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Sedimentary C_{org}:P ratios, paleocean ventilation, and Phanerozoic atmospheric pO_2

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Abstract

The C_{org}:P ratios of organic-rich facies (TOC > 1%) exhibit considerable variation through the Phanerozoic, from < 10:1 in the Permian Phosphoria Formation to > 1000:1 in some Devonian black shales. Relative to the composition of phytoplankton (C:P ~ 106:1), which provide the bulk of organic C and P to organic-rich marine sediments, the range of Phanerozoic sedimentary C_{org}:P ratios largely reflects the influence of benthic redox conditions on diagenetic pathways of C and P remobilization. Enhanced preservation of organic C at lower redox potentials combined with enhanced sedimentary retention of remineralized organic P at higher redox potentials results in a strong relationship between benthic redox conditions and sedimentary C_{org}:P ratios. The strong secular coherence of the Phanerozoic C_{org}:P record (i.e., limited variation within narrow time slices) suggests that these ratios are controlled primarily by factors influencing benthic redox conditions on a global scale, such as atmospheric pO_2. Inversion and scaling of the Phanerozoic C_{org}:P record yields a new atmospheric pO_2 model that has strong similarities to existing models based on elemental and isotopic mass balances, yet differs in some potentially significant respects. In particular, the new model suggests that atmospheric pO_2 was markedly lower during the Early to Middle Paleozoic than previously inferred. During most of the Devonian, atmospheric O_2 levels may have been sufficiently low (< 13%) as to prevent the sustained combustion of plant material. This feature of the model may account for an anomalous gap in the fossil charcoal record during the Devonian. The redox-dependent burial of P in the ocean results in positive and negative feedback mechanisms that tend to stabilize atmospheric oxygen concentrations on geologic timescales. Temporal variations in the burial of P relative to C suggest that the strength of these feedback mechanisms varied over the Phanerozoic.

Keywords: Phosphorus; Organic carbon; Oxygen; Redox; Nutrient cycling

1. Introduction

1.1. The marine phosphorus cycle

The marine P cycle is closely linked to the production of molecular oxygen and, hence, atmospheric O_2 levels. The influence of redox-sensitive P burial in marine sediments on marine productivity has been explored in a number of recent global models (Van Cappellen and Ingall, 1994, 1996; Lenton and Watson, 2000a,b; Wallmann, 2003). One idea incorporated in these models is that at comparatively short timescales ($<10^3$ yr) enhanced benthic P fluxes in oxygen-depleted depositional environments, i.e., from the sediment to the overlying water column, have the potential to enhance primary productivity. Greater primary production increases the sinking flux of organic C, which intensifies

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respiratory oxygen demand in the water column, thus creating a positive feedback loop. At longer timescales ($>10^6$ yr), benthic P fluxes are part of a larger, negative feedback system that operates via its influence on atmospheric pO_2. Burial of organic C greatly reduces its chances for respiration by oxygen, which ultimately leads to increasing atmospheric oxygen concentrations. Increases in atmospheric oxygen and, subsequently, dissolved oxygen in seawater eventually counteract decreases in bottomwater oxygen associated with locally enhanced organic C sinking fluxes (Van Cappellen and Ingall, 1996). This combination of positive and negative feedbacks has been hypothesized to act as a key control that stabilizes atmospheric O_2 levels on geologic timescales (Van Cappellen and Ingall, 1994, 1996; Colman and Holland, 2000).

Owing to its importance in these feedback cycles, an improved understanding of benthic P fluxes through time is needed. C:P ratios in marine phytoplankton are commonly cited as ~106:1 (the “Redfield ratio”; Redfield, 1958; Redfield et al., 1963). In fact, phytoplankton C:P can vary from ~50:1 to ~150:1 (Ryther and Dunstan, 1971; Martin and Knauer, 1973; Broecker and Peng, 1982; DeMaster et al., 1996; Hedges et al., 2002; Li and Peng, 2002; Van der Zee et al., 2002) and may average closer to 117:1 (Anderson and Sarmiento, 1994). Bacterial decay of organic matter tends to preferentially remineralize P-rich compounds such as proteins and nucleic acids; the organic residue is typically enriched several-fold in P-poor carbohydrates (Cauwet, 1978; Peng and Broecker, 1987; Clark et al., 1999). This typically results in a 2- to 10-fold increase of the organic carbon-to-organic phosphorus ratio, $(C{:}P)_{org}$, in marine sediments relative to that of marine plankton (Toth and Lerman, 1977; Krom and Berner, 1981; Haddad and Martens, 1987; Martens, 1993; Li and Peng, 2002). Depending in part on benthic redox conditions, some or all of the P released during organic matter decomposition may remain in the sediment as a result of adsorption and complexation reactions, storage of polyphosphates by microorganisms, and, ultimately, formation of authigenic phosphate minerals (Froelich et al., 1988; Glenn et al., 1994; Jarvis et al., 1994; DeMaster et al., 1996; Hensen et al., 1998; Sannigrahi and Ingall, 2005). Sedimentary $(C{:}P)_{org}$ ratios have been used to proxy benthic nutrient fluxes in paleoenvironments (Krom and Berner, 1981; Mach et al., 1987; Ingall et al., 1993; Murphy et al., 2000a,b; Werne et al., 2002), but the ratio of organic carbon to reactive P (see Section 2.1), $C_{org}{:}P_{reac}$, may provide a better measure of the retention versus diffusive loss of remineralized organic P in ancient depositional systems (Ruttenberg and Berner, 1993; Filippelli and Delaney, 1996; Ruttenberg and Goñi, 1997; Anderson et al., 2001; Latimer and Filippelli, 2001). Unfortunately, the measurements required to calculate the $C_{org}{:}P_{reac}$ proxy ratio have been undertaken in comparatively few studies. In this study, we (1) demonstrate that $C_{org}{:}P_{reac}$ ratios can be effectively proxied in organic-rich facies by $C_{org}{:}P$, the ratio of organic carbon to total phosphorus; (2) document secular variation in the $C_{org}{:}P$ ratios of organic-rich facies through the Phanerozoic; (3) investigate connections between Phanerozoic $C_{org}{:}P$ ratios, the ventilation of paleoseas, and secular trends in atmospheric pO_2; and (4) consider the implications of these connections for feedbacks between the marine P cycle and atmospheric oxygen.

1.2. Redox controls on the marine phosphorus cycle

Most phosphorus (P) in organic-rich facies, defined here as having a total organic carbon (TOC) concentration >1% (dry bulk weight), is delivered to the sediment bound in organic matter. The ultimate fate of P derived from remineralization of organic matter depends on bottomwater oxygen concentrations (Fig. 1). Under anoxic bottomwaters, organic P released to sediment porewater during degradation of organic matter mostly diffuses out of the sediment (Ingall et al., 2005). Under

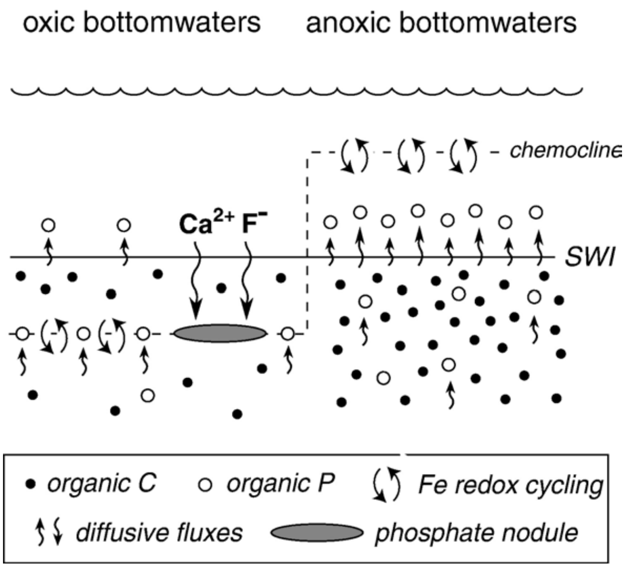

Fig. 1. Sedimentary P cycle model (e.g., Froelich et al., 1988; Glenn et al., 1994; Jarvis et al., 1994; Föllmi, 1996; Filippelli, 2002). Under oxic bottomwaters (left), redox cycling of Fe within the sediment facilitates retention of remineralized organic P. P that is initially sorbed onto Fe-oxyhydroxides subsequently may be fixed in authigenic carbonate fluorapatite phases as Ca^{2+} and F^- diffuse into the sediment. Under anoxic bottomwaters (right), the lack of ferric iron phases allows most remineralized P to diffuse out of the sediment. SWI = sediment–water interface.

oxic conditions, on the other hand, a greater proportion of remineralized organic P can be trapped in the sediment through a combination of mechanisms including adsorption and complexation reactions (mainly involving Fe-oxyhydroxides; Slomp et al., 1996) and biological sequestration of polyphosphates (Davelaar, 1993; Sannigrahi and Ingall, 2005). These P trapping mechanisms can ultimately lead to conditions in sediment porewaters conducive to the formation of authigenic phosphate minerals which represent a long-term sink for P (Froelich et al., 1982, 1988; Heggie et al., 1990; Glenn et al., 1994; Jarvis et al., 1994; Föllmi, 1996; Filippelli, 2002).

The sensitivity of the P burial flux to benthic redox conditions (i.e., the concentration of dissolved O_2 or H_2S at the seafloor) has commonly been explained by cycling of P associated with reducible ferric oxyhydroxide phases (Froelich et al., 1979; Bostrom et al., 1988; Sundby et al., 1992; McManus et al., 1997; Filippelli, 2002). When Fe-oxyhydroxides are reductively dissolved, the associated phosphate is released. In sediments overlain by anoxic bottomwaters, the released iron and phosphate can readily diffuse out of the sediments (Fig. 1). On the other hand, at sites overlain by oxic bottomwaters, the transition between oxidizing and reducing conditions is located within the sediment. Oxic conditions in the upper few centimeters of sediment prevent the reduction of ferric oxyhydroxides and subsequent release of associated P. Additionally, in this situation ferrous ions diffusing from the deeper anoxic regions of the sediment column can precipitate as ferric oxyhydroxides in the oxic/suboxic upper sediment layers. These newly precipitated ferric oxyhydroxides can absorb and trap phosphate released during early diagenesis. Another potential mechanism for redox-sensitive P cycling is polyphosphate metabolism by organisms living at the oxic–anoxic transition in the sediment. This mechanism is based on the ability of certain bacteria and protozoan genera to store P as intercellular polyphosphate granules under aerobic conditions (Schulz and Schulz, 2005; Sannigrahi and Ingall, 2005; Ingall et al., 2005). Polyphosphate metabolism occurs along a redox potential range that overlaps microbially mediated iron reduction (Davelaar, 1993). Thus, in a similar fashion to the cycling of Fe and P around the sediment oxic–anoxic transition, P from polyphosphates remineralized in the deeper anoxic portions of the sediment can be sequestered by polyphosphate formation by organisms in the higher, oxic portions of the sediment column. Both redox-sensitive cycling mechanisms may retain P in the sediment for a period sufficient to allow for the slow growth of authigenic phosphate phases, which typically requires $\sim 10^2$–10^6 yr (Burnett, 1980; Burnett et al., 1982; Van Cappellen and Berner, 1988; O'Brien et al., 1990; Anderson et al., 2001). Because P retention is promoted by oxic bottomwaters whereas organic P delivery to the sediment is enhanced by benthic oxygen deficiency, net sedimentary P accumulation rates are often greatest in suboxic settings (e.g., within the NO_3^- reducing zone) and, in particular, under fluctuating redox conditions (Jarvis et al., 1994).

