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Phosphorus, a Servant Faithful to Gaia? Biosphere Remediation Rather Than Regulation

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Abstract

The global cycles of the biophile elements phosphorus and carbon are closely linked through their profound implication in two major biogeochemical processes, photosynthesis and biogeochemical weathering. In photosynthetic processes phosphorus may limit the transformation of atmospheric CO_2 into organic carbon, and in biogeochemical weathering processes atmospheric CO_2 may limit the mobilization of phosphorus. During environmental change, changes in both cycles are coupled and associated feedback mechanisms have important implications on the biosphere.

In this chapter, we study the character of the coupled changes in the phosphorus and carbon cycles during the last 160 million years and propose feedback mechanisms between the two cycles. We explore the effects of the proposed feedback systems on the biosphere and especially their capacity to regulate environmental conditions in a Gaian sense. For this purpose, we use marine phosphorus and carbon burial rates, a modeled atmospheric CO_2 curve, and stable carbon isotopes as proxies for temporal change in the global phosphorus and carbon cycles. Based on the temporal changes within these proxies, we postulate a period of fundamental change in feedback between weathering, productivity, and climate at around 32 million years ago, which is explained by the onset of major glaciation. This suggests that feedback mechanisms may not be uniform throughout Earth's history but may change during environmental change. We also observe evidence for complex interactions between the carbon and phosphorus cycles, which suggests that the two cycles are not necessarily coupled in a linear fashion.

Our general conclusion is that the phosphorus and carbon cycles are characterized by interactions and resulting feedback mechanisms, which show stabilizing effects only to a certain extent. The effects of global change extrinsic to the biosphere, such as volcanic events, changes in orbital parameters, and impacts, and intrinsic change related to biological evolution appear to overrule the tendency toward stable conditions, and the associated feedback mechanisms are considered to be remediative rather than regulatory.

Introduction

Phosphorus is an element essential to life. Within the biosphere, it drives plant growth and fosters the transformation of atmospheric CO_2 into organic carbon through photosynthesis. This vital process provides a close link between phosphorus and carbon and their respective cycles (figure 7.1).

The delivery of phosphorus to the biosphere is accomplished predominantly by biogeochemical weathering of continental rocks. This process is highly dependent on the availability of atmospheric CO_2, which—under natural conditions—forms a weak acid with water and dissolves rocks. For this reason, weathering provides a second interface with the carbon cycle, albeit with reversed signs. In photosynthetic processes, phosphorus provides a driving force for an important phase change within the carbon cycle, whereas in weathering processes carbon is instrumental in pushing an important phase change within the phosphorus cycle (figure 7.1). These two interfaces tightly couple both cycles, and therefore these cycles temporal and spatial changes occur interdependently.

Biogeochemical weathering is a process which involves biological participation, and photosynthesis is a biological process per se. There is thus an important biological momentum in linking the two cycles, and the question to be posed here is in how far this momentum shows Gaian properties—that is, regulative capacities in a homeostatic sense (Lovelock and Margulis, 1974; Lovelock, 1988). The approach taken here in trying to provide an answer is to reconstruct how temporal changes in the global phosphorus cycle have been linked to those in the carbon cycle during the last 160 million years (myr) of the history of the biosphere, and to evaluate whether these changes can

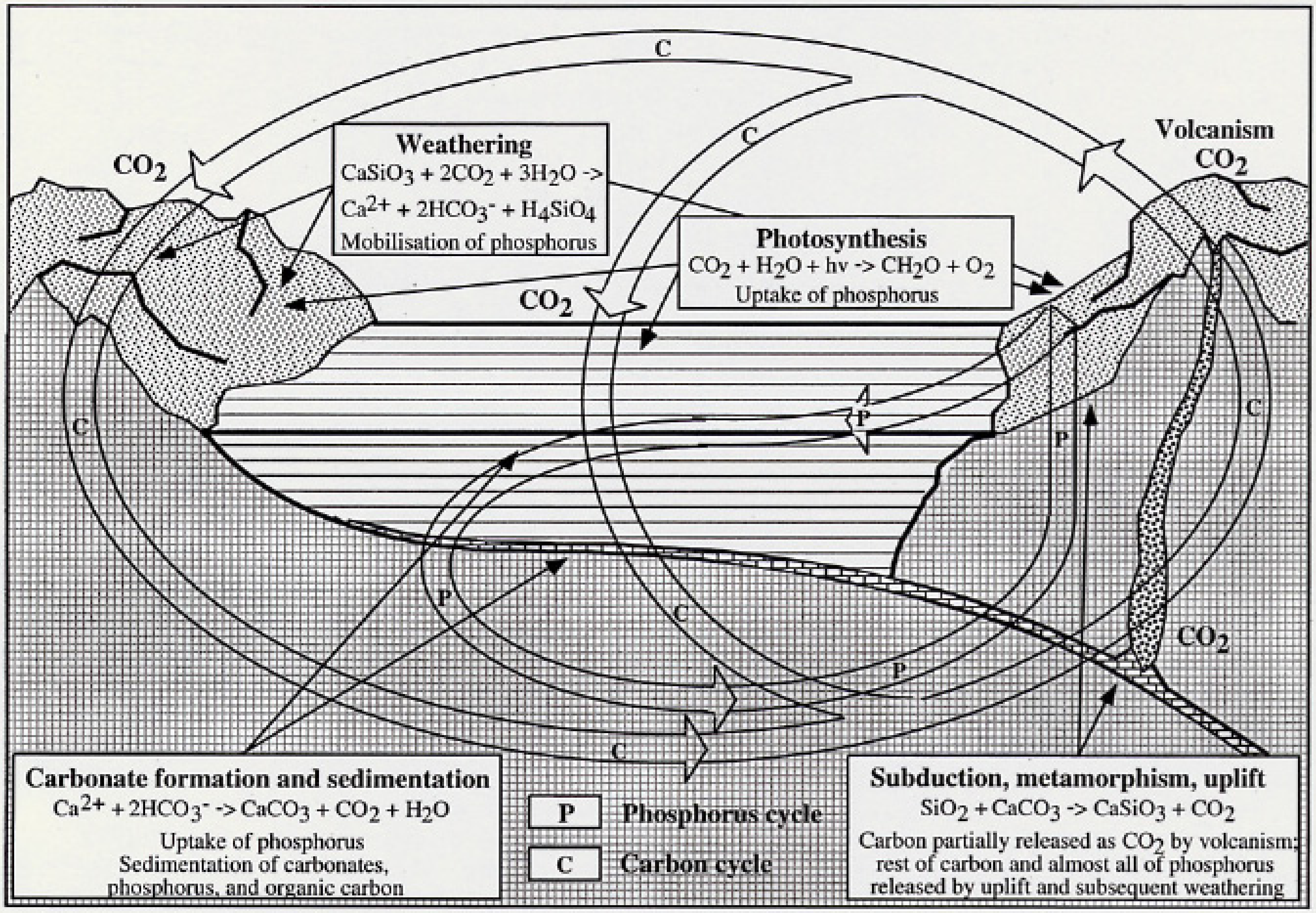

Figure 7.1
Qualitative and schematic overview of the long-term carbon and phosphorus cycles and the model reactions essential in the transfer and phase changes of carbon and phosphorus.

be interpreted as favorable to the biosphere (i.e., leading to a negative, and therefore stabilizing, feedback effect on environmental conditions). It will be shown here that—related to the nonlinear and complex character of change within the biosphere—no simple and uniform answer can be given.

