Sea Level Change, Anaerobic Methane Oxidation, and the Glacial-Interglacial Phosphorus Cycle

Bjorn Sundby[1], Alfonso Mucci[1], Pascal Lecroart[2], and Pierre Anschutz[2]

[1]McGill University
[2]Université de Bordeaux

November 22, 2022

Abstract

The oceanic phosphorus cycle describes how phosphorus moves through the ocean, accumulates with the sediments on the sea floor, and participates in biogeochemical reactions. We propose a new two-reservoir scenario of the glacial-interglacial phosphorus cycle. It relies on diagenesis in methane hydrate-bearing sediments to mobilize sedimentary phosphorus and transfer it to the ocean during times when falling sea level lowers the hydrostatic pressure on the sea floor and destabilizes methane hydrate. Throughout the cycle, primary production assimilates phosphorus and inorganic carbon into biomass which, upon settling and burial, returns phosphorus to the sedimentary reservoir. The impact of the two processes is not balanced: the former increases the oceanic phosphorus inventory whereas the latter decreases it. Primary production also lowers the partial pressure of COin the surface ocean, potentially drawing down COfrom the atmosphere. Concurrent with this slow 'biological pump', but operating in the opposite direction, a 'physical pump' brings metabolic COenriched waters from deep-ocean basins to the upper ocean. The two pumps compete, but the direction of the COflux at the air-sea interface depends on the nutrient content of the deep waters. Because of the transfer of reactive phosphorus to the sediment throughout a glaciation cycle, low phosphorus/ high COdeep waters reign in the beginning of the deglaciation, resulting in rapid transfer of COto the atmosphere. The new scenario provides another element to the suite of processes that may have contributed to the rapid glacial-interglacial climate transitions documented in paleo records.

Hosted file

`06 table 1. chronology of events .docx` available at https://authorea.com/users/533357/articles/598172-sea-level-change-anaerobic-methane-oxidation-and-the-glacial-interglacial-phosphorus-cycle

Sea Level Change, Anaerobic Methane Oxidation, and the Glacial-Interglacial Phosphorus Cycle

Bjorn Sundby [1,2], Pierre Anschutz [3], Pascal Lecroart [3], and Alfonso Mucci [2]

[1]ISMER, Université du Québec à Rimouski, Rimouski, QC, Canada H4C 3J9; [2]GEOTOP and Earth& Planetary Sciences, McGill University, Montreal, QC, Canada H3A 0E8; [3]EPOC, Université de Bordeaux, 33615 Pessac, France.

Correspondance to: Bjorn Sundby (bjorn.sundby@mcgill.ca)

ABSTRACT The oceanic phosphorus cycle describes how phosphorus moves through the ocean, accumulates with the sediments on the sea floor, and participates in biogeochemical reactions. We propose a new two-reservoir scenario of the glacial-interglacial phosphorus cycle. It relies on diagenesis in methane hydrate-bearing sediments to mobilize sedimentary phosphorus and transfer it to the ocean during times when falling sea level lowers the hydrostatic pressure on the sea floor and destabilizes methane hydrate. Throughout the cycle, primary production assimilates phosphorus and inorganic carbon into biomass which, upon settling and burial, returns phosphorus to the sedimentary reservoir. The impact of the two processes is not balanced: the former increases the oceanic phosphorus inventory whereas the latter decreases it. Primary production also lowers the partial pressure of CO_2 in the surface ocean, potentially drawing down CO_2 from the atmosphere. Concurrent with this slow 'biological pump', but operating in the opposite direction, a 'physical pump' brings metabolic CO_2 enriched waters from deep-ocean basins to the upper ocean. The two pumps compete, but the direction of the CO_2 flux at the air-sea interface depends on the nutrient content of the deep waters. Because of the transfer of reactive phosphorus to the sediment throughout a glaciation cycle, low phosphorus/ high CO_2 deep waters reign in the beginning of the deglaciation, resulting in rapid transfer of CO_2 to the atmosphere. The new scenario provides another element to the suite of processes that may have contributed to the rapid glacial-interglacial climate transitions documented in paleo records.

Key Points

*A 2-reservoir scenario of the oceanic P-cycle predicts that the oceanic P- inventory expands during the onset of a glaciation but contracts and reaches its lower limit during the deglaciation.

*The scenario predicts that transfer of phosphorus from the oceanic to the sedimentary P-reservoir weakens the power of the biological nutrient pump to draw down atmospheric CO_2.

*Upwelling of nutrient poor water near the end of a glaciation takes control of outgassing and produces a spike in the atmospheric CO_2.

Keywords: diagenesis; methane; gas hydrate; carbon dioxide; SMT-sulfate methane transition zone; atmosphere

1. INTRODUCTION

Each of the glacial cycles that characterize the Pleistocene lasted roughly 100 Kyr. During each cycle, about 90 Kyr were glacial (cold), allowing continental ice sheets to build up, and 10 Kyr were interglacial (warm), allowing the ice to melt. The large volumes of water transferred from the ocean to the continents during the glacial part of the cycle and the return flow of water to the ocean during the interglacial caused the globally-averaged sea level to fall by more than 100 meters and then rise again (e.g. Siddal et al., 2003; Lambeck et al., 2014). Seasonality changes, caused by cyclic variations in Earth's orbit around the Sun (Milankovitch cycles), are the fundamental drivers of the glacial cycles, but orbital variations by themselves cannot account for the rapid climate transitions documented in paleo-records. This implies that positive feedbacks within Earth's climate system must amplify the orbital driver (Sigman & Boyle, 2000). Much research has focused on processes that might provide such feedbacks. Since carbon dioxide (CO_2) is a greenhouse gas and since the ocean is the largest CO_2 reservoir on Earth (fifty times larger than the atmospheric reservoir), processes that influence the exchange of CO_2 between the ocean and the atmosphere top the list of candidates.

Measurements on air samples trapped in ice cores have shown that the partial pressure of CO_2 (pCO_2) in the atmosphere during the glacial period of a cycle was substantially lower than during the intervening interglacial (Barnola et al., 1987; Petit et al., 1999). The atmospheric pCO_2 decreased slowly throughout the glacial part of the cycle, as did sea-level. By comparison, both the rise of atmospheric pCO_2 and the rise of the sea level at the end of the glaciation (termination) were remarkably rapid, lasting 10 Kyr or less. The similarity between the sea-level change and the change in atmospheric pCO_2 through time suggests that the two phenomena are linked, but the nature of the link has remained elusive (e.g. Sigman & Boyle, 2000; Kohfeld et al., 2005; Peacock et al., 2006; Sigman et al., 2010).

Another greenhouse gas, methane, is abundant in continental margin sediments where it occurs as a solid in the form of methane hydrate (clathrate) (Kvenvolden, 1993; Bohrmann & Torres, 2006; Ruppel & Kessler, 2017). Paull et al. (1991) proposed a direct link between sea level fall and global warming as follows: As the sea level falls, the pressure on the sediment column decreases, methane hydrate become destabilized, and methane gas is released into the pore water. They further proposed that methane released in this way could reach the atmosphere and initiate a warming event, but it is doubtful that the vast quantities of methane that would be required to trigger substantial warming could reach the atmosphere before being oxidized in the sediments and the overlying water (Archer et al., 2000; Archer,

2007). The search for mechanisms that may explain the glacial-interglacial variation in atmospheric pCO_2 has therefore focused on other scenarios.

Common to many scenarios is the idea that the whole ocean inventory of major nutrients may have varied on glacial-interglacial time scales: If the nutrient inventory in the global ocean were to increase, mixing and upwelling could increase the flux of nutrients to the surface ocean. This would stimulate primary productivity, increase the flux of organic matter to the seafloor, and lower the pCO_2 in the surface ocean. If the pCO_2 in the surface ocean were to fall below the atmospheric pCO_2, CO_2 would be drawn down from the atmosphere. A temporally variable nutrient inventory could thus explain the glacial-interglacial pCO_2 difference. The combination of processes involved in this scenario has become known as the biological pump (e.g. Falkowski, 1997; Hain et al., 2014).

Searching for a temporary sink for phosphorus, the nutrient often considered to be limiting on geological time scales, Broecker (1982a, 1982b) developed a scenario whereby phosphorus is removed from the global ocean by deposition of P-containing sediment on continental shelves during sea-level high stands and returned to the ocean by erosion of shelf sediments during sea-level low stands. This scenario, which is known as the "shelf nutrient hypothesis" suffers a major weakness: The amount of sediment that has to be deposited and eroded on the relevant time scale appears to be far greater than can be supported by observations (Peacock et al., 2006). Another weakness of the hypothesis is the absence of an explicit mechanism that would release phosphate into the aqueous phase once the sediments are eroded. Indeed, as Archer et al. (2000) stated, it seems that all of the simple mechanisms for lowering pCO_2 in the surface ocean have been eliminated. Broecker (2018) made the point that although alternate scenarios may exist to explain glacial cycles, one must take into account that the situation is complex, and that no single scenario may be the 'best'.

