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Lithium isotope constraints on the plume world hypothesis for the Marinoan Snowball Earth

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ABSTRACT

The Snowball Earth hypothesis predicts that continental chemical weathering was curtailed substantially during but rebounded strongly after the Marinoan ice age some 635 million years ago. Defrosting the planet would result in a plume of fresh glacial meltwater with a different chemical composition than underlying hypersaline seawater, generating an onshore-offshore geochemical gradient. Here we test the plume world hypothesis using lithium isotope abundances in the basal Ediacaran
Doushantuo cap dolostone that accumulated in the aftermath of the Marinoan snowball Earth along an onshore-offshore transect in South China. Critical to this analysis is whether the cap dolostone formed simultaneously at different water depths, or whether it accumulated sequentially in shallow marine environments as sea level rose in the glacial aftermath. Our data shows an overall decreasing $\delta^7$Li trend with distance from the shoreline, which is consistent with either variable mixing of a meltwater plume with high $\delta^7$Li and hypersaline seawater with low $\delta^7$Li under the isochronous accumulation scenario, or with the progressive dominance of the meltwater plume under the diachronous end member, wherein cap dolostone accumulation accompanied sea level rise. In contrast to the modern oceans with high $\delta^7$Li, our geochemical model explains the evolution of low $\delta^7$Li of syn-glacial silica-rich seawater through enhanced silicate reverse weathering.

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

**INTRODUCTION**

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

The geochemical cycle of lithium in modern oceans is generally well understood [14, 15]. Because of their substantial mass difference (~17%), $^6$Li and $^7$Li fractionate strongly during mineral-fluid interactions [15]. Importantly, the fractionation factors are largely constant, with negligible dependence on temperature, salinity, Li/Ca ratios, biological processes, and redox conditions [16-19]. In the modern ocean, the two primary Li sources are riverine flux ($1.0 \times 10^{10}$ mol/yr) derived from
continental silicate weathering with an average $\delta^7$Li of $\sim$23% and marine hydrothermal flux (1.3×10$^{10}$ mol/yr) with an average $\delta^7$Li of 8.3% [20]. The two major sinks are authigenic clay formation associated with silicate reverse weathering and low-temperature basalt alteration [21, 22]. As $^6$Li is preferentially partitioned into clays during mineral-fluid interactions (e.g., incongruent silicate weathering and reverse weathering) [19], $\delta^7$Li of modern seawater ($\sim$31%) is higher than that of average riverine input. Additionally, since the residence time of lithium in modern oceans is 0.3–1.5 Myr [23], much longer than the oceanic mixing time of $\sim$10$^3$ years [20], $\delta^7$Li of modern seawater is homogeneous.

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

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

GEOLOGICAL SETTING AND SAMPLING

The Ediacaran Doushantuo Formation in the Yangtze Block of South China (Fig. 1a–b) consists of carbonate, siltstone, black shale, and phosphorite that overlie glacial diamictites of the Marinoan-age Nantuo Formation and underlie the terminal Ediacaran Dengying Formation or its correlative Liuchapo Formation. The basal Doushantuo Formation is represented by a cap dolostone (Fig. 1c; Supplementary
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Figures 1a and 2) that is a few meters in thickness, but is widely distributed across the Yangtze platform from shelf to basinal environments [4]. The cap dolostone is laterally persistent and traceable with consistent lithology and internal stratigraphy for at least 350 km in platform-to-basin transects. It consists of thick beds of thinly laminated dolostone accumulated below storm wave base [4]. A distinctive suite of closely associated tepee-like structures, stromatolite-like cavities, layer-parallel sheet cracks, and cemented breccias occurs in the cap dolostone, particularly in the lower interval. While the top of the cap dolostone in slope and basinal facies appear to grade into overlying strata, proximal facies reveal evidence of a locally developed karstic unconformity (Supplementary Figures 1b and 2) [26, 27]. Two indistinguishable zircon U–Pb ages from South China—a 634.6 ± 0.9 Ma age from the uppermost Nantuo Formation [28] and a 635.2 ± 0.6 Ma age from an ash bed immediately above the cap dolostone [29]—constrain the age of the cap dolostone to ~635 Ma.

