A MODEL FOR CALCIUM, MAGNESIUM AND SULFATE IN SEAWATER OVER PHANEROZOIC TIME

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ABSTRACT. A theoretical model has been constructed for calculating the concentrations of dissolved calcium, magnesium and sulfate in seawater over the past 550 million years (Phanerozoic time). It is demonstrated that the weathering of Ca carbonates and silicates by carbonic acid can be generally ignored in the modeling. A previous model of the carbon cycle is used to guide input to the oceans of Mg from carbonate and silicate weathering by H_2CO_3. Similarly a previous model of the sulfur cycle is used to guide input fluxes to the ocean by calcium sulfate weathering and the weathering of Ca and Mg carbonates and silicates by sulfuric acid. The sulfuric acid is derived from the oxidation of pyrite during weathering plus the oxidation of sulfur gases derived from the metamorphic/volcanic decomposition of pyrite and $CaSO_4$. Calcium is removed from seawater as sedimentary carbonates and sulfates, SO_4 is removed as sedimentary pyrite and $CaSO_4$, and Mg is removed by exchange for Ca via basalt-seawater reaction and/or dolomitization (plus minor burial in sediments with pyrite as anoxic dolomite).

By adjusting starting conditions modeling results can be found that agree well with results of studies of salt fluid inclusions for variations of Ca and SO_4. This is especially true of the timing when Ca was more abundant in seawater than SO_4 and vice versa. General agreement was also found with fluid inclusion results for changes in the Mg/Ca ratio thereby distinguishing "calcite seas" from "aragonite seas". Because of this overall agreement the modeling offers a new perspective on why oceanic Ca, Mg and SO_4 have varied over Phanerozoic time.

INTRODUCTION

Recent studies have conclusively demonstrated that the chemical composition of the oceans, in terms of the concentrations of major ions, has varied significantly over geologic time. The basis for this discovery is the study of the composition of fluid inclusions in bedded halite (Horita and others, 1991; Hardie, 1996; Kovalovich and others, 1998; Zimmermann, 2000; Lowenstein and others, 2001; Brennan and Lowenstein, 2002; Horita and others, 2002; Kovalovich and others, 2002; Lowenstein and others, 2003). Also, the ratio of Mg/Ca has been found to vary over time in a way that is in accord with predictions based on the mineralogy of shallow water carbonates (Sandberg, 1983; Hardie, 1996; Stanley and Hardie, 1998; Dickson, 2002). When applied to both biologically and inorganically precipitated carbonates, high Mg/Ca ratios are found associated with "aragonite seas" and low Mg/Ca with "calcite seas". The mineralogy of bitterns (minerals formed from extremely highly evaporated seawater) also correlate with the Mg/Ca ratio of seawater (Hardie, 1996); bitterns characterized by $MgSO_4$ minerals occur at times of high Mg/Ca and those characterized by KCl at times of low Mg/Ca.

Explanation of these observations in terms of chemical models for seawater evolution have been offered by Spencer and Hardie (1990), Hardie (1996), Holland and Zimmermann (2000) and Holland (unpublished ms). The model of Spencer and Hardie has received the greatest attention. In this model Na, Ca, Mg, K, SO_4 and Cl concentrations are calculated over time by mixing fluxes of river water with water resulting from hydrothermal reactions with mid-ocean ridge basalts. Variations of composition are due primarily to variations in the degree of basalt-seawater reaction as guided by the history of seafloor spreading rate (Gaffin, 1987). It is assumed that all Mg is removed by reaction with basalts. By contrast, Holland and Zimmermann (2000) and
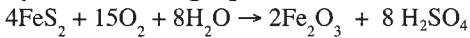
Table 1

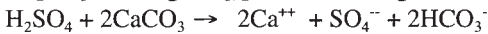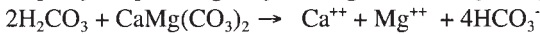*Inputs and Outputs of Ca, Mg and SO$_4$ to/from the Ocean*

Calcium sulfate weathering input

$CaSO_4 \rightarrow Ca^{++} + SO_4^{-}$

Pyrite weathering input

$4FeS_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 8 H_2SO_4$

Silicate and Carbonate weathering input

$2 H_2CO_3 + H_2O + CaSiO_3 \rightarrow Ca^{++} + 2HCO_3^- + H_4SiO_4$

$H_2CO_3 + CaCO_3 \rightarrow Ca^{++} + 2HCO_3^-$

$2H_2CO_3 + H_2O + MgSiO_3 \rightarrow Mg^{++} + 2HCO_3^- + H_4SiO_4$

$2H_2CO_3 + CaMg(CO_3)_2 \rightarrow Ca^{++} + Mg^{++} + 4HCO_3^-$

$H_2SO_4 + 2CaCO_3 \rightarrow 2Ca^{++} + SO_4^{--} + 2HCO_3^-$

$H_2SO_4 + CaSiO_3 + H_2O \rightarrow Ca^{++} + SO_4^{--} + H_4SiO_4$

$2H_2SO_4 + 2CaMg(CO_3)_2 \rightarrow 2Ca^{++} + 2Mg^{++} + 2SO_4^{--} + 4HCO_3^-$

$H_2SO_4 + MgSiO_3 + H_2O \rightarrow Mg^{++} + SO_4^{--} + H_4SiO_4$

Basalt-seawater reaction and dolomitization (output of Mg and input of Ca)

$Mg^{++} + Ca\text{-basalt} \rightarrow Ca^{++} + Mg\text{-basalt}$

$Mg^{++} + 2CaCO_3 \rightarrow Ca^{++} + CaMg(CO_3)_2$

Outputs of Ca, Mg and SO$_4$ from the ocean

$Ca^{++} + 2HCO_3^- \rightarrow CO_2 + H_2O + CaCO_3$

$Ca^{++} + SO_4^{--} \rightarrow CaSO_4$

$2Fe_2O_3 + 8 Ca^{++} + 8SO_4^{--} + 8CO_2 \rightarrow 4FeS_2 + 15O_2 + 8 CaCO_3$

$2Fe_2O_3 + 4 Ca^{++} + 4Mg^{++} + 8SO_4^{--} + 8CO_2 \rightarrow 4FeS_2 + 15O_2 + 4 CaMg(CO_3)_2$
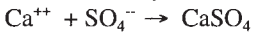
Holland (unpublished ms) emphasize reaction with carbonates to form dolomite as the principal process of Mg removal from seawater.

As a check on these models independent dynamic modeling is needed which tracks all of the principal fluxes over time for the input and output of the principal ions of seawater. One such dynamic model, for Ca, Mg, SO$_4$ and HCO$_3$ over the past 150 Ma, is that of Hansen and Wallmann (2003). Some others that treat the entire Phanerozoic are Mackenzie and others (2003) and Bergman and others (2004). The purpose of the present paper is to offer a new dynamic model that focuses only on Ca, Mg and SO$_4$ over the Phanerozoic (past 550 million years). Processes include variations in riverine input from weathering and output by burial in sediments, as well as changes in rates of basalt-seawater reaction or dolomitization.

