Extreme methane signals in a low sulfate world

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Marine sulfate has a major controlling effect on sedimentary carbon cycling; sulfate reduction accounts for the majority of organic carbon mineralization in the modern ocean, and consumes almost all biogenic sedimentary methane. However, modern sulfate levels are anomalously high in comparison to current estimates of past conditions. It is therefore expected that sulfate-dependent sedimentary processes will have operated differently during much of the phanerozoic, particularly during the late Mesozoic where sulfate concentrations may have been up to 50% lower than current levels.

Exceptionally well preserved thick-shelled fossil bivalves collected from the Cretaceous/Palaeogene boundary sequence of Seymour Island, Antarctica (65°S) provide rare insights into the sub-annual behaviour of marine bottom-water conditions during this low sulfate interval. We present an extensive high resolution investigation of $\delta^{18}O$, $\delta^{13}C$ and trace element composition in a number of individual fossil shells spanning several million years of geological time. $\delta^{13}C$ records in particular show annual isotopic depletion unprecedented in modern shell material, of up to –34‰.

These records are thought to provide evidence for periods of seasonal domination of bottom waters by methane-derived dissolved inorganic carbon. However, the magnitude of these annual fluctuations is difficult to reconcile with our current understanding of methane production and release in modern systems. This suggests methane release may have been operating under a more environmentally responsive mechanism during low sulfate regimes. We use simple mass balance calculations to discuss the mechanisms which may have produced this difference in behaviour.