Evidence in modern sediments derived either from direct measurement of benthic fluxes or fluxes calculated from porewater profiles suggests that the presence of anoxic bottomwaters enhances the release of P relative to C from organic matter (Ingall and Jahnke, 1994, 1997; McManus et al., 1997; Colman and Holland, 2000). In certain situations, suboxic bottomwaters may also enhance the release of P from marine sediments (McManus et al., 1997; Colman and Holland, 2000). The strong influence of redox potential on benthic P fluxes is underscored by a recent work in Effingham Inlet, where an anoxic site yielded a ~5× greater flux to the overlying water column than an otherwise similar oxic site (Ingall et al., 2005; Sannigrahi and Ingall, 2005). Highly significant, small-scale relationships between redox potential and benthic P fluxes have been demonstrated in various marine settings, including the Baltic Sea (Emeis et al., 2000) and the northeast Atlantic (Van der Zee et al., 2002). In other areas, the spatial distribution of authigenic phosphate phases provides indirect evidence for control of benthic P fluxes by redox potential. For example, phosphate nodules are found in abundance along the upper and lower boundaries of the oxygen minimum zone on the Peru Shelf (Burnett, 1980; Burnett et al., 1982; Froelich et al., 1988). Redox control of sedimentary P retention has been shown to operate also in intermittently anoxic lakes (Gächter et al., 1988; Carignan and Lean, 1991; Gächter and Meyer, 1993) and soils (Melillo and Gosz, 1983; Stevenson, 1994).

A survey of C_{org}:P ratios in modern marine environments and their relationship to bottomwater O_2 and H_2S concentrations confirms the importance of redox controls on sedimentary P retention (Fig. 2). Although the ranges of C_{org}:P ratios for these environments can be large (e.g., ~30–400:1 for the Black Sea) and broadly overlapping, statistically significant differences exist between the median values for most environments. The highest median C_{org}:P ratios are exhibited by permanently anoxic environments, including the inner basin of Effingham Inlet (~200:1), Framvaren Fjord (~180:1), and the Black Sea (~150:1). Intermediate C_{org}:P ratios are exhibited by suboxic and intermittently anoxic environments, including the outer basin of Effingham

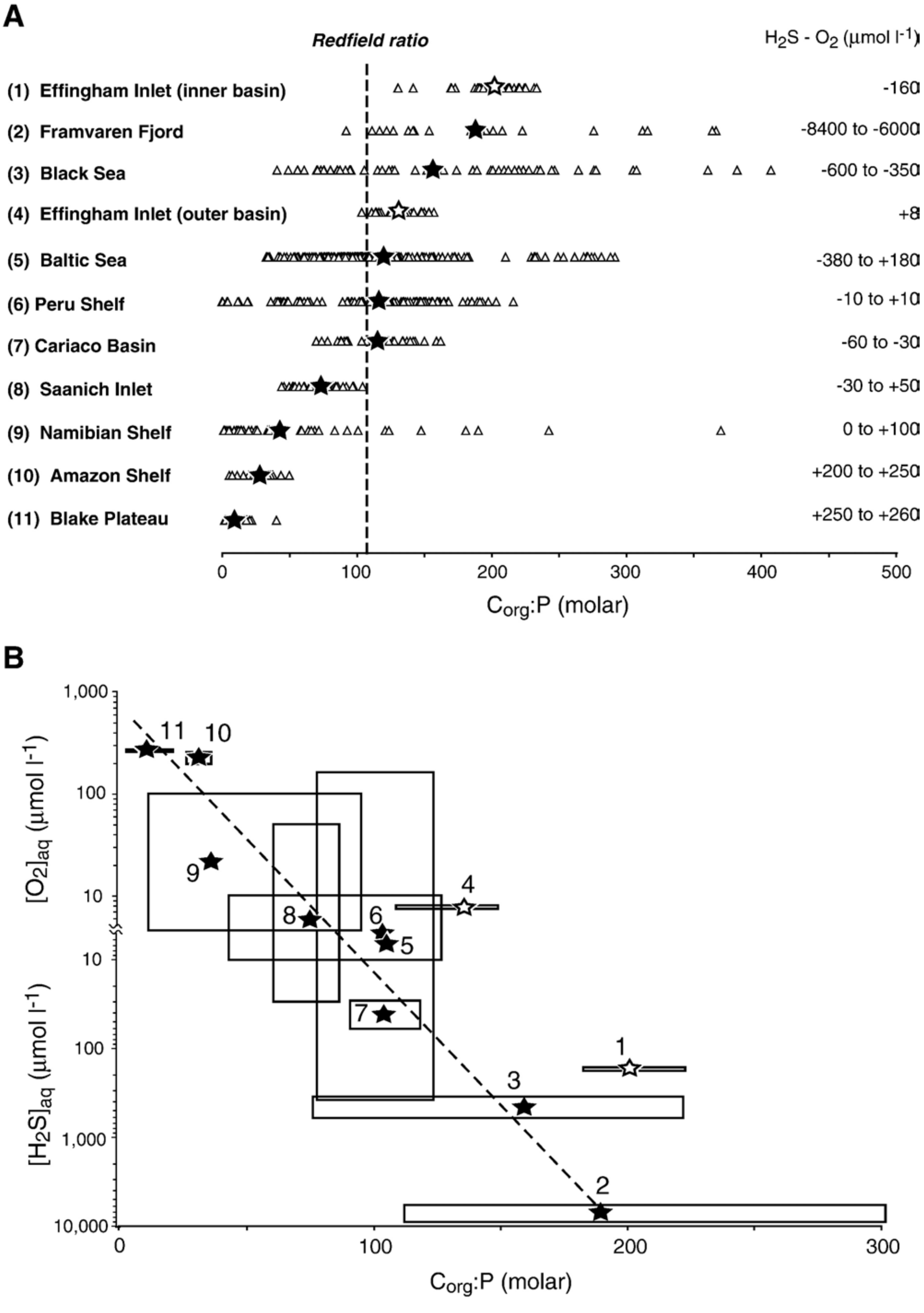

Fig. 2. (A) C_{org}:P ratios of modern marine sediments (open triangles; median values given by solid stars). The Redfield ratio of 106:1 is shown for reference. Sediment C_{org}:P ratios are mostly <50:1 in oxic–suboxic environments and ~50–300 in anoxic environments. The range of observed deepwater redox conditions for each environment is given at the right. (B) Relationship of C_{org}:P ratios to deepwater redox status. Boxes represent the median (±1 s.d.) for C_{org}:P ratios and the full range of observed redox conditions. Dashed diagonal line is a best-fit regression through the data, excluding the two Effingham Inlet data points ($r^2 = 0.95$, $p(\alpha) < 0.01$). Data sources: Hirst (1974), Suess (1981), Calvert and Price (1983), Skei (1986), François (1987), Froelich et al. (1988), Brumsack (1989), Lyons (1992), Ruttenberg et al. (1997), Yarincik (1997), Bianchi et al. (2000), Emeis et al. (2000), Anderson et al. (2001), Emelyanov (2001), Filippelli (2001), and Ingall et al. (2005).

Inlet (~130:1), the Baltic Sea, Peru Shelf, the Cariaco Basin (all ~110:1), and Saanich Inlet (~75:1). Still lower median C_{org}:P ratios are encountered on the oxic–suboxic Namibian Shelf (~40:1) and fully oxic Amazon Shelf and Blake Plateau (<30:1). These median values exhibit a strong correlation to benthic redox potential as represented by O_2 and H_2S concentrations (Fig. 2B; $r^2 = 0.95$, $p(\alpha) < 0.01$). The data points representing the outer suboxic and inner sulfidic basins of Effingham Inlet were excluded from this calculation as the benthic redox status of these locales has been determined only once (Hurtgen et al., 1999); nonetheless, the differences in C_{org}:P ratios between the two basins are consistent with a dominant redox control. The strength of the relationship shown in Fig. 2 suggests that benthic redox conditions generally exert a strong, albeit locally variable, control on sedimentary C_{org}:P ratios. Although aqueous H_2S concentrations probably do not directly modify sedimentary C_{org}:P ratios, they do influence the rate of consumption of dissolved oxygen in sinking hyperpycnal watermasses and, hence, the likelihood that molecular oxygen will penetrate to the seafloor during a given deepwater renewal event. For this reason, the correlation of C_{org}:P ratios with benthic redox potential extends to sulfidic environments (Fig. 2B).

2. Results

2.1. Phosphorus speciation

Total sedimentary P is comprised of exchangeable (or adsorbed), Fe-bound, authigenic, organic, and detrital fractions (Berner, 1973; Filippelli, 2002). These different fractions can be quantified using sequential extraction procedures (Aspila et al., 1976; Filipek and Owen, 1981; Ruttenberg, 1992). The Fe-bound fraction consists of P associated with ferric oxyhydroxide phases. The authigenic fraction is generally dominated by P in diagenetically precipitated carbonate fluorapatites. Because of the operational nature of the chemical separation procedures used in the sequential extraction methods the authigenic fraction can also include P in allochthonous biogenic apatite and carbonate minerals (Suess, 1981; Froelich et al., 1988). The detrital fraction is hosted mainly by apatite of igneous or metamorphic origin, although P can reside in rare earth phosphate minerals, feldspars, and clay minerals as well (Rasmussen, 1996). Apart from that bound in the crystal lattices of detrital minerals, P is delivered to the sediment mainly as a component of organic matter. Release of organic P to porewaters during degradation of organic matter and its subsequent incorporation into mineral phases accounts for most P in the exchangeable, Fe-bound, and authigenic fractions. Owing to differences in diagenetic mobility, a distinction is made between P that is organically sourced ("reactive P") and P that is detritally sourced ("non-reactive P") (Ruttenberg, 1992; Filippelli, 2002).

P speciation analysis has been carried out on a relatively limited number of marine sediments. Averaging the published data available for 18 units, the following proportions of different P fractions are obtained (mean ± 1 s.d.): 18(±12)% for organic P, 9 (±13)% for exchangeable P, 21(±16)% for Fe-bound P, 40(±25)% for authigenic P, and 13(±10)% for detrital P (Fig. 3). Total reactive P, comprised of the first four fractions above, averages 87(±10)%. Thus, total P in marine sediments is usually dominated by reactive P. The amount of detritally sourced P is generally <20% of total P, and in only one of the units surveyed does detrital P substantially exceed 20%: the FOAM site in Long Island Sound, where detrital P comprises 42% of total P (Ruttenberg and Berner, 1993). The high proportion of detrital P at the FOAM site is likely a reflection of the close proximity of the site to local sources of apatite-bearing igneous and metamorphic rocks and of enhanced weathering fluxes of detrital minerals as a consequence of Pleistocene glaciation.