A summary of the generalized reactions for the input to and output from the oceans for Ca, Mg and SO$_4$ are shown in table 1. As one can see there is considerable involvement of the cycles of carbon and sulfur as they accompany the addition of calcium and magnesium to the ocean, and their removal from the ocean. This is due to the weathering of Ca and Mg silicates and carbonates by carbonic and sulfuric acids, and by the removal of Ca from the oceans as calcium carbonate, calcium sulfates and a combination of pyrite plus CaCO$_3$. Because a model for the fluxes of bicarbonate and sulfate to/from the ocean over Phanerozoic time is already available (Berner, 2001), the approach of the present paper will be to add mass balance expressions for Ca and Mg to those already existing for carbon and sulfur.

MODELING ASSUMPTIONS

Carbon

It is important to present the mass balance expressions for carbon input and output fluxes to/from the ocean before discussing the Ca, Mg and SO_4 cycles themselves. From long term (multimillion year) carbon modeling (Berner, 2001; Berner, 2004), the appropriate C mass balance expression, involving fluxes of carbon F, is:

$$F_{wc} + F_{mc} + F_{wg} + F_{mg} = F_{bc} + F_{bg} \qquad (1)$$

where:

F_{wc} = weathering of Ca and Mg carbonates
F_{mc} = metamorphic/diagenetic/volcanic degassing from carbonates
F_{wg} = weathering of organic matter
F_{mg} = metamorphic/diagenetic/volcanic degassing from organic matter
F_{bc} = sedimentary burial of Ca and Mg carbonates
F_{bg} = sedimentary burial of organic matter

This expression shows that the total input flux is assumed to balance the total output flux. This is a reasonable approximation because of the limited capacity for storing carbon in the oceans, resulting in a very short residence time (about 100,000 years) when compared to the multimillion year time scale of the Phanerozoic (Berner and Caldeira, 1997). To further simplify modeling, the approach of Berner (2001) is assumed here whereby the metamorphic/diagenetic/volcanic fluxes are combined with the weathering fluxes to give a combined "weathering" flux that lumps carbonate weathering with silicate weathering. In other words, the degassed CO_2 from volcanism + metamorphism + diagenesis is reacted with carbonates and silicates to form HCO_3 along with the HCO_3 derived from the carbonate minerals themselves. Also, the metamorphic breakdown flux of organic matter, followed by atmospheric oxidation of reduced gases, is combined with the flux for low temperature oxidative weathering so that the sites of oxidation of organic matter to CO_2 are not distinguished. In this manner equation (1) simplifies to:

$$F_{wmc} + F_{wmg} = F_{bc} + F_{bg} \qquad (2)$$

where $F_{wmg} = F_{wg} + F_{mg}$ and $F_{wmc} = F_{wc} + F_{mc}$. By using data on the carbon isotopic composition of carbonates over time it is possible to calculate the values for each of the fluxes in equation (2), and this procedure is repeated in the present model. To lend negative feedback stability to the modeling, the weathering fluxes are divided into fluxes from old and young rocks via rapid recycling and the fractionation of carbon isotopes during photosynthesis is assumed to be a function of atmospheric O_2 concentration (see Berner, 2001 for further details).

Sulfate

The expression for the rate of change of sulfate over time is derived from sulfur mass balance modeling (Berner, 2001), but with the modification here that sulfate is not at steady state. The appropriate equation is:

$$d[SO_4]/dt = F_{wmp} + F_{wms} - F_{bp} - F_{bs} \qquad (3)$$

where:

$[SO_4]$ = mass of sulfate-sulfur in the oceans
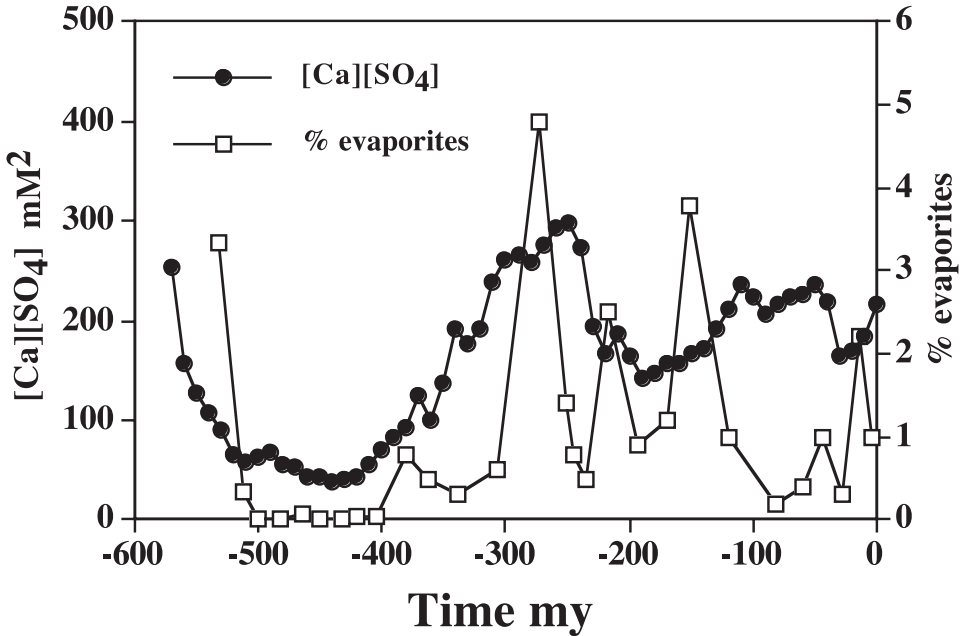F_{wmp} = weathering and metamorphic/volcanic release of pyrite sulfur

Fig. 1. Plot of the model-derived product of dissolved Ca and SO_4 concentrations $[Ca][SO_4]$ and percent evaporites versus time. Data for evaporites, representing a running two-point average, are from Ronov (1993).

F_{wms} = weathering and metamorphic/volcanic release of calcium sulfate sulfur
F_{bp} = burial of pyrite sulfur in sediments
F_{bs} = burial of calcium sulfate sulfur in sediments

Similar to the calculations for carbon the use of rapid recycling, O_2-dependent sulfur isotope fractionation, and the inclusion of metamorphic and volcanic degassing in the "weathering" terms is employed (Berner, 2001). For a detailed treatment of degassing the reader is referred to the model by Hansen and Wallmann (2003) where degassing is considered separately from weathering. Removal of sulfate from seawater to form hydrothermal $CaSO_4$ at mid-ocean rises is not considered because this material readily re-dissolves later.

