

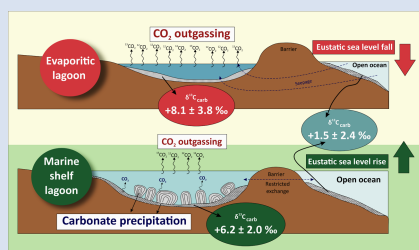
Can CO₂ outgassing and carbonate precipitation explain the Lomagundi Excursion?

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Abstract

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The Lomagundi-Jatuli event (2.3–2.0 Ga) is one of the striking carbon isotopic ($\delta^{13}\text{C}_{\text{carbonate}}$) excursion events in the Earth's history, marked by anomalously high $\delta^{13}\text{C}_{\text{carbonate}}$ reaching up to +30 ‰. The conventional explanation attributes it to enhanced organic carbon burial. However, the lack of organic-rich strata synchronous with the excursion demands the reconsideration of alternative biogeochemical processes to explain this isotopic anomaly. Moreover, the excursion is observed only in the evaporitic and near shore carbonates, with no evidence from the open ocean, demanding a facies based biogeochemical explanation. Here, we propose a depositional framework for Lomagundi successions and explore the possibility of CO₂ outgassing and carbonate precipitation as potential drivers responsible for this excursion, as these processes remain the least explored among the proposed hypotheses. Through sedimentological evidence from previous studies and Rayleigh fractionation calculations, we argue that dominant loss of dissolved inorganic carbon (DIC) through CO₂ outgassing in the evaporitic facies and carbonate precipitation in the near shore facies along with a well mixed DIC reservoir in the open ocean explains the observed Lomagundi Excursion.

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Introduction

The carbon isotopic composition of carbonates ($\delta^{13}\text{C}_{\text{carbonate}}$) reflects the isotopic composition of the dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) pool from which they precipitate with minimal fractionation ($\epsilon_{\text{carbonate-bicarbonate}}$ ~0.9 ‰ to 2.7 ‰; Robinson and Clayton, 1969). Certain time intervals in geological history record highly positive $\delta^{13}\text{C}_{\text{carbonate}}$ (>4 ‰), which are known as carbon isotope excursions (Kump and Arthur, 1999; Hodgskiss *et al.*, 2023). The most prominent among such excursions, in terms of both magnitude and duration, is the Lomagundi-Jatuli Event (LJE), which occurred at ~2.2–2.0 Ga with $\delta^{13}\text{C}_{\text{carbonate}}$ as high as 30 ‰ (Schidlowski *et al.*, 1975; Hodgskiss *et al.*, 2023).

Conventionally, global enhancement in organic carbon burial has the most traction among the researchers as the cause of LJE (e.g., Schidlowski *et al.*, 1975; Bekker and Holland, 2012). According to this hypothesis, a significant increase in global marine productivity and associated organic carbon burial (~60 %; Schidlowski *et al.*, 1975) during the LJE led to the preferential removal of ¹²C from DIC pool, thereby enriching the residual DIC and carbonates precipitating from them in ¹³C. Such a huge organic carbon burial should manifest a significant accumulation of organic-rich sedimentary rocks synchronous with the excursion (Melezhik *et al.*, 1999). But the lack of such organic-rich strata in the sedimentary rock records during the LJE (Melezhik *et al.*, 1999; Hodgskiss *et al.*, 2023) led to the proposition of alternative explanatory models, which are reviewed in Hodgskiss *et al.* (2023). However, two processes that

have been least explored in explaining the LJE are carbon dioxide (CO₂) outgassing (Stiller *et al.*, 1985) and carbonate precipitation along with their potential interactions (Beeler *et al.*, 2020), which are the focus of this study.

Why CO₂ Outgassing?