2. OBJECTIVES AND APPROACH

In a recent modeling study, we drew attention to the fact that methane is a fuel that can drive diagenesis in sediments. Using manganese as an example, we showed that methane-fuelled diagenesis can reduce and redistribute solid-phase oxidized manganese throughout the sediment column (Sundby et al., 2015). Building on that study, we now focus on methane-fuelled reduction of oxidized sedimentary iron-phases and the consequent release of iron oxide-bound phosphorus into the pore water. The objective is to develop a chronological scenario of phosphorus cycling in the global ocean over a full glacial cycle. In this scenario, which capitalizes on the two-reservoir model of Broecker (1982a, 1982b),

phosphorus cycles between two principal reservoirs: the ocean and the sediments that accumulate on continental margins.

We focus on the mechanisms that promote the release of sedimentary phosphorus into the pore waters and the transfer of phosphorus to the oceanic reservoir. We then explore the mechanisms that return phosphorus to the sedimentary reservoir throughout a glacial cycle. Finally, we examine the interaction of the glacial-interglacial phosphorus cycle with the carbon system to discover how this interaction might affect variations in atmospheric pCO_2. The approach focuses on large scale temporal and spatial processes, but it does not preclude eventual incorporation of shorter timescale and broader spatial-scale processes in a more detailed scenario. By including diagenesis, we can revive elements of Broecker's original hypothesis by providing a set of mechanisms that do not rely on large scale erosion to release phosphate from sediments. We will also re-examine the idea proposed by Paull et al. (1991, 2002) that sedimentary methane may be directly involved in the atmospheric carbon cycle by escaping to the atmosphere during periods of sea-level fall. By invoking diagenesis (anaerobic methane oxidation produces sulfide that reduces iron oxides and releases soluble phosphate into pore waters) we can show that methane plays an indirect but essential role in the redistribution of phosphate between the oceanic and the sedimentary reservoirs.

3. DIAGENESIS AND FLUXES OF PHOSPHORUS IN CONTINENTAL MARGIN SEDIMENTS

3.1 Sources and sinks of phosphorus. The inventory of the oceanic phosphorus reservoir depends on the supply of phosphorus from the continents, remineralization of organic phosphorus in the water column and the upper sediment column, burial of solid phases with which phosphorus is associated, release of soluble phosphorus from the sediments, and removal by hydrothermal activity (e.g. Wallmann, 2010). Burial on the abyssal seafloor is the ultimate sink for phosphorus, but an amount equivalent to about half of the total phosphorus flux from the continents to the modern ocean does not reach the abyssal seafloor but settles out and is buried on continental margins (Colman & Holland, 2000; Ruttenberg, 2003). The particulate phosphorus that is delivered to the seafloor contains, on average, one third each of organic phosphorus, iron oxide-bound phosphorus, and poorly - reactive apatite minerals (Delaney, 1998; Fillipelli, 1997; Ruttenberg, 2003). Organic phosphorus exists in a variety of forms (primarily phosphate esters) that originate from excretion, decomposition, death, and autolysis of organisms. Microbial degradation of organic matter during the earliest stages of diagenesis converts

organic phosphorus to dissolved inorganic phosphate. Part of the remineralized phosphorus escapes into the water column and is added to the oceanic phosphorus reservoir; part of it is co-precipitated with or adsorbed onto iron (hydr)oxide minerals or may be converted to poorly reactive phases such as calcium fluoroapatite (Delaney, 1998).

In its simplest expression, the marine phosphorus cycle consists of a source and a sink of P-bearing material and a set of processes that act upon this material (figure 1). Erosion and weathering of continental rocks supply phosphorus to the ocean, and burial on the sea floor removes it. Until recently, the phosphorus sink was thought to be represented by poorly reactive (stable) apatite minerals. This view had presumably its origin in the analytical procedures that were used to quantify individual P-containing components in marine sediments. This view is now changing, and other phosphorus minerals are thought to be involved. This is exemplified by autogenesis of vivianite, a hydrous ferrous phosphate that can form in sulfate poor sediments such as those in brackish estuaries. Egger et al. (2015) suggested that vivianite may act as an important burial sink for phosphorus in brackish environments worldwide. Vivianite authigenesis requires porewater with elevated ferrous iron (Fe^{2+}) and phosphate concentrations (e.g. Liu et al., 2018). Low-sulfate lacustrine settings typically satisfy these criteria, and vivianite is commonly reported from freshwater sediments (e.g., Rothe et al., 2014).

In more sulfate-rich settings, the presence of a sulfate–methane transition zone (SMT) has been shown to provide favourable conditions for vivianite authigenesis (Egger et al., 2015a, 2016; Hsu et al., 2014; März et al., 2008a, 2018; Slomp et al., 2013). The production of dissolved sulfide by anaerobic oxidation of methane (and the associated conversion of Fe-oxides to Fe-sulfides, result in elevated porewater PO4 concentrations around the SMT (März et al., 2008a). The subsequent downward diffusion of PO4 into sulfide-depleted porewater below the SMTZ may lead to precipitation of vivianite if sufficient reduced Fe is available (e.g., Egger et al., 2015a; März et al., 2018).

Porewater profiles of phosphate in marine sediments tend to display a concentration maximum within or near the sulfate methane transition zone (SMT) (e.g. März et al., 2008a). The associated concentration gradients imply vertical transport of soluble phosphate both in the downward and the upward direction. To sustain these fluxes requires the presence of phosphate sinks both below as well as above the SMT zone. This conclusion is in agreement with the postulated presence of a phosphate sink and its strength, but it does not provide information about the nature of the sink.

A large body of research shows that phosphate is in fact released from continental margin sediments into the overlying oceanic water. Perhaps the most prominent result of this research is the paper by Colman and Holland (2000). They analyzed nearly 200 published porewater profiles of dissolved phosphate in sediment cores from a variety of marine environments and calculated phosphate fluxes into the overlying water. They concluded that the return flux of phosphate from margin sediment was more than one order of magnitude larger than the riverine flux of total dissolved phosphorus towards the ocean. Wallmann (2010) used a mass balance approach to estimate phosphate fluxes in the ocean and came up with the remarkable conclusion that the pre-human modern ocean is losing dissolved phosphate (to the sedimentary reservoir) at a rate of about 5% Kyr-1. Studies of phosphorus diagenesis in continental margin sediments have also shown that phosphate is released to the overlying waters (Sundby et al., 1992). These observations point to the important role that diagenesis (oxidation of reduced carbon) plays in the marine phosphorus cycle. Methane being prominently present in continental margin sediments suggests that our scenario, whereby sea level variations have important consequences for methane oxidation, has merit. Beyond the data, the next step could well be a better quantification of methane-fuelled diagenesis, but we are not convinced that the understanding of phosphorus and iron reservoirs, processes, and boundary conditions have progressed to the point where we are ready to attempt meaningful modelling of the oceanic phosphorus cycle.

3.2 Phosphorus diagenesis. The term *phosphorus* usually stands for the sum total of all phosphorus species, organic as well as inorganic, particulate as well as dissolved. It is typically defined operationally according the analytical methods by which it is determined (e.g., Poulton and Canfield, 2006; Ruttenberg, 2003). Phosphorus bound to iron oxides is defined operationally as "reactive particulate phosphorus" but the latter definition typically includes particulate organic phosphorus, phosphate reversibly adsorbed to other mineral surfaces, as well as phosphate in carbonate fluorapatite minerals and fish bones. In sediment pore waters, soluble reactive phosphorus (also referred to as orthophosphate or dissolved inorganic phosphorus) is a minor component of the reactive phosphorus pool and occurs chiefly as the hydrogen phosphate species (HPO_4^{2-}). Particulate and soluble forms of phosphorus are subjected to different modes of transport. Particulate phosphorus is transported to the sea floor by settling through the oceanic water column and is buried in the sediment. Soluble forms of phosphorus are transported by diffusion along concentration gradients that often develop in sediment pore waters. Transport via bioirrigation can be important in the upper sediment column.

