Authigenic origin for a massive negative carbon isotope excursion

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ABSTRACT

The Neoproterozoic contains several pronounced negative carbon isotope excursions that have been the topic of intense debate. The foremost of these, the “Shuram excursion,” represents the largest known carbon isotope excursion in Earth’s history. These negative carbon isotope excursions have been variably interpreted to record primary seawater values and massive carbon cycle perturbations, diagenetic alteration, or porewater authigenic carbonate formation. Although there are abundant examples of recent and Phanerozoic authigenic carbonates with markedly negative carbonate carbon isotope values, these carbonates are clearly identifiable as diagentic products, making it difficult to link them to Neoproterozoic carbon isotope excursions. Here, we report the occurrence of a Middle Triassic, shallow-marine formation within the sediment pile that contains a negative carbon isotope excursion in fine crystalline and peloidal carbonates that is comparable—in terms of its magnitude and stratigraphic structure and variability—to several Neoproterozoic carbon isotope excursions. A coupled petrographic and multiple isotope (C-O-Sr-U) approach suggests that the excursion was driven by carbonate precipitation within anoxic porewaters. Extensive carbon precipitation in the upper portion of the sediment pile was likely linked to inhibited bioturbation and a high background carbonate saturation state in an evaporative setting. The discovery of a Phanerozoic authigenic carbon isotope excursion bolsters the case that some stratigraphically continuous Neoproterozoic negative carbon isotope excursions may be tied to carbonate formation within the sediment pile.

INTRODUCTION

The input of carbon to Earth’s surface reservoirs ($\delta^{13}C_{\text{org}}$) is balanced mainly by the burial of depleted organic carbon ($\delta^{13}C_{\text{org}}$, $\sim-25\%e$), and the burial of marine calcium carbonate ($\delta^{13}C_{\text{calc}}$, $\sim-0\%e$). Marine calcium carbonate ($\delta^{13}C_{\text{calc}}$) is similar in isotopic composition to dissolved inorganic carbon (DIC) in seawater, which has remained relatively constant at $-0\%e$ throughout Earth’s history. The $\delta^{13}C_{\text{calc}}$ record of sedimentary calcium carbonate has been used to reconstruct the history of the global carbon cycle and to correlate poorly fossiliferous Precambrian strata globally (e.g., Halverson et al., 2010). Although baseline carbonate carbon isotope values are near $0\%e$, there are numerous large swings in carbonate carbon isotope values that have been the topic of intense debate (Knauth and Kennedy, 2009; Derry, 2010; Halverson et al., 2010; Grotzinger et al., 2011; Swart and Kennedy, 2012; Schrag et al., 2013). The largest of these excursions occurs in Neoproterozoic strata, where there are shifts from markedly positive to markedly negative carbonate $\delta^{13}C$ values (Grotzinger et al., 2011).

The largest-amplitude negative carbon isotope excursion in Earth history ($\delta^{13}C_{\text{calc}}$ drop from $+5\%e$ to $-12\%e$) is the “Shuram excursion” (SE). Multiple globally distributed late Ediacaran sections have been linked to the SE, but there are no direct age constraints on any of these sections (e.g., Fike et al., 2006; Le Guerroué et al., 2006; Jiang et al., 2007; Kaufman et al., 2007; Grotzinger et al., 2011). Numerous authors have proposed a primary seawater origin for the markedly negative carbon isotope values in these sections—typically linked to massive, pulsed organic carbon oxidation (Fike et al., 2006; Li et al., 2017; Zhou et al., 2017). However, the difficulty of modeling these values as a global excursion (Bristow and Kennedy, 2008), and the observed correlation between $\delta^{13}C_{\text{calc}}$ and $\delta^{18}O_{\text{calc}}$ have led numerous authors to propose that these “isotope excursions” are instead linked to diagentic alteration—either by meteoric waters (Swart and Kennedy, 2012) or by burial fluids (Derry, 2010).

More recently, there has been a renewed interest in linking the markedly negative Neoproterozoic carbon isotope values to authigenic carbonate formation within the sediment pile (e.g., Schrag et al., 2013). This model is attractive given that authigenic carbonates have long been known to record markedly negative $\delta^{13}C_{\text{calc}}$ values (e.g., Aller et al., 1996). However, Phanerozoic authigenic carbonates commonly have macroscopic features that clearly point toward formation within the sediment pile (e.g., carbonate nodules, void-filling cements, and diageneric beds) and generally do not show any clear stratigraphic trends (Irwin et al., 1977; Loyd et al., 2012; Zhao et al., 2016), clearly distinguishing them from isotopically depleted Neoproterozoic SE carbonates. The lack of an obvious Phanerozoic analogue has made it difficult to link stratigraphically well-resolved $\delta^{13}C_{\text{calc}}$ trends to varying amounts of authigenic carbonate precipitation. Although new metal isotope systems may be able to improve our ability to track depositional and/or diageneric conditions of marine carbonates (e.g., Blättler et al., 2015; Higgins et al., 2018; Hood et al., 2018), there is still a need

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to explore Phanerozoic and modern carbonate successions that can help us to better understand the enigmatic Proterozoic carbonate record.

