

# Sedimentary constraints on the duration of the Marinoan Oxygen-17 Depletion (MOSD) event

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The ~635 Ma Marinoan glaciation is marked by dramatic Earth system perturbations. Deposition of nonmass-dependently <sup>17</sup>O-depleted sulfate (SO<sub>4</sub><sup>2-</sup>) in worldwide postglacial sediments is, thus far, unique to this glaciation. It is proposed that an extremely high-*p*CO<sub>2</sub> atmosphere can result in highly <sup>17</sup>O-depleted atmospheric O<sub>2</sub>, or the Marinoan Oxygen-17 Depletion (MOSD) event. This anomalous <sup>17</sup>O signal was imparted to sulfate of oxidative weathering origin. However, <sup>17</sup>O-depleted sulfate occurs in limited sedimentary intervals, suggesting that Earth surface conditions conducive to the MOSD had a finite duration. An MOSD duration can, therefore, provide much needed constraint on modeling Earth system responses at that time. Unfortunately, the sulfate <sup>17</sup>O record is often sparse or lacks radiometric dates. Here, we report 11 barite layers from a post-Marinoan dolostone sequence at Wushanhu in the South China Block. The <sup>17</sup>O depletion fluctuates in magnitude in lower layers but is persistently absent up section, providing the most confident first and last sedimentary appearance of the anomaly. δ<sup>13</sup>C chemostratigraphy is used to correlate the Wushanhu section to two proximal sections on the same shallow platform that lack barite layers but have published U-Pb dates that occur in dolostone and shale. Assuming a similar pattern and rate for carbonate and shale deposition among the different sections, we estimate the MOSD duration at 0–0.99 My. This number can be further constrained by new radiometric dates from equivalent sequences worldwide, thus underpinning models on the nonsteady-state Earth system response in the immediate aftermath of the Marinoan meltdown.

Neoproterozoic | snowball Earth | cap carbonates | Doushantuo | atmospheric oxygen

The Marinoan glaciation (~635 Ma) may be the most extreme glacial period in Earth history, with widespread occurrence of glacial sediments at low paleolatitudes near the tropics (1). The central theme of the original snowball Earth hypothesis, which was developed to explain this glacial record, is the buildup of atmospheric CO<sub>2</sub> to bring the Earth out of an indefinite deep freeze (2). This idea has been expanded (3–5), undergone debate (1, 6), and driven new modeling work (7–14). Thanks to well-preserved sedimentary records (15, 16) and decent geochronological controls (17–19), many of the theories pertaining to the Marinoan glaciation can be tested.

The most unusual evidence that is consistent with a snowball Earth hypothesis is the nonmass-dependently <sup>17</sup>O-depleted sulfate (SO<sub>4</sub><sup>2-</sup>) in barite (BaSO<sub>4</sub>) deposited in the post-Marinoan dolostones in South China and West Africa (20, 21), carbonate-associated sulfate in carbonate lenses within diamictites in Svalbard (22), and carbonate-associated sulfate of cap dolostones in the Kimberley region, Western Australia (23). A probable cause of the anomalously <sup>17</sup>O-depleted sulfate [a nadir of Δ<sup>17</sup>O = –1.64‰ (22), with Δ<sup>17</sup>O ≡ ln(δ<sup>17</sup>O + 1) – 0.52ln(δ<sup>18</sup>O + 1)] is suggested to be an ultra-high *p*CO<sub>2</sub> atmosphere. Chapman reactions in the stratosphere (24) under extremely high *p*CO<sub>2</sub> (with other conditions unchanged) could result in a large reservoir of <sup>17</sup>O being transferred to CO<sub>2</sub> while leaving atmospheric O<sub>2</sub> extremely depleted in <sup>17</sup>O (20). Here, we refer to this unusual atmospheric

O<sub>2</sub> isotope state as the Marinoan Oxygen-17 Depletion (MOSD) event. Sulfate derived from oxidative weathering of sulfide minerals inherits atmospheric O<sub>2</sub> signal, with a variable portion (0–50%) of the product sulfate oxygen sourced from O<sub>2</sub> and the rest sourced from ambient water (20, 25, 26). By comparison, under modern *p*CO<sub>2</sub> conditions, a Δ<sup>17</sup>O of –0.26‰ for tropospheric O<sub>2</sub> (27) is matched by a Δ<sup>17</sup>O of –0.10‰ to –0.20‰ for sulfate of oxidative weathering origin (20). We, therefore, use sulfate with a Δ<sup>17</sup>O value more negative than –0.30‰ to indicate the presence of a distinctly <sup>17</sup>O-depleted atmospheric O<sub>2</sub>. The anomalously <sup>17</sup>O-depleted sulfate is the expression of the MOSD as it is recorded in post-Marinoan or basal Ediacaran sediments.