Because of slowly varying oceanic sulfate concentration, the burial rate of $CaSO_4$, F_{bs}, cannot be obtained from a steady state sulfur mass balance equation analogous to (1) by eliminating the time derivative as is done for carbon. Instead the following rate law for calcium sulfate precipitation is assumed:

$$F_{bs} = \{[Ca][SO_4]/[Ca](o)[SO_4](o)\}F_{bs}(o) \qquad (4)$$

where $[Ca]$ is the mass of Ca in seawater and (o) refers to present values. The value of $F_{bs}(o)$ is not well known but a reasonable value for the past few million years ("present") is 1.3×10^{18} mol/My (Berner and Berner, 1996).

The formulation of equation (4) is not the most realistic. Calcium sulfate results from the evaporation of seawater and it forms only when two independent preconditions occur, an arid climate with intense evaporation and topographically restricted seawater circulation. Nevertheless, there is a crude correlation of total evaporite formation (mainly as NaCl) and the product $[Ca][SO_4]$ (based on the present model) as shown in figure 1 (data for evaporites from Ronov, 1993). This correlation cannot be
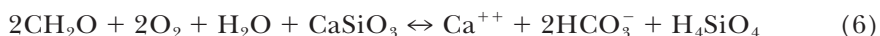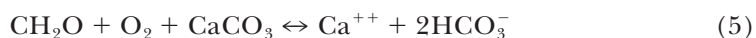
carried too far, however. Use of the Ronov evaporite abundance as a *direct* measure of $CaSO_4$ precipitation in computer calculations led to impossible and negative values for Ca and SO_4 concentrations because of the enormous variability of the evaporite data set. I believe that $CaSO_4$ precipitation may be more continual over time than indicated by the age distribution of evaporites. This is especially true because of the likelihood of preferential and discontinuous loss of evaporites over time due to their high solubility (Garrels and Mackenzie, 1971).

<center>*Calcium*</center>

Because of the short residence time of carbon in seawater, the input of Ca from the weathering of silicates and carbonates by carbonic acid, when added to the input of Ca from exchange with Mg (via basalt-seawater reaction or dolomitization), can be assumed to be balanced by the output flux of Ca to form calcium carbonate. This is a consequence of equation (2) and the stoichiometry of the reactions of table 1. This means that, in a time dependent model for seawater calcium concentration, the input weathering flux of Ca from the reaction of carbonic acid with carbonates and silicates, and the output flux of Ca as $CaCO_3$, can be ignored as a first approximation. Further explanation of this reasoning, along with an independent equilibrium argument, is presented in appendices A and B.

In the present paper it is also implicitly assumed that the much lower fluxes of HCO_3 accompanying Na and K silicate weathering by carbonic acid (only 5% of the total HCO_3 flux-Berner and Berner, 1996), are essentially balanced by the destruction of HCO_3 by the formation of authigenic Na and K silicates in sediments (Mackenzie and Garrels, 1966). Sodium and potassium do not form major carbonates. A possible feedback mechanism for this to occur is that greater physical erosion, resulting from enhanced chemical weathering of primary Na and K silicates such as feldspars, should lead to greater sedimentation of clay-rich siliciclastic debris (Berner and Canfield, 1989). More clayey sedimentation should aid in the formation of authigenic silicates as shown, for example, by authigenic K silicates forming at present in major clay depositional sites, such as river deltas (Michalopoulos and Aller, 2004).

The oxidation during weathering of organic matter involves the production of CO_2 and globally this CO_2 can then react with carbonates and silicates to form HCO_3^-. The combined reactions can be written as:

$$CH_2O + O_2 + CaCO_3 \leftrightarrow Ca^{++} + 2HCO_3^- \tag{5}$$

$$2CH_2O + 2O_2 + H_2O + CaSiO_3 \leftrightarrow Ca^{++} + 2HCO_3^- + H_4SiO_4 \tag{6}$$

The HCO_3^- derived from organic matter oxidation plus silicate and carbonate weathering, is assumed in the present modeling to be balanced by that consumed by organic matter and calcium carbonate burial in the oceans, in other words, reaction (5) reading backwards (which is the sum of carbonate precipitation plus net photosynthesis/burial). This is a further simplification due to the short residence time of carbon in the oceans.

The simplest input reaction for Ca to the oceans is the weathering of $CaSO_4$ minerals. Each sulfate added via weathering is accompanied by an equivalent of calcium. This equivalency is also maintained during $CaSO_4$ deposition. Thus:
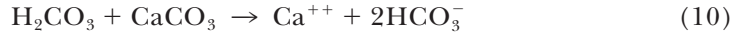
$$F_{wmCa}(CaSO_4) = F_{wms} \tag{7}$$

$$F_{bCa}(CaSO_4) = F_{bs} \tag{8}$$

where F_{wmca} and F_{bca} refer to the combined weathering plus metamorphic breakdown and marine burial of specified Ca minerals respectively.

The oxidation of pyrite during weathering produces sulfuric acid and this acid reacts with Ca carbonates and silicates (table 1). The overall reaction of H_2SO_4 with $CaCO_3$ given in table 1 represents the sum of the following reactions:

$$H_2SO_4 + CaCO_3 \rightarrow Ca^{++} + SO_4^- + H_2CO_3 \qquad (9)$$

with the H_2CO_3 reacting with $CaCO_3$:

$$H_2CO_3 + CaCO_3 \rightarrow Ca^{++} + 2HCO_3^- \qquad (10)$$

To conserve carbon reaction (10) is balanced by $CaCO_3$ precipitation in the ocean (see the above discussion and the appendices) and thus, can be ignored. This means that, for the purposes of the present Ca modeling, carbonate weathering by sulfuric acid is represented by reaction (9). Thus, the oceanic input flux of Ca from both calcium carbonate and calcium silicate weathering by sulfuric acid is equal to that for the input of sulfate from pyrite oxidation (less that from Mg weathering-see below). Reaction (9) also represents the overall reaction for the metamorphic and volcanic breakdown of pyrite with the liberated reduced sulfur gases emitted to the atmosphere where they are rapidly oxidized to sulfuric acid and afterwards react with $CaCO_3$.