Samples of the Doushantu cap dolostone were collected from five sections, including the Zhangcunping (ZCP) section (N31°17′34″, E111°12′30″) and Jiulongwan (JLW) section (N30°48′54″, E111°03′20″) in Hubei Province, the Daping (DP) section (N28°59′01″, E110°27′42″) and Siduping (SDP) section (N28°55′05″, E110°26′55″) in Hunan Province, and the Wuhe (WH) section (N26°45′46″, E108°25′7″) in Guizhou Province (Fig. 1b). Together with the previously published δLi data from the Daotuo (DT) section in Guizhou Province [30], these sections represent a transect from inner shelf to slope facies (Fig. 1b) [31].

RESULTS

Lithium isotope compositions of the 36 cap dolostone samples from the five sections were analyzed on a Q-ICP-MS at University of North Carolina at Chapel Hill. The data, along with previously published δLi data from the Daotuo section [30], are presented in Fig. 1d–h and Supplementary Table S1. Twenty-one of these samples were also analyzed for δLi on a MC-ICP-MS at University of Maryland for inter-laboratory comparison, and the results are presented in Supplementary Figure 3 and Supplementary Table S1. The two sets of data agreed excellently, although the UMD dataset has much better analytical uncertainties (approximately ±0.3‰, 2σ) than the UNC dataset (approximately ±1.9‰, 2σ). We choose to use the UNC dataset for discussion because of its better stratigraphic coverage. Consistent with the previously published data [30], the 36 new measurements show that the δLi values range from −1.7 to 14.9‰ with an average of 4.4‰ (n = 36, SD = 4.1‰), which is significantly lower than those of previously published Precambrian (average = 7.7‰, n = 217, SD = 5.7‰; p-value ≈ 5.0 × 10⁻⁴, one-tailed T-test), Paleozoic (average = 10.1‰, n = 263, SD = 4.3‰, p-value ≈ 3.7 × 10⁻¹¹, one-tailed T-test), and Cenozoic–Mesozoic carbonates (average = 23.1‰, n = 45, SD = 3.8‰, p-value ≈ 1.0 × 10⁻³⁴, one-tailed T-test) [22].

The δLi data show a decreasing trend from inner shelf (the ZCP section, average = 14.3‰, n = 3; Fig. 1e) to upper slope (the DT section, average = 7.4‰, n = 30; and the WH section, average = 6.1‰, n = 10; combined average = 7.1‰; Fig. 1g) to lower slope facies (the SDP section, average = 3.4‰, n = 16; and the DP section, average = 0.3‰, n = 4; combined average = 2.6‰; Fig. 1h), with the intrashelf JLW section (average = 0.5‰, n = 3; Fig. 1f) representing an anomaly to this trend. The overall
difference in $\delta^7$Li between inner shelf and lower slope facies reaches 14.6‰ (Fig. 1d).

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

**DISCUSSION**

**Diagenesis and clay mineral contamination**

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

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

To aid the assessment of clay mineral contamination during sample leaching processes, the leachate for $\delta^7$Li measurement was also analyzed for elemental concentrations. Because clay and carbonate minerals have different Al and Rb concentrations, these elements were chosen as proxies for clay contamination. The Rb/(Mg+Ca) ratios of Doushantuo cap dolostone samples ($n = 36$) range from $6.39 \times 10^{-8}$ to $2.11 \times 10^{-6}$ ppm/ppm (Supplementary Figure 5a), all below the proposed threshold value of $3.0 \times 10^{-5}$ ppm/ppm [22], suggesting minimal clay mineral contamination. In contrast, Al/(Mg+Ca) ratios of Doushantuo cap dolostone samples range from 0.42 to 9.31 ppb/ppm (Supplementary Figure 5b), and many are above the 0.54 ppb/ppm threshold chosen to screen for clay contamination [22]. Nonetheless, no correlation is observed between $\delta^7$Li and element ratios of Rb/(Mg+Ca), Al/(Mg+Ca), and Li/(Mg+Ca) (Supplementary Figure 5a–c), indicating that clay mineral contamination is unlikely to be a major driver of the observed $\delta^7$Li variations. To further assess clay mineral contamination in samples with elevated Al/(Mg+Ca) ratios, Monte Carlo modeling was conducted to quantify the probability of likely clay content in our samples (see SI text). The model suggests that the maximum probability corresponds to a clay mineral content ≤ 0.5 wt.% (Supplementary Figures 6 and 7; see SI text).
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An effort was made to correct the measured $\delta^7$Li for potential clay mineral contamination because even 0.5 wt.% clay mineral contamination could have a notable impact on $\delta^7$Li owing to the higher Li content of clay compared to carbonate minerals. As clay minerals typically have lower $\delta^7$Li values than carbonates [33], corrected carbonate $\delta^7$Li values would be higher than measured values if clay contamination had occurred. Using a binary mixing model, we show that the corrected carbonate $\delta^7$Li values could be 1‰ to 6‰ higher than the measured values (Supplementary Table S4; see SI text). However, the corrected data do not change the temporal and onshore-offshore patterns of $\delta^7$Li, and thus we use the measured values for discussion.

