

Geochemical Balance of Ca and Mg during Sedimentation. Part 1. Balance of Fluxes in the Geochemical Cycle of Ca, Mg, and CO₂

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This paper is dedicated to the memory of my friend
and colleague Areg Artashesovich Migdisov

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INTRODUCTION

Data on the carbonate abundance in the Earth's sedimentary shell and, respectively, the average composition of the latter [1, 2] indicate an excess of Ca, i.e., its amount in magmatic rocks feeding the sedimentary process is significantly lower than that in the average composition of sedimentary rocks. Moreover, a strange carbonate deficiency was noted in Precambrian metasediments [2]. These observations were independently confirmed by many geologists (table) and leave no doubts, unambiguously indicating that Ca and CO₂ fluxes in the surface geochemical cycle are poorly studied and require explanation. Various concepts considered in the literature (evolution of the CO₂ content in the atmosphere by Daly [3], Vinogradov [4], and Ronov [5]; changes in the facies conditions of carbonate deposition by Cameron [6]; influence of metamorphism on Ca mobility by Yaroshevsky [7], and others) were not confirmed by independent observations and provoke doubt.

Another aspect in the problem of Ca balance in the sedimentary shell is related to Mg involvement in carbonate accumulation. According to the available data, dolomites predominated among sedimentary carbonates up to the Early Mesozoic and disappeared as the principle component of the sedimentary shell in the Jurassic (Fig. 1) [3, 8]. These data were supplemented by facts of secondary dolomite formation in modern environments during dolomitization (for example, [9]) and a seemingly unbalanced Mg content in the modern ocean [10]. The hypotheses of the dependence of dolomite formation on CO₂ pressure in the atmosphere by Ronov [5] and Veizer [11] and a significant role of secondary dolomitization in Lower Phanerozoic deposits by Strakhov [12] or Friedman and Sanders [13] have not been confirmed by independent evidence and have been the subject of much controversy. Only the involvement of marine waters in hydrothermal circulation with Mg consumption by basaltic material of oceanic crust

[14, 15] could explain Mg imbalance in seawater. However, it remains uncertain as to what extent this consumption resolves the problem and whether this process was efficient in the past.

Relative abundance of major types of sedimentary rocks (after Ronov, Yaroshevskii, and Migdisov, 1990 [2])

Clays and shales	Sands and sandstones	Carbonates and salts	Reference
<i>Mass-balance calculations</i>			
82	12	6	Mead, 1907
80	15	5	Clarke, 1924
	91	9	Goldschmidt, 1933
79.6	11.9	8.5	Engelhardt, 1936
70	16	14	Holms, 1937
83	8	9	Wickman, 1954
	95	5	Goldberg and Arrhenius, 1958
83	10	7	Brotzen, 1966
73	20	7	Horn, 1966
81	11	8	Garrels and Mackenzie, 1971
56	24	19	Sibley and Wilband, 1977
<i>Direct measurements</i>			
46	32	22	Leith and Mead, 1915
44	37	19	Schuchert, 1931
56	14	29	Kuenen, 1941
42	40	18	Krynin, 1948
60	20	20	Ronov, 1948
60	15	25	Poldervaart, 1955
52	25	23	Ronov and Yaroshevsky, 1967
49	23	28	Ronov and Yaroshevsky, 1976
52	28	20	Ronov and Yaroshevsky, 1990

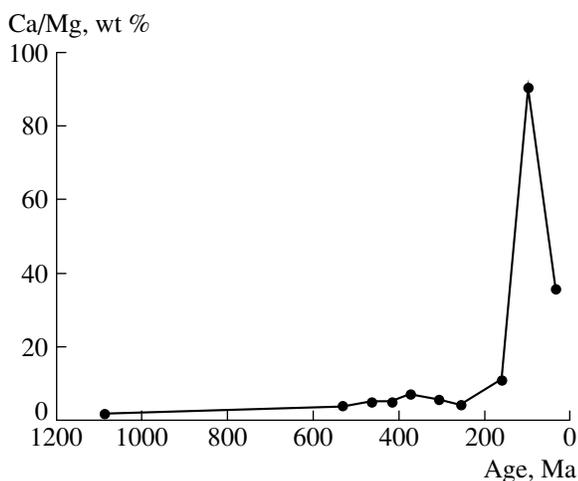


Fig. 1. Evolution of the Ca/Mg ratio in the carbonates of the Russian platform depending on their age, based on the data of Vinogradov and Ronov (1956) [8].

It is clear that the mass and composition of sedimentary rocks accumulating per time unit (sedimentation rate) are quantitatively determined by the total flux of feeding material and the abundance of chemical elements in it. Ca and Mg are supplied mainly by decomposed continental rocks. It is also clear that the formation of Ca and Mg carbonates consumes CO_2 from a source independent of continental rocks. According to Goldschmidt [16], CO_2 belongs to excess volatiles, which are considered to originate from deep-seated material in the Earth during its degassing. Therefore, in order to interpret the observed geochemical balance (rather, imbalance) of Ca and Mg and its possible evolution in the geological history of sedimentary shell, it is important to decipher the composition of fluxes of these elements. Our model is based on the following empirical geological principles.

First, the values of the Ca and Mg fluxes during sedimentation depend on the denudation rate and the average composition of surface continental rocks, while the value of juvenile CO_2 flux is determined by the degassing of the Earth's interiors. This indicates that these processes are independent and controlled by different geological factors. Hence, the Ca and Mg fluxes should not be correlated, and, moreover, quantitatively balanced with juvenile CO_2 flux.