In this study we refer to soluble inorganic phosphorus as "*phosphate*" and to insoluble forms as "*particulate phosphorus*" or "*total phosphorus*". The term *reactive iron* has been applied to the fraction of iron in marine sediments that reacts readily with sulfide (Canfield, 1989). By analogy, we define *reactive particulate phosphorus* as the fraction of total P that is adsorbed on or is co-precipitated with iron oxides and can therefore be released to pore waters when iron oxides are reductively dissolved. The challenge presented by the original shelf nutrient scenario is to find mechanisms that can trigger reciprocal changes in the sedimentary and oceanic phosphorus inventories over a glacial cycle. Diagenesis is a strong candidate for such a mechanism. Diagenesis is defined as the sum of the physical, chemical, and biological processes that bring about changes in a sediment subsequent to deposition (Berner, 1980). Phosphorus diagenesis is intimately linked to the diagenesis of iron oxide minerals, as these are the most important carrier phases for reactive phosphorus in sediments (Ruttenberg, 2003). Surface sediments contain both detrital and authigenic forms of oxidized iron, of which the most reactive occur in the authigenic fraction. Iron oxides have been characterized operationally by their reactivity towards hydrogen sulfide (e.g. Canfield, 1989; Roberts, 2015), and various sequential extraction schemes have been designed and applied to distinguish the reactivity of iron oxides towards a variety of reductants (Anschutz et al., 1998; Kostka & Luther, 1994; Poulton & Canfield, 2005; Ruttenberg, 2003). For a recent review of the extensive literature on sequential extraction procedures, we refer to Anschutz & Deborde (2016).

Authigenic iron oxides form in the upper part of the sediment column above the depth where the stability boundary for the Fe(II)/Fe(III) redox couple is located. Reactive iron buried below this boundary is reduced to soluble Fe(II) at a rate that depends on the reactivity of Fe(III) phases and organic matter, the availability of which decreases with depth below the sediment surface. Fe(II) is then immobilized as sulfides (in organic-rich sediment) or is transported up by diffusion across the Fe(II)/Fe(III) redox boundary and reoxidized by various oxidants (O_2, NO_3^-, MnO_2). This "freshly precipitated" iron oxide is reactive and can be recycled multiple times across the Fe(II)/Fe(III) redox boundary before it is finally permanently buried (Canfield et al., 1993). The presence of authigenic iron oxides in the sediment can be quantified according to its reactivity towards a "weak" reductant such as buffered ascorbic acid (Hyacinthe & Van Cappellen, 2004; Kostka & Luther, 1994). Once buried, authigenic iron oxides go through an aging process that includes stepwise dehydration of amorphous phases such as ferrihydrite to goethite and diminishing specific surface area (Lijklema, 1977). This renders reactive iron oxides more refractory, which in addition to diagenetic remobilization is reflected by a diminishing content of ascorbate-extractible iron with depth in the sediment. Thus, the bulk

reactivity of the sedimentary iron oxides decreases with time (depth of burial). The reactivity of the sedimentary organic matter that survives burial below the oxic surface sediment is also important because the reduction rate of sulfate and production rate of H_2S depend on it. In the section that follows we will introduce methane, a highly mobile form of organic matter that can be oxidized anaerobically in sediments by micro-organisms that use sulfate as terminal electron acceptor.

3.3 Linking phosphorus diagenesis to sea level changes via anaerobic methane oxidation.

Much of our understanding of the early stages of diagenesis rests on the notion that diagenesis is fuelled by the organic carbon that settles to the seafloor and is buried, and that diagenesis comes to an end when this carbon has been fully consumed. However, in continental margin sediments, where immense sub-surface accumulations of methane are present in the form of methane hydrate (e.g., Bohrmann & Torres, 2016; Ruppel & Kessler, 2017), methane can support diagenesis above and beyond that fueled by organic matter settling from the water column (Burdige & Komada 2011, 2013; Komada et al., 2016). Methane fuels diagenesis via a number of microbially-mediated processes of which the most important is anaerobic microbial methane oxidation (AOM) using sulfate as terminal electron acceptor (e.g. Boetius et al., 2000; Jørgensen & Kasten, 2006; Nauhaus et al., 2002). AOM has been described as a process that intercepts methane that migrates through anoxic pore water, thereby preventing significant quantities of methane from reaching the atmosphere. However, AOM coupled to sulfate reduction does more than just remove methane; it also produces sulfide and bicarbonate (equation 1).

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \qquad (1)$$

The sediment layer within which AOM takes place is known as the sulfate methane transition zone (SMT). It can be located at depths varying from centimeters to tens of meters below the sediment surface (Borowski et al., 1999). Riedinger et al. (2014) have made the case for coupled anaerobic oxidation of methane via iron oxide reduction, and Egger et al. (2017) have proposed that a potential coupling between iron oxide reduction and methane oxidation likely affects iron cycling and related biogeochemical processes such as burial of phosphorus. Of special interest here is the production of sulfide, a strong reductant that can reductively dissolve iron oxides and thereby release the associated phosphate into the sediment pore water.

At steady state, the SMT would be located at a fixed distance from the sea floor, and the flux of soluble phosphate from the SMT would be controlled by the burial rate of reactive phosphorus.

However, the depth of the SMT in continental margin sediments has not necessarily been at steady state on glacial time scales. Meister et al. (2007, 2008) linked diagenetic dolomite formation in hemipelagic sediments to sea level changes, showing that the SMT migrates upwards and downwards within the sediment column. They hypothesized that the SMT persists within an organic carbon-rich interglacial sediment layer sandwiched between layers of organic carbon-poor glacial sediment. Contreras et al. (2013) reported evidence showing that the SMT in organic carbon-rich sediments from the highly productive Peruvian shelf was located at much shallower burial depths than the present SMT.

The location of the SMT in the sediment column is critical since this is where the reduction of iron oxides releases phosphate to the pore water. The closer the SMT is to the sediment surface, the greater is the flux of sulfate into the sediment and the shorter is the path that phosphate travels before it escapes the sediment. The upward displacement of the SMT and the instantaneous flux of phosphate to the ocean can be linked to the rate of sea-level fall if we assume that a time-variable supply of methane from methane hydrate-bearing sediment layers can also bring about a fluctuating SMT.

3.4 Background (steady - state) fluxes of methane and phosphate in methane hydrate bearing sediment. The depth distribution of methane hydrate in sediments is constrained by the relatively narrow pressure and temperature range within which methane hydrate is stable and can exist as a solid (e.g., Ruppel & Kessler, 2017). The lower and upper boundaries of the methane hydrate stability field respond to the accumulation and burial of successive layers of fresh sediment by migrating upward towards the seafloor. Methane hydrate located at the lower stability boundary is thereby transported below this boundary, where it becomes unstable, dissociates, and releases methane into the pore water. Consequently, the downward directed burial flux of sediment is accompanied by an upward directed flux of methane.

The lower stability boundary for methane hydrate can be observed seismically as a discontinuity in sound transmission as a gas-rich layer develops. Recent high-resolution seismic data from the Blake Ridge crest (Borowski et al. 1999) show that methane gas, produced by hydrate dissociation at the lower stability boundary, can be injected well into the overlying hydrate stability zone. The data indicate that methane, in the form of free gas, can migrate hundreds of meters into the hydrate stability zone before re-forming as solid phase hydrate (Gorman et al., 2002). The ability of gaseous methane to migrate across a thermodynamic regime where it should be trapped as a hydrate suggests that gas migration through the sediment column plays an important role in the interaction of sub-seafloor methane with the overlying ocean. Under steady state conditions, the upper boundary of the methane hydrate stability field

would keep pace with the rate of sediment accumulation, which would create a zone in the upper sediment column within which methane can be removed from the pore water by solid phase hydrate precipitation. In the presence of sulfate, which is in abundant supply in the overlying ocean, methane can also be removed from the pore water by anaerobic methane oxidation. According to the stoichiometry of AOM (Equation 1), the upward flux of methane into the SMT should equal the downward flux of sulfate. In the absence of electron donors other than methane, a linear pore-water sulfate gradient is expected and can be used to estimate the instantaneous methane flux (Borowski et al., 1999).

3.5 Sea-level changes and methane and phosphate fluxes in the sediment. Because of the sensitivity of methane hydrate deposits to changes in temperature and pressure, one can expect that fluctuations in sea level and temperature, both of which are associated with glacial cycles, will perturb the depth distribution of methane in the sediment. For example, the hydrostatic pressure decrease that was associated with the 120 m sea-level drop during the last glacial maximum has been estimated to lower the hydrostatic pressure enough to raise the lower boundary of the gas hydrate stability field by as much as 20 m (Dillon & Max, 1983). There can therefore be little doubt that a perturbation such as a sea-level drop can cause methane to be released into the pore water and thereby increase the instantaneous fluxes of methane and phosphate above and beyond the slower background fluxes sustained by steady-state sediment accumulation (section 3.4).

The stoichiometry of anaerobic methane oxidation requires that the flux of sulfate into the sediment must increase in order to accommodate an increased upward flux of methane (Equation 1). This implies that the sulfate gradient grows steeper and that the SMT migrates upward. As the SMT moves upward, so does the Fe(II)/Fe(III) redox boundary, expanding the pool of iron oxides that is exposed to reducing conditions. An upward directed migration of the SMT and the expansion of the pool of oxidized Fe can also be expected to increase the abundance of dissolved ferrous iron and generate a downward directed flux of Fe(II) into the sediment region located below the SMT. It has been suggested (März et al. 2018) that this might be one of the conditions (among others) that would lead to autigenesis of Fe(II) minerals, such as vivianite.

