



# CO<sub>2</sub> buildup drove global warming, the Marinoan deglaciation, and the genesis of the Ediacaran cap carbonates

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## ABSTRACT

What caused ocean/climate changes that drove Marinoan deglaciation, and the subsequent genesis of Ediacaran cap carbonates remains unclear. To address this issue, we examined the Hg records in Ediacaran cap carbonates from shelf to slope depositional settings in exposures from South China. These cap carbonates show higher total Hg (THg) concentrations (4.9 to 405 ppb), most of which are comparable to that observed in carbonates deposited during non-LIPs periods. The lack of THg/TOC anomalies in these cap carbonates suggests that background volcanic activity, rather than a short-term large igneous province event, drove the Marinoan deglaciation. The cap carbonates show positive  $\Delta^{199}\text{Hg}$  values (0.18 to 0.34 ‰) in slope settings and slightly negative to slightly positive  $\Delta^{199}\text{Hg}$  values (−0.16 to 0.11 ‰) in shelf settings, suggesting a binary mixing of seawater- and terrestrial-derived Hg in early Ediacaran Ocean. We infer that the accumulation of greenhouse gases, due to ongoing volcanic emissions of CO<sub>2</sub> and enhanced release of gas hydrates, triggered global warming. This warming led to melting of sea ice cover, enhanced terrestrial inputs of alkalis (e.g., K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>), and large-scale dissolution of atmospheric CO<sub>2</sub> into seawater, driving widespread deposition of Ediacaran cap carbonates.

## 1. Introduction

Cap carbonates, that are meter- to decameter-thick dolostone or limestone layers overlying Marinoan glacial diamictites (Hoffman et al., 2017), represent the abrupt termination of the Marinoan Ice Age at ca. 635 Ma (Condon et al., 2005; Yu et al., 2020). These cap carbonates are characterized by negative carbon isotope ( $\delta^{13}\text{C}$ ) excursions reflecting profound changes in ocean chemistry soon after the Cryogenian glaciation (Wang et al., 2008; Sansjofre et al., 2011); which may have an important connection to oceanic/atmospheric oxygenation (Lang et al., 2018) and the early evolution of complex multicellular eukaryotes in the following Ediacaran period (Zhao et al., 2021).

The formation of cap carbonates was associated with sea-level rise during the Marinoan deglaciation (Fairchild et al., 2016) and has been interpreted by multiple models, including the upwelling of alkalinity-rich deep-ocean seawater (Knoll et al., 1996), postglacial chemical

weathering of silicate and carbonate rocks (Hoffman et al., 2017; Myrow et al., 2018), oxidation of methane from gas hydrate destabilization (Jiang et al., 2006; Kennedy et al., 2008), and microbially mediated carbonate precipitation from deglacial meltwater (Shields, 2005). In each of these models, changes in ocean chemistry during the Marinoan deglaciation could provide a favorable environment for cap carbonates deposition, such as high alkalinity (Hoffman, 2011) and enhanced biotic activity (Meyer et al., 2012).

The ultimate driving force for the Marinoan deglaciation remains unclear but has been linked to global warming driven by rising greenhouse gas (e.g., CO<sub>2</sub>) levels in the atmosphere (Hyde et al., 2000; Kennedy et al., 2001). Events such as large igneous provinces (LIPs) eruptions, can lead to transient emissions of large amounts of CO<sub>2</sub> to the atmosphere. When LIPs are absent, background volcanism could also cause a slow accumulation of CO<sub>2</sub> in the atmosphere if normal processes of CO<sub>2</sub> drawdown are inhibited. We examine these two possibilities here

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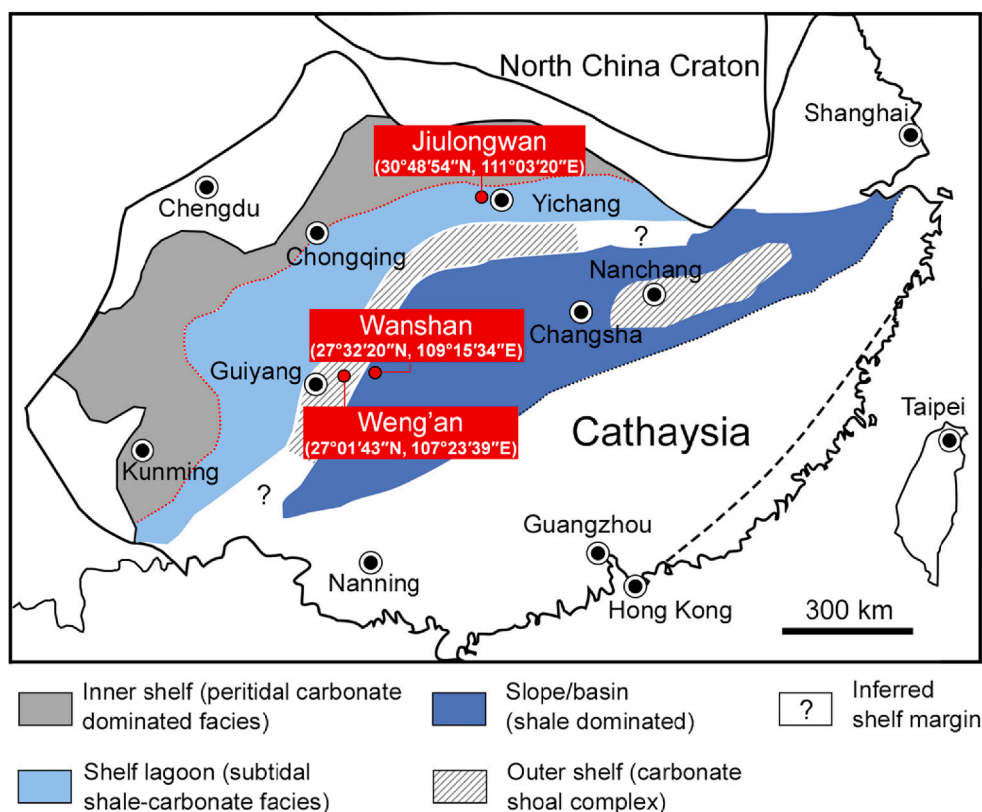


Fig. 1. Geological map showing the paleogeography of the Yangtze platform during the Ediacaran Doushantuo deposition and the location of sampling sites (Modified from Jiang et al., 2011).

using mercury (Hg) as a proxy.