Proxy for Temporal Change in the Global Phosphorus Cycle

The choice of a reliable proxy for temporal change in phosphorus input and sedimentary removal is limited to the oceanic sedimentary record. Such a record reflects changes in the phosphorus budget on local, regional, and global levels. This phenomenon is related to the observation that phosphorus is a reactive element and its residence time in oceanic systems is considered to be short (around 10,000 years; Colman and Holland, 2000). This means that its spatial distribution within the different ocean basins is not homogeneous, and is biased by its importance as an essential nutrient relative to other nutrients (Codispoti, 1989; Tyrell, 1999), by local to regional differences in phosphorus uptake through primary productivity and subsequent remineralization, and by the capacity of sediments to efficiently store phosphorus (Colman and Holland, 2000), among other factors. It is therefore crucial to use a record which is representative for large parts of the oceans, in order to extract a signal of wider significance.

The record we propose here is based on a compilation of phosphorus accumulation rates, which were calculated from systematically measured phosphorus contents in a great variety of Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) cores (figure 7.2; Föllmi, 1995, 1996). This record is used as

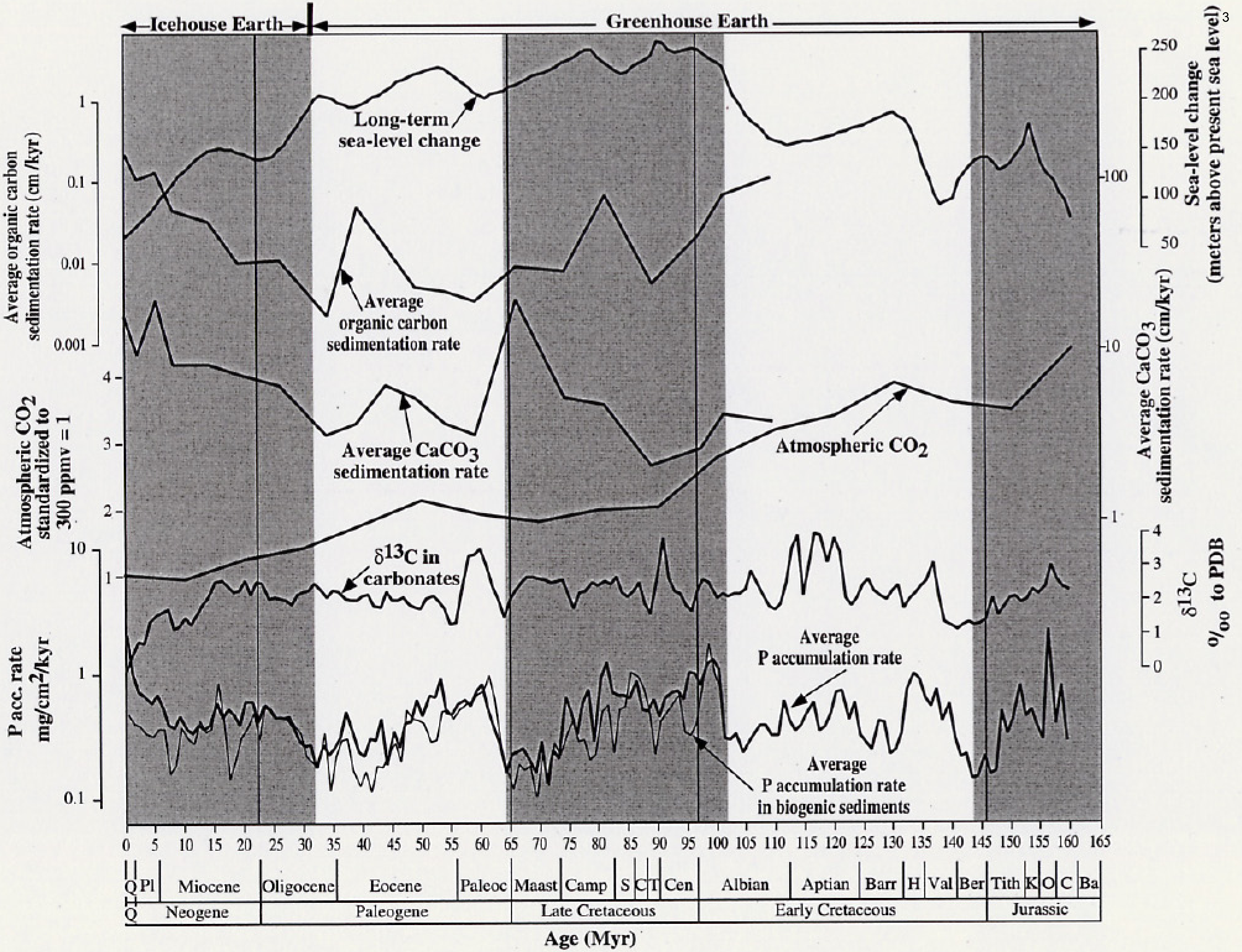

Figure 7.2
Evolution of marine phosphorus burial rates (for all types of sediments and separately for biogenic sediments) (Föllmi, 1995); the $\delta^{13}C$ whole-rock record of marine carbonates (Föllmi, 1996); atmospheric CO_2 contents (Berner, 1994); carbonate and organic carbon sedimentation rates (Southam and Hay, 1981); and long-term sea-level change (Haq et al., 1987).

a proxy for temporal changes in the global phosphorus cycle over the last 160 myr, which are coupled to changes in the intensity of continental weathering. It is suggestive of a close coupling between overall and chemical weathering rates, and between overall sediment and phosphorus accumulation rates. It shows also evidence for an important change in the coupling between climate, weathering, and productivity at around 32 myr. For the period prior to 32 myr, a positive correlation is observed, suggesting a link between warm climates, increased biogeochemical weathering rates, and phosphorus release and burial rates, whereas from 32 myr on, this correlation appears to be inverse, thereby suggesting a link between cooling periods, intensified weathering rates, and phosphorus mobilization and burial rates. The cause of this inversion is identified as the onset of widespread glaciation (Föllmi, 1995, 1996).

Since its first publication, we have received several criticisms challenging the assumption that this record is representative on a global scale. These concerns evolve around four observations: (1) older portions of the curve are constructed on fewer data relative to younger portions, and may not be as reliable; (2) glaciation is associated with mechanical weathering rather than biogeochemical weathering, and periods of increased glaciation should lead to lower mobilization rates of phosphorus rather than higher; (3) DSDP and ODP drill sites are for a large part located in the deeper waters of open oceans, and the shallower parts of shelf areas are generally underrepresented—this means that the effect of sea-level change and the associated shift in sedimentary depo-centers and phosphorus burial rates may influence phosphorus burial rates; and (4) ocean-inherent changes, such as the capacities to transform occluded phosphate phases into bio-available phases and to store phosphate, also may interfere (e.g., Van Cappellen and Ingall, 1994; Colman and Holland, 2000).