Second, Ca silicates and aluminosilicates are unstable in sedimentation environments. The major stable phase of Ca during the entire geological evolution of the sedimentary shell is carbonate (CaCO_3). In other words, CO_2 pressure in the Earth's atmosphere and the corresponding content of dissolved CO_2 in the hydrosphere during carbonatization were higher than those in equilibrium Ca silicates and aluminosilicates.

Third, unlike Ca minerals, both Ca–Mg carbonates [MgCO_3 , more precisely, $\text{CaMg}(\text{CO}_3)_2$] and silicates

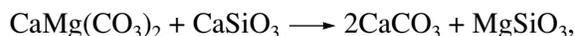
(hydrosilicates, more specifically, clay minerals) are stable during sedimentation. These observations are of principle significance for understanding the geochemical balance during the formation of carbonates, because they indicate that the CO_2 pressure in the atmosphere during the geological history of the sedimentary shell could not significantly deviate from that in equilibrium with Mg silicates (hydrosilicates) during carbonatization and must be close to the modern values. Any possible deviations of pressure (either its increase or decrease) should relax with a rate defined by the geological kinetics of weathering–sedimentation reactions, which, unfortunately is unstudied as of yet (for example, [17]), making it impossible to evaluate the scales of such deviations accurately enough. It is generally accepted that the kinetic restrictions of chemical reactions of continental weathering and mineral precipitation do not prevent the attainment of a local equilibrium, at least, on the scales of geological processes: supposedly hundreds of thousands of years to a few million years.

It is pertinent to mention that the equilibrium between Mg carbonate and silicates (hydrosilicates) exerts a buffering effect on the CO_2 pressure in the atmosphere [18], since the concepts of possible significant variations in the CO_2 concentrations in the atmosphere, up to formation of “hydrocarbonic” atmosphere in the Precambrian, are widely accepted in geology. There were many attempts to evaluate these amounts based on the assumption that the mass of carbonate in sedimentary rocks is functionally related to the mass of CO_2 in biospheric exchange reservoirs (for example, [19–21]). This approach to the problem of CO_2 evolution in the atmosphere is principally misleading, because the amount of CO_2 consumed during carbonate accumulation is determined by its degassing flow from the interior rather than by the resource of this gas in exchange reservoirs.

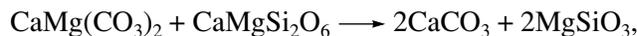
In order to understand the geochemical balance of Ca and Mg and their modes of occurrences (proportions of carbonates and silicates) in the sedimentary shell, it is important to consider another aspect of the stability of Mg carbonates and hydrosilicates. Indeed, mineral equilibria with Ca and Mg in sedimentary rocks can be written in a simplified form, for example:



$$\Delta G^0 = -8.26 \text{ kcal mol},$$



$$\Delta G^0 = -5.56 \text{ kcal mol},$$



$$\Delta G^0 = -2.15 \text{ kcal mol},$$



$$\Delta G^0 = -4.67 \text{ kcal mol}.$$

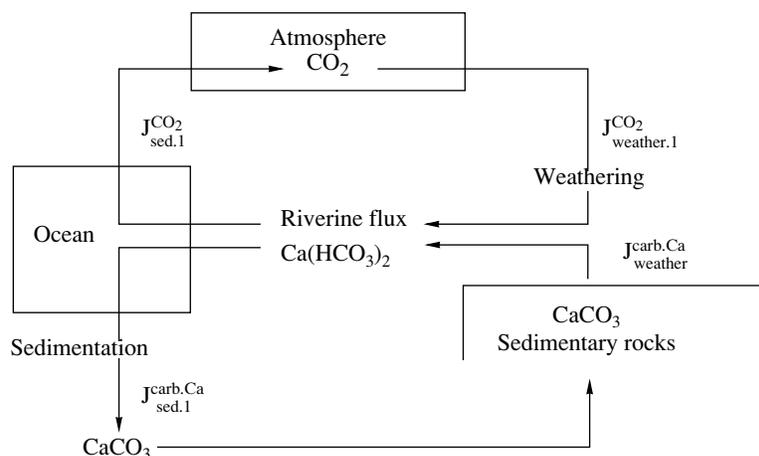


Fig. 2. Scheme of the first cycle of Ca: the cycling of Ca carbonate. Indices of fluxes are explained in text.

Empirical data show that the quantitative proportions of the masses and fluxes of Ca, Mg, and CO_2 in the biosphere caused the shift of the reaction to the right, which led to the exhaustion of Ca silicates and to the stability of the assemblage of Mg silicates and Ca and Mg carbonates. The CO_2 atmospheric pressure is buffered by this assemblage owing to variations in the amounts of Mg carbonates and silicates: an increase in CO_2 flux in the atmosphere, for example, owing to interior degassing, causes the transformation of Mg silicates into carbonates, while a decrease induces a shift of the reaction toward silicate formation. Geological observations indicate that this flux compensated by Mg decarbonatization has never been lower than that required for the complete transformation of Ca silicates into carbonates and has never reached values at which Mg hydrosilicates become unstable. These buffering properties of the mineral assemblage of Ca–Mg carbonates and Mg silicates and resulting balance proportions serve as the basis to quantify the geological evolution of sedimentation and degassing of the Earth's interiors.

GEOCHEMICAL CYLCE OF Ca

The first cycle of Ca is the cycle of Ca carbonate. The surface cycling of Ca carbonate includes the following reactions and processes (Fig. 2).