Mercury (Hg), a highly volatile metal, is capable of tracing volcanism through geological history (Grasby et al., 2019) as LIP events transiently emit large amounts of Hg (Sanei et al., 2012; Grasby et al., 2020). This Hg is mainly in gaseous Hg(0) form that is transported globally in the atmosphere before depositing into terrestrial and marine systems (Selin, 2009), resulting in anomalously high Hg concentrations in sediments. Owing to the affinity of Hg to organic matter, anomalous high Hg to total organic carbon (Hg/TOC) ratios in sediments can better reveal large volcanic eruptions (Grasby et al., 2019). Other potential drawdown mechanisms have to be excluded though, as well as using isotope systems to ascribe a Hg source. Mercury isotopes undergo mass-dependent fractionation (MDF, defined as  $\delta^{202}\text{Hg}$ ) and unique mass-independent fractionation (MIF, defined as  $\Delta^{199}\text{Hg}$ ). Hg-MDF occurs ubiquitously during physical, chemical, and biological processes, therefore  $\delta^{202}\text{Hg}$  is not easily used as a Hg source tracer (Kwon et al., 2020). Volcanic Hg usually has  $\Delta^{199}\text{Hg} \sim 0$  (Zambardi et al., 2009), but photochemical processes in the surface environment can alter this signal, resulting in positive  $\Delta^{199}\text{Hg}$  in marine systems (e.g., seawater and marine sediments) and negative  $\Delta^{199}\text{Hg}$  in terrestrial systems (e.g., soil and vegetation) (Blum et al., 2014). The Hg-MIF signatures are not altered by sedimentation and diagenesis processes, therefore,  $\Delta^{199}\text{Hg}$  can be used to constrain Hg sources in sediments (Grasby et al., 2019). Recent studies have reported Hg (or Hg/TOC) anomalies with significant  $\Delta^{199}\text{Hg}$  shifts during the Cryogenian interglacial greenhouse (Zhou et al., 2021), end-Permian mass extinction (Grasby et al., 2017; Shen et al., 2019a, 2019b) and Triassic-Jurassic (T-J) mass extinction (Thibodeau et al., 2016), highlighting LIP eruptions as drivers of these events. However, Hg records of the Marinoan deglaciation have not been well explored.

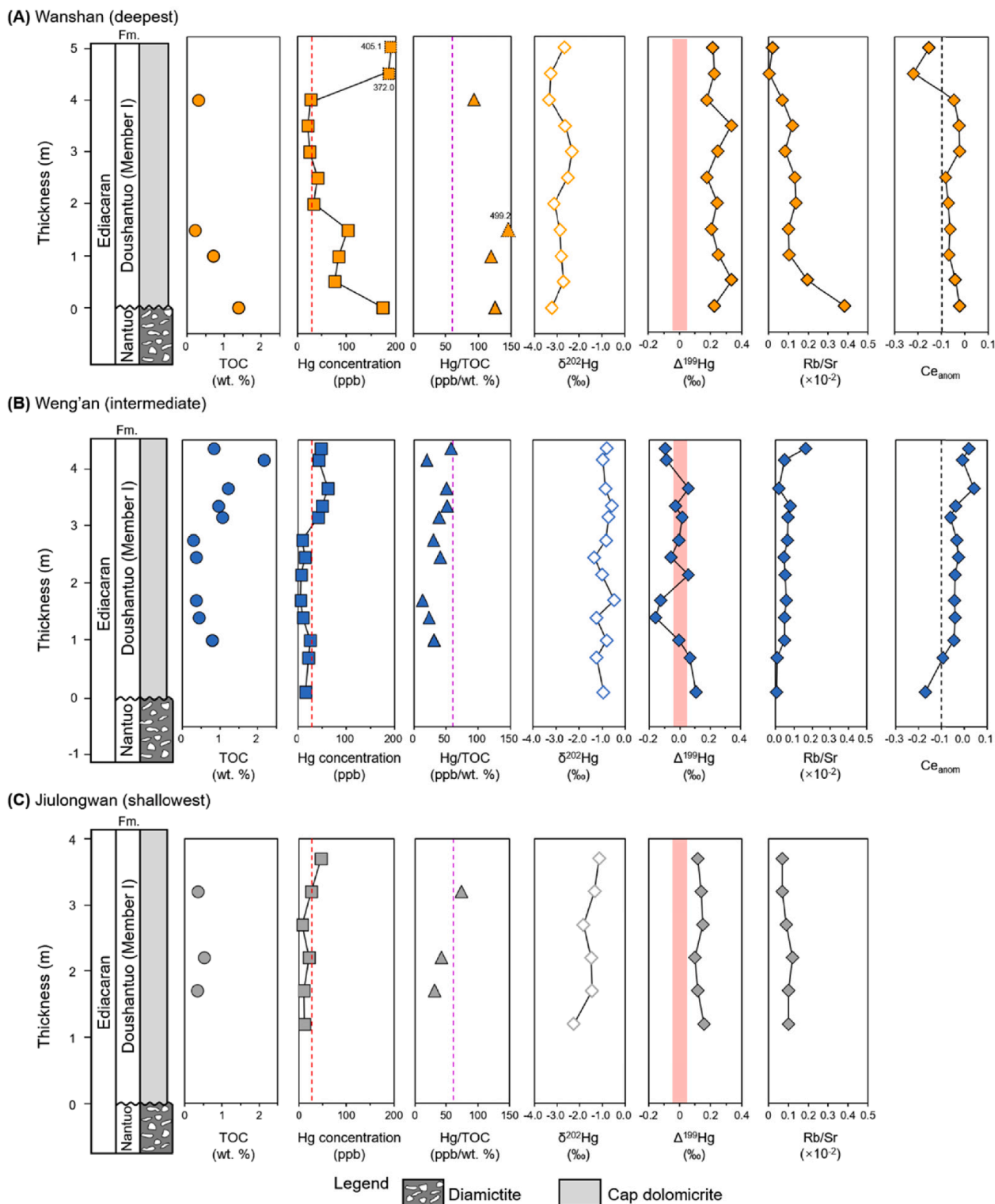
Sections of Ediacaran cap carbonates are widely distributed in the Yangtze Platform, South China. Here, we investigate Hg concentration and isotopic composition, trace elements, and TOC content of cap