Dissolved CO₂ is an important component of DIC pool, and variations in its proportion have the potential to modulate $\delta^{13}\text{C}_{\text{DIC}}$, and in turn $\delta^{13}\text{C}_{\text{carbonate}}$. CO₂ outgassing to the atmosphere has been shown to cause significant increase in $\delta^{13}\text{C}$ in the residual DIC pool in modern day aquatic systems with fractionation factors ranging from –15 to –23 ‰ (Stiller *et al.*, 1985), which makes it a plausible mechanism to explain the LJE. The air-water flux of CO₂ (F_{CO_2}) can be expressed as:

$$F_{\text{CO}_2} = \Delta p\text{CO}_2 * K_w * K_s \quad \text{Eq. 1}$$

where $\Delta p\text{CO}_2$ is the pCO₂ gradient (pCO_{2-surface water} – pCO_{2-atmosphere}), which determines the direction of the CO₂ flux; K_w is the gas transfer velocity (a quadratic function of wind speed); and K_s is the CO₂ solubility (a function of temperature and salinity) (Nicholson *et al.*, 2022). The pCO_{2-atmosphere} during the LJE has been calculated to be 20 to 620 times higher than the present day atmospheric level (Kanzaki and Murakami, 2015), which may appear to limit CO₂ outgassing from the water column. However, air-sea gas exchange under such high pCO_{2-atmosphere} drives the surface ocean rapidly towards equilibrium with the atmosphere, resulting in high pCO₂ in surface

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waters (Galbraith *et al.*, 2015). Under equilibrium condition, the partial pressure of CO₂ in surface water equals that of the atmosphere ($p\text{CO}_{2\text{-surface-water}} = p\text{CO}_{2\text{-atmosphere}}$; $\Delta p\text{CO}_2 = 0$) resulting in no net flux of CO₂, *i.e.* neither net outgassing nor in-gassing. In cases where surface water pCO₂ increases due to enhanced organic matter degradation and/or carbonate precipitation ($p\text{CO}_{2\text{-surface-water}} > p\text{CO}_{2\text{-atmosphere}}$; positive $\Delta p\text{CO}_2$), outgassing of CO₂ to the atmosphere is favoured. Outgassing of CO₂ is further enhanced potentially in cases of increased surface water temperature due to reduced CO₂ solubility (low K_s ; Dai *et al.*, 2022) and stronger winds leading to high gas transfer velocity (high K_w ; Nicholson *et al.*, 2022). Sedimentological observations in Lomagundi successions suggest higher temperatures associated with greenhouse climate (potentially low K_s ; Shang *et al.*, 2024) and stronger winds (high K_w) due to prevalence of storm events (Pambo *et al.*, 2006; Hill-Svehla and Corcoran, 2023; Shang *et al.*, 2024). Therefore, we argue that, positive $\Delta p\text{CO}_2$ along with higher temperature and high wind speed during the LJE could have likely favoured CO₂ outgassing from the aquatic systems, leading to high $\delta^{13}\text{C}_{\text{DIC}}$ and eventually high $\delta^{13}\text{C}_{\text{carbonate}}$; this needs to be explored for its role in the LJE.

Facies Dependency of the Lomagundi Excursion

The lithology of Lomagundi successions worldwide constitutes evaporitic deposits (with calcites and dolomites), dolostones, stromatolitic dolostones, and siliciclastic rocks (Melezhik *et al.*, 1999; Brasier *et al.*, 2011; Melezhik *et al.*, 2013) inferred to be deposited across a range of sedimentological facies ranging from coastal sabkhas and near shore to open ocean environments (Melezhik *et al.*, 1999). Accordingly, a facies based screening of the global Lomagundi carbonates showed that anomalously high $\delta^{13}\text{C}_{\text{carbonate}}$ were confined only to coastal evaporites ($+8.1 \pm 3.8$ ‰) and near shore carbonates ($+6.2 \pm 2.0$ ‰), whereas the open ocean carbonates ($+1.5 \pm 2.4$ ‰) remained unperturbed (Prave *et al.*, 2022). This facies based compilation of Lomagundi carbonates revealed that the LJE was a global near shore carbon anomaly and not a global carbon anomaly (Melezhik *et al.*, 1999; Prave *et al.*, 2022; Hodgskiss *et al.*, 2023). Therefore, any model proposed to explain the LJE should account for both the lack of organic-rich strata as well as the facies dependency of the excursion. Here, we propose and explain a facies dependent, water column scale biogeochemical explanation for the LJE, rather than invoking global scale mechanisms.