In order to explore the relevance of these observations, we decided to perform three tests. The first test considered observation (1) and consisted of a reexamination of an important part of its early Cretaceous portion (137 to 132 myr; Valanginian-Hauterivian), which is an older part within this compilation and based is on relatively few data in comparison to younger parts. For this test, 575 phosphorus concentrations were measured in eight continental sections in central and southern Europe for their Valanginian and Hauterivian portions (Van de Schootbrugge et al., in press). The resulting compilation correlates very well with the DSDP- and ODP-based data set, which suggests that the curve is robust for this time interval.

The second test considered observation (2) and consisted of a close-up study of the last full glaciation phase. Here different phosphorus phases were analyzed in a selection of eight ODP cores using a sequential extraction method (Ruttenberg, 1992; Anderson and Delaney, 2000; Tamburini, 2001). An important result was that during this last phase of glaciation, variations in phosphorus burial were coupled to climate change, albeit on a shorter time scale, in the range of the precession band frequency. In addition, glacial periods during this last glaciation show comparable to slightly higher phosphorus burial rates than interglacial stages (Tamburini, 2001; Tamburini et al., 2003).

The third test also considered observation (2) and included a detailed analysis of the importance of biogeochemical weathering processes in glaciated areas. Here we selected the Rhône and Oberaar glacier catchments—both situated within the crystalline basement of the Aare massif (central Switzerland)—and performed analyses on the geochemistry of the outlet waters, mineralogy of suspended material, and geochemistry and mineralogy of moraine material of different ages. One outcome was that glaciers have an important potential for increasing biogeochemical weathering rates during and especially immediately after glaciation phases (Hosein et al., in press).

With regard to observation (3), a positive correlation between sea-level change and phosphorus burial rates is given for a major part of the curve, indicating that the effect of sea-level rise in shifting depo-centers toward the continent is negligible relative to the increase in burial rates observed. Finally, with regard to observation (4), ocean-inherent changes in the capacity to transform and store phosphorus may considerably change the ocean residence time of phosphorus. For instance, it may very well be that during a period of increased anoxic conditions, such as the late Cenomanian to early Turonian, may have decelerated phosphorus burial rates on a wider scale (Van Cappellen and Ingall, 1994; see also below). However, the robustness of the curve displayed by the resemblance of the data extracted from biogenic sediments to the total curve (self-similarity) and by the meaningful correlation of the phosphorus burial curve with other paleo-environmental proxies such as sea-level change encourages us to consider the phosphorus burial curve as representative on a global scale.

Proxies for Temporal Change in the Global Carbon Cycle

There are several types of proxies for temporal change in the carbon cycle, all of which will be examined here. A first type is comparable with the one used for phosphorus, a compilation of carbonate and organic carbon burial rates, which is based on a series of DSDP drill sites (figure 7.2; Southam and Hay, 1981). The disadvantages this compilation is that it does not include the data sets of the more recent DSDP and ODP drill legs, and it does not show the same time resolution as the phosphorus curve. Unfortunately, more recent compilations are not available.

The organic carbon curve suggests high organic carbon sedimentation rates prior to approximately 100 myr, at around 80 and 40 myr, and from approximately 25 myr on. The carbonate curve shows maxima for the period around 65 and 45 myr and an increasing trend from approximately 25 myr onwards. The two curves show quite good correlation in the time intervals prior to 90 myr and from 65 myr on. The period between 90 and 65 myr is characterized by poor correlation between the two proxies.

A second type of proxy is based on the $\delta^{13}C$ whole-rock record of marine carbonates, which is interpreted as a measure of the ratio of carbonate carbon burial and organic carbon production and burial at a given time. Here sufficient data sets are available and the resolution is comparable with that of the phosphorus burial curve (figure 7.2). The $\delta^{13}C$ record correlates poorly to the sedimentation curves of carbonates and organic carbon, which is probably related to the differences in resolution and data density, in addition to original differences between production and burial rates.

A third type consists of modeled atmospheric CO_2 concentrations and temporal changes therein (figure 7.2; Berner, 1994). Here, too, resolution is poor in comparison with the phosphorus and $\delta^{13}C$ data sets. The curve shows a rather steady decrease toward the present, with relative maxima around 130 and 50 myr.

For the purpose of this chapter, we will concentrate on the $\delta^{13}C$ curve as a reference curve, and compare its evolution against the trends shown by the phosphorus curve. The other proxy curves will be used as additional sources of information.

Temporal Links Between the Carbon and Phosphorus Cycles and Their Interpretation

From a comparison of the phosphorus burial and the $\delta^{13}C$ curves, we intend to gain information on the character of coupling between the carbon and phosphorus cycles for the last 160 myr, as well as on the types of reactions and feedback mechanisms during periods of major environmental change. For this purpose, we divided this time period into five distinct intervals (figure 7.2), which we will examine separately.

Interval 160–143 myr

The oldest interval includes the last 160–143 myr (Bajocian–Berriasian), and is characterized by an increase in both $\delta^{13}C$ and phosphorus burial values up to 154 myr, followed by an unsteady decrease in values. With regard to the main trend, the two curves correlate rather well. This general trend is also seen in sea level (albeit with an offset between the two maxima). Atmospheric CO_2 values decrease until 150 myr and slowly increase thereafter. The rather good correlation between the $\delta^{13}C$ and phosphorus burial curve is explained by a period of warming and sea level rise until 154 myr, which led to intensified continental weathering and phosphorus mobilization (e.g., Bartolini and Cecca, 1999). The increased availability of phosphorus induced higher productivity and organic carbon burial rates (relative to carbonate carbon), which again is expressed by increasing $\delta^{13}C$ values. The period between 154 and 143 myr was one of sea-level fall, which probably was linked to a period of cooling (drop in atmospheric CO_2) and less intense weathering. Productivity levels were lowered and $\delta^{13}C$ values became lighter. This change is explained by a negative feedback reaction following the period of warming (figure 7.3).

The causes of the warming and sea-level rise have not been identified yet. Among the proposed mechanisms, an episode of intense volcanism and increased volcanic CO_2 outgassing is a likely candidate (Bartolini and Cecca, 1999).