(1) Dissolution of Ca carbonate in ancient sedimentary rocks during weathering and the formation of easily soluble bicarbonate (main modes of occurrence of dissolved Ca in the riverine flux) by the reaction

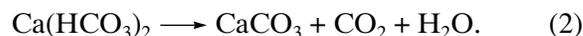


The value of the dissolved Ca flux ($J_{\text{weather}}^{\text{carb.Ca}}$) is determined by the rate of chemical weathering during the denudation of surface continental rocks and the abundance of Ca carbonate in them; the partial flux of Ca carbonate in sedimentation basins in the form of partic-

ulate matter owing to incomplete dissolution is not involved in the balance system, but reflects only the mechanical redistribution of Ca from the denudation to the sedimentation zone.

(2) The rate of chemical weathering of Ca carbonate unambiguously defines the value of the CO_2 flux consumed from the atmosphere according to reaction (1); in equivalent units (each 40 g of Ca coming into the chemical weathering zone consume 44 g of CO_2 from the atmosphere), $J_{\text{weather.1}}^{\text{CO}_2} = J_{\text{weather}}^{\text{carb.Ca}}$.

(3) The deposition of Ca carbonate in sedimentation basins accompanied by the decomposition of bicarbonate and the return of CO_2 consumed during weathering according to the reaction (reaction of “reverse weathering”) in the atmosphere by the reaction



The value of the precipitation flux of Ca carbonate ($J_{\text{sed.1}}^{\text{carb.Ca}}$) is determined by the rate of the continental sink of Ca bicarbonate. Since Ca is not accumulated in route to the hydrosphere owing to seawater saturation with respect to Ca carbonate, this value should be equal to the weathering flux ($J_{\text{sed.1}}^{\text{carb.Ca}} = J_{\text{weather}}^{\text{carb.Ca}}$).

(4) The rate of Ca carbonate precipitation unambiguously defines the value of the reverse CO_2 flux from the hydrosphere (sedimentation basins) into the atmosphere, which should accordingly be strictly equal to the rate of CO_2 consumption during weathering ($J_{\text{sed.1}}^{\text{CO}_2} = J_{\text{weather.1}}^{\text{CO}_2}$). There are no grounds for anticipating the disturbance of either this balance or the steady state of the first Ca cycle.

The participation of water in weathering and precipitation reactions does not limit the Ca and CO_2 fluxes, because of the giant water resource in the hydrosphere and a high rate of its surface cycling (H_2O flux con-

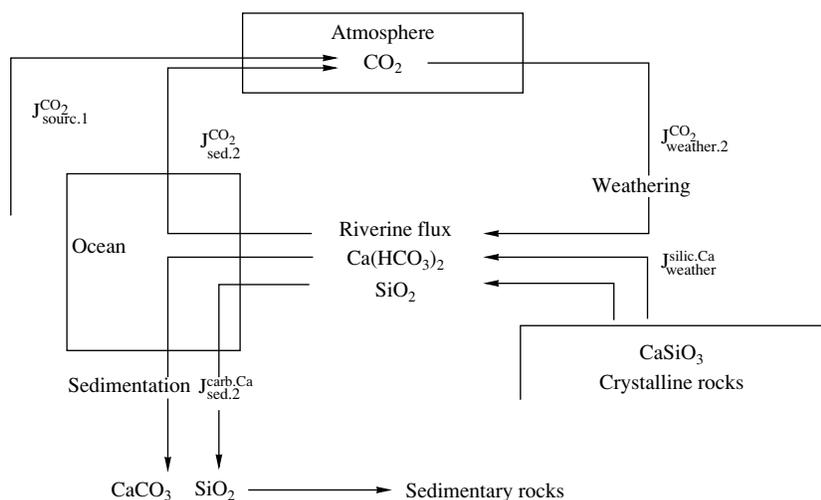
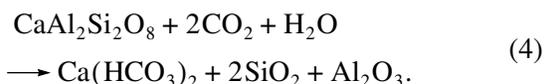


Fig. 3. Scheme of the second cycle of Ca: the weathering of silicates and aluminosilicates and the precipitation of newly formed Ca carbonate. Indices of fluxes are explained in text.

sumed by weathering accounts for only a small fraction of the atmospheric hydrological cycle).

The second cycle of Ca is the weathering of silicates and aluminosilicates and the precipitation of a newly formed Ca carbonate. This cycle includes the following reactions and processes (Fig. 3).

(1) The carbonatization of Ca silicates and aluminosilicates in crystalline (magmatic and metamorphic) rocks during weathering with the formation of a readily soluble Ca bicarbonate



The value of the dissolved Ca flux ($J_{\text{weather}}^{\text{silic.Ca}}$) is determined, as in the first Ca cycle, by the chemical weathering rate of continents and the abundance of Ca silicates and aluminosilicates in them.

(2) The rate of chemical weathering of Ca silicates and aluminosilicates uniquely determines the flux of CO_2 , which is consumed from the atmosphere according to reactions (3) and (4); in equivalent units, $J_{\text{weather.2}}^{\text{CO}_2} = 2 J_{\text{weather}}^{\text{silic.Ca}}$.

(3) The deposition of Ca carbonate in sedimentation basins, which is accompanied by the decomposition of bicarbonates and the return of CO_2 consumed during weathering to the atmosphere according to reaction (2). The precipitation flux value of newly formed Ca carbonate ($J_{\text{sed.2}}^{\text{carb.Ca}}$) depends on the rate of the newly formed Ca bicarbonate flux from continents and should be equal to the Ca silicate weathering flux ($J_{\text{sed.2}}^{\text{carb.Ca}} = J_{\text{weather}}^{\text{silic.Ca}}$).