A Depositional Framework for Lomagundi Deposits

Eustatic sea level fluctuations are common in greenhouse climates (Warren, 2010). Studies on evaporite deposits globally suggest that greenhouse climate results in the formation of sub-sea level seepage lagoons in which eustatic sea level fluctuations cause the deposition of platform evaporites (during low sea level) alternating with marine shelf carbonates (during high sea level) (Warren, 2010). The presence of such alternating evaporite and carbonate depositional cycles during Lomagundi successions (Brasier *et al.*, 2011; Melezhik *et al.*, 2013) is consistent with the influence of greenhouse climate inferred during the LJE (Shang *et al.*, 2024). Additionally, these evaporites and carbonates are inferred to be deposited in restricted to partially restricted lagoonal environments (Brasier *et al.*, 2011; Melezhik *et al.*, 2013). Therefore, we argue that the evaporites with a mean $\delta^{13}\text{C}$ of $+8.1 \pm 3.8$ ‰ (Prave *et al.*, 2022) might have likely

deposited during periods of low sea level, where the lagoons become hydrographically isolated leading to hypersaline conditions (evaporitic lagoon; Fig. 1a). On the other hand, the near shore dolostones and stromatolitic dolostones of Lomagundi with a mean $\delta^{13}\text{C}$ of $+6.2 \pm 2.0$ ‰ (Prave *et al.*, 2022) might have deposited during high sea level in partially restricted marine shelf lagoons (Fig. 1b). These enclosed lagoons are separated from the open ocean by elevated barriers and hence would be characterised by minimal or intermittent input of sea water from the open ocean (Fig. 1). This proposed depositional framework accounts for the observed irregular appearance of evaporitic signatures and hence anomalous values in the Lomagundi successions (Melezhik *et al.*, 1999, 2013).

Facies Dependent Biogeochemical Processes

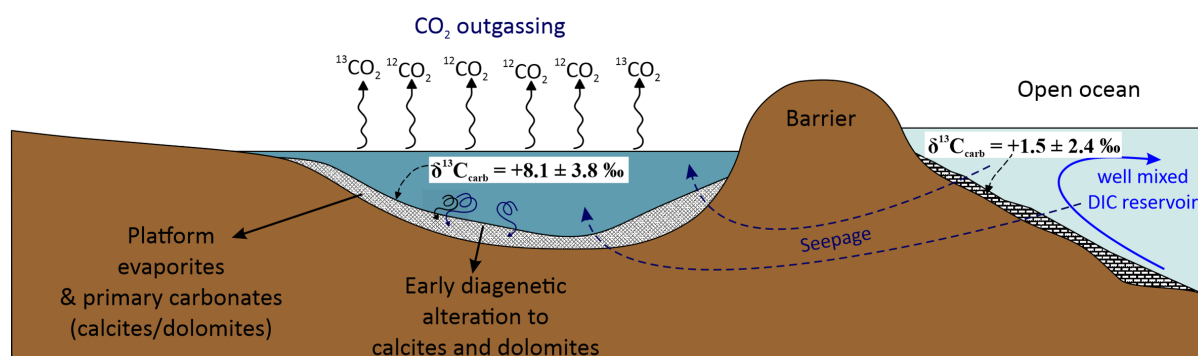
The sources of DIC in any aquatic system include external inputs (riverine, volcanic, and atmospheric), organic matter degradation, and carbonate dissolution; whereas the sinks include primary productivity and associated organic burial, CO₂ outgassing, and carbonate precipitation. Productivity and outgassing leads to a decrease in DIC concentration and increase in $\delta^{13}\text{C}$ of the remaining DIC pool. Organic matter degradation, on the other hand, increases the DIC pool with a decrease in $\delta^{13}\text{C}_{\text{DIC}}$. Carbonate dissolution and precipitation act opposite to each other where dissolution increases both concentration and isotopic composition of DIC pool, while precipitation decreases both (Alling *et al.*, 2012). Therefore, $\delta^{13}\text{C}_{\text{DIC}}$ in our hypothesised lagoon system during the LJE could also be the resultant of these biogeochemical processes and their interactions. Carbonate dissolution appears to be the least relevant process in the context of LJE due to a predominantly carbonate precipitating environment in the water column. Hence, the LJE might have resulted due to the interplay of four processes (productivity, organic matter degradation, CO₂ outgassing, and carbonate precipitation) in the lagoonal setting. Although productivity and associated organic burial have the potential to increase the $\delta^{13}\text{C}_{\text{DIC}}$, low organic carbon concentration in lagoonal LJE carbonates (Karhu, 1993) and absence of organic-rich strata simultaneous or prior to the LJE (Melezhik *et al.*, 1999), suggests that the organic matter produced in the lagoons might have largely undergone remineralisation. Such extensive remineralisation would have resulted in minimal net organic burial, thereby having negligible effects on both size and isotopic composition of DIC pool during the LJE. Therefore, primary productivity and mineralisation (organic matter degradation) may be assumed to have a neutralising effect on the $\delta^{13}\text{C}_{\text{DIC}}$ during the LJE with CO₂ outgassing and carbonate precipitation being the dominant processes controlling the $\delta^{13}\text{C}_{\text{DIC}}$ of the lagoons.

