

On the control of the carbon-oxygen system

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ABSTRACT

The dynamical aspects of the carbon-oxygen system in the ocean and atmosphere are considered. The analysis is based on the stoichiometry of the main reactions, relevant continuity constraints and assumptions about feedback from the state of the system. It is found that silicate weathering, though necessary for the forcing of the system, may be unimportant for the control of the system. It is thus fully possible that the stability is taken care of by feedback on the burials of carbonate, reduced carbon and sulphide, which flows may have the potential to be very sensitive to modest perturbations of the state of the ocean-atmosphere system. It is shown that the coupling between the carbon and oxygen cycles becomes stronger, if silicate weathering is less important for the control, which has interesting consequences. In general, the need to keep the carbon cycle balanced on the long time scale characterizing the oxygen cycle has important implications. If feed back from $p\text{CO}_2$ on silicate weathering is sufficiently weak, we thus find that a positive feedback from $p\text{O}_2$ on the rate of burial of reduced carbon may be favourable for the stability of the system, contrary to what is commonly assumed. It is discussed how the frequency of forest fire may have a key position in the control system together with the degree of oxygen depletion in oceanic deep water, since these phenomena may provide "switches" for the formation of charcoal (i.e., deposition of reduced carbon) and burial of sulfide.

1. Introduction

Some dynamical aspects of the carbon-oxygen system will be considered in this paper. In the spirit of the Bolin 65 Symposium, an effort is made to shake up current ideas about controls of the carbon-oxygen system by applying asymptotic analysis to the balance requirements that can be derived for the dominant geochemical fluxes.

The ocean atmosphere system is subjected to a continuous flow of material passing through the system. On a short time scale, these flows may appear small compared with the size of the various reservoirs in the ocean and atmosphere. For a longer time perspective, this is not the case; on the contrary, the flow is hectic as discussed by Garrels et al. (1976) and Whitfield (1981). Despite the fast turnover of material, it is believed that the state of the ocean-atmosphere has remained remarkably constant (Garrels and Perry, 1974; Lovelock and Margulis, 1974).

This observation calls for a control system capable of keeping the ocean-atmosphere reasonably close to the observed state.

Sillén (1961) argued for control of ocean acidity by the vast amounts of silicate minerals available in the bottom sediments. However, Sillén did not recognize the importance of the flow of material through the system for the long term control.

A kinetic model considering the importance of net supplies was discussed by Broecker (1971) in a pioneering work. However, Broecker did not put all his suggested control mechanisms into a coherent picture by the application of the constraints posed by continuity.

Lovelock and Margulis (1974) presented the GAIA hypothesis, postulating that the biosphere is capable of optimizing the environment for its own benefit. Lovelock thereby provoked a lot of interesting scientific work and also discussions on whether his proposal is truly scientific, religious or perhaps a truism. Many interesting ideas have grown out of Lovelock's initiative, e.g., a study of the sensitivity of fire to increased $p\text{O}_2$ (Watson et al., 1978).

Very ambitious efforts to build a quantitative picture have been provided by Berner et al. (1983) and Lasaga et al. (1985) modeling the carbon cycle

and by Kump and Garrels (1986) and Berner and Canfield (1989) modeling the oxygen cycle. With the exception of the paper by Lasaga et al. (1985), the interaction between the carbon and oxygen cycles is only touched upon in these models.

In the paper by Lasaga et al. (1985), the oxygen development is calculated essentially as a byproduct of the carbon system and the authors notice the need to balance the oxygen cycle as a problem. Furthermore, their treatment of the burial of reduced carbon and sulphide is diagnostic, i.e., the authors calculate the flows from geological observations of isotope distributions. Accordingly, the question of feedback from the state of the system on the magnitude of these flows never enters the analysis.

In the analysis of the oxygen cycle by Berner and Canfield (1989) and Kump and Garrels (1986), the interaction with the carbon cycle is avoided with an implicit assumption that silicate weathering automatically compensates for the influence on the carbon system by the oxygen cycle. Such an assumption calls for very efficient feedback from $p\text{CO}_2$ on the weathering of silicate (as compared with other interactions), which was not explicitly required by the authors.

In the modeling work mentioned above and in most previous work on the subject, it is taken for granted that silicate weathering controls the carbon cycle on long time scales, while burial of reduced carbon, assisted by burial of sulfide, is in charge for the control of atmospheric oxygen. Ideas in favour of a stronger biogenic interference have been expressed by Garrels and Perry (1974) and Garrels and Lerman (1981) and by Veizer et al. (1980) on the basis of the record of carbon and sulfur isotopes, though they have not explicitly questioned the approach used in the above mentioned models.

In this paper, we consider some dynamical aspects of the carbon-oxygen system. Essentially, we adopt the kinetic approach introduced by Broecker (1971). We will thus emphasize the necessity to balance the various flows that interact with the system rather than look for states characterized by chemical equilibrium.

Our starting point is a set of continuity equations based on the stoichiometry of the most important transfer reactions. An important step is to cast these equations into a form suitable for dynamical considerations. A central question is

whether the dominating role of silicate weathering for the control of the system may be questioned. The analysis in this paper is related to the ideas presented by Garrels and Perry (1974), in particular with respect to the importance assigned to the interaction of the sulfur and carbon cycles.

Our emphasis is on the coupling between the carbon and oxygen cycles and on the feedback properties. We will consider only feedback from the state of the ocean-atmosphere on to the relevant flows, since such feedback is needed to protect the ocean-atmosphere from very large excursions away from its present life-supporting state. It may be pointed out though that the feedback may be indirect via some other substance or property such as the abundance of nutrients or the mean temperature at the surface of the earth.

A somewhat surprising conclusion from our study of the coupled carbon-oxygen system is that a positive rather than a negative feedback from $p\text{O}_2$ on the burial of reduced carbon may be favourable for the control of the system. Inspired by this result, the possible role of continental forest fires and deep-ocean oxygen depletion as critical agencies for feedback is discussed and illustrated with an idealized scenario.

2. Continuity considerations

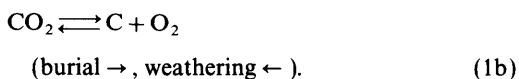
The carbon-oxygen system is mainly influenced by the following transfer processes which define the dominant fluxes interacting with the system (Berner et al., 1983 and Berner and Canfield, 1989)

(A) Rate of metamorphic production of carbon dioxide (V_a) defined by



This process occurs under high pressure and temperature in subduction zones where carbonates and silica previously deposited on the sea floor are forced to react and release carbon dioxide.

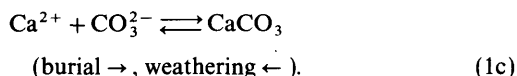
(B) Net rate of burial, i.e., burial minus weathering, of reduced carbon (B_a) defined by



Weathering of reduced carbon ($B_a < 0$) occurs on

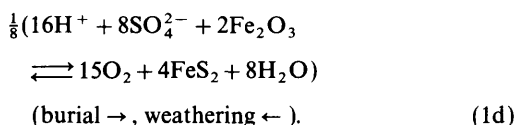
the continents. Burial of reduced carbon ($B_a > 0$) occurs on the continents as well as on the ocean floor.

