

Enhanced marine biological carbon pump as a trigger for Early Mississippian marine anoxia and climatic cooling

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The mid-Tournaisian carbon isotope excursion (TICE) marks a major perturbation in the global carbon cycle with the largest positive carbon isotope excursion in the late Paleozoic. The TICE is coincident with a climatic transition from greenhouse to icehouse. While enhanced organic carbon burial caused by high marine productivity is largely invoked to explain the TICE event, direct evidence for enhanced marine productivity is lacking, leaving the causes of the TICE event and its links to broadly contemporaneous climatic and biotic events poorly constrained. Here, we analyze barium isotopes ($\delta^{138}\text{Ba}$) of marine limestones from the Pahrnaghat Range (PR) section and the Sacagawea Peak (SP) section, which are separated by ~1200 km, from the USA to place constraints on the relative changes in regional marine productivity across the TICE event. The PR section yielded the largest positive $\delta^{138}\text{Ba}$ shift in the geological record with $\delta^{138}\text{Ba}$ values ranging from -0.15‰ to 1.12‰ . While the SP section also exhibits a positive $\delta^{138}\text{Ba}$ excursion, the magnitude of the shift is significantly smaller compared to the PR section (ranging from -0.20‰ to 0.26‰). The lack of covariation among $\delta^{138}\text{Ba}$ values, proxies for local depositional and diagenetic influences, and facies changes from both sections suggest that the $\delta^{138}\text{Ba}$ trends represent primary seawater signals in the studied marine basins. We interpret our new $\delta^{138}\text{Ba}$ data to suggest an increase in regional marine export productivity followed by the expansion of marine anoxia. The differences in the magnitude of $\delta^{138}\text{Ba}$ excursions between the PR and SP sections suggest the marine export production at the two sites is different. This scenario can be reasonably reproduced using Earth system model cGENIE where the $[\text{PO}_4]$ at the PR site was higher than at the SP site. Enhanced marine biological carbon pump would have strongly influenced the redox state of the ocean-atmosphere system with notable impacts on atmospheric CO_2 . In aid of the cGENIE model, we show that the scenario of $8\text{PAL } p\text{CO}_2 - 1.2 \times [\text{PO}_4] > 4\text{PAL } p\text{CO}_2 - 1.6 \times [\text{PO}_4] > 2\text{PAL } p\text{CO}_2 - 1.6 \times [\text{PO}_4]$ can best reproduce the observed