Assuming negligible DIC input to alter the pool size and isotopic composition through seepage or restricted exchange in evaporitic and marine shelf lagoons, the range of possible $\delta^{13}\text{C}_{\text{DIC}}$ values that can be achieved in the lagoons from an initial open ocean seawater composition ($\delta^{13}\text{C} \sim 0 \pm 4$ ‰; Prave *et al.*, 2022) through CO₂ outgassing and carbonate precipitation can be approximated by treating the lagoons as a closed system and applying a Rayleigh fractionation model. The $\delta^{13}\text{C}_{\text{DIC}}$ of the lagoons at a given time will then be governed by the relative contributions of outgassing and carbonate precipitation.

$$\delta^{13}\text{C}_{\text{DIC}} = (\delta^{13}\text{C}_{\text{initial}}) + (\epsilon_{\text{og}}X_{\text{og}} + \epsilon_{\text{cp}}X_{\text{cp}}) \ln(f) \quad \text{Eq. 2}$$

where, $\delta^{13}\text{C}_{\text{initial}}$ is the initial $\delta^{13}\text{C}_{\text{DIC}}$. X_{og} is the fraction of DIC being outgassed whereas X_{cp} is the fraction of DIC precipitated

(a) Eustatic sea level fall (evaporitic lagoon): CO_2 outgassing > carbonate precipitation ($X_{\text{og}} > 50\%$)



(b) Eustatic sea level rise (marine shelf lagoon): carbonate precipitation > CO_2 outgassing ($X_{\text{cp}} > 50\%$)

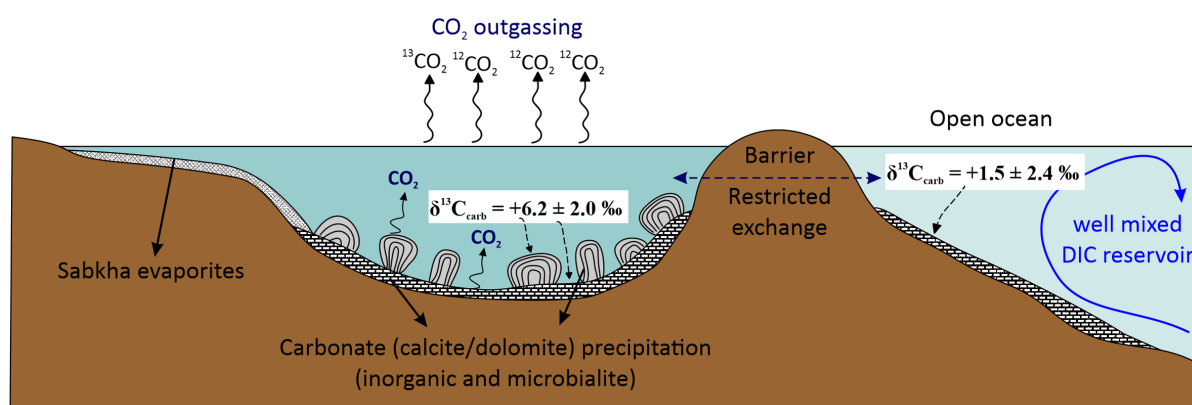


Figure 1 Schematic of a conceptual model of carbonate deposition in lagoons during periods of eustatic sea level (a) fall and (b) rise. $\delta^{13}\text{C}_{\text{carb}}$ means $\delta^{13}\text{C}_{\text{carbonate}}$.