Interval 143–101 myr

During the period between 143 and 101 myr (Berriasian to Albian), the general trends in phosphorus burial and $\delta^{13}C$ curve also correlate rather well. A pronounced increase in phosphorus burial at the beginning of this period was followed by an increase in $\delta^{13}C$ values. A relative minimum is seen for both curves at around 130–125 myr, whereas a relative

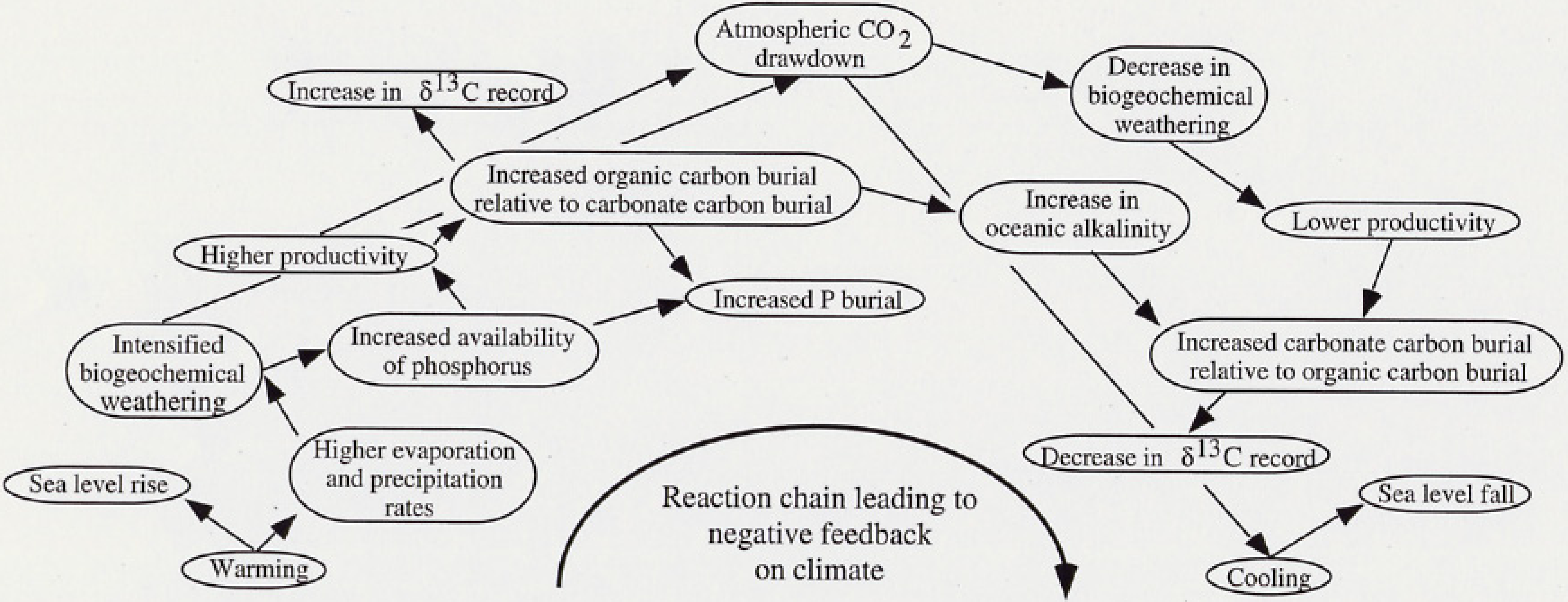

Figure 7.3
Network of reactions leading to negative feedback proposed for the period between 160 and 32 myr (after Föllmi et al., 1994).

maximum is present between 120 and 112 myr. During this period, the large increases in phosphorus burial led the increases in $\delta^{13}C$ by several million years. This may hint at a delay in response time by the $\delta^{13}C$ record to phosphorus-induced changes in productivity, due eventually to a difference in response time between phosphorus (short present-day oceanic residence time of around 10 kyr) and carbon (longer present-day oceanic residence time of several 100 kyr). It may also be noted here that the general shape of the phosphorus burial curve is mirrored by the long-term trend in sea-level change. This link may confirm the type of interaction between climate, continental weathering, and phosphorus mobilization, as was postulated for the previous period (e.g., Föllmi et al., 1994).

The period between 136 and 133 myr is characterized by a decoupling between the two signatures: The phosphorus burial record remains high until 133 myr, whereas the $\delta^{13}C$ record shows a decline in values at around 136 myr. This decoupling is interpreted as the consequence of the following chain of events (figure 7.3; Van de Schootbrugge, 2001; Van de Schootbrugge et al., in press): Analogous to the scenario invoked for the previous period, a warming period associated with a phase of pronounced sea-level rise led to intensified weathering on the continents, and therefore to increased phosphorus availability and higher productivity rates. One of the consequences of this environmental change was a widespread drowning episode of carbonate platforms (Schlager, 1981; Föllmi et al., 1994) and a presumed general increase in the ratio of buried organic carbon and carbonate carbon indicated by the positive excursion in $\delta^{13}C$ values (Lini et al., 1992). This increase and sustained high weathering rates led to a build up of oceanic alkalinity, which was then compensated for by a large increase in carbonate production and a second change in the ratio of buried organic carbon to carbonate carbon toward lower values (figure 7.3; Weissert et al., 1998; Van de Schootbrugge et al., in press).

Episodes of intensified volcanism and increased CO_2 output during the Valanginian, and Aptian and Albian (Larson, 1991; Föllmi et al., 1994; Van de Schootbrugge et al., in press) have been identified as the general cause of global warming during this time period.

Interval 101–65 myr

The time period of 101–65 myr (Albian–Maastrichtian) shows a rather positive correlation between phosphorus burial and long-term sea-level change, and the low-resolution organic carbon sedimentation curve appears to confirm both trends in such a way that the link between volcanism, warming, intensified weathering, mobilization of phosphorus, higher productivity, and higher organic carbon burial rates may also apply to this time period (figure 7.3).

In contrast to the two previous periods, the $\delta^{13}C$ curve shows almost no correlation with the phosphorus burial curve. An explanation may be found in the shape of the carbonate carbon sedimentation curve, which shows a decrease between 101 and 90 myr, followed by a marked increase in values from 90 myr on. This increase is correlated with an important phase of proliferation in planktonic carbonate-producing calcisphaerulides and Foraminifera (e.g., Scholle et al., 1983), and a corresponding increase in sedimentation rates of pelagic carbonates. This new mechanism of carbonate production leading to an efficient transfer of carbonate carbon to the oceanic sedimentary reservoir may have had an influence on the $\delta^{13}C$ signature in a way which has not yet been explored in detail. Possibly the formation of organic carbon associated with pelagic carbonate production was high as well, and this may have had a buffering effect on the global planktonic $\delta^{13}C$ signature. The burial rate of organic carbon, however, remained relatively low, which was eventually related to longer transfer ways (from 80 myr on).

A particular case is the "anoxic event" at around 90 myr (Cenomanian-Turonian boundary; e.g., Arthur and Schlanger, 1979; Arthur et al., 1985; Jenkyns, 1980), which is characterized by a pronounced positive excursion in $\delta^{13}C$ values, and relatively low corresponding values for phosphorus burial. Here the scenario developed by Van Cappellen and Ingall (1994) may help to explain this particular decoupling. The period around 90 myr is considered to be a time with particularly widespread dysaerobic conditions in oceanic bottom waters and a corresponding poor retention potential for phosphorus in anoxic oceanic sediments. The positive $\delta^{13}C$ excursion during this period was probably the expression of a shift in the ratio of carbonate carbon burial and organic carbon burial in favor of organic carbon, due in part to a widespread drowning event on carbonate platform systems (e.g., Jenkyns, 1991).