The location of the SMT is important because the closer it is to the sediment surface the steeper will be the phosphate gradient that drives phosphate towards and across the sediment-water interface. Recent syntheses of global sea-level records (Foster & Rohling, 2013; Lambec et al., 2014; Wallmann et al., 2016) show that there were several episodes of sea-level fall during the last glaciation, each episode interrupted by periods of stable sea level. This suggests that there could also have been several pulses of

methane release into the pore water, which would cause the sub-bottom depth of the SMT and the reactions associated with it to fluctuate.

The phosphate flux cannot be expected to mirror directly the fluxes of methane and sulfate because the reductive dissolution rate of the sedimentary iron oxide pool is not constant but depends on the reactivity of the individual iron oxides present in the sediment (Canfield, 1989). Furthermore, the efflux of phosphate is ultimately limited by the pool of reactive phosphorus that is present in the sediment column when sea-level falls.

3.6 Transport of phosphate in sediment pore waters: adsorption and desorption. Relative to the sediment surface, burial moves reactive particulate phosphorus downward into the sediment column while diffusion moves soluble phosphate upwards. The two oppositely directed phosphorus fluxes interact by partitioning soluble phosphate between solution and sorption sites on solid surfaces, mostly to iron oxides (e.g. Krom and Berner, 1980, 1981; Sundby et al., 1992). Phosphate also adsorbs onto other solids, including Mn-oxides and carbonate minerals (Millero et al., 2001; Yao and Millero, 1996). It can also form authigenic carbonate fluorapatite (März et al., 2018). It has been observed that all the iron oxide surfaces found in oxic continental margin sediments are “saturated” with phosphate (all available sorption sites are occupied) and that the detrital iron oxide fraction is already saturated in phosphate by the time it arrives on the sea floor (Anschutz and Chaillou, 2009). Irrespective, sorption sites soon become saturated upon burial below the sediment-water interface where organic phosphorus is rapidly remineralized and pore-water phosphate reaches saturation levels (Sundby et al., 1992). Sorption should therefore not restrict the transport of phosphate diffusing up from the SMT towards the sea floor.

Evidence that phosphate can be transported over large depth intervals in sediments without the pore-water profile being visibly affected by sorption onto sediment particles can be found in the data set of Niewohner et al. (1998). Four 12-15 m long cores collected in 1300-2000 m water depth from gas hydrate-bearing sediments on the continental margin off Namibia display linear pore-water phosphate profiles. In two of the cores, the phosphate profile is linear over a 15 m depth interval, from the sediment-water interface to the bottom of the cores; the two other cores display a slope change at about 2 m depth, below which the profile is linear. We do not wish to imply that these profiles are representative of glacial sediments, but they do illustrate an important point: It is possible for phosphate to diffuse over long distances in sediment pore water without encountering significant impediment by secondary diagenetic reactions.

4. LINKING THE PHOSPHORUS CYCLE TO CHANGES IN ATMOSPHERIC CO_2

4.1. The concept of a limiting nutrient. A nutrient is limiting if its addition to the system increases the rate of net primary production. Because phosphorus and nitrogen both are essential elements for life, there has been much debate about which of these elements limits photosynthetic primary production in the ocean (e.g. Falkowski, 1997; Galbraith et al., 2008; Lenton & Watson, 2000; Smith, 1984; Tyrrell, 1999). Oceanic inventories of nitrogen have undergone large changes between glacial and interglacial periods (Ganeshram et al., 1995, 2002), which has been attributed to greatly diminished water column denitrification and consequent increase in the nitrate inventory during glacial periods. In the modern ocean, it appears that nitrogen is the limiting nutrient. Therefore, increasing the flux of phosphate into the ocean would not necessarily increase the rate of primary production. Nevertheless, irrespective of which nutrient element is limiting, primary production assimilates phosphate into biomass, which settles to the sea floor and is buried under successive layers of new sediment. In this way, phosphorus is transferred from the oceanic reservoir to the sedimentary reservoir. Likewise, the net result of methane-fuelled diagenesis is to return phosphate, a nutrient element, from the sedimentary to the oceanic phosphorus reservoir.

4.2. Expansion and contraction of phosphorus reservoirs during a glacial cycle. The central idea of the simple two-reservoir representation of the phosphorus cycle proposed by Broecker (1982a, 1982b) is that the phosphorus inventory in a reservoir can contract and expand on glacial time scales, eventually impacting the CO_2 level in the atmosphere. This simple representation of otherwise complex phenomena has stimulated research on the mechanism that control nutrient fluxes in the ocean.

Boyle (1986) showed that the oceanic phosphorus inventory can vary on a glacial time scale. He concluded, based on the cadmium content of foraminifera and carbon isotope measurements, that the phosphate content of the ocean during the last glacial maximum was 17% larger than it is at present. Likewise, Wallmann (2010) found that the pre-human modern ocean was losing dissolved phosphate (to the sedimentary P-reservoir) at a rate of about 5% Kyr^{-1}. The 'lost' phosphate is assimilated into biomass and/or adsorbed onto mineral particles, the settling of which returns reactive phosphorus to the sediment. Colman & Holland (2000), who examined phosphate cycling in modern continental margin sediments, concluded that the current efflux of phosphate from continental margin sediments is about one half of the total settling flux of particulate reactive phosphorus. The portion that settles through the

ocean water column to the sea floor is eventually converted to stable minerals and lost from the oceanic phosphorus cycle.

4.3. Chronology of events during a glacial phosphorus cycle. With the initiation of a glacial cycle, the global temperature decreases, ice builds up on the continents, the sea level falls, the pressure on the sea floor decreases, and the upper and lower boundaries of the methane hydrate stability field in the sediment column shift upward. Methane hydrate located below the lower stability boundary becomes unstable and decomposes. Methane gas is released to the pore water, the concentration gradient becomes steeper, and the upward methane flux increases. Upward migrating methane encounters downward diffusing sulfate in the sulfate-methane transition zone (SMT). Here, methane is oxidized to CO_2 and sulfate is reduced to sulfide (Eqn. 1). The reaction between sulfide and oxidized Fe-species reduces Fe(III) to Fe(II), and phosphate associated with oxidized Fe is released into the pore waters, increasing the phosphorus flux into the oceanic reservoir. Irrespective of which nutrient is limiting, primary production in the photic zone assimilates nutrients into biomass, lowering the inventory and concentration of reactive phosphorus and other nutrients in the oceanic reservoir. The fraction of reactive phosphorus that becomes buried on the continental margin is not necessarily lost to the marine phosphorus cycle. It may conceivably become remobilized by diagenesis during an eventual new glacial cycle.

During times when the sea level remains stable, and assuming that sediment accumulation and burial still take place, methane fuelled diagenesis can nevertheless occur. This is because the migration of the upper and lower boundaries of the methane hydrate stability field tracks the burial of sediment. When this happens, gas hydrates previously located within the hydrate stability field—and thus stable—become exposed to destabilizing conditions and release methane, and subsequently phosphate, to the pore water. A flux of phosphate—what we call a 'background' flux— can therefore be delivered to the ocean even when the sea level remains stable. When sea level change is then superimposed, the net result is to amplify the phosphate flux to the ocean beyond the background flux.

Sea level driven diagenetic transfer of phosphate from sediment to ocean continues throughout the glaciation period, perhaps in spurts because of intervals of stable sea level. When, finally, after the deglaciation, when sea level and pressure on the seafloor have reached stable values, diagenetically driven fluxes from the sediment stabilize on pre-glaciation background values. Towards the end of the glaciation period, the stratification of the water column destabilizes (e.g., Basak et al., 2008), which facilitates vertical mixing and brings CO_2-rich deep water to the photic zone. The biological pump having been weakened by the ongoing biological removal of soluble reactive phosphorus from the

oceanic reservoir and the physical pump having gained strength, transport of nutrient-poor / CO_2 -rich water to the surface ocean will favour the escape (outgassing) of CO_2 into the atmosphere.

4.4. The timing of the exchange of phosphorus between ocean and sediment. The key to understanding the glacial phosphorus cycle lies in the timing of the transformation of phosphorus from one form to another and the transfer from one phosphorus-reservoir to the other. Under the two-reservoir methane-fuelled diagenetic scenario, the transfer of phosphate from the sedimentary reservoir to the oceanic reservoir begins when the sea-level falls. The initial phosphate release from the sedimentary reservoir would likely be a pulse because, occurring at the end of a long time (nearly a complete glacial cycle) of transfer of reactive phosphorus to the sedimentary reservoir, this is when the sedimentary phosphorus inventory would be at a maximum.