(4) The precipitation rate of newly formed Ca carbonate directly defines the value of reverse CO_2 flux from the hydrosphere into the atmosphere, which should be, accordingly, strictly equal to half of the CO_2 amount consumed during the weathering of silicates and aluminosilicates ($J_{\text{sed.2}}^{\text{CO}_2} = 0.5 J_{\text{weather.2}}^{\text{CO}_2}$), since the other half is incorporated in sedimentary rocks with newly formed CO_2 . To maintain a CO_2 balance in exchange reservoirs (hydrosphere and atmosphere), it is important to compensate CO_2 by an ingress from additional source. The evident additional source could be juvenile CO_2 flux or, as will be shown below, CO_2 redistribution between the cycles of Ca and Mg. To preserve the balance, this additional flux (source) of CO_2 , designated here as $J_{\text{sourc.1}}^{\text{CO}_2}$ (Fig. 2), should be equal to $0.5 J_{\text{weather.2}}^{\text{CO}_2}$.

The scheme of the overall (total) surface cycle of Ca is shown in Fig. 4. Symbols in this figure are the same as in Fig. 1 and 2, with the exception of a combination of the same fluxes:

$$J_{\text{weather.Ca}}^{\text{CO}_2} = J_{\text{weather.1}}^{\text{CO}_2} + J_{\text{weather.2}}^{\text{CO}_2};$$

$$J_{\text{sed.Ca}}^{\text{CO}_2} = J_{\text{sed.1}}^{\text{CO}_2} + J_{\text{sed.2}}^{\text{CO}_2};$$

$$J_{\text{sed.}}^{\text{carb.Ca}} = J_{\text{sed.1}}^{\text{carb.Ca}} + J_{\text{sed.2}}^{\text{carb.Ca}}.$$

The mass balance condition requires equality between the precipitation fluxes of Ca carbonates and the total of the weathering fluxes of Ca carbonates and silicates, which serves as the boundary condition for the total rate of the surface Ca cycle.

$$J_{\text{sed.}}^{\text{carb.Ca}} = J_{\text{weather.}}^{\text{carb.Ca}} + J_{\text{weather.}}^{\text{silic.Ca}},$$

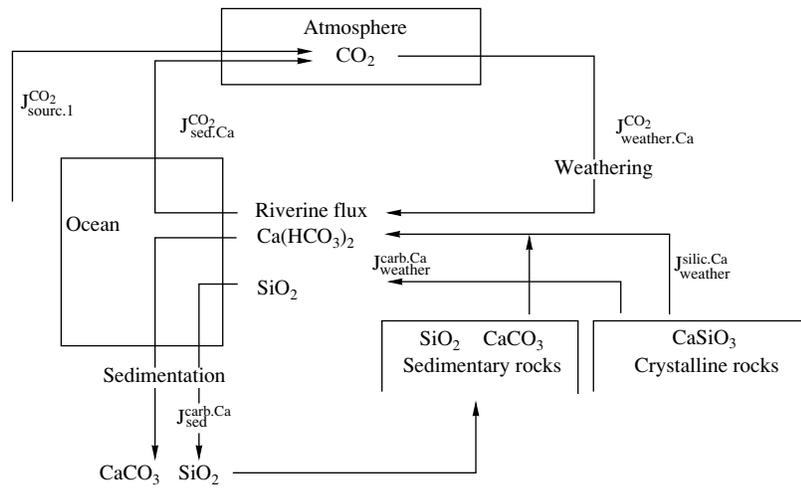


Fig. 4. Scheme of combined (integral) surface Ca cycling. Indices of fluxes are explained in text.

and equality between the consumption flux and the total atmospheric flux of CO_2 during weathering

$$J_{\text{weather.Ca}}^{\text{CO}_2} = J_{\text{sed.Ca}}^{\text{CO}_2} + J_{\text{sourc.1}}^{\text{CO}_2};$$

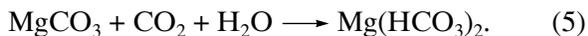
with

$$J_{\text{sourc.1}}^{\text{CO}_2} = J_{\text{weather}}^{\text{silic.Ca}}.$$

GEOCHEMICAL CYCLES OF Mg

The first cycle of Mg is the cycling of Mg carbonate and silicates in sedimentary rocks. The surface cycling of Mg carbonate and hydrosilicates involves the following reactions and processes (Fig. 5).

(1) Dissolution of Mg carbonate from ancient sedimentary rocks during weathering with the formation of highly soluble bicarbonate (the major mode of occurrence of Mg dissolved in the riverine flux) by the reaction



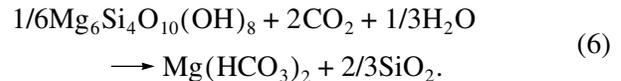
The value of the dissolved Mg flux ($J_{\text{weather}}^{\text{carb.Mg}}$) is determined by the rate of chemical weathering during the denudation of the continental surface rocks and by the abundance of Mg carbonate in them; the partial sink of Mg carbonate (dolomite) in the form of particulate matter in the sedimentation basin owing to incomplete dissolution is not considered in the balance system because it reflects only the mechanical redistribution from the denudation into the sedimentation zone.

(2) The rate of chemical weathering of Mg carbonate directly controls the value of the CO_2 flux consumed from the atmosphere according to reaction (5);

in equivalent units, $J_{\text{weather.3}}^{\text{CO}_2} = J_{\text{weather}}^{\text{carb.Mg}}$.

(3) Dissolution of Mg hydrosilicates in ancient sedimentary rocks during weathering, with the formation

of readily soluble Mg bicarbonate by the reaction (Mg hydrosilicate is exemplified by chlorite)



The value of the dissolved Mg flux ($J_{\text{weather.1}}^{\text{silic.Mg}}$) is determined by the rate of chemical weathering during the denudation of continental surface rocks and by the abundance of Mg hydrosilicates in them.