as carbonates ($X_{\text{og}} + X_{\text{cp}} = 1$). ε_{og} and ε_{cp} are the respective fractionation factors ($\varepsilon = \delta^{13}\text{C}_{\text{product}} - \delta^{13}\text{C}_{\text{reactant}}$). The term f denotes the fraction of DIC remaining. Equation 2 suggests that varying proportions of CO_2 outgassing (X_{og}) and carbonate precipitation (X_{cp}) could have resulted in DIC loss from a Lomagundi lagoonal setting, where the former might have increased the $\delta^{13}\text{C}_{\text{DIC}}$ of water column while the latter could have decreased it. Solving Equation 2 for $\delta^{13}\text{C}_{\text{DIC}}$ shows that

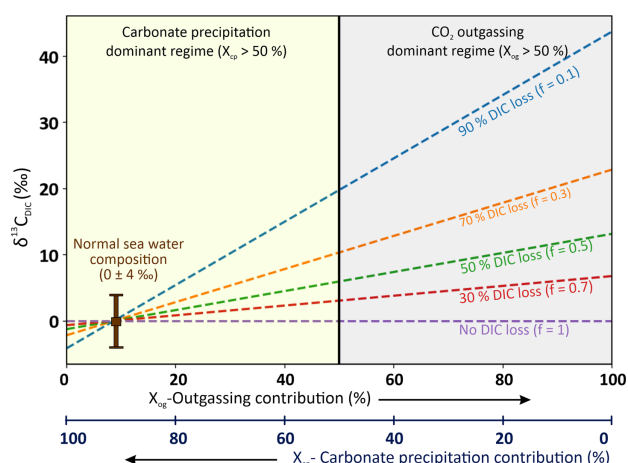


Figure 2 $\delta^{13}\text{C}_{\text{DIC}}$ obtained for varying proportions of outgassing (X_{og}) and carbonate precipitation (X_{cp}) from Equation 2 at different DIC loss proportions (f).

varying contributions in DIC loss through outgassing and carbonate precipitation can result in different $\delta^{13}\text{C}_{\text{DIC}}$ (see Fig. 2 and Supplementary Information for values used in calculation).

Lomagundi Excursions in an Evaporitic Environment

The carbonates in the Lomagundi evaporites show anomalously high $\delta^{13}\text{C}_{\text{carbonate}}$ ($+8.1 \pm 3.8\%$; Prave *et al.*, 2022), which we infer to be deposited in the evaporitic lagoons during eustatic sea level fall (Fig. 1a). The restricted nature of the lagoon and warmer temperatures during the LJE should have preferably favoured DIC loss through evaporative outgassing of CO_2 to the atmosphere ($X_{\text{og}} > 50\%$; the outgassing dominant regime in Fig. 2). Such non-equilibrium CO_2 transfer to the atmosphere is observed in the present day Dead Sea brine, which causes a significant increase in $\delta^{13}\text{C}$ of the residual DIC pool with fractionation factors ranging between -15 and -23% (Stiller *et al.*, 1985; Barkan *et al.*, 2001). Hence, we infer that intense evaporative loss of CO_2 through outgassing might have resulted in significant loss of DIC, thereby enriching remaining DIC pool in ^{13}C in the evaporitic lagoon's water column during the LJE. Such intense evaporation promotes the precipitation of calcium sulphates (CaSO_4) including gypsum and anhydrite. A large proportion of calcites in these settings are interpreted to have formed through early diagenetic calcitisation of the deposited CaSO_4 (Brasier *et al.*, 2011; Melezhik *et al.*, 2013). Furthermore, selective removal of Ca^{2+} from the water column during CaSO_4 precipitation increases the Mg/Ca ratio

(Brasier *et al.*, 2011). Such Mg-rich conditions would have also favoured dolomite formation, either through direct precipitation or through dolomitisation of pre-existing calcites (Brasier *et al.*, 2011). In this context, we argue that the ^{13}C enriched DIC of the lagoonal waters likely served as the fluid source for such calcitisation and dolomite precipitation (or dolomitisation of calcite) processes, thereby resulting in the formation of anomalously high $\delta^{13}\text{C}$ evaporitic carbonates. This is evidenced through carbonates in the evaporitic environments of Tulomozero formations from Onega basin where syn-sedimentary calcitisation and dolomitisation have been observed (Brasier *et al.*, 2011; Melezhik *et al.*, 2013).