(C) Net rate of burial of carbonate (B_b) defined by



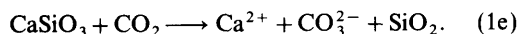
Carbonates are weathered on the continents ($B_b < 0$) and deposited ($B_b > 0$) on the sea floor. Magnesium carbonates are also involved, which, however, makes no difference for the present purpose. Some acid is needed as a catalyst in the weathering process and may be temporarily consumed for the formation of bicarbonate ions (HCO_3^-). This, however, does not influence the overall stoichiometry.

(D) Net rate of burial of sulfide (B_s) defined by



Sulfides are weathered on the continents ($B_s < 0$) through oxidation with atmospheric oxygen and deposited under anoxic conditions ($B_s > 0$) mainly in marine sediments.

(E) Rate of weathering of silicates (W_{Si}) defined by



Silicate minerals of various types, here typified by Wollastonite, are weathered on the continents ($W_{\text{Si}} > 0$). As with weathering of carbonates, some acid is needed as a catalyst.

The symbols V_a , B_a , B_b , B_s , W_{Si} denote the rate at which these chemical transformations occur (positive from left to right). Note that B_a , B_s , B_b represent the burial minus the weathering of reduced carbon, sulfide and carbonate. Furthermore, V_a , B_a , B_b , W_{Si} measure moles of carbon involved in the reaction per unit time, while B_s measures moles of sulfur involved. Formation of 1 mole of FeS_2 per unit time thus corresponds to $B_s = 2$ moles per unit time. We also note that $W_{\text{Si}} + B_b$ represents the exact reversal of V_a . Should we require that the system is in complete

steady state with respect to all reservoir sizes (including the rock reservoirs), we thus obtain

$$B_a = B_s = 0, \quad (2a)$$

$$V_a = W_{\text{Si}} = B_b. \quad (2b)$$

In the state represented by eqs. (2), the burial and weathering balance out for reduced carbon and reduced sulphur while the metamorphic production of carbon dioxide is balanced by silicate weathering combined with burial of carbonate. It should be noted at this point that we have no reason to expect that eqs. (2) represent a typical state of the system. In fact, because of the large size of the rock reservoirs, we cannot justify an assumption of vanishing net flow to individual rock reservoirs except possibly for the very longest time scales larger than 10^9 years.

The state of the carbon-oxygen system is described by the oceanic total carbon (C_T) and alkalinity (A), the atmospheric carbon dioxide pressure, $p\text{CO}_2$, and atmospheric oxygen pressure, $p\text{O}_2$, or by the associated reservoirs:

M_{Alk} = the integrated ocean alkalinity (equivalents),

M_T = the integrated oceanic total carbon (moles),

M_g = the integrated atmospheric carbon dioxide (moles),

M_{ox} = the integrated atmospheric oxygen (moles).

Considering the stoichiometry of eq. (1a-e) or, e.g., the rules given by Dyrssen and Sillén (1967), we obtain the following continuity relations

$$\frac{d}{dt} (M_T + M_g) = V_a - B_a - B_b, \quad (3a)$$

$$\frac{d}{dt} M_{\text{Alk}} = -2B_b + 2B_s + 2W_{\text{Si}}, \quad (3b)$$

$$\frac{d}{dt} M_{\text{ox}} = B_a + rB_s, \quad (3c)$$

where

$$r = \frac{15}{8}. \quad (3d)$$

Note that r is determined by the stoichiometry of sulfate reduction as given by eq. (1d). We note that r is a number significantly different from unity, which, as we will find, is important for the properties of the system.

From eq. (3a) one gets the impression that B_a and B_b have essentially the same effect on the system. As every ocean chemist knows, this is quite the opposite of the truth. The reason for this false impression is the somewhat unfortunate choice of the variable M_T to describe the oceanic carbon system. We will thus choose to switch to the new variables acid carbon (M_a) and base carbon (M_b) defined by

$$M_a = M_T - \frac{1}{2}M_{\text{Alk}}, \quad (4a)$$

$$M_b = \frac{1}{2}M_{\text{Alk}}. \quad (4b)$$

From eq. (3), we easily find

$$\frac{d}{dt}(M_a + M_g) = V_a - B_a - B_s - W_{\text{Si}}, \quad (5a)$$

$$\frac{d}{dt}M_b = -B_b + B_s + W_{\text{Si}}, \quad (5b)$$

$$\frac{d}{dt}M_{\text{ox}} = B_a + rB_s. \quad (5c)$$

Correspondingly, we define the acid (aC) and base (bC) oceanic carbon concentrations with the relations:

$$^aC = C_T - \frac{1}{2}A, \quad (6a)$$

$$^bC = \frac{1}{2}A. \quad (6b)$$

Since the alkalinity (A) and total carbon (C_T) are given by

$$A = 2\text{CO}_3^{2-} + \text{HCO}_3^- + \text{H}_2\text{BO}_3^-,$$

$$C_T = \text{CO}_3^{2-} + \text{HCO}_3^- + \text{CO}_2,$$

we obtain for aC and bC from eqs. (6)

$$^aC = \text{CO}_2 + \frac{1}{2}\text{HCO}_3^- - \frac{1}{2}\text{H}_2\text{BO}_3^-, \quad (7a)$$

$$^bC = \text{CO}_3^{2-} + \frac{1}{2}\text{HCO}_3^- + \frac{1}{2}\text{H}_2\text{BO}_3^-. \quad (7b)$$

In this definition of alkalinity, we have ignored some minor contributions (Fiadeiro, 1980), e.g., from H_3SiO_4^- , which are very small in the range of

pH encountered in the ocean. This simplification has no consequence at all for the present purpose.

It should be pointed out that eqs. (5) may be derived directly from continuity considerations applied to the involved ions. Here, we have started with alkalinity and total carbon because of their widespread use in ocean chemistry. The use of the variables aC and bC (or a similar pair including $\pm \frac{1}{2}\text{NO}_3^-$) has previously been suggested by Fiadeiro (1980), motivated by the need to separate the effects of precipitation of organic carbon and calcium carbonate.

We can see from eq. (5) that the supply of carbon dioxide (given by $V_a - B_a$) enters only in the equation for ($M_a + M_g$) while the supply of carbonate ions (CO_3^{2-}) from carbonate dissolution (given by $-B_b$) enters only in the equation for M_b .

The reservoir $M_a + M_g$ may thus be considered as the total amount of CO_2 in the ocean-atmosphere, despite the fact that the main part is hidden in bicarbonate ions by dissociation processes. Likewise, M_b may be considered as the total amount of dissolved carbonate.

The remaining terms B_s and W_{Si} appearing with opposite sign in eqs. (5a, b) represent a transfer between the acid reservoir ($M_a + M_g$) and the base reservoir M_b . Such a transfer occurs as the result of the supply or removal of hydrogen ions.