A global occurrence of <sup>17</sup>O-depleted sulfate within post-Marinoan sedimentary sequences has been established by our recent findings in South China, West Africa, Svalbard, and Western Australia. This global occurrence is consistent with an event of atmospheric origin. In fact, the <sup>17</sup>O-depleted sulfate can be confidently used as a marker for a global synchronous event. However, although the anomalous sulfate occurs in one or two layers of barite or several horizons of dolostones, in all cases, it occurs only in limited intervals in the postglacial sediments. Viewed on the scale of geologic time, the MOSD is a transient event, and when looked at closely, the MOSD event has a finite duration. This mode of occurrence suggests that there was a limited window of time when the postglacial Earth surface conditions were favorable for atmospheric O<sub>2</sub> to possess distinct <sup>17</sup>O depletion.

Exactly how long the MOSD event lasted is of paramount importance to understanding and modeling the Earth system in response to extreme perturbations. If the snowball hypothesis offers a viable explanation for the observed sulfate <sup>17</sup>O depletion, then, in the immediate aftermath of the Marinoan meltdown, ultra-high *p*CO<sub>2</sub> was probably being drawn down by rock weathering, *p*O<sub>2</sub> was rising, and biosphere CO<sub>2</sub>–O<sub>2</sub> fluxes were evolving because of photosynthesis, respiration, and organic burial in response to tectonics, climate, sediment supply, and numerous feedbacks. The Δ<sup>17</sup>O value of atmospheric O<sub>2</sub> and the duration of the MOSD should be the results of dynamic interplay between these variables.

Currently, modeling exercises on all of the aforementioned variables are too open and unconstrained to be informative. Although certain constraints can be placed on some of these variables, we believe that the first one that should be and can be constrained is the duration of the MOSD event. After a general number of the duration is given, modeling work can put additional constraints on the rates of *p*CO<sub>2</sub> drawdown, *p*O<sub>2</sub> rise, and biological fluxes at this critical transition in Earth system history.

Constraining the duration of MOSD using sedimentary records faces two main issues: (i) the dearth of minerals or host rocks that

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bear  $^{17}\text{O}$ -depleted sulfate and (ii) the lack of radiometric dates at the same sites where  $^{17}\text{O}$ -depleted sulfate occurs. The presence of sulfate  $^{17}\text{O}$  depletion attests to the MOSD event. However, the absence of sulfate  $^{17}\text{O}$  depletion does not necessarily mean that the MOSD event has ended. This absence of sulfate  $^{17}\text{O}$  depletion can be attributed to (i) a lack of suitable sulfate mineral (e.g., barite) to record  $\Delta^{17}\text{O}$ , (ii) processes that destroy or poorly preserve the sulfate mineral (e.g., erosion or lack of sedimentation), (iii) mixing with  $^{17}\text{O}$ -normal  $\text{SO}_4^{2-}$  seawater, and (iv) erasing of anomalous  $^{17}\text{O}$  signals by microbial sulfur cycling processes. Only when sedimentary sulfate remains consistently  $^{17}\text{O}$ -normal can we conclude that atmospheric  $\text{O}_2$  no longer had a distinct  $^{17}\text{O}$  depletion. Therefore, to resolve the first issue of duration constraint, we must locate a sedimentary sequence with a high abundance of barite layers to confidently pin down the first and last appearances of the  $^{17}\text{O}$  depletion signal in a postglacial sedimentary sequence. The establishment of such a reference sequence is analogous to the effort of defining a Global Boundary Stratotype Section and Point. To resolve the second issue of geochronology, we can use carbon isotope chemostratigraphy (e.g.,  $\delta^{13}\text{C}$  of dolostones) combined with regional facies change (e.g., from carbonates to shales) to stratigraphically correlate the reference section to proximal sections where radiometric dates are available.