Lomagundi Excursion in Marine Shelf Lagoon Environment

It has been observed that carbonates not associated with evaporitic mineral phases also record Lomagundi Excursion, suggesting deposition in a non-hypersaline basin (Goswami *et al.*, 2023). Moreover, these carbonates show relatively lower $\delta^{13}\text{C}_{\text{carbonate}}$ ($+6.2 \pm 2.0$ ‰) compared to carbonates of evaporite deposits (Prave *et al.*, 2022). We infer these carbonates to be marine shelf carbonates deposited in the lagoon during eustatic sea level rise (Fig. 1b). These marine shelf lagoonal carbonates constitute both dolostones (which are inorganically precipitated) and stromatolitic dolostones, which are microbialites formed through microbially induced precipitation of carbonates, where microbial mats influence their mineralisation (Dupraz *et al.*, 2009; Melezhik *et al.*, 2013). The precipitation of carbonate from the water column produces CO_2 ; therefore, stromatolitic and inorganic carbonate precipitation in the marine shelf lagoonal setting should eventually produce CO_2 . This CO_2 could either be consumed by phytoplankton or outgassed to the atmosphere (Dupraz *et al.*, 2009). Moreover, microbialites should have also produced CO_2 due to their characteristically rapid decomposition of biomass, which should have resulted in negligible organic matter accumulation (Jørgensen *et al.*, 1992). Evidently, the low organic matter preservation in the LJE carbonates (Karhu, 1993) likely indicates that most of the microbialite produced organic matter was mineralised to CO_2 . The CO_2 sourced from carbonate precipitation and biomass remineralisation should have likely led to build up of CO_2 in the lagoon. Given the warmer temperature (high K_s) due to greenhouse climate, higher wind speeds (high K_w) due to storm events and partially restricted nature of the lagoon, the air-sea flux of CO_2 should likely be higher. For the lagoon to outgas CO_2 into the atmosphere, the $p\text{CO}_{2\text{surface}}$ should exceed the $p\text{CO}_{2\text{atmosphere}}$. In restricted water bodies like lakes and lagoons, stratification in the water column is common, which can be disrupted by strong winds, promoting vertical redistribution of CO_2 from bottom layers to the top layers and resulting in an increase in $p\text{CO}_2$ in the surface water (Jennings *et al.*, 2012). Therefore, we hypothesise that the CO_2 produced due to carbonate precipitation and organic matter remineralisation in the Lomagundi marine shelf lagoon should have increased the surface water $p\text{CO}_2$ (high $\Delta p\text{CO}_2$) due to disturbance of stratification through strong winds, which might have favoured outgassing. However, the presence of stromatolitic carbonates and dolostones indicates that even though CO_2 outgassing occurred, carbonate precipitation was likely dominant in the shelf lagoons. Therefore, in the marine shelf lagoonal facies, carbonate precipitation (X_{cp}) might have likely dominated, *i.e.* the carbonate precipitation dominant regime in Figure 2. As is evident from the fractionation factor of carbonate precipitation, the process over time tends to lower the $\delta^{13}\text{C}$ of water column DIC (Rubinson and Clayton, 1969), which could be the reason for comparatively lower $\delta^{13}\text{C}_{\text{carbonate}}$ in the marine

shelf lagoonal carbonates compared to evaporitic carbonates, where outgassing dominated. Our Rayleigh fractionation calculation using Equation 2 for the $\delta^{13}\text{C}_{\text{DIC}}$ and residual DIC (f) data of Lake Laguna Negra (Beeler *et al.*, 2020), a modern day analogy for the lagoonal environment discussed here, suggests that ~ 80 % DIC loss through 30–40 % CO_2 outgassing can explain the observed $\delta^{13}\text{C}_{\text{DIC}}$ as high as ~ 15 ‰ in the lake. We refrain from flux estimates of these processes during LJE due to uncertainty in quantification of several parameters, particularly $p\text{CO}_{2\text{surface-water}}$.