Some general conclusions can be reached based on the P speciation data in Fig. 3 and the studies from which the data are drawn. First, with the exception of the detrital fraction, there is no apparent relationship between depositional setting and the proportions of different P species. P species vary asystematically among open-marine, restricted marine, continental shelf, and coastal environments. As expected, detrital P fractions tend to be lower in open-marine settings, consistent with a proportionally lower flux of detrital material into deep-ocean basins. Second, the correlation between average TOC content and detrital P fraction for the 18 units shown in Fig. 3 is statistically insignificant. Although the range of TOC values for these units is more limited (0.1–4.0%) than for the Phanerozoic organic-rich shales of Table 1 (1.0–25.5%), this observation suggests that the latter may be expected to have similar proportions of detrital P to the former. Third, P speciation reflects the cumulative effect of diagenetic transformations of P with time. Authigenic P tends to increase at the expense of exchangeable, Fe-oxide, and organic P with depth and age in sediments (Ruttenberg and Berner, 1993; Filippelli and Delaney, 1996; Ruttenberg et al., 1997; Anderson et al., 2001). The $(C{:}P)_{org}$ ratio of a sediment generally increases during diagenesis, whereas its C_{org}:P_{reac} ratio often does not. For reasons discussed above, the reactive P fraction more accurately reflects the degree

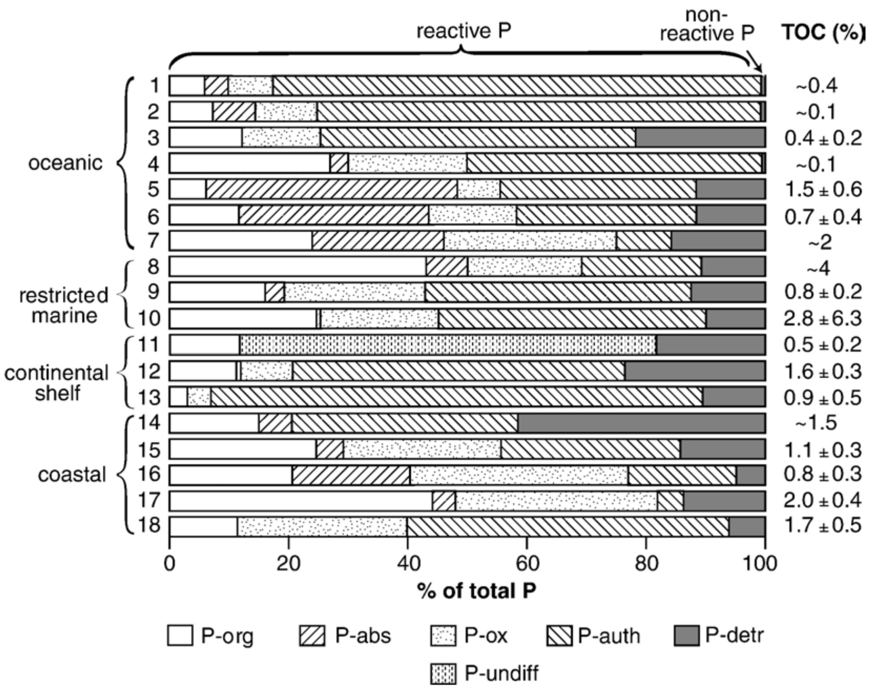

Fig. 3. Phosphorus speciation data. The non-reactive (i.e., detrital) P fraction ranges from <1% to 42% of total P, but a majority of units (11 of 18) yield values between 10 and 20%. The mean (±1 s.d.) TOC content of each unit is shown to the right; note that many of these are not organic-rich facies (i.e., mean TOC<1%). "P-undiff" represents undifferentiated, non-organic reactive P in unit 11. Data sources: (1–2) Filippelli and Delaney (1996); (3) Tamburini et al. (2002); (4, 8, 16) Berner et al. (1993); (5–6) Schenau et al. (2005); (7) Schenau and De Lange (2001); (9) Eijsink et al. (2000); (10) Slomp et al. (2004); (11) Filipek and Owen (1981); (12) Delaney and Anderson (2000); (13) Tamburini et al. (2003); (14–15) Ruttenberg and Berner (1993); (17) Vink et al. (1997); (18) Filippelli (2001).

of retention of organic P in the sediment than the organic P fraction, and C_{org}:P_{reac} ratios are to be preferred over $(C{:}P)_{org}$ ratios in assessing organic P regeneration. The reactive P fraction can be effectively proxied by total P because the non-reactive (i.e., detrital) P fraction is generally a minor component (mean ~13%) of total P in marine sediments (Fig. 3). This inference is critical to an evaluation of sedimentary C_{org}:P relationships in pre-Cenozoic sediments, for which P speciation data are largely unavailable.

2.2. Phanerozoic sedimentary C_{org}:P ratios

C_{org}:P ratios were determined using data from 91 "formation-studies" of 58 different organic-rich facies of Late Cambrian through Recent age (Table 1; n.b., each "formation-study" represents the data for one formation from one study). For each formation-study, C_{org}, total P, and C_{org}:P ratios were tabulated for all samples; these data are reported as mean (±1 s.d.) values for C_{org} and total P and as the median value (with a 16th to 84th percentile range) for C_{org}:P ratios. For C_{org}:P, the median is used in preference to the mean because small denominators in simple ratios can produce extreme values that will skew the latter measure of central tendency. Although there is some degree of variance in C_{org}:P ratios within any given unit, modern or ancient, central-tendency measures such as the median appear to provide an average value that can be interpreted in terms of environmental factors (e.g., Fig. 2). Data sources were limited to "organic-rich facies" (TOC>1%) deposited in marine environments. In sediments from these marine environments, the bulk of the sedimentary organic matter was derived from marine algal precursors, as determined by organic petrographic and geochemical proxies in the original studies. For the pre-Cretaceous, most units necessarily represent epicontinental settings; for the Neogene, a wider range of settings, including deep-ocean environments, is represented.

Phanerozoic sedimentary C_{org}:P ratios range from 1.7:1 (Upper Permian Phosphoria Formation) to ~1625:1 (Middle Devonian Marcellus Group; Table 1). Secular variation in C_{org}:P ratios appears to be non-random (Fig. 4). Relatively high values are associated with the Late Cambrian (~400–500:1) and the Early to Late Devonian (~200–1625:1), with intermediate values characterizing the Ordovician and Silurian (~50–150:1). Beginning in the Late Devonian, C_{org}:P ratios commence a sustained decline that continues to the Late Permian, when values are typically <20:1 (Fig. 4). C_{org}:P ratios for

Table 1
C_{org}:P ratios for Phanerozoic anoxic marine facies

	Unit	Age	Location	C_{org} [a]	P_{total} [a]	C_{org}:P [b]	Reference
				(%)	(ppm)	(molar ratio)	
1	Alum Shale	Mid–Upr Cambrian	Sweden–Norway	16.5±1.0; 10.0±4.2; 11.3±4.3; 13.7±2.1	2589±448; 658±231; 761±222; 867±208	403 (327–436); 423 (304–533); 444 (264–486); 387 (331–525)	(Assarsson and Grundulis, 1961; Armands, 1972; Andersson et al., 1985; Leventhal, 1990)
2	Humber Arm Supergroup	Mid Cambrian–Lwr Ordovician	Newfoundland	1.5±0.7	602±253	77 (46–79)	Botsford (1987)
3	Meguma/St. John/Cookson/Tetagouche/Fournier Groups	Upr Cambrian–Upr Ordovician	New Brunswick/Nova Scotia	3.1±1.8; 2.5±0.7	518±148; 538±289	144 (94–180); 117 (92–219)	(Fyffe and Pickerill, 1993; Fyffe, 1994)
4	Llandeilo Shales	Mid Ordovician	Wales	1.9±1.4	388±158	114 (26–268)	Lev (1994)
5	Glenwood Shale	Mid Ordovician	Iowa	22.1±6.9	1258±472	478 (330–592)	T. Algeo, unpubl.
6	Utica Shale	Mid–Upr Ordovician	N. Appalachian Basin	2.5±0.5	1112±202	61 (52–71)	Mickler (1998)
7	Martinsburg Shale	Upr Ordovician	N. Appalachian Basin	1.6 ±0.5	759±100	52 (45–67)	Mickler (1998)
8	Athens Shale	Upr Ordovician	S. Appalachian Basin	2.4±0.6; 1.0±0.1	436±44; 497±86	149 (114–162); 52 (40–62)	(Saunders and Savrda, 1993; Mickler, 1998)
9	Maquoketa Shale	Upr Ordovician	Iowa	8.2±2.6	14,024±23,474	51 (28–77)	T. Algeo, unpubl.
10	Gull Island Fm.	Upr Ordovician	Newfoundland	1.7±0.3	162±74	338 (219–462)	Brüchert et al. (1994)
11	Graptolitic shales	Upr Ordovician–Upr Silurian	France	8.6±5.2; 2.1±2.8; 5.7±3.1	378±110; 393±319; 1172±888	571 (419–716); 80 (52–165); 121 (79–320)	(Dabard and Paris, 1986; Saupé and Vegas, 1987; Chauris, 1990)
12	Graptolitic shales	Lwr Silurian	Spain	5.7±2.8	1091±157	132 (94–170)	Saupé (1990)
13	Graptolitic shales	Lwr Silurian	Czech	3.1±1.0	753±577	147 (78–306)	Štorch and Pašava (1989)
14	Graptolitic shales	Lwr Silurian–Lwr Devonian	Southern Germany	12.7±4.5; 12.5±4.5	4523±4177; 10,765±9143	120 (41–321); 72 (39–302)	(Dill, 1985, 1986; Dill and Nielsen, 1986)
15	Graptolitic shales	Upr Silurian–Lwr Devonian	Poland	3.8±1.4	214±196	977 (151–1477)	Porebska and Sawlowicz (1997)
16	Marcellus Group	Mid Devonian (Givetian)	N. Appalachian Basin	6.9±3.4; 7.5±4.0	248±76; 254±76	1625 (894–2388); 1606 (822–2392)	(Werne et al., 2002, Sageman et al., 2003)
17	Carpenter Fork Bed, New Albany Shale	Mid Devonian (Givetian)	C. Appalachian Basin	8.4±5.3	2098±2410	186 (84–413)	Robl et al. (1984), unpubl.
18	Genesee–Sonyea–West Falls–Canadaway	Upr Devonian (Frasnian)	N. Appalachian Basin	3.3±1.0	415±283	507 (305–1522)	Sageman et al. (2003)
19	Chattanooga Shale	Upr Devonian	S. Appalachian Basin	16.1±1.8	1172±1360	598 (267–1211)	Rheams and Neathery (1988)
20	Woodford Shale	Upr Devonian	Ouachita–Anadarko region	18.5±4.9	1142±76	424 (339–492)	Kolowith and Berner (2002)