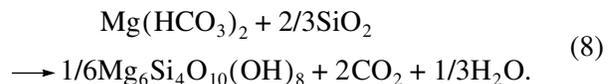
(4) The rate of chemical weathering of Mg hydrosilicates unambiguously determines the value of the CO_2 flux consumed from the atmosphere according to reaction (6); in equivalent units, $J_{\text{weather.4}}^{\text{CO}_2} = 2 J_{\text{weather.1}}^{\text{silic.Mg}}$.

(5) Deposition of Mg carbonate in sedimentation basins associated with the decomposition of bicarbonate and the return of CO_2 consumed during weathering to the atmosphere following the "reverse weathering" reaction



(6) The precipitation rate of Mg carbonate defines part of the reverse CO_2 flux from the hydrosphere to the atmosphere ($J_{\text{sed.3}}^{\text{CO}_2}$), which equals, in equivalent amounts in accordance to the stoichiometry of reaction (7), the value of the Mg carbonate flux ($J_{\text{sed.1}}^{\text{carb.Mg}}$).

(7) Deposition of Mg hydrosilicates in sedimentation basin associated with the decomposition of dissolved bicarbonate and interaction with dissolved (and, perhaps, also particulate) silica according to the reaction



(8) The precipitation rate of Mg hydrosilicate defines part of the reverse CO_2 flux from the hydro-

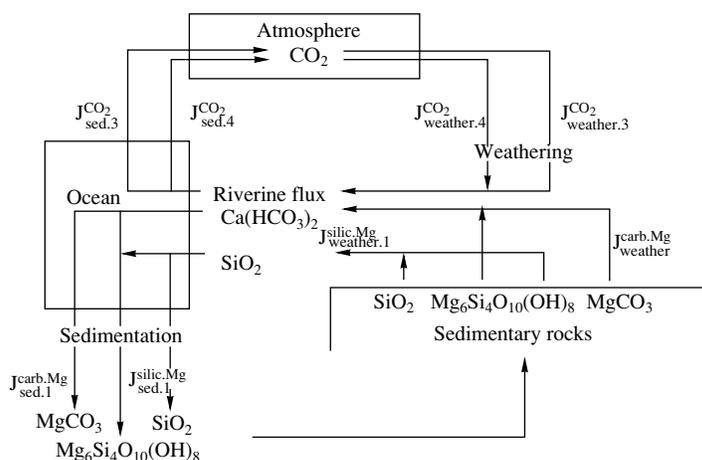


Fig. 5. Scheme of the first cycle of Mg: the cycling of Mg carbonate and hydrosilicates in sedimentary rocks. Indices of fluxes are explained in text.

sphere to atmosphere ($J^{\text{CO}_2}_{\text{sed.4}}$), which is, in equivalent amounts, twice as high as the value of the Mg hydrosilicate flux ($J^{\text{silic.Mg}}_{\text{sed.1}}$).

When a system is completely closed with respect to CO_2 cycling, a complete balance is kept,

$$J^{\text{carb.Mg}}_{\text{sed.1}} = J^{\text{carb.Mg}}_{\text{weather}}$$

$$J^{\text{silic.Mg}}_{\text{sed.1}} = J^{\text{silic.Mg}}_{\text{weather.1}}$$

$$J^{\text{CO}_2}_{\text{sed.3}} + J^{\text{CO}_2}_{\text{sed.4}} = J^{\text{CO}_2}_{\text{weather.3}} + J^{\text{CO}_2}_{\text{weather.4}},$$

and cycling is maintained in a steady state.

However, the “double” carbonate–silicate cycle of Mg has a feature that may be very important for a system open with respect to CO_2 . The appearance of additional fluxes (for example, CO_2 consumption during the weathering of Ca silicates and aluminosilicates) should cause an increase in the reverse CO_2 flux in the atmosphere owing to the additional precipitation of Mg hydrosilicate instead of carbonates, thus compensating the consumption of atmospheric CO_2 for the precipitation of newly formed Ca carbonate. An additional supply of, for example, juvenile CO_2 must cause a partial compensating transfer from the Mg hydrosilicate into carbonate fluxes. The possibility of compensating the external influence of the redistribution of Mg fluxes between carbonate and silicate constituents follows from the conditions of the thermodynamic stability of the assemblage of Ca and Mg carbonates and silicates and reflects the aforementioned buffering role of coexisting Mg carbonate (dolomite) and hydrosilicates (clay minerals) throughout the whole geological evolution of the sedimentary shell.

The second cycle of Mg involves the weathering of silicates and the precipitation of newly formed Mg car-

bonates and hydrosilicates. This cycle comprises of the following reactions and processes (Fig. 6).

(1) Carbonatization of Mg silicates in crystalline (magmatic and metamorphic) rocks during weathering with the formation of an easily soluble Mg bicarbonate

$$\text{MgSiO}_3 + 2\text{CO}_2 + \text{H}_2\text{O} \longrightarrow \text{Mg}(\text{HCO}_3)_2 + \text{SiO}_2. \quad (9)$$

The value of the dissolved Mg flux ($J^{\text{silic.Mg}}_{\text{weather.2}}$) is determined, like in the first cycle, by the rate of the chemical weathering of the continental surface and abundance of crystalline rocks bearing Mg silicates.

