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

Kang-Jun Huang^{a,b,c}, Fang-Zhen Teng^d, Bing Shen^{a,1}, Shuhai Xiao^e, Xianguo Lang^a, Hao-Ran Ma^a, Yong Fu^f, and Yongbo Peng^g

^aMinistry of Education Key Laboratory of Orogenic Belts and Crustal Evolution, School of Earth and Space Sciences, Peking University, Beijing 100871, People's Republic of China; ^bShaanxi Key Laboratory of Early Life and Environments, Department of Geology, Northwest University, Xi'an 710069, People's Republic of China; ^cState Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an 710069, People's Republic of China; ^dIsotope Laboratory, Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195; ^eDepartment of Geosciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061; ^fCollege of Resource and Environmental Engineering, Guizhou University, Guiyang 550025, People's Republic of China; and ^gDepartment of Geology and Geophysics, Louisiana State University, Baton Rouge, LA 70803

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Cryogenian (~720–635 Ma) global glaciations (the snowball Earth) represent the most extreme ice ages in Earth's history. The termination of these snowball Earth glaciations is marked by the global precipitation of cap carbonates, which are interpreted to have been driven by intense chemical weathering on continents. However, direct geochemical evidence for the intense chemical weathering in the aftermath of snowball glaciations is lacking. Here, we report Mg isotopic data from the terminal Cryogenian or Marinoan-age Nantuo Formation and the overlying cap carbonate of the basal Doushantuo Formation in South China. A positive excursion of extremely high $\delta^{26}\text{Mg}$ values (+0.56 to +0.95)—indicative of an episode of intense chemical weathering—occurs in the top Nantuo Formation, whereas the siliciclastic component of the overlying Doushantuo cap carbonate has significantly lower $\delta^{26}\text{Mg}$ values (<+0.40), suggesting moderate to low intensity of chemical weathering during cap carbonate deposition. These observations suggest that cap carbonate deposition postdates the climax of chemical weathering, probably because of the suppression of carbonate precipitation in an acidified ocean when atmospheric CO_2 concentration was high. Cap carbonate deposition did not occur until chemical weathering had consumed substantial amounts of atmospheric CO_2 and accumulated high levels of oceanic alkalinity. Our finding confirms intense chemical weathering at the onset of deglaciation but indicates that the maximum weathering predated cap carbonate deposition.

snowball Earth | magnesium isotopes | cap carbonate | chemical weathering | South China

The worldwide distribution of Cryogenian glacial deposits (~720–635 Ma) implies the occurrence of global glaciations or snowball Earth events, with ice sheet extending to paleo-equatorial regions (1, 2). The termination of the end-Cryogenian Marinoan glaciation was followed by ocean oxygenation and diversification of complex eukaryotes (3–5), suggesting the possible linkage between glaciation and evolution (6). As a marker for the end of the Marinoan glaciation, globally distributed cap carbonates immediately above the glacial deposits indicate a sharp transition from an icehouse to a greenhouse climatic condition (7–9). The “snowball Earth” hypothesis posits that deglaciation was abrupt and was triggered by extremely high atmospheric CO_2 concentration ($p\text{CO}_2$) [~350× present atmospheric level (PAL), about $10^{-3.5}$ bar] accumulated during global freezing for tens of million years (8, 10). High atmospheric $p\text{CO}_2$ levels are expected to cause intense chemical weathering on continents, which, in turn, elevates seawater alkalinity and results in the rapid precipitation of cap carbonates all over the world (10, 11). This interpretation also explains the consistently negative carbon isotopic signatures of cap carbonates (10). Thus, cap carbonate precipitation coupled with intense chemical weathering is one of the key predictions of the snowball Earth hypothesis. However, direct geochemical evidence for intense chemical weathering during deglaciation is not available (12), and the temporal

relationship between intense chemical weathering and cap carbonate precipitation remains equivocal. In this study, we use Mg isotopes as a geochemical proxy to constrain the intensity of chemical weathering during the deposition of the terminal Cryogenian Nantuo Formation and the overlying cap carbonate of the basal Ediacaran Doushantuo Formation in the Yangtze Platform of South China.

