

## Deoxygenation in warming oceans—Looking back to the future

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Earth's climate has varied dramatically over its long history, from snowball glaciations to greenhouse extremes. Ancient warming is one reason we study the past—to get the fullest possible picture of what might lie ahead. No episode of past warming was more dramatic than the Paleocene–Eocene Thermal Maximum (PETM) ~55 m.y. ago: a rapid temperature increase of ~5–8 °C unfolded over a mere tens of thousands of years, driving severe perturbations to the marine and terrestrial carbon cycles and concomitant impacts on ecologies in both settings. As we anticipate the impacts possible via modern climate trends, with similar levels of projected carbon release and temperature rise but over only centuries, the PETM has become a conservative poster child for why we look back in time to inform our understanding of the future.

Among the growing list of concerns in the face of the current warming trend are widespread decreases in the dissolved oxygen content of seawater, or 'ocean deoxygenation' (Keeling et al., 2010), in part because O<sub>2</sub> is less soluble in warmer water. In this regard, however, the PETM's potential as an ancient window to view modern climate has been only partly realized. Oxygen loss has been implicated in perturbations to organisms living on the deep seafloor, but little is known about the intensity and global extent of those O<sub>2</sub>-challenged conditions. Dickson et al. (2012, p. 639 in this issue of *Geology*) set their sights on filling this gap through the use of molybdenum isotope measurements applied to an exceptional set of drill-core samples collected in the Arctic Ocean. Their data point convincingly to low-O<sub>2</sub> conditions during the PETM that were more expansive than today's.

The causes and consequences of O<sub>2</sub> loss in the ocean during PETM warming are best digested within the full context of the event's many manifestations. The PETM was marked by severe isotopic perturbation to the marine (Kennett and Stott, 1991) and terrestrial (Koch et al., 1992) carbon cycles; widespread seafloor carbonate dissolution (Zachos et al., 2005); and extinction, migration, and/or rapid turnover of benthic marine organisms and a number of terrestrial floral and faunal clades (reviewed in McInerney and Wing, 2011). Other signatures are changes to the surface hydrologic cycle (Pagani et al., 2006) and rapid and extreme temperature increase on a global scale (e.g., Tripathi and Elderfield, 2005).

Although there is little debate that the carbon isotope excursion that marks the PETM required a significant release of isotopically light carbon to Earth's surface system, the source of that carbon and the ultimate causal mechanisms behind the PETM remain contested. Early models posited the destabilization of seafloor methane clathrates (Dickens et al., 1995). Discussions about the role of methane still remain very much in the mix, but subsequent interpretations have invoked a wider range of carbon sources, including the oxidation of organic carbon within widespread epicontinental seas (Higgins and Schrag, 2006), the burning of Paleocene coal and peat deposits (Kurtz et al., 2003), and orbitally paced release of permafrost carbon (DeConto et al., 2012). The feedbacks associated with recovery from the PETM are also unclear, with hypotheses that include drawdown attendant to silicate weathering (Zachos et al., 2005), the rapid regrowth of organic carbon stocks (Bowen and Zachos, 2010), and increases in marine export production (Bains et al., 2000).

What elevates the importance of the Dickson et al. study is that many of the mechanisms for extreme carbon cycling and warming during the PETM are linked to changing levels of dissolved O<sub>2</sub> in the

oceans, as a cause and effect, and specifically the spatiotemporal fabric of low-O<sub>2</sub> settings. These redox-dependent controls include (1) the size and internal dynamics of the oceanic methane hydrate reservoir during the Paleogene, (2) shifting redox-dependent microbial ecosystems and associated efficiency of organic degradation, and (3) constraints on benthic macrofaunal ecology and bioturbation intensity—among other factors modulating the burial and long-term sequestration of organic carbon beneath Earth's surface.

A number of studies have documented local changes to benthic redox associated with the PETM (Kaiho et al., 1996; März et al., 2011, and references therein), and models predict that widespread deoxygenation of the oceans during this period was probable (e.g., Winguth et al., 2012). The studies to date, however, are inherently regional in scope and provide little perspective on the broader spatial extent of low-O<sub>2</sub> conditions generally and total O<sub>2</sub> loss (anoxia) specifically and the full scope of the redox-dependent feedbacks at play during the perturbation.