The scenarios that have been proposed to explain variations of the CO2 concentration in the atmosphere fall into two groups. A biological pump relies on photosynthesis to convert CO_2 to biomass, thereby lowering the partial pressure of CO_2 in the surface ocean. A physical pump relies on the vast quantity of CO_2 sequestered in the deep ocean that can be brought to the surface ocean by vertical mixing and advection. The net effect of each type of pump—draw-down from the atmosphere or outgassing into the atmosphere— depends on the resulting partial CO_2 pressure gradient across the air-sea interface (e.g., Hain et al., 2014). The ice-core record of atmospheric CO_2 (Petit et al., 1999; Sigman & Boyle, 2000) shows that, during glacial periods, the atmospheric CO_2 concentration decreased gradually from values as high as 280-300 ppm near the beginning of a glaciation to less than 200 ppm at the end. The decrease in atmospheric CO_2 typically took place over about 90,000 years, and was similar for each of the previous three glaciation cycles.The average rate at which atmospheric CO_2 *decreased* throughout the last glacial period was roughly 1 ppm Kyr^{-1}. This is slower than the rate at which atmospheric CO_2 *increased* during the transition from the glacial period to the interglacial period that preceded it (Sowers and Bender, 1995). Ice-core data also show that the atmospheric CO_2 level peaked rapidly during the termination of each glacial period. The methane-driven phosphorus scenario predicts that phosphate is transferred to the ocean from the sedimentary phosphorus reservoir during the early stages of a glacial cycle, after the sea level has begun to fall.

The concentration of CO_2 sequestered in the deep (> 1000m) waters of the oceanic reservoir is higher than in the surface ocean reservoir because a fraction of the organic matter produced in the surface ocean settles towards the deep seafloor and is remineralized by microbial processes. The deep ocean contains nearly ten times more carbon than the atmosphere, surface-ocean, and terrestrial systems combined, and the pCO_2 of the deep-ocean water is well buffered on long time scales via reactions of the carbonate system, including the dissolution of biogenic carbonates. The dissolved inorganic carbon inventory in the deep ocean does not, therefore, respond rapidly to changes in the sinking flux of mineralizable organic matter, but remains high. Deep water is exposed at the ocean surface roughly every 1,000 years or 100 times during a complete glacial cycle (Broecker & Peng, 1982; DeVries & Primeau, 2011; Sigman & Boyle, 2000), which attenuates CO_2 changes on the time scale of glaciations.

5. SUMMARY AND CONCLUSIONS

We have modified the two-reservoir scenario of the marine phosphorus cycle proposed by Broecker (1982a, 1982b) to include a diagenetic mechanism that allows for phosphorus to be exchanged between the sedimentary and the oceanic phosphorus reservoirs on glacial time scales. Within the scenario a coupled series of processes acts upon the glacial – interglacial marine phosphorus cycle (table 1).

During a glaciation period, water is transfered from the ocean to continental ice sheets. The falling sea level lowers the hydrostatic pressure on the seafloor. The pressure change perturbs the stability field of methane hydrates, and methane gas is released into the pore water. The release of methane gas from gas hydrates amplifies the upward flux of methane through the sediment column. In the sulfate-methane-transition zone (SMT), where methane is removed via anaerobic methane oxidation, the increased methane supply increases the demand for sulfate. The sulfate gradient steepens, and the SMT zone moves closer to the sediment-water interface. Reactions within the SMT produce hydrogen sulfide, which reductively dissolves iron oxides. Iron-bound phosphate can then be released into the pore water. The upward directed phosphate gradient steepens, which increases the flux of phosphate towards and across the sediment-water interface and increases the phosphate inventory of the ocean.

Phosphorus is transferred from the oceanic to the sedimentary reservoir by sedimentation and burial of phosphorous-containing biogenic particulate matter resulting from primary production and abiotic particulate matter on which phosphate is adsorbed. Unlike the release of phosphate from the

sediment, the return flux of phosphorus to the sediment and the associated depletion of the oceanic reactive phosphorus inventory do not occur as an event but take place throughout the glacial cycle. Burial of organic matter causes a corresponding loss of phosphorus from the oceanic inventory. If phosphorus were the nutrient limiting primary production at the time leading up to the release, primary production would be stimulated by the added phosphate to the surface ocean, CO_2 would be drawn down from the atmosphere, and the phosphorus inventory would begin to decrease. If, on the other hand, nitrogen nutrients were to become limiting, which is likely when new phosphate is added to the surface ocean reservoir, the rates of primary production, phosphorus burial, and draw-down of atmospheric CO_2 would slow down until the fixed nitrogen to phosphorus ratio became similar to the Redfield ratio. It is therefore not unreasonable to expect that with a gradual depletion of phosphorus in the ocean, a stable N:P ratio would develop, co-limiting primary production in the ocean (e.g., Lenton & Watson, 2000; Lenton & Klausmeier, 2007). As the glaciation progresses, the ocean will gradually become nutrient depleted irrespective of which is the limiting nutrient. This would weaken the biological pump relative to the physical pump (upwelling of deep CO_2-rich water) and set the stage for a tipping point beyond which atmospheric CO_2 is controlled by upwelling of CO_2-rich deep water. The next glaciation period, which is accompanied by sea-level fall, methane-hydrate decomposition, anaerobic methane oxidation, and phosphate release allows the biological pump to once again take control over atmospheric CO_2.

Inventories of reactive particulate phosphorus in the ocean and in continental margin sediments can change on glacial-interglacial time scales as phosphorus is transferred from the sediment column to the water column and *vice versa*. Responding to a fall in sea level, phosphorus is transferred from the sediment to the ocean. This involves destabilization of methane hydrate, an increase of the methane flux through the sediment column, and an increase in the rate of anaerobic methane oxidation. The elevated methane flux drives an increasing demand for sulfate and consequent production of sulfide. Sulfide reduces sedimentary iron oxides and releases associated phosphate to the pore water through which it can migrate across the sediment-water interface and increase the surface ocean inventory of phosphorus. Since sea level fall may not occur as a single event but may include stable periods, phosphate release may likewise occur episodically. The latter would depend on the extent to which the phosphate contained in the sedimentary reservoir has been depleted and on the amount of time available to recharge the sedimentary reservoir between sea-level change events. The link between sea level fall, gas hydrate destabilization and the upward migration of the sulfate-methane-transition zone establishes the timing of phosphate releases to the surface ocean reservoir during the glaciation period, likely during the initial episode of sea level fall.

The proposed scenario capitalizes on elements of Broecker's model and provides another potential trigger to the suite of processes that may have contributed to the rapid glacial-interglacial climate transitions documented in paleo-records.

ACKNOWLEDGEMENTS

No new data are presented in this manuscript, which is inspired by and developed with data in the public domain. These are cited in the references included in the manuscript. B.S. and A.M. gratefully acknowledge the financial support from the Natural Sciences and Engineering Research Council of Canada through their Discovery grants.

REFERENCES

Anschutz, P. & Chaillou, G. (2009). Deposition and fate of reactive Fe, Mn, P, and C in suspended particulate matter in the Bay of Biscay. Continental Shelf Research, 29(8), 1038-1043.

Anschutz, P. & Deborde, J. (2016). Spectrophotometric determination of phosphate in matrices from sequential leaching of sediments. Limnology and Oceanography: Methods, 14(4), 245-256.

Anschutz, P., Zhong, S., Sundby, B., Mucci, A. & Gobeil, C. (1998). Burial efficiency of phosphorus and the geochemistry of iron in continental margin sediments. Limnology and Oceanography, 43(1), 53-64.

Archer, D. (2007). Methane hydrate stability and anthropogenic climate change. Biogeosciences Discussions, 4(2), 993-1057.

Archer, D., Winguth, A., Lea, D. & Mahowald, N. (2000). What caused the glacial/interglacial atmospheric pCO2 cycles? Reviews of Geophysics, 38(2), 159-189.

Barnola, J.M., Raynaud, D.Y.S.N., Korotkevich, Y.S. & Lorius, C. (1987). Vostok ice core provides 160,000-year record of atmospheric CO2. Nature, 329(6138), 408-414.

Basak C., Fröllje, H., Lamy, F., Gersonde, R. Benz, V. Anderson R. F. et al. (2018). Breakup of last glacial deep stratification in the South Pacific. Science, 359, 900–904.

Berner, R.A. (1980). Early Diagenesis: A Theoretical Approach, Princeton University Press.

Berner, R.A., Ruttenberg, K.C., Ingall, E.D. & Rao, J.L. (1993). The nature of phosphorus burial in modern marine sediments. In R. Wollast, F. T. Mackenzie & L. Chou (eds) Interactions of C, N, P and S biogeochemical cycles and global change (pp. 365-378). Springer, Berlin, Heidelberg.

Boetius, A., Ravenschlag, K., Schubert, C.J., Rickert, D., Widdel, F., Gieseke, A., et al. (2000). A marine microbial consortium apparently mediating anaerobic oxidation of methane. Nature, 407(6804), 623-626.

Bohrmann G. & Torres M.E. (2006). Gas hydrates in marine sediments. In H. D. Schulz & M. Zabel (eds.) Marine Geochemistry. (pp. 481-512) Springer, Berlin, Heidelberg.