Tracer for the Intensity of Chemical Weathering

Traditional proxies for the intensity of chemical weathering include chemical index of alteration (CIA) and strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$). However, CIA is sensitive to the compositions of source rocks (13), and Sr isotopes are susceptible to diagenetic alterations (14). Magnesium (Mg) isotopes have several advantages to surmount these obstacles. First, owing to the limited fractionation during magmatic processes (15), the primary components of the upper continental crust (UCC, e.g., granitoids and basalts) display a narrow range of Mg isotopic compositions [$\delta^{26}\text{Mg} = -0.3$ to -0.1 , Fig. 1A; $\delta^{26}\text{Mg}$ is the per mil deviation of $^{26}\text{Mg}/^{24}\text{Mg}$ with respect to the standard Dead Sea Magnesium (DSM3) (16)], minimizing the source effect encountered in CIA study. In addition, unlike Sr isotopes, the Mg isotopic system in dolomite and siliciclastic rocks is immune to secondary alteration related to low-grade metamorphism and diagenesis (17, 18). More importantly, Mg isotopes significantly fractionate (up to 2‰) during chemical weathering, with the preferential retention of ^{26}Mg in weathering residues (Fig. 1A) (19–21), and, as such, $\delta^{26}\text{Mg}$ values of weathering residues become progressively higher with increasing intensity of chemical weathering (22). As

Significance

At least two extreme glaciations (dubbed as snowball Earth events), each lasting millions of years and affecting the entire globe, occurred during the Cryogenian Period (~720–635 Ma). These glaciations are recorded by globally distributed glacial deposits overlain by cap carbonates. According to the snowball Earth hypothesis, cap carbonate deposition was driven by intense continental weathering during deglaciation, but geochemical evidence is lacking. Using Mg isotopes as a proxy, we reconstruct the history of chemical weathering during and following the terminal Cryogenian Marinoan glaciation in South China. Our data confirm an episode of strong chemical weathering during the termination of the 635-Ma Marinoan glaciation, but its climax occurred before cap carbonate deposition.

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¹To whom correspondence should be addressed. Email: bingshen@pku.edu.cn.

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Fig. 1. Compilation of Mg isotope data. (A) Boxplots showing the Mg isotopic compositions of major Mg reservoirs. The box encompasses the 25 and 75 percentiles, the vertical line inside the box represents the median value, the whiskers represent the 2.5 and 97.5 percentiles, and the gray dots are outliers. The cyan and orange vertical dashed lines represent average $\delta^{26}\text{Mg}$ of seawater (SW, -0.83) (47) and UCC (-0.22) (32), respectively. See [SI Text](#) and [Dataset S1](#) for references. (B) Cross-plot of $\delta^{26}\text{Mg}$ versus CIA for weathered residues in basalt weathering profiles. Green bar, fresh basalt (21, 22); cyan squares, sapolites developed from basaltic dike, South Carolina (22); purple triangles, soils above basalts, Iceland (48); red circles, sapolites developed from tholeiitic basalts South China (21); orange diamonds, bauxites developed from Columbia River basalts, United States (19). (Inset) In detail, the relationship between CIA and $\delta^{26}\text{Mg}$ values of sapolites from South China and Columbia River.

shown in the weathered basalt profiles, $\delta^{26}\text{Mg}$ values of weathering residues increase gradually from unaltered bedrock to the most weathered sapolites, displaying a positive (although not necessarily linear) correlation with CIA (19, 22) (Fig. 1B). Given the aforementioned merits, Mg isotopes can serve as a more reliable tracer for chemical weathering.

Geological Setting and Sample Description

The Cryogenian succession in the Yangtze Platform consists of, in ascending order, the Chang'an/Tiesiao Formation, representing the early Cryogenian (or Sturtian) glacial deposits, the interglacial Fulu/Datango Formation, and the Nantuo Formation equivalent

to the terminal Cryogenian or Marinoan glaciation (23). The Nantuo Formation is dated between 654 ± 3.8 Ma and 635.2 ± 0.6 Ma (24, 25), and is overlain by the 3- to 5-m-thick cap carbonate of the basal Doushantuo Formation (25, 26). Although cap carbonate atop Marinoan glacial deposits may be time-transgressive, the magnitude of this diachroneity is likely $<10^3$ – 10^4 y (9). In South China, the contact between the Nantuo glacial deposits and the Doushantuo cap carbonate is continuous, without a sedimentary break, particularly in the sampled sections that were deposited in deep basinal environments beyond the reach of wave activities (26).