In a recent field campaign, we located such a reference sequence. Here, we report sulfate  $\Delta^{17}\text{O}$  data from the Wushanhu section in the South China Block, where 11 layers of barite occur within 1 m of a postglacial dolostone sequence. By correlating sedimentary packages and  $\delta^{13}\text{C}$  data, we are able to extrapolate the stratigraphic positions of uranium-lead (U-Pb) dated layers in two sections, which are nearby to the Wushanhu section, and offer a quantitative estimate of the duration of the MOSD event.

### Wushanhu Section: A Barite Reference Sequence

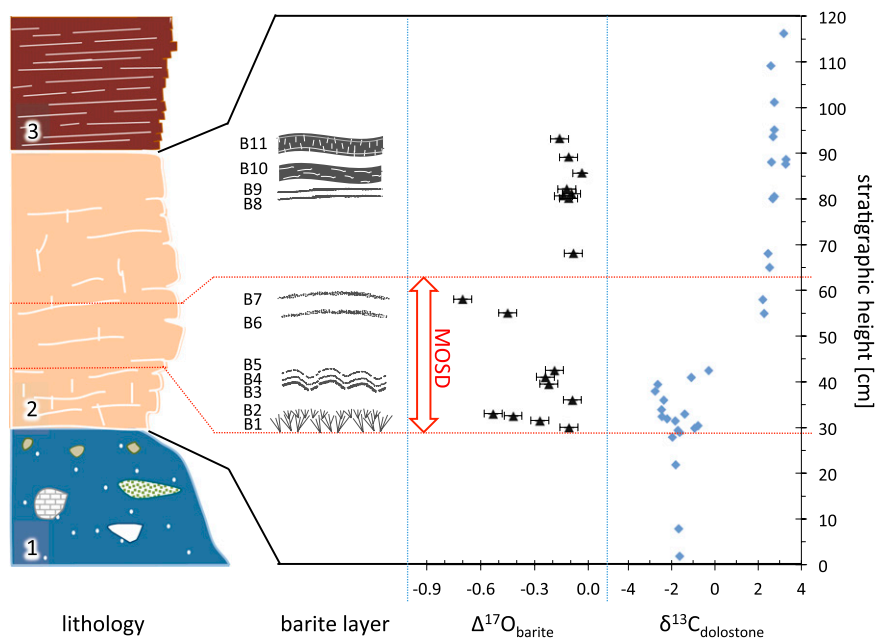
The sampled section at Wushanhu, Hubei Province, China (31° 41.74' N, 110° 47.20' E) is a well-exposed post-Marinoan or basal Ediacaran sedimentary sequence that overlies the Nantuo Formation diamictite (Fig. 1). This basal Doushantuo Formation consists of 0.30 m cap dolostones (defined as the dolostone

package below the first layer of barite) (28) and 0.88 m micritic dolostones topped by phosphorite-bearing shales. The cap dolostones have a disrupted and karstified appearance, bear cavity fillings of isopachous dolomitized aragonite fans and quartz spar, and lack barite. The 0.88 m dolostones overlying the cap dolostones host 11 identified barite layers (B1 ... B11) (Figs. 1 and 2). The lowest barite layer (B1) consists of ~2 cm in height radiating bladed barite crystal fans, consistent with the basal Ediacaran barite occurrence observed in other shallow-platform sections in South China. All 11 discretely occurred barite layers occur within the 0.6-m interval above the cap dolostones. Dolostones continue above the last barite layers for 0.25 m before being overlain by shales (Fig. 1). Overall, because of the shallow depositional setting, the basal Ediacaran sediments in the Wushanhu section are much more condensed than most in South China. Probably for this same reason, Wushanhu hosts more discrete barite layers than any equivalent sequence in South China.