Borowski, W.S., Paull, C.K. & Ussler, W. (1999). Global and local variations of interstitial sulfate gradients in deep-water, continental margin sediments: Sensitivity to underlying methane and gas hydrates. Marine Geology, 159(1-4), 131-154.

Boyle, E.A. (1986). Paired carbon isotope and cadmium data from benthic foraminifera: Implications for changes in oceanic phosphorus, oceanic circulation, and atmospheric carbon dioxide. Geochimica et Cosmochimica Acta, 50(2), 265-276.

Broecker, W.S., (1982a). Glacial to interglacial changes in ocean chemistry. Progress in Oceanography, 11(2), 151-197.

Broecker, W.S. (1982b). Ocean chemistry during glacial time. Geochimica et Cosmochimica Acta, 46(10), 1689-1705.

Broecker, W.S. (2018). Glacial Cycles. Geochemical Perspectives, 7(2), 167-181.

Broecker, W.S. & Peng, T.H. (1982). Tracers in the Sea. Eldigio Press, New York, 1-690

Burdige, D.J. & Komada, T. (2011). Anaerobic oxidation of methane and the stoichiometry of remineralization processes in continental margin sediments. Limnology and Oceanography, 56(5), 1781-1796.

Burdige, D.J. & Komada, T. (2013). Using ammonium pore water profiles to assess stoichiometry of deep remineralization processes in methanogenic continental margin sediments. Geochemistry, Geophysics, Geosystems, 14(5), 1626-1643.

Canfield, D. E. (1989). Reactive iron in marine sediments. Geochimica et Cosmochimica Acta, 53, 619-632

Canfield, D.E., Thamdrup, B. & Hansen, J.W. (1993). The anaerobic degradation of organic matter in Danish coastal sediments: iron reduction, manganese reduction, and sulfate reduction. Geochimica et Cosmochimica Acta, 57(16), 3867-3883.

Cartapanis, O., Bianchi, D., Jaccard, S.L. and Galbraith, E.D., 2016. Global pulses of organic carbon burial in deep-sea sediments during glacial maxima. *Nature communications*, *7*(1), pp.1-7.

Colman, A.S. & Holland, H.D. (2000). The global diagenetic flux of phosphorus from marine sediments to the oceans: redox sensitivity and the control of atmospheric oxygen levels. SEPM Special Publication No. 66. 53-75. doi.org/10.2110/pec.00.66.0053

Contreras, S., Meister, P., Liu, B., Prieto-Mollar, X., Hinrichs, K.U., Khalili, A., et al. (2013). Cyclic 100-ka (glacial-interglacial) migration of subseafloor redox zonation on the Peruvian shelf. Proceedings of the National Academy of Sciences, 110(45), 18098-18103.

Delaney M. (1998). Phosphorus accumulation in marine sediments and the oceanic phosphorus cycle. Global Biogeochemical Cycles, 12, 563-572.

DeVries, T. & Primeau, F. (2011). Dynamically and observationally constrained estimates of water-mass distributions and ages in the global ocean. Journal of Physical Oceanography, 41(12), 2381-2401.

Dillon, W.P. & Max, M.D. (2000). Oceanic Gas Hydrate. In M.D. Max (ed.) Natural Gas Hydrate in Oceanic and Permafrost Environments (pp. 61-76), Dordrech, NL: Kluwer.

Egger M., Hagens M., Sapart C. J., Dijkstra N., van Helmond N. A. G. M., Mogollón J. M., et al. (2017). Iron oxide reduction in methane-rich deep Baltic Sea sediments. Geochimica et Cosmochimica Acta, 207, 256–276.

Egger, M., Jilbert, T., Behrends, T., Rivard, C. & Slomp, C.P. (2015) Vivianite is a major sink for phosphorus in methanogenic coastal surface sediments. Geochimica et Cosmochimica Acta, 169, 217–235.

Egger, M., Kraal, P., Jilbert, T., Sulu-Gambari, F., Sapart, C. J., Röckmann, T. & Slomp, C. P. (2016) Anaerobic oxidation of methane alters sediment records of sulfur, iron and phosphorus in the Black Sea, Biogeosciences, 13, 5333–5355.

Falkowski, P.G. (1997). Evolution of the nitrogen cycle and its influence on the biological sequestration of CO2 in the ocean. Nature, 387(6630), 272-275.

Filippelli, G.M. (1997). Controls on phosphorus concentration and accumulation in oceanic sediments. Marine Geology, 139(1-4), 231-240.

Foster, G.L. & Rohling, E.J. (2013). Relationship between sea level and climate forcing by CO2 on geological timescales. Proceedings of the National Academy of Sciences, 110(4), 1209-1214.

Galbraith, E. D, Sigman, D., Pedersen, T. & Robinson, R. S. (2008). Past changes in the marine nitrogen cycle. In D. Capone, D. Bronk, M. Mulholland & E. Carpenter (eds.) Nitrogen in the Marine Environment, 2nd edition (pp. 1497-1535), Elsevier. doi 10.1016B978-0-12-372522-6.00034-7.

Ganeshram, R.S., Pedersen, T.F., Calvert, S. & François, R. (2002). Reduced nitrogen fixation in the glacial ocean inferred from changes in marine nitrogen and phosphorus inventories. Nature, 415(6868), 156-159.

Ganeshram, R.S., Pedersen, T.F., Calvert, S.E. & Murray, J.W. (1995). Large changes in oceanic nutrient inventories from glacial to interglacial periods. Nature, 376(6543), 755-758.

Gorman, A.R., Holbrook, W.S., Hornbach, M.J., Hackwith, K.L., Lizarralde, D. & Pecher, I. (2002). Migration of methane gas through the hydrate stability zone in a low-flux hydrate province. Geology, 30(4), .327-330.

Hain, M.P., Sigman, D.M. & Haug, G.H. (2014). The biological Pump in the Past. Treatise on Geochemistry (Second Edition), The Oceans and Marine Geochemistry, 8, 485-517.

Hsu, T. W., Jiang, W. T. & Wang, Y. (2014) Authigenesis of vivianite as influenced by methane-induced sulfidization in cold-seep sediments off southwestern Taiwan. Journal of Asian Earth Sciences. 89, 88–97.

Hyacinthe, C. & Van Cappellen, P. (2004). An authigenic iron phosphate phase in estuarine sediments: composition, formation and chemical reactivity. Marine Chemistry, 91(1-4), 227-251.

Jørgensen, B.B. & Kasten, S. (2006). Sulfur cycling and methane oxidation. In H. D. Schulz & M. Zabel (eds.), Marine Geochemistry (pp. 271-302). Springer,

Kohfeld, K.E., Le Quéré, C., Harrison, S.P. & Anderson, R.F. (2005). Role of marine biology in glacial-interglacial CO2 cycles. Science, 308(5718), 74-78.

Komada, T., Burdige, D.J., Li, H.L., Magen, C., Chanton, J.P. & Cada, A.K. (2016). Organic matter cycling across the sulfate-methane transition zone of the Santa Barbara Basin, California Borderland. Geochimica et Cosmochimica Acta, 176, 259-278.

Kostka, J.E. & Luther III, G.W. (1994). Partitioning and speciation of solid phase iron in saltmarsh sediments. Geochimica et Cosmochimica Acta, 58(7), 1701-1710.

Krom M. D. & Berner, R. A. (1981). The diagenesis of phosphorus in a nearshore marine sediment. Geochimica et Cosmochimica Acta, 45(2), 207-216.

Krom, M.D. & Berner, R.A. (1980). The diffusion coefficients of sulfate, ammonium, and phosphate ions in anoxic marine sediments. Limnology and Oceanography, 25, 327-337.

Kvenvolden, K.A. (1993). Gas hydrates – Geological perspective and global change. Reviews of Geophysics, 31(2), 173-187.

Lambeck, K., Rouby, H., Purcell, A., Sun, Y. & Sambridge, M. (2014). Sea level and global ice volumes from the Last Glacial Maximum to the Holocene. Proceedings of the National Academy of Sciences, 111(43), 15296-15303.Lenton, T.M. & Klausmeier, C.A. (2007). Biotic stoichiometric controls on the deep ocean N: P ratio. Biogeosciences, 4, 353-367.

Lenton, T.M. & Watson, A.J. (2000). Redfield revisited: 1. Regulation of nitrate, phosphate, and oxygen in the ocean. Global Biogeochemical Cycles, 14(1), 225-248.

Lijklema, L. (1977). The role of iron in the exchange of phosphate between water and sediments. In: H. L. Golterman (ed.), Interactions Between Sediments and Fresh Water. (pp. 313-317) Dr W. Junk Publishers, The Hague.

Liu, J., Izon, G., Wang, J., Antler, G., Wang, Z. & Egger, M. (2018) Vivianite formation in methane-rich deep-sea sediments from the South China Sea. Biogeosciences, 15, 6329-6348.