21	New Albany Shale	Upr Devonian	Illinois Basin	5.8±2.2;	412±1160;	516 (267–1296);	(Frost et al., 1985;
				8.1±2.9;	289±78;	691 (490–1047);	Calvert et al., 1996;
				9.4±0.3	434±115	504 (476–743)	Kolowith and Berner, 2002)
22	Ohio–Sunbury Shales	Upr Devonian–Lwr Mississippian (Famennian–Tournaisian)	C. Appalachian Basin	8.4±3.2;	762±118;	400 (297–487);	(Robl et al., 1984, unpubl.,
				8.6±3.3	411±268	556 (397–749)	Jaminski, 1997)
23	Exshaw Fm.[c]	Upr Devonian–Lwr Mississippian (Famennian–Tournaisian)	Alberta	II: 8.1±3.9;	II: 1274±2082;	II: 282 (163–380);	(Caplan, 1997; Hartwell, 1998)
				III: 2.8±3.4;	III: 1364±855;	III: 66 (2–169);	
				11.5±3.5	1036±1082	142 (124–180)	
24	Alum & Kulm shales	Lwr Mississippian	Germany	1.9±0.9	967±647	44 (32–134)	Urban et al. (1995)
25	Cyclothemic shales	Lwr Pennsylvanian	England	4.5±2.3	655±218	176 (N/A)	Spears and Amin (1981)
26	Cyclothemic shales	Mid Pennsylvanian	Illinois Basin/ Midcontinent U.S.	12.9±2.7;	3633±1480;	97 (76–119);	(Shaffer et al., 1985;
				25.5±11.1;	8677±11,719;	124 (47–986);	Coveney et al., 1987;
				15.9±6.5	11,833±9073	36 (24–125)	Hatch and Leventhal, 1997)
27	Cyclothemic shales[c]	Upr Pennsylvanian	Midcontinent U.S.	BS: 17.3±7.6;	BS: 12,930±15,859;	BS: 55 (17–766);	Algeo et al. (2004), unpubl.
				GS: 1.6±1.0	GS: 1198±1641	GS: 49 (22–101)	
28	Dollarhide Fm.	Lwr Permian	Idaho	5.1±3.0	873±225	89 (78–272)	Wavra et al. (1986)
29	Meade Peak & Retort mbrs., Phosphoria Fm.	Upr Permian (Guadalupian)	Western U.S.	6.2±5.2;	100,000±86,400;	4.3 (1.0–14.2);	(Cressman and Swanson, 1964;
				2.7±1.9;	134,700±99,500;	1.7 (0.4–4.0);	Medrano and Piper, 1992;
				3.8±3.6	62,700±80,310	7.3 (1.3–17.4)	Perkins et al., 2003)
30	Cumnock Fm.	Upr Triassic–Lwr Jurassic	Eastern U.S.	7.5±10.2	7441±11,638	26 (12–60)	Krohn et al. (1988)
31	Posidonia Shale	Lwr Jurassic (Toarcian)	FranceGermany	6.5±4.8;	873±480;	192 (N/A);	(Brumsack, 1991;
				6.0±1.3	1309±524	128 (N/A)	Robl et al., 1993)
32	Oxford Clay	Upr Jurassic (Oxfordian)	N. England	1.2±0.7;	1850±1809;	35 (1053);	(Dypvik, 1984;
				5.1±1.7	990±319	142 (94–196)	Norry et al., 1994)
33	Kimmeridge Clay	Upr Jurassic (Kimmeridgian)	North Sea	3.9±1.6;	1362±608;	86 (42–127);	(Dypvik, 1984;
				3.5±1.8	1111±373	75 (62–164)	Tribovillard et al., 1994)
34	Greenhorn Fm./lwr. Mancos Shale	Upr Cretaceous (Cenomanian–Turonian)	U.S. Western Interior	4.0±1.2	423±113	241 (169–326)	Dean and Arthur (1998)
35	Niobrara Fm./upr. Mancos Shale	Upr Cretaceous (Turonian–Coniacian)	U.S. Western Interior	4.2±1.6;	452±150;	234 (164–377)	Dean and Arthur (1998)
36	Ghareb Formation	Upr Cretaceous (Campan.–Maastricht.)	Israel	16.9±6.9	11,346±3616	36 (30–47)	Shirav and Ginzburg (1983)
37	Monterey Fm.	Tertiary (Miocene)	California	5.0±3.9	4077±5485	43 (16–79)	Leventhal (1989)
38	Marine sediment	Tertiary (Mioc.)–Quaternary	Sea of Japan	1.5±0.8	1771±341	22 (12–30)	Föllmi and von Breymann (1992)
39	Sapropels	Quaternary	E. Mediterranean	1.9±3.5;	460±280;	53 (14–127);	(Calvert, 1983;
				1.7±1.1;	522±120;	99 (16–135);	Sutherland et al., 1984;
				6.1±8.7	513±115	112 (62–537)	Slomp et al., 2004)

(continued on next page)

Table 1 (*continued*)

	Unit	Age	Location	C_{org} [a]	P_{total} [a]	C_{org}:P [b]	Reference
				(%)	(ppm)	(molar ratio)	
40	Marine sediment	Quaternary	Black Sea	1.3±1.8; 3.9±4.0; 2.2±1.6	739±257; 718±143; 589±80	30 (12–64); 104 (24–244); 71 (45–192)	(Hirst, 1974; Brumsack, 1989; Lyons, 1992)
41	Marine sediment	Quaternary	Cariaco Basin	1.8±1.0; 3.4±2.0	572±135; 874±249	78 (37–121); 107 (26–136)	Yarincik (1997), T. Lyons, unpubl.
42	Marine sediment	Quaternary	Saanich Inlet	2.0±1.4; 1.7±0.5	780±185; 674±61	61 (23–102); 71 (46–85)	(Francois, 1988;, Filippelli, 2001)
43	Marine sediment	Quaternary	Arabian Sea	1.8±1.2	967±405	51 (24–68)	Lückge et al. (1999)
44	Marine sediment	Quaternary	Peru margin	8.0±3.8; 7.4±3.9	6379±7403; 10,924±25,550	43 (25–98); 115 (42–155)	(Suess, 1981; Froelich et al., 1988)
45	Marine sediment	Quaternary	NW African margin	2.0±0.8	644±113	78 (54–108)	Hartmann et al. (1976)
46	Marine sediment	Quaternary	SW African margin	9.7±3.8	3680±853	69 (57–77)	(Calvert and Price, 1970; Brongersma-Sanders et al., 1980)
47	Marine sediment	Quaternary	Oman margin	1.5±0.5	1781±1003	27 (15–32)	Tamburini et al. (2003)
48	Marine sediment	Quaternary	Namibian shelf	6.9±4.6	12,250±17,930	42 (10–94)	Calvert and Price (1983)
49	Marine sediment	Quaternary	Baltic Sea	2.3±0.5; 5.4±2.8; 3.3±1.0	752±59; 1246±545; 883±272	81 (64–92); 107 (78–149); 96 (64–140)	(Bianchi et al., 2000; Emeis et al., 2000; unpubl., Emelyanov, 2001)
50	Marine sediment	Quaternary	Framvaren Fjord	10.7±3.5	1478±354	186 (123–302)	Skei (1986)
51	Marine sediment	Quaternary	California margin	2.2±0.3; 1.6±0.5; 2.3±0.4; 2.1±1.4	1330±109; 1028±72; 680±119; 710±136	42 (39–45); 39 (28–52); 85 (74–106); 61 (48–100)	(Sholkovitz, 1973; Vink et al., 1997; Tada et al., 2000; Delaney and Anderson, 2000)
52	Marine sediment	Quaternary	Pacific shelf, Mexico	6.1±2.5	2445±2229	86 (55–104)	Ganeshram et al. (2002)
53	Marine sediment	Quaternary	Gulf of California	4.5±0.5	1074±138	108 (99–118)	Brumsack (1989)
54	Marine sediment	Quaternary	Canadian Arctic shelf	1.5±0.3	1008±242	40 (29–51)	Ruttenberg and Goñi (1997)
55	Marine sediment	Quaternary	Gulf of Mexico shelf	1.2±0.2	751±129	41 (38–48)	Ruttenberg and Goñi (1997)
56	Marine sediment	Quaternary	deep ocean	1.4±0.7	564±86	59 (40–86)	Van der Zee et al. (2002)
57	Marine sediment	Quaternary	Venice lagoon	7.9±4.9	419±98	48 (34–57)	(Lucchini et al., 2001–2002; Sfriso et al., 2003)
58	Marine sediment	Quaternary	Long Island Sound	1.2±0.2	611±86	48 (45–53)	Krom and Berner (1981)

[a] C_{org} and P values are given as the mean of the sample set plus or minus one standard deviation.

[b] C_{org}:P molar ratios are given as the median of the sample set with the standard deviation range (i.e., 16th–84th percentiles) in parentheses; these statistics are used in preference to the mean and standard deviation in order to avoid the influence of extreme values on the latter.

[c] C_{org}:P ratios given separately for type II and type III organic matter, or for black shale (BS) and gray shale (GS) facies.

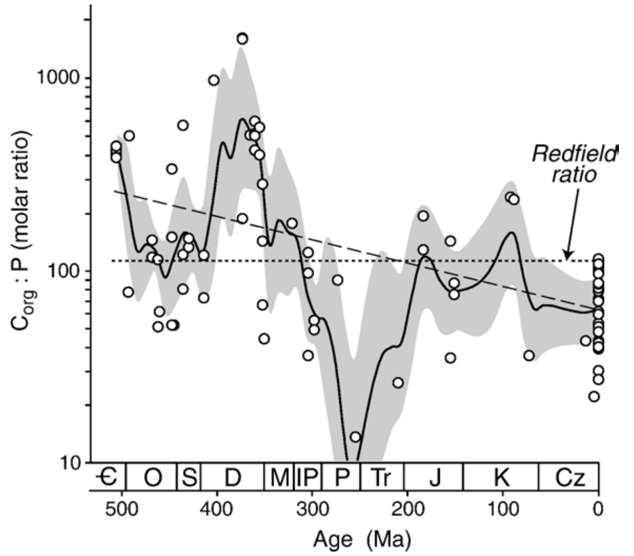

Fig. 4. Median C_{org}:P ratios from 91 "formation-studies" of 58 different Phanerozoic organic-rich facies (Table 1). For each unit, the median C_{org}:P ratio was calculated in preference to the mean to avoid undue influence by outliers. Two Late Permian units with C_{org}:P ratios <10 are not shown but are included in calculations of the linear regression (dashed line), running mean (solid line), and standard deviation range (shaded). Trend line calculations are based on logarithms of median C_{org}:P ratios. The linear regression line shows that C_{org}:P ratios have declined on average by a factor of four from the Cambrian (~260:1) to the Recent (~65:1). The running mean curve demonstrates the existence of coherent secular variation in the dataset. The Redfield ratio of 106:1 is shown for reference. The timescale used is that of Gradstein et al. (2004).

Mesozoic–Cenozoic formations are mostly within the range encountered in (sub)Recent sediments (~30–120:1), although a few Cretaceous black shales yield ratios as high as ~220:1. Recent organic-rich facies yield a mean C_{org}:P ratio of 65(±25):1. For the Phanerozoic as a whole, the mean C_{org}:P ratio declines by a factor of four, from ~260:1 in the Late Cambrian to ~65:1 in the Recent (Fig. 4, dashed line), a statistically robust result ($r^2=0.18$; $d.f.=90$; $p(\alpha)<0.01$). By comparison, organic-poor facies of all ages typically have C_{org}:P ratios of <50:1 (e.g., Fig. 2; Ruttenberg et al., 1997; Anderson et al., 2001; Sageman et al., 2003).