If the oceanic concentration of aC and bC are known, we may calculate the oceanic carbon dioxide pressure pCO_2 and the concentration of carbonate ions (CO_3^{2-}). The calculation is implicit and a little complicated, see, e.g., Broecker and Peng (1982) or Walin (1990). However we find that, irrespective of the details, pCO_2 as well as CO_3^{2-} is sensitive to variations in the difference ($^bC - ^aC$). In fact, we have the approximate relations

$$\text{pCO}_2 \approx \text{const.} (^aC)^2 / (^bC - ^aC), \quad (8a)$$

$$\text{CO}_3^{2-} \approx ^bC - ^aC, \quad (8b)$$

where (const.) in eq. (8a) depends on the dissociation constants for carbonic acid and the solubility of CO_2 in ocean water. In terms of A and C_T these equations are well known and frequently used (Broecker and Peng, 1982) in the form

$$\text{pCO}_2 \approx \text{const.} (C_T - \frac{1}{2}A)^2 / (A - C_T),$$

$$\text{CO}_3^{2-} \approx A - C_T.$$

Eqs. (8) involve a comparatively large error, of the order of 20%, in the range of states typical for the ocean. We have, e.g., ignored the presence of boric acid in the derivation. In the case ${}^bC \leq {}^aC$, eqs. (8) are obviously incorrect. These limitations have to be kept in mind in the use of these simplified relations.

Eqs. (8) demonstrate the importance of the difference Δ defined by

$$\Delta = {}^bC - {}^aC, \quad (9a)$$

and the associated reservoir

$$M_{\Delta} = M_b - M_a. \quad (9b)$$

In view of the sensitivity to changes in Δ , e.g., as expressed by eq. (8), it is favourable in studies of the dynamical properties to go one step further and introduce M_{Δ} instead of M_b as variable in our continuity equations. We thus obtain from eq. (5), making use of eq. (9b):

$$\frac{d}{dt}(M_{\Delta} - M_g) = -B_b + 2(B_s + W_{Si}) - V_a + B_a, \quad (10a)$$

$$\frac{d}{dt}(M_a + M_g) = V_a - B_a - B_s - W_{Si}, \quad (10b)$$

$$\frac{d}{dt}M_{ox} = B_a + rB_s. \quad (10c)$$

3. Magnitude of involved quantities

To understand the qualitative properties of eqs. (10), we need some knowledge about the magnitude of the involved quantities. For the reservoirs we have (Garrels and Perry, 1974; Broecker and Peng, 1982):

$$M_{\Delta} \approx 0.1, \quad M_a \approx 1.5, \quad M_b \approx 1.7, \\ M_{ox} \approx 38, \quad M_g \approx 0.07 \quad (10^{18} \text{ moles}). \quad (11)$$

The magnitudes of the involved flows are much more uncertain. The estimates that can be found in the literature (Garrels and Perry, 1974; Sundquist, 1985) concern the gross burial and weathering fluxes. However, the net burials remain very uncertain. Accordingly, we have only the following

very rough order of magnitude estimates for the flows involved

$$V_a \approx W_{Si} \approx B_b \approx 8 \pm 5, \quad B_a \approx 0 \pm 3, \\ B_s \approx 0 \pm 1, \quad (10^{12} \text{ moles/year}). \quad (12)$$

For comparison, we recall (Sundquist, 1985) that the flow induced by the burning of fossil fuels corresponds to

$$B_a \approx -500 \quad (10^{12} \text{ moles/year}).$$

In order to estimate the involved time-scales, we introduce a reference flow rate F_0 which is taken to be representative for the net flows appearing on the right-hand sides of eqs. (10). Since M_g and M_{Δ} are of the same order of magnitude, we have three widely differing characteristic time-scales for the system

$$T_{\Delta} = M_{\Delta}/F_0, \quad T_a = M_a/F_0, \\ T_{ox} = M_{ox}/F_0, \quad (13a-c)$$

With F_0 taken to be $5 \cdot 10^{12}$ moles/year, we obtain

$$T_{\Delta} \approx 20, \quad T_a \approx 300, \quad T_{ox} \approx 8000 \\ (10^3 \text{ years}). \quad (13d-f)$$

The fact that these time-scales differ so widely is of profound importance for the dynamics and immensely simplifies the dynamical behaviour of the system.

4. Stoichiometric constraints on very long time scales

The importance of the time derivatives on the left-hand side of eqs. (10) depend on the time scale under consideration. Assuming that the maximum variation of any one of the reservoirs M_{Δ} , M_a , M_{ox} is at most of the same order of magnitude as its present size, we find that all the time derivatives may be dropped if $T \gg T_{ox}$, where T is the time scale under consideration.

From eqs. (10), we thus obtain solving for B_a , B_s and B_b :

$$B_a = [r/(r-1)](V_a - W_{Si}), \quad (14a)$$

$$B_s = -[1/(r-1)](V_a - W_{Si}), \quad (14b)$$

$$B_b = -[1/(r-1)](V_a - W_{Si}) + W_{Si}, \quad (14c)$$

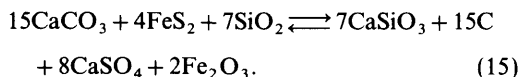
where all the flows B_a , V_a , etc., should be interpreted as mean values over a time much longer than T_{ox} .

Note that eqs. (14) should not be interpreted as a "steady state" based on the assumption that the size of the reservoirs M_Δ , M_a , M_{ox} are independent of time. The correct interpretation is that eqs. (14) represent a constraint on the involved mean flows. This constraint remains valid despite variations in the state of the system as long as the variations stay within certain limits. The critical assumption is thereby that the atmospheric pO_2 is not allowed to take on values very much in excess of, say, twice the present value. It appears likely that restrictions posed by the presence of life are at least that stringent.

We note that eqs. (14) differ from eqs. (2) in that they allow non-zero B_a and B_s . Eqs. (2) thus represents a much more stringent constraint valid only on time scales so large that even the rock reservoirs are too small to absorb any mean supplies.

In our description so far, we have not worried about what happens to the oceanic reservoirs of sulphate (SO_4^{2-}) and silicic acid (H_4SiO_4), since these components do not interact with the carbon-oxygen system as long as silica (SiO_2) is deposited biogenically as fast as it is supplied and sulphate ions are present in sufficient amount.

Assuming that silica and sulphate do not accumulate in the ocean and are thus deposited at the same rate as they are supplied (on this long time scale), eq. (14) corresponds to a stoichiometry as follows:



Eq. (15) was given by Garrels and Perry (1974) in their discussion of possible exchanges between rock reservoirs that do not require any net exchange with the ocean-atmosphere.

Flow to the right in eq. (15) occurs when $(V_a - W_{Si}) > 0$. A net formation of reduced carbon ($B_a > 0$) is thus by necessity accompanied by a net weathering of sulfide ($B_s < 0$). If this fails to occur (or if eqs. (14) are violated in any way), then the ocean atmosphere will "run away" to a qualitatively different state.

The building up of the rock reservoirs of reduced

carbon which presumably have taken place without such "run aways" has thus been paralleled by a corresponding loss of reduced sulfur satisfying (in view of eqs. (14)):

$$B_a \approx -rB_s, \quad (16)$$

where we recall that B_a and B_s represent mean values over times long compared with T_{ox} .

Evidence in support of eq. (16) based on isotope records has been given by Veizer et al. (1980) and Garrels and Lerman (1981). These authors also suggest that the controlling agency behind this balance is of biogenic origin.