März, C., Hoffmann, J., Bleil, U., De Lange, G. & Kasten, S. (2008) Diagenetic changes of magnetic and geochemical signals by anaerobic methane oxidation in sediments of the Zambezi deep-sea fan (SW Indian Ocean). Marine Geology, 255, 118–130.

März, C., Riedinger, N., Sena, C. & Kasten, S. (2018). Phosphorus dynamics around the sulphate-methane transition in continental margin sediments: Authigenic apatite and Fe (II) phosphates. Marine Geology, 404, 84-96.

Meister, P., Bernasconi, S.M., Vasconcelos, C. & McKenzie, J.A. (2008). Sea level changes control diagenetic dolomite formation in hemipelagic sediments of the Peru Margin. Marine Geology, 252(3-4), pp.166-173.

Meister, P., McKenzie, J.A., Vasconcelos, C., Bernasconi, S., Frank, M., Gutjahr, M. & Schrag, D.P. (2007). Dolomite formation in the dynamic deep biosphere: results from the Peru Margin. Sedimentology, 54(5),1007-1032.

Millero F.J., Huang F., Zhu X. & Zhang J.-Z. (2001). Adsorption and desorption of phosphate on calcite and aragonite in seawater. Aquatic Geochemistry, 7(1), 33-56.

Nauhaus, K., Boetius, A., Krüger, M. & Widdel, F. (2002). In vitro demonstration of anaerobic oxidation of methane coupled to sulphate reduction in sediment from a marine gas hydrate area. Environmental Microbiology, 4(5), 296-305.

Niewöhner, C., Hensen, C., Kasten, S., Zabel, M. & Schulz, H.D. (1998). Deep sulfate reduction completely mediated by anaerobic methane oxidation in sediments of the upwelling area off Namibia. Geochimica et Cosmochimica Acta, 62(3), 455-464.

Paull, C.K., Brewer, P.G., Ussler, W., Peltzer, E.T., Rehder, G. & Clague, D. (2002). An experiment demonstrating that marine slumping is a mechanism to transfer methane from seafloor gas-hydrate deposits into the upper ocean and atmosphere. Geo-Marine Letters, 22(4), 198-203.

Paull, C.K., Ussler, W. & Dillon, W.P. (1991). Is the extent of glaciation limited by marine gas hydrates? Geophysical Research Letters, 18(3), 432-434.

Peacock, S., Lane, E. & Restrepo, J.M. (2006). A possible sequence of events for the generalized glacial-interglacial cycle. Global Biogeochemical Cycles, 20, GB2010. doi.org/10.1029/2005GB002448

Petit, J.R., Jouzel, J., Raynaud, D., Barkov, N.I., Barnola, J.M., Basile, I., et al. (1999). Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. Nature, 399(6735), 429-436

Poulton, S.W. & Canfield, D.E. (2005). Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. Chemical Geology, 214(3-4), 209-221.

Riedinger, N., Formolo, M.J., Lyons, T.W., Henkel, S., Beck, A. & Kasten, S. (2014). An inorganic geochemical argument for coupled anaerobic oxidation of methane and iron reduction in marine sediments. Geobiology, 12(2), 172-181.

Roberts, A.P. (2015). Magnetic mineral diagenesis. Earth-Science Reviews, 151, 1-47.

Rothe, M., Kleeberg, A. & Hupfer, M. (2016) The occurrence, identification and environmental relevance of vivianite in waterlogged soils and aquatic sediments. Earth-Science Review, 158, 51–64.

Ruppel, C.D. & Kessler, J.D. (2017). The interaction of climate change and methane hydrates. Reviews of Geophysics, 55(1), 126-168.

Ruttenberg, K.C. (2003). The global phosphorus cycle. In: W.H. Schleisinger (ed.), Treatise on Geochemistry, Vol. 8, pp. 585-643.

Siddall, M., Rohling, E.J., Almogi-Labin, A., Hemleben, C., Meischner, D., Schmelzer, I. & Smeed, D.A. (2003). Sea level fluctuations during the last glacial cycle. Nature, 423(6942), 853-858.

Sigman, D.M. & Boyle, E.A. (2000). Glacial/interglacial variations in atmospheric carbon dioxide. Nature, 407(6806), 859-869.

Sigman, D.M., Hain, M.P. & Haug, G.H. (2010). The polar ocean and glacial cycles in atmospheric CO2 concentration. Nature, 466(7302), 47-55.

Slomp, C. P., Mort, H. P., Jilbert, T., Reed, D. C., Gustafsson, B. G. & Wolthers, M. (2013) Coupled dynamics of iron and phosphorus in sediments of an oligotrophic coastal basin and the impact of anaerobic oxidation of methane, PloS one, 8, e62386

Smith, S.V. (1984). Phosphorus versus nitrogen limitation in the marine environment. Limnology and Oceanography, 29(6), 1149-1160.

Sowers, T. & Bender, M. (1995). Climate records covering the last deglaciation. Science, 269(5221), 210-214.

Sundby B., Gobeil C., Silverberg N. & Mucci A. (1992). The phosphorus cycle in coastal marine sediments. Limnology and Oceanography, 37, 1129-1145.

Sundby, B., Lecroart, P., Anschutz, P., Katsev, S., & Mucci, A. (2015). When deep diagenesis in Arctic Ocean sediments compromises manganese-based geochronology. Marine Geology, 366, 62-68.

Tyrrell, T. (1999). The relative influences of nitrogen and phosphorus on oceanic primary production. Nature, 400(6744), 525-531.

Wallmann, K. (2010). Phosphorus imbalance in the global ocean? Global Biogeochemical Cycles, 24(4), GB4030. doi:10.1029/2009GB003643.

Wallmann, K., Schneider, B. & Sarnthein, M. (2016). Effects of eustatic sea level change, ocean dynamics, and nutrient utilization on atmospheric pCO2 and seawater composition over the last 130 000 years: a model study. Climate of the Past, 12(2), 339-375.

Yao, W. & Millero, F.J. (1996). Adsorption of phosphate on manganese dioxide in seawater. Environmental Science & Technology, 30(2), 536-541.

Figure captions

Figure 1. A simple two-reservoir representation of the oceanic phosphorus cycle.

Figure 2. Porewater profiles for relevant species (CH_4/SO_4/Fe(II)/H_2S). Note that the SMT migrates vertically when forced by variable CH4 fluxes.

Table captions

Table 1. The glacial-interglacial phosphorus cycle: Events and consequences.

Figure 1.

