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Simulating the biogeochemical effects of volcanic CO_2 degassing on the oxygen-state of the deep ocean during the Cenomanian/Turonian Anoxic Event (OAE2)

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ABSTRACT

Cretaceous anoxic events may have been triggered by massive volcanic CO_2 degassing as large igneous provinces (LIPs) were emplaced on the seafloor. Here, we present a comprehensive modeling study to decipher the marine biogeochemical consequences of enhanced volcanic CO_2 emissions. A biogeochemical box model has been developed for transient model runs with time-dependent volcanic CO_2 forcing. The box model considers continental weathering processes, marine export production, degradation processes in the water column, the rain of particles to the seafloor, benthic fluxes of dissolved species across the seabed, and burial of particulates in marine sediments. The ocean is represented by twenty-seven boxes. To estimate horizontal and vertical fluxes between boxes, a coupled ocean–atmosphere general circulation model (AOGCM) is run to derive the circulation patterns of the global ocean under Late Cretaceous boundary conditions. The AOGCM modeling predicts a strong thermohaline circulation and intense ventilation in the Late Cretaceous oceans under high pCO_2 values. With an appropriate choice of parameter values such as the continental input of phosphorus, the model produces ocean anoxia at low to mid latitudes and changes in marine $\delta^{13}C$ that are consistent with geological data such as the well established $\delta^{13}C$ curve. The spread of anoxia is supported by an increase in riverine phosphorus fluxes under high pCO_2 and a decrease in phosphorus burial efficiency in marine sediments under low oxygen conditions in ambient bottom waters. Here, we suggest that an additional mechanism might contribute to anoxia, an increase in the C:P ratio of marine plankton which is induced by high pCO_2 values. According to our AOGCM model results, an intensively ventilated Cretaceous ocean turns anoxic only if the C:P ratio of marine organic particles exported into the deep ocean is allowed to increase under high pCO_2 conditions. Being aware of the uncertainties such as diagenesis, this modeling study implies that potential changes in Redfield ratios might be a strong feedback mechanism to attain ocean anoxia via enhanced CO_2 emissions. The formation of C-enriched marine organic matter may also explain the frequent occurrence of global anoxia during other geological periods characterized by high pCO_2 values.

1. Introduction

1.1. Oceanic Anoxic Events — OAEs

The deposition of dark-gray to black laminated organic carbon-rich shales at certain times during the Cretaceous period (~140–65 Ma) led to the concept of Oceanic Anoxic Events (OAEs; Schlanger and Jenkyns, 1976) which implies that large portions of the world's oceans became anoxic throughout the water column. However, recent high-resolution studies have highlighted problems with a single definition of OAEs that relies purely on the stratigraphic distribution of organic matter because local variations in depositional and diagenetic conditions have affected the preservation and accumulation of such material (Tsikos et al., 2004). Generally, OAEs are characterized by unusually enhanced deposition and/or preservation of organic matter across marine environments ranging from the deep oceans to the shelf seas. Enhanced productivity of siliceous and primary producers and/or better preservation under dysaerobic to anoxic conditions in large portions of the major ocean basins have been suggested as likely causes (Erba, 2004; Jenkyns, 2003; Mattioli et al., 2009). Enhanced ocean stratification (Bralower and Thierstein, 1987, Tyson, 2005) and the expansion of warm saline intermediate waters during high CO_2 periods (Poulsen et al., 2001, 2003) may also have played an important role. The OAEs led to fundamental chemical and biological changes in the world ocean.

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Common to all OAE models is the assumption that a massive increase in magmatic activity raised the pCO_2 thus preconditioning the climate system and/or triggering the OAEs (Kerr, 2005; Sinton and Duncan, 1997; Turgeon and Creaser, 2008). The most likely candidate for enhanced CO_2 degassing is the emplacement of large igneous provinces (LIPs) such as the Caribbean LIP. By using $^{40}Ar/^{39}Ar$ from feldspar and groundmass, the oldest exposed lava flows of this oceanic plateau volcanism have recently been dated to 93.4–90.9 Ma (Duncan et al., 2008). These oceanic plateaus are the equivalent of continental flood basalts and strongly support a close relation between OAE2 and submarine volcanism. This time period is characterized by the formation of Caribbean–Colombian LIP and the Kerguelen plateau in the Indian Ocean and probably the Ontong Java Plateau in the western Pacific as well. Around the Cenomanian/Turonian OAE2 there was additional volcanic activity associated with the rifting of Madagascar and India and continuous breakup of Gondwana, thus increasing the length of the global ridge system (Kerr, 2005). The associated global warming was accompanied by a more vigorous hydrological cycle, increased continental weathering, enhanced nutrient fluxes to the oceans, changes in upwelling intensity, and elevated organic productivity (Jenkyns, 2010).

While the geographic extent of most Cretaceous black shale intervals is still under debate, the two main OAEs in the early Aptian (Selli Event: OAE1a, ~119 Ma) and at the Cenomanian–Turonian boundary (Cenomanian/Turonian Boundary Event: OAE2, ~93.5 Ma), have a near-global distribution (Erba, 2004; Schlanger and Jenkyns, 1976). Estimates of organic matter accumulation rates and recent findings of biomarkers for cyanobacteria indicate photic zone anoxia during the deposition of organic-carbon rich sediments of both OAEs (Kuypers et al., 1999). They suggest high levels of productivity as observed in extreme upwelling environments of the modern world. Carbon-isotope studies demonstrate that both the Aptian and the Cenomanian–Turonian black shales are associated with a positive carbon-isotope excursion in marine pelagic and shallow-water carbonates, marine organic matter and terrestrial higher-plant material. The isotopic shift is generally thought to have resulted from a strong increase in sedimentary burial of ^{13}C depleted organic carbon due to prevailing anoxic conditions (Arthur et al., 1988). These carbon-isotope excursions thus offer a means of correlation between sediments deposited in the oceans and on the continents (Gale et al., 1993).