Eqs. (14) form a strong constraint on the system which pinpoints the crucial importance of the sulfur cycle for the operation of the carbon-oxygen cycle. Mechanisms that may control the proportions of organics and sulfide in sediments were discussed by Berner and Raiswell (1983) against the background provided by eq. (16).

Here, a strong reservation is needed. Eq. (14) derives from our assumption about which processes are essentially controlling the system. This assumption is approximate and furthermore applies only to an ocean-atmosphere-biosphere system behaving essentially as the present system does.

The constraint posed by eq. (14) will not be satisfied by sheer good luck; it requires efficient control processes which have to originate in the state of the ocean-atmosphere as given by our state variables M_Δ , M_a , M_{ox} .

Although, as pointed out by Veizer et al. (1980), eq. (16) suggests a biogenic control, we have to remember that eqs. (14) are nothing but a direct consequence of the stoichiometry of the system. Even the most convincing evidence in support of the validity of eqs. (14) proves nothing about the mechanisms controlling the carbon-oxygen system.

5. Feedback properties

The stability of the system depends on appropriate feedback on the flows B_a , B_s , B_b , W_{Si} from the state variables M_Δ , M_a , M_{ox} . Such a feedback can be expected to manifest itself in that the state variables determine pCO_2 , pO_2 and (CO_3^{2-}) , which properties interact with the above-

mentioned flows. From this point of view, the flow V_a may be considered as an externally prescribed forcing on the system.

It should be pointed out here that there is presently little firm knowledge about the feedback properties of the various flows. An exception is the interaction between the net burial of carbonate, B_b , and the degree of saturation as represented by Δ or M_Δ , which rests on a very solid foundation (see below). With respect to the remaining flows, our knowledge is at best qualitative. In fact, we do not even know for sure the sign of certain interactions, or which feedback is more important than another.

In Sections 6–8, we will analyse the consequences of different assumptions regarding the feedback properties which can be done in a reasonably conclusive way. The very qualitative and not very conclusive discussion in this section is meant to serve as a background for the analysis in the later sections.

5.1. Silicate weathering (W_{Si})

Silicate weathering is the result of chemical reaction between silicate-containing rock material and rain or ground water. The reaction consumes hydrogen ions. We thus expect W_{Si} to increase with pCO_2 .

It has been argued, however, that the main part of silicate weathering occurs in the ground where organic material is broken down, creating a locally very acid environment (Broecker and Peng, 1982). As a result, silicate weathering would become less dependent on the atmospheric pCO_2 and depend more on the abundance of such regions.

However, we may expect that plant productivity will be stimulated in various ways by increased pCO_2 (Garrels and Perry, 1974; Idso, 1989). This may result in faster turnover of organic material and larger vegetated areas, thus increasing the below-ground biological activity and the associated breakdown of silicates. Furthermore, increased weathering will increase the supply of nutrients, thus further stimulating productivity.

Many authors emphasize the importance of increased temperature resulting from a higher pCO_2 (Walker et al., 1981; Berner et al., 1983). Since chemical reactions in general go faster at higher temperature, a presumed relation between pCO_2 and temperature provides a working feedback link.

Although there are several possible feedback links between pCO_2 and the weathering of silicates, the strength and sensitivity of the feedback may be questioned.

5.2. Burial of organic carbon (B_a)

Burial of organic carbon is presently a very small part, less than 0.1%, of the gross overturning of organic material in the biosphere. We expect increased pCO_2 to stimulate the biosphere in many ways, such as through direct fertilization, increased temperature and rainfall, increased areas of vegetation, better resistance against drought, increased supply of nutrients from weathering which may increase productivity on land as well as in the ocean (Idso, 1989).

Furthermore, even a modest increase in the rate of overturning organic material could produce a large increase in the rate of loss of organic material; the loss would still be very small compared with the gross overturning (Garrels et al., 1974). One might dare a comparison with an engine which quickly loses efficiency when run over its design power. In particular, we note that whatever the ultimate upper limit of B_a might be, it is still far away, since the flow is drawn from such a large gross flow. We may compare with silicate weathering in this respect, noting that silicate weathering is itself a gross flow.

It has been pointed out (Berner and Canfield, 1989; Broecker and Peng, 1982) that burial of organics, particularly in the ocean, depletes the biosphere of phosphorus which may provide a limitation on the possible magnitude of B_a . It should be noted here that burial of organic carbon on land, which presumably requires less phosphorus, has been important at least in the past as witnessed by so-called coal swamps.

It should also be pointed out here that calculations based on the geological record of carbon isotopes, indicate that B_a has not undergone dramatic variations in the past (Garrels and Lerman, 1981). Of course such evidence does not altogether exclude stronger variations in the future.

In conclusion, we expect that B_a might be a sensitive function of pCO_2 and that its potential range of variation may be considerably larger than its estimated present magnitude. The above-mentioned interaction with phosphorous should, however, be kept in mind as well as the geological

record, indicating modest variations of B_a in the past.

When it comes to the dependence of B_a on pO_2 , the situation is contradictory. It has long been assumed that feedback from pO_2 on B_a , and in particular the part associated with organic deposition on the ocean floor, is the dominant factor in the control of pO_2 (Broecker and Peng, 1982; Holland, 1978). This view has been questioned, however, e.g., by Kump (1988), who designed a fairly complicated scenario involving fire to transfer nutrients from the continents to the ocean where the nutrients are supposed to create a smaller rate of organic burial. However, Kump did not question the need for a negative feedback from pO_2 to B_a .

Here, we will mention two circumstances of importance which put the negative feedback from pO_2 to B_a into question.

(i) Burial of organic material in ocean sediments does not increase markedly, if at all, when the oxygen content of the water is depleted, since oxidation with sulfate to a large extent takes over when the supply of oxygen is exhausted.

(ii) Increased occurrence of fire in response to higher pO_2 may lead to increased burial of reduced carbon (i.e., further increasing pO_2) through the production of very resistant charcoal (Herring, 1985). Possibly, the massive depositions of reduced carbon in coal swamps could be related to such fire-induced deposition.

We thus consider the response of B_a to increased pO_2 as an open question even with respect to its sign.

5.3. Burial of sulfide (B_s)

Burial of sulfide occurs when organic material is oxidized through the reduction of sulphate in the absence of free oxygen. B_s may be very sensitive to deep-ocean pO_2 because of the following mechanism.

Suppose that deep-water oxygen has been depleted by oxidation of organic material in an ocean basin and that an excess of organic material descends, for which there is no free oxygen available.

The flow of organic material creates no net result as long as it is oxidized with free oxygen.

A net contribution to B_a results only from burial of the small part of the organic flow which escapes oxidation. When the deep water becomes anoxic, the situation changes dramatically. Essentially, all excess organic material now becomes oxidized with sulfate, leading to a corresponding sulfide burial. Despite the fact that practically all the organic material may become oxidized and the carbon returned to the ocean, we obtain a rate of sulfide burial related to the flow of organic material in excess of what is oxidized with free oxygen.

The burial of sulfide in this situation no longer forms a very small proportion of the gross biogenic flow, but becomes of the same magnitude as the gross flow, or more precisely, the gross flow in excess of the part oxidized by the available free oxygen.