The dolomite problem

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

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

Low $\delta$Li values and synglacial distillation

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

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

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

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

In this model, the seawater lithium reservoir ($M$) depends on the influxes from riverine input ($F_{\text{riv}}$) and high temperature alteration at the mid-ocean ridges ($F_{\text{HT}}$), as well as outfluxes through authigenic clay mineral formation ($F_2$) and low-temperature alteration ($F_{\text{LT}}$). The isotopic composition of seawater ($\delta^7\text{Li}_{\text{SW}}$) depends on the size of the lithium reservoir, influxes, outfluxes, and their isotopic compositions ($\delta^7\text{Li}_{\text{riv}}$ and $\delta^7\text{Li}_{\text{HT}}$) or fractionation factors ($\Delta^7\text{Li}_s = \delta^7\text{Li}_s - \delta^7\text{Li}_{\text{SW}}$ and $\Delta^7\text{Li}_{\text{LT}} = \delta^7\text{Li}_{\text{LT}} - \delta^7\text{Li}_{\text{SW}}$). We set the model time to 10 Myr in light of the estimated duration of the Marinoan glaciation of $<15$ Myr and most likely $\sim12$ Myr [2, 56]. The high temperature input ($F_{\text{HT}}$ and $\delta^7\text{Li}_{\text{HT}}$) was set the same as modern values since geophysical models estimate hydrothermal heat flux to be near-modern and to have stayed constant during our studied time interval [57, 58]. A series of sensitivity tests were performed to explore a wide range of possible values for $F_{\text{riv}}$ (0%, 10%, and 20% of modern values; Fig. 2), $\Delta^7\text{Li}_s$ ($-20\%$ to 0%; Fig. 2), $\Delta^7\text{Li}_{\text{LT}}$ ($-18\%, -10\%, -8\%$; and $-8\%$; Fig. 2), and $\delta^7\text{Li}_{\text{riv}}$ ($= 10\%$ to the modern value of $23\%$; Fig. 3). Additional parameter details for the model are provided in Supplementary Table S5.

The model results show that within the parameter space explored and under the conditions of low or no riverine fluxes ($F_{\text{riv}} \approx 0\%$; Fig. 2g and Fig. 3) and minimal fractionation ($\Delta^7\text{Li}_s \approx 0\%$; $\Delta^7\text{Li}_{\text{LT}} \approx -8\%$), $\delta^7\text{Li}_{\text{SW}}$ can evolve from a modern seawater value of $31\%$ to $<13\%$ on a timescale of $\sim7$–8 Myr.
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(Fig. 2g). These conditions would be favored in a snowball Earth scenario, particularly with the exceedingly limited riverine flux towards the peak of glaciation [1, 59]. Additionally, elevated reverse weathering, driven by the high concentrations of dissolved silica in Precambrian oceans prior to the ecological rise of Si-biomiminerlizing organisms [52], may have effectively limited Li isotopic fractionation during rapid formation of authigenic clay minerals [22]. Thus, it is plausible that evolved seawater at the end of the Marinoan snowball Earth could have a δLiSW value of ~13‰ (Fig. 4b), much lower than that of the modern seawater (31‰) and even lower than that of the modern riverine input (23‰). If so, upon the termination of the snowball Earth when riverine input resumes, the Li isotopic gradient between seawater and freshwater plume would be reversed (Fig. 4c) relative to the modern ocean (Fig. 4a).

