

Geologic history of seawater: a MAGic approach to carbon chemistry

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I. Introduction

In his paper *Geologic history of sea water: An attempt to state the problem* (Rubey, 1951), W. W. Rubey presented one of the first quantitative efforts at obtaining an understanding of the paleochemistry of seawater and the atmosphere. Rubey concluded that throughout much of geologic time, seawater chemistry has been relatively uniform in composition. Dick Holland (Holland, 1972), to whom our paper in this volume is dedicated, employing a play of words on the title of Rubey's article, in the paper *The geologic history of sea water—An attempt to solve the problem* reached a conclusion somewhat in agreement with Rubey. Based on the relative abundance of minerals in marine evaporites, their depositional sequence, and the absence of many minerals typical of non-marine evaporites, Holland concluded “that the concentration of the major constituents of seawater has rarely, if ever, been more than twice or less than half their present concentration during the past 700 million years.” Holland further stated that the “chemistry of seawater has been highly conservative” through geologic time. Garrels and Mackenzie (1971, 1972) based on the relative similarity of the mineralogy and chemistry of sedimentary rocks through geologic time, and accounting for diagenetic reactions and overprinting, had previously come to the same conclusion. However, in the latter part of the twentieth century and on into the twenty-first, these latter three authors and others using different methodologies (e.g., Mackenzie, 1975; Garrels and Perry, 1974; Berner et al., 1983; Veizer and Compston, 1974; Horita et al., 2002; Holland, 2004) concluded that Phanerozoic and also Precambrian seawater exhibited important compositional variations. Although both Rubey (Rubey, 1951) and Holland (Holland, 1972) discussed the role of carbon in the chemistry of seawater, neither author was able to resolve the geologic history of compositional variations in the seawater CO₂-carbonic acid system [the system that includes CO₂ (gas), CO₂ (aq), H₂CO₃ (aq), HCO₃⁻ ion, CO₃²⁻ ion, H⁺ ion, dissolved inorganic carbon (DIC), total alkalinity, and carbonate saturation state]. More recently there have been attempts to resolve Phanerozoic variations in this important seawater chemical system for at least part of the Phanerozoic using Earth system models (Zeebe, 2012; Arvidson et al., 2006, 2011, Kump et al. 2009, Ridgwell, 2005, Ridgwell and Zeebe, 2005; Locklair and Lerman, 2005; Hardie et al., 1996; Lowenstein et al. 2003; see also additional references in Arvidson et al. 2006).

As the quest for an understanding of the geologic history of seawater was developing, model calculations were leading to an increasingly robust understanding of paleoatmospheric CO₂ variations during the Phanerozoic (e.g., Berner et al., 1983; Mora et al., 1996; Pearson and Palmer, 2000; Wallman, 2001; Nordt et al., 2002; Demicco et al., 2003; Edmond and Huh, 2003; Hansen and Wallman, 2003; Royer et al., 2004; Haworth et al., 2005; Guidry et al. 2007; Mackenzie et al., 2008; Arvidson et al., 2006, 2011; Berner, 2004, 2006; Royer, 2006). Proxy information for Phanerozoic CO₂ variability was later derived from fossilized plant stomata, paleosols, phytoplankton, boron isotopes, and liverworts (e.g., Royer, 2006) confirming to some extent the CO₂ modeling calculations. The ability to calculate paleoatmospheric CO₂ places one constraint on the history of the CO₂-carbonic acid system of seawater. However, unlike atmospheric CO₂, there are no sedimentary proxies for the complete seawater CO₂-carbonic acid system applicable on the time scale of the whole Phanerozoic: thus model estimates are mainly

relied on. In this article we employ principally a modeling approach that is supported to some degree by sedimentological and paleontological data to investigate seawater carbon chemistry.

II. Methodology

We use primarily the numerical output from the Earth system model *MAGic* (Fig. 1; Mackenzie, Arvidson, Guidry interactive cycles, e.g., Arvidson et al., 2006, 2011; Guidry et al., 2007; Mackenzie et al., 2008) to explore the evolution of the trend in the Phanerozoic carbonic acid system of seawater. The data we present are for the standard runs of *MAGic* based on the original *MAGic* model (Arvidson et al., 2006) as revised in Arvidson et al. (2011). Briefly *MAGic* deals with the long-term, deep-time Phanerozoic evolution of 11 coupled biogeochemical element cycles, including atmospheric CO₂ and O₂, in the exogenic system of land-ocean-atmosphere-sediment and includes interactions with the deeper endogenic system. In addition and of importance to this paper, not only can the compositional changes in atmospheric CO₂ and O₂ be explored in *MAGic* but also those of the seawater CO₂-carbonic acid system chemistry and carbonate sediment composition throughout the Phanerozoic Eon. To our knowledge this is the only coupled biogeochemical 11 element model that is capable of doing this.

In *MAGic*, the 11 element cycles are explicitly coupled to one another via a reaction network. This network incorporates the basic reactions controlling atmospheric CO₂ and O₂ concentrations, continental and seafloor weathering of silicate and carbonate rocks, net ecosystem productivity, basalt-seawater exchange reactions, precipitation and diagenesis of chemical sediments and authigenic silicates, oxidation–reduction reactions involving C, S, and Fe, and subduction-decarbonation reactions. Coupled reservoirs include shallow and deep cratonic silicate and carbonate rocks and sediments, seawater (as a single reservoir with no proviso for shallow and deep domains), atmosphere, oceanic sediments and basalts, and the shallow mantle (Fig. 1). In addition, the model has parameterizations of the interactions between seawater and oceanic crust, the cycling and complex feedbacks between O₂, iron (Fe), phosphorus (P), and organic matter, the complex feedback relationships between atmospheric CO₂, global temperature, the terrestrial biosphere, and the rate of chemical weathering. *MAGic* is set up in an initial steady state condition that can be perturbed and the time course of changes in the atmosphere, ocean, and sediment composition followed through Phanerozoic time.

MAGic has been mainly employed to investigate the long-term millions to tens of million-year deep time compositional history of the Phanerozoic ocean-atmosphere-carbonate sediment system. Relatively short-term events like the changes accompanying mass extinctions have not been dealt with to date in any detail in the model. This should be kept in mind in the following discussion since these events, whatever their ultimate cause, be they meteorite impacts, volcanic eruptions, or rapid sea level changes, can reset the “compositional clock” and disturb the otherwise smoother changes in geochemical and environmental parameters calculated for the long time scale.

III. Calcium-Magnesium-Silicate-Carbonate-CO₂ Subcycle of the Model *MAGic*

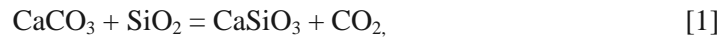
We begin our discussion of the CO₂-carbonic acid system of seawater by first considering the reservoir domains and biogeochemical processes involving components that have a significant effect on the behavior of the system over geologic time (Fig. 2). These include CO₂, calcium (Ca), magnesium (Mg), dissolved inorganic carbon, silica, and carbonate.

Figure 2 illustrates in detail one subcycle of the model that has particular relevance to the seawater CO₂-carbonic acid system (Arvidson et al., 2006, 2011).

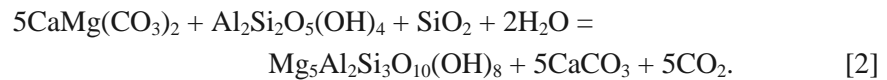
With reference to Figure 2, Ca and Mg are initially weathered from continental silicates and carbonates by carbonic and sulfuric acids. The Ca in river water is mainly derived from the weathering of calcite and dolomite and the dissolution of silicate minerals, particularly felsic plagioclase (Ca, Na aluminosilicate). Mg is derived from dolomite [CaMg(CO₃)₂] weathering and the weathering of mafic silicate minerals such as amphibole, pyroxene, and biotite (Fe- and Mg-

rich silicate minerals). The dissolved inorganic carbon (mainly bicarbonate at the pH of river water) is derived from the weathering of carbonate and silicate rocks in the presence of CO₂-charged soil and ground waters; the CO₂ being mainly derived from terrestrial plant photosynthesis and subsequent degradation of organic carbon and root respiration in soils. Ca and Mg are also produced during weathering from the dissolution of evaporite minerals. The resultant dissolved constituents are transported to the oceans by rivers, and less importantly, by ground waters. Once present in seawater, these components are re-deposited in shelf environments as primary or secondary calcite (CaCO₃), dolomite, and CaSO₄ and MgSO₄ salts in evaporite deposits. Subsequent to deposition, these minerals either re-enter the weathering cycle through uplift and exposure or can be removed to deeper burial regimes.

In pelagic environments (slope, rise, and deep-sea), only calcium carbonate is deposited, and as far as we are aware in the present and past oceans, no dolomite; thus, the total carbonate flux is partitioned between shelf and pelagic regimes. Although other factors may play a role (Arvidson et al., 2011), the precipitation rate of shelf dolomite in *MAGic* is controlled by seawater saturation state and temperature (Arvidson and Mackenzie, 1999). In addition, the accumulation of dolomite is a function of the shelf area available for deposition of carbonate sediment. This function is estimated from Quaternary dolomite depositional fluxes in shallow water environments and the submerged shelf area as a function of time and is normalized to its Quaternary value. Dolomite is also formed in the shelf environment in locales where the oxidation of organic matter (so-called organogenic dolomitization) is tied to the rate of microbial sulfate reduction and production of dissolved inorganic carbon. After deposition, pelagic calcite is either subducted to the mantle or removed to a metamorphic regime, such as deep burial in sedimentary basins like the Gulf Coast, USA. Both of these pathways lead to decarbonation reactions that serve to return material to the weathering cycle. This is the classic Urey-Ebelmen reaction, written simply as:



leading to the release of CO₂ to the atmosphere via volcanism and metamorphism in the subsurface of deep sedimentary basins. The latter process can be represented by the burial metamorphic reaction involving the reactants dolomite, kaolinite, quartz, and water and the products of chlorite, calcite, and CO₂ (Hutcheon et al., 1980; Holser et al., 1988):



The mantle itself does not constitute a reservoir *per se* in the *MAGic* model but simply represents a collection point for return fluxes to either the silicate (basaltic or continental crust) or atmospheric reservoirs. Basalt-seawater reactions result in the uptake of Mg and the release of Ca. Mg uptake is assumed to be first order with respect to the Mg²⁺ concentration in seawater and its uptake is modified by a time-dependent parameter reflecting the rate at which the seafloor spreads. The complementary release of Ca²⁺ from basalt during seawater-basalt reactions, although identical to the Mg uptake flux in the steady state (Quaternary) condition, is allowed to vary during time to balance with the uptake fluxes. This variation is related to the maintenance of the proton (i.e., CO₂) balance between seawater and hydrothermal fluids within the basalt (see detailed explanation in Arvidson et al., 2006). In addition, some of the Ca derived from reactions with mafic silicate minerals in seafloor basalts during basalt-seawater reactions in the shallow seafloor is precipitated within the basalt and can be subducted to depth where its decarbonization leads to release of CO₂ to the atmosphere via volcanism.

Diagenetic alteration of shelf and pelagic sediments also results in release of Ca to seawater that is first order with respect to sediment mass. Mg uptake by reverse weathering reactions in the sediment to form chlorite, a composition representative of a neofomed magnesium silicate clay mineral, is allowed to vary according to the mass of Mg²⁺ in the ocean. The Mg from the chlorite formed is transferred from the chlorite reservoir to react with buried calcite to form burial dolomite, an important process of secondary dolomite formation. The rate of burial dolomite

formation is consequently limited by the size of the chlorite reservoir. This dolomite is eventually returned by uplift to the continental weathering regime, and burial calcite not consumed by dolomitization or uplift eventually returns CO₂ to the atmosphere and Ca to the silicate reservoir by metamorphic decarbonation.

As has been known for some time now, the coupled cycle of Ca, Mg, carbonate, and CO₂ is tied to that of the biogeochemical cycle of silica. Silica is released to river and ground waters during the chemical weathering of silicate minerals in rocks and in more recent geologic time, and less importantly, because of the dissolution of silica phytoliths in plants (see e.g., Katz et al., 2007). Since the appearance of organisms such as diatoms, radiolarians, dinoflagellates, and sponges that secrete siliceous opal-A skeletons, the dissolved silica entering the ocean from the weathering source, and from both low- and high-temperature basalt–seawater reactions, has been removed from the ocean primarily by the precipitation of the biogenic silica phase opal-A (SiO₂ · 2H₂O). During early diagenesis on the seafloor, some of this silica, upon dissolution in the pore waters of sediments, may precipitate in reverse weathering reactions, leading to the neof ormation of silicate phases in the sediments (Mackenzie and Garrels, 1966a, b; Mackenzie et al., 1981; Michalopoulos and Aller, 1995). The net amount of opal-A buried in the sediments goes through a series of diagenetic reactions that convert it to quartz (SiO₂) on the longer time scale. Some of the buried quartz reacts with calcium carbonate at the higher temperatures of the subducted slab of the seafloor or in deep sedimentary basins to form calcium silicate (CaSiO₃) and release CO₂ to the atmosphere via volcanism or seepage from the deep sedimentary basins (Mackenzie and Pigott, 1981; Berner et al., 1983; Berner and Kothavala, 2001; Berner, 2004; Milliken, 2004). However, most of the quartz silica is uplifted to the surface environment where it can be dissolved during weathering or recycled in the solid phase (Wollast and Mackenzie, 1983). Now with some appreciation of the scheme for the Ca-Mg-carbonate-CO₂-Si subcycle of the *MAGic* model, we can consider some of the numerical results of the model and their accordance with proxy or other data for the evolution of the ocean-atmosphere-carbonate sediment system during the Phanerozoic Eon.