We can see here a possibly very powerful and sensitive feedback. The sensitivity of this mechanism derives from the fact that it is mediated by the deep ocean oxygen pressure, which is considerably smaller than the atmospheric pressure. A small change in the atmospheric pressure will give rise to a larger relative change in the deep ocean oxygen pressure and a correspondingly large change in the rate of burial of sulfides.

Here an important reservation should be made namely that pyrite formation depends on the availability of iron. Though one of the most common substances in the earth's crust, iron is very sparse in ocean water. It is essentially present only in particles supplied from the continents. The limited supply of iron most likely limits the strength of the sulfide formation that can be initiated in anoxic deep waters, in particular distant from the coasts. It should be recalled, however, that the feedback process does not require very large flows to be efficient in the control of the system. The important thing is that a change in the rate of sulfide formation can be initiated by a small change in the state of the system. We may thus envision that the deep ocean oxygen pressure, by undergoing only small excursions around an almost completely oxygenated state, can create the modest variations in the rate of sulfide formation that might be required as part of the entire control system.

Analysis of sediments seems to confirm that burial of sulfide is sensitive to the abundance of free oxygen at least in ocean water where sulfate is

available (Berner and Canfield, 1989). Records of sulfur isotopes in sedimentary material indicate that the rate of pyrite formation has not varied drastically (Garrels and Lerman, 1981). However, this does not preclude that sulfide formation is involved in an efficient feedback process. In fact, an efficient control system reacts quickly, but with small modifications to perturbations.

Increased $p\text{CO}_2$ may be expected to increase burial of sulfide for essentially the same reasons as burial of organics, i.e., as a direct result of increased biogenic activity. We have, however, an additional effect which may be more important.

Ocean productivity is essentially controlled by the abundance of nutrients. Making the reasonable assumption that the supply of nutrients to the ocean will increase with $p\text{CO}_2$, we can thus expect an increased ocean productivity in response to increased $p\text{CO}_2$. This effect may well be amplified by more efficient nutrient utilization in the surface layer stimulated by the higher $p\text{CO}_2$. As a result, the consumption of oxygen in the ocean will increase, giving rise to larger anoxic areas and increased rate of sulfide burial. Note that for modest perturbations of the system, the main part of the deep ocean will still be oxygenated. The relative increase in the size of the anoxic areas may, however, be substantial.

In this context, it may be pointed out that increased temperature at the sites of bottom water formation will influence the oxygen content of the deep water in a fashion similar to an increased ocean productivity or a lowered atmospheric $p\text{O}_2$, which might delude the control system. We could, however, consider such a response to higher temperature as part of a feedback chain from $p\text{CO}_2$, since high $p\text{CO}_2$ causes an increase in the temperature as well as ocean productivity. This and many other complications associated with the oceanic nutrient balance make the picture more complicated. However, it is still believed that such complications do not change the overall picture.

A further reason to emphasize the potential importance of sulfide burial is that this process does not deplete the ocean of nutrients as effectively as burial of organics.

We thus expect sulfide burial to be sensitive to $p\text{O}_2$ and in particular to $p\text{CO}_2$, recalling, however, that the rate of sulfide formation is probably limited by the availability of iron in the marine environment.

5.4. Burial of carbonates (B_b)

Burial of carbonates is controlled by the rate of dissolution of biogenically-produced carbonate particles persistently raining through ocean water. The mechanism is thoroughly described by Broecker and Peng (1982). The ocean is thus kept close to a state of saturation with respect to calcium carbonate. Perturbations away from this state will be compensated for by variations in the rate of burial of carbonates on the sea floor.

This means that B_b is sensitive to deviations of (CO_3^{2-}) from its saturation value. This saturation value depends on the concentration of calcium ions in the ocean. Since (Ca^{2+}) is influenced by independent processes (Broecker and Peng, 1982), most importantly ion exchange associated with volcanic-seawater reactions, we consider (Ca^{2+}) as externally controlled.

The situation is further complicated by the variation of properties within the ocean which are influenced by biological activity, variation of solubility between different types of carbonate, pressure dependence of the solubility, etc. These complications, though of the utmost importance for ocean chemistry, do not change the overall picture outlined here.

Recalling the close relation between Δ and (CO_3^{2-}) in the ocean (eq. 8b), we thus expect a very efficient feedback from variations of M_Δ on B_b .

6. Perturbation analysis

Let us now return to eqs. (10) derived from the stoichiometry of the processes controlling the carbon-oxygen system. We recall that the system is characterized by three time-scales T_Δ , T_a , T_{ox} , which differ greatly in size (eqs. 13). We will mainly be concerned with the control properties on time scales of order T_a and larger. Our first task will be to essentially eliminate the first of eqs. (10).

We recall from Section 2 that M_a and M_Δ represent the oceanic reservoirs of ^aC (acid carbon) and $^b\text{C} - ^a\text{C}$ (base minus acid carbon). In view of eq. (8a), we thus have the approximate relation

$$M_g = \text{const.} (M_a)^2 / M_\Delta. \quad (17)$$

Because of this link between the atmospheric CO_2 reservoir and the state of the ocean, eqs. (10)

represent a closed system, if the flows can be expressed in terms of our state variables M_Δ , M_a , M_{ox} .

6.1. Control of M_Δ or acid carbon versus base carbon

We now turn our interest to the intermediate and long time scales, assuming

$$T \gg T_a, \quad (\text{i.e., } T \gg T_\Delta). \quad (18)$$

Making use of the estimates given by eqs. (13), we find that the time-derivative in eq. (10a) may be dropped and we obtain:

$$0 = -B_b + 2(B_s + W_{Si}) - V_a + B_a, \quad (19a)$$

$$\frac{d}{dt}(M_a + M_g) = V_a - B_a - B_s - W_{Si}, \quad (19b)$$

$$\frac{d}{dt}M_{ox} = B_a + rB_s. \quad (19c)$$

Note that this simplification is made possible because of the choice of M_Δ as state variable to replace M_b . Eq. (19a) now appears as a constraint for the development on time scales of order T_a and larger. Furthermore, this constraint can be given a very simple interpretation.

The most important term in eq. (19a) is the net deposition of carbonates represented by B_b . As discussed by Broecker and Peng (1982) and briefly in Subsection 5.4, this flow adjusts in order to keep the ocean close to a state which is marginally saturated with respect to carbonates. This amounts to keeping Δ close to some target value Δ^0 . The remaining terms in eq. (19a) will act to push Δ somewhat away from Δ^0 . The powerful mechanism produced by the persistent rain of carbonate particles in the ocean will, however, act to keep such perturbations relatively small.

Note that this mechanism does not stop M_a from varying with time. The implication of eq. (19a) is that the base reservoir M_b has to follow variations in M_a in order to keep M_Δ approximately constant.