The output of SO_4^- from the oceans to form sedimentary pyrite involves a number of reactions. These include (Berner, 2004): the photosynthetic production of organic matter, the bacterial reduction of dissolved sulfate to H_2S by this organic matter, the reaction of H_2S with iron minerals to form pyrite, and the precipitation of $CaCO_3$ from the HCO_3^- formed during bacterial sulfate reduction. The overall reaction from table 1 is:

$$2Fe_2O_3 + 8Ca^{++} + 8SO_4^{--} + 8CO_2 \rightarrow 4FeS_2 + 15O_2 + 8CaCO_3 \qquad (11)$$
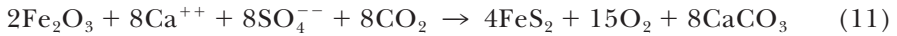
Mg is also added to the oceans along with sulfate as a result of the weathering by H_2SO_4 of Mg carbonates and silicates. In modern rivers about 70 percent of the flux of Ca + Mg consists of Ca (Berner and Berner, 1996). If we assume the same proportion for sulfuric acid weathering, we obtain for calcium carbonate and calcium silicate weathering (weathering of K and Na silicates by sulfuric acid is assumed negligible):

$$F_{wmCa(pyrite)} = 0.7F_{wmp} \qquad (12)$$

The same reasoning can be applied to the precipitation of carbonates during sedimentary pyrite formation. Thus,

$$F_{bCa(pyrite)} = 0.7F_{bp} \qquad (13)$$

where F_{wmCa}(pyrite) refers to the weathering of both Ca carbonates and Ca silicates and $F_{bCa(pyrite)}$ refers to the burial of $CaCO_3$ accompanying sedimentary pyrite formation.

Finally, appreciable calcium is added to the oceans by the reaction of seawater Mg with basalt at mid-ocean ridges (Hardie, 1996) or by reaction with $CaCO_3$ to form dolomite (Holland and Zimmermann, 2000). In either case there is a mole for mole loss of Mg and gain of Ca. (Ca precipitated at ridges as $CaSO_4$ is later released to seawater resulting in net one-for-one Mg exchange—Berner and Berner, 1996). At steady state for Mg (see below), there is no net change in Ca concentration by this process because the HCO_3 and SO_4 that accompanied the input of Mg from carbonic and sulfuric acid weathering is precipitated with a Ca flux that is equivalent to the Ca flux from the exchange of Mg for Ca. Change in Ca due to exchange with Mg occurs only when there is an imbalance between the Mg inputs and outputs (see appendix A):

$$d[Ca]/dt_{exch} = -d[Mg]/dt = -(F_{wmHg} - F_{exchMg}) \qquad (14)$$

where:

$d[Ca]/dt\ exch$ = variation of mass of Ca in seawater due to exchange with, and variation of, Mg in seawater

F_{wmMg} = input flux of Mg to the oceans from weathering and metamorphism (see next section)

F_{exchMg} = output flux of Mg due to mole-for-mole exchange with Ca (see next section)

Combining all the above expressions for oceanic Ca:

$$d[Ca]/dt = F_{wmCa(CaSO_4)} + F_{wmCa(pyrite)} - F_{bCa(CaSO_4)} - F_{bCa(pyrite)} + d[Ca]/dt_{exch} \quad (15)$$

which on substituting from equations (7), (8) (12), (13) and (14) is:

$$d[Ca]/dt = F_{wms} + 0.7F_{wmp} - F_{bs} - 0.7F_{bp} - d[Mg]/dt \qquad (16)$$

Magnesium

Magnesium is added to the oceans via carbonate and silicate weathering and is removed mainly by the mole for mole exchange for Ca via basalt-seawater reaction (Hardie, 1996) or via dolomite formation (Holland and Zimmermann, 2000) (table 1). Because Mg is not removed entirely as carbonates, the input fluxes of HCO_3 from the weathering of Mg carbonates and silicates by H_2CO_3 (including H_2CO_3 from organic matter) are not balanced by equivalent output fluxes of Mg carbonates. Thus, in contrast to Ca, input fluxes of Mg from silicate and carbonate weathering by carbonic acid must be considered in a time dependent model. In the modern oceans 30 percent of the total weathering flux of Ca plus Mg consists of Mg. Thus, for weathering by H_2CO_3 (since there are two HCO_3 ions released for each Mg):

$$F_{wmMg} = 0.15(F_{wmc} + F_{wmg})(H_2CO_3\ only) \qquad (17)$$

Weathering by H_2SO_4 from pyrite oxidation affects Mg silicates and carbonates as well as those of Ca, with 30 percent of the total flux of Ca plus Mg released as Mg (see reaction 12). Combining the carbonic and sulfuric acid reactions:

$$F_{wmMg} = 0.15(F_{wmc} + F_{wmg}) + 0.3F_{wmp} \qquad (18)$$

The output of Mg from seawater is mainly by means of exchange for Ca via basalt seawater reaction at midocean rises or by dolomitization (table 1). In either case we have:

$$F_{exchMg} = k\{[Mg](t)/[Mg](o)\}F_{exchMg}(o) \qquad (19)$$

where F_{exchMg} is the exchange flux, [Mg] refers to the mass of Mg in the oceans and (o) refers to the present. Rather than have k be a constant over time, it is reasonable to have it vary in direct proportion to rates of ridge formation in terms of seafloor spreading rate (Hardie, 1996). Sea level is often used as a proxy for seafloor spreading rate (Gaffin, 1987) and can also be used as an indicator of dolomitization (Holland, unpublished ms). In the latter case the reasoning is that at higher sea level there are more shallow seas on the continents where evaporation can lead to dolomitization.

An additional but small removal term for Mg is needed to account for the Mg carbonate formed during bacterial sulfate reduction and pyrite formation. In equation (13) it was assumed that 70 percent of the carbonate precipitated during pyrite formation occurs as $CaCO_3$. This means that the remaining 30 percent is as Mg

carbonates, principally the Mg component of "anoxic" dolomite. This leads to the expression:

$$F_{bMg}(pyrite) = 0.3F_{bp} \tag{20}$$

In summary, the mass balance expression for oceanic Mg over time is:

$$d[Mg]/dt = F_{wmMg} - F_{exchMg} - F_{bMg}(pyrite) \tag{21}$$

which on substituting equations (18), (19) and (20) yields:

$$d[Mg]/dt = 0.15(F_{wmc} + F_{wmg}) + 0.3F_{wmp}$$
$$- f_{SR}(t)\{[Mg](t)/[Mg](o)\}F_{exchMg}(o) - 0.3F_{bp} \tag{22}$$

The value for $F_{exchMg}(o)$ is assumed to be 5×10^{18} moles per million years, the value needed to balance the present day input of Mg to the oceans by rivers (Berner and Berner, 1996); $f_{SR}(t)$ = spreading rate (t)/spreading rate (o).

Method of Calculation

Expressions (2), (3), (4), (16) and (22) were combined with expressions for carbon and sulfur isotopic mass balance, based on the isotopic data of Veizer and others (1999) and Strauss (1999), assuming rapid recycling and O_2-dependent fractionation of carbon and sulfur isotopes (Berner, 2001). The numerical computational procedure was the same as that used earlier for calculating carbon and sulfur fluxes over the Phanerozoic (Berner, 2001). This involves calculation forward in time with a time step of one million years for determination of all fluxes and concentrations. Initial (550Ma) starting concentrations of Ca, Mg, and SO_4 were varied until reasonable agreement was obtained with independent data for concentrations over time based on the study of halite fluid inclusions. Unfortunately, all investigated initial concentrations that give a good match to the fluid inclusion data resulted in final values for concentrations of Ca, Mg and SO_4 only approximately equal to those in modern seawater. Values of $f_{SR}(t)$ were from Gaffin (1987) and Engebretson and others (1992).