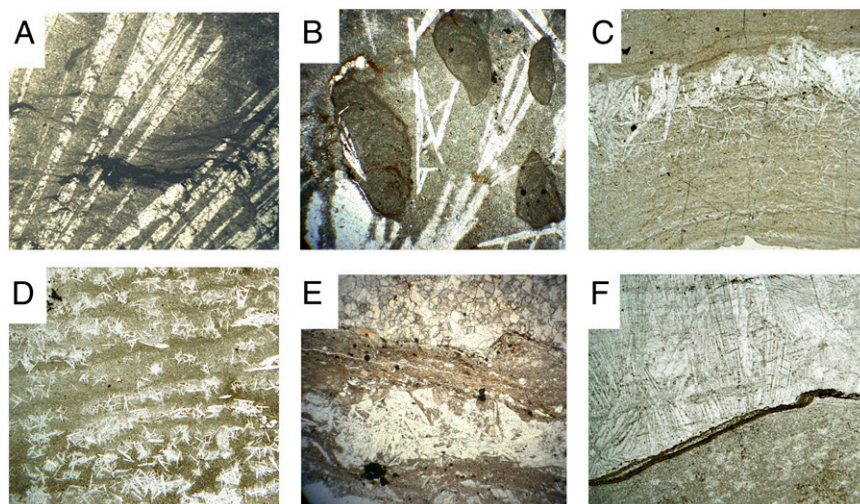
The syn-depositional origin of the barite fans in the basal Doushantuo Formation, an important precondition for their use as a record of a temporal event, has been recognized in earlier studies (21, 28). The following petrographic and sedimentological features in the Wushanhu barite further support the conclusion. (i) Domal laminations continue through barite growth bands in layers B1 and B2 (Fig. 2 A and B), (ii) macroscopic crystal growth follows dolostone lamination (Fig. 2 A and C), (iii) different barite layers do not connect by fractures, and (iv) a rich variety of barite occurs in a small hand specimen (Fig. 2).

### Stable Isotope Results

Isotope parameters analyzed for the Wushanhu section include barite  $\Delta^{17}\text{O}$  and dolostone  $\delta^{13}\text{C}$ . The magnitude of the  $^{17}\text{O}$  depletion initially increases (or the  $\Delta^{17}\text{O}_{\text{barite}}$  value decreases) upward but decreases to a nondistinct level ( $-0.09\text{‰}$ ) 6 cm above the top of the cap dolostone (*sensu stricto*) (28), or the first barite layer. The magnitude again increases farther up until it reaches  $-0.70\text{‰}$  (sample B7) at 30 cm above the first layer. Farther up in stratigraphic level, none of four layers of barite (B8 to B11), including a small barite mass between B8 and B9, show any distinct  $^{17}\text{O}$



**Fig. 1.** The post-Marinoan or basal Ediacaran stratigraphic sequence at Wushanhu, Hubei Province, China: (1) the Nantuo diamictite, (2) the basal Doushantuo dolostone, and (3) the first unit of the Doushantuo shale. The occurrence and  $^{17}\text{O}$  anomaly ( $\Delta^{17}\text{O}\text{‰}$ ) of barite and the  $\delta^{13}\text{C}$  [‰ Vienna Pee Dee Belemnite (VPDB)] of the dolostones are displayed by height above base of the dolostones. Stratigraphic interval of the MOSD event is denoted.



**Fig. 2.** Photomicrographs of barite layers in thin sections under plane polarized light. The layers, features, and fields of view are (A) B1, soft sediment deformation cross-cutting barite crystal fans, 3 mm; (B) B1, stromatolitic features in association with barite, 3 mm; (C) B3, disrupted barite layer and laminations, 12 mm; (D) B6, layers of barite microcrystals in dolomite matrix, 8 mm; (E) B9, chaotically arranged barite crystal layers bounded by mud above and below, 4 mm; and (F) B11, densely packed sheaves of radiating barite crystals, 12 mm.

depletion, with  $\Delta^{17}\text{O}$  values ranging from  $-0.15\text{‰}$  to  $-0.04\text{‰}$ . The  $\Delta^{17}\text{O}_{\text{barite}}$  from crystals within the dolomite matrix, not in discrete layers, was obtained from between layers B2 and B3 and between layers B7 and B8, with results of  $-0.09\text{‰}$  and  $-0.08\text{‰}$ , respectively (Fig. 1).

Dolostone  $\delta^{13}\text{C}$  (‰VPDB) (Fig. 1) begins with a negative value of  $-1.6\text{‰}$ , decreases to a low of  $-2.8\text{‰}$  just below barite layer B3 (8 cm above the first layer of barite), then increases to positive values, and is maintained at  $\sim 2.7\text{‰}$  in the upper one-half of the dolostone sequence. All stable isotope data and their corresponding stratigraphic levels are tabulated in Tables S1 and S2.