carbonates deposited in different depositional settings in the Yangtze Platform, to gain an understanding of the cause of the Marinoan deglaciation and the mechanisms of cap carbonate formation.

## 2. Geological background

During the breakup of supercontinent Rodinia, a passive continental margin was formed on the southeastern edge of the Yangtze Platform, providing favorable conditions for Neoproterozoic sedimentation (Fig. 1, Jiang et al., 2003). The Neoproterozoic succession in the Yangtze Platform consists of three lithostratigraphic units, the Tonian unit consisting of siliciclastic rocks, the Cryogenian glacial-interglacial unit consisting of mixed deposition of siliciclastic rocks and glacial diamictites, and the Ediacaran unit consisting of mixed deposition of carbonate and siliciclastic rocks. The upper part of the Cryogenian glacial sequence (Nantuo Formation) consists of glacial diamictites and corresponds to the Marinoan Ice Age deposition (Jiang et al., 2003; Zhou et al., 2019). The lower part of the Ediacaran Doushantuo Formation lies over the Nantuo Formation (Jiang et al., 2011) and consists of cap carbonates, which are predominantly composed of massive dolostones with typical sedimentary structures, such as tepees, crossbedding, and rip-up clasts (Shields, 2005). During the Early Ediacaran the Yangtze Platform can be divided, from northwest to southeast, into shelf, slope, and basin depositional settings (Fig. 1). The Doushantuo cap carbonates are observed in the shelf and slope settings.

The Hg data of the Ediacaran cap carbonates ( $n = 6$ ) was recently reported from the inner shelf setting of the Jiulongwan section (Fig. 2, Fan et al., 2020). To identify if the Hg isotope pattern observed is of broader significance, two sections in the Yangtze Platform (Fig. 1), including the Weng'an section ( $27^{\circ}01'43''\text{N}$ ,  $107^{\circ}23'39''\text{E}$ ) from the outer shelf setting and the Wanshan section ( $27^{\circ}32'20''\text{N}$ ,  $109^{\circ}15'34''\text{E}$ ) from the slope setting, were sampled in this study. In these sections, the Doushantuo cap carbonates are well exposed (Jiang et al., 2011). As



**Fig. 2.** TOC concentrations, Hg concentrations, Hg/TOC ratios,  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$ , Rb/Sr ratios, and  $\text{Ce}_{\text{anom}}$  values of (A) the Wanshan section, (B) the Weng'an section, and (C) the Jiulongwan section (after Fan et al., 2020). The red dashed line represents the mean value for Hg in carbonates ( $28.3 \pm 91.9$  ppb) and the purple dashed line represents the mean value for Hg/TOC ratios of ancient carbonates during non-LIPs periods ( $59.5 \pm 86.5$  ppb/wt.%). The red bars represent the  $\Delta^{199}\text{Hg}$  of the volcanic Hg ( $0 \pm 0.05$  ‰, Zambardi et al., 2009). The black dashed lines mean the redox boundary of the  $\text{Ce}_{\text{anom}}$  value (-0.1). TOC concentrations and Hg/TOC ratios have not been involved for samples with TOC content lower than 0.2 wt%. The data of the Jiulongwan section are from Fan et al. (2020). Fm = Formation.

shown in Fig. 2, the Wanshan and Weng'an sections contain glacial diamictites in the upper part of the Nantuo Formation (~1 m), and cap dolostones in the Doushantuo Formation Member I (~5 m), similar to the Jiulongwan section.

### 3. Methods

Ediacaran cap carbonates were sampled from the Wanshan ( $n = 11$ ) and Weng'an ( $n = 13$ ) sections (Fig. 1). The samples were trimmed to