IV. Ca, Mg, and DIC Weathering and Basalt-Seawater Reaction Fluxes

Let us start with the weathering and basalt-seawater reaction fluxes. Figures 3 – 5 show the calculated Ca, Mg, and DIC weathering and basalt-seawater reaction fluxes during the Phanerozoic. Notice first the roughly long-term, multi-million year cyclic pattern in these fluxes. The Phanerozoic starts out with low values of the weathering fluxes, gradually increasing into the middle of the Paleozoic and then falling to the Carboniferous, at which time the fluxes began to increase into the Mesozoic and then fall dramatically into the Cenozoic. Despite some time lags, this general pattern is remarkably similar to the calculated long-term paleoatmospheric CO₂ curves of the models *MAGic* and *GEOCARB* (e.g., Berner, 2004; Arvidson et al., 2006) and to proxy data for this atmospheric variable (e.g., Royer, 2006). As atmospheric CO₂ concentrations rose, the radiative forcing due to this greenhouse gas increased and planetary temperatures rose leading to enhanced loading of the atmosphere with water vapor and hence increased precipitation (Kasting et al., 1988). The increase in temperature and precipitation rate led in turn to increasing weathering rates on land. The opposite combination of decreasing atmospheric CO₂, radiative forcing, and precipitation appears to be responsible for falling weathering rates. The overall pattern of weathering fluxes is modified by sea level changes, a reflection at least in part of plate accretion rate, and the carbonate land area and carbonate rock type available for weathering, plus the location of the continents during Phanerozoic time. Notice that the cyclic weathering flux changes are somewhat muted for Mg. This probably reflects the more rapid dissolution rate of calcite than that of dolomite and the mass distribution of dolomite versus limestone, and hence surface exposure to weathering (Garrels et al., 1976), as a function of geologic age in the sedimentary rock column.

Figures 3 – 5 also show the Ca, Mg, and DIC combined low and high temperature exchange fluxes due to basalt-seawater reactions in the seafloor during the Phanerozoic. These fluxes only vary by about a factor of 1.5 to 2.5 in magnitude. The uptake-age trend of the DIC basalt uptake flux exhibits a distinct cyclic pattern with uptake fluxes low in the early Paleozoic climbing slightly into the Ordovician and then falling into the late-Paleozoic/early-Mesozoic minimum, followed by a rise into the Cretaceous and then falling again into the Cenozoic. To some extent this pattern roughly mimics that of the seafloor accretion rate (Fig. 7), with lower fluxes at times of low accretion rate and higher fluxes at times of high accretion rates. This might be anticipated as more DIC (mainly HCO_3^-) is flushed through the global ridge system and precipitates as CaCO_3 (the Ca being derived mainly from minerals like the Ca-rich anorthite component of plagioclase feldspar within the basalt) releasing CO_2 as accretion rates increase; the converse is true for lower accretion rates. Calcite found in seafloor basalts as veins and other fillings of voids is recognized as an important sink of carbon (Alt and Teagle, 1999). This seafloor calcite on subduction acts as a CO_2 source to the atmosphere owing to the Urey-Ebelmen reaction (eq. 1).

The Ca basalt release and Mg uptake fluxes due to basalt-seawater exchange reactions in the seafloor show only moderate variations over Phanerozoic time. This is to be expected because of the strong buffering of these exchange fluxes controlled by the stoichiometry of basalt-seawater reactions (Arvidson et al., 2006). However, the temporal patterns of uptake of Mg and release of Ca due to basalt-seawater reactions are similar and their exchange is not simply one to one due to the complex nature of the processes giving rise to the basalt exchange fluxes (Arvidson et al., 2006).

V. Sinks of Ca, Mg, and DIC through the Phanerozoic Eon

The dissolved constituents delivered to the ocean by rivers and ground water discharges and those from other sources during Phanerozoic time must be removed from the oceans by various mechanisms and processes, otherwise the ocean would become much more saline than the present day ocean. Variations in the input and output fluxes of dissolved constituents involving the ocean determine seawater composition during geologic time. The *MAGic* model permits one to make calculations of the magnitude of these fluxes, and in addition, the changes in seawater and atmospheric CO_2 and O_2 composition deriving from changes in these fluxes. These variations in composition exert an influence on the evolution of life in the Phanerozoic that in turn through feedback mechanisms influence the composition of the ocean and atmosphere. In this section, we present a description and quantification of the sinks of Ca, Mg, and DIC, three major components related to carbonate biomineralization and production and to organic productivity through Phanerozoic time. The oceanic uptakes or sinks of Ca, Mg, and DIC into solid marine deposits are shown in Figures 8 – 10. The strength of each sink is shown as a percentage of the total constituent flux into the solid phase. Let us first consider the nature of the sinks for Ca, Mg, and DIC.

The flux of dissolved Ca to the oceans from weathering on land of carbonate and silicate rocks and that released through reactions at the seafloor involving basalt and seawater at low and high temperatures (Thompson 1983; Wollast and Mackenzie, 1983; Mottl and Wheat, 1994; de Villiers and Nelson, 1999; Arvidson et al., 2006) is removed from the ocean in five sinks (Fig. 8): accumulation of CaCO_3 on the shelf and in deep sea sediments; accumulation of dolomite [$\text{CaMg}(\text{CO}_3)_2$] on the shelf; accumulation of CaCO_3 in the pores, cracks, and fractures in submarine basalts; and accumulation as evaporite CaSO_4 . Until the onset and rapid expansion of the planktonic Coccolithophoridae and foraminiferal calcifiers in the mid Mesozoic, unless there were inorganic deposition of calcium carbonate in the deep sea (see previous discussion and Berner and Mackenzie, 2011), there was no accumulation of laterally extensive beds of carbonate sediments in the pre-Mesozoic deep sea.

Mg mainly derived from weathering reactions on land of carbonate and silicate rocks is primarily removed from the ocean during dolomite formation on the shelves (Morse and

Mackenzie, 1990; Mackenzie and Morse, 1992); in low-temperature, diagenetic reverse weathering reactions in seafloor sediments (e.g., Mackenzie and Garrels, 1966a; Mackenzie et al., 1981; Michalopoulos and Aller, 1995; Holland, 2004); during reactions involving basalts and seawater (Thompson, 1983; Mottl and Wheat, 1994); and during formation of evaporite MgSO_4 (Babel and Schreiber, 2013) (Fig. 9).

The sinks for dissolved inorganic C released via weathering of carbonate and silicate rocks (in the latter the CO_2 comes ultimately only from the atmosphere) and seafloor basalt-seawater reactions are the accumulation of inorganic carbon in shelf CaCO_3 and dolomite, the accumulation of CaCO_3 in seafloor basalts, and the accumulation of calcite and aragonite in the deep sea (Morse and Mackenzie, 1990) (Fig. 10). Organic carbon sinks include shelf and pelagic storage of organic matter and the burial of organic matter in coal basins. Variations in the flux to the latter sink are especially important to the history of atmospheric oxygen (Berner and Canfield, 1989; Berner, 2004; Arvidson et al., 2006).

Now let us consider how these sinks of Ca, Mg, and DIC vary throughout Phanerozoic time. First, we will consider the pattern of Ca and Mg flux variations as shown in Figures 8 and 9. It can be seen from the figures that an important sink of Mg, and less so for Ca, through the Phanerozoic Eon is in the accumulation of dolomite on the shelf. Storage of these elements in dolomite is relatively high for much of the Mesozoic and mid-Paleozoic and low in the Cenozoic and Permo-Carboniferous. The downward trend from the high dolomite accumulation rate of the Cretaceous toward the present is well established by observational records of the distribution of dolomite through Phanerozoic time (Wilkinson and Walker, 1989; Wilkinson and Algeo, 1989; Morse and Mackenzie, 1990; Holland and Zimmermann, 2000). The high of the mid-Paleozoic and the subsequent low of the Permo-Carboniferous have been debated in the literature based on interpretations of observations of the dolomite mass-age distribution (Wilkinson and Algeo, 1989; Mackenzie and Morse, 1992; Holland and Zimmermann, 2000; Veizer and Mackenzie, 2004), but nevertheless, the results of the numerical simulations from *MAGic* suggest the possibility of a cyclic pattern in the dolomite accumulation flux-age distribution. This pattern is in accord with the distribution of preserved dolomite as a function of age in the Phanerozoic sedimentary rock column (e.g., Morse and Mackenzie, 2000). This cyclic pattern also mimics to some extent the first-order sea level curves of Vail et al. (1977) and Hallam (1984), with high sea level stands being times of high dolomite accumulation rates. This would be anticipated since dolomite is a shallow-water deposit and is not deposited as vast extensive beds of dolomite in the deep sea. One can see from Figure 9 that as the sink for Mg in dolomite accumulation becomes more significant, the sink in submarine basalt uptake, the second most important sink of Mg, weakens as more of the Mg entering seawater is removed in the accumulation of dolomite.

For Ca, the most important sink through Phanerozoic time is in the accumulation of CaCO_3 in shelf carbonate deposits (Fig. 8). Until the advent of open ocean pelagic calcifying organisms, there probably was scant accumulation of biogenic CaCO_3 in the deep sea (Boss and Wilkinson, 1991), and as mentioned previously, there may or may not have been inorganic deposition of CaCO_3 in the deep sea. The accumulation of deep-sea biogenic carbonates only became significant in the early Mesozoic, resulting in the transfer of CaCO_3 from the shallow water continental regime to the deep sea. Most, if not all, extant Paleozoic carbonates were deposited in cratonic, continental environments as mainly organo-detrital limestones and not in the deep sea, as evidenced by the sedimentologic characteristics of the carbonate rock record and the near-absence of deep-sea carbonate deposits associated with Paleozoic ophiolites (ancient sea floor metamorphosed basalt complexes; Boss and Wilkinson, 1991). The latter authors contend that some of the occurrences of dark limestone and rhythmically layered marble associated with the scant record of Paleozoic ophiolites may represent inorganic CaCO_3 deposition on the deep seafloor. This observation would lend credence to the hypothesis of Berner and Mackenzie (2011) mentioned above that there was inorganic accumulation of carbonate in the Paleozoic deep sea. The accumulation of calcite in submarine basalts is of further importance to the record of Ca

accumulation in the deep sea. In this case, the Ca is derived from the reaction of primary basaltic minerals with seawater mainly at hydrothermal temperatures and accumulates during the precipitation of CaCO₃ in the pores, cracks, and fractures of submarine basalt. Arvidson et al. (2006) hypothesize that this sink can be an important source of CO₂ to the atmosphere. Subduction of this CaCO₃, along with pelagic calcareous oozes, results in decarbonation at higher temperatures and pressures and ultimate release of CO₂ by volcanism to the Earth's atmosphere. Evaporite minerals form an additional, albeit minor, sink for both Ca and Mg.

Ca and Mg also accumulate in evaporite deposits. The age distribution of extant evaporites in the sedimentary rock record is irregular, reflecting the infrequent coincidence of requisite tectonic, paleogeographic, and paleoclimatic conditions necessary for evaporite deposition. For example, vast quantities of evaporite salts accumulated in the Upper Permian that may actually have resulted in a lowering of the mean salinity of seawater at this time by 1% to 4% (Holser, 1984). The current version of the *MAGic* model does not incorporate these episodic evaporite depositional events and thus the modeled pattern of Ca and Mg accumulation reflects more the integrated strength

The Phanerozoic oceanic sinks of inorganic and organic C derived from land and organic C produced *in situ* by productivity in the ocean are shown in Figure 10. Shelf accumulation of both C in organic matter and inorganic C in calcite and dolomite are very important sinks of C during the Phanerozoic. The trend in the rate of accumulation of inorganic C in dolomite, as might be expected, mimics the trend in accumulation of Mg in this phase. Pelagic calcite accumulation of inorganic C becomes important in the Mesozoic and inorganic accumulation of CaCO₃ in submarine basalts occurs with only minor variation in magnitude through the past 500 million years. Accumulation of terrestrially derived organic C is particularly important in the Permian-Carboniferous, a time of vast coal deposits, whereas pelagic accumulation of organic C varies only slightly throughout Phanerozoic time (not shown).

Because to a significant extent, the ratio of the reduced carbon as organic C flux to the oxidized carbon as inorganic carbonate flux determines the $\delta^{13}\text{C}$ ratio of seawater and hence that of sedimentary carbonates, it is possible to calculate using *MAGic* this ratio during Phanerozoic time and compare its trend with the carbon isotopic curve. It has been shown that the trend in calculated ratio agrees well with the isotopic curve with intervals of high organic C accumulation being periods of ¹³C-enriched carbonate deposits, and hence presumably seawater, at the time (Guidry et al., 2007). This finding lends some credence to the temporal distribution of carbon sinks shown in Figure 10.

VI. Changes in Ca, Mg, DIC, pH, and Carbonate Saturation State of Seawater

The balance between the fluxes of dissolved constituents to seawater and their accumulation fluxes is the basic control on variations in seawater chemistry through geologic time. Several authors have tried to document variations in the CO₂-carbonic acid system and carbonate saturation state of seawater for portions of the Phanerozoic (e.g., Lasaga *et al.*, 1985; Tyrrell and Zeebe, 2004; Locklair and Lerman, 2005; Guidry et al., 2007; Arvidson *et al.*, 2006, 2011). The changes in Ca, Mg, and DIC concentrations, pH, and seawater saturation state with respect to calcite in the ocean during Phanerozoic time calculated from the *MAGic* model are shown in Figure 11. In addition, the sulfate concentration trend with age is also shown in Figure 11 since the concentration-age trend of this dissolved species is one that is recorded in the fluid inclusions of evaporites (Babel and Schreiber, 2013) and can be compared with model output.

In general there is a cyclic pattern of variation in the Ca, Mg, and DIC concentrations of seawater and hence the Mg/Ca and SO₄/Ca ratios through Phanerozoic time. Times of slow plate accretion rates and low sea level are times of high Mg/Ca and SO₄/Ca ratios; the converse is true for high plate accretion rates and high sea levels. The composition of fluid inclusions in evaporites in terms of Ca, Mg, and sulfate tracks the modeled compositional trends. As would be expected, the pH and carbonate mineral saturation state of seawater track each other closely, with

a decrease in pH and saturation state with respect to calcite, and therefore aragonite and dolomite, at times of dolomite accumulation during first order high sea level stands and flooded continental freeboards. The cyclicity in seawater pH and calcite saturation state to some degree also tracks the paleoatmospheric CO₂ curve with high CO₂ levels correlating with lower seawater pH and calcite saturation state; the converse is true for lower pCO₂ levels. The extended times of low seawater pH and likely carbonate saturation state are natural periods of ocean acidification.

With respect to DIC concentrations, the total inventory of DIC in the ocean reflects the sum of fluxes derived from continental weathering, basalt-seawater exchange, reverse weathering, and global deposition of carbonate. In the *MAGic* model, the pattern of DIC concentrations through the Phanerozoic is very sensitive to the dolomite accumulation rate, which acts to buffer the DIC concentration. Indeed varying the dolomite flux alone in the *MAGic* model can produce quite a different pattern of the DIC versus age trend (as cf. Arvidson et al., 2006; Arvidson et al., 2011). Thus, this trend still remains an important question for future investigation, although it is likely that DIC seawater concentrations were elevated during Hothouse intervals (Phanerozoic geologic periods of extended warmth).