The upper part of the Nantuo Formation and the overlying Doushantuo cap carbonate were sampled from two localities: a drill core (14ZK) from the Songtao county and an outcrop section (Bahuang) in the Tongren city, both in northeastern Guizhou Province, South China. These two sections are paleogeographically located in the deep-water basinal facies in Neoproterozoic (23) (Fig. S1). The Nantuo Formation recovered from the 14ZK core is 225 m thick and consists of alternating siltstone, sandstone, pebbly sandstone, and diamictite (Fig. 2). The focus of this study is on the upper Nantuo Formation, which can be divided into six lithological units (Fig. 2). Unit I is composed of 40-m-thick massive diamictite (only the upper 20 m was sampled), followed by 15-m-thick pebbly sandstone/siltstone alternations (unit II). The rest of the Nantuo Formation can be subdivided into, in stratigraphic order, 28-m-thick sandstone and siltstone of unit III, 8-m-thick pebbly sandstone intercalated with siltstone (unit IV), 10-m-thick siltstone (unit V), and 3-m-thick diamictite associated with siltstone (unit VI). In the Bahuang section, only siltstone of the topmost 1 m of the Nantuo Formation was sampled, and the sampled interval can be correlated with unit VI in the 14ZK core (Fig. S2). The Nantuo diamictites and pebbly sandstone/siltstone are generally considered as deposition in a glacial marine environment, representing proximal glaciomarine and distal glaciomarine facies, respectively, whereas the pebble-free sandstone and siltstone may represent normal marine deposition without the influence of glaciation (27, 28). The Nantuo Formation in these two sections is capped by the basal Ediacaran Doushantuo cap carbonates, which are composed of microcrystalline dolomite and dolomicrite with widespread sheet cracks (Fig. S2).

Results

In the 14ZK core, $\delta^{26}\text{Mg}$ remains constant at $\sim +0.05$ in the diamictite of unit I and pebbly sandstone and siltstone of unit II, but displays a sharp increase to $+0.56$ at the base of unit III (Fig. 2 and Table S1). High $\delta^{26}\text{Mg}$ values ($+0.56$ to $+0.95$) persist throughout units III and IV, followed by a sharp decline to $\sim +0.14$ in unit V. The topmost part of the Nantuo Formation (units V and VI) is characterized by relatively low $\delta^{26}\text{Mg}$, varying between -0.15 and $+0.28$. The siliciclastic component of the Doushantuo cap carbonate in the 14ZK core also has low $\delta^{26}\text{Mg}$, varying between $+0.17$ and $+0.24$ (Fig. 2). In the Bahuang section, both the siltstone in the top of Nantuo Formation (equivalent to unit VI in the 14ZK core) and the siliciclastic component of the cap carbonate have relatively low $\delta^{26}\text{Mg}$ values, ranging from -0.36 to $+0.40$ and -0.46 to $+0.42$, respectively. The $\delta^{13}\text{C}$ of the Doushantuo cap carbonate ranges from -11.6 to -4.0 in the 14ZK core and from -5.5 to -2.8 at the Bahuang section (Fig. 2 and Table S1).

Discussion

Stratigraphic fluctuation in $\delta^{26}\text{Mg}$ observed here cannot be attributed to the lithological variation alone, because $\delta^{26}\text{Mg}$ is not dependent on lithologies, as shown in Fig. 2. For example, siltstones and sandstones in units III and IV have exclusively high $\delta^{26}\text{Mg}$ values, whereas these same lithologies in units II and V have significantly lower values (Fig. 2). Nor could $\delta^{26}\text{Mg}$ variations be attributed to changes in sediment sources (e.g., fluctuations in hydrodynamic sorting of sediments and modification of the fluvial system), because consistently high $\delta^{26}\text{Mg}$ values occur in units III

14ZK

Fig. 2. Stratigraphic profiles of $\delta^{26}\text{Mg}$ and $\delta^{13}\text{C}$ of the upper Nantuo Formation and the basal Doushantuo Formation cap carbonate in the 14ZK core and the Bahuang section. Units I through VI refer to six lithostratigraphic units in the upper Nantuo Formation. Pink dashed line represents the stratigraphic correlation line. For different grain sizes, c/s is clay/silt, f is fine sand, m is medium sand, c is coarse sand, and q is granules.