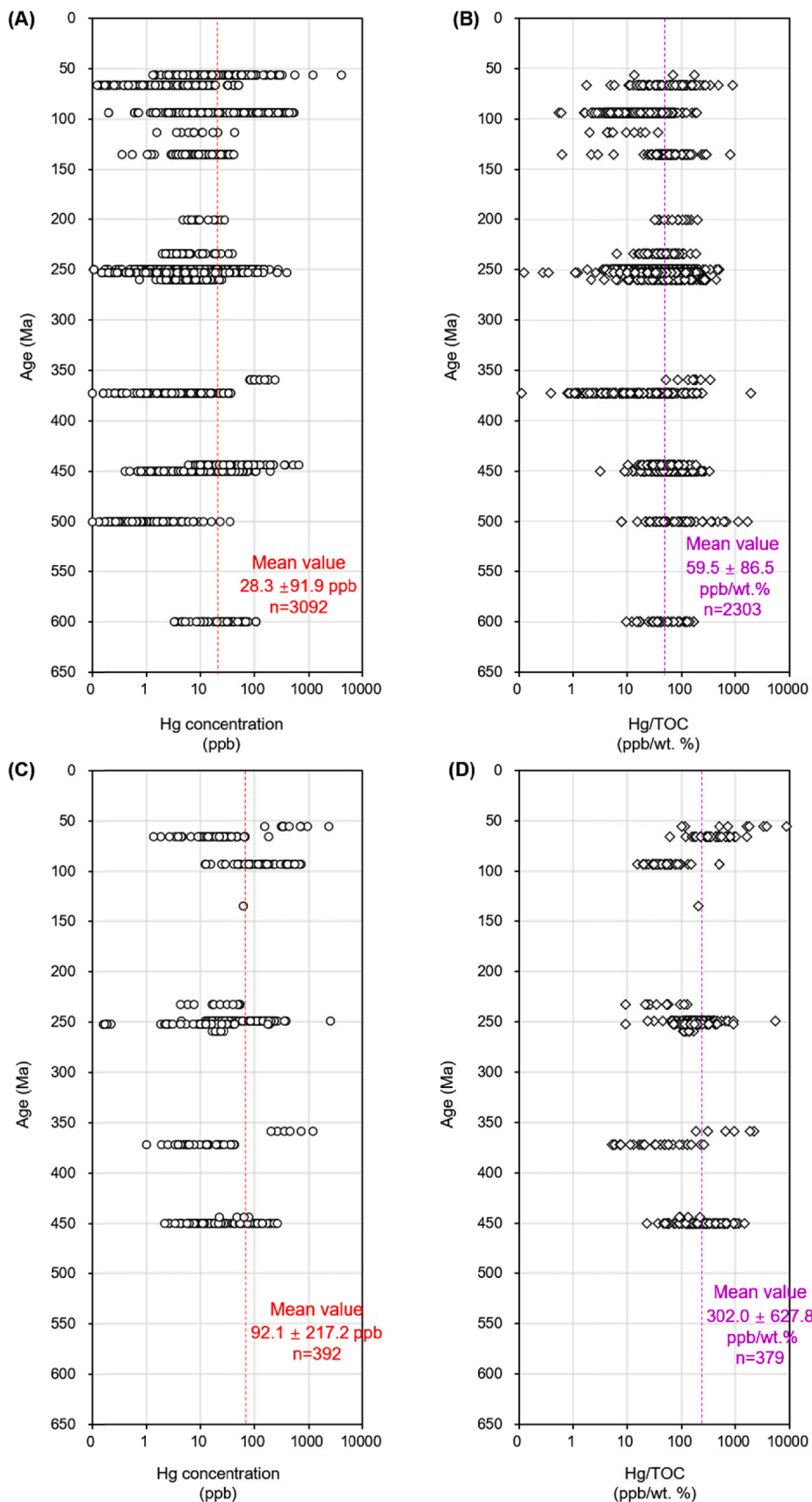


Fig. 3. Plots of (A) Hg concentrations and (B) Hg/TOC values for ancient carbonates during non-LIPs period and plots of (C) Hg concentrations and (D) Hg/TOC values for ancient carbonates during LIPs period. The dashed lines represent the mean values. Data source: see Supplementary Table S3 and references therein.

remove weathered surfaces, pulverized to ~ 200 mesh, and homogenized before chemical analyses at the Institute of Geochemistry, Chinese Academy of Sciences.

For total organic carbon (TOC) analyses, the sample powders were acidified using 2 M HCl to remove the carbonate fraction. After centrifuging, the residual samples were washed thrice using deionized purified water. After washing, the residual samples were analyzed for total carbon, representing the TOC fraction. TOC concentrations in sediment samples were measured using the potassium dichromate oxidation spectrophotometric method (detection limit: 0.1 wt%, Schumacher, 2002). Trace elements (e.g., Rb, Sr, and rare earth elements) were measured by an Agilent 8900 inductively coupled plasma mass spectrometry (ICP-MS), following the procedures of Liang et al. (2000). The analytical uncertainty for trace elements was better than  $\pm 5\%$  based on the long-term results of two reference materials (carbonate, COQ-1; shale, SBC-1).

Total Hg (THg) concentration was measured using a Lumex RA-915F Hg analyzer (detection limit: 0.05 ng/g). About 350 mg of samples were used in this analysis. Results were calibrated to the standard reference material (SMR) GSS-5 (soil, 290 ppb). One replicate and a standard were analyzed every-five samples. Data quality was monitored via multiple analyses of standard GSS-5, yielding an analytical precision of 90–110 % for GSS-5 and uncertainty of  $< 10\%$  (2SD) for triplicate samples.

Hg in sedimentary samples was preconcentrated into 5 mL of 40 % anti aqua regia ( $\text{HNO}_3/\text{HCl} = 2/1$ , v/v) using a double-stage combustion method developed for Hg isotope analysis (see more details in Zerkle et al., 2020). After the preconcentration, the trapping solution was diluted to 1 ppb Hg and the highest acid concentration of ~ 20 %, for the analysis using a Neptune Plus multi-collector-inductively coupled plasma mass spectrometer (MC-ICP-MS), following the method by Yin et al. (2016). Standard reference material (GSS-4, soil) was prepared in the same way as the samples. Hg concentrations and acid matrices in the bracketing National Institute of Standards and Technology 3133 (NIST-3133) solutions were matched well with the neighboring samples. Mercury isotopic compositions were reported following Blum and Bergquist (2007). MDF is expressed in  $\delta^{202}\text{Hg}$  notation in units of permil (‰) referenced to the NIST-3133 Hg standard:

$$\delta^{202}\text{Hg}(\text{‰}) = \left[ \left( \frac{{}^{202}\text{Hg}/{}^{198}\text{Hg}_{\text{sample}}}{{}^{202}\text{Hg}/{}^{198}\text{Hg}_{\text{standard}}} \right) - 1 \right] \times 1000 \quad (1)$$