Here, we present new isotope data from an early Middle Triassic, shallow-marine, subsurface carbonate and evaporite succession in the Sichuan Basin, China. This succession contains a prominent negative carbon isotope excursion generally comparable in scale and sedimentary fabric to Neoproterozoic negative carbon isotope excursions, including the SE. We argue—based on petrographic and C-Sr-O-U isotope data—that the negative δ13C values are linked to carbonate precipitation in anoxic porewaters. The Triassic carbonates described here are unique (for authigenic carbonates) in being composed of fine crystalline or peloid carbonate that is not easily identified as a diagenetic product. These textures are linked in part to the evaporative setting, which resulted in the sediments being unbioturbated and the overlying waters likely having a high carbonate saturation state, conditions that, although rare through the Phanerozoic, were likely part of the baseline Earth state in the Proterozoic (e.g., Wright and Cherns, 2016).

GEOLOGIC SETTING AND RESULTS

During the Middle Triassic, the Sichuan Basin was a restricted evaporitic platform under an arid climate, with a platform-margin shoal that developed on the northwest side during the Leikoupo period. The Leikoupo Formation conformably overlies the Lower Triassic Jialingjiang Formation carbonates and evaporites, and it is unconformably overlain by the Upper Triassic Xujiahe sandstone. The Leikoupo Formation is characterized by repetitive, laterally persistent beds of evaporites, dolostone, limestone, and minor interbedded siliclastic rocks.

Within this succession, we focused on dolomitic samples from the lower Middle Triassic strata (3045–3100 m in the PetroChina drill core Guang 100; Fig. 1). The lower part of this succession is characterized by cyclic deposition of carbonate and evaporite, with putative microbialite textures and a typical mineral assemblage of anhydrite and dolomite, with few magnesite and detrital materials. Dolostone is mainly a finely crystalline dolomite layer on top of the cyclic evaporitic sequence, and it is overlain by finely crystalline limestone. Marine biotic grains (e.g., brachiopod and mollusk) occur only in the uppermost dolostone and limestone interval. Evidence for bioturbation is lacking from the lower portion of the examined section.

The δ13C and δ18O, and δ238U values of this Early Triassic carbonate interval show significant variations: carbon, oxygen, and uranium isotopic compositions display a wide range between −11.5‰ and +5.9‰, between −9.2‰ and +1.2‰, and between −0.76‰ ± 0.08‰ and −0.33‰ ± 0.04‰, respectively (Fig. 2). In contrast, organic carbon isotope values (δ13Corg) range from −26.0‰ to −29.1‰ and do not show a clear stratigraphic trend; i.e., there is organic-carbonate δ13C decoupling. At the bottom of the section, δ18O and δ238U values are relatively high, with a value of ~−1.0‰ and ~−0.36‰ ± 0.03‰, respectively, in dolomite. In a 25 m interval between 3100 m and 3075 m, there are coherent negative isotope excursions, with most of values lying between −11.5‰ and −8.0‰ for δ13C and between −0.76‰ ± 0.08‰ and −0.39‰ ± 0.08‰ for δ238U. The δ13Corg values maintain negative (averaging −10.0‰), whereas δ238Uorg values show a prominent positive shift toward −0.33‰ ± 0.04‰ between 3075 m and 3065 m. The δ18Oorg values rise abruptly from −1.6‰ to −5.0‰ (Fig. 2) at the upper part of the section between 3065 m to 3055 m. The 87Sr/86Sr values are strongly correlated with δ13C values (see Fig. DR2 in the GSA Data Repository1)

1 GSA Data Repository item 2019047, supplementary information, figures, and data tables, including diagenesis modeling conditions, methods, and results, is available online at http://www.geosociety.org/datarepository/2019/; or on request from editing@geosociety.org.

In contrast to δ13Corg, δ18Oorg, and δ238Uorg carbonates in the studied section display a narrow range of 87Sr/86Sr ratios from 0.708179 to 0.708530. The lower part of this section yields 87Sr/86Sr ratios that range from ~0.7082 to 0.7085, whereas the upper part of this section, composed by finely crystalline carbonates, yields 87Sr/86Sr ratios of ~0.7082 to 0.7083—all roughly comparable to the contemporaneous seawater estimates at this time (87Sr/86Sr ~0.7082–0.7083; Korte et al., 2003).