Interval 65–32 myr

The period between 65 and 32 myr (Paleocene–Oligocene) is characterized by a steep increase in phosphorus burial at its onset, followed by a long and irregular decrease in values. The general trend toward lower values was superimposed on by relative maxima around 52, 43, and 37 myr. The general trend in phosphorus burial is only partly mirrored by the $\delta^{13}C$ curve. Sea-level change appears to follow phosphorus burial, which may suggest that the feedback between climate, phosphorus mobilization, and productivity may be also applicable for this period. The trend in rising atmospheric CO_2 values until 50 myr, the initial marked increase in $\delta^{13}C$ values, and the initial decrease in the ratio of carbonate carbon and organic carbon burial are compatible with this scenario.

The increases in organic carbon and carbonate carbon burial from 60 myr on (with maxima at 45 and 40 myr, respectively) are not correlatable to any other trend, with the possible exception of the phosphorus burial curve. It would be good to have more detailed compilations of organic and carbonate carbon burial for this time period, in order to corroborate this lack of correlation.

Interval 32–0 myr

This last interval differs from the previous periods in a substantial way. Phosphorus burial and sea-level change are inversely correlated, which may indicate that continental weathering and phosphorus mobilization are favored in periods of long-term cooling (Föllmi, 1995). With regard to the phosphorus burial and the $\delta^{13}C$ curves, a similar inverse correlation is seen for the period between 32 and 28 myr, and between 6 myr and the present. The entire period is characterized by a long-term increase in carbonate carbon and organic carbon sedimentation rates, and by a long-term decrease in atmospheric CO_2 values. A first step of cooling from 32 to 25 myr was accompanied by an increase in phosphorus burial and in carbonate carbon and organic carbon sedimentation. This was followed by an interval of warming (25–14 myr), characterized by relatively high phosphorus burial rates and by a slower increase in carbonate and organic carbon sedimentation rates. The period from 14 myr on was again characterized by a period of cooling, which is correlated to further important increases in phosphorus burial rates, and in carbonate carbon and organic carbon sedimentation rates.

The inverse correlation between phosphorus burial rates and sea-level change suggests that the rates of phosphorus influx into the oceans covaried with climate change in such a way that phases of cooling were coupled with increased phosphorus mobilization rates. As already stated, the change in this coupling at 32 myr is explained by the onset of widespread glaciation, which may have acted as the driving force in continental weathering from 32 myr on (Föllmi, 1995, 1996). Glacial activity is very efficient in abrading and grinding bedrock, thereby providing fine-grained material which may subsequently be subjected to biogeochemical weathering. The change from a positive correlation between sea-level rise and phosphorus mobilization to an inverse one suggests that the effect of glaciation was powerful enough to change an entire chain of feedback mechanisms (figure 7.4). The uplift of the Himalaya and the Alps during this period may have been an additional factor which helped to raise weathering rates in general (e.g., Raymo, 1994).

The mechanisms invoked to slow down and stop this chain of positive feedback are not yet positively identified. The development of permafrost soils in periglacial areas and the change from warm-based to cold-based glaciers, which are frozen to the underlying bedrock, may have been important factors. Both phenomena may slow down physical weathering (and with that biogeochemical weathering) and transport of weathered material in such a way that the chain of positive feedback is halted.

In addition to the reversal in signs on the feedback chain, it appears that the rate of carbonate sedimentation was less hampered by the higher rates of phosphorus availability during cooling phases within this last period, whereas in the previous periods—during phases of warming—high phosphorus mobilization rates often led to drowning events of carbonate platforms and a general decrease in carbonate sedimentation. This may explain why the $\delta^{13}C$ signal becomes more negative in times of cooling and sea-level fall, in spite of the increased availability of phosphorus.

Relationships Between Phosphorus and Carbon in Changing Ecosystems

The coupling between phosphorus and carbon is also of interest in regionally confined ecosystems. An example is given here, in which we suggest a nonlinear coupling of the two elements, due to the dynamics of the ecosystem concerned.

The example concerns the temporal evolution of a shallow-water carbonate platform system during the latest Jurassic and early Cretaceous (approximately 147–112 myr). This platform developed along the former northern Tethyan margin, and large portions are presently preserved in the central Europe Jura Mountains and Helvetic Alps (Funk et al., 1993; Föllmi et al., 1994). Three phases have been distin-

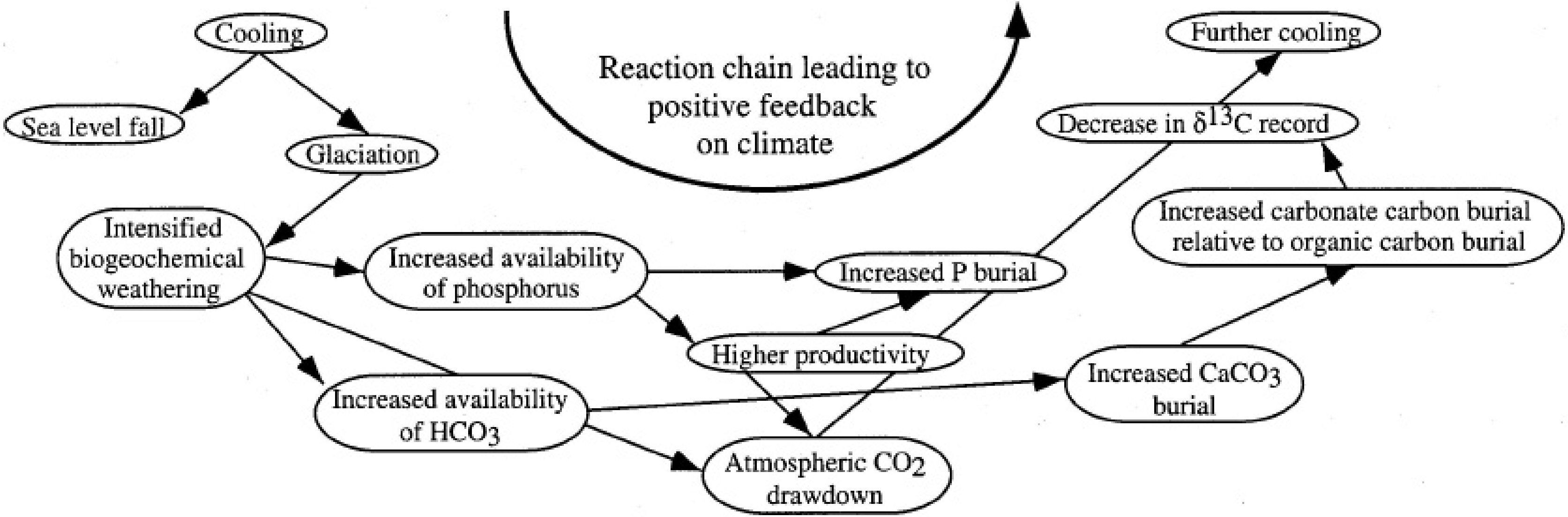

Figure 7.4
Network of reactions leading to positive feedback proposed for the period between 32 myr and present (after Föllmi, 1996).