RESULTS AND DISCUSSION

Calculated concentrations of calcium and sulfate in seawater over Phanerozoic time are shown in figure 2 where all processes are considered by the modeling. Figure 3 shows the effect on Ca and SO_4 of considering only the weathering and burial of pyrite and calcium sulfate and ignoring the exchange of Mg for Ca (steady state Mg concentration). These figures show that in order to obtain an appreciable variation in Ca concentration, it is necessary to consider *both* exchange of Mg for Ca and the weathering and burial of pyrite and calcium sulfate.

Crossovers of the curves of Ca and SO_4 are important because it means that there may have been times in the geological past when Ca in seawater was more abundant than SO_4, the opposite of the present situation. Actual crossovers have been observed as a result of the study of brine inclusions trapped in halite (Horita and others, 2002; Lowenstein and others, 2003). At certain times in the past, after evaporation to NaCl saturation, appreciable Ca was found in solution within halite brine inclusions with no SO_4. This means that during evaporation continued calcium sulfate precipitation resulted in the almost complete loss of SO_4 but not Ca, the opposite situation as is found for modern seawater. This could only happen if Ca was more abundant than SO_4 in the original unevaporated seawater.

Measurements of halite fluid inclusions provide directly only the differences between the concentrations of Ca and SO_4 for the original unevaporated seawater, not
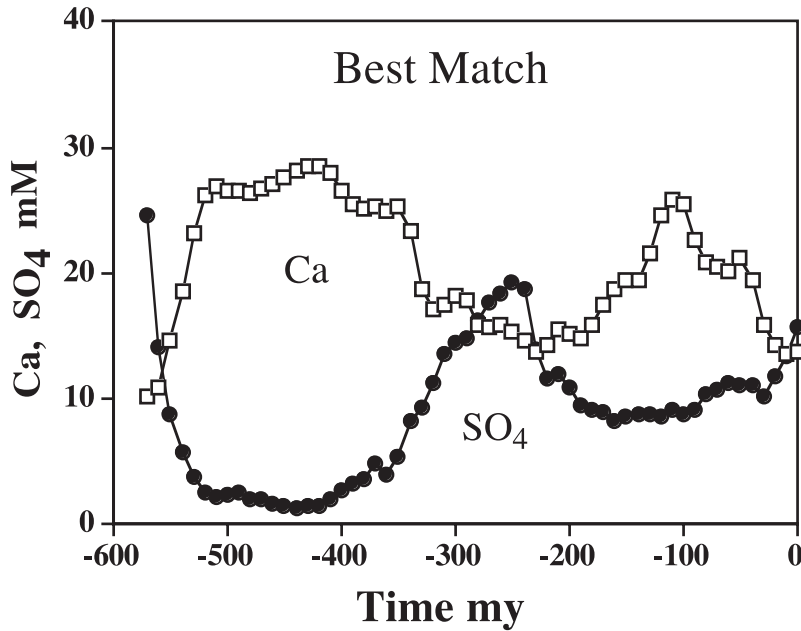
Fig. 2. Plots of dissolved Ca and SO_4 in seawater over Phanerozoic time based on the modeling of the present paper. "Best Match" refers to the best fit to halite fluid inclusion data (fig. 4) by varying initial concentrations at 550 Ma.

the actual concentrations. These differences result from the precipitation of $CaSO_4$ and the exchange of Mg for Ca during evaporation and are expressed mathematically (Horita and others, 2002) as:

$$Mg(S)/DE = Mg(o) - b \tag{23}$$

$$Ca(S)/DE = Ca(o) - a + b \tag{24}$$

$$SO_4(S)/DE = SO_4(o) - a \tag{25}$$

where: (S) represents the measured concentration in the halite brine inclusions, (o) represents the original concentration in seawater, DE the degree of evaporation (obtained from measured bromide concentrations), a the precipitated $CaSO_4$, and b the increase of Ca due to exchange with Mg. Combining (23) to (25):

$$Ca(o) - SO_4(o) + Mg(o) = [Ca(S) - SO_4(S) + Mg(S)]/DE \tag{26}$$

If b is small during evaporation (true for salt deposits with little accompanying dolomite), then b can be assumed to be small compared to a. In this case equation (26) simplifies to:

