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Paired carbonate-organic carbon and nitrogen isotope variations in Lower Mississippian strata of the southern Great Basin, western United States

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ABSTRACT

The Early Mississippian K-O (Kinderhookian-Osagean) carbon isotope ($\delta^{13}C$) excursion or TICE (mid-Tournaisian carbon isotope excursion) is one of the most prominent positive $\delta^{13}C$ excursions of the Phanerozoic. Recent studies raise uncertainties about the representative shape (single vs. double spikes) and magnitude of this $\delta^{13}C$ excursion (3‰ to ≥6‰ in South China; ≥5.5‰ in Europe; and ≥7‰ in North America) and the 3‰ unidirectional increase in nitrogen isotopes across the $\delta^{13}C$ excursion, which is unanticipated considering the amount of organic carbon burial required to form the $\delta^{13}C$ excursion and the resultant oxygen increase and global cooling. To test if stratigraphic completeness and spatial isotope variations caused such uncertainties, we have conducted paired carbonate carbon ($\delta^{13}C_{carb}$), organic carbon ($\delta^{13}C_{org}$) and nitrogen ($\delta^{15}N$) isotope analyses across the K-O interval in two well-exposed sections of the southern Great Basin, western United States. The two sections represent proximal shallow-water and distal deep-water depositional settings of a west-dipping carbonate ramp. In the distal ramp section where no exposure surface is present, both $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ show double spikes with peak $\delta^{13}C_{carb}$ values up to 7‰ and a negative shift down to 4‰ between the peaks. In the proximal shallower-water section where two karstic disconformities are observed, $\delta^{13}C_{org}$ shows similar double spikes but $\delta^{13}C_{carb}$ displays only a single peak with the highest value of 5.5‰. The missing $\delta^{13}C_{carb}$ spike is likely caused by diagenetic alteration below a karstic disconformity that lowered $\delta^{13}C_{carb}$ but not $\delta^{13}C_{org}$ values, resulting in smaller magnitude of the $\delta^{13}C_{carb}$ excursion. These features suggest that the 7‰ magnitude and double spikes are more representative of the K-O $\delta^{13}C$ excursion in the southern Great Basin. The smaller magnitude of the K-O $\delta^{13}C_{carb}$ excursion in some sections of the Great Basin and the TICE in other sections globally may have overprinted with local environmental/diagenetic signal or resulted from stratigraphic hiatus/truncation, which needs to be clarified in future research.

The $\delta^{15}N$ across the K-O $\delta^{13}C$ excursion in the distal ramp section is decoupled from $\delta^{13}C$, with the majority of $\delta^{15}N$ values around 4 ± 1‰ that do not show any obvious temporal trend. In contrast, $\delta^{15}N$ values in the shallow-water section is coupled with the K-O $\delta^{13}C$ excursion, with a 3‰ positive shift from 4‰ to 7‰ at the rising limb of the $\delta^{13}C$ excursion and a negative shift from 7‰ to 1–2‰ at the falling limb of the $\delta^{13}C$ excursion. The $\delta^{15}N$ trend from the distal ramp section is, in some extent, comparable with that documented from a section in South China, while the coupled $\delta^{13}C$–$\delta^{15}N$ pattern in the proximal section seems better explain the potential redox change across a prominent $\delta^{13}C$ excursion. Considering the sensitivity of $\delta^{15}N$ to redox conditions of depositional environments, a more comprehensive $\delta^{15}N$ study in a broader paleogeographic context is required to better understand the interactions between carbon and nitrogen cycles across the K-O interval—a critical transition from the mid-Paleozoic greenhouse clime to Late Paleozoic Ice Age (LPIA).

1. Introduction

The Lower Mississippian strata host one of the largest positive carbon isotope ($\delta^{13}C$) excursions of the Phanerozoic. This $\delta^{13}C$ excursion, referred to as the K-O (Kinderhookian-Osagean) $\delta^{13}C$ excursion in North America (Saltzman, 2002) or TICE (mid-Tournaisian carbon isotope excursion; Yao et al., 2015) in other global places, strides across the *Siphondella isosticha* and *Gnathodus typicus* conodont zones around ca. 352 Ma and has a duration of 2–4 million years (Saltzman et al., 2004; Buggisch et al., 2008; Yao et al., 2015). The K-O $\delta^{13}C$ excursion has been documented from many sections globally, mostly through carbonate carbon isotope ($\delta^{13}C_{carb}$) analyses, but the shape and