MIF is reported in  $\Delta$  notation, which describes the difference

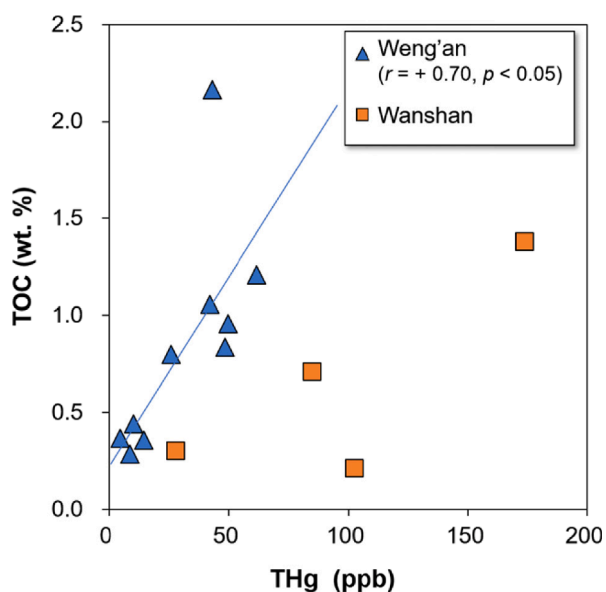


Fig. 4. The relationship between THg concentration and TOC content in the studied sections.

between the measured  $\delta^{\text{xxx}}\text{Hg}$  and the theoretically predicted  $\delta^{\text{xxx}}\text{Hg}$  value, in units of ‰, with xxx = 199, 200, or 201:

$$\Delta^{\text{xxx}}\text{Hg} = \delta^{\text{xxx}}\text{Hg} - \delta^{202}\text{Hg} \times \beta \quad (2)$$

$\beta$  equals to 0.2520 for  $^{199}\text{Hg}$ , 0.5024 for  $^{200}\text{Hg}$ , and 0.7520 for  $^{201}\text{Hg}$  (Blum and Bergquist, 2007). Analytical uncertainty was estimated based on the replicates of the NIST-3177 secondary standard solution and full procedural analyses of SRM GSS-4 (soil). The overall average and uncertainty of NIST-3177 ( $\delta^{202}\text{Hg}$ :  $-0.50 \pm 0.10\%$ ;  $\Delta^{199}\text{Hg}$ :  $-0.01 \pm 0.03\%$ ;  $\Delta^{200}\text{Hg}$ :  $0.02 \pm 0.04\%$ ;  $\Delta^{201}\text{Hg}$ :  $0.01 \pm 0.04\%$ , 2SD,  $n = 6$ ) and GSS-4 ( $\delta^{202}\text{Hg}$ :  $-1.53 \pm 0.10\%$ ;  $\Delta^{199}\text{Hg}$ :  $-0.44 \pm 0.05\%$ ;  $\Delta^{200}\text{Hg}$ :  $-0.02 \pm 0.08\%$ ;  $\Delta^{201}\text{Hg}$ :  $-0.37 \pm 0.06\%$ , 2SD,  $n = 3$ ) agree well with previously reported studies (Blum and Bergquist, 2007; Deng et al., 2021). The larger 2SD values of either NIST-3177 or GSS-4 are used to reflect analytical uncertainties.

## 4. Results

Hg concentrations, isotopic compositions, and TOC contents of Ediacaran cap carbonates in the two studied sections are shown in Table S1 and Fig. 2. In the Wanshan section (Fig. 2A), the samples show low TOC contents ( $0.65 \pm 0.53$  wt%, SD), and some are even lower than the detection limit (0.1 wt%). The samples have large variation in THg concentrations (4.9 to 405 ppb) and Hg/TOC ratios (93.7 to 499 ppb/wt. %). Only samples with TOC values  $> 0.2$  wt% are calculated and plotted in Fig. 2A to avoid error (Grasby et al., 2019). In the Weng'an section (Fig. 2B), the samples show slightly higher TOC contents ( $0.85 \pm 0.57$  wt%, SD), but obviously lower Hg concentrations (4.9 to 61.8 ppb) and Hg/TOC ratios (lower than 60 ppb/wt.%) than the Wanshan section.

Negative  $\delta^{202}\text{Hg}$  values are observed in the Wanshan section ( $-3.34$  to  $-2.32\%$ ) and Weng'an section ( $-1.34$  to  $-0.48\%$ ). In the Wanshan section (Fig. 2A), positive  $\Delta^{199}\text{Hg}$  values are observed (0.18 to 0.34 ‰). In the Weng'an section (Fig. 2B), the  $\Delta^{199}\text{Hg}$  shows positive values (0.11 ‰) at the bottom of the section, and then show a shift toward negative values ( $-0.10\%$ ) at the top of cap carbonates. There is then a positive excursion in the  $\Delta^{199}\text{Hg}$  values from  $-0.16\%$  to  $0.06\%$ , followed by a return to negative values in the upper part of the section.

Concentrations of redox-sensitive elements are listed in Table S2. The Ce anomalies ( $\text{Ce}_{\text{anom}}$ ) are calculated by formulae:  $\text{Ce}_{\text{anom}} = \text{Lg}(3 \times \text{Ce}_N / (2 \times \text{La}_N + \text{Nd}_N))$  (Haskin et al., 1968; Tylor and McLennan, 1985). Elements with subscript N represent the concentration normalized to Post-Archaean Australian Shale (PAAS, McLennan, 1989). The Wanshan and Weng'an cap carbonate samples sections show negative  $\text{Ce}_{\text{anom}}$  values of  $-0.07 \pm 0.06$  (SD) and  $-0.04 \pm 0.05$  (SD), respectively). The Rb/Sr ratios in the Wanshan section ( $0.15 \pm 0.10$ , SD) are higher than the Weng'an section ( $0.06 \pm 0.05$ , SD).

