sink as altered oceanic crust (Δ^7Li$_{AOC}$ = −10‰) and 80% Li sink as marine authigenic

778 aluminosilicate clay (Δ^7Li$_{MAAC}$ = −5‰) (Kalderon-Asael et al., 2021). The riverine Li fluxes

779 are calculated by products of Li concentration and run-off. The continental run-off in the post-

780 Marinoan interval is suggested 1.2 times higher than that of present time (Le Hir et al., 2009).

781 For model sensitivity test, modern ocean Li cycle is presented in (B) with 52% Li sink as altered

782 oceanic crust (Δ^7Li$_{AOC}$ = −13‰) and 48% Li sink as marine authigenic aluminosilicate clay

783 (Δ^7Li$_{MAAC}$ = −20‰) (Li and West, 2014). The circle in (A) and (B) represent the estimated Li

784 isotope budgets of Marinoan and post-Marinoan seawater in this study (see Supplementary

785   materials for model parameters).

Figure 2_R1   Click here to access/download;Figure;Figure 2_R1.pdf ⬇

Jiulongwan section

Siduping section

Figure 3_R1   Click here to access/download;Figure;Figure 3_R1.pdf ⬇

Figure 5_R1

Click here to access/download;Figure;Figure 5_R1.pdf ⬇

Figure 1_R2

Figure 4_R2   Click here to access/download;Figure;Figure 4_R2.pdf ±

Figure 6_R2