For the following discussion concerning the behaviour of the system on time scales much larger than T_Δ , we will thus replace eq. (19a) with the constraint

$$\Delta = \Delta^0 \quad \text{or} \quad M_\Delta = M_\Delta^0. \quad (20)$$

Adopting eq. (20), we have ignored the influence other than B_b in eq. (19a) as mentioned above. More important is, however, that we essentially consider the ocean as a well-mixed entity. We thus bypass the possibility to redistribute properties within the ocean. Such redistributions may be responsible for substantial variations of the atmospheric $p\text{CO}_2$ as suggested by model computations reported, e.g., by Knox and McElroy (1984). For the present analysis, all these complications are equivalent, to considerable uncertainty connected with the target value Δ^0 , which must be accepted in the present context.

6.2. Control of M_a and M_{ox} or acid carbon versus oxygen

Let us now consider the control properties of eqs. (19b, c) subject to the constraint given by eq. (20). For this purpose, we introduce perturbations relative to a presumed balanced state. We thus write:

$$M_a = M_a^0(1 + x), \quad (21a)$$

$$M_{ox} = M_{ox}^0(1 + y), \quad (21b)$$

where

$$x = {}^aC'/{}^aC^0 \quad (21c)$$

$$y = p\text{O}'_2/p\text{O}_2^0, \quad (21d)$$

$${}^aC' = {}^aC - {}^aC^0, \quad (21e)$$

$$p\text{O}'_2 = p\text{O}_2 - p\text{O}_2^0, \quad (21f)$$

$$x \ll 1, \quad y \ll 1. \quad (21g, h)$$

We expect that the control of the system is related to feedback from $p\text{O}_2$, $p\text{CO}_2$. It is therefore essential that the perturbations x and y are directly related to perturbations of $p\text{O}_2$ and $p\text{CO}_2$. This is obviously true for y according to eq. (21d) above. The relation between ${}^aC'$ and $p\text{CO}'_2$ is in general more complicated. It is at this point that the constraint on Δ enters the analysis.

From eq. (8a) and (20), we obtain the approximate relation

$$p\text{CO}_2 = \text{const} \cdot ({}^aC')^2/\Delta^0,$$

where Δ^0 is now a constant, implying that

$$p\text{CO}'_2/p\text{CO}_2^0 = 2 {}^aC'/{}^aC^0 = 2x, \quad (22)$$

which is the relation between $p\text{CO}_2'$ and x required for the present discussion.

In view of the direct proportionality between (x, y) and $(p\text{CO}_2', p\text{O}_2')$, we expect that the perturbations x and y are associated with perturbations on the flows B_a , B_s , and W_{Si} according to:

$$B_a = B_a^0 + F_0(\alpha_1 x - \beta_1 y), \quad (23a)$$

$$B_s = B_s^0 + F_0(\alpha_2 x - \beta_2 y), \quad (23b)$$

$$W_{\text{Si}} = W_{\text{Si}}^0 + F_0 \alpha_3 x, \quad (23c)$$

where F_0 is the reference flow used in eqs. (13) and the mean flows B_a^0 , B_s^0 , W_{Si}^0 represent a steady state solution to eqs. (19b, c).

The strength of the feedback is represented by the constants α_v and β_v in eqs. (23).

We note that α_v and β_v as defined by eqs. (23) are positive if the feedback conforms with what is commonly expected (B_a , B_s , W_{Si} increasing with $p\text{CO}_2$ and B_a , B_s decreasing with $p\text{O}_2$).

From eqs. (19, 21, 23), the definition of the time scales given by eqs. (13a–c), and recalling that $M_g \ll M_a$, we obtain:

$$T_a \frac{d}{dt} x = -(\alpha_1 + \alpha_2 + \alpha_3) x + (\beta_1 + \beta_2) y, \quad (24a)$$

$$T_{\text{ox}} \frac{d}{dt} y = +(\alpha_1 + r\alpha_2) x - (\beta_1 + r\beta_2) y. \quad (24b)$$

Eqs. (23) may be solved exactly with elementary methods. The resulting expressions become somewhat complicated. In the limit when

$$T_a \ll T_{\text{ox}},$$

which is relevant in view of eqs. (13), the solution simplifies to

$$x(t) = (x_0 - py_0) \exp(-q_a t) + py(t), \quad (25a)$$

$$y(t) = y_0 \exp(-q_{\text{ox}} t), \quad (25b)$$

where

$$q_a = (\alpha_1 + \alpha_2 + \alpha_3)/T_a, \quad (25c)$$

$$q_{\text{ox}} = [(r-1)(\alpha_1 \beta_2 - \alpha_2 \beta_1) + \alpha_3(\beta_1 + r\beta_2)]/$$

$$[(\alpha_1 + \alpha_2 + \alpha_3) T_{\text{ox}}], \quad (25d)$$

$$p = (\beta_1 + \beta_2)/(\alpha_1 + \alpha_2 + \alpha_3),$$

and (x_0, y_0) are the initial values for (x, y) .

We note that $|q_a| \gg |q_{\text{ox}}|$ in accordance with our expectation that $y(t)$ develops on a much longer time-scale than $x(t)$. We also note that $x(t)$ has two time-scales, since $x(t)$ first adjusts with the time scale T_a to become equal to $py(t)$, which decays slowly with the time scale T_{ox} .

Obviously we must require that

$$q_a > 0, \quad q_{\text{ox}} > 0, \quad (26a, b)$$

for the system to be stable. If all (α_v, β_v) are positive, then q_a is obviously positive. The parameter q_{ox} , however, contains a negative contribution (assuming that α_2 and β_1 are positive). We note that this possibly negative contribution is associated with the response of B_a to increased $p\text{O}_2$. This is an interesting observation in view of the doubts cast on the feedback properties of B_a as discussed in Subsection 5.2.

We may recall here that the feedback parameters (α_v, β_v) are not known. Our "solution" to the small perturbation problem is thus nothing but a procedure to illustrate the consequences of different assumptions about particular feedback properties. The reader is thus invited to check his own ideas in this respect versus the implications of continuity as expressed by eqs. (25).

7. Control with or without silicate weathering

We may now consider the consequences of different assumptions concerning the relative strength of the feedback parameters (α_v, β_v) . Let us first try the assumption that feedback from $p\text{CO}_2$ is dominated by silicate weathering in the sense that

$$\alpha_3 \gg (\alpha_1, \alpha_2). \quad (27)$$

We then obtain for the decay constants

$$q_a \approx \alpha_3/T_a,$$

$$q_{\text{ox}} \approx (\beta_1 + r\beta_2)/T_{\text{ox}},$$

$$p = (\beta_1 + \beta_2)/\alpha_3, \quad (28a, b)$$

which is precisely the mathematical expression for control by silicate weathering on the short time scale and by reduced carbon and sulphide burial on the longer time scale.

We should recall, however, that an interaction between the carbon and oxygen systems is still present in that a perturbation of the oxygen system imposes a perturbation on the carbon system (the term $py(t)$ in eq. (25a)).

Let us now look at the opposite possibility, namely, that silicate weathering does not enter the control at all. We thus consider $(V_a - W_{Si})$ as a prescribed external forcing when considering the stability properties of our system.