$$Ca(o) - SO_4(o) = [Ca(S) - SO_4(S)]/DE \tag{27}$$

In order to obtain the individual concentrations of Ca and SO_4 in original unevaporated seawater, using equation (27), it is necessary to make an additional assumption. The assumption made by Horita and others (2002) and Lowenstein and others (2003) is that the product of Ca and SO_4 concentrations in the original seawater was constant at all past times. However, there is no independent reason that this is
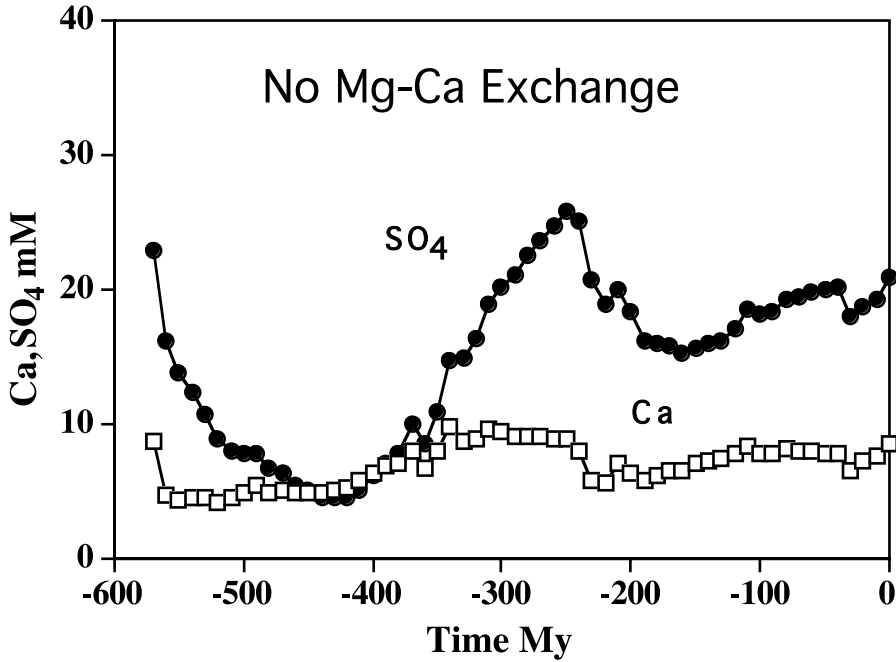
Fig. 3. Model-derived plots of dissolved Ca and SO_4 considering only the weathering and burial of pyrite and calcium sulfates and ignoring changes in dissolved Ca as a result of exchange with Mg during basalt-seawater reaction or dolomitization.
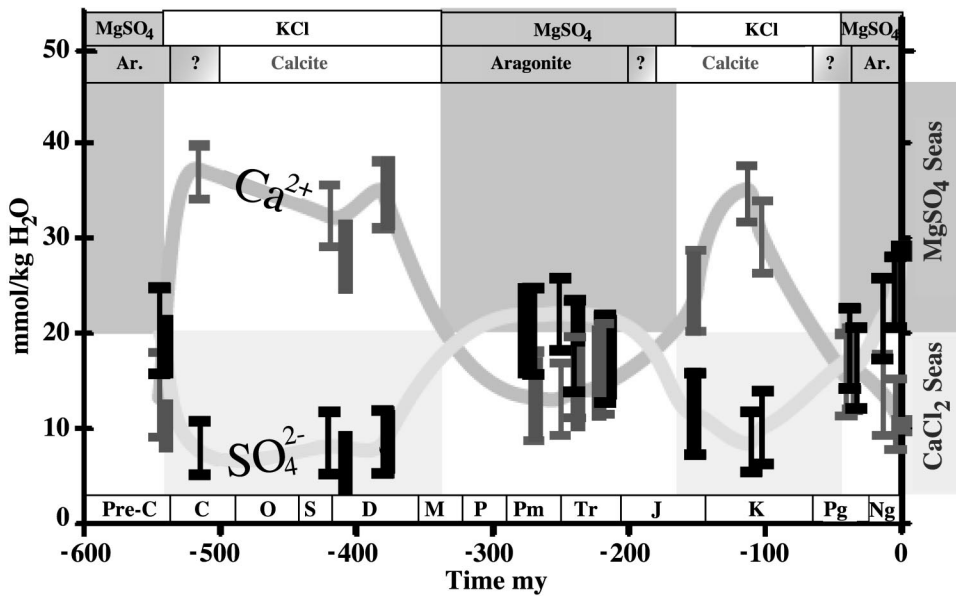

Fig. 4. Plots of dissolved Ca and SO_4 as determined by the analysis of fluid inclusions in halite. Black bars are SO_4^{2-} data, gray bars are Ca^{2+} data. The wider vertical bars represent the data of Horita and others (2002); all other data are from Lowenstein and others (2003). Predominant carbonate and bittern minerals shown at top. (Modified from Lowenstein and others, 2003).

necessarily true. Figure 1 shows that, based on the present modeling, the product could have varied by up to a factor of six over the Phanerozoic. Nevertheless, the concentrations of Ca and SO_4 obtained by Horita and others and Lowenstein and others, are in reasonable agreement with those from the modeling of the present paper. This can be seen by comparing figure 4 with the complete model shown in figure 2. (Ranges of concentration at any specific time in figure 4 are derived from variation of the product of Ca and SO_4 concentration by $\pm$ 50 percent from the present value of 300 mM^2.) Much more significant than the actual values for the individual concentrations of Ca and SO_4 is the good agreement, between the fluid inclusion studies and the modeling results, for the *timing and extent of crossovers.* It is the difference between concentrations that is firmly established by the fluid inclusion measurements and the ability to reasonably match the values and times for these differences that gives some credence to the modeling.

A factor of major importance to the history of seawater is changes in the ratio of Mg to Ca. The modeling results of the present paper are shown in figure 5. The results compare well with data based on halite fluid inclusions, shown in figure 6 (Lowenstein and others, 2001; Horita and others, 2002). High Mg/Ca ratios (greater than 2) correlate with periods when shallow water carbonate deposition was dominated by aragonite and high Mg-calcite and low ratios (less than 2) with calcite deposition. This is an expected consequence of what is known about the precipitation of these minerals (Sandberg, 1983; Stanley and Hardie, 1998) and agreement of the modeling with the independent observations gives further credence to the modeling.

The rise of Mg/Ca over the past 100 million years (fig. 5) is due to both a rise in Mg concentration and a drop in Ca concentration. This is in contrast to the opposite changes in Mg and Ca calculated by the earlier BLAG model (Berner and others, 1983). Differences between the two studies are mainly due to very different, parameterizations of weathering. Weathering in the present paper is based on coupling with
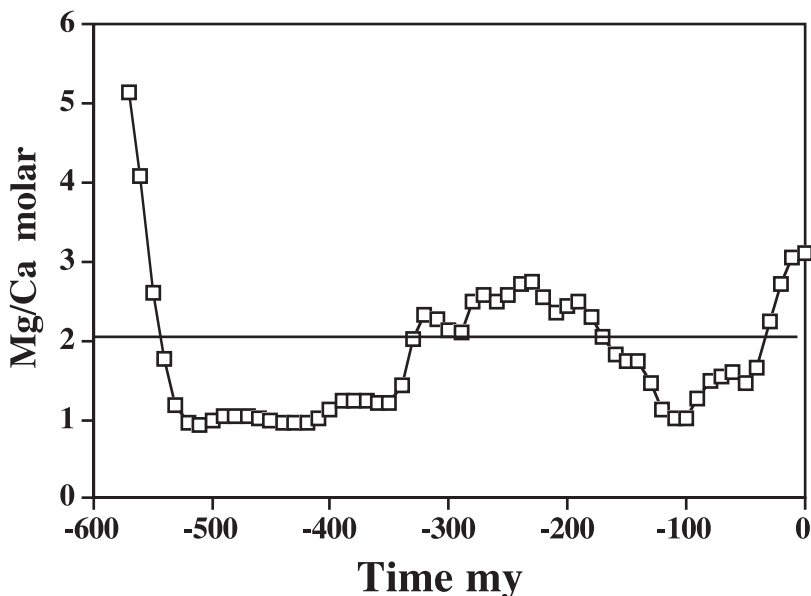