guished in the evolution of this platform system: (1) platform growth in a "coral-oolith" mode, with carbonate production dominated by reef-type organisms (corals, chaetetids, rudists, stromatoporoids, calcareous sponges), as well as green algae and benthic Foraminifera. Another important mechanism is oolite formation ("chlorozoan mode," according to Lees and Buller, 1972); (2) platform growth in a "crinoid-bryozoan" mode, with carbonate production dominated by crinoids, bryozoans, bivalves, and brachiopods. Reef-related organisms are lacking ("foramol" mode, according to Lees and Buller, 1972); and (3) phases of platform drowning which are characterized by erosion and dissolution of preexisting carbonates, as well as the formation of thin and highly condensed, phosphate-rich horizons. The principal cause of change between the different modes was changes in nutrient levels, especially of phosphorus, as is shown by the changes in phosphorus burial rates in dependency of facies and the presence of macroscopic accumulations of phosphate-rich sediments during periods of platform drowning. Other factors such as changes in water temperature, related to sea-level change and the opening of gateways to the Boreal realm, were also of consequence (Van de Schootbrugge, 2001; Van de Schootbrugge et al., in press).

Sedimentation rates in the "coral-oolith" mode average around 2 cm/kyr and are maximally around 10 cm/kyr, whereas in the "crinoid-bryozoan" mode, they amount to average values around 5 cm/kyr and maximal values around 50 cm/kyr. The change from the first mode to the second was usually rather rapid and led to the buildup of well distinguishable lithostratigraphic formations. This suggests a link between phosphorus and carbonate carbon production (and sedimentation) in the following way: Carbonate production in the "coral-oolith" mode was under mostly oligotrophic conditions; an increase in phosphorus availability led to a rather rapid change in the composition of the platform ecosystem, including the loss of reef-related organisms. Carbonate production rates in the "crinoid-bryozoan" mode are significantly higher in comparison with the previous mode. Further increases in phosphorus availability led to a strong reduction in carbonate production and to the development of phosphate-rich drowning surfaces. In figure 7.5, we depict this development in a qualitative way to illustrate the development and the links observed between phosphorus availability and carbonate production.

Similar relationships are likely to occur in other ecosystems, such as coastal marine upwelling centers, where calcareous phytoplankton may be replaced by siliceous phytoplankton as a function of upwelling intensity, or in basins that become progressively eutrophic. In the analysis of population dynamics, Robert May pioneered the use of this type of "bifurcation" diagram (e.g., May and Oster, 1976), stating that dynamics are predictable until a threshold value is reached, from which point two states are possible (bifurcation). Within these two states, threshold values may be reached again, and four states are possible. Bifurcation may continue until a fully undeterminable situation is reached. From the research by May and many others, it appears that the relationships depicted in this example may be widespread in the biosphere.

Nonlinear Elements in the General Coupling of Phosphorus and Carbon and Its Importance to the Gaia Hypothesis

The relationships between phosphorus and carbon in the above-mentioned example are indicative of a nonlinear and complex system. This system has imminent properties which set it off from a linear and determinable system in a mathematic sense.

1. Figure 7.5 is characteristic of a nondetermined, complex system, in which different states are possible for the same set of conditions. In our example, production rates are dependent on the type of ecosystem available; once an ecosystem is not replaced by an ecosystem capable of coping with increased trophic conditions, productivity rates may break down, such as during phases of platform drowning.

2. The long-term evolution of phosphorus burial between 160 and 32 myr is characterized by the presence of an asymmetric pattern of development with main periodicities of around 33 and 18 myr (Tiwari and Rao, 1999). The asymmetry is expressed by short periods (3–5 myr) of rapid increase in phosphorus burial, followed by longer periods (12–30 myr) of irregular decrease. Superimposed on this long-term trend, shorter trends are visible which show a similar asymmetry (i.e., rapid increases in phosphorus burial followed by longer periods of decrease). This repetition of the same pattern on different time scales resembles a pattern of self-similarity, which is again indicative of a complex system. Comparable asymmetric patterns are known from other proxies, such as sea-level change (Haq et al., 1987), the $\delta^{18}O$ record in

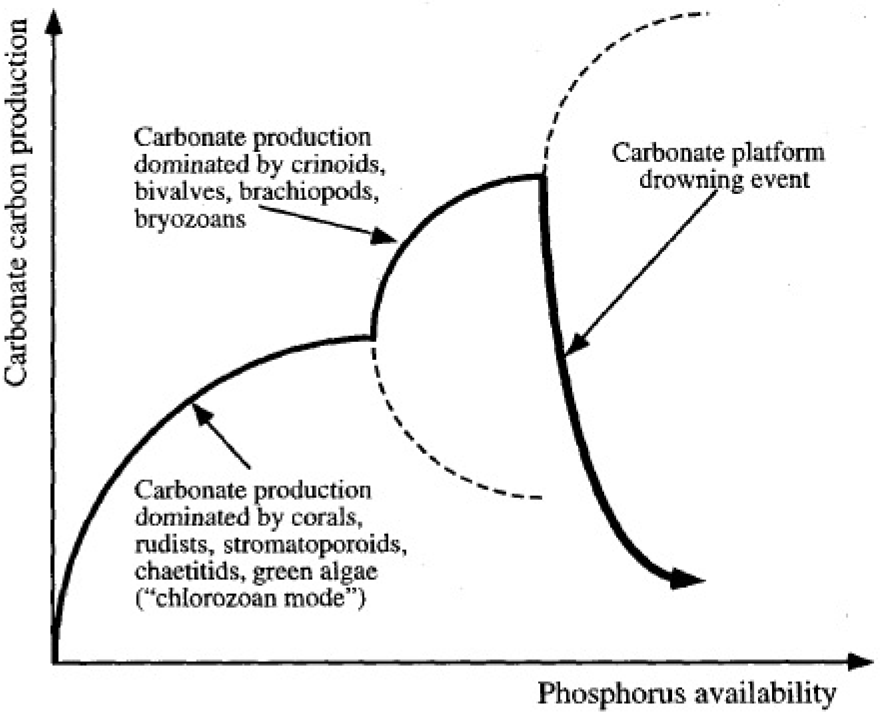

Figure 7.5
Qualitative bifurcation diagram depicting nonlinear relationships between phosphorus availability and carbonate carbon production.

ice cores, and the atmospheric CO_2 record measured in ice cores (e.g., Petit et al., 1999).