### MOSD Duration

To estimate the duration of the MOSD, an unusual atmospheric event, the first step is to establish with maximum confidence that sulfate  $^{17}\text{O}$  depletion closely registers the MOSD within a well-defined stratigraphic interval. At Wushanhu, distinct sulfate  $^{17}\text{O}$  depletion begins at 0.31 m above the base of the dolostone (i.e., above the top of diamictite) within the top of B1 barite fans (Fig. 1). However, the MOSD stratigraphic end might easily be misidentified at 0.36 m (B3 in Fig. 1) because of a lack of distinct sulfate  $^{17}\text{O}$  depletion at that horizon. Undersampling can also result in misidentification. For example, had we not sampled B6 and B7, we would have determined that the  $^{17}\text{O}$ -depleted signal disappeared at 0.36 m above the top of the Nantuo diamictite. However, because of the many barite layers at Wushanhu, we can confidently conclude that the MOSD event existed through the dolostone depositional interval of 0.31–0.58 m (B1 to B7), and the lack of distinct sulfate  $^{17}\text{O}$  depletion in between could be caused by sulfate mixing, microbial reprocessing, and many other factors that could result in no record of the anomaly. The underlying hypothesis is, of course, that the MOSD event had occurred only one time and not two times at the aftermath of the Marinoan meltdown. Although it is not absolute proof, the persistent absence of distinct  $^{17}\text{O}$  depletion in the four upper barite layers (B8 to B11), including barite occurring between layers (i.e., between B7 and B8 and between B8 and B9), suggests that atmospheric  $\text{O}_2$  was no longer distinctly depleted in  $^{17}\text{O}$ . Therefore, the MOSD interval is at 0.31 m to somewhere between 0.58 and 0.68 m above the top of the diamictite at Wushanhu, a total of  $\sim 0.3$  m.

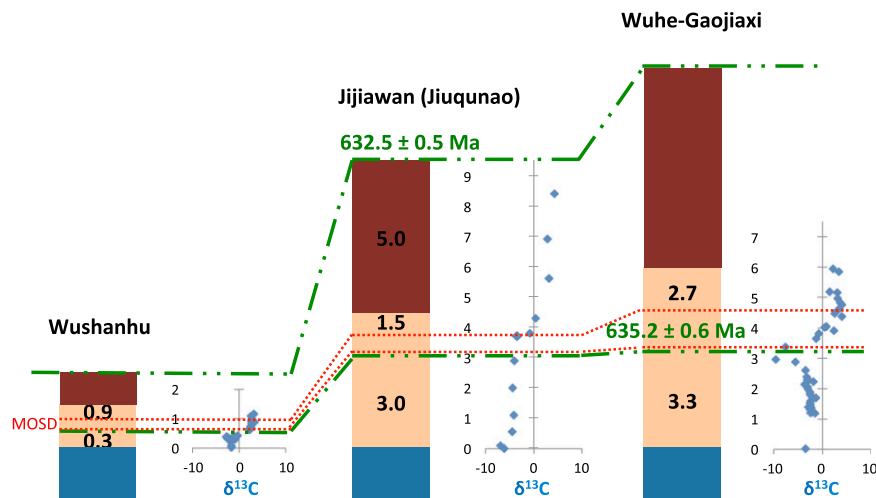
With the MOSD interval being positioned at the Wushanhu section, we need to correlate this interval to a proximal section

that has radiometric dates so that the duration can be estimated. To do the correlation, we need a reproducible  $\delta^{13}\text{C}$  profile that is shared by shallow-platform postglacial sedimentary sequences in the region. At Wushanhu, the  $\delta^{13}\text{C}$  of the dolostones turns to more negative values before it turns positive at 0.43 m above the base of the dolostones (Fig. 1). This  $\delta^{13}\text{C}$  trend is well-reproduced in most of the published  $\delta^{13}\text{C}$  profiles in the Yangtze Gorges area in South China (29). Specifically, the Wushanhu  $\delta^{13}\text{C}$  curve is similar to the  $\delta^{13}\text{C}$  curves of the two Yangtze-Gorges sections ( $\sim 150$  km south of Wushanhu), the Jijiawan (Jiuqunao), and the Wuhe-Gaojiayi sections, where radiometric dates are available (18). The similarity in the  $\delta^{13}\text{C}$  trend also suggests that, despite an apparently condensed section at Wushanhu, no major sedimentary hiatus had occurred. This  $\delta^{13}\text{C}$  trend similarity offers us confidence to correlate horizons among sections where the MOSD record and radiometric dates do not co-occur (Fig. 3).