Fig. 5. Plot of the ratio Mg/Ca in seawater over Phanerozoic time as determined by the modeling of the present paper.
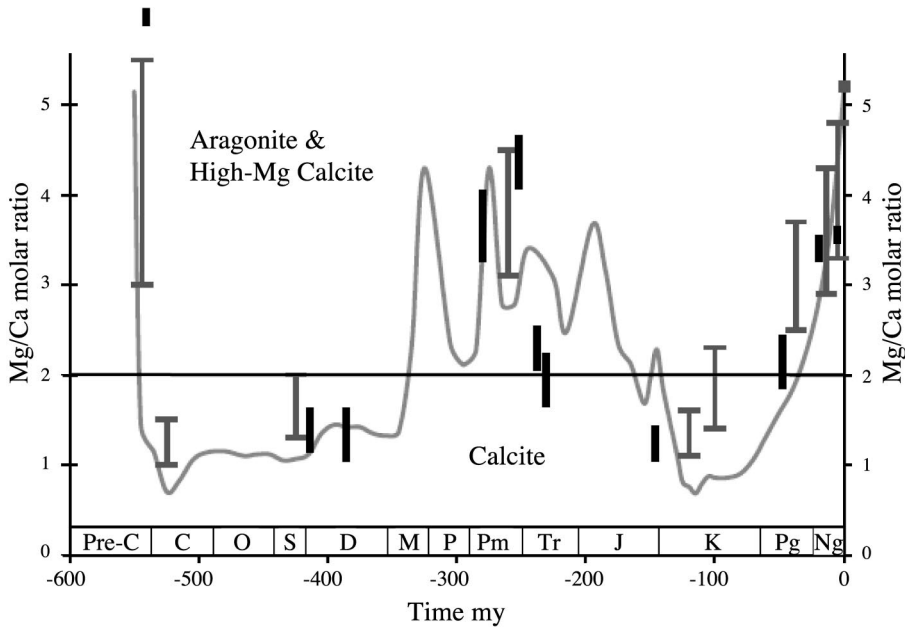
Fig. 6. Plot of Mg/Ca in seawater as determined by the analysis of fluid inclusions in halite. Black vertical bars represent data of Horita and others (2002); all other data (in gray) from Lowenstein (2001). The gray line represents model calculations by Hardie (1996). (Modified from Lowenstein and others, 2001).

models of the carbon and sulfur cycles whereas in the BLAG paper weathering follows a series of modifying factors which have subsequently been found to be inaccurate and/or incomplete.

The rate of exchange of Mg for Ca in the modeling, as a result of either basalt-seawater reaction or the dolomitization of carbonate sediments, is assumed to track changes in sea level. In the basalt-seawater reaction scenario sea level is used as an indicator of the relative rate of seafloor area creation (Gaffin, 1987) (spreading rate) with faster seafloor area creation meaning more exposure of basalt to reaction with seawater per unit time (Hardie, 1996). If the recent calculations of Rowley (2002) are correct, seafloor spreading rate has *not* changed over time and, thus, exchange rates of Mg uptake by basalt-seawater reaction have not changed with time. For varying oceanic Mg/Ca this means that changes in Mg concentration must occur only via changes in rates of dolomitization (Holland, unpublished ms) and not by changes in rates of basalt-seawater reaction. The use of sea level as a guide to spreading rate may instead be used as a guide to the abundance of shallow seas where dolomitization is favored (Holland, unpublished ms). However, new comprehensive data on seafloor area creation and subduction rate for the past 150 million years (Gaina and others, 2003) is in serious disagreement with the conclusions of Rowley. Thus, the principal process of Mg removal from seawater is still to be determined. The model of the present paper attempts to avoid the controversy of which Mg removal mechanism dominates by using the Gaffin (1987) formulation for seafloor spreading rates that are tied to changes in sea level.

Plots of the weathering and burial of pyrite and calcium sulfate versus time are shown in figures 7 and 8. Results show that the early Paleozoic (550-400 Ma) was a time of high rates of pyrite formation and low rates of $CaSO_4$ formation with the opposite

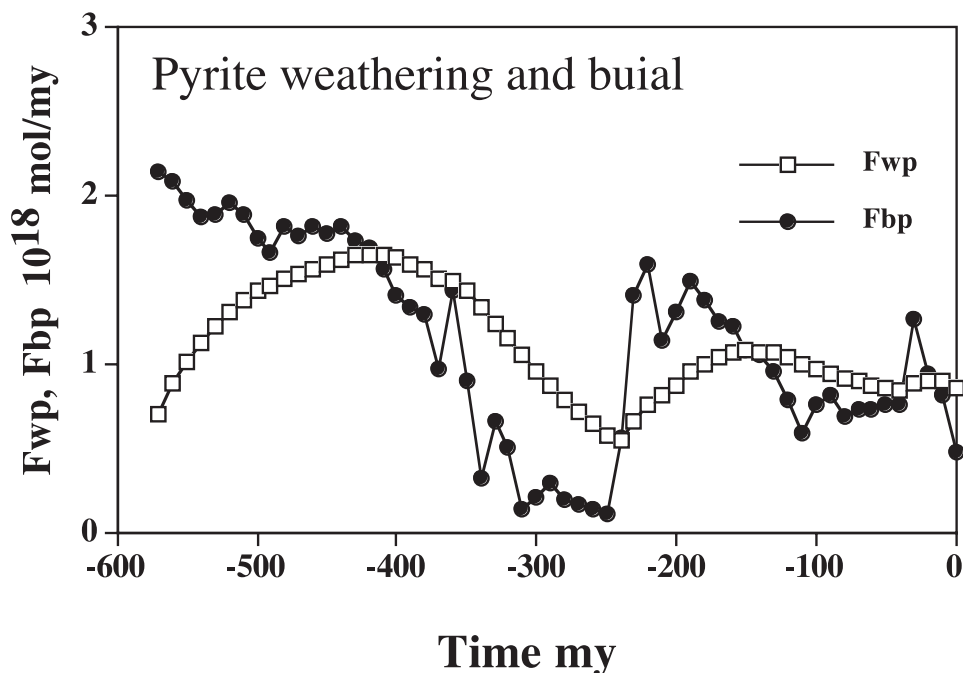Fig. 7. Plots of the weathering (Fwp) and burial (Fbp) fluxes for pyrite (FeS$_2$) over Phanerozoic time calculated by the model of the present paper.

situation occurring in the late Paleozoic ($\approx$300 Ma). These results have been noted elsewhere (for example, Berner and Raiswell, 1983; Garrels and Lerman, 1984). The new thing here is that the weathering of pyrite and calcium sulfate closely track their deposition with a lag of about 50 million years. This is a consequence of the introduction of rapid recycling (Berner, 2001) to the modeling. Excessive deposition of a substance is followed by excessive weathering of the same material after exposure due to uplift or recession of the seas. This process provides stabilization via negative feedback. By including variations in the inputs from pyrite and CaSO$_4$ weathering, the present modeling is distinguished from that of Hardie (1996).

CONCLUSIONS

Good agreement is found between the results of the present model and measurements of halite fluid inclusions for the variations of Ca, and SO$_4$ over the Phanerozoic. This is especially true of the timing when Ca was more abundant than SO$_4$ and vice versa. The two approaches are also in agreement for the evolution of the Mg/Ca ratio of seawater. The major processes driving variations in the abundance of Ca, Mg and SO$_4$ are variations in rates of CaSO$_4$ versus pyrite burial and weathering, and rates of exchange of Mg for Ca via either basalt seawater reaction or dolomitization.

