

The Carbonate Geochemical Fingerprint of an Early Paleozoic OAE

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The Paleozoic Era contains many large, commonly globally expressed positive carbon isotope excursions recorded in carbonate rocks. In younger Mesozoic rocks, similar excursions are often linked to organic-rich deposits formed from enhanced carbon burial under ocean-scale anoxia – i.e., oceanic anoxic events (OAEs). These events are important since voluminous organic carbon and pyrite burial in anoxic settings can be a central player in modulating the amount of oxygen and carbon dioxide in the atmosphere, and many of Earth's major extinctions are coeval with ocean-scale anoxia. In contrast, physical records of organic carbon burial tied to carbon isotope excursions are scarce in the Paleozoic, leading to ambiguity in the interpretation of the isotope data. These data become less cryptic when viewed in light of coeval seawater sulfur isotope trends.

For the globally expressed, Late Cambrian (SPICE) carbon isotope excursion, carbonate-C and sulfate-S preserved in the carbonate lattice reveal parallel, positive isotope shifts suggesting enhanced burial of organic C and pyrite S. Additionally, isotope data from the Alum Shale of Sweden for both organic C and pyrite S record the SPICE Event, putting to rest questions of the primary nature of the carbonate records. Comparison of the SPICE to similar isotope data from the Toarcian OAE and results from geochemical box modeling for both events lead us to conclude that the SPICE Event is a prime candidate for an early Paleozoic OAE.

Additional evidence for increased ocean anoxia coincident with the SPICE also comes from the Alum Shale. Molybdenum concentrations show muted enrichment during the extent of the SPICE, despite data that show the basin was persistently euxinic before, during and after. Significant increases in molybdenum concentration occur only immediately after the event, suggesting a depleted seawater Mo inventory associated with a greatly expanded (global) anoxic Mo sink during the SPICE.

An interesting result from geochemical box modeling of the SPICE and Toarcian records is the suggestion of large-scale oxidation of ³⁴S-depleted sulfur at the end of both events. A likely source of this sulfur is the oxidation of destabilized euxinic water masses. The driver of this oxidation was most likely increasing atmospheric pO_2 in conjunction with lowered pCO_2 – a result of the enhanced organic carbon and pyrite burial that marked the events. Lowered pCO_2 allowed for lower global temperatures, invigorated ocean circulation and thus delivery of O_2 to the deep ocean, leading to the demise of each anoxic event. Our ongoing work is exploring patterns of early Paleozoic biotic extinction and radiation in light of newly recognized oceanic anoxia.