The Phanerozoic C_{org}:P record exhibits a moderately strong degree of secular coherence. In other words, the C_{org}:P ratios within narrow (e.g., 10 myr) time slices generally vary by only a factor of two to three. For example, nine formation-studies of Upper Devonian organic-rich facies yield C_{org}:P ratios within the range of 280:1 to 600:1 (Table 1). This is similar to the variance in median C_{org}:P ratios among modern anoxic marine environments (Fig. 2), which is perhaps not coincidental. Rather, it may be an indication of the degree to which local factors such as water depth, vertical stratification, and deepwater renewal processes can introduce variance into the sedimentary C_{org}:P record (see Section 3.2.1). Although there is variation in median C_{org}:P ratios within a given time slice, the overall long-term secular trends in C_{org}:P ratios likely reflect variation in a global quantity such as atmospheric pO_2 (see Section 3.3).

With the exception of the (sub)Recent, C_{org}:P data are sparser for the post-Carboniferous than for the Cambrian-to-Carboniferous interval. This observation is significant for two reasons. First, the age distribution of C_{org}:P data is not an artifact of data collection procedures; rather, organic-rich facies of post-Carboniferous age are less common than for earlier geologic periods. This pattern may reflect secular changes in the partial pressure of oxygen in the oceanic–atmospheric system and its influence on the prevalence of anoxic marine environments (see Section 3.2.3). Second, owing to the comparatively short residence time of oxygen in the atmosphere (~4 myr; Walker, 1977), the Phanerozoic pO_2 model generated from the C_{org}:P data of this study (Fig. 5) provides an incomplete representation of secular variation in this parameter at timescales of one to a few million years. The attendant uncertainties are larger for geologic periods with sparser C_{org}:P data, such as the Permian to Recent (Fig. 4). As a note of caution, it

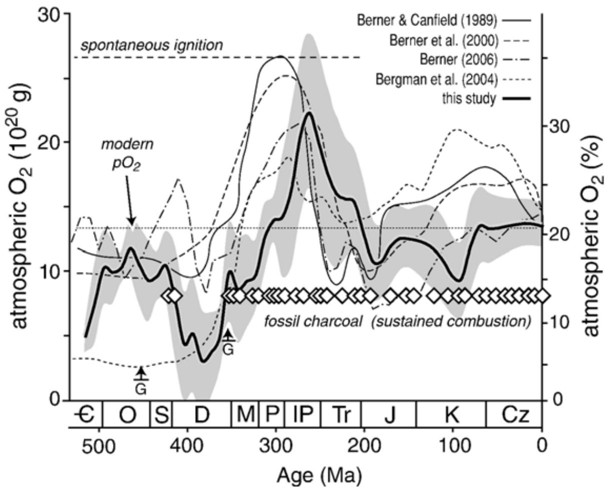

Fig. 5. Phanerozoic atmospheric pO_2 models. The model of the present study (thick line) was generated by inversion and scaling of the Phanerozoic C_{org}:P curve (Fig. 4). The curve is anchored to the present atmospheric O_2 level of 21% (horizontal line), and Phanerozoic variation is maximized consonant with range constraints imposed by (1) diffusion modeling of Late Ordovician and Late Devonian soils (arrows with "G"; Yapp, 1996), (2) fossil charcoal occurrences, which require O_2 levels >13% for sustained combustion (diamonds; Chaloner, 1989; Robinson, 1989), and (3) spontaneous ignition of wood at O_2 levels of ~35% (Chaloner, 1989; Wildman et al., 2004). Four published atmospheric pO_2 models are shown for comparison (thin lines; Berner and Canfield, 1989; Berner et al., 2000; Bergman et al., 2004; Berner, in press).

should be emphasized that models of long-term secular variation in geochemical systems characterized by relatively short residence times (e.g., atmospheric pO_2 and pCO_2) cannot be used to infer short-term variation in such systems; misuse of such models has unfortunately become common in the literature (e.g., Weidlich et al., 2003; Raymond and Metz, 2004; cf. Royer et al., 2004).

3. Discussion

3.1. Potential non-environmental influences on Phanerozoic sedimentary C_{org}:P ratios

Several considerations may potentially limit the utility of Phanerozoic sedimentary C_{org}:P data (Fig. 4) as a record of a global environmental variable such as atmospheric pO_2. One issue is whether the average C:P ratio of marine phytoplankton has changed through time. Direct determination of ancient biotic C:P ratios is precluded by pervasive post-depositional alteration of sedimentary organic matter. However, despite limited knowledge regarding the relative importance of various phytoplankton groups as contributors to sedimentary organic matter in the past (Tappan, 1980; Martin, 1995), an assumption of uniformitarianism with respect to biotic C:P ratios may be warranted. The reason is that all marine phytoplankton are composed of the same few types of compounds, each having a known range of compositions. Modern phytoplankton consist of ~75% proteins and 5–10% each of nucleic acids, lipids, and carbohydrates (Cauwet, 1978; Libes, 1992; Hedges et al., 2002). Typical P concentrations in these compounds are ~2–3% (by weight) for lipids and 0.5–1.0% for proteins and carbohydrates. Lipid-poor phytoplankton such as coccolithophorids and cyanobacteria have C:P ratios close to the Redfield ratio (Takahashi et al., 1985; Fu et al., 2005), which is based on a carbohydrate, $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$ (Redfield et al., 1963). Comparatively lipid-rich diatoms, on the other hand, tend to have somewhat lower C:P ratios (~80–90:1; De Baar et al., 1997; Bozec et al., 2005).

Potentially more important than comparatively small differences in cell biology among phytoplankton groups is ecophenotypic compositional variation within individual groups. Rather sizable variations in biotic C:P ratios are known to occur as a function of nutrient availability. During the early stages of a phytoplankton bloom when nutrient levels are high, P uptake per unit organic C is also high and, hence, C:P ratios are low; this effect is known as “luxury consumption” of nutrients (Droop, 1973; Thomas et al., 1999). Conversely, when nutrient levels are low, C:P ratios can increase substantially. Diazotrophic cyanobacteria exhibit C:P ratios within ±10% of the Redfield ratio when P is non-limiting but can generate C:P ratios as high as ~400:1 under strongly P-limited conditions (Letelier and Karl, 1996; Sañudo-Wilhelmy et al., 2001; Fu et al., 2005). Thus, some variation in phytoplankton C:P ratios through time might be expected as a consequence of changes in the nutrient status of ancient oceans. Unfortunately, there is no consensus regarding past variations in ocean nutrient status. Tappan (1980) and Bambach (1993) invoked generally high nutrient levels for the Early Paleozoic, but Martin (1995, 1999) has argued the converse, that oligotrophic conditions generally prevailed during the Cambrian through Devonian. Most recently, Saltzman (2005) used variance in carbonate $\delta^{13}C$ data to identify alternating intervals of P-limited and N-limited conditions during the Paleozoic, which should theoretically be linked to higher and lower phytoplankton C:P ratios, respectively. Because his pattern, which predicts P limitation for the Late Cambrian but N limitation for most of the Devonian, does not show any systematic relationship to the sedimentary C_{org}:P trends documented in this study, it is likely that either carbonate $\delta^{13}C$ does not vary strongly as a function of nutrient status, or that ocean nutrient status is not a strong control on phytoplankton C:P ratios at geologic timescales. In summary, the issue of past variations in the primary composition of phytoplankton is one that cannot be resolved at present.

One additional issue is differential loss of organic carbon and phosphorus during burial diagenesis. Early diagenetic fluxes of C and P (e.g., Froelich et al., 1988; Martens, 1993; Ruttenberg and Berner, 1993; Hensen et al., 1998; Van der Zee et al., 2002) are related to benthic environmental conditions and, hence, potentially to global environmental variables such as atmospheric pO_2. On the other hand, loss of organic C or P as a result of late-stage burial (catagenetic) reactions would alter sedimentary C_{org}:P ratios in a manner unrelated to primary environmental conditions. Organic carbon is more prone to thermal remobilization and loss than sedimentary P, especially that hosted by comparatively refractory authigenic phosphate phases (Anderson et al., 2001). Such a pattern of differential loss should result in a progressive decrease in C_{org}:P ratios in more deeply buried and, hence, generally older study formations—a pattern analogous to that for sedimentary C/S ratios (Raiswell and Berner, 1987). Although not controlled for explicitly, the older formations of the present study almost certainly experienced higher burial temperatures on average than the younger ones. If this relationship has contributed to (an undiagnosed) secular bias in reported sedimentary C_{org}:P ratios, it is one that can only have attenuated (rather than reinforced) the secular pattern shown in Fig. 4. Hence, burial diagenetic factors are unlikely to negate the general conclusions of the present study.

3.2. Significance for paleocean ventilation

3.2.1. Benthic redox variability

Although all of the modern organic-rich facies surveyed in this study were deposited in oxygen-deficient (and commonly anoxic) environments, benthic redox conditions in most depositional systems are rarely static for any extended interval. Anoxic marine environments are subject to episodic renewal of the deep (subpycnoclinal) watermass through processes such as hyperpycnal overspills at basin-margin sills, water-column overturn via surface cooling, turbulent vertical mixing via storms, and density flows generated around basin margins as a function of slope instability, seismicity, or human activity (e.g., Anderson and Devol, 1973; Skei, 1983; Östlund and Dyrssen, 1986; Stigebrandt and Molvaer, 1988; Friedrich and Stanev, 1989; Holmen and Rooth, 1990; Lyons, 1991; Thomson et al., 1998; Scranton et al., 2001; Popescu et al., 2004). The influence of these processes on benthic redox potential depends on the frequency and magnitude of the renewal events relative to the volume of the deep watermass.

The average rate of deepwater renewal in a given environment is reflected in its deepwater "age" or renewal time, τ_{dw}, as measured by proxies such as ^{14}C or ^{3}H. In the Recent, deepwater renewal times range from >500 yr for the Black Sea to ~50–150 yr for Framvaren Fjord and the Cariaco Basin and ~2 yr for Saanich Inlet (Algeo and Lyons, 2006). Basin size and geometry as well as local hydrographic factors are key influences on τ_{dw}. For instance, deepwater renewal is very limited in Framvaren Fjord owing to its shallow sill depth (~2 m) relative to its total basin depth (~180 m) and to a steep vertical density gradient. In comparison, deepwater renewal is much more frequent in the similarly sized Saanich Inlet owing to its comparatively deep sill depth (~70 m) relative to its total basin depth (~240 m) and to local hydrographic factors that promote quasi-annual hyperpycnal incursions. In the Baltic Sea, which may be the best modern analog for many ancient epicratonic seas, redox conditions in the deeper basins have fluctuated erratically between moderately oxic and strongly sulfidic at timescales of a few years to a few decades as a consequence of regulation of inflow of oxygenated hyperpycnal watermasses through the Danish Straits by regional atmospheric pressure systems (Algeo et al., in press). In the Black Sea, the effects of deepwater renewal are strongly attenuated by large basin size, but small quantities of dissolved oxygen nonetheless penetrate episodically to the seafloor, as shown by the presence of bioturbated abyssal-plain "turbidites" (Lyons, 1991). In ancient marine environments, similar short-term ($<10^2$ yr) redox fluctuations are commonly evidenced by juxtaposition of conflicting redox proxies, e.g., trace or body fossils indicative of oxic–suboxic conditions with geochemical indicators documenting anoxic or euxinic conditions (e.g., Wignall and Myers, 1988; Kenig et al., 2004; Schwark and Frimmel, 2004).