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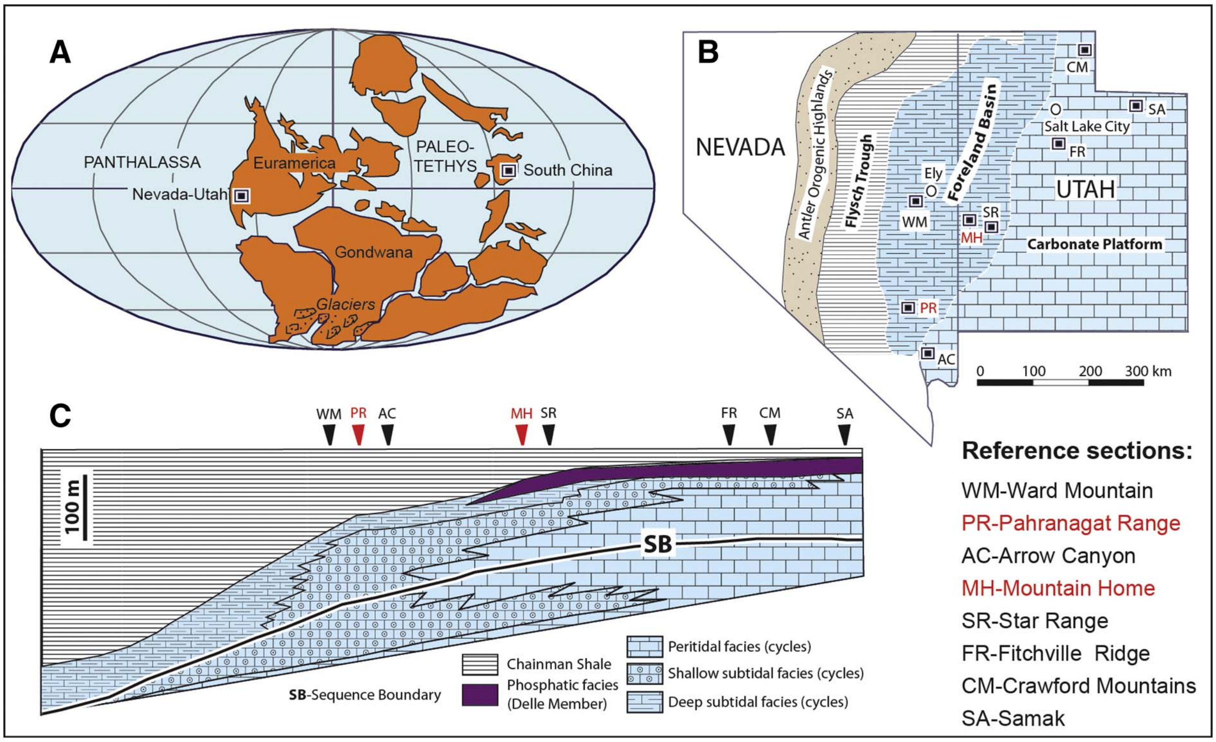

Fig. 1. Paleogeographic location of the measured sections. (A) Paleogeographic location of the southern Great Basin and South China during the Early Mississippian (after Scotese and McKerrow, 1990; Saltzman et al., 2004). (B) Early Mississippian paleogeography of the southern Great Basin (Nevada and Utah) in western U.S. showing a few representative sections including Pahranagat Range (PR) and Mountain Home (MH) (after Stevens et al., 1991; Saltzman et al., 2004). (C) Schematic cross section from eastern Nevada to northeastern Utah showing the facies changes in a west-dipping Early Mississippian carbonate ramp and the approximate location of a few representative sections including PR and MH (after Giles, 1996).

magnitude of this excursion vary significantly. In North America, the K-O $\delta^{13}C_{carb}$ excursion has a magnitude of $\geq 7‰$ and in many sections a secondary 2–3‰ negative shift is present at the peak of the excursion, making a "double spike" appearance (e.g., Saltzman, 2002, 2003; Saltzman et al., 2000, 2004; Katz et al., 2007). In Europe and Russia, the amplitude of the TICE is about 5.5‰ and the double spikes are present in some sections but are less apparent (Saltzman et al., 2004; Buggisch et al., 2008). In South China, the magnitude of the TICE varies from 3‰ to $\geq 6‰$ in two sections but the low stratigraphic resolution of $\delta^{13}C_{carb}$ data are insufficient to show the double spikes (Qie et al., 2011; Yao et al., 2015).