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

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

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

The plumeworld model may also help to explain the δLi chemostratigraphic trend observed in the Doushantuo cap dolostone (Fig. 5). The most complete chemostratigraphic profiles show that the basal cap dolostone (stage I) has the lowest δLi values and lowest Li/(Mg+Ca) ratios (Fig. 1g and Supplementary Figure 1d, e, j). These low values are consistent with the predicted low δLi values and Li concentrations in evolved hypersaline seawater (Fig. 5b). We hypothesize that stage I cap dolostone was deposited during early deglaciation but prior to the development of the plumeworld ocean, and was thus strongly influenced by hypersaline seawater (Fig. 5c). During this stage, the melting of sea ice may have diluted the Li concentrations of seawater, but it would not have influenced the δLiSW because sea
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ice contains little Li.

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

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

SUMMARY

Lithium isotope data from the basal Ediacaran Doushantuo cap dolostone in South China are consistent with enhanced reverse silicate weathering during the Marinoan snowball Earth and a plumeworld ocean in the aftermath. The $\delta^7$Li values are lower than those of Phanerozoic carbonates, and they show a decreasing trend from inner shelf facies to slope facies. We hypothesize that the spatial trend reflects differential mixing between meltwater with a relatively high $\delta^7$Li$_{sw}$ value and evolved hypersaline seawater with a low $\delta^7$Li$_{sw}$ value, irrespective of whether the caps were isochronous or diachronous, the latter of which is our preferred interpretation. The Li isotope contrast between proximal and distal cap dolostones is thus consistent with a post-glacial plumeworld ocean, where a persistent, terrestrially derived meltwater plume occurred on top of evolved hypersaline seawater. The Doushantuo cap dolostone also exhibits a recognizable stratigraphic trend, beginning with low $\delta^7$Li and Li/(Mg+Ca) values followed by an increasing and then a decreasing trend. Although this chemostratigraphic trend remains to be confirmed, it is also consistent with the development of a post-glacial meltwater plume, reflecting the influence of evolved seawater in the beginning of cap dolostone deposition, followed by increasing impact of terrestrial meltwater, and then mixing of meltwater and seawater. Additionally, the
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Inferred $\delta^{7}$Li of the evolved seawater (~13‰) requires isotopic distillation of the ocean during the Marinoan snowball Earth, with little riverine influx and muted isotopic fractionation associated with enhanced reverse weathering of the seafloor in a silica-rich ocean. The lithium isotope data presented here may ultimately allow us to test the severity of the Marinoan glaciation, and extreme biogeochemical reorganization associated with its aftermath.
METHODS

Lithium isotopic analyses and elemental analyses

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

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

Elemental concentrations were analyzed in Agilent ultra-high matrix introduction (UHMI) mode. Samples were calibrated against matrix-matched multi-element standards before being analyzed under UHMI mode, in which helium gas was used to reduce potential isobaric interferences. Background intensities were monitored periodically by aspirating 2% v/v HNO$_3$ blank, and an internal standard solution containing Be, Ge, In, and Bi was used to correct for the instrumental drift. A limestone standard, NIST-1d, obtained from the National Institute of Standards and Technology (NIST), was measured routinely, yielding long-term accuracy of <10% for major elements [63].
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DATA AVAILABILITY
All geochemical data generated here are included in Supplementary Table S1. A description of the Li mass-balance model and quantifying clay contamination through Monte Carlo sampling are available in Supplementary Information. Additional code (in Python) has been posted on GitHub (https://github.com/cart0381/BoxModel).

SUPPLEMENTARY DATA
Supplementary data are available at NSR online

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AUTHOR CONTRIBUTIONS
T.G., M.T., and S.X. designed research; T.G., M.T., X.W., and S.X. performed research; T.G., M.T., 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., 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. wrote the paper, with input from other co-authors.

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