Given the highly dynamic character of most anoxic marine environments, it is worth reflecting on differences in the degree of time-averaging recorded by different paleoredox proxies. Proxies such as sediment biofabric, syngenetic pyrite framboids, and PZE (photic-zone euxinia) biomarkers record more-or-less instantaneous (<1 yr) redox conditions (Bromley, 1996; Ohfuji and Rickard, 2005; Smittenberg et al., 2005). Trace-metal concentrations and pyrite $\delta^{34}S$ values, which are set by early diagenetic reactions within the sediment, may be expected to respond to redox changes at the sediment–water interface as long as sediment porewaters remain in contact with the overlying water column, typically for intervals of up to a few hundred years or so for bioturbated sediments (Thomson et al., 1998; Schoonen, 2004), although these reactions can proceed to equilibrium at much shorter timescales (Gee and Bruland, 2002). Benthic P fluxes can also respond to "instantaneous" fluctuations in benthic redox conditions, probably through reactions involving Fe-sorbed P and biogenic cycling of polyphosphates (Emeis et al., 2000; Sannigrahi and Ingall, 2005). However, C_{org}:P ratios differ from other commonly used redox proxies in their tendency to remain responsive to fluctuations in benthic redox potential for longer periods. This extended responsiveness is due to the slow kinetics of authigenic phosphate mineral growth, a process that typically operates at timescales from a few years for phosphate pellets (<1 mm diam.; Burnett, 1990) to 10^2 to $>10^6$ yr for phosphate nodules (>1 mm diam.; Burnett, 1980; Burnett et al., 1982; Thomson et al., 1984; Van Cappellen and Berner, 1988; O'Brien et al., 1990; Anderson et al., 2001). This property of C_{org}:P ratios is advantageous for evaluation of *time-averaged* benthic redox conditions.

3.2.2. Local versus global redox controls

In view of the strong control of Recent sedimentary C_{org}:P ratios by benthic redox conditions (Fig. 2), it seems reasonable to interpret Phanerozoic sedimentary C_{org}:P ratios (Fig. 4) primarily in terms of paleocean ventilation. There are, however, a multitude of factors, both local and global, that influence time-averaged redox conditions at any given point on the seafloor. Local factors include water depth, degree of watermass stratification, and the type and scale of deepwater renewal processes (see Section 3.2.1). Modern anoxic marine environments exhibit large differences in all of these variables. Water depths range from <200 m (Framvaren Fjord) to >2200 m (the Black Sea). Degree of water-column stratification, as measured by $\Delta\sigma_{t(\text{deep-shallow})}$, varies from ~3 (the Black Sea) to ~10 (Framvaren Fjord) (Brewer and Spencer, 1974; Skei, 1986). Deepwater renewal processes vary between environments also, with hyperpycnal overspills dominant in Framvaren Fjord and the Baltic Sea but tectonically induced turbidite flows probably more important in the Black Sea. With regard to paleoenvironments, such local controls are generally poorly known. However, almost all of the pre-Recent units surveyed (Table 1) were deposited in epicratonic settings, hence at water depths that are typically estimated in the range of tens to a few hundred meters. The relatively shallow water depths typical of ancient epicratonic seas would be expected to favor good communication between the benthic watermass and the paleoatmosphere, allowing the former to respond to compositional variations in the latter.

In addition to bottomwater oxygen concentrations, sediment accumulation rates influence the preservation versus remineralization of sedimentary organic C and P through their control of diffusive and advective fluxes of dissolved oxygen into the sediment (Berner, 1980; Henrichs and Reeburgh, 1987; Canfield, 1989, 1994; Betts and Holland, 1991). In general, these studies indicate that organic C preservation in marine sediments is enhanced at higher sedimentation rates. In contrast, the relationship between P preservation and sedimentation rate is less clear. The $(C:P)_{org}$ ratio of sedimentary organic matter has been shown to be a complex function of sedimentation rate (Ingall and Van Cappellen, 1990). Low $(C:P)_{org}$ ratios (<200) are found in sediments with sedimentation rates both <0.002 cm yr^{-1} and >1 cm yr^{-1}. At sedimentation rates between these extremes, $(C:P)_{org}$ ratios up to 600:1 are encountered. At comparable sedimentation rates, the $(C:P)_{org}$ ratio of sedimentary organic matter is consistently higher in sediments deposited under low-oxygen and anoxic conditions in comparison to those deposited from oxic waters. The difference in $(C:P)_{org}$ ratios between oxic and anoxic facies is greatest at sites with low sedimentation rates (<0.01 cm yr^{-1}), whereas $(C:P)_{org}$ ratios tend to converge at sites with high sedimentation rates (>1 cm yr^{-1}) (Van Cappellen and Slomp, 2002). However, it is unclear whether these observations for $(C:P)_{org}$ ratios necessarily apply to $C_{org}:P_{reac}$ ratios as well.

Despite considerable variability in local controls on benthic redox conditions as well as in sedimentation rates, modern anoxic marine environments exhibit a relatively limited range of median C_{org}:P ratios, from ~110:1 (the Baltic Sea and Cariaco Basin) to ~180–200:1 (Framvaren Fjord and the inner basin of Effingham Inlet; Fig. 2). Thus, the full range of variation in median C_{org}:P ratios for modern anoxic marine environments is *less than a factor of two*. This observation is significant because (1) no modern anoxic marine environment yields a median C_{org}:P ratio approaching that of many Early to Middle Paleozoic organic-rich facies, in which C_{org}:P ratios of >400:1 are common, and (2) the full range of median C_{org}:P ratios in modern anoxic marine environments (~110–200:1) is much smaller than that observed for the Phanerozoic as a whole (~2–1625:1; Table 1). The implications of these observations are that the local factors discussed above are probably not the dominant influence on Phanerozoic C_{org}:P ratios, and that some other factor is responsible for much of the variance in the Phanerozoic record. The strong secular coherence shown by Phanerozoic C_{org}:P ratios (Fig. 4) implies that much of the variance in this record can be attributed to a *global* rather than a local control on benthic redox conditions, most probably atmospheric pO_2 (see Section 3.3).

3.2.3. Ventilation of Phanerozoic seas

If the Phanerozoic C_{org}:P record can be interpreted primarily in terms of paleocean ventilation, as argued in the preceding section, then epochs characterized by high C_{org}:P ratios had poorly ventilated seas, and epochs characterized by low C_{org}:P ratios had well-ventilated seas. The Phanerozoic C_{org}:P record suggests that Early to Middle Paleozoic seas were poorly ventilated, especially during the Late Cambrian and Early to Late Devonian, and that post-Devonian seas were generally well-ventilated. This interpretation is consonant with inferences from earlier paleoceanographic studies. Precambrian oceans are thought to have been largely anoxic (Anbar and Knoll, 2002; Poulton et al., 2004), although ventilation may have improved somewhat in association with widespread Late Proterozoic glaciation (Canfield and Teske, 1996; Kaufman et al., 1997; Hoffman et al., 1998; Lenton et al., 2004). Nonetheless, the Early to Middle Paleozoic was characterized by widespread deepwater anoxia, especially in the Iapetan region (Berry and Wilde, 1978; Wilde and Berry, 1982; Wilde, 1987) but also in many large epicratonic basins (e.g., Goodfellow and Jonasson, 1984).

The cause of the apparent shift from poorly ventilated to well-ventilated seas around the Devonian–Carboniferous transition is uncertain. One possibility is a fundamental change in deepwater formation processes. Whereas modern deepwaters form through cooling at high northern and southern latitudes, ancient deepwaters may have been generated through evaporation in epicratonic or marginal marine seas and subsequent sinking of hypersaline, hyperpycnal watermasses. This model has been applied to the Early–Middle Paleozoic (Railsback et al., 1990; Jeppsson, 1990; Aldridge et al., 1993; Brenchley et al., 1994; Wenzel and Joachimski, 1996) as well as to the Late Cretaceous and Early Cenozoic (Brass et al., 1982; Kennett and Stott, 1991; Pak and Miller, 1992; Bice et al., 1997). Whether such a shift in deepwater formation processes could have occurred within the epicratonic seas that are the source of virtually all of the pre-Neogene data in this study is unclear. In comparatively shallow epicratonic seas, transfer of dissolved oxygen to the seafloor probably was more dependent on the types of deepwater renewal processes operating in modern anoxic silled basins (see Section 3.2.1) than on formation of thermohaline or haline deep watermasses as in modern oceans. For this reason, we infer that the apparent improvement in ventilation of epicratonic seas beginning in the Late Devonian records a change not in deepwater formation processes but, rather, in paleoatmospheric O_2 levels.

3.3. Significance for Phanerozoic atmospheric pO_2

3.3.1. Atmospheric pO_2 as a global redox control

The most important global control on bottomwater oxygenation and, therefore, benthic redox conditions is atmospheric pO_2. If variance in the Phanerozoic C_{org}:P record primarily reflects a global control rather than local factors (see Section 3.2.2), then this record can be interpreted in terms of secular variation in atmospheric pO_2. In this case, systematic differences in C_{org}:P ratios between, for example, Late Devonian (~300–600:1) and Recent (~110–200) organic-rich facies reflect differences in the concentration of dissolved oxygen in downwelling watermasses during deepwater renewal events. According to this interpretation, such events imparted a more oxygen-depleted signature to Late Devonian organic-rich facies because lower atmospheric pO_2 resulted in lower dissolved oxygen concentrations in contemporaneous surface waters and in the downwelling watermasses formed from these surface waters. Although the dissolved oxygen content of surface waters is dependent on sea-surface temperatures as well as atmospheric pO_2, the influence of sea-surface temperatures on benthic redox conditions through time has probably been limited: assuming a maximum 10 °C range in Phanerozoic sea-surface temperatures, this corresponds to only a 14% change in the solubility of O_2 in seawater (Wright and Colling, 1995). This is almost certainly insufficient to account for the much larger range of variation in Phanerozoic C_{org}:P ratios (Fig. 4).

3.3.2. The Phanerozoic atmospheric pO_2 model

The Phanerozoic sedimentary C_{org}:P curve (Fig. 4) readily conveys a sense of qualitative changes in paleoatmospheric pO_2, with low pO_2 levels during the Late Cambrian and Devonian and high pO_2 levels during the Permian (cf. Fig. 5). Although the lack of a reaction-based relationship between sedimentary C_{org}:P ratios and atmospheric pO_2 is an impediment to deriving a quantitative pO_2 model from the Phanerozoic C_{org}:P record, a simple heuristic approach is available. This approach is based on the use of "anchor points" and "range constraints." The principal anchor point is the present: the mean value for 29 median C_{org}:P ratios of (sub)Recent organic-rich facies (~65:1) was set equal to present atmospheric O_2 (21%), and lower (higher) C_{org}:P ratios were equated with higher (lower) O_2 levels. The Phanerozoic pO_2 model of the present study (Fig. 5) was then scaled using range constraints, i.e., limits beyond which pO_2 variation was impermissible. The vertical scale of the inverted logarithmic C_{org}:P curve (Fig. 4) was expanded to the maximum degree possible without violating specified lower or upper range constraints. The rationale for maximizing Phanerozoic pO_2 variation within the limits imposed by these range constraints is that atmospheric O_2 levels have almost certainly varied considerably through the Phanerozoic, and the range of this variation has probably been limited by such constraints at some times in the geologic past.