Results in this study are partially different from previous results of the cap carbonates in the Jiulongwan section (Fig. 2C, Fan et al., 2020). Cap carbonates in the Jiulongwan section show similar TOC contents ( $0.40 \pm 0.10$  wt%, SD), Hg concentrations (7.9 to 46.5 ppb), and Hg/TOC ratios (32 to 74 ppb/wt.%) to the Wanshan and Weng'an sections. The Jiulongwan section is also characterized by negative  $\delta^{202}\text{Hg}$  ( $-2.25$  to  $-1.13\%$ ) and positive  $\Delta^{199}\text{Hg}$  values (0.10 to 0.16 ‰) (Fig. 2C, Fan et al., 2020).  $\Delta^{199}\text{Hg}$  shows a shift toward less positive values in the Jiulongwan section, similar to the trend in the Weng'an section, but with a steadier decline. Overall, the Weng'an section shows the lowest Hg concentrations and Hg/TOC ratios, and the Wanshan section shows the most positive  $\Delta^{199}\text{Hg}$  values amongst these three sections.

## 5. Discussion

### 5.1. Mercury host phases in Ediacaran cap carbonates

The large volume of data produced over the last several years provides great insight into Hg in carbonates in the geologic record. We have

examined previous studies on Hg in carbonates and sorted out the Hg concentrations and Hg/TOC ratios of ancient carbonates (see **Table S3** and references therein). These studies found Hg enrichment in carbonates at boundaries related to LIPs eruptions, but low Hg concentrations in carbonates below or above these Hg-rich boundaries (Fig. 3). Based on previous results on carbonates deposited during non-LIPs periods, we propose a background Hg value of  $28 \pm 92$  ppb (SD,  $n = 3092$ , Fig. 3A) and a background Hg/TOC ratio of  $60 \pm 43$  ppb/wt.% (SD,  $n = 2303$ , Fig. 3B) for non-LIPs carbonates (Meyer et al., 2019; Tremblin et al., 2022; Font et al., 2016, 2021; Sial et al., 2013, 2016; Scaife et al., 2017; Benigno et al., 2021; Charbonnier et al., 2017; Percival et al., 2015; Thibodeau et al., 2016; Zhao et al., 2022a, 2022b; Shen et al., 2019a, 2019b; Kailho et al., 2020; Wang et al., 2018; Grasby et al., 2017; Hu et al., 2021; Huang et al., 2018; Rakociński et al., 2021; Zhang et al., 2021; Racki et al., 2018, 2020; Jones et al., 2017; Gong et al., 2017; Pruss et al., 2019; Fan et al., 2020). In this study, Hg concentrations in Ediacaran cap carbonates show the 16th to 84th percentile range of 10.5 to 76.8 ppb, which are comparable to previous results on carbonates deposited during non-LIPs periods, according to the lack of statistical difference through *t*-test analysis ( $t = 1.924$ ,  $p = 0.064$ ). Mercury potentially occurs in marine sediments as organic-bound, clay-bound, and sulfides species (Sanei et al., 2012; Shen et al., 2020). As shown in Fig. 4, significant positive correlations between THg and TOC can be observed in Ediacaran cap carbonates in the Weng'an ( $r = +0.70$ ,  $p < 0.05$ ) section, suggesting that Hg is mainly hosted in organic matter in the Weng'an section.

### 5.2. Lack of large-scale volcanic eruption of short-term duration during the Marinoan deglaciation?

Anomalous high Hg/TOC ratios can be used to trace large volcanism (Grasby et al., 2019). In this study, most of the cap carbonates samples show Hg/TOC ratios ( $\sim 50$  ppb/wt.%) that are comparable to the background Hg/TOC ratio for non-LIPs ancient carbonates (59.5 ppb/wt.%) and global marine sediments (71.9 ppb/wt.%, Grasby et al., 2019) deposited during non-LIP periods. Only three cap carbonates in the Wanshan sections show elevated Hg/TOC ratios of  $> 100$  ppb/wt.%, which may be explained by their low TOC values and/or local reduced condition (Shen et al., 2022).

The lack of widespread Hg/TOC peaks in the Ediacaran cap carbonates suggest overall low levels of regional volcanic activity during the Marinoan deglaciation. This is consistent with there being no known LIP eruption during that time except for Lan et al. (2022), which proposed that prolonged magmatic activity during 641–637 Ma may have shortened the Marinoan Ice Age. In this case, our results support the earlier hypothesis that the Marinoan deglaciation was triggered by global warming caused by the buildup of  $\text{CO}_2$  emitted by the continuous background volcanism during the Marinoan Ice Age (Kirschvink, 1992; Hoffman et al., 1998). The Cryogenian Ice Age was dominated by the breakup of the Rodinia supercontinent and following the amalgamation of the Gondwana supercontinent (Cawood et al., 2016; Merdith et al., 2017). Long-lasting subduction-related magmatism would have occurred in the collision of Gondwana continental fragments during the Marinoan Ice Age (Merdith et al., 2017), although we acknowledge the duration of the Marinoan Ice Age (6 to 15 Ma, Bao et al., 2018; Gong et al., 2021) is shorter than that of the subduction-related magmatism during the collision of Gondwana continental fragments. This continuous background volcanic activity would emit a substantial amount of  $\text{CO}_2$  and Hg into the atmosphere. The emitted  $\text{CO}_2$  would have accumulated in the atmosphere, building to a tipping point that triggered global warming and the Marinoan deglaciation (Kirschvink, 1992; Hoffman et al., 1998). The released Hg, due to its short residence time (0.5 to 2 years) in the atmosphere, would have been deposited into the ocean (Grasby et al., 2020) and evenly buried in glacial deposits during the Marinoan Ice Age, explaining the lack of Hg anomalies in the Marinoan cap carbonates.