and IV regardless of lithological variations. This inference is further supported by the poor correlations of $\delta^{26}\text{Mg}$ with K/Ti, Mg/Ti, and Fe/Ti (Fig. S3), suggesting that variations in $\delta^{26}\text{Mg}$ are largely independent of lithological compositions. Furthermore, postdepositional alterations of $\delta^{26}\text{Mg}$ can also be ruled out on the basis of a dearth of characteristic metamorphic minerals and the poor correlation between $\delta^{26}\text{Mg}$ and K metasomatism indicator (e.g., K/Ti molar ratio) (Fig. S34). These observations agree with previous studies that found limited Mg isotope fractionations in siliciclastic sedimentary rocks during diagenesis and low-grade metamorphism (17, 29). A possible influence of modern outcrop weathering can also be excluded because both Bahuang outcrop and the 14ZK core show consistent $\delta^{26}\text{Mg}$ profiles. Finally, the observed $\delta^{26}\text{Mg}$ patterns are not artifacts associated with incomplete carbonate leaching, because there is no significant correlation between Ca/Ti and $\delta^{26}\text{Mg}$ in leached residues (Fig. S3C).

Both X-ray diffraction (XRD) results and major elemental data reveal that siliciclastic components dispersed in the cap carbonate are compositionally similar to the matrix of the underlying siliciclastic rocks of the Nantuo Formation (Fig. S4 and Table S2), indicating a common and predominantly terrestrial source for the fine-grained siliciclastic components in both the Nantuo Formation and the overlying Doushantuo cap carbonate (30). As such, fine-grained siliciclastic extractions from the Nantuo Formation and the Doushantuo cap dolostone carry information about chemical weathering on continents and hence are sensitive records of chemical weathering (31). Despite their similar mineralogical compositions, siliciclastic extractions from the Nantuo and Doushantuo formations have different Mg isotopic compositions, probably because $\delta^{26}\text{Mg}$ is a more sensitive indicator of extremely intense chemical weathering when mineralogical and elemental indices such as CIA become saturated (Fig. 1B, ref. 20). Thus, we suggest

Seawater pH at equilibrium with an atmospheric $p\text{CO}_2$ level of 550 PAL would be ≤ 6.5 (39), which is significantly lower than the seawater pH of 8.3 to 8.7 during cap carbonate deposition as estimated from boron isotopes (41) (Fig. 3A). Thus, cap carbonate precipitation seems to require a substantial rise in seawater pH as well as a sharp decline in atmospheric $p\text{CO}_2$ levels, so as to raise the carbonate saturation state (Ω) in seawaters (Fig. 3). Assuming cap carbonate deposition at pH of 8.3 (40, 41) and seawater dissolved inorganic carbon (DIC) of 10 mM (SI Text), the equilibrated atmospheric $p\text{CO}_2$ level would be ~ 5.2 PAL (Fig. 3A) and Ω would be 4.5 (Fig. 3B), implying that cap carbonate deposition did not occur until more than 97 to 99% of atmospheric CO_2 (210 PAL to 550 PAL) had been consumed by chemical weathering. Similarly, if we accept an atmospheric $p\text{CO}_2$ level of 33 PAL on the basis of triple-oxygen isotopes of cap carbonates (42), cap carbonate deposition began after 85 to 95% CO_2 consumption, at seawater pH of 7.5, and carbonate Ω of 1.54 (Fig. 3). The gap between deglaciation and cap carbonate precipitation might be on the order of 10^5 y, inferred from a previous modeling study that estimated the length of time needed for chemical weathering to reduce atmospheric $p\text{CO}_2$ levels from 270 PAL (assumed $p\text{CO}_2$ levels at end of glaciation) to 1 PAL (background $p\text{CO}_2$ level) at 40 °C (43).

A drop in atmospheric $p\text{CO}_2$ levels is consistent with persistently low $\delta^{26}\text{Mg}$ values and thus low intensity of chemical weathering in the topmost part of the Nantuo Formation and the Doushantuo cap carbonate (Fig. 2). We suggest that, as chemical weathering consumes atmospheric CO_2 , seawater alkalinity would be elevated, leading to the progressive increase of carbonate saturation state in seawater (Fig. 3B) and eventually cap carbonate precipitation. In this scenario, the cap carbonate precipitated from supersaturated seawater with DIC mainly derived from atmospheric CO_2 , explaining the negative carbon isotope signals (Fig. 2) and widespread isopachous cements and aragonite fans in the cap carbonate (7, 44, 45).