DISCUSSION

Authigenic Carbonate Formation

In the upper part of the section, fine crystalline carbonates and shell hash display δ13C, δ18O, and 87Sr/86Sr values similar to early Middle Triassic (Anisian) seawater (Korte et al., 2003, 2005), suggesting they preserve the original seawater signals. The strongly depleted δ13C and δ18O values in the lower part of the studied section, in contrast, clearly do not record open-marine signals (Korte et al., 2005). Early or late
diagenetic alteration is a potential explanation for the depleted isotope signatures, but the lack of any petrographic evidence for late diagenetic modification coupled with the very low porosity (<<1%) and seawater-like Sr isotope values suggest very limited diagenetic alteration. Therefore, the markedly depleted \( \delta^{18}O \) and \( \delta^{13}C \) during the \( \delta^{18}C \) excursion, similar to that found in Neoproterozoic SE carbonates (e.g., Derry, 2010), suggests that the negative carbon and oxygen isotope values are genetically linked. Both meteoric water diagenesis (Melim et al., 2004; Swart and Kennedy, 2012) and burial diagenesis (Derry, 2010; Jiang et al., 2015) are able to significantly alter sedimentary marine carbonate isotopic compositions toward more negative values. However, as outlined above, limited diagenetic alteration argues against either the meteoric or the burial diagenesis hypothesis. The oxygen variations could be driven by temperature variations, but the observed spread in oxygen isotope values would represent an extreme range of temperatures (roughly 30 °C, e.g., from 20 °C to 50 °C). However, depletion of \( \delta^{18}O \) and \( \delta^{13}C \) in early diagenetic carbonates can be a direct consequence of anaerobic organic matter decomposition (e.g., Sass et al., 1991), providing a simple explanation for the coupled \( \delta^{18}O \) and \( \delta^{13}C \) records.

In contrast to the carbon and oxygen isotopes, seawater \( \delta^{238}U \) values for the examined time interval are not well constrained. Nonetheless, the Middle Triassic was not marked by any major biogeochemical perturbations that would have dramatically shifted seawater \( \delta^{238}U \) values, making it unlikely that the large swings in carbonate U isotopes reflect global marine values. The negative U isotope values are similar to predicted values if carbonate precipitation occurred during early diagenesis where anaerobic organic matter remineralization triggered carbonate precipitation (through an alkalinity increase). Uranium reduction results in solid phase accumulation (a rapid drop in \( \delta^{13}C \)) rather than water-column DIC \( \delta^{13}C \) values. Significantly, the \( \delta^{13}C \) excursion observed in the Middle Triassic profile is comparable to the SE in terms of magnitude (\( \delta^{13}C \) range from \( -12 \%_c \) to \( +6 \%_c \)), stratigraphic structure and variability (a rapid drop in \( \delta^{13}C \) followed by a more gradual recovery), and thickness (\( ~45 \) m), at least comparable to the SE of the Doushantuo Formation from South China (Jiang et al., 2007), and the isotopically depleted interval in the Johnnie Formation in the United States (Verdel et al., 2011).

Although the nature and processes driving Neoproterozoic carbon isotope excursions need to be evaluated on a case by case basis, this study adds to the framework that can be used to explore the Neoproterozoic record. The discovery of a large swing in carbonate \( \delta^{13}C \) values within the Middle Triassic Leikoupo Formation strengthens the case that stratigraphically coherent Neoproterozoic carbonate isotope excursions could be linked to carbonate formation within the sediment pile—and, critically, it seems this process can produce carbonate textures that are not easily identified as secondary phases (e.g., fine crystalline laminated

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**Figure 2.** Carbon, oxygen, strontium, and uranium isotope records (in %) of carbonate and carbon isotope record (in %) of organic matter from studied lower Middle Triassic Leikoupo interval (Sichuan Basin, China; depth in m).
carbonates or peloids). The Leikoupo Forma-

tion was deposited in a distinctive (evapo-

rative) setting. Because of extensive evaporation and enhanced salinity, the Leikoupo Formation appears to have been bioturbated and likely had an elevated background carbonate saturation state. These factors were likely key in allowing extensive authigenic carbonate formation in the upper portion of the sediment pile while preserving typical sedimentary fabrics (e.g., non-carbonate nodules or diagenetic beds) despite extensive carbonate authigenesis. However, limited or no bioturbation and a high carbonate saturation state were the background state in the Neoproterozoic (Ridgwell and Zeebee, 2005). We suggest that although the setting of the Leikoupo Formation is not analogous to commonly examined Neoproterozoic successions (which are clearly not evaporative), the processes driving the Leikoupo excursion are likely to have operated in the Neoproterozoic.

CONCLUSIONS

The Middle Triassic shallow-marine, lagoonal Leikoupo Formation contains markedly depleted carbonate carbon isotope values that form a stratigraphically coherent negative carbon isotope excursion. The excursion is comparable to the Neoproterozoic Shuram excursion in terms of its shape and magnitude, and a strong correlation between $\delta^{13}$C and $\delta^{18}$O. However, petrographic and Sr isotope evidence suggests that it is unlikely that the markedly negative $\delta^{13}$C values and the correlation between $\delta^{13}$C and $\delta^{18}$O values were linked to meteoric and/or burial diagenesis alteration. Therefore, we propose that the $\delta^{13}$C and $\delta^{18}$O shifts were related to varying amounts of authigenic carbonate precipitation in reducing sediment porewaters. Although negative Neoproterozoic carbon isotope excursions almost certainly have multiple origins, this work provides support for the idea that these excursions could be linked to syndepositional authigenic carbonate formation within the sediment pile.

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