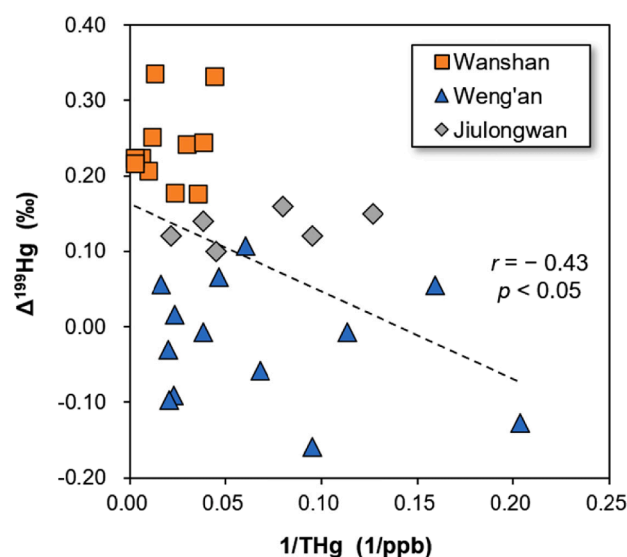


Fig. 5. The relationship between THg concentration and  $\Delta^{199}\text{Hg}$  values in the studied sections. The  $r$  and  $p$  values are calculated from all three sections. The data of the Jiulongwan section are from Fan et al. (2020).

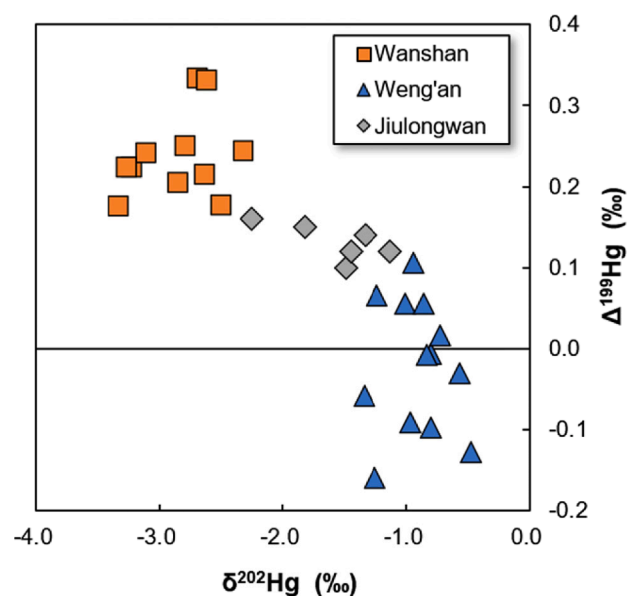


Fig. 6. Plot of  $\Delta^{199}\text{Hg}$  versus  $\delta^{202}\text{Hg}$  in the cap carbonates of the studied sections. The data of the Jiulongwan section are from Fan et al. (2020).

### 5.3. Mixing of seawater- and terrestrial-derived Hg in Ediacaran cap carbonates

Mercury isotopes provide insight into the sources of Hg in sediments. The negative  $\delta^{202}\text{Hg}$  values of the studied Ediacaran cap carbonates fall into the range of that is reported for global marine sediments ( $-3.02$  to  $0.23$  ‰, Blum et al., 2014; Grasby et al., 2019; Yin et al., 2017). However, the variation of Hg-MDF can result from various geochemical processes. Below we use Hg-MIF signals to trace the source of Hg in our samples. As shown in Fig. 5, THg and  $\Delta^{199}\text{Hg}$  values of cap carbonates demonstrate a decreasing pattern from the Wanshan section (THg: 22.7 to 405 ppb;  $\Delta^{199}\text{Hg}$ : 0.18 to 0.34 ‰), to the Weng'an section (THg: 4.91 to 61.8 ppb;  $\Delta^{199}\text{Hg}$ :  $-0.16$  to 0.11 ‰) and continuing to the Jiulongwan section (THg: 7.9 to 46.5 ppb;  $\Delta^{199}\text{Hg}$ : 0.10 to 0.16 ‰). A negative correlation can be observed between  $\Delta^{199}\text{Hg}$  and  $1/\text{THg}$  ( $r = -0.43$ ,  $p < 0.05$ ), possibly suggesting a binary mixing of Hg from

