

The Phanerozoic carbon cycle with a Gas hydrate Capacitor

DICKENS, G R.

Department of Earth Sciences, Rice University, Houston, TX
77005, USA

The carbon isotopic composition of the exogenic carbon cycle has varied significantly over the Phanerozoic because of changes in external fluxes to and from the ocean and atmosphere. For nearly three decades, these secular variations in $\delta^{13}\text{C}$ have been interpreted using a common template with three major inputs (silicate weathering, organic oxidation and volcanism) and two major outputs (carbonate and organic matter). Despite widespread acceptance of these models, they are being challenged, increasingly and appropriately, because they exclude CH_4 fluxes to and from deep marine sediment. Upwards of 10,000 to 15,000 gigatons (Gt) of ^{12}C -rich methane ($\delta^{13}\text{C}$ -40 to -80 ‰) exist as gas hydrate and free gas in the upper few hundred meters of sediment on continental margins at present-day and presumably throughout much of the Phanerozoic. This CH_4 is clearly connected to the ocean through microbially mediated fluxes with magnitudes sensitive to external conditions, particularly bottom water temperature. How then should we incorporate deep sea CH_4 into global carbon cycle models and what are the implications of such a partial reconstruction? Several brief intervals of the geological record, perhaps best exemplified by the Paleocene/Eocene Thermal Maximum (PETM) ca. 55 Ma, are characterized by rapid warming of intermediate to deep ocean waters and prominent global negative $\delta^{13}\text{C}$ excursions. Thermal dissociation of gas hydrate followed by release and oxidation of CH_4 from the seafloor provides the best and perhaps only explanation for these extraordinary carbon cycle perturbations (Dickens et al., 1995). However, this requires that global carbon cycle models include a "gas hydrate capacitor" that stores and releases large quantities of ^{12}C -rich carbon at rates linked to bottom water temperature. In the simplest case, the capacitor contains three internal reservoirs: dissolved gas, gas hydrate and free gas. Carbon enters dissolved gas through decomposition of organic matter (methanogenesis), gas hydrate through saturation of pore waters, and free gas through thermal dissociation of gas hydrate. Carbon leaves free gas to the ocean through anaerobic CH_4 oxidation or, if overlying gas hydrate has been completely dissociated, direct injection to the water column and aerobic CH_4 oxidation. Massive amounts of ^{12}C -rich carbon can escape the capacitor during bottom water warming and refill the capacitor during cooling because the amount and location of free gas depends on the geotherm. Numerical simulations of a Palaeogene carbon cycle with a gas hydrate capacitor shows that a rapid 5 °C warming of intermediate to deep ocean waters, as inferred from benthic foraminiferal $\delta^{18}\text{O}$ records across the PETM, causes a $\delta^{13}\text{C}$ excursion very similar to geological observations. But this same treatment extended throughout the Palaeogene demonstrates that variable CH_4 outputs from gas hydrates nicely explain other $\delta^{13}\text{C}$ excursions, rapid and slow, large and small, negative and positive. Acceptance of a vast, thermally regulated gas hydrate capacitor at the PETM and other brief events will ultimately force us to consider global $\delta^{13}\text{C}$ records as proxies for the release and storage of seafloor CH_4 .

The effects and implications of anaerobic methane oxidation on the geochemical cycling of barium in marine sediment

DICKENS, G R

Department of Earth Sciences, Rice University, Houston, TX
77005, USA

Many sediment sequences along continental margins contain substantial amounts of microbially generated CH_4 . In most of these sequences, upward moving CH_4 encounters downward diffusing SO_4^{2-} , a meeting that drives anaerobic methane oxidation (AMO) by Archaea-Bacteria consortia at a shallow sulfate/methane interface (SMI). Although considerable efforts have been directed at understanding AMO in marine sediment, the potential effects and implications of this process on the marine barium cycle have generally been overlooked. During sediment burial, particulate barite moves downward from SO_4^{2-} -rich pore water into SO_4^{2-} -depleted pore water where it slowly dissolves. In turn, dissolved Ba^{2+} slowly diffuses upward from SO_4^{2-} -depleted pore water into SO_4^{2-} -rich pore water where it precipitates as barite. In most sediment systems, AMO occurs several meters beneath the seafloor, and upward Ba^{2+} diffusion exceeds downward barite burial. The continual cycling of Ba should therefore trap enormous amounts of dissolved Ba^{2+} beneath shallow sedimentary "barite fronts". Barium cycling in and above gas-charged sediment sequences can potentially influence our understanding of AMO and the deep biosphere in at least four different ways: (1) precipitation of barite above the SMI may consume a large fraction of the SO_4^{2-} typically assumed to react with CH_4 , (2) dissolution of barite beneath the SMI may provide a solid-phase SO_4^{2-} source for microbial consumption of organic carbon or CH_4 in deep, anaerobic sediments, (3) preserved barite fronts may mark past depths of AMO, especially in sequences where upward CH_4 fluxes have decreased over time, and (4) anomalous barite accumulation may occur on the seafloor when CH_4 (and Ba) has escaped AMO in shallow sediment and vented into the ocean. In this presentation, I review the above theory and provide specific examples from gas-charged sediment sequences recovered by Ocean Drilling Program (ODP) Legs 164, 181 and 201.