Unperturbed Open Ocean and Coeval $\delta^{13}\text{C}_{\text{Org}}$

The open ocean carbonates of the LJE show $\delta^{13}\text{C}_{\text{carbonate}} \sim +1.5 \pm 2.4$ ‰, which lies within the range of normal sea water isotopic composition (0 ± 4 ‰; Prave *et al.*, 2022) observed throughout the geologic past. This reflects the conservative nature of open ocean $\delta^{13}\text{C}_{\text{DIC}}$. Previous studies suggested that the Proterozoic ocean likely had a larger DIC inventory than that of the present day ocean (Bartley and Kah, 2004; Cantine *et al.*, 2020) and hence could likely be the reason for the unperturbed nature of open ocean $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{carbonate}}$. With unperturbed open ocean $\delta^{13}\text{C}_{\text{DIC}}$ and elevated lagoonal $\delta^{13}\text{C}_{\text{DIC}}$, open ocean organic matter would be expected to have a lower $\delta^{13}\text{C}_{\text{Org}}$ than lagoonal organic matter during the LJE. Supporting the above argument, the open ocean deposited Sengoma shales of the Silverton Formation showed $\delta^{13}\text{C}_{\text{Org}}$ ranging from -33.7 to -20.8 ‰ with an average of -27.0 ± 3.0 ‰ (Bekker *et al.*, 2008), while the overlying Lomagundi carbonates ($\delta^{13}\text{C}_{\text{carbonate}}$ ranging from $+8.3$ to $+11.2$ ‰) showed relatively higher $\delta^{13}\text{C}_{\text{Org}}$ ranging from -24.8 to -13.9 ‰ (Bekker *et al.*, 2008). Available data indicate a wide range of $\delta^{13}\text{C}_{\text{Org}}$ values during the LJE, from as low as -48.2 ‰ to as high as -11 ‰ (Farrell *et al.*, 2021). We attribute the deposits with relatively high $\delta^{13}\text{C}_{\text{Org}}$ during the LJE to be associated with lagoons, whereas those with comparatively lower $\delta^{13}\text{C}_{\text{Org}}$ to likely represent open ocean depositional settings.

Uniqueness of Anomalous $\delta^{13}\text{C}$ to the LJE

The LJE coincided with the subaerial emergence of continents which should have resulted in widespread creation of (partially) restricted intracontinental shallow basins, favouring evaporite deposition and abundant stromatolite reef accretion (Melezhik *et al.*, 1999; Hodgskiss *et al.*, 2023). Such restricted basins/lagoons are suitable for CO_2 outgassing and carbonate precipitation to dominate the carbon cycling (Fig. 1). Specifically, the sea surface temperature was very high (~ 60 °C) during the Paleoproterozoic compared to later time intervals, as inferred from resurrected proteins (Gaucher *et al.*, 2008) and oxygen isotope studies (Robert and Chaussidon, 2006). Therefore, we argue that such high temperatures during the LJE could have resulted in increased evaporation and reduced CO_2 solubility (K_s in Equation 1), leading to enhanced CO_2 outgassing in the lagoons. The observed decline in sea surface temperatures post-LJE (Robert and Chaussidon, 2006; Gaucher *et al.*, 2008) could likely explain the absence of anomalous values in evaporitic carbonates of later geological intervals. Moreover, the Lomagundi carbonates in many regions are overlain by organic-rich shales, which are attributed to the cessation of shallow marine restricted, carbonate precipitating environments post-LJE (Bekker *et al.*, 2003; Hodgskiss *et al.*, 2023). Termination of such environments along with the observed decline in sea surface temperature should

have resulted in reduced dominance of CO₂ outgassing and carbonate precipitation, which likely explains the abrupt termination of the LJE.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2627>.



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Can CO₂ outgassing and carbonate precipitation explain Lomagundi excursion?

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Supplementary Information

The Supplementary Information includes:

- Calculations for Figure 2
- Supplementary Information References

Calculations for Figure 2

- The $\delta^{13}\text{C}_{\text{DIC}}$ for varying proportions of CO₂ outgassing and carbonate precipitation at differential DIC loss (f) was calculated from Eq. 2 (Figure 2 of the paper).
- DIC input ($\delta^{13}\text{C}_{\text{input}}$) to the lagoon was assumed to be dominantly from the open ocean with normal seawater composition i.e., $\delta^{13}\text{C}_{\text{initial}} = 0 \pm 4 \text{ ‰}$ (Prave *et al.*, 2021).
- Average fractionation factors were used for the calculations :
 - $\epsilon_{\text{og}} = -19\text{‰}$ (-15.9 ‰ to -23 ‰ ; Stiller *et al.*, 1985).
 - $\epsilon_{\text{cp}} = 1.8\text{‰}$ (0.9 ‰ to 2.7 ‰ ; Romanek *et al.*, 1992; Robinson and Clayton, 1969).
 - Residual DIC fraction (f) was varied from 1 to 0.

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