3. The asymmetric patterns in the phosphorus burial curve are characterized by the presence of minimal and maximal values between the periods of slow decrease and rapid increase. The extreme values are considered here to be threshold values, which mark a turning point within the chain of feedback reaction (i.e., the maximal values may mark the moment where negative feedback starts to have an effect on the environment (figure 7.3), whereas the minimal values appear to mark the effect of extrinsic events, which have a large impact on the entire system. The asymmetric shape appears, therefore, to be an expression of the interplay between extrinsic events (such as volcanic episodes; e.g., Courtillot, 1994), eventually helped by positive feedback (e.g., release of methane from clathrates during warming; Dickens et al., 1995; Kennett et al., 2000), and the effect of negative feedback, which tends to stabilize and prolong "stable" environmental conditions. The asymmetric shape is less pronounced in the phosphorus burial curve from the period from 32 myr to present, and this may be related to the change in sign on the postulated feedback mechanism (figure 7.4).

The presence of asymmetry in reaction, self-similarity in patterns, threshold values, nondeterminable behavior, and feedback reactions which may change signs according to environmental conditions—as suggested by the proxies used here to trace temporal change in the global phosphorus and carbon cycles—is characteristic of the complex, nonlinear dynamic character of the biosphere. It is the interaction of changes extrinsic to the biosphere, such as cyclic changes in astronomic parameters (Milankovitch cycles) and episodes of intense volcanism, and intrinsic to the biosphere, such as evolutionary patterns and degree of diversity in ecosystems, which renders this complexity to the biosphere system.

Within this pattern of complexity, we identify periods—such as those of slow and irregular decrease in phosphorus burial—in which negative feedback may have led to conditions of greater stability. In such periods, the pattern of change may be considered Gaian, albeit marked by great irregularity, as is shown by the repetitive character of change on different time scales. Of interest here is that during such periods, sea level was lowered, climate became cooler, weathering rates decreased, and phosphorus burial rates decreased. A feedback-guided convergence emerges from this pattern toward conditions of minimal energy use, toward a "saving mode," in which the transfer of energy and matter within the biosphere is minimalized. A similar trend is observed during

Pleistocene glaciation phases, where the trend goes toward colder temperatures in a comparable way (e.g., Petit et al., 1999).

The long-term trend toward a cooler climate was followed by a shorter phase of sea-level rise, warming, increased weathering rates, and increased phosphorus burial rates. Here the speed of change is related to the effect of extrinsic forcing—eventually helped by positive feedback; and it is during such periods that efficient negative feedback and regulation along Gaian pathways become important, in order to avoid protracted destabilization of the entire biosphere.

The period from 32 myr to the present is a different case: the role of phosphorus has changed in such a way that—in this last period—it has become an important driver in pushing positive feedback reactions, which seem to accelerate climate cooling (figure 7.4), whereas prior to 32 myr, it catalyzed negative feedback in times of warming (figure 7.3). This switch in feedback was forced by the change in the type of climate responsible for enhancing biogeochemical continental weathering rates. This change in the role of a biophile element in feedback processes has important implications for our understanding of the way the system Earth functions. The possibility of switching roles, and thereby changing signs on feedback mechanisms, adds an additional degree of complexity to environmental change and biosphere response.

In how far is the Gaia hypothesis compatible with the nonlinear dynamics described here? Signs of negative, stabilizing feedback are present in the records of the carbon and phosphorus cycles, and they allude to the regulative capacities of the Earth system. The shape of the patterns themselves, however, suggests that the nonlinear dynamics displayed during environmental change and induced by an interplay of intrinsic and extrinsic factors, prevent full-fledged stable conditions during longer time periods. During the last 160 myr, the feedback mechanisms described here appear to have remediated rather than regulated environmental conditions in response to the perils of global change, be it by extrinsic events, cyclic extrinsic change, intrinsic evolution and adaptation, or the unexpected consequences of complex dynamics.

Conclusions

Proxies used here in order to reconstruct temporal change in the global phosphorus and carbon cycles for the past 160 myr suggest the presence of feedback reactions which may change in character through time, the importance of threshold values, the possibility of self-similarity in patterns on different time scales, and the probability of nondetermined states of carbonate carbon and organic carbon production that depend on the trophic level. These phenomena are all indicative of the nonlinear and complex character of coupling between the elemental cycles of phosphorus and carbon, and associated change in environmental conditions in response to extrinsic and intrinsic change. Within the patterns of change, the effect of negative feedback is important; it plays a role in counteracting the effects of extrinsic change and stabilizes environmental conditions. The overall trend is toward a state of minimal transfer of energy and material within the biosphere. Even if the effect of negative feedback is important, it is not an element that permanently stabilizes environmental conditions. Global change related to extrinsic factors such as volcanic events, impacts, and cyclic change in astronomical parameters, as well as intrinsic factors such as the evolution and adaptation of ecosystems within the biosphere, overrules this tendency and imposes itself in such a way that the associated feedback mechanisms remediate rather than regulate environmental conditions.

The initial question posed here, if phosphorus is a servant faithful to Gaia, is negated. Due to the change in climate conditions at around 32 myr, continental biogeochemical weathering—the prime mechanism through which phosphorus is mobilized—is enhanced by glaciation rather than warm and humid climates. This change turns the sign on feedback mechanisms in which phosphorus is involved as an essential nutrient, and the servant appears to trim its sails to the wind (climate) rather than remaining trustworthy to Gaia.

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References

Anderson, L. D., and M. L. Delaney. 2000. Sequential extraction and analysis of phosphorus in marine sediments: Streamlining of the SEDEX procedure. *Limnology and Oceanography*, 45, 509–515.

Arthur, M. A., W. E. Dean, and S. O. Schlanger. 1985. Variations in the global carbon cycle during the Cretaceous related to climate, volcanism, and changes in atmospheric CO_2. In E. T. Sundquist and W. S. Broecker, eds., *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present*, American Geophysical Union, Geophysical Monograph, 32, pp. 504–529. Washington, DC: American Geophysical Union.

Arthur, M. A., and S. O. Schlanger. 1979. Cretaceous "oceanic anoxic events" as causal factors in development of reef-reservoired giant oil fields. *American Association of Petroleum Geologists, Bulletin*, 63, 870–885.

Bartolini, A., and F. Cecca. 1999. 20 My hiatus in the Jurassic of Umbria–Marche Apeninnes (Italy): Carbonate crisis due to eutrophication. *Comptes Rendus, Académie des Sciences* (Paris), *Sciences de la Terre et des Planètes*, 329, 587–595.

Berner, R. A. 1994. Geocarb II: A revised model of atmospheric CO_2 over Phanerozoic time. *American Journal of Science*, 194, 56–91.

Codispoti, L. A. 1989. Phosphorus vs. nitrogen limitation of new and export production. In W. H. Berger, V. S. Smetacek, and G. Wefer, eds., *Productivity of the Ocean: Present and Past*, pp. 377–394. Chichester, UK: John Wiley.