The two U-Pb absolute ages of  $635.2 \pm 0.6$  and  $632.5 \pm 0.5$  Ma do not occur in the same section. At Wuhe-Gaojiayi, the 635.2-Ma U-Pb age comes from a tuff bed in the postglacial dolostones at 2.3 m above the top of diamictite on the outcrop (18). Dolostone  $\delta^{13}\text{C}$  data come from a drill core in a thicker portion of that same section (30). The 635.2  $\pm$  0.6-Ma age at Wuhe-Gaojiayi occurs on top of the cap dolostone and is pinned on the  $\delta^{13}\text{C}$  curve from the thicker portion accordingly (Fig. 3). At Jijiawan the 632.5-Ma age comes from a tuff bed in the shale unit at 5.0 m above the top of the 4.5-m-thick postglacial dolostones. Here, the dolostone  $\delta^{13}\text{C}$  data come from the same section (31) (Fig. 3).

With this information, we now can estimate the MOSD duration at Wushanhu, where it is represented by the 0.3-m-thick dolostone interval (Figs. 1 and 3). Using the  $\delta^{13}\text{C}$  curve alone, we match the 635.2-Ma age at Wuhe-Gaojiayi at both 0.3 m above the diamictite at Wushanhu and 3.0 m above the diamictite at Jijiawan. This 635.2-Ma age is the horizon right at the top of the cap dolostone (*sensu stricto*) (28). It is also where the lowest of the many  $^{17}\text{O}$ -depleted barite layers, or the onset of the MOSD, occurs at the Wushanhu section. Pinning the younger date of 632.5 from Jijiawan to Wushanhu and correlating the 0.3-m MOSD interval at Wushanhu to the Jijiawan section are achieved through the following scheme. (i) The  $\delta^{13}\text{C}$  curves put the onset of the MOSD at 635.2 Ma at 3.0 m above the base of the 4.5-m-thick dolostone section at Jijiawan. (ii) Assuming an equal deposition rate for the dolostones and the shales through the  $2.7 \pm 0.781$ -My duration





**Fig. 3.** Carbon isotope chemostratigraphy, MOSD event stratigraphic interval, and correlation of radiometric age for three shallow-platform post-Marinoan sections in the Yangtze Gorges area, South China Block. Stratigraphic sequences from the bottom up are the Nantuo diamictite (blue or medium gray), the basal Doushantuo dolostone sequence with the lower portion being the cap dolostone [*sensu stricto* (28); pink or light gray], and shale (brown or dark gray), with thicknesses marked in meters, including thickness of dolostones above and below the lower radiometric date. Jijiawan upper and Wuhe-Gaojiaxi lower absolute ages are from ref. 18. Carbon isotope data are given for Wushanhu (this study), Jijiawan (31), and Wuhe-Gaojiaxi (30). The MOSD position is marked within the dolostone sequence at the Wushanhu section.

constrained by the two U-Pb dates, the upper 1.5 m dolostones at Jijiawan represent a time interval of  $0.623 \pm 0.781$  My. (iii) This upper 1.5-m dolostone section at Jijiawan is equivalent to the 0.9-m dolostone section above the first layers of barite at Wushanhu. Because only 0.3 m of the 0.9-m dolostone section at Wushanhu represent the MOSD interval, by proportioning, we have an estimated number of  $0.208 \pm 0.781$  or 0–0.99 My for the MOSD duration (Figs. 1 and 3).

## Discussion

There are uncertainties associated with this estimate. First, it is difficult to determine the first and last appearances of sulfate  $^{17}\text{O}$  depletion in sedimentary records. The discovery of the Wushanhu section has helped us narrow this uncertainty as described previously. Second, the assumption of equal dolostone and shale sedimentation rates is rather conservative. Typically, dolostones are expected to precipitate rapidly after the deglaciation compared with the later deposition of shales. For example, if dolostones deposited five times faster than the phosphorite-bearing shales, our estimated duration would be  $0.051 \pm 0.781$  or 0–0.83 My. It is clear from these two very different assumptions on the relative rate of shale and dolostone deposition that this possibility of varying depositional rates does not make a huge difference in the final estimate of the MOSD duration. The main uncertainty comes from the uncertainties ( $\pm 0.781$  My) associated with the two U-Pb dates.