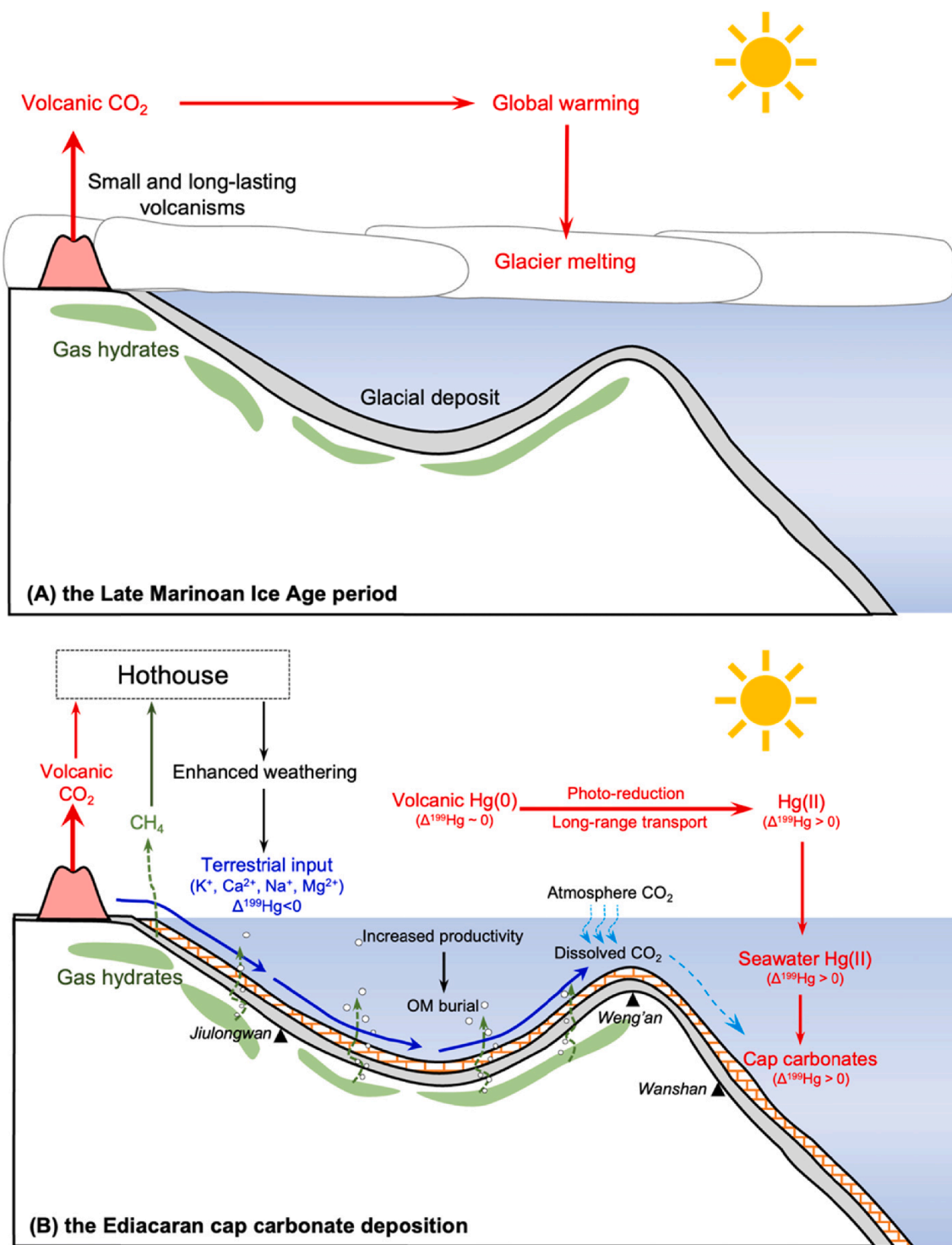


Fig. 7. Scenarios of Hg cycling during (A) the Late Marinoan Ice Age period and (B) the Ediacaran cap carbonate deposition. The sketch is not to scale.

seawater- and terrestrial-derived sources. In the  $\delta^{202}\text{Hg}-\Delta^{199}\text{Hg}$  diagram (Fig. 6), the Jiulongwan section appears to show a mixing of Hg from two sources. The positive  $\Delta^{199}\text{Hg}$  values in the Wanshan slope section are comparable to that reported for modern seawater (0.1 to 0.4 ‰, Štok et al., 2015), suggesting a dominance of seawater Hg deposition. The relatively lower  $\Delta^{199}\text{Hg}$  values in shelf sections (Weng'an and Jiulongwan) could be attributed to enhanced terrestrial input, given terrestrial systems (e.g., soil) have negative  $\Delta^{199}\text{Hg}$  values (Blum et al., 2014). Plants preferentially uptake atmospheric Hg(0) into the soil, resulting in negative  $\Delta^{199}\text{Hg}$  values in terrestrial material (Biswas et al.,

2008; Yin et al., 2013). A recent study by Žárský et al. (2022) demonstrated the expansion of the first terrestrial flora during the Cryogenian interglacial, which may support the presence of terrestrial soil with negative  $\Delta^{199}\text{Hg}$  values in the Precambrian.

## 6. Implications for the genesis of Ediacaran cap carbonates

The negative  $C_{\text{anom}}$  values in our samples, which are indicative of oceanic oxic conditions, are in line with the negative  $\delta^{13}\text{C}_{\text{carb}}$  excursion in Ediacaran cap carbonates due to the oxidation of dissolved organic

matter (DOM) in deeper seawater (Kennedy et al., 2001; Shield et al., 2019; Chen et al., 2021). The Hg data in our study provide further insight into the genesis of Ediacaran cap carbonates, as shown in Fig. 7 and discussed below.

Continuous magmatism, due to the final stages of the breakup of supercontinent Rodinia during the late stage of Marinoan Ice Age (Merdith et al., 2017), would have slowly released CO<sub>2</sub> into the atmosphere and gradually increased atmospheric CO<sub>2</sub> to a tipping point that triggered global warming and melting of sea ice cover. As sea ice was melted, the global ocean warmed up to a point to then trigger the destabilization of gas hydrates (methane) in the ocean, causing the release of methane, an even more efficient greenhouse gas than CO<sub>2</sub>, into the atmosphere, pushing global temperature to higher levels (Ruppel and Kessler, 2017).

High atmospheric CO<sub>2</sub> level during the Marinoan deglaciation would have had profound consequences on the land–ocean system. Not only would it have increased the dissolved CO<sub>2</sub> level (as HCO<sub>3</sub><sup>-</sup>) in seawater due to the melting of sea ice cover but also facilitated chemical weathering of continents, by which large amounts of alkalis (e.g., K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) would have been released from terrestrial materials and entered the ocean (Hoffman et al., 2011). In shelf or slope settings, the abundant HCO<sub>3</sub><sup>-</sup>, along with large inputs of terrestrial Ca<sup>2+</sup> and Mg<sup>2+</sup>, would have resulted in extensive deposition of Ediacaran cap carbonates. In the early Ediacaran Ocean, driven by global warming, oceanic productivity would be enhanced, forming organic particles that could scavenge Hg from seawater, as indicated by the largest positive Δ<sup>199</sup>Hg values being in the Wanshan slope section. Enhanced continental weathering also transported large amounts of terrestrial-derived Hg to the Ediacaran cap carbonates, as supported by the less positive to negative shifts of Δ<sup>199</sup>Hg in the Jiulongwan and Weng'an shelf sections. Enhanced deposition of seawater-derived Hg and terrestrial-derived Hg explains the higher THg levels of Ediacaran cap carbonates than non-LIPs carbonates.

#### CRedit authorship contribution statement

**Ruiyang Sun:** Data curation, Investigation, Writing – original draft. **Jun Shen:** Supervision. **Stephen E. Grasby:** Conceptualization, Methodology, Supervision. **Jiawei Zhang:** Data curation, Investigation. **Jianshu Chen:** Data curation, Investigation. **Chuang Yang:** Data curation, Investigation. **Runsheng Yin:** Conceptualization, Methodology, Supervision, Writing – original draft.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.precamres.2022.106891>.

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