Formally, we require just the opposite of eq. (27), i.e.,

$$(\alpha_1, \alpha_2) \gg \alpha_3. \quad (29)$$

We obtain

$$q_a \approx (\alpha_1 + \alpha_2)/T_a, \quad (30a)$$

$$q_{ox} \approx (r-1)(\alpha_1\beta_2 - \alpha_2\beta_1)/[(\alpha_1 + \alpha_2)T_{ox}], \quad (30b)$$

$$p \approx (\beta_1 + \beta_2)/(\alpha_1 + \alpha_2). \quad (30c)$$

Eqs. (30) demonstrate that the system may work altogether independently of the operation of silicate weathering. We note the crucial appearance of the factor $(r-1)$ in front of the expression for q_{ox} . It follows from the stoichiometry of sulphide burial (Section 2) that $(r-1) > 0$. As demonstrated by eq. (30b), this is a necessary condition for the system to function without silicate weathering.

A condition for stability is that q_{ox} remains positive despite the possibly negative contribution from the term $\alpha_2\beta_1$ in eq. (30b), i.e., that

$$\alpha_1\beta_2 - \alpha_2\beta_1 > 0. \quad (31)$$

We conclude that stability of the system could be violated, even though all the feedback parameters (α_v, β_v) are positive.

8. Control by the deep ocean and continental fire

Let us now outline a speculative scenario for the control of the carbon oxygen system involving

only two feedback processes related to continental fire and the oxygenation of the deep ocean.

We have in mind two important features of the system namely, the following.

(i) The frequency of continental fires is sensitive to changes in the atmospheric pO_2 . It has been suggested that even a small increase in atmospheric oxygen from 21 % to say 25 % of the total atmospheric pressure would increase the frequency of fire beyond tolerable limits (Watson et al., 1978). This is probably an exaggeration as pointed out by Robinson (1989), in a paper discussing the capacity of terrestrial vegetation to adjust to the higher frequency of fire associated with higher pO_2 . However, also a more modest assumption concerning the relation between fire and pO_2 calls for a feedback mechanism that can protect the biosphere from too high pO_2 .

(ii) The deep ocean is in a state such that the concentration of free oxygen is barely depleted in those regions of the ocean which are occupied by the oldest water. This state of the ocean is hardly a matter of good luck but can be expected to be the result of feedback processes emanating directly from the oxygen state of the deep ocean.

Against this background, it appears inevitable that continental fire as well as the state of saturation with respect to oxygen in the deep ocean is involved in the system of feedback which controls the carbon oxygen system. In what follows, we will outline an extreme version of such a system which for its operation depends only on feedback related to the frequency of fire and the state of the deep ocean. Our intention is thereby not to provide the most realistic picture but rather to demonstrate a possibility and perhaps present a starting point for a much more comprehensive analysis.

We thus make the following assumptions about feedback. (i) Burial of reduced carbon increases when pO_2 is high because of increased formation of charcoal associated with increased frequency of fire. (ii) Burial of sulfide increases with atmospheric pCO_2 , since pCO_2 is expected to increase the nutrient supply to the ocean and thus increase ocean productivity. High productivity of the ocean will give rise to larger anoxic areas, resulting in increased burial of sulfide. (iii) All other feedback mechanisms may be neglected in comparison with (i) and (ii).

In terms of the formal perturbation scheme presented in Section 6, we thus have

$$\beta_1 < 0, \quad \alpha_2 > 0, \quad \alpha_1 = \alpha_3 = \beta_2 = 0, \quad (32a)$$

$$q_a = \alpha_2/T_a, \quad q_{ox} = -(r-1)\beta_1/T_{ox}. \quad (32b)$$

Eqs. (32) represent a stable system, since q_a as well as q_{ox} are positive. Eqs. (32) represent a control system with complete coupling between the carbon and oxygen systems. This is the extreme counterpart of the silicate-dominated control described by eqs. (28), in which the carbon and oxygen systems operate essentially independently.

In order to clarify the operation of the system described by eqs. (32), we write the perturbation equations in the form:

$$\frac{d}{dt} M'_a = -B'_a - B'_s, \quad (33a)$$

$$\frac{d}{dt} M'_{ox} = B'_a + rB'_s, \quad (33b)$$

which are obtained by introducing

$$B_a = B_a^0 + B'_a, \quad B_s = B_s^0 + B'_s,$$

$$W_{Si} = W_{Si}^0$$

into eqs. (19b and c) and subtracting the mean flows (B_a^0 , etc.) which are assumed to be balanced. (Note that $W'_{Si} = 0$ by assumption.)

On the longer time scale, T_{ox} , the flows on the right-hand side of eq. (33a) have to balance (in view of the smallness of M_a), and we obtain

$$B'_a + B'_s = 0 \quad \text{when } T \gg T_a. \quad (34)$$

Eq. (34) represents a constraint on the development of the system on the longer time scale T_{ox} . Suppose now that we have at some time a positive perturbation on M_{ox} , i.e.,

$$M'_{ox} > 0,$$

which in order to decay calls for a negative flow on the right-hand side of eq. (33b), i.e., we require

$$B'_a + rB'_s < 0. \quad (35)$$

In view of the constraint provided by eq. (34) and

recalling that $r > 1$, such a negative flow can only be obtained if

$$B'_a > 0 \quad \text{and} \quad B'_s < 0,$$

which demonstrates that we actually need an increased burial of reduced carbon in order to bring down the oxygen pressure to its equilibrium value.

Let us now try to give an intuitively oriented description of the operation of the control system outlined in this section. Let us thus try to describe the sequence of events that will result if pO_2 initially is "too high" for some reason.

(1) The high pO_2 will increase the frequency of fire and consequently increase the burial of reduced carbon (in the form of charcoal).

(2) The increased burial of reduced carbon will reduce pCO_2 and increase pO_2 . The effect on pO_2 will, however, be negligible in view of the relative sizes of the carbon and oxygen reservoirs.

(3) The depletion of pCO_2 will continue until the ocean productivity is influenced through decreased supply of nutrients or otherwise. Anoxic areas in the ocean will become more rare and as a consequence the burial of sulfide is reduced.

(4) As a result of these events, the system will establish a slowly developing state characterized by a net oxidation of sulfides combined with a net burial of reduced carbon. The relative size of these flows is such that the oxygen reservoir is reduced while the carbon reservoir is essentially untouched.

(5) As a consequence of this combination of flows, the initial positive perturbation on pO_2 decays together with the negative perturbation on pCO_2 created by the system in the course of events. The final decay will take some 10 million years.

9. Concluding remarks

The analysis in this paper is based on the stoichiometry of the main reactions controlling the carbon-oxygen system and the requirements posed by continuity. An effort has been made to cast this fairly solid information into a form which illuminates the dynamical properties of the system, in particular the consequences for the system of different assumptions about feedback properties.

We have found that the system has three distinct time scales associated with the reservoirs (M_Δ ,

M_a , and M_{ox}) representing the state of the carbon oxygen system. The shortest time scale under consideration is dominated by the burial of carbonates which controls Δ , i.e., the difference between the "acid" and "base" carbon reservoirs, and thereby the short-term variations of pCO_2 . Here, it should be recalled that we have altogether ignored the entire world of disturbances that is associated with redistribution of properties within the ocean which may give rise to substantial variations of pCO_2 .

On the longer time scales, silicate weathering and the net burial of reduced carbon and sulfide remain to control the system.