(2) The chemical weathering rate of Mg silicates unambiguously defines the value of the atmospheric CO_2 flux according to reaction (9); in equivalent units,

$$J^{\text{CO}_2}_{\text{weather.5}} = 2J^{\text{silic.Mg}}_{\text{weather.2}}.$$

(3) The deposition of Mg hydrosilicates in sedimentation basins according to reaction (8), which is accompanied by the decomposition of bicarbonate and the return of CO_2 consumed during weathering to the atmosphere; in the system closed with respect to CO_2 , the precipitation flux of newly formed Mg hydrosilicates ($J^{\text{silic.Mg}}_{\text{sed.2}}$) must be exactly equal to the weathering flux of Mg silicates ($J^{\text{silic.Mg}}_{\text{weather.2}}$).

(4) The precipitation rate of newly formed Mg hydrosilicates partly defines the reverse CO_2 flux from the hydrosphere into atmosphere ($J^{\text{CO}_2}_{\text{sed.5}}$), which is equal to doubled precipitation flux of newly formed Mg hydrosilicates.

However, as geological observations indicate that juvenile CO_2 was continuously supplied to and involved in surface cycling, part of the weathered Mg silicates in crystalline rocks can be transformed into carbonates. This process must be involved in the general scheme of fluxes of second Mg cycle.

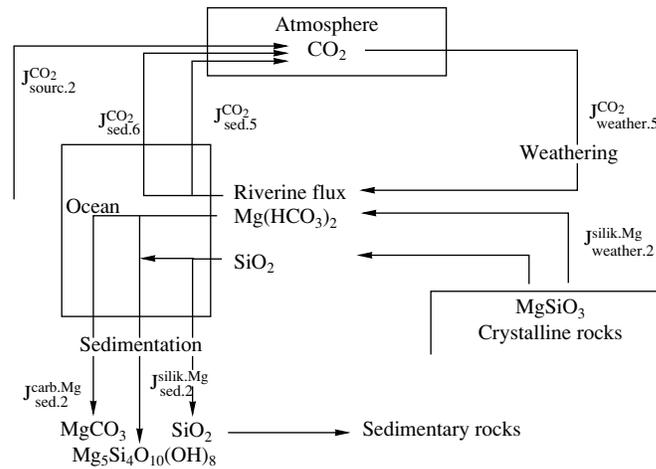


Fig. 6. Scheme of the second cycle of Mg: the weathering of silicates and the precipitation of newly formed Mg carbonate and hydrosilicates. Indices of fluxes are explained in text.

(5) The precipitation of newly formed Mg carbonate in sedimentation basins according to reaction (7), which is accompanied by the decomposition of bicarbonate and the partial return of CO₂ consumed during the weathering of silicates to the atmosphere ($J_{sed.6}^{CO_2}$). The value of the precipitation flux of newly formed Mg carbonate ($J_{sed.2}^{carb.Mg}$) is determined by the supply rate of the required amount of CO₂ from an external source ($J_{sourc.2}^{CO_2}$). Correspondingly, the precipitation flux of Mg carbonate increases by the value of this flux, in equivalent amounts; the precipitation flux of Mg hydrosilicates and the reverse CO₂ flux from the hydrosphere to the atmosphere by the same value.

A scheme of combined (total) surface cycling of Mg is shown in Fig. 7. Symbols in the figure are the same as in Figs. 4 and 5, with the exception of the combination of the same fluxes:

$$J_{weather.Mg}^{CO_2} = J_{weather.3}^{CO_2} + J_{weather.4}^{CO_2} + J_{weather.5}^{CO_2} ;$$

$$J_{sed.Mg}^{CO_2} = J_{sed.3}^{CO_2} + J_{sed.4}^{CO_2} + J_{sed.5}^{CO_2} + J_{sed.6}^{CO_2} ;$$

$$J_{sed}^{carb.Mg} = J_{sed.1}^{carb.Mg} + J_{sed.2}^{carb.Mg} ;$$

$$J_{sed}^{silic.Mg} = J_{sed.1}^{silic.Mg} + J_{sed.2}^{silic.Mg} .$$

The maintenance of a balance requires that the precipitation fluxes of Mg carbonates and hydrosilicates should be equal to the total of the weathering fluxes of Mg carbonate and hydrosilicates and Mg silicates in ancient crystalline rocks, which is the boundary conditions for the total rate of surface Mg cycling,

$$J_{sed}^{carb.Mg} + J_{sed}^{silic.Mg} = J_{weather}^{carb.Mg} + J_{weather.1}^{silic.Mg} + J_{weather.2}^{silic.Mg} ,$$

and that the CO₂ consumption flux during weathering should be equal to the total of CO₂ fluxes supplying the atmosphere

$$J_{weather.Mg}^{CO_2} = J_{sed.Mg}^{CO_2} + J_{sourc.2}^{CO_2} ;$$

at the same time,

$$J_{sourc.2}^{CO_2} = J_{sed.2}^{carb.Mg} .$$

An important feature of surface Ca and Mg cyclings, which is of principal significance for the scheme of balances considered in this publication, is their relation through CO₂ redistribution, which depends on the balance of two independent fluxes, the weathering rate, which determines the weathering fluxes of Ca and Mg and the degassing rate of CO₂. This relation predetermines the relative sedimentation rates of Ca and Mg carbonates and, respectively, the proportions of these elements in the precipitating sedimentary rocks. Variations in the values of the fluxes of weathering, on the one hand, and degassing, on the other hand, are geological factors that control the composition of carbonates during the geochemical evolution of the sedimentary shell.