Although the results of modeling agree well with those from the study of halite fluid inclusions, the modeling is still conceptually unsatisfactory in that the rate law for calcium sulfate precipitation and burial is not geologically realistic. Areally extensive gypsum and anhydrite formation requires the concatenation of two apparently independent phenomena: an arid climate with high evaporation rates, and locally restricted ocean circulation due to the trapping of a body of water within a silled basin. Future models need to take this observation into account quantitatively. Also, non-equivalent
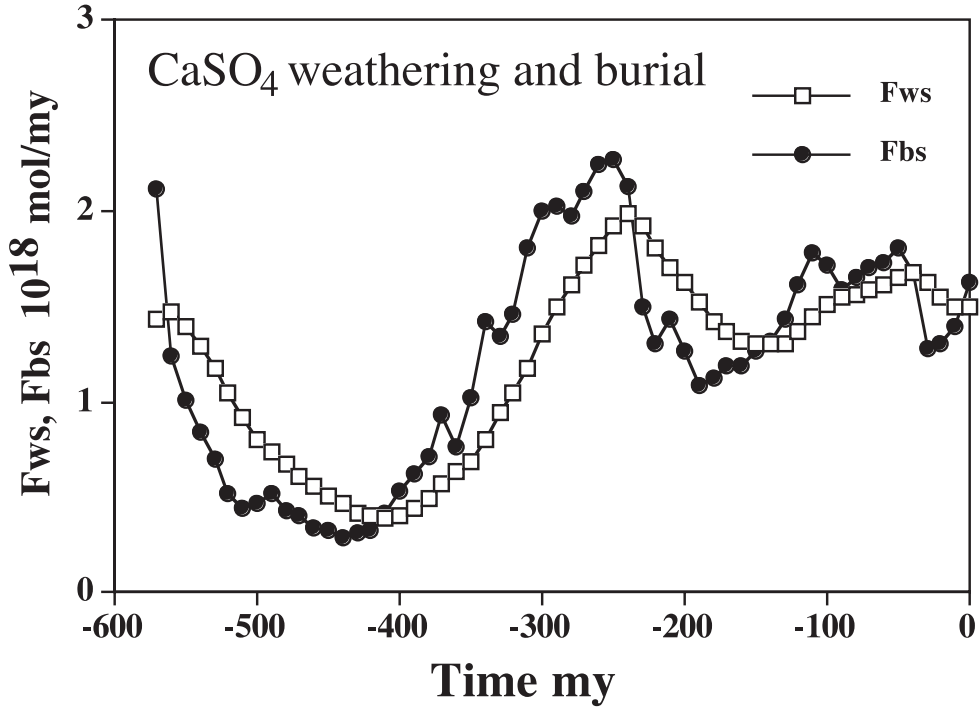
Fig. 8. Plots of the weathering (Fws) and burial (Fbs) fluxes of calcium sulfate over Phanerozoic time calculated by the model of the present paper.

concentrations of Ca and SO_4 in seawater were likely in the past. This means that upon evaporation and precipitation, the near exhaustion of one ion or the other would limit $CaSO_4$ formation. Nevertheless, additional calculations show that, if only the mass in seawater of the lesser ion is used in the expression for precipitation rather than the product of Ca and SO_4 (equation 4), results turn out to be similar to those reported here.

APPENDIX A

Mass Balances In a Sulfur-free System

The appropriate mass balance equations for the weathering of Ca and Mg carbonates and silicates only by carbonic acid, when combined with the burial of $CaCO_3$ and the exchange of Mg for Ca, from the reactions of table 1 are:

$$d[Ca]/dt = F_{wmCa} + F_{exch} - F_{bCa} \qquad (A-1)$$

$$d[HCO_3]/dt = 2F_{wmCa} + 2F_{wmMg} - 2F_{bCa} \qquad (A-2)$$

$$d[Mg]/dt = F_{wmMg} - F_{exch} \qquad (A-3)$$

where: [Ca], [HCO_3], [Mg] represents the mass of each element in seawater

F_{wmCa} = the weathering flux of Ca from carbonates and silicates
F_{wmMg} = the weathering flux of Mg from carbonates and silicates
F_{exh} = the mole-for-mole exchange of Mg for Ca via basalt-seawater reaction or dolomitization
F_{bCa} = burial of $CaCO_3$
t = time

Since carbon in seawater is essentially at steady state, $d(HCO_3)/dt = 0$. Thus:

$$F_{bCa} = F_{wmCa} + F_{wmMg} \tag{A-4}$$

Substituting (A-4) in (A-1):

$$d[Ca]\}/dt = F_{exch} - F_{wmMg} = -d[Mg]/dt \tag{A-5}$$

This shows that, for weathering solely by H_2CO_3 the input flux of Ca from weathering can be ignored and that change with time of the concentration of Ca in seawater is the inverse of that for Mg.

<center>APPENDIX B</center>

<center>*Equilibrium Considerations*</center>

Additional calculation is presented here to illustrate that changes in the calcium concentration of seawater over geologic time are due mainly to processes other than those involving the carbon cycle. If excess Ca accumulates in the ocean it is because inputs > outputs. This means that HCO_3^- and/or SO_4^- also accumulates. But HCO_3^- cannot accumulate because of $CaCO_3$ precipitation: Over time and as a first approximation, the oceans cannot be far from equilibrium with $CaCO_3$ and atmospheric CO_2. Therefore, for the reaction:

$$CO_2 + H_2O + CaCO_3 \leftrightarrow Ca^{++} + 2HCO_3^-$$

at equilibrium we have:

$$M_{Ca}M_{HCO_3^2}/M_{CO_2} = K \tag{B-1}$$

where M refers to masses in moles in each reservoir. One can rearrange this to:

$$M_{HCO_3} = [KM_{CO_2}/M_{Ca}]^{1/2} \tag{B-2}$$

For two different times (present = 0 and past = t):

$$R_{HCO_3} = [R_{CO_2}/R_{Ca}]^{1/2} \tag{B-3}$$

where R = M(t)/M(0).

For a maximum Phanerozoic oceanic Ca concentration of about 30 mM or R_{Ca} = 3 (from Horita and others, 2002; Lowenstein and others, 2003) and a maximum R_{CO_2} of about 25 (Berner and Kothavala, 2001), from equation (B-3) one obtains a maximum Phanerozoic R_{HCO_3} value of about 3, which means a HCO_3^- concentration of 3 × 2 mM (the present value) = 6 mM. From this, the change from the present HCO_3 concentration is 6 − 2 = 4 mM. The corresponding change in Ca is 30 − 10 (the present value) = 20 mM. This much larger value indicates that most of the change in Ca concentration over time is NOT due to imbalances in the carbon cycle resulting in changes in HCO_3^-.

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