We have demonstrated that the control of the system may operate independently of silicate weathering on all time scales. With this view of the system, metamorphic degassing and silicate weathering may be considered as an externally-prescribed forcing. The task of controlling the long-term behaviour of the carbon-oxygen system would then be left to the flows corresponding to net burial of reduced carbon and sulfide. Correspondingly, the stability of the system would depend on feedback from the state of the system on these flows.

As demonstrated by our set of continuity eqs. (10), the coupling between the carbon and the oxygen system shows up very clearly on the long time scale characteristic for adjustments of pO_2 . Because of the small size of the acid carbon reservoir, M_a , compared with the oxygen reservoir, M_{ox} , the adjustment of the longest time scale has to operate under the constraint that the net flow to M_a vanishes. This constraint has important consequences for the stability properties, which is demonstrated with the perturbation procedure in Section 6. In particular, we arrive at the interesting

conclusion that it may be favourable for the stability properties of the system if burial of organic carbon increases in response to high pO_2 rather than the opposite, which is commonly assumed.

An extreme alternative for the control of the system is presented. In this scenario, the control is based on: (i) feedback from pO_2 on the frequency of forest fires, assuming that fire increases the rate of formation of charcoal; (ii) feedback from pCO_2 on the deep ocean oxygen depletion, assuming that oxygen abundance in the deep ocean provides an efficient switch for burial of sulphides.

It is demonstrated that these two mechanisms alone could provide efficient control of the carbon oxygen system on the long and intermediate time scales.

An obvious conclusion of this paper is that even the most qualitative aspects of the control properties of the carbon-oxygen system are largely open for debate. Most importantly, we need information regarding feedback, i.e., how the system reacts in response to perturbations. This might seem a hopeless task in view of the complexities of the system. Thus, there is still room for ingenuity in approach to the problem.

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REFERENCES

- Berner, R. A., Lasaga, A. C. and Garrels, R. M. 1983. The carbonate-silicate geochemical cycle and its effect on carbon dioxide over the past 100 million years. *Am. Journ. of Sc.* 283, 641–683.
- Berner, R. A. and Raiswell, R. 1983. Burial of organic carbon and pyrite sulfur in sediments of Phanerozoic time: a new theory. *Geochimica et Cosmochimica Acta* 47, 855–862.
- Berner, R. A. and Canfield, D. E. 1989. A new model for atmospheric oxygen over Phanerozoic time. *American Journ. of Sc.* 289, 333–361.
- Broecker, W. S. 1971. A kinetic model for the chemical composition of sea water. *Quaternary Res.* 6, 188–207.
- Broecker, W. S. and Peng, T.-H. 1982. *Tracers in the sea*. Eldigio Press. Lamont-Doherty Geological Observatory, Columbia University, Palisades, New York.
- Dyrssen, D. and Sillén, L. G. 1967. Alkalinity and total carbonate in sea water. A plea for p-T-independent data. *Tellus* 19, 113–121.
- Fiadeiro, M. 1980. The Alkalinity of the deep Pacific. *Earth and Planetary Sc. Letters*. 49, 499–505.
- Garrels, M. G. and Lerman, A. 1981. Phanerozoic cycles

- of sedimentary carbon and sulfur. *Proc. Natl. Acad. Sci. USA* 78, 8, 4652–4656.
- Garrels, M. G., Lerman, A. and Mackenzie, F. T. 1976. Controls of Atmospheric O₂ and CO₂. *Past, Present, and Future. American Sc.* 64, 306–315.
- Garrels, M. G. and Perry, E. A. 1974. Cycling of carbon, sulfur, and oxygen through geologic time. In: (ed. E. D. Goldberg) *The Sea*. New York, Wiley, 5, 303–316.
- Herring, J. R. 1985. Charcoal fluxes into sediments of the north Pacific ocean: The Cenozoic record of burning. In, *The carbon cycle and atmospheric CO₂: Natural variations Archean to present*. (eds. E. T. Sundquist and W. S. Broecker) American Geophysical Union, Geophysical Monograph 32, 397–411.
- Holland, H. D. 1978. *The chemistry of the Atmosphere and Oceans*. New York, Wiley.
- Idso, S. B. 1989. Carbon dioxide and global change: earth in transition. IBR Press Inst. for Biospheric Research. Tempe, Arizona USA. Available from author.
- Kasting, J. F., Richardson, S. M., Pollack, J. B. and Toon, O. B. 1986. A hybrid model of the CO₂ geochemical cycle and its application to large impact events. *Am. J. Sc.* 286, 361–389.
- Knox, F. and McElroy, M. B. 1984. Changes in atmospheric CO₂: Influence of the marine biota at high latitude. *J. Geophys. Res.* 89, D3, 4629–4637.
- Kump, L. R. 1988. Terrestrial feedback in atmospheric oxygen regulation by fire and phosphorus. *Nature* 335, 152–154.
- Kump, L. R. and Garrels, R. M. 1986. Modelling atmospheric O₂ in the global sedimentary redox cycle. *Am. J. Sci.* 286, 337–360.
- Lasaga, C. G., Berner, R. A., and Garrels, R. M. 1985. An improved geochemical model of atmospheric CO₂ fluctuations over the past 100 million years. In, *The carbon cycle and atmospheric CO₂: Natural variations Archean to present*. (eds. E. T. Sundquist and W. S. Broecker) American Geophysical Union, Geophysical Monograph 32, 397–411.
- Lovelock, J. E. and Margulis, L. 1974. Atmospheric homeostasis by and for the biosphere. The GAIA hypothesis. *Tellus* 26, 1–20.
- Robinson, J. M. 1989. Phanerozoic O₂ variation, fire, and terrestrial ecology. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* (Global and Planetary change section) 75, 223–240.
- Sillén, L. G. 1961. The physical chemistry of sea water. In: *Oceanography, Publ. No. 67*, Amer. Assoc. Adv. of Sc.
- Sundquist, E. T. 1985. Geological perspectives on carbon dioxide and the carbon cycle. In, *The carbon cycle and atmospheric CO₂: Natural variations Archean to present*. (eds. E. T. Sundquist and W. S. Broecker) American Geophysical Union, Geophysical Monograph 32, 5–60.
- Veizer, J., Holser, W. T. and Wilgus, C. K. 1980. Correlation of ¹³C/¹²C and ³⁴S/³²S secular variations. *Geochimica et Cosmochimica Acta* 44, 579–587.
- Walén, G. 1990. Continuity equations for the carbon oxygen system. On the control of ocean acidity and atmospheric oxygen. Dept. Oceanography Univ. of Gothenburg Report no. 50.
- Walker, J. C. G., Hays, P. B. and Kasting, J. F. 1981. A negative feedback mechanism for the long term stabilization of earth's surface temperature. *J. Geophys. Res.* 86, C10, 9776–9782.
- Watson, A. J., Lovelock, J. E. and Margulis, L. 1978. Methanogenesis, fires and the regulation of atmospheric oxygen. *Biosystems* 10, 293–298.
- Whitfield, M. 1981. The world ocean. Mechanism or machination. *Interdisciplinary Sc. Reviews* 6, no. 1.