SIMULTANEOUS CYCLING OF Ca AND Mg

The described scheme of the balances of Ca, Mg, and CO₂ fluxes makes it possible to construct a general scheme of fluxes, which can be represented as follows. Note that this scheme considers empirical geological observations, which indicate that the ratio between the rates of the chemical weathering of continental rocks and ingress of juvenile CO₂ during the evolution of the sedimentary shell provided conditions for the stability of only one Ca compound, carbonate (CaCO₃), incomplete Mg carbonatization, and the existence of two pre-

A balance system can also be written for CO₂ fluxes involved in the weathering and precipitation of Ca and Mg compounds.

The CO₂ bounding flux during weathering (indices of the fluxes are shown above) is as follows:

$$\begin{aligned} J_{\text{weather}}^{\text{CO}_2} &= J_{\text{weather.Ca}}^{\text{CO}_2} + J_{\text{weather.Mg}}^{\text{CO}_2} = J_{\text{weather.1}}^{\text{CO}_2} + J_{\text{weather.2}}^{\text{CO}_2} \\ &+ J_{\text{weather.3}}^{\text{CO}_2} + J_{\text{weather.4}}^{\text{CO}_2} + J_{\text{weather.5}}^{\text{CO}_2} \\ &= J_{\text{weather}}^{\text{Ccarb.Ca}} + 2 J_{\text{weather}}^{\text{silic.Ca}} + J_{\text{weather}}^{\text{carb.Mg}} + 2 J_{\text{weather}}^{\text{silic.Mg}} \end{aligned} \quad (18)$$

In other words, the rate of CO₂ consumption from biospheric exchange reservoirs (atmosphere and hydrosphere) is given by the denudation rate of continental sedimentary, magmatic, and metamorphic rocks and is the boundary conditions for the surface cycling of CO₂.¹

The CO₂ flux in exchange reservoirs consists of two components: the flux of juvenile CO₂ and the reverse flux of CO₂ from sedimentation basins owing to the decarbonatization of dissolved Ca and Mg:

$$\begin{aligned} J_{\text{juven}}^{\text{CO}_2} + J_{\text{sed}}^{\text{CO}_2} \\ = J_{\text{juven}}^{\text{CO}_2} + J_{\text{sed.Ca}}^{\text{CO}_2} + J_{\text{sed.carb.Mg}}^{\text{CO}_2} + J_{\text{sed.silic.Mg}}^{\text{CO}_2} \end{aligned}$$

With regard for the relations of the precipitation fluxes of Ca carbonate, Mg carbonate, and hydrosilicates to the corresponding weathering fluxes (Eqs. (10), (14), (15)), we obtain:

$$\begin{aligned} J_{\text{juven}}^{\text{CO}_2} + J_{\text{sed}}^{\text{CO}_2} &= J_{\text{juven}}^{\text{CO}_2} + J_{\text{weather}}^{\text{carb.Ca}} + J_{\text{weather}}^{\text{silic.Ca}} + J_{\text{weather}}^{\text{carb.Mg}} \\ + J_{\text{juven}}^{\text{CO}_2} - J_{\text{weather}}^{\text{silic.Ca}} &+ 2 J_{\text{weather}}^{\text{silic.Mg}} + 2 J_{\text{weather}}^{\text{silic.Ca}} - 2 J_{\text{juven}}^{\text{CO}_2} \\ &= J_{\text{weather}}^{\text{carb.Ca}} + J_{\text{weather}}^{\text{carb.Mg}} + 2 J_{\text{weather}}^{\text{silic.Mg}} + 2 J_{\text{weather}}^{\text{silic.Ca}} \end{aligned} \quad (19)$$

The right-hand side of Eqs. (18) and (19) are the same, implying a simple condition of CO₂ mass balance in the biospheric exchange reservoirs:

$$J_{\text{weather}}^{\text{CO}_2} = J_{\text{juven}}^{\text{CO}_2} + J_{\text{sed}}^{\text{CO}_2} \quad (20)$$

Equation (20) is the condition of a steady state of biospheric exchange reservoirs, which is evidently related to the steady state of the surface cycling of Ca and Mg.

¹ CO₂ cycling in the biosphere includes CO₂ consumption by living organisms during photosynthesis. It should be emphasized that, first, the biogeochemical cycling of C_{org} is geologically minute and is always (>99.5%) closed, and, second, the global CO₂ balance is contributed only by the flux of C_{org} buried in sedimentary rocks, but it is negligible (less than 0.5% of the primary production) and exerted almost no effect on the global balance of carbonate carbon.

Equations (10) and (14) can be used to obtain a relation that controls the composition (Ca/Mg ratio) of carbonates in the sedimentary shell:

$$\begin{aligned} J_{\text{sed}}^{\text{carb.Ca}} / J_{\text{sed}}^{\text{carb.Mg}} \\ = (J_{\text{weather}}^{\text{carb.Ca}} + J_{\text{weather}}^{\text{silic.Ca}}) / (J_{\text{weather}}^{\text{carb.Mg}} \\ + J_{\text{juven}}^{\text{CO}_2} - J_{\text{weather}}^{\text{silic.Ca}}) \end{aligned} \quad (21)$$

This equation demonstrates a simple relation between the Ca/Mg ratio in carbonates and the flux of juvenile CO₂: an increase in the latter leads to an increase in the denominator and, correspondingly, a decrease in the proportion of the limestone to dolomite abundances (decrease in Ca/Mg ratio), and, on the contrary, a decrease in the degassing rate of the Earth's interior leads to a decrease in dolomite abundance. This equation can be used to obtain the conditions of a constant Ca/Mg ratio in carbonates during sedimentation, i.e., a relation between weathering and degassing rates at which the Ca/Mg ratio in newly formed carbonates is similar to that in the weathered ancient carbonates:

$$\begin{aligned} J_{\text{sed}}^{\text{carb.Ca}} / J_{\text{sed}}^{\text{carb.Mg}} &= J_{\text{weather}}^{\text{carb.Ca}} / J_{\text{weather}}^{\text{carb.Mg}} \\ &= (J_{\text{weather}}^{\text{carb.Ca}} + J_{\text{weather}}^{\text{silic.Ca}}) / (J_{\text{weather}}^{\text{carb.Mg}} \\ &+ J_{\text{juven}}^{\text{CO}_2} - J_{\text{weather}}^{\text{silic.Ca}}) \end{aligned}$$