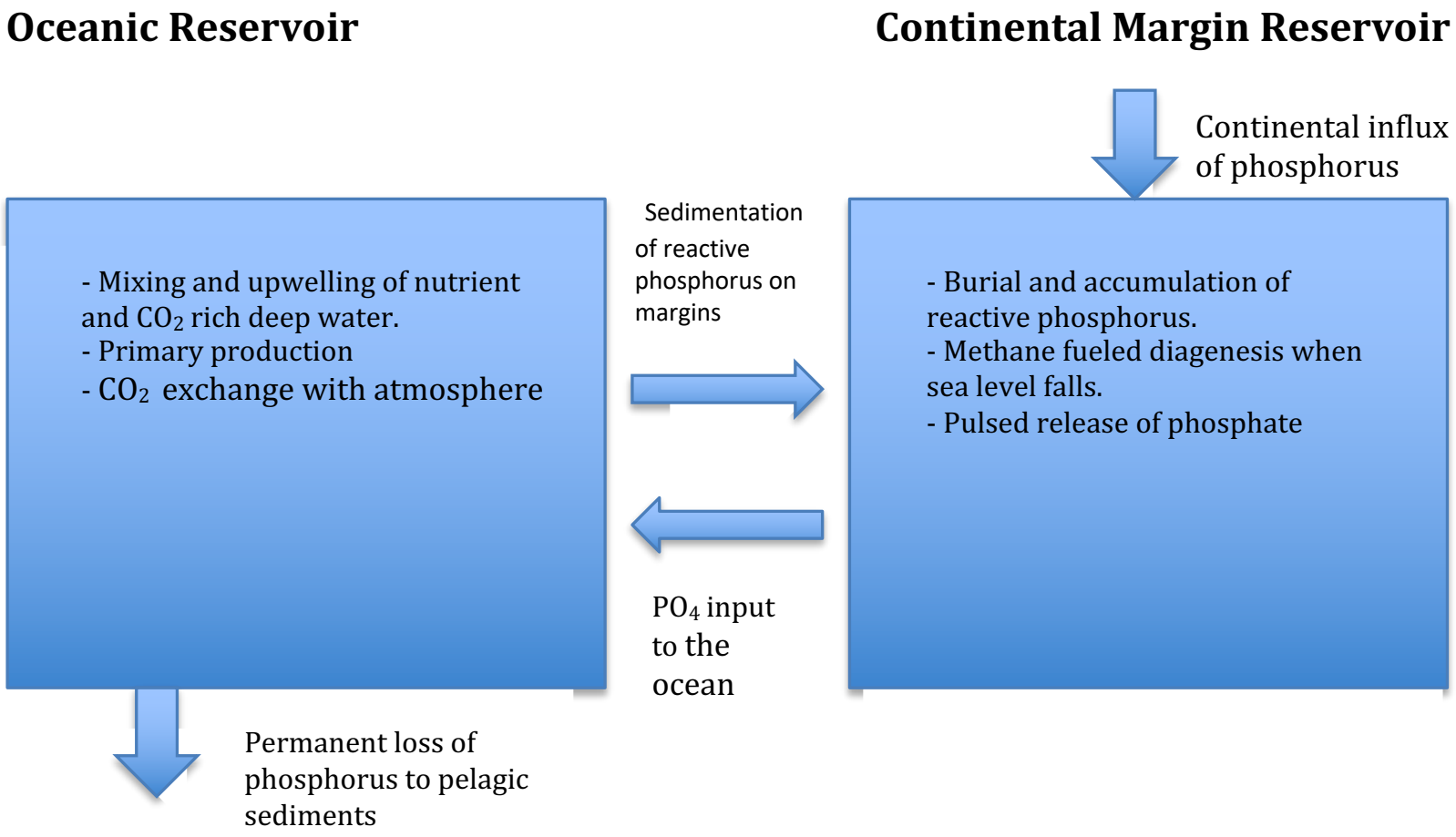
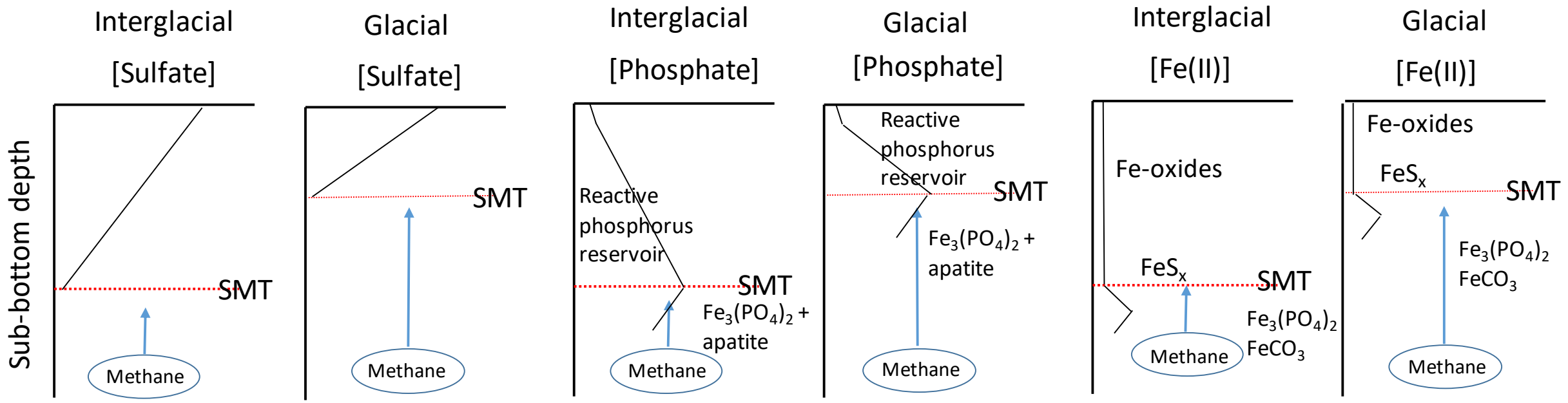

Oceanic Reservoir
Continental Margin Reservoir
Continental influx of phosphorus
- Mixing and upwelling of nutrient and CO_2 rich deep water.
- Primary production
- CO_2 exchange with atmosphere
Sedimentation of reactive phosphorus on margins
- Burial and accumulation of reactive phosphorus.
- Methane fueled diagenesis when sea level falls.
- Pulsed release of phosphate
PO_4 input to the ocean
Permanent loss of phosphorus to pelagic sediments

Figure 2.


Sub-bottom depth
Interglacial
[Sulfate]
SMT
Methane
Glacial
[Sulfate]
SMT
Methane
Interglacial
[Phosphate]
Reactive
phosphorus
reservoir
SMT
$Fe_3(PO_4)_2$ +
apatite
Methane
Glacial
[Phosphate]
Reactive
phosphorus
reservoir
SMT
$Fe_3(PO_4)_2$ +
apatite
Methane
Interglacial
[Fe(II)]
Fe-oxides
FeS_x
SMT
$Fe_3(PO_4)_2$
$FeCO_3$
Methane
Glacial
[Fe(II)]
Fe-oxides
FeS_x
SMT
$Fe_3(PO_4)_2$
$FeCO_3$
Methane

EVENTS	IMPACTS	NOTES
1. A glacial cycle begins	Temperature decreases globally, ice builds up on the continents, sea level begins to fall	
2. The pressure on the sea floor decreases	The upper and lower boundaries of the methane hydrate stability field in the sediment column shift upward	
3. Methane hydrate located below the lower stability boundary becomes unstable and decomposes	Methane is released to the pore water, the methane concentration gradient steepens, and the upward methane flux increases	*Had the sea level remained stable, methane fuelled diagenesis would nevertheless have taken place and a flux of phosphate—which we call a 'background' flux—would have been delivered to the ocean. This is because the slow upward displacement of the methane hydrate stability field caused by accumulation and burial of sediment would support an upward directed methane flux. The result of sea level fall is therefore to increase the phosphate flux above and beyond the background.*
4. Upward diffusing methane encounters downward diffusing sulfate, which increases the rate of anaerobic methane oxidation (AMO) in the sulfate-methane transition zone (SMT)	The SMT moves upward in the direction of the sediment water interface	*Methane can also be oxidized using other electron acceptors such as manganese oxides, which would also release adsorbed phosphate to the pore water.*
5. Pore-water hydrogen sulfide accumulates at the displaced SMT	Hydrogen sulfide reduces Fe (III) to Fe (II), thereby releasing phosphate associated with Fe oxides into the pore water. A phosphate maximum appears within the SMT, which supports upward and downward fluxes of phosphate. Ferrous sulfide precipitates.	*The upper part of the sediment column, located above the methane oxidation zone, contains reactive phosphorus that was delivered and buried during the previous glacial cycle. This accumulated mass of phosphorus is available for conversion to phosphate and may be thought of as a limiting factor controlling the expansion of the oceanic phosphorus inventory during a glaciation cycle.*
6. The zone in the sediment column within which phosphate associated with iron oxides can be released expands in the direction of the sea floor	The phosphate concentration gradient steepens and the phosphate flux towards the sediment-water interface and into the ocean increases	*The kinetics of iron oxide reduction by H2S depends on the reactivity of the oxides, which depends on the mineralogy, time since deposition, etc. Sequential analysis of sediments suggests that the most reactive forms of iron oxide occur in the upper part of the sediment column. With time these oxides become exhausted or converted to less reactive forms with depth (time) in the sediment.*
7. Nutrients are assimilated by primary producers and incorporated in biomass.	Irrespective of which nutrient is limiting, primary production incorporates nutrient elements in organic matter, which settles to the seafloor and is progressively buried	*The part of the export production that reaches the seafloor in the deep abyssal ocean is oxidized aerobically, and the phosphorus it contains is converted to stable poorly soluble minerals such as fluorapatite and is removed from the oceanic phosphorus cycle. Reactive phosphorus in the material that settles on the continental*

		margin is available for diagenesis and may be remobilized and returned to the ocean.
8. Phosphate is released into the oceanic surface layer, temporarily decoupling the oceanic P and C cycles	Reduction of Fe oxides in continental margin sediments delivers phosphate to the upper water column. Oxidation of organic matter settling through the abyssal water column enriches deep water in CO_2. Oxidation in the underlying sediment converts phosphorus to stable phosphorous minerals	This is supported by observations: global rate of organic matter burial is maximal during the glaciation (Cartapanis et al. 2016); Boyle (1986); Wallmann, (2010)
9. Stratification of the water column breaks down during the termination of the deglaciation, destabilizes the water column, and facilitates vertical mixing. CO_2 rich bottom water is transported to the surface ocean. Degassing releases CO_2 to the atmosphere.	CO_2 rich, nutrient poor water is brought to the surface. This weakens of the biological pump, which would otherwise draw down CO_2 from the atmosphere. The partial pressure difference would be controlled by the supply of CO_2 from the deep ocean. The CO_2 flux would be directed from the ocean to the atmosphere and create a peak in atmospheric CO_2.	
10. Upon termination of the glaciation the sea level rises and lowers the pressure on the sea floor.	The fluxes of methane and diagenetically released phosphate become weaker and return to pre-glaciation background levels	