Colman, A. S., and H. D. Holland. 2000. The global diagenetic flux of phosphorus from marine sediments to the oceans: Redox sensitivity and the control of atmospheric oxygen levels. In C. R. Glenn, L. Prévôt-Lucas, and J. Lucas, eds., *Marine Authigenesis: From Global to Microbial*, SEPM spec. vol. 66, 53–75. Tulsa, OK: Society of Sedimentary Geology.

Courtillot, V. 1994. Mass extinctions in the last 300 million years: One impact and seven flood basalts? *Israel Journal of Earth Sciences*, 43, 255–266.

Dickens, G. R., J. R. O'Neil, D. K. Rea, and R. M. Owen. 1995. Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene. *Paleoceanography*, 10, 965–971.

Föllmi, K. B. 1995. 160 m.y. record of marine sedimentary phosphorus burial: Coupling of climate and continental weathering under greenhouse and icehouse conditions. *Geology*, 23, 859–862.

Föllmi, K. B. 1996. The phosphorus cycle, phosphogenesis and marine phosphate-rich deposits. *Earth-Science Reviews*, 40, 55–124.

Föllmi, K. B., H. Weissert, M. Bisping, and H. Funk. 1994. Phosphogenesis, carbon-isotope stratigraphy, and carbonate-platform evolution along the Lower Cretaceous northern Tethyan margin. *Geological Society of America, Bulletin*, 106, 729–746.

Funk, H., K. B. Föllmi, and H. Mohr. 1993. Evolution of the Tithonian-Aptian carbonate platform along the northern Tethyan margin, eastern Helvetic Alps. In T. Simo, R. W. Scott, and J. P. Masse, eds., *Atlas of Cretaceous Carbonate Platforms*, American Association of Petroleum Geologists Memoir 56, pp. 387–408. Tulsa, OK: The Association.

Haq, B. U., J. Hardenbol, and P. R. Vail. 1987. Chronology of fluctuating sea levels since the Trias. *Science*, 235, 1156–1167.

Hosein, R., K. Arn, P. Steinmann, and K. B. Föllmi. In press. Calcite, the principal control on cation fluxes from the Rhône and Oberaar glaciers, Switzerland. *Geochimica et Cosmochimica Acta*.

Jenkyns, H. C. 1980. Cretaceous anoxic events: From continents to oceans. *Journal of the Geological Society of London*, 137, 171–188.

Jenkyns, H. C. 1991. Impact of Cretaceous sea-level rise and anoxic events on the Mesozoic carbonate platform of Yugoslavia. *American Association of Petroleum Geologists, Bulletin*, 75, 1007–1017.

Kennett, J. P., K. G. Cannariato, I. L. Hendy, and R. J. Behl. 2000. Carbon isotopic evidence for methane hydrate instability during Quaternary interstadials. *Science*, 288, 128–133.

Larson, R. L. 1991. The latest pulse of the Earth: Evidence for a mid-Cretaceous superplume. *Geology*, 19, 547–550.

Lees, A., and A. T. Buller. 1972. Modern temperate water and warm water shelf carbonate sediments contrasted. *Marine Geology*, 13, 1767–1773.

Lini, A., H. Weissert, and E. Erba. 1992. The Valanginian carbon isotope event: A first episode of greenhouse climate conditions during the Cretaceous. *Terra Nova*, 4, 374–384.

Lovelock, J. 1988. *The Ages of Gaia: A Biography of Our Living Earth*. New York: Norton.

Lovelock, J. E., and L. Margulis. 1974. Atmospheric homeostasis by and for the biosphere: The Gaia hypothesis. *Tellus*, 26, 2–10.

May, R. M., and G. F. Oster. 1976. Bifurcations and dynamics complexity in simple ecological models. *American Naturalist*, 110, 573–599.

Petit, J. R., J. Jouzel, N. I. Raynaud, N. I. Barkov, J. M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V. M. Kotlyakov, M. Legrand, V. Y. Lipenkov, C. Lorius, L. Pépin, C. Ritz, E. Saltzman, and M. Stievenard. 1999. Climate and atmosphric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature*, 399, 429–436.

Raymo, M. E. 1994. The Himalayas, organic carbon burial, and climate in the Miocene. *Paleoceanography*, 9, 399–404.

Ruttenberg, K. C. 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnology and Oceanography*, 37, 1460–1482.

Schlager, W. 1981. The paradox of drowned reefs and carbonate platforms. *Geological Society of America, Bulletin*, 92, 197–211.

Scholle, P. A., M. A. Arthur, and A. A. Ekdale. 1983. Pelagic environment. In P. A. Scholle, D. G. Bebout, and C. H. Moore, eds., *Carbonate Depositional Environments*, American Association of Petroleum Geologists Memoir 33, pp. 620–691. Tulsa, OK: The Association.

Southam, J. R., and W. W. Hay. 1981. Global sedimentary mass balance and sea level changes. In C. Emiliani, ed., *The Sea*, vol. 7, pp. 1617–1684. New York: John Wiley and Sons.

Tamburini, F. 2001. Phosphorus in marine sediments during the last 150,000 years: Exploring relationships between continental weathering, productivity, and climate. Ph.D. thesis, University of Neuchâtel.

Tamburini, F., et al. 2003. Sedimentary phosphorus record from the Oman margin: New evidence of high productivity during glacial periods. *Paleoceanography*, 18.10.102g/2000PA000616.

Tiwari, R. K., and K. N. N. Rao. 1999. Periodicity in marine phosphorus burial records. *Nature*, 400, 31–32.

Tyrrell, T. 1999. The relative influences of nitrogen and phosphorus on oceanic primary production. *Nature*, 400, 525–531.

Van Cappellen, P., and E. D. Ingall. 1994. Benthic phosphorus regeneration, net primary production, and ocean anoxia: A model of the coupled marine biogeochemical cycles of carbon and phosphorus. *Paleoceanography*, 9, 677–692.

Van de Schootbrugge, B. 2001. Influence of paleo-environmental changes during the Hauterivian (early Cretaceous) on carbonate deposition along the northern margin of the Tethys: Evidence from geochemical records (C-, O-, Sr-isotopes, P, Fe, Mn. Ph.D. thesis, University of Neuchâtel.

Van de Schootbrugge, B., K. B. Föllmi, L. G. Bulot, and S. J. Burns. 2000. Paleoceanographic changes during the early Cretaceous (Valanginian–Hauterivian): Evidence from oxygen and carbon stable isotopes. *Earth and Planetary Science Letters*, 181, 15–31.

Van de Schootbrugge, B., O. Kuhn, T. Adatte, P. Steinmann, and K. B. Föllmi. In press. Mesotrophic carbonate production and high P-accumulation rate during the Hauterivian: Regulating the Valanginian global carbon cycle perturbation. *Palaeogeography, Palaeoclimatology, Palaeoecology*.

Weissert, H., A. Lini, K. B. Föllmi, and O. Kuhn. 1998. Correlation of early Cretaceous carbon isotope stratigraphy and platform drowning events: A possible link? *Palaeogeography, Palaeoclimatology, Palaeoecology*, 137, 189–203.