The range constraints applied in the present study have been widely discussed in the literature (see Berner, 2004, for a review). A lower O_2 limit on atmospheric oxygen content (~13%) is imposed by the threshold for sustained combustion of vegetative matter (Chaloner, 1989; Robinson, 1989). This constraint applies to the Late Silurian–Early Devonian and the Late Devonian-to-Recent intervals, for which a record of fossil charcoal exists (Fig. 6) (Cope and Chaloner, 1980, 1985; Jones and Chaloner, 1991; Robinson et al., 1997; Scott, 2000; Rowe and Jones, 2000; Edwards and Axe, 2004; Glasspool et al., 2004; Uhl et al., 2004). Soil-diffusion modeling of goethite $\delta^{13}C$ values provides lower O_2

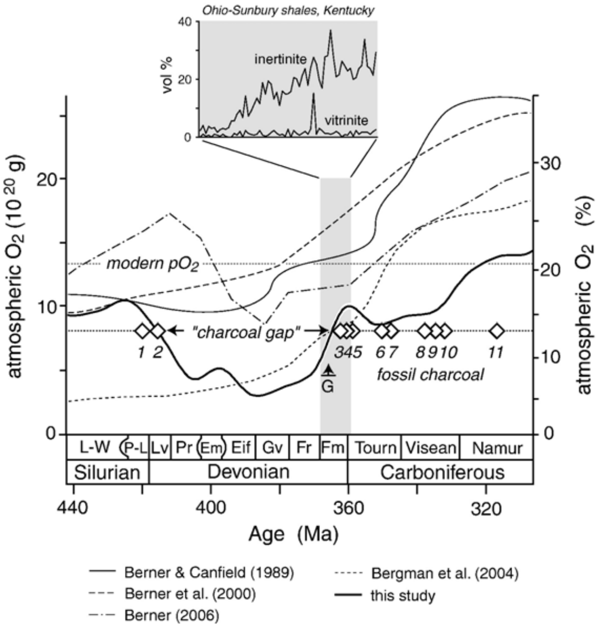

Fig. 6. Silurian–Carboniferous atmospheric pO_2 and the “Devonian charcoal gap.” Atmospheric pO_2 curves are from Fig. 5. Fossil charcoal records: (*1*) *Platyschima* Shale Member, Downton Castle Formation (Glasspool et al., 2004); (*2*) Ditton Formation (Edwards and Axe, 2004); (*3*) Duncannon Member, Catskill Formation (Cressler, 2001); (*4*) Hangenberg Sandstone (Rowe and Jones, 2000); (*5*) Berea Sandstone (Beck et al., 1982); (*6*) Cementstone Group (Scott et al., 1985); (*7*) Horton Group (Falcon-Lang, 2000); (*8*) Moyny Limestone (Falcon-Lang, 1998); (*9*) Upper Shalwy Beds (Nichols and Jones, 1992); (*10*) Strathclyde Group (Scott and Jones, 1994); (*11*) Namurian B units, Staffordshire, England (Scott et al., 1997). The presence of fossil charcoal implies atmospheric O_2 levels >13% for sustained combustion of plant tissue; soil diffusion modeling imposes an O_2 minimum of 8% for the Late Devonian (arrow with “G”; Yapp, 1996). Inset at top: stratigraphic trends in inertinite and vitrinite abundances in the Famennian Ohio Shale and Early Tournaisian Sunbury Shale (Rimmer et al., 2004).

constraints of ~3% and ~8% for the Late Ordovician and Late Devonian, respectively (Yapp, 1996). An upper O_2 constraint of ~35% is imposed by the spontaneous ignition of woody material (Cope and Chaloner, 1980; Chaloner, 1989; Robinson, 1989; Jones and Chaloner, 1991; Beerling et al., 1998; Wildman et al., 2004). More qualitative limits are provided by biological factors such as Carboniferous insect gigantism (Graham et al., 1995; Harrison and Lighton, 1998; though see Hannibal, 1998, for counter arguments) and post-Devonian tetrapod and, especially, post-mid-Cretaceous mammalian evolution (Holland, 1984), which are considered to require high (but unspecified) O_2 levels.

3.3.3. Comparison with existing Phanerozoic atmospheric pO_2 models

Variation in atmospheric pO_2 during the Phanerozoic has been modeled on the basis of sediment mass and elemental fluxes (Kump, 1988; Berner and Canfield, 1989; Van Cappellen and Ingall, 1996; Colman et al., 1997), isotope mass balances (Veizer et al., 1980; Garrels and Lerman, 1984; Kump and Garrels, 1986; Berner, 1987, 1989; Berner and Canfield, 1989; Lasaga, 1989; Kump, 1990; Petsch and Berner, 1998; Berner, 1999; Berner et al., 2000), and, most recently, integrated global geochemical redox systems (“COPSE,” Bergman et al., 2004; “GEOCARBSULF,” Berner, in press). The most widely cited models, the “Berner curves,” exhibit Phanerozoic atmospheric O_2 variation within the range of ~15 to 35% (Berner and Canfield, 1989; Berner et al., 2000), or ~12 to 30% in the most recent version (Fig. 5; Berner, in press). However, the published uncertainties on these models are typically large, averaging ±8% O_2 for the Berner et al. (2000) curve and ±4% O_2 for the Berner (in press) curve (although much larger uncertainty ranges were obtained in varying some model parameters in the latter study). A problem with all such models is the extreme sensitivity of atmospheric pO_2 estimates to small imbalances in the burial and weathering fluxes of reduced C and S (Berner, 1999, 2004).

The atmospheric pO_2 model based on the sedimentary C_{org}:P record of this study is broadly consonant with both the Berner and the Bergman–Lenton–Watson (subsequently “BLW2004”) curves. General similarities include: (1) sub-Recent O_2 levels during the Early to Middle Paleozoic; (2) a steep rise and subsequent decline in pO_2 during the Late Paleozoic (due to increased rates of burial of organic C in contemporaneous coal swamps; Berner and Raiswell, 1983; Berner, 1987, 1989); and (3) near-modern and less variant O_2 levels during the Mesozoic–Cenozoic (Fig. 5). In detail, however, the atmospheric pO_2 model of this study differs from these earlier models in some important respects. First, the present model exhibits more dynamic fluctuations in atmospheric O_2 levels during the Early to Middle Paleozoic than either the BLW2004 or Berner curves (except for Berner, in press). Second, the present model exhibits higher pO_2 values than the BLW2004 curve for the Cambrian to Early Devonian interval and lower pO_2 values than the Berner curves throughout the Paleozoic. Third, the Late Paleozoic increase in pO_2 of the present model is a stepwise rise that peaks in the mid-Permian, whereas this feature is a monotonic rise culminating in the Late Pennsylvanian or Early Permian in both the BLW2004 and Berner curves (Fig. 5; although Berner, 2005, appears to show a mid-Permian maximum). The Late Paleozoic O_2 maximum (~31%) is greater than that of BLW2004 and less than that of the older Berner curves (but comparable to Berner, 2005, in press). Finally, the BLW2004 and older Berner curves exhibit a mid- to late Cretaceous O_2 maximum of 25–30% that is not found in the present model (or in Berner, in press).

Certain features of the Berner and BLW2004 atmospheric pO_2 curves are difficult to reconcile with existing geologic evidence. First, the Early to Middle Paleozoic was characterized by extensive seafloor anoxia (Berry and Wilde, 1978; Goodfellow and Jonasson, 1984; Wilde, 1987). This is inconsistent with O_2 levels similar to or only marginally less than the Recent level of 21%, as in the Berner curves (Fig. 5). Second, the same interval was characterized by large changes in global climate, for example, a cooling trend during the Middle and Late Ordovician (Hambrey, 1985; Crowley and North, 1991; Frakes et al., 1992; Brenchley et al., 1994; Marshall et al., 1997; Crowell, 1999; Sutcliffe et al., 2000; Brenchley et al., 2003; Pope and Steffen, 2003; Shields et al., 2003) and strong climate fluctuations during the Silurian (Leggett et al., 1981; Jeppsson, 1990; Aldridge et al., 1993). These fluctuations were linked to perturbations in the global carbon cycle such as changes in the inorganic–organic C burial ratio (Hatch et al., 1987; Ludvigson et al., 1996; Patzkowsky et al., 1997; Saltzman, 2005), which would certainly have caused atmospheric O_2 levels to vary. The invariance of the Cambrian–Devonian portions of the Berner and BLW2004 models (Fig. 5) is at odds with the climate data. On the other hand, the model of the present study exhibits patterns consistent with the geologic evidence: generally low atmospheric O_2 levels during the Cambrian–Devonian interval but with a transient rise to near-Recent values peaking in the Late Ordovician.

3.3.4. The "Devonian charcoal gap"

Particularly interesting are differences between the Devonian portions of the atmospheric pO_2 models considered here. All of the models show a steep rise beginning in the Middle Devonian, but the pre-rise baseline is ~13–18% O_2 in the Berner curves versus ~5–7% O_2 in the BLW2004 curve and the present model (Fig. 6). The BLW2004 curve and the present model differ in that the latter infers moderately high Late Silurian O_2 levels (~15–17%) before falling to an Early to Middle Devonian low. These differences are potentially significant in that the various models implicitly make different predictions about when sufficient atmospheric O_2 was available to sustain combustion of vegetation (based on the ~13% threshold of Chaloner, 1989) and, hence, about secular trends in charcoal production. The atmospheric pO_2 model of the present study seems to match most closely the extant record of fossil charcoal occurrences.

A survey of the literature on fossil charcoal occurrences shows that the earliest reported charcoals are of late Late Silurian (Pridolian) and early Early Devonian (Lokhovian) age (Fig. 6), associated with low-growing rhyniophytoid assemblages (Robinson et al., 1997; Edwards and Axe, 2004; Glasspool et al., 2004), although such occurrences are not universally accepted (Rowe and Jones, 2000). Middle and Upper Devonian coals are rare and typically contain little or no charcoal. For example, thin (0.2–0.5 m) Givetian and Frasnian coals from Arctic Canada are reported to contain <4% inertinite and 'negligible' fusinite (Goodarzi and Goodbody, 1990). Beginning in the late Late Devonian (Famennian), fossil charcoal is found in greater abundances (Rowe and Jones, 2000; Cressler, 2001), and the Carboniferous record of fossil charcoal is extensive (Beck et al., 1982; Scott et al., 1985; Jones and Chaloner, 1991; Nichols and Jones, 1992; Scott and Jones, 1994; Scott et al., 1997; Falcon-Lang, 1998, 2000; Rowe and Jones, 2000; Scott, 2000).

The significance of the fossil charcoal record lies in the fact that charcoal production requires both fuel in the form of vegetative matter and sufficient oxygen to sustain combustion. Combustible fuel has probably existed since the Late Silurian as evidenced by reports of fossil charcoal in association with the primitive rhyniophytoid vascular plants that inhabited lowland areas during that time (e.g., Gensel and Andrews, 1987; Thomas and Spicer, 1987; Edwards and Berry, 1991; Beerbower et al., 1992). By the Givetian (late Middle Devonian), secondary woody tissues had evolved and forests had appeared (Chaloner and Sheerin, 1979; Mosbrugger, 1990), and by the Frasnian (early Late Devonian) extensive forests of the progymnosperm *Archaeopteris* were present on many continents (Meyer-Berthaud et al., 1999). Thus, woody plant tissues were abundantly present during the Givetian–Frasnian, conditions that should have been conducive to widespread wildfires (Scott, 2000). The lack of documented occurrences of fossil charcoal from these epochs, despite the apparent availability of fuels, suggests that atmospheric O_2 levels may have been too low to sustain combustion at that time (e.g., Fig. 6). This inference is independently supported by paleoecological data (Lethiers and Whatley, 1994). An interesting speculation is that low atmospheric O_2 levels may have delayed the terrestrial invasion of vertebrates until the latest Devonian (Thomson, 1993; Clack, 2005).