In summary, Mg isotopic data indicate that the deposition of the Doushantuo cap carbonate was preceded by an episode of intense chemical weathering during the termination of the 635 Ma Marinoan glaciation, and cap carbonate precipitation occurred when atmospheric $p\text{CO}_2$ and chemical weathering intensity returned to lower levels. In this scenario, cap carbonate deposition was a delayed response to an episode of intense chemical weathering, which ultimately supplied Ca^{2+} and bicarbonate to support cap carbonate precipitation. This episode of intense chemical weathering not only led to the global precipitation of cap carbonate after the Marinoan glaciation but may have also brought abundant nutrients to the ocean, which in turn might have triggered primary productivity, ocean oxygenation (3), and, eventually, the diversification of complex eukaryotes in the early Ediacaran Period (46).

Methods

Sample Preparation. To minimize the effect of modern weathering, drill core samples and least-weathered outcrop samples were selected for analysis. Thin

sections were prepared to guide the sampling of fine-grained siliciclastic components, so as to keep away from pebbles or large-sized clasts in diamictites. Powders (300 mg to 500 mg) were obtained from different parts of the matrix using a handheld drill and were mixed to produce a homogenous sample. To remove calcareous contents, sample powder (~ 30 mg) was first leached in 10 mL of 0.5 N acetic acid in an ultrasonic incubator for 3 h. After centrifugation, the residue was further leached in 5 mL of 1 N hydrochloric acid for 1 h to ensure complete removal of carbonate minerals. After centrifugation, leaching residues were washed in deionized water at least three times, and then dried down overnight at 60 °C.

Elemental and Mineralogical Analyses. Postleaching residues were completely dissolved in a mixture of concentrated HF, HNO_3 , and HCl. Elemental compositions were determined on a Spectro Blue Sop Inductively Coupled Plasma Optical Emission Spectrometer at Peking University. Elemental concentrations were calculated on the basis of residue mass. The external reproducibility for major and minor elements (Na, Mg, Al, K, Ca, Fe, Mn, Ti, and Sr) is better than 5%. Mineral compositions of Doushantuo cap carbonate (whole-rock powders) and Nantuo Formation (postleaching residues) were analyzed using a PANalytical X'Pert Pro MPD X-ray Diffractometer. Mineral phases were identified by peak positions, and mineralogical abundances were quantitatively determined by peak areas.

Carbon Isotope Analysis. About 0.2 mg of carbonate sample powders was weighted to react with 1 mL of 100% phosphoric acid at 72 °C to liberate CO_2 from carbonate. CO_2 gas was introduced to MAT253 mass spectrometry at Louisiana State University for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analysis. Carbon and oxygen isotope values are reported in the delta notation as permil (‰) deviation relative to the Vienna-Pee Dee Formation belemnite standard. The analytical precision is $\pm 0.1\text{‰}$ (1σ).

Magnesium Isotope Analysis. About 5 mg of postleaching residue was dissolved in a mixture of Optima-grade HF, HNO_3 , and HCl. Mg was purified by cation exchange chromatography (loaded with Bio-Rad AGW50-X8 resin, 200 to 400 mesh). Two standards (Hawaii seawater and San Carlos olivine) were processed with samples for column chemistry. The purified Mg solutions with Na/Mg, Ca/Mg, Al/Mg, K/Mg, Fe/Mg < 0.05 were analyzed by the standard-sample bracketing method on a Nu plasma Multi-Collector Inductively Coupled Plasma Mass Spectrometer at University of Washington, Seattle. Three Mg isotopes (24–26) were measured simultaneously in separate Faraday cups (H5, Ax, and L4) at low-resolution mode. The procedure blank for ^{24}Mg ($< 10^{-4}$ V) was negligible relative to the sample signals (2 V to 4 V). Mg isotope values are reported in δ -notation as permil deviation relative to the standard DSM3: $\delta^{26}\text{Mg} = [(\delta^{26}\text{Mg}/^{24}\text{Mg})_{\text{sample}}/(\delta^{26}\text{Mg}/^{24}\text{Mg})_{\text{DSM3}} - 1] \times 1,000$, where x refers to mass 25 or 26. Multiple analyses of the San Carlos olivine and Hawaii seawater standards during the course of this study yielded $\delta^{26}\text{Mg}$ values ranging from -0.25 to -0.21 and from -0.87 to -0.78 , respectively, which are consistent with published values. All samples and standards analyzed in this study fall in a single mass-dependent fractionation line with a slope of 0.519 (Fig. S5).

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