Global stratigraphic correlation of post-Marinoan, or basal Ediacaran, dolostone sequences reveals a general upward negative and then positive excursion (32), which is a pattern similar to what is observed in the shallow settings of the South China Block. It is, therefore, feasible to further constrain the duration of the MOSD if future U-Pb dates are tied to their respective  $\delta^{13}\text{C}$  curves, regardless of where the basal Ediacaran section is located. For example, in the post-Marinoan dolostone sequence in Mauritania, Southwest Africa, distinct  $^{17}\text{O}$  depletion has been observed in barite (20), and a  $\delta^{13}\text{C}$  curve with characteristic negative and then positive excursion has also been observed (33). As the sulfate  $^{17}\text{O}$  record is expanded and more accurate radiometric age controls are available worldwide, the uncertainties on MOSD duration estimate can be reduced.

The less than 1 My MOSD duration, which we estimated based on records and dates from South China, is consistent with the time that it may take for ultra-high  $p\text{CO}_2$  (350 times present atmospheric level) to be drawn down to a moderate level or presumed background Neoproterozoic levels at the aftermath of a snowball meltdown. The exact duration is dependent on different scenarios, as shown by a modeling study (7). There is a lot of room for speculation on the initial condition of the atmosphere at the onset of the meltdown. It could be extremely high in  $p\text{CO}_2$  but extremely low or even devoid of  $\text{O}_2$ . The rate of  $\text{O}_2$  flux into the atmosphere could be increasing dramatically, which is ultimately controlled by the rate of organic burial that is, in turn, linked to the rate of sedimentation as well as  $p\text{O}_2$ . Eventually, the  $p\text{CO}_2$ ,  $p\text{O}_2$ , organic C burial, and  $\text{O}_2$  fluxes reached a new steady state. Therefore, during the reestablishment of a new Earth system steady state, we might expect no  $\text{O}_2$   $^{17}\text{O}$  depletion in the very beginning of the meltdown because of the low  $p\text{O}_2$ , and then low to high depletion and low to no depletion again after a certain duration with the decreasing of  $p\text{CO}_2$  and increasing of  $p\text{O}_2$ . However, all this speculation would do little to concrete scientific progress if there were no sedimentary records to offer constraints or tests. The 0–0.99 My MOSD duration that we estimated here will help constrain models on how the Earth system responded to one of the most dramatic transitions in Earth history. In turn, those models will be of great reference value for us in gauging the resilience of the Earth system to extreme perturbations.

## Materials and Methods

Hand specimens were taken nearly continuously in the 1.18-m post-Marinoan dolostone sequence at Wushanhu. Each dolostone sample was cut for thin sections and polished slabs for petrographic examination. Powders were drilled from identified individual barite crystal fans or within layers. Sulfate was extracted and purified from an aliquot of the powders using a sequence of HCl and DTPA dissolution and reprecipitation (DDARP) treatment. Triple oxygen isotope composition of sulfate,  $\Delta^{17}\text{O}$ , was measured using a  $\text{CO}_2$ -laser fluorination method and run as  $\text{O}_2$  in dual-inlet mode on a MAT 253 at Louisiana State University. Detailed procedures have been described in earlier publications (21, 34, 35). The whole-process SD (starting from the same well-mixed powders) for sulfate  $\Delta^{17}\text{O}$  is better than 0.05‰. The dolomite matrix was sampled for isotope analysis beginning at the base of the cap dolostone up to just below the contact with the shale unit. The  $\delta^{13}\text{C}$  was measured for each hand specimen at Nanjing Institute of Geology and Palaeontology using an aliquot of 80–100  $\mu\text{g}$ , which reacted with ortho-

phosphoric acid for 150–200 s at 72 °C in a Kiel IV carbonate device automatically connected to an MAT 253. The  $\delta^{13}\text{C}$  is reported in per mil (‰) with respect to VPDB, with SD ( $1\sigma$ ) for multiple runs of a reference sample better than 0.05‰.

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