The solution of this equation with respect to J_{juven}^{CO₂} yields

$$J_{\text{juven}}^{\text{CO}_2} = J_{\text{weather}}^{\text{silic.Ca}} (J_{\text{weather}}^{\text{carb.Mg}} / J_{\text{weather}}^{\text{carb.Ca}} + 1) \quad (22)$$

As can be seen from Eq. (22), to preserve a constant Ca/Mg ratio in carbonates, the flux of juvenile CO₂ should exceed the weathering flux of Ca silicates by a value proportional to the ratio of the weathering fluxes of Ca and Mg carbonates (the expression in parentheses in the right-hand side of the equation is universally greater than one). A higher flux of juvenile CO₂ leads to a decrease in Ca/Mg ratio [see Eq. (21)]. At a lower degassing rate, the contribution of Mg carbonate (dolomite) decreases.

CONCLUSIONS

The most interesting features of the balances, which were revealed by examining the scheme proposed for the surface cycles of Ca, Mg, and CO₂, are as follows: (1) the regulation of Ca and Mg carbonate fluxes by Mg redistribution between carbonate and hydrosilicate modes and (2) the compensation of variations in juvenile CO₂ fluxes by the internal redistribution of the forms of Mg fluxes. These two features provide the basis for the solution of the very important problems of the internal (endogenous) and external (exogenic) geodynamics.

First, the denudation of continents, which consist of primary (juvenile) silicates and aluminosilicates of Ca and Mg, throughout the entire geological history of the sedimentary shell suggests that the degassing of the Earth's interior existed for the entire geological history; the supply of juvenile volatiles to the Earth's surface and their involvement in surface cycling is evident of weathering. The structure of the sedimentary shell cannot be explained by an "initial reserve" of volatiles in the hypothetical "primary" atmosphere; the concepts of this atmosphere have no factual basis. It is pertinent to clarify the meaning of fairly indefinite terms of "juvenile" and "the Earth's interiors". In this context, the term "the interiors" as a source of "juvenile" rocks and volatiles includes mantle and deep-seated crustal material. The operation of both of the sources during geological history of the sedimentary shell is an evident fact. The exposure of granitoids and metamorphic rocks, which were affected by decarbonatization during metamorphism and granite formation, to weathering distinctly demonstrates the input of a "rejuvenated" (phreatic, according to V.I. Vernadsky) component in juvenile flux of CO₂, while the outflow of magmatic (volcanic) mantle rocks at the surface and their incorporation in sedimentation definitely testify to truly "juvenile" mantle CO₂.

Second, the obligatory correspondence between the juvenile CO₂ flux and the amounts of Ca and Mg silicates and aluminosilicates supplied to the weathering zone may be abandoned when the quantitative relations of carbonate formation during the geological evolution of the sedimentary shell are interpreted. This condition seems to be peculiar since there is no evidence of any quantitative correlations between these processes. The only limitation of this conclusion is that the juvenile CO₂ flux (in equivalent units) could not be lower than the weathering rates of Ca silicates and aluminosilicates and the complete decarbonatization rate of Mg and could not be higher than the limiting flux at which hydrosilicates would disappear as equilibrium Mg compounds from the biosphere. However, this range of values is fairly wide.

Third, to explain the variations in the proportions of Ca and Mg carbonates with geological time within the framework of our stationary model, neither the change in the CO₂ resource in the exchange biospheric reservoirs, nor corresponding variations in the abundance of Ca and Mg supplied to the weathering zone (constant ratio of fluxes of these elements in the continental sink) are required.

In this aspect, very important consequences follow from the drastic decrease in the dolomite abundance in the sedimentary shell starting at Mesozoic time. Within the scope of the model, this means only a sharp decrease in the flux of juvenile CO₂ from this moment, i.e., a dramatic decrease in the degassing rate of the Earth's interiors. Accepting this conclusion, we have to admit that the onset of the formation of recent oceanic

structures was accompanied by a significant modification of the dynamics of endogenous and exogenic processes, which was primarily expressed in a sharp deceleration of the degassing process.

Of course, this conclusion is of model character and its significance depends on the plausibility of our model for surface Ca and Mg cycles. However, the model is based on the only assumption that local chemical equilibrium in weathering and sedimentation was maintained throughout the entire geological evolution of the sedimentary shell, with all other characteristics of the model seeming evident from geological viewpoint. However, any complications of the model (for example, due to the consideration of the geological kinetics of these processes) will not affect the equation system, and require only incorporation of the members in the corresponding equations that take into account the finite (on the geological scale) relaxation rates of the reservoirs in response to outer disturbances. Evidently, these considerations will require the incorporation of the regime of relaxation fluctuations into the system dynamics but will not modify the principal interrelations. However, the problem does not concern abandoning the model but rather the deviations from equilibrium permissible in the system, including deviations from the stationary CO₂ content in the atmosphere, a parameter believed to be critical in many schemes proposed for the geological evolution of the biosphere. However, this problem is beyond the scope of the model considered in the paper.

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