One further study with implications for the "Devonian charcoal gap" is that of Rimmer et al. (2004). They generated a high-resolution record of organic maceral frequencies through the Famennian Ohio Shale and the early Tournaisian Sunbury Shale of the Central Appalachian Basin. This record shows a sharp increase in the burial flux of inertinite during the latest Devonian (Famennian), even as vitrinite concentrations remain almost uniform (Fig. 6, inset). Because both of these maceral types are sourced from higher plants, the divergence in their abundances during the Famennian cannot be explained simply as a function of proximity to terrestrial sources. The pattern is consistent with a sharp increase in atmospheric pO_2 levels across the critical ~13% threshold during the Late Devonian (cf. Lethiers and Whatley, 1994, their fig. 1). Other interpretations of the data are possible, e.g., that the rise in inertinite abundance is associated with the advent and spread of seed plants into drier upland areas during the Late Devonian (Algeo et al., 1995, 2001). However, these processes are potentially interrelated, e.g., the spread of seed plants into drier habitats may have accelerated the production of charcoal which, when buried in sufficient quantity, contributed to a rise in atmospheric pO_2. This represents a potential positive feedback on atmospheric pO_2 levels that may operate in the range of the 13% combustion threshold.

3.4. Implications for feedbacks between the marine phosphorus cycle and atmospheric pO_2

The comparatively short residence time of oxygen in the atmosphere (~4 myr; Walker, 1977) and the apparent stability of atmospheric O_2 concentrations for periods of tens to possibly hundreds of millions of years (Watson et al., 1978; Holland, 1984; Lenton and Watson, 2000a, b) require that some types of stabilization mechanism exist. Simple models show that, without such feedback mechanisms, slight imbalances in the biogeochemical cycle of O_2 can result in extremely large fluctuations in atmospheric oxygen concentrations, even to the point of producing an anoxic atmosphere (Van Cappellen and Ingall, 1996). Although diverse stabilization mechanisms have been proposed (see Lenton and Watson, 2000b, for a review), the most important may involve feedbacks between the marine P cycle and atmospheric pO_2.

The influence of redox-sensitive P burial on marine productivity has been explored in a number of models (Van Cappellen and Ingall, 1994, 1996; Lenton and Watson, 2000a,b; Wallmann, 2003). One feature of these models is the "anoxia-productivity feedback," in which oxygen depletion in bottomwaters enhances the benthic flux of P from sediments, remineralized P stimulates primary productivity in surface waters, and an increase in the sinking flux of organic C intensifies respiratory oxygen demand in the water column (Fig. 7A, cycle I). This cycle represents a positive feedback loop that operates in local environments on a sub-million-year timescale (Fig. 7B). Redox-sensitive benthic P fluxes are also part of a larger feedback system termed the "C_{org} burial-pO_2 feedback" (Fig. 7A, cycle II). As the extent and intensity of low-oxygen seafloor conditions increase, more organic C is buried and more oxygen is released to the atmosphere. Increases in atmospheric oxygen and subsequent increases in the dissolved oxygen concentration of seawater eventually counteract decreases in bottomwater oxygen associated with enhanced organic C sinking fluxes (Van Cappellen and Ingall, 1996). This cycle represents a negative feedback loop that operates globally on a multi-million-year timescale (Fig. 7B). The concurrent operation of these two feedbacks has important implications for marine anoxic events, which may be self-sustaining on a sub-million-year timescale

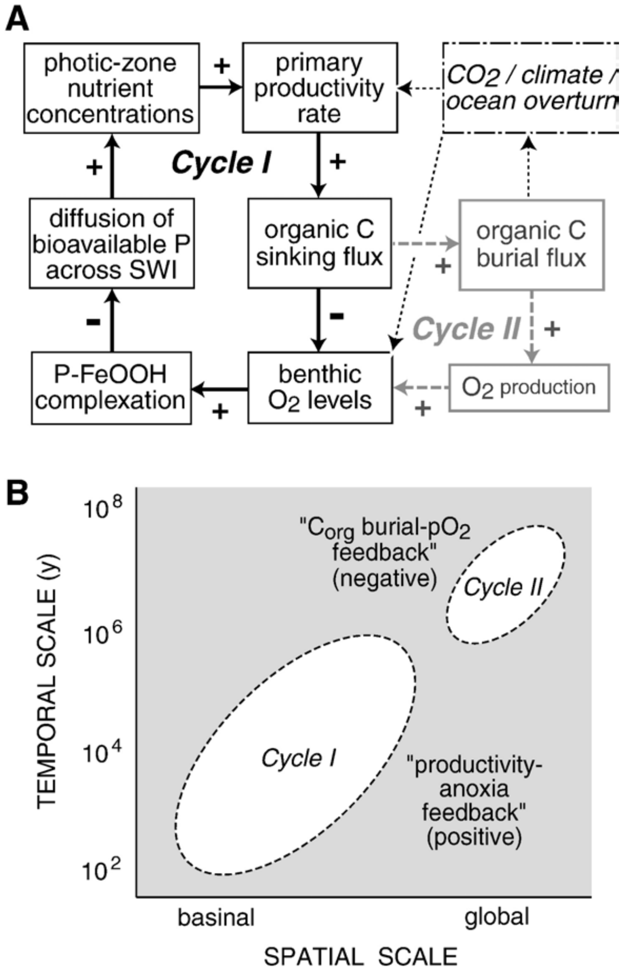

Fig. 7. (A) Model of feedbacks between the marine P cycle and atmospheric pO_2. Cycle I represents the "productivity-anoxia feedback" and cycle II the "C_{org} burial-pO_2 feedback" (see text for discussion). (B) Characteristic spatio-temporal scales of operation of these feedbacks. Differences in scale between cycles I and II imply that marine anoxic events should be self-reinforcing on sub-million-year timescales and self-limiting on multi-million-year timescales.

due to the productivity-anoxia feedback but are inherently self-limiting on a multi-million-year timescale due to the C_{org} burial-pO_2 feedback. Other feedbacks between the marine P cycle and atmospheric pO_2 may exist as well, although the scale and, in some cases, the sign of these feedbacks are in doubt. For example, changes in the burial flux of organic C can influence atmospheric pCO_2, global climate, and ocean overturn rates. Changes in ocean overturn rates affect upwelling of nutrients and downwelling of dissolved oxygen, both important links in the marine P-atmospheric pO_2 feedback system (Fig. 7A). Whether an increase in ocean overturn rates has a stronger effect on primary productivity rates (cycle I) or benthic O_2 levels (cycle II) will ultimately determine if the net effect is a positive or a negative feedback; indeed, the sign of this relationship may be influenced by epoch-specific paleogeographic and paleoclimatic factors (e.g., Broecker et al., 2004).

The C_{org} burial-pO_2 feedback in particular has been hypothesized to act as a key control in the stabilization of atmospheric pO_2 on a multi-million-year timescale (Van Cappellen and Ingall, 1994, 1996; Colman and Holland, 2000; Lenton and Watson, 2000a,b; Wallmann, 2003). The secular coherence of the Phanerozoic C_{org}:P record at a similar multi-million-year timescale (Fig. 4) is consistent with this inference. However, the variability in C_{org}:P ratios that characterizes the Early and Middle Paleozoic may indicate a weaker feedback at that time. This inference appears to be at odds with the model results of Van Cappellen and Ingall (1996), who showed that larger degrees of C–P fractionation (i.e., higher sedimentary $(C{:}P)_{org}$ ratios) have a stronger stabilizing effect on atmospheric pO_2 perturbations. On this basis, the generally high C_{org}:P ratios of Early to Middle Paleozoic organic-rich facies (Fig. 4) should be associated with more uniform atmospheric O_2 levels. One explanation may be that the strength of this stabilizing feedback is pO_2-dependent, and that it operates most effectively at higher atmospheric O_2 concentrations. At lower O_2 concentrations, as during the Early and Middle Paleozoic, the effect may have been weakened by a positive feedback between atmospheric pO_2 and charcoal production and burial (see Section 3.3.4). Alternatively, the apparent increase in stability of atmospheric pO_2 since the Carboniferous might be linked to negative feedbacks involving the terrestrial biosphere, as proposed by Kump (1988). In his model, higher atmospheric O_2 levels result in an increase in terrestrial wildfires, which cause a transfer of nutrients from land areas to oceans, where smaller quantities of organic C are buried per unit P. A smaller $(C{:}P)_{org}$ ratio for the cumulative burial flux of terrestrial and marine organic matter would result in a lower rate of release of oxygen to the atmosphere, counteracting the initial increase. Further research will be needed to determine the time- and pO_2-dependence of feedbacks in the marine P-atmospheric pO_2 system.

4. Conclusions

The C_{org}:P ratios of marine sediments are strongly influenced by benthic redox conditions. Oxygen depletion simultaneously enhances preservation of organic C and diffusive loss of remineralized organic P, whereas the presence of oxygen simultaneously promotes oxidative destruction of organic C and retention of remineralized organic P in the sediment. Modern marine environments exhibit a strong relationship between benthic redox status and C_{org}:P ratios, with anoxic facies yielding median C_{org}:P ratios of ~110–200:1. A survey of 58 different organic-rich facies (TOC>1%) of Late Cambrian to Recent age shows considerably greater variation in median C_{org}:P ratios, from a low of 1.7:1 in the Late Permian to a high of ~1625:1 in the Middle Devonian. In general, Cambrian to Devonian organic-rich facies yield markedly higher C_{org}:P ratios (mostly >100:1) than Carboniferous to Recent organic-rich facies (mostly <100:1). The limited range of variation in median C_{org}:P ratios among modern anoxic marine environments in combination with the strong secular coherence of the Phanerozoic C_{org}:P record implies that local influences on benthic redox potential (e.g., water depth, vertical stratification, and deepwater renewal processes) exert only moderate control over these ratios, and that a global variable (e.g., atmospheric pO_2) is responsible for most of the variance at geologic timescales. An atmospheric pO_2 model generated from the Phanerozoic C_{org}:P record implies that O_2 levels were generally lower during the Early to Middle Paleozoic than inferred by existing models, and that very low O_2 levels (<10%) during the Devonian may account for an anomalous lack of contemporaneous fossil charcoal (the "Devonian charcoal gap"). The redox-dependent burial of phosphorus in the ocean results in positive and negative feedbacks that influence atmospheric oxygen concentrations over geologic time. The secular coherence of the Phanerozoic C_{org}:P record is consistent with the inferred dominant role of the "C_{org} burial-pO_2 feedback" mechanism in the long-term stabilization of atmospheric O_2 concentrations. The interaction of this mechanism with the positive "productivity-anoxia feedback" implies that marine anoxic events should be self-reinforcing at sub-million-year timescales but are inherently self-limiting at multi-million-year timescales.

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