Despite decades of research, the mechanisms underlying OAEs still remain a topic of vigorous debate. In order to investigate these driving mechanisms and time scales for the onset and spread of OAE2 we have developed a biogeochemical box model for the Cenomanian/Turonian (Late Cretaceous) that allows us to test the influence of ocean circulation, continental weathering, O_2 dependent phosphorus (P) burial, and pCO_2 dependent C:P ratio. The latter is a mechanism that has been considered in the prediction of future ocean change (Oschlies et al., 2008) but has not been previously incorporated in biogeochemical models simulating the triggering of oceanic anoxic events in the geological past. To test the influence of circulation on biogeochemical cycles, we drive the biogeochemical box model using output from a Late Cretaceous climate simulation performed using an Atmosphere–Ocean General Circulation Model (AOGCM).

Phosphorus is the limiting nutrient on geological time scales (Tyrrell, 1999). The total inventory of dissolved phosphorus in the oceans is regulated by continental inputs, burial at the seafloor, and hydrothermal processes (Wallmann, 2010). Phosphorus availability in the marine environment is strongly affected by the ambient redox conditions (Kraal et al., 2010). Under anoxic bottom waters, P regeneration from organic matter is enhanced (Slomp et al., 1996). Enhanced P regeneration in response to bottom water oxygen depletion might have further increased marine productivity and ocean anoxia in a positive feedback loop (Van Cappellen and Ingall, 1994; Wallmann, 2003). Earlier modeling studies indicated that P regeneration from anoxic sediments fueled black shale deposition during mid-Cretaceous OAEs (Bjerrum et al., 2006; Handoh and Lenton, 2003; Nederbragt et al., 2004; Tsandev and Slomp, 2009). Bottom water oxygen depletion may have resulted from enhanced primary productivity, which was driven by increased riverine input of P from the continents (Handoh and Lenton, 2003). Additionally, enhanced P recycling from a low oxygenated proto-Atlantic (Slomp et al., 2004; Tsandev and Slomp, 2009) might have added to elevated productivity. These ideas, increased productivity and associated P burial prior to OAE 2 followed by intense P regeneration during the event are supported by geological evidence from various basins (Mort et al., 2007).

Changes in bottom water oxygen availability affect not only the burial of P, but also the relative importance of the various sedimentary P reservoirs (Kraal et al., 2010 and references therein). Under anoxic conditions, preservation of apatite in fish debris increases. As a result, biogenic Ca–P can become an important P sink under anoxic bottom waters (Slomp and Van Cappellen, 2007).

Phosphorus cycling around the Cenomanian/Turonian boundary has been previously investigated (Gertsch et al., 2010; Mort et al., 2007, 2008; Nederbragt et al., 2004). Phosphorus records that encompass the complete OAE 2 interval are scarce (Gertsch et al., 2010; Mort et al., 2007). Such data are crucial to validate model predictions regarding P cycling around the termination of ocean anoxia. Furthermore, the records of P burial during OAE 2 published so far are all from relatively shallow settings on the continental margin and slope (Gertsch et al., 2010; Mort et al., 2007, 2008). Insight into P cycling at deep locations, e.g. in the expanding and deepening mid-Cretaceous proto-Atlantic Ocean is needed when constructing a global picture of the marine P cycle during OAE 2. Lastly, the role of biogenic mineral P phases (i.e. fish debris) as a sink for P in the mid-Cretaceous oceans has not yet been assessed.

The primary impacts of increased CO_2 emissions on marine biogeochemical cycles include ocean acidification, global warming induced shifts in biogeographical provinces, and a possible negative feedback on atmospheric CO_2 levels by CO_2-fertilized biological production. Oschlies et al. (2008) have indicated an additional impact on the oxygen-minimum zones of the tropical oceans. Using a model of global climate, ocean circulation, and biogeochemical cycling, they have extrapolated mesocosm derived experimental findings from Riebesell et al. (2007) of a pCO_2-sensitive increase in biotic carbon-to-nitrogen and carbon-to-phosphate drawdown to the global ocean. Riebesell et al. (2007) have shown that dissolved inorganic carbon consumption of a natural plankton community maintained in mesocosm enclosures at initial CO_2 partial pressures of 350, 700 and 1050 µatm increases with rising CO_2. The community consumed up to 39% more dissolved inorganic carbon at increased CO_2 partial pressures compared to present levels, whereas nutrient uptake remained the same. The stoichiometry of carbon to nitrogen drawdown increased from 6.0 at low CO_2 to 8.0 at high CO_2, thus exceeding the Redfield carbon to nitrogen ratio of 6.6 in today's ocean. At the same time no change in the N:P ratio has been observed implying a corresponding increase in the C:P ratio. A similar mechanism is described from a study by Barcelos e Ramos et al. (2007) which has shown a rise in the C:P ratio of *Trichodesmium* from ~70 to ~125 at pCO_2 levels of 180 and 750 ppm respectively. Up to now, this mechanism is based on mesocosm experiments only indicating that further open ocean experiments and studies are needed to confirm this new concept.

2. The AOGCM and biogeochemical box model

2.1. AOGCM

To generate a circulation for our biogeochemical model, we have performed a Cretaceous climate simulation using the GENESIS version 3.0 Earth system model coupled to the MOM2 oceanic GCM (Zhou et al., 2008). GENESIS is composed of an atmospheric General Circulation Model (GCM) coupled to multilayer models of vegetation,