The proxies for tracking local bottom-water redox conditions include many that are particularly well suited to fingerprinting low-O<sub>2</sub> and fully anoxic settings, which can be euxinic (anoxic and hydrogen-sulfide-containing) in the extreme. Among these tracers are trends in benthic ecology and specifically the persistence versus disruption of depositional microlaminar by burrowing animals as a function of O<sub>2</sub> availability; organic biomarkers for anoxygenic photosynthesizing bacteria that oxidize hydrogen sulfide when euxinia extends into the light-rich, shallow portions of the ocean; and distributions of redox-sensitive metals, such as iron and molybdenum, in muds and shales (Lyons et al., 2009). Such approaches have contributed to our understanding of the PETM, but estimates for the full oceanic extent of low O<sub>2</sub> based on local proxies are only as good as our ability to correlate local records across very broad regions.

A newer generation of proxies seeks to constrain global extents of anoxia via local measurements, even for intervals in geologic time for which much of the seafloor has been lost to subduction. These methods typically involve either mass balance assessments of metal enrichments in organic-rich shales (Scott et al., 2008) or novel metal isotope systems (Arnold et al., 2004). They are unified via their shared prerequisite for local settings known independently to have been euxinic, based on the iron relationships mentioned above, for example, and the testable assumption that the local setting was sampling global ocean chemistry.

The molybdenum isotope system has emerged as one of the most promising tracers of changes in ocean redox on a global scale. The basic principle is that the Mo isotope composition of seawater is regulated by a simple isotope mass balance controlled by the relative amount of O<sub>2</sub>-rich and O<sub>2</sub>-lean seafloor and that the isotopic composition of seawater through time can be tracked by analyzing euxinic shales. The method is simple in theory but more challenging in practice.

The burial of Mo in association with manganese (Mn) oxides in oxic settings imposes a characteristic isotope fractionation associated with sorption to the oxide surface (Barling and Anbar, 2004). In contrast, strongly sulfidic environments that support the quantitative conversion and authigenic uptake of seawater MoO<sub>4</sub><sup>2-</sup> as MoS<sub>4</sub><sup>2-</sup> will record no fractionation from ambient seawater (Lyons et al., 2009). In principle, then, the Mo isotope composition of seawater can be constrained through analysis of euxinic sediments, and this isotope composition responds

to the balance between oxic and euxinic removal fluxes from the oceans (Arnold et al., 2004).

Two significant complications to this model have emerged over recent years. One concern is conventionally referred to as the 'suboxic' sink, represented by environments where Mo is authigenically buried in sulfidic pore water beneath non-sulfidic bottom waters at rates lower than those seen in euxinic settings—but with a significant isotopic offset from coeval seawater. The second involves the isotope systematics of conversion between  $\text{MoO}_4^{2-}$  and  $\text{MoS}_4^{2-}$ . Theoretical analysis predicts that the inter-conversions among the various oxythiomolybdate species, as oxygen is replaced by sulfur, should produce significant equilibrium isotope effects (Tossell, 2005), and the isotopic manifestation of incomplete conversion at lower than optimal, albeit euxinic, dissolved  $\text{H}_2\text{S}$  concentrations has been described in some natural settings (Neubert et al., 2008). Because the kinetics of conversion among the oxythiomolybdate species is relatively slow, the marine environment must be stably euxinic with elevated dissolved  $\text{H}_2\text{S}$  concentrations to serve as a robust recorder of the isotopic composition of coeval seawater.

Dickson et al. are well aware of the ground rules. For example, organic biomarkers fingerprinting shallow microbial sulfide oxidation and high Mo enrichments (Lyons et al., 2009) point to euxinia in a basin with a strong connection to the global ocean. A conservative interpretation of their data, which they wisely favor, suggests "small global expansion of low-oxygen marine environments in the upper part of the PETM." And it is worth noting that their estimate, although low, could still be an overestimation; the uncertainties that can confound efforts to characterize the ancient ocean tend, if anything, to move the  $\delta^{98/95}\text{Mo}$  recorded in the sediment to values lower than the seawater's, thus exaggerating the extent of reducing conditions.

The Dickson et al. study is an important chapter and a great proof of concept, but it is certainly not the end of the story. For example, data from the lower portion of the PETM, missing because of a gap in core recovery, are needed to assess the full impact of deoxygenation during the event. Also, the numerical models used in the Mo isotope approach still struggle to distinguish global extents of true euxinic seafloor, in a quantitative way, from settings with low or no  $\text{O}_2$  in the water column but  $\text{H}_2\text{S}$  confined to the pore waters. Nevertheless, the data of Dickson et al. tell us that the upper PETM was not marked by vast expanses of anoxic/sulfidic conditions across the global deep ocean, either in the water column or sediments. This is not a big surprise. Establishing and maintaining highly reducing waters away from productive margins is difficult—even in warm oceans. That said, the Mo data do point to less  $\text{O}_2$  during the PETM than in today's oceans, and that difference remains a point of interest, a platform to launch future work, and a major concern as the modern oceans continue to warm at a record breaking pace.

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