The varying magnitudes of the K-O $\delta^{13}C_{carb}$ excursion or TICE raise uncertainties on the representative seawater isotope signature across the K-O interval. Saltzman et al. (2004) interpreted that the higher magnitude ($\geq 7‰$) of the K-O $\delta^{13}C$ excursion in North America may have overprinted with signature from local carbon cycling in a broad epeiric sea and suggested that the magnitude of 5.5‰ from the European sections is more representative of the global seawater signature. However, later organic carbon isotope ($\delta^{13}C_{org}$) analyses in some European sections (e.g., Buggisch et al., 2008) indicated that the positive $\delta^{13}C_{org}$ shift across the K-O interval has an amplitude of $\geq 6.5‰$. The small magnitude of the TICE ($\sim 3‰$) in one of the South China sections is interpreted as resulting from meteoric alteration and stratigraphic truncation (Yao et al., 2015), which suggests that the larger ($\geq 6‰$) magnitude is more representative of the TICE. In North America, the 7‰ magnitude of the K-O $\delta^{13}C_{carb}$ excursion is not present in all measured sections; there are sections that have peak $\delta^{13}C_{carb}$ values of $\leq 5‰$ (e.g., Saltzman et al., 2004; Koch et al., 2014). One of the questions is to what extent the variable shape and magnitude of the K-O $\delta^{13}C$ excursion are caused by incomplete stratigraphic record and/or paleogeographically controlled isotope variations.

The K-O $\delta^{13}C_{carb}$ excursion, even with a magnitude of 5.5‰, requires significant amount of organic carbon burial ($\geq 7.5 \times 10^{19}$ g carbon; Saltzman et al., 2004) that would result in drawdown of atmospheric CO_2, increase of oxygen, global cooling, and sea-level fall (Mii et al., 1999; Saltzman et al., 2000; Saltzman, 2002; Buggisch et al., 2008). Because at higher partial pressure of atmospheric O_2 (pO_2), marine phytoplankton may increase isotopic discrimination for ^{12}C (Berner et al., 2000; Beerling et al., 2002; Saltzman et al., 2011), it is anticipated that carbonate-organic isotope fractionation or $\Delta^{13}C$ ($\Delta^{13}C = \delta^{13}C_{carb}–\delta^{13}C_{org}$) across the K-O $\delta^{13}C$ excursion would increase. Although some $\delta^{13}C_{org}$ data from the K-O interval have been reported (Buggisch et al., 2008), the general lack of stratigraphically continuous, paired $\delta^{13}C_{carb}–\delta^{13}C_{org}$ data makes it difficult to test this prediction.

The increase of oxygen and global cooling resulting from organic carbon burial may cause ocean redox changes that impact the nitrogen (N) biogeochemical cycle in the ocean. Nitrogen fixation and denitrification are the major source and sink of bioavailable nitrogen in oxygenated oceans, respectively (DeVries et al., 2012). Nitrogen fixation provides bioavailable nitrogen to the ocean and its nitrogen isotope ($\delta^{15}N$) value is close to that of atmospheric N_2 ($\delta^{15}N \approx 0‰$; Junium and Arthur, 2007). In oxygenated oceans, fixed nitrogen is quantitatively transferred to nitrate without significant isotope change. Denitrification, a bacterial reduction of nitrate, reduces nitrogen species in sediments and water column where oxygen is nearly absent and results in higher $\delta^{15}N$ values of the seawater nitrate reservoir ($\delta^{15}N \approx +5‰$ in the modern ocean; Algeo et al., 2014; Ader et al., 2016; Stüeken et al., 2016). Evidence from the Quaternary (e.g., Altabet et al., 1995; Deutsch et al., 2004), Pleistocene (e.g., Liu et al., 2005) and Late Carboniferous (Algeo et al., 2008) has shown that high $\delta^{15}N$ values indicative of enhanced water-column denitrification are commonly associated with interglacial stages, while low $\delta^{15}N$ values are found during glacial periods. In this context, lower $\delta^{15}N$ values are anticipated during the late stage of the K-O $\delta^{13}C_{carb}$ excursion when enhanced organic carbon burial led to cooling, oxygen increase and shrink of the oxygen minimum zone (OMZ) in the ocean. In contrast to this expectation, recent $\delta^{15}N$ data from South China reveal a 3‰