VII. Atmospheric O₂ and the Seawater CO₂-Carbonic Acid System

VII.1. Introduction

Atmospheric O₂ exhibits significantly major changes in its concentration-age distribution during the Phanerozoic Eon. The various model calculations for O₂ are shown in Figure 12, and although variable, appear robust in terms of the most important features: (1) atmospheric O₂ concentrations started out at the beginning of the Phanerozoic similar to those of the more recent past; (2) from Cambrian to Devonian time, O₂ concentrations were slightly higher or slightly lower than modern day; (3) in the Carboniferous and on into the Permian, O₂ concentrations apparently rose dramatically to values reaching 1.5 to 2 times present day values; (4) following the relatively high O₂ concentrations of the Permo-Carboniferous, O₂ concentrations fell to values perhaps lower than today during the Triassic/early Jurassic and then rose once more into the late Mesozoic, falling then into the Cenozoic toward present day levels.

What caused this pattern in paleoatmospheric O₂ concentrations during the Phanerozoic? The simplest explanation has been mainly tied to the development of the vast Permo-Carboniferous and Cretaceous/early Tertiary coal basins that stored large quantities of organic carbon recalcitrant to oxidation (Bernier and Canfield, 1989). Oxygen on the geologic time scale is mainly controlled by two major processes: (1) the accumulation of organic carbon and pyrite (FeS₂) in sediments leading to accumulation of O₂ in the atmosphere, and (2) the weathering of uplifted sediments containing fossil organic matter (kerogen) and FeS₂ by atmospheric O₂ that removes O₂ from the atmosphere (e.g., Garrels et al., 1976; Bernier and Canfield, 1989; **more refs**). During the Permo-Carboniferous and the Cretaceous/early Tertiary, with the large fluxes of organic carbon stored in coal basins, O₂ weathering fluxes could not keep up and atmospheric O₂ concentrations increased. Decreased coal basin development and carbon storage then led to O₂ weathering fluxes being sufficient to drawdown atmospheric O₂ levels.

Recently Ozaki et al. (2011) calculated secular changes in the state of ocean oxygenation during the Phanerozoic employing an oceanic biogeochemical cycle model and estimates from the literature of the variations in atmospheric concentrations of CO₂ and O₂ and continental shelf area. The results of the model demonstrated that although the first-order variations in the degree of oxygenation of the ocean are mainly regulated by the partial pressure of atmospheric O₂, changes in continental shelf area also exert a crucial control on the long-term degree of oxygenation of the ocean. Although controversial it appears that well oxygenated open oceans could have prevailed in the Hothouse (Greenhouse) high CO₂ and warm global climates of the early to middle Paleozoic and the Cretaceous Period. This would require the large epicontinental seas, resulting from continental flooding due to the high global sea levels characteristic of these

times, acting as major repositories of nutrients derived via runoff from the land, thus enhancing marine productivity and the sequestration of important amounts of the organic carbon produced in shelf sediments.

VII.2. *MAGic* model parameterizations of the O₂ cycle

In the standard run of *MAGic* applicable to the discussion in this paper of controls on the long-term evolution of atmospheric O₂, marine productivity of organic matter in the ocean, which is the one of the first steps in the burial of organic carbon on the seafloor and the accumulation of O₂ in the atmosphere, is strongly dependent on the flux of P from weathering of continental apatite. The net oxygen production is ultimately a power function of the mass of the reactive P pool. A degree of anoxia (DOA) function (Van Cappellen and Ingall, 1996) controls the C/P ratio of the buried organic matter and the fraction of the reactive iron pool in sediments involved in iron sulfide formation is inversely tied to atmospheric oxygen, and thus acts as a strong brake on the growth of this reservoir during periods of high marine productivity and carbon burial. This regulatory tie between sulfide formation and atmospheric O₂ is a very similar approach to that of Garrels et al. (1976) in their study of the controls on atmospheric CO₂ and O₂ on a million-year time scale. In the current *MAGic* model, the description of oxidative weathering of organic matter on land involves only an exchange of CO₂ for O₂, and does not include any flux of terrestrial organic matter from land to ocean. In addition, the sedimentation of organic matter in the paralic or more open ocean environments is not directly tied to clastic sedimentation rate. However, *MAGic* employs an organic carbon and coal burial flux from a modification of the dataset of Budyko et al. (1987) (see Arvidson et al., 2006, for explanation), which is a Phanerozoic record of both *preserved* terrestrial and marine organic carbon burial in sediments and consequently should represent the *net* amount of O₂ released to the ocean/atmosphere system involving the organic carbon biogeochemical cycle.

The major input of sulfate to seawater is via continental runoff and is derived through pyrite weathering on land, and less importantly, by weathering of sulfate-bearing evaporite deposits. Thus, at least part of this runoff sulfate-oxygen represents original atmospheric oxygen utilized in the oxidation of pyrite on land. The sulfate is reduced to sulfide in the pore waters of marine sediments by microbial processes. The reduced sulfur then reacts with ferrous iron and is stored in the sediments as pyrite. The pyrite buried represents oxygen accumulation in the atmosphere. During uplift this oxygen is removed from the atmosphere in the oxidation of the uplifted pyrite (see e.g., Garrels et al., 1976; Berner and Canfield, 1989; [more refs](#)). Free oxygen in the *MAGic* model is also returned to the atmosphere via the reduction of iron oxide (magnetite). This oxide formed originally as a product of an overall reaction involving ferrous silicate oxidation, sulfate reduction, and formation of pyrite in the basaltic crust of the ocean. The iron oxide, if subducted and sequestered in the mantle, represents oxygen that is not returned to the atmosphere. In the current *MAGic* model, this oxide is simply reduced to produce molecular oxygen. The details of how this reduction reaction occurs are problematic. The return was introduced in the model to balance the oxygen cycle and allow examination of the history of atmospheric O₂ without the complication of a mantle sink. In addition, the O₂ flux involved is small in comparison to the O₂ flux deriving from the burial of pyrite in sediments.

In the *MAGic* model, the ultimate regulatory nutrient on the geologic time scale is taken as P because of its low solubility and tendency to be sequestered in solid phases such as iron oxyhydroxides, carbonate fluorapatite (CFA), and organic matter. The rate of uptake of P in organic matter is proportional to the mass of reactive P in the ocean:

$$F_P = k_1 \times v_{\text{mix}} \times M_P, \quad [3]$$

where F_P is the flux of P into organic matter fixation (bioproductivity), k_1 is a rate constant calculated from the initial steady state of the model, v_{mix} is a rate function that describes the ocean's ventilation rate, and M_P is the mass of reactive P in the ocean. The latter includes both

dissolved inorganic P and that portion of the organic P and other particulate P that is reactive in the ocean reservoir. The ventilation rate is the rate at which surface waters exposed to the atmosphere penetrate the interior portion of the ocean, that is enter or ventilate it. Bioproductivity is determined by the P fixation rate such that:

$$BP = C/P_{\text{Redfield}} \times F_P \quad [4]$$

BP is bioproductivity (gross organic production) and C/P is the Redfield C to P ratio of 106:16. The degree of anoxicity of the ocean (DOA) is fundamentally a measure of the amount of O₂ dissolved in the ocean; the less the O₂ concentration, the more the ocean tends toward hypoxia or anoxia. DOA in *MAGic* is defined as:

$$DOA = (1 - k_2) \times v_{\text{mix}} \times M_{O_2} \quad [5]$$

where k_2 is a rate constant and M_{O_2} is the mass of oxygen in the atmosphere. DOA affects the burial C/P ratio and thus the total amount of P that gets buried or recycled, as well as the extent of sulfate reduction and these effects are all linear with respect to v_{mix} . However, the organic carbon burial flux has a non-linear dependence on these variables such that:

$$F_B = k_3 \times (F_p)^n \quad [6]$$

where F_B is the burial flux of organic carbon and $n = 2.5$ (adapted from Van Cappellen and Ingall, 1996). This non-linear dependence is a strong negative feedback on atmospheric oxygen because F_p , despite its scaling to v_{mix} , is dependent on the reactive P mass (M_p), and DOA and its dependence on v_{mix} are modulated by their inverse proportionality to the mass of atmospheric O₂.

As a summary of the discussion above, Figure 13 shows diagrammatically the coupling between the organic carbon subcycle of *MAGic* and its ties to atmospheric O₂ in which net production of marine organic carbon is driven by phosphorus and net burial of *total* organic carbon is related to the Budyko et al. (1987) preserved rock record of accumulation of organic carbon (organic carbon survival or preservation rate: Gregor, 1985; Veizer and Mackenzie, 2004) with that of the biogeochemical cycles of iron and sulfur. The latter elements are related to the geologic history of atmospheric O₂ concentrations primarily through the burial of sulfide, mainly as pyrite (FeS₂), in sediments. This burial of pyrite along with that of organic carbon results in the accumulation of O₂ in the atmosphere and later oxidation by atmospheric O₂ of this sedimentary pyrite and organic carbon on uplift of host sediments removes O₂ from the atmosphere and releases dissolved sulfate to rivers and CO₂ to the atmosphere (see Arvidson et al., 2006 for details).

VII.3. Oceanic mixing and atmospheric oxygen

There is little doubt that the intensity of turbulent and diffusional mixing processes in the modern and paleocean play a role in the bulk concentration and concentration gradient of O₂ in the ocean (e.g., Wyrski, 1961, 1962; Wilde and Berry, 1982; Wilde, 1987; Algeo and Ingall, 2007; Dahl et al., 2010; Ozaki et al., 2011). Even at a 100% present atmospheric level (PAL) of O₂, Wilde (1987) suggested that global anoxic conditions could have prevailed on the continental shelf during the warm climates of the Early Paleozoic due to the lack of oxygen ventilation into deep water. As a means of exploring the long term coupling between atmospheric oxygen, the inorganic carbon system, and their manifold linkages to weathering and related redox-sensitive processes, we conducted a series of sensitivity runs in which we varied the ventilation rate (v_{mix} , eq. 3). To provide a reference picture for these results, we include detailed results from a baseline run in which v_{mix} was fixed at a value of 3, for pH and saturation state (Fig. 14A), atmospheric oxygen relative to present day (RO₂, Fig. 14B), major seawater electrolytes (Fig. 14C), atmospheric CO₂ (Fig. 14D), Mg/Ca and SO₄/Ca ratios together with the fluid inclusion data of Hardie et al. (1996) and Lowenstein et al. (2003), respectively (Fig. 14E), and fluxes relevant to organic matter cycling (Fig. 14F). [Discuss Figure 14 some more? Some results have been shown in previous figures, but some stuff is new, particularly in 14F. Fred/Michael?]

In the sensitivity runs, v_{mix} was fixed and elevated ($v_{\text{mix}} = 4$) or allowed to oscillate in a sinusoidal fashion between (3,4), with one pattern (arbitrarily labeled “normal”) being exactly out of phase with the other (“inverse”). Thus in the normal oscillation, v_{mix} starts the run close to its maximum value (4), decreases to the minimum (3) at $t \sim -350$ Ma, climbs back its maximum (4) at $t \sim -150$ Ma, and decreases thereafter until the end of the run (a full cycle of 400 Ma). The inverse oscillation follows the opposite schedule, with minima at -545 and -150 Ma and a maximum at -350 Ma. The results of these runs, shown in Figures **15** and **16**, are expressed as the deviation (Δ) from those obtained from the run in which $v_{\text{mix}} = 3$, i.e.,

$$\Delta(t) = y(t) - y(t)|_{(v_{\text{mix}} = 3)}. \quad [7]$$

Figure **15B** clearly shows the effect on atmospheric oxygen. In comparison with the results obtained with $v_{\text{mix}} = 3$, imposing an increased ventilation rate ($v_{\text{mix}} = 4$) *decreases* oxygen mass (O_2). The effect on oxygen from changes in ventilation rate is best shown when v_{mix} is allowed vary between these limits (3,4) in antithetical fashion, producing results that show precisely contrasting minima and maxima (“normal” versus “inverse” curves of Fig. **15B**).

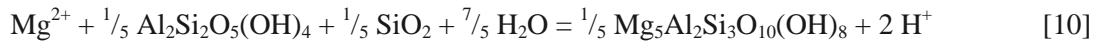
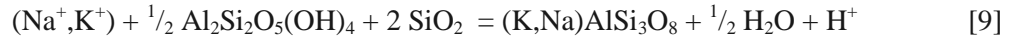
This result is anticipated, and shows the strong productivity-driven feedback effect of oxygen buffering described in eqs. 3 – 6. However, even higher ventilation rates at the close of the Paleozoic (fixed $v_{\text{mix}} = 4$ and “inverse” curves) reduce but do not eliminate the O_2 maximum over this interval, related to the burial of *terrestrial* organic matter accumulating in extensive coastal swamp and paludal environments. In contrast, marine organic matter burial rates are reduced during this period (Fig. **14F**). This latter effect is complex and cannot be explored in detail here, but reflects changes in marine productivity brought about by an overall decrease in the delivery of reactive phosphorous (Fig. **14F**) as CO_2 and weathering rates decline during this interval, versus an increase, *relative to the weathering flux*, in the net flux of phosphorous that is buried (thus ultimately becoming sedimentary apatite), and not returned to the water column. In the model, this negative feedback in reactive phosphorous cycling is the primary cause of reduced marine productivity and carbon burial at a time when O_2 concentrations are actually at a global maximum (Fig. **14B**).

In addition to the burial- and productivity-based controls on atmospheric O_2 , the model results also show significant but expected differences in the oxidation of both marine organic matter (i.e., carbon that is first buried and later exhumed to undergo oxic weathering) and pyrite. We should note for clarity that the latter includes both pyrite that is formed during microbial sulfate reduction (and thus for which marine organic matter is the electron donor) as well as that formed by hydrothermal sulfate reduction during seawater-basalt interaction (for which ferrous iron silicate, generically represented as Fe_2SiO_4 in the model, is the electron donor). This pyrite tied up in basalt will ultimately undergo subduction; in the model, the subsequent “return” of this phase to the continent is done in order maintain strict redox balance and prevent a long term “leak” of ferric iron into the mantle (see Fig. **13** and discussion in Arvidson et al., 2006). These fluxes are shown in Figure **16A** and **16C**, respectively, again expressed as the difference with the results of $v_{\text{mix}} = 3$. The overall pattern shown by both these fluxes is similar. A constant, enhanced ventilation rate ($v_{\text{mix}} = 4$, brown curve) and the resulting decrease in atmospheric O_2 (Fig. **15B**) brings about an overall reduction in the oxidation flux of organic carbon (Fig. **16A**) and pyrite (Fig. **16C**) throughout the entire Phanerozoic model run. Comparison of cyclic variation in v_{mix} is also, not surprisingly, consistent, with “normal” (green) and “inverse” (magenta) curves closely resembling their O_2 counterparts in Figure **15B**.

The responses of both pH and CO_2 (Figs. **16B** and **16D**, respectively) are more complex, with identifiable but subtle differences in response to v_{mix} – driven O_2 shifts. Overall, a reduction in atmospheric O_2 during constant enhanced mixing (brown curve, Fig. **15B**) results in a decrease in pH (brown curve, Fig. **16B**) over the entire run. The pH change seems to primarily reflect elevated CO_2 (brown curve, Fig. **16D**). The results of the cyclic forcing runs (“normal” and “inverse” v_{mix} variations) show similar results, with greater mixing (and lower atmospheric O_2

concentrations) giving rise to a drop in pH and an increase in CO₂. At first glance the *direction* of these changes seems inconsistent with the organic matter and pyrite oxidation fluxes expressed in Figures **16A** and **16C**, respectively. One might expect that increases in organic matter oxidation should result in an increase in CO₂ (as CH₂O + O₂ = CO₂ + H₂O is driven to the right). Similarly, one might have a similar expectation for pH, for which increases in pyrite oxidation flux should decrease its value, as in acid mine drainage. The trends, at least in terms of CO₂, are precisely the opposite. In the normal oscillation, CO₂ is elevated at the beginning of the run when oxidation fluxes are relatively low, reaches a minimum around $t \sim -350$ Ma when oxidation fluxes are high, and increases to a second maximum at $t \sim -150$ Ma, when fluxes are again low. This can be understood by differentiating cause and effect, and recognizing the importance of productivity feedbacks as they appear in the model. Model changes in v_{mix} control bioproductivity (Fig. **16E**) and marine organic matter burial (Fig. **16F**) fluxes through eqs. **3–6**. In addition, the sensitivity to changes in O₂ concentration and v_{mix} is brought about through DOA (eq. **5**), which influences the ratio of C/P in the organic matter undergoing burial and provides an essential negative feedback. Thus, although oxidation rates, which have a first order sensitivity to O₂ concentrations in the model, increase during periods of suppressed mixing (O₂ maxima), organic matter burial rates *also* increase (Fig. **15F**), sequestering greater amounts of organic carbon, and thus leaving relatively *more* oxygen (and thus less CO₂) in the atmosphere [Fred please let me know if this makes sense].

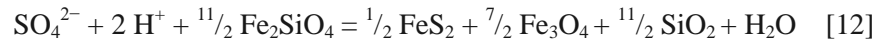
The effect of coupled (v_{mix} , O₂) changes on CO₂ (and thus pH) can be understood through evaluation of the results of DIC and SO₄, shown in Figures **17A** and **17B**, respectively. As explained in detail in Arvidson et al. (2006), DIC and SO₄ are both importantly involved in the basalt-seawater exchange reactions. Seawater SO₄, together with Mg and alkalis (Na + K), all undergo uptake during these reactions, for which the following reaction network can be written:



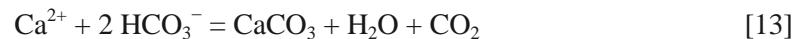
Eqs. **9** and **10** show that alkali and Mg uptake effectively consumes a degraded silicate (shown here as normative kaolinite), to yield an acid. In the model, this acid is used to drive a reaction that results in the decomposition of calcic plagioclase in the basalt (represented in eq. **11** as normative anorthite):



In contrast, the hydrothermal reduction of SO₄ can be written (consistent with the observations of Mottl and Holland, 1978) to consume ferrous silicate and produces pyrite and iron oxide (magnetite):



Because the model does not maintain hydrogen as a component, the above reactions are written in terms of carbonic acid. These reactions thus describe the basic exchange of Mg for Ca during seawater-basalt reactions as a function of whether acid is released or consumed. The fluxes involving these reactions are given simple first order dependence with respect to dissolved concentrations of alkalis, Mg, and SO₄ (eqs. **9**, **10**, and **12**, respectively), meaning that these fluxes can vary more or less independently, at least to the extent that they are involved in other processes. Lastly, the model represents the uptake of bicarbonate in order to account for the observation of basalt carbonate formation (vein calcite) observed by Alt and Teagle (1999),



thus providing an additional sink (other than seawater) for the Ca liberated during eq. **11**.

The critical point we wish to make here is that the model thus links the concentrations of CO₂, DIC and SO₄ via their basalt-seawater exchange reactions, and provides a means of comparing the effect of O₂-promoted changes in seawater and atmosphere composition in terms of the contribution high temperature inorganic (hydrothermal basalt-seawater exchanges), low

temperature weathering, and organic matter burial. Evaluating the results of Fig. 17 in this light, we see that the inverse oscillation of v_{mix} has relatively effect on SO_4 concentration, and also corresponding little change in hydrothermal SR fluxes, reflecting the simple first order dependency. In contrast, both the normal mode oscillation and constant elevated run ($v_{\text{mix}} = 4$) show a virtually identical pattern. This response suggests that it is the timing of the O_2 peaks relative to the change in Mg/Ca ratio (Fig. 14E) that determines the change in SO_4 . Note that the *all* sensitivity runs deliver the same Mg/Ca ratio curve results in terms of fidelity to the fluid inclusion constraint data. In this sense, the normal mode variation in O_2 imposed by v_{mix} is roughly synchronous with the Mg/Ca ratio curve. As discussed previously, the maxima and minima of the Mg/Ca ratio curve correspond in changes in spreading rate, which in turn drive changes in the uptake fluxes of Mg and SO_4 (eqs. 10 and 12). When MOR uptake is low (e.g., in the early Paleozoic just after the start of the run), shifts in O_2 bring about only a muted response in SO_4 (albeit the trend roughly follows the O_2 curve), as seen by the similarity in the inverse (magenta) and baseline (blue, $v_{\text{mix}} = 3$) curves. It is when the Mg/Ca ratio and O_2 changes are roughly in phase that the greatest reduction in sulfate is observed, corresponding to the normal oscillation (green) and fixed, elevated mixing (brown, $v_{\text{mix}} = 4$) curves in Figure 17C. The pattern we see suggests that it is the *timing* of mixing and O_2 variations, relative to corresponding changes in electrolyte uptake within the basalt, that strongly calibrates the system's response.

Although the pattern is complex, the pattern of sulfate changes with respect to O_2 appears to roughly oppose those we observe in DIC concentration (Fig. 17A). The reasons for this are not immediately apparent, and will require further sensitivity analysis to resolve. One interesting observation is that the comparison of the various DIC curves shows that there are intervals over which the normal oscillation and fixed but elevated modes are in rough agreement (e.g., between $t \sim -300$ and -100 Ma); during other intervals (e.g., between $t \sim -500$ and -300 , -100 to 0 Ma), they clearly diverge.

[Fred, I'm uncertain of how to finish this thread, or even if what I have thus far makes much sense. In hindsight, we could use a sensitivity run in which mixing is *less than 3* to determine the system's response (I can't recall if I able to do this or not). Also in hindsight, we would have been better off using $v_{\text{mix}} = 3.5$ as the baseline, and normalizing the (3, 4, variational) results to this marker, thus providing a "positive" and "negative" forcing. Anyway, enough of my griping: these results are more complex than even I first surmised, and I do need to take a break, get some feedback from you, and just think about this a bit more in order to say something intelligent to finish this section. Help!]

Notes on final points to make after the above section (tentative list):

1. strong fundamental coupling, most importantly with respect to inorganic and organic carbon, limits the system's response (atmosphere and hydrosphere) to internal perturbation (i.e., changes in heat flow, volcanism, glacio-eustasy, paleogeographic redistribution and assembly, etc., etc.)

2. the sensitivity to changes involving physics, chemistry, and biology of the system: chemostatic nature enforces a strong return to a stable state after a perturbation (e.g., after resetting initial conditions, the system returns to a stable configuration that reflects the relative values of the matrix of flux coefficients governing basic exchange dynamics). The system is thus quasi-linear in behavior, i.e., reactions at the molecular level are non-linear, but competing and back reactions usually provide negative feedbacks that maintain the system within fairly close limits: this is particularly true for seawater and atmosphere. However biological evolution *does* provoke one-way, irreversible changes in the systems distribution of mass, and thus overprints the slow, long-legged cyclic pattern brought about by basic mass transfer and energy flow.

3. What have we learned?

VIII. Conclusions and Final Remarks

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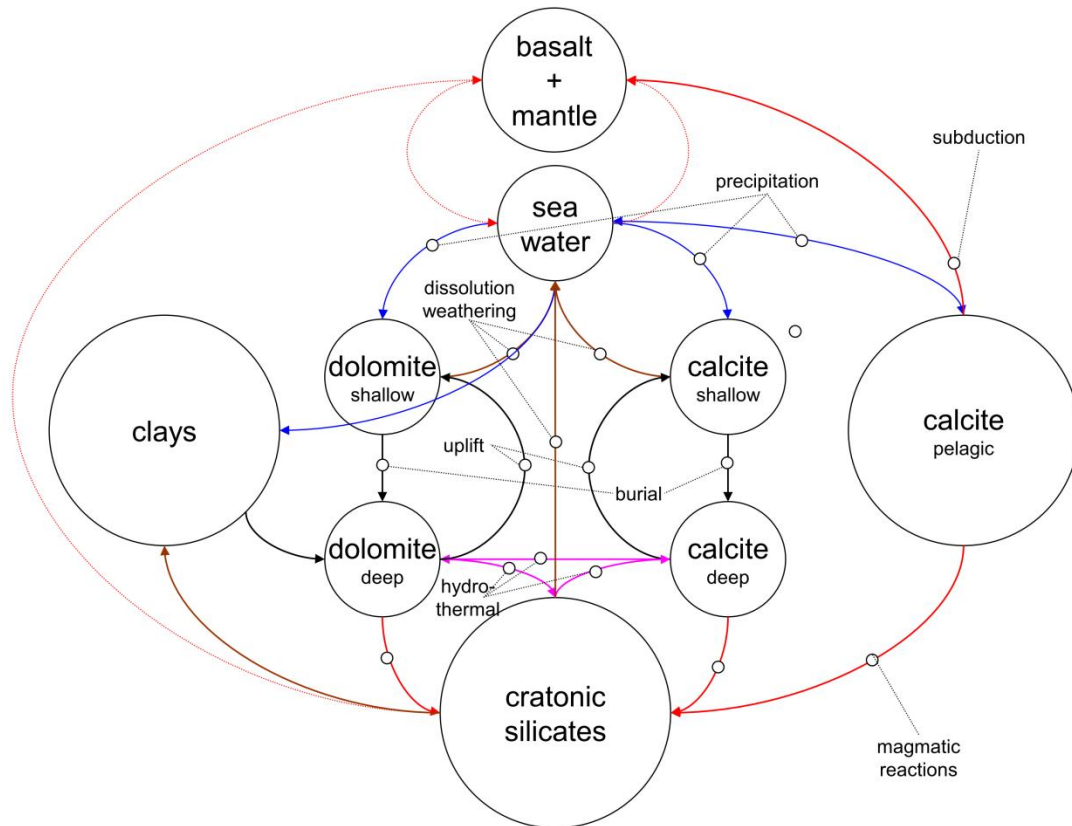


Figure 1. Schematic diagram of the Earth system model MAGic (Mackenzie, Arvidson, Guidry interactive cycles) showing the major reservoirs and the coupling network among the reservoirs. Size of reservoirs is not proportional, and many fluxes are generalized. Precipitation fluxes are indicated by blue arrows, weathering or (diagenetic) dissolution by brown, hydrothermal interactions by magenta arrows, and magmatic or metamorphic transfers by red. Virtually all reservoirs contain links to the atmospheric (CO_2 and O_2), and thus these are omitted for clarity.

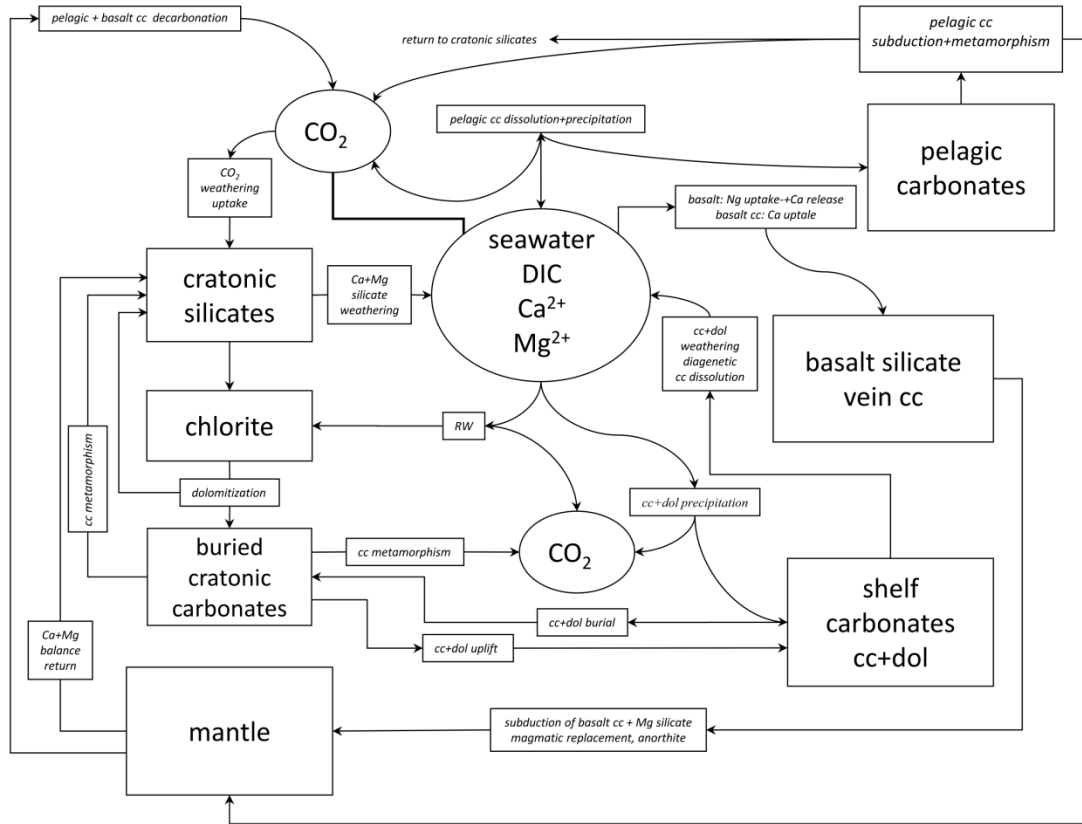


Figure 2. The calcium-magnesium-silicate-carbonate- CO_2 subcycle of the model MAGIC showing reservoirs and processes moving constituents from reservoir to reservoir. This subcycle is coupled to several others in the reaction network of MAGIC and is important in terms of controls on atmospheric CO_2 and ocean carbon chemistry on the geologic deep time scale (adapted from Arvidson et al., 2006).

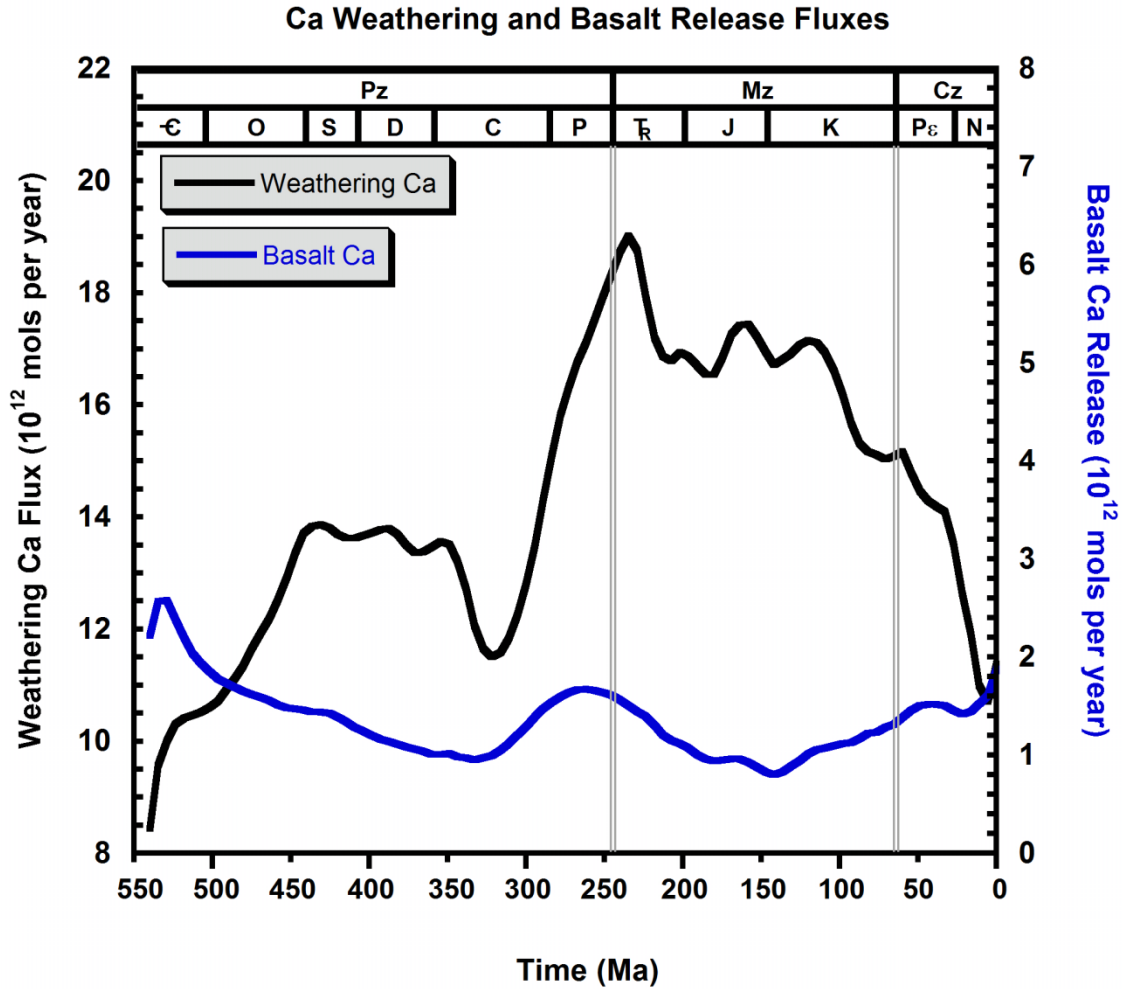


Figure 3. The results of numerical calculations from MAGic showing the calcium flux to the ocean via rivers and groundwaters from weathering reactions on land and the calcium released to the ocean due to basalt-seawater reactions in the seafloor in 10^{12} mol y^{-1} . Notice in particular the rough cyclic pattern of higher weathering fluxes of the mid-Paleozoic and much of the Mesozoic and the lower fluxes of the early Phanerozoic, late Paleozoic, and Cenozoic. The basalt calcium release fluxes vary by about a factor of two and appear slightly higher at times of low plate accretion rates and lower at times of higher plate accretion rates [data from numerical model output of MAGic (Arvidson et al., 2006)] as modified in Arvidson et al. (2011).

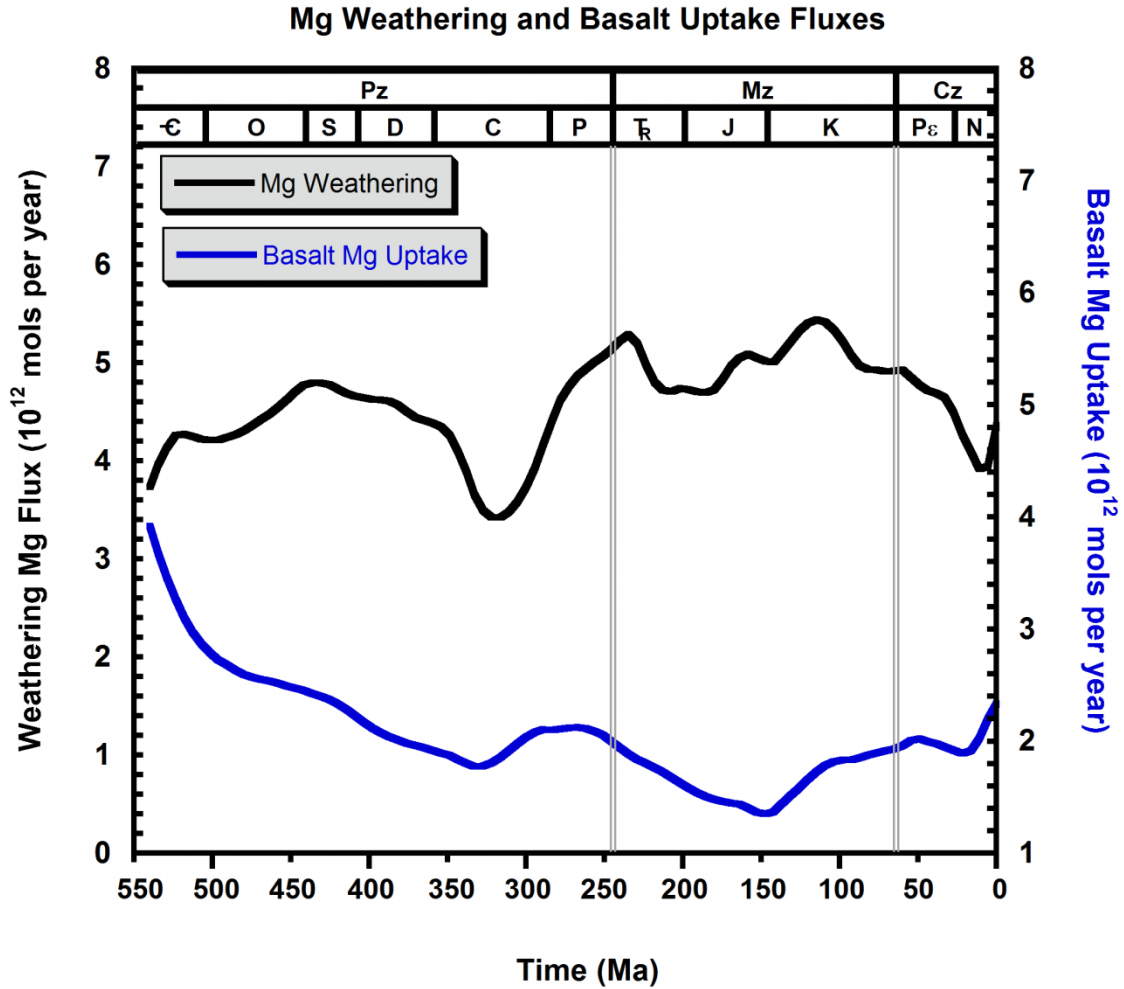


Figure 4. The results of numerical calculations from MAGic showing the magnesium flux to the ocean via rivers and groundwaters from weathering reactions on land and the magnesium taken up from seawater due to basalt-seawater reactions in the seafloor in 10^{12} mol y^{-1} . Similar to the calcium fluxes in Figure 3 but not as pronounced, notice in particular the rough cyclic pattern of higher weathering fluxes of the mid-Paleozoic and much of the Mesozoic and the lower fluxes of the early Phanerozoic, late Paleozoic, and Cenozoic. The basalt magnesium uptake fluxes vary by about a factor of 2.5 and appear slightly higher at times of low plate accretion rates and lower at times of higher plate accretion rates (*ibid*).

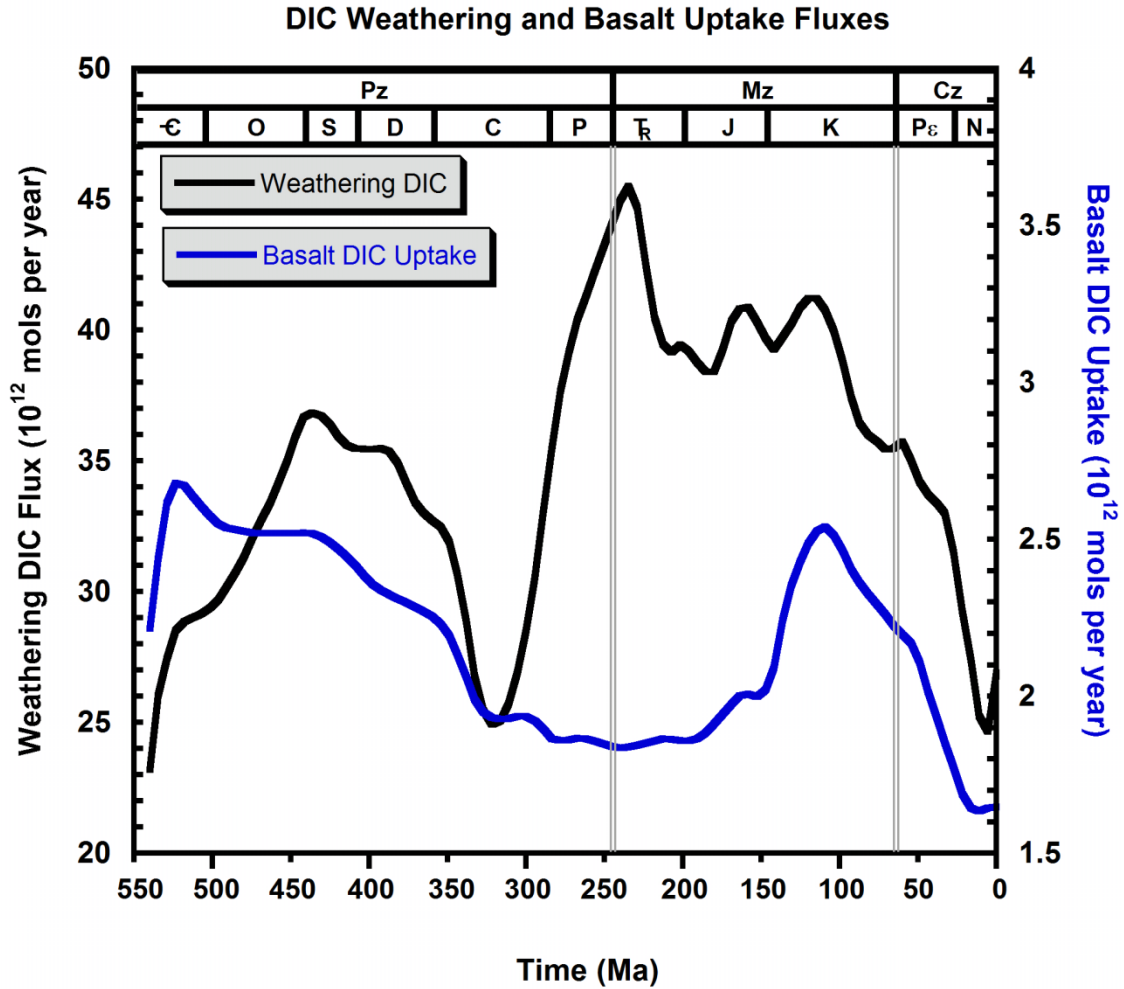


Figure 5. The results of numerical calculations from MAGic showing the dissolved inorganic carbon (DIC, mainly bicarbonate) flux to the ocean via rivers and groundwaters from weathering reactions on land and the DIC taken up from seawater due to basalt-seawater reactions in the seafloor in $10^{12} \text{ mol y}^{-1}$. Similar to the calcium fluxes in **Figure 3**, notice in particular the pronounced cyclic pattern of higher weathering fluxes of the mid-Paleozoic and much of the Mesozoic and the lower fluxes of the early Phanerozoic, late Paleozoic, and Cenozoic. The basalt DIC uptake fluxes also exhibit a cyclic pattern and vary by about a factor of 1.5, appearing higher at times of high plate accretion rates and lower at times of lower plate accretion rates (*ibid*).

Atmospheric CO₂

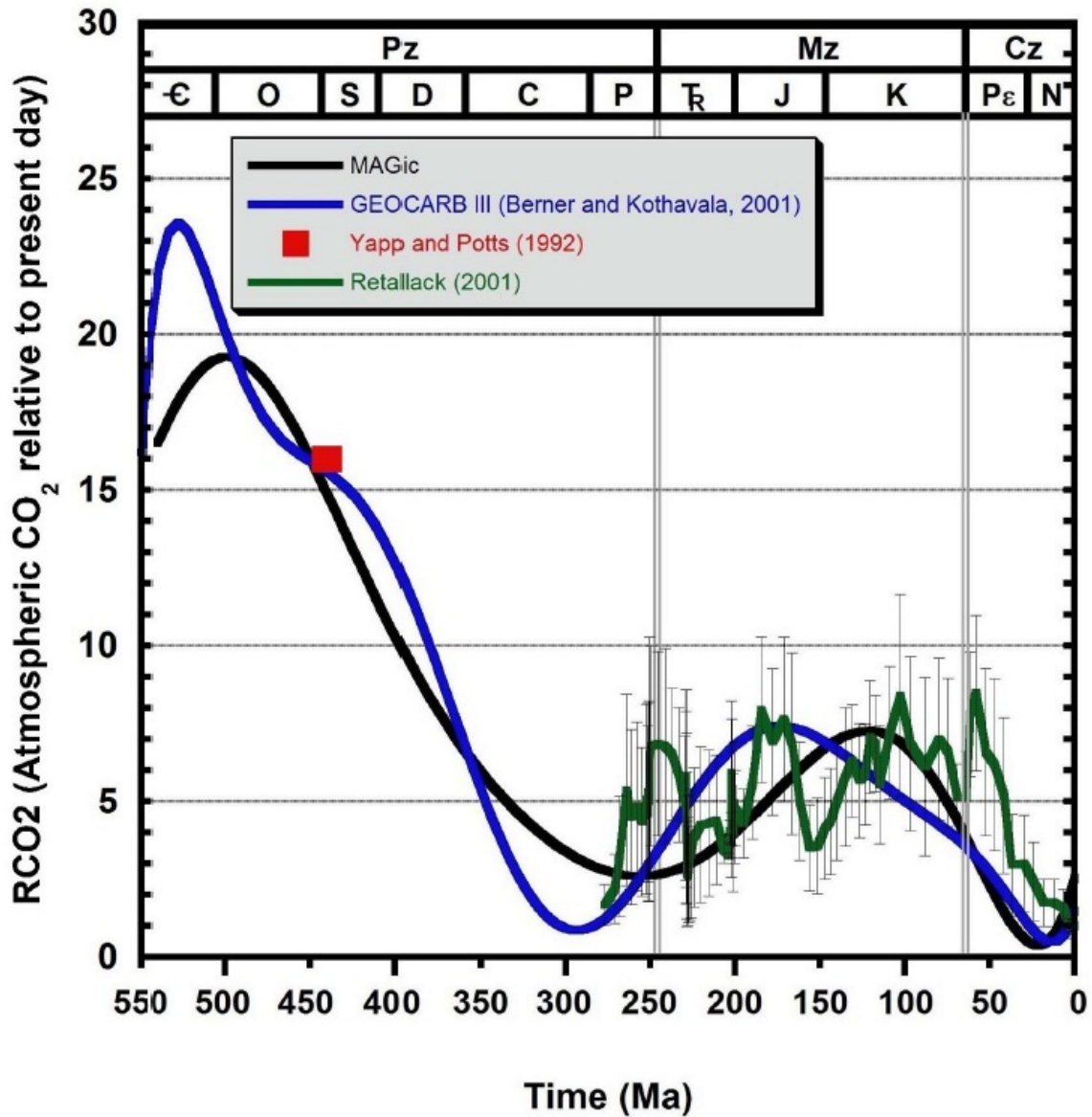


Figure 6. Phanerozoic long-term deep time generalized paleoatmospheric CO₂ concentrations relative to the pre-Anthropocene value of ~300 ppmv. Model calculations from MAGic (Arvidson et al., 2006, 2011) and GEOCARB III (Berner and Kothavala (2001) are shown for comparison. The green line is a trend line through the ranges (bars) in proxy fossil plant stomatal data for atmospheric CO₂ of Retallack (2001). The red square is Yapp and Potts (1992) data point of paleoatmospheric CO₂ derived from paleosols. Notice the overall cyclic pattern in Phanerozoic atmospheric CO₂ levels with concentration values increasing from the beginning of the Cambrian into the mid-Paleozoic and then falling toward the end of the Paleozoic and rising once more into the mid-Mesozoic and then falling into the Cenozoic.

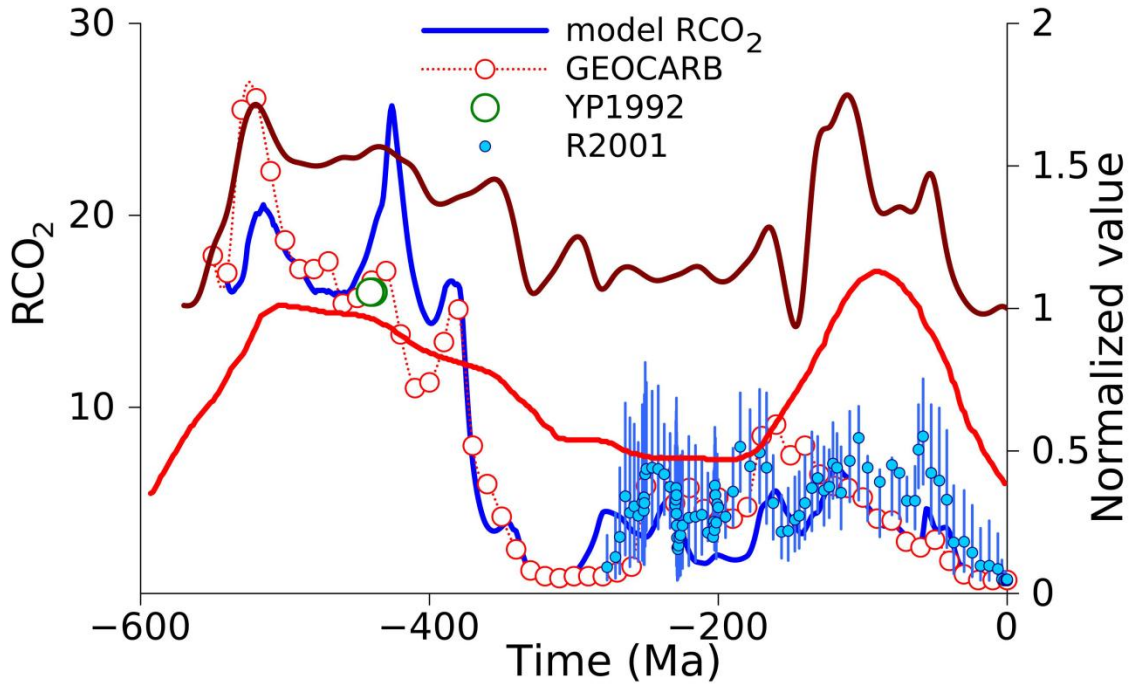


Figure 7. First order sea level changes, accretion rate, and paleoatmospheric CO₂ through the Phanerozoic Eon. The brown curve is a normalized forcing function used in the GEOCARB and MAGic models to simulate sea floor accretion rate (e.g., Berner and Kothavala, 2001); the red curve is an estimate of relative eustatic sea level variation, based on data from Vail et al. (1977) modified by Arvidson and Mackenzie (1997). Atmospheric CO₂ is shown as plotted relative to present day concentration (RCO₂). The proxy CO₂ data from Yapp and Potts (1992) obtained from paleosols and from the fossil plant stomata of Retallack (2001) are also shown (after Mackenzie et al., 2011).

Ocean Calcium Relative Sink Strength

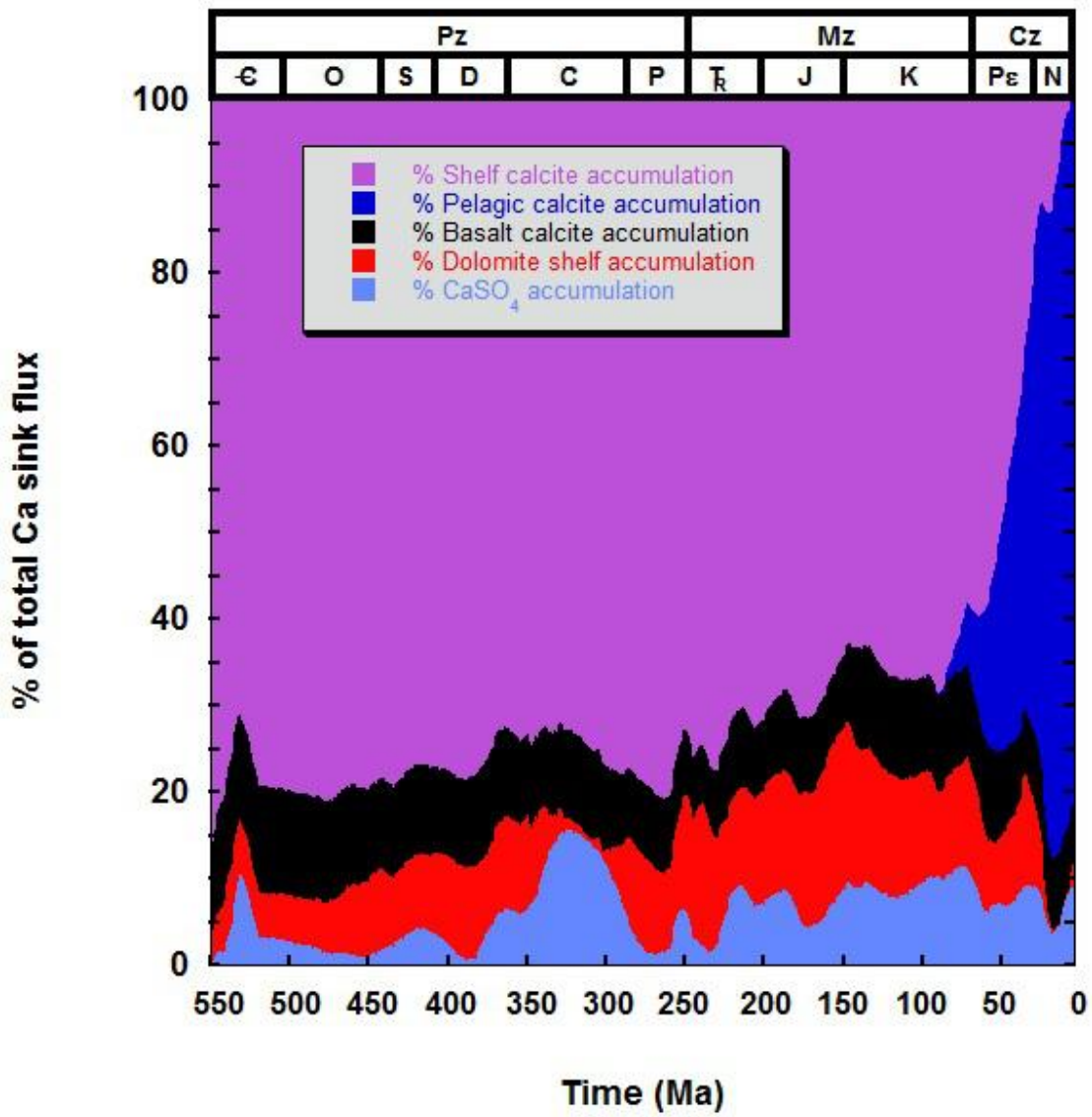


Figure 8. The relative sink strengths of various solid phase marine reservoirs of calcium in percent of total calcium flux to the reservoirs through Phanerozoic time [data from numerical model output of MAGic (Arvidson et al., 2006)], as modified in Arvidson et al. (2011).

Ocean Mg Relative Sink Strength

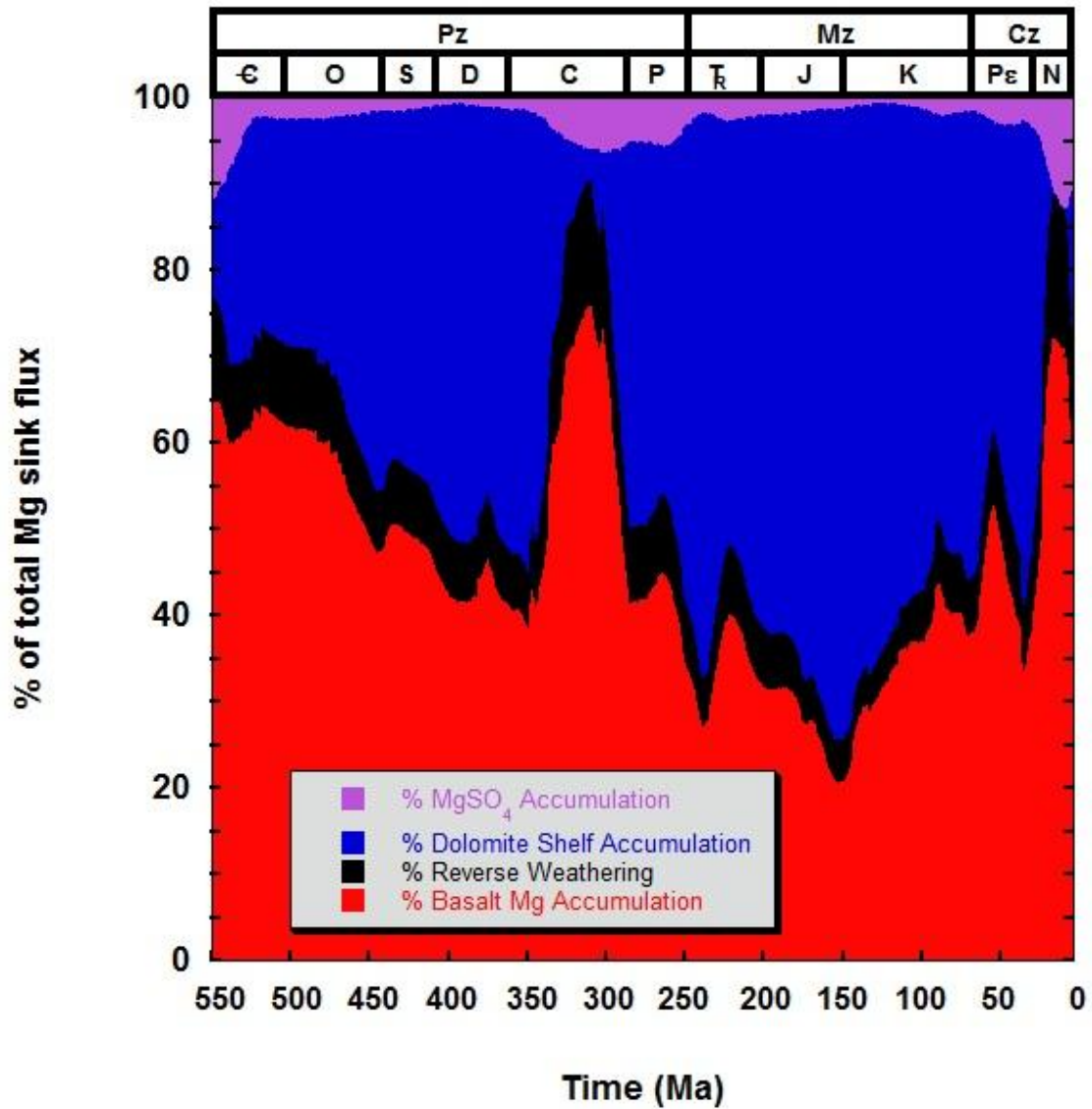


Figure 9. The relative sink strengths of various solid phase marine reservoirs of magnesium in percent of total magnesium flux to the reservoirs through Phanerozoic time (*ibid*).

Ocean Carbon Relative Sink Strength

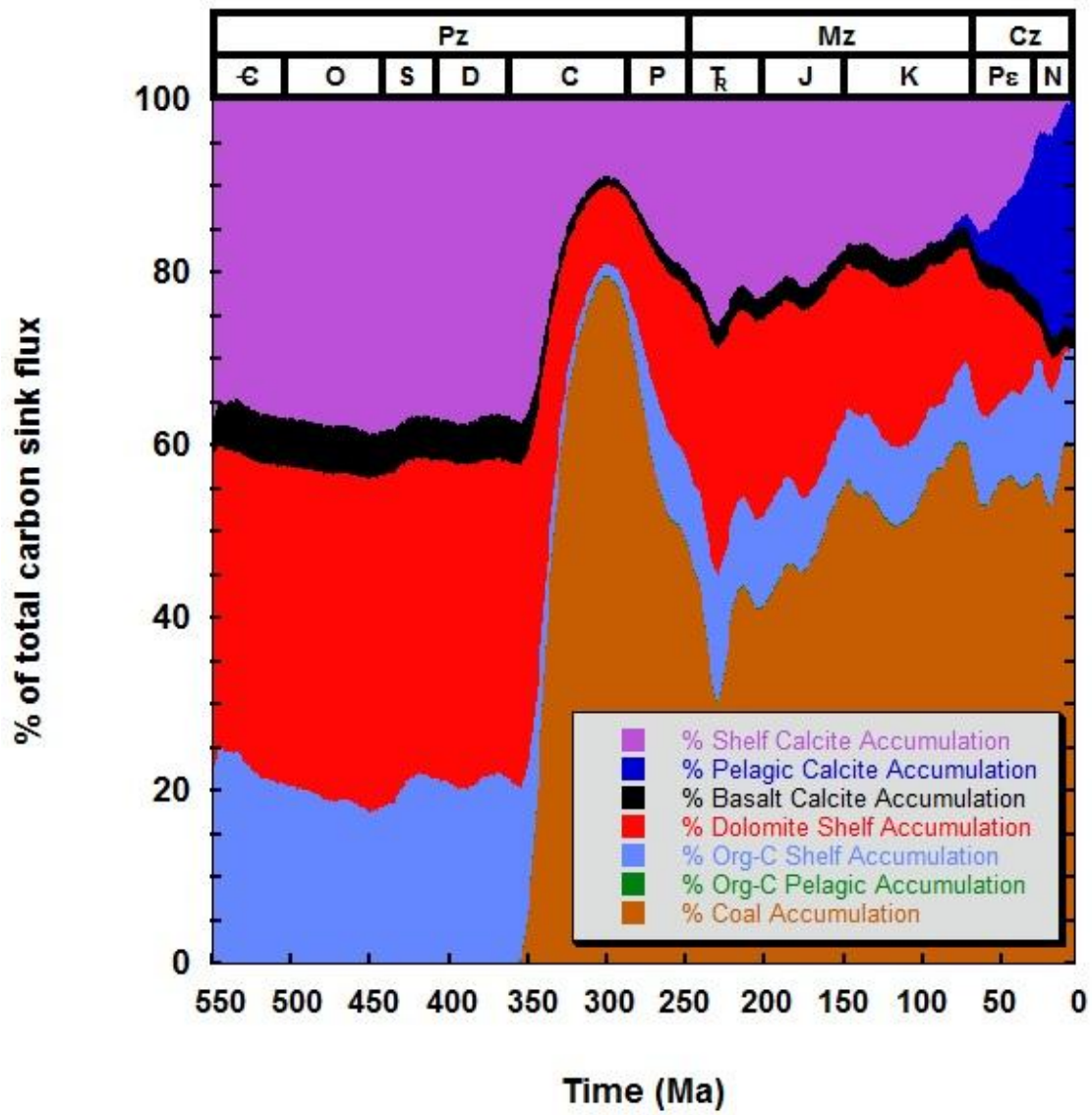


Figure 10. The relative sink strengths of various solid phase marine reservoirs of carbon in percent of total carbon flux to the reservoirs through Phanerozoic time (*ibid*).

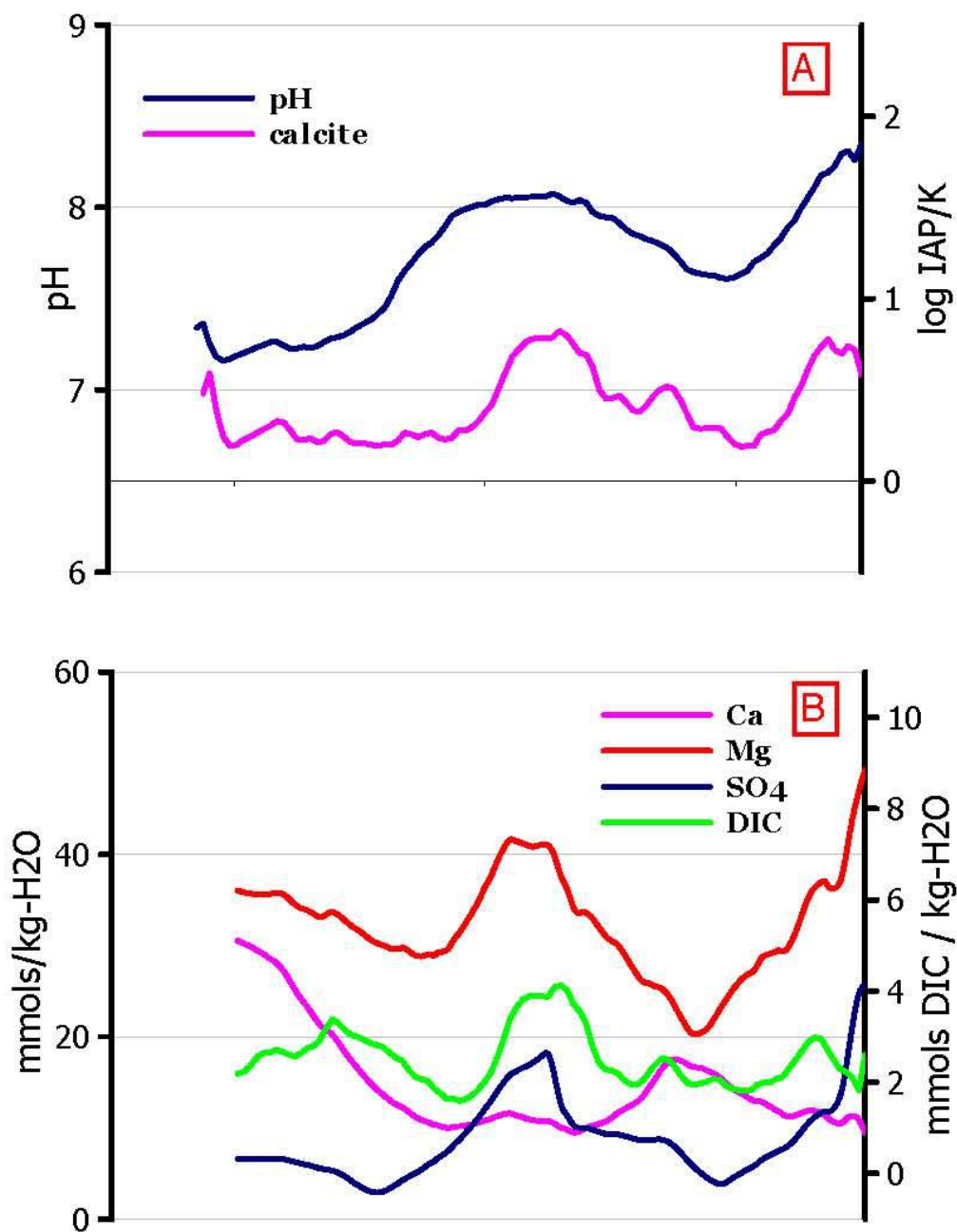


Figure 11. MAGic seawater concentration-age trends through the Phanerozoic. (A) pH and seawater saturation state with respect to calcite, computed from Pitzer equations; (B) Seawater dissolved Ca, Mg, DIC, and sulfate concentrations. There is a general cyclic variation in Mg/Ca and SO₄/Ca ratios (Fig. 14E), thus times of slow plate accretion rates, low sea levels, and low CO₂ are times of high Mg/Ca and SO₄/Ca ratios; conversely, low ratios are associated with high plate accretion rates, sea levels, and CO₂ (cf. Fig. 7). The cyclicality in calcite saturation state and pH also tracks the paleoatmospheric CO₂ curve (Figs. 6, 7, 12, and 14), with high CO₂ levels correlating with lower seawater pH and calcite saturation state, and lower pCO₂ levels with higher pH and saturation state. Extended periods of low seawater pH are natural periods of ocean acidification (OA) [data from Arvidson et al. (2006) as modified in Arvidson et al. (2011)].

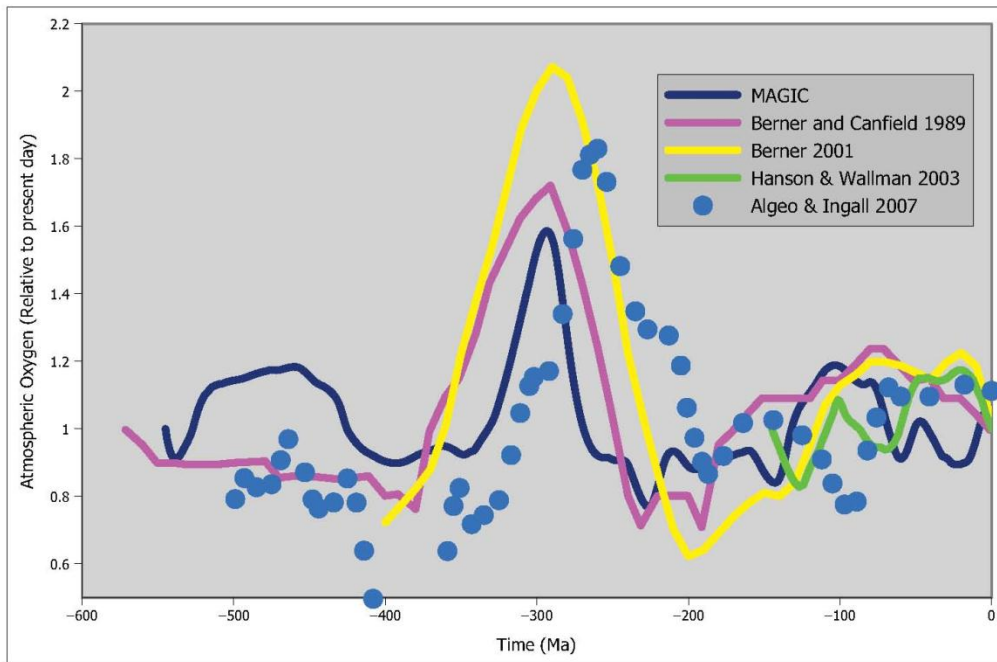


Figure 12. Comparison of atmospheric oxygen estimates. [Describe MAGIC (yellow), Berner and Canfield (1989), Berner (2001), Hanson and Wallmann (2003; figure legend shows “Wallman”, needs correction), and Algeo and Ingall (2007).]

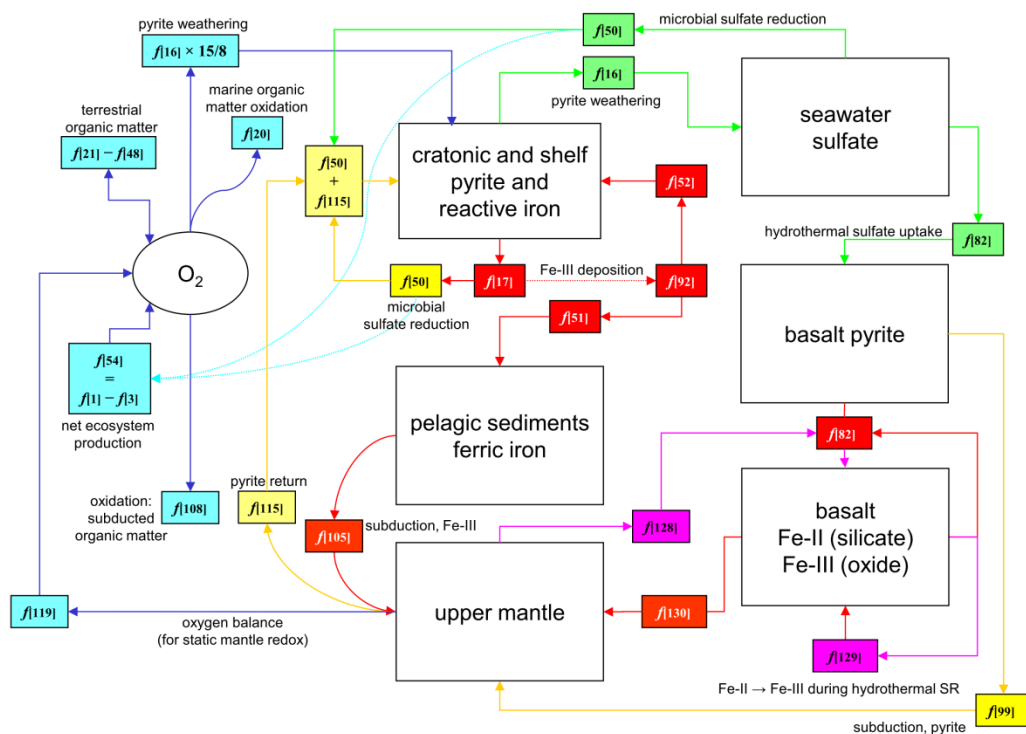


Figure 13. Interactions of organic carbon, iron, and sulfur biogeochemical cycles and their role in regulating atmospheric oxygen through the Phanerozoic Eon. The numbered labels refer to either reservoirs identified by bold italic font, or flux indices ($f[i]$) in the MAGic model (see Table A1, Arvidson et al., 2006). The flows related to oxygen are shown in blue, sulfate in green, ferric iron in gold, and reduced iron silicate as magenta. In addition to terrestrial organic matter cycling (burial – oxidation, $f[21] - f[48]$), oxidation of marine-derived organic matter on land ($f[20]$), and oxidation of pelagic organic matter, atmospheric oxygen is also controlled by the partitioning of iron between reduced and oxidized phases of sulfur and iron. Pyrite is produced both by microbial sulfate reduction ($f[50]$) in sediments and by hydrothermal sulfate reduction within seafloor basalt ($f[82]$). Pyrite oxidation ($f[16]$) consumes oxygen, as does hydrothermal pyrite formation, which involves production of ferric iron ($f[129]$). Although its flux is small, for purposes of the steady state maintenance of O_2 , the oxygen bound within this phase is ultimately returned to the atmosphere in the model ($f[119]$). The precise mechanism for this return flux is problematic and not well understood (after Arvidson et al., 2006).

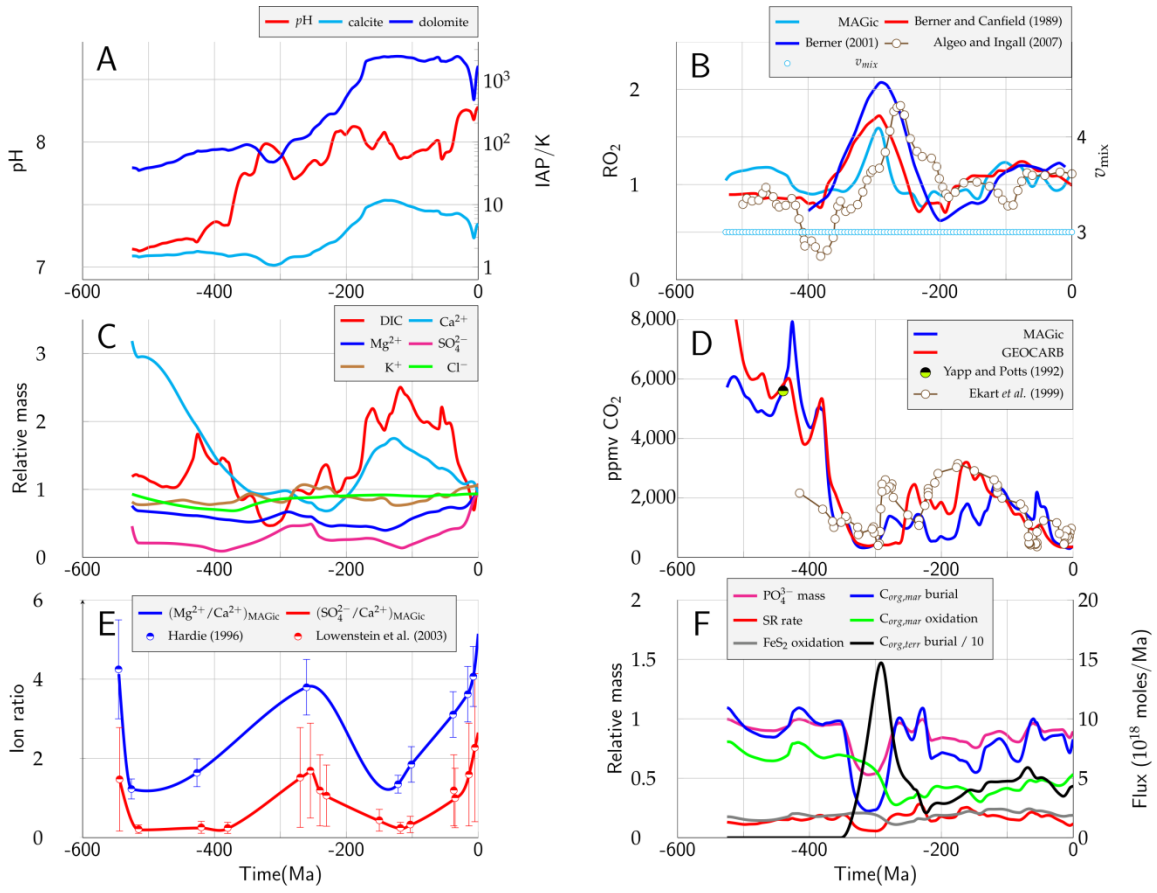


Figure 14. Summary figure of MAGic baseline run (fixed $v_{mix} = 3$). [To do]

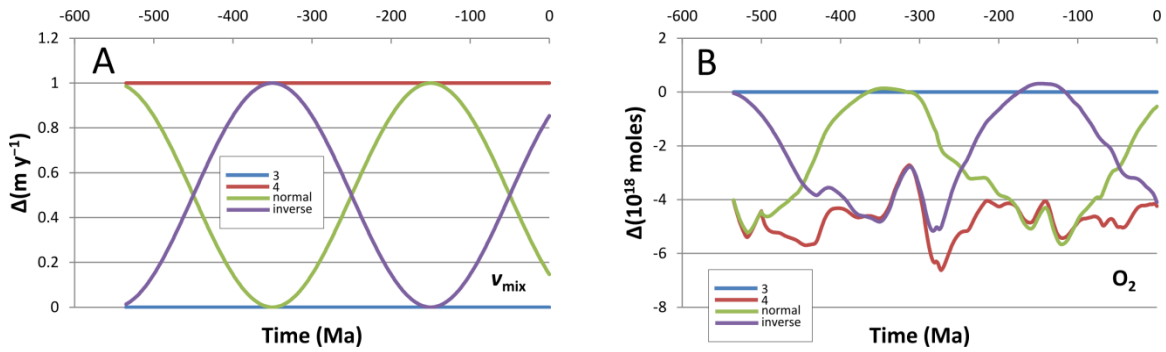


Figure 15. Sensitivity of atmospheric oxygen to simple variations in mixing rate (v_{mix}) over the Phanerozoic. (A) Four runs were made, in which the value of v_{mix} was fixed at 3 (blue curve) or 4 (brown curve), or cycled between these fixed values; the cyclic runs are arbitrarily differentiated as “normal” (green curve) and “inverse” (magenta curve). (B) The resulting variation in the total mass of atmospheric oxygen, expressed as an absolute deviation, $\Delta(O_2)$, from the $v_{mix} = 3$ (blue line at $\Delta = 0$) results; colors for other curves as in (A). In general, an *increase* in the mixing rate brings about a *decrease* in atmospheric O_2 , as more oxygen is consumed in the aerobic decomposition of organic matter, oxic weathering of pyrite, and related processes. See Figures 16, 17 and supporting text for discussion.

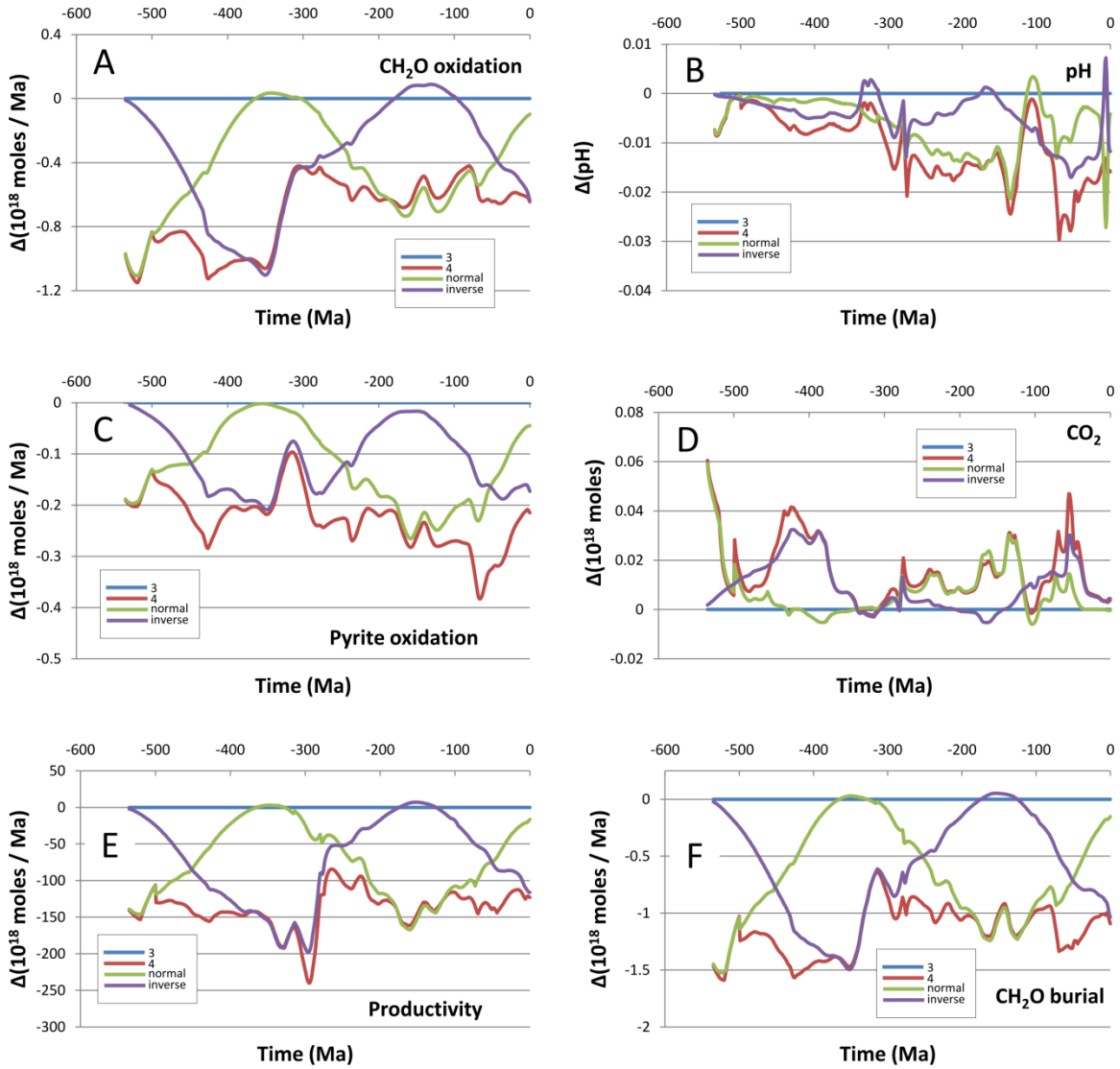


Figure 16. Variations in oxidation fluxes of marine organic matter (A) and pyrite (C), compared to changes in pH (B) and CO₂ (D), as well as bioproductivity (E; BP term of eq. 4), and marine organic matter burial (F; F_B term of eq. 6) brought about by v_{mix} -forced changes in O₂ concentration (Fig. 15B), expressed as Δ values relative to $v_{\text{mix}} = 3$ (color scheme identical to Fig. 15). See text for discussion.

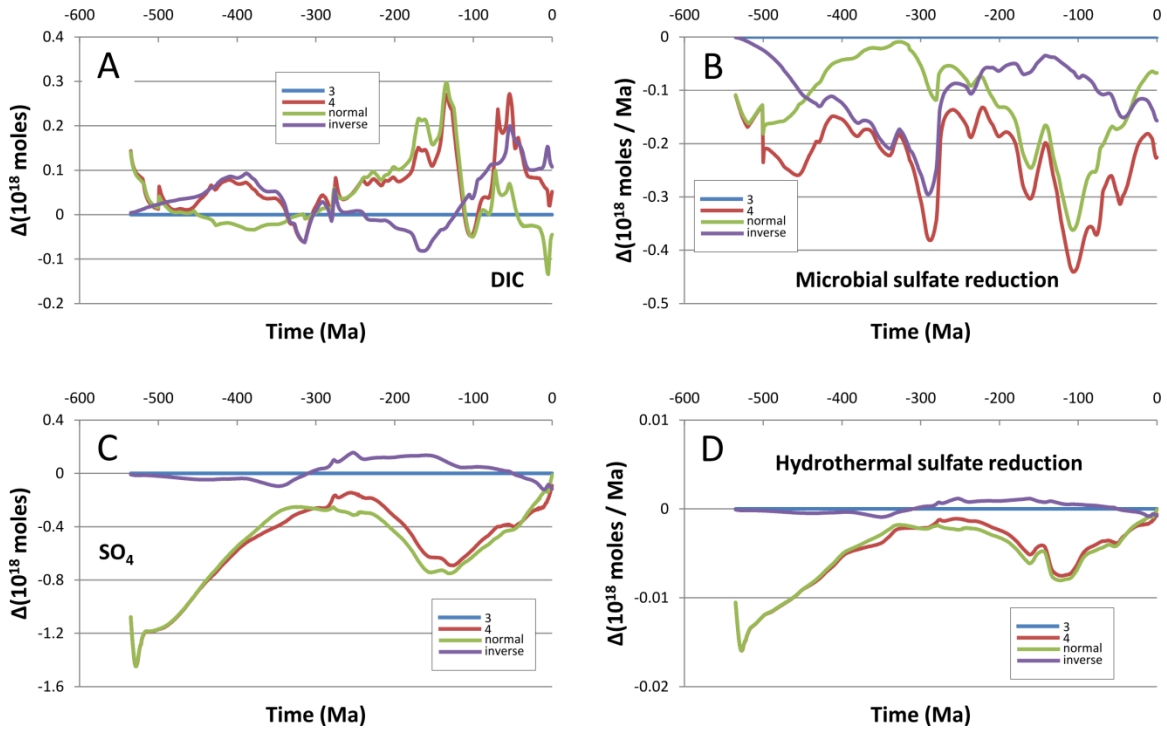


Figure 17. Variations in the seawater masses of DIC (A) and SO_4 (C), and sulfur fluxes of arising from sulfate reduction during anaerobic oxidation of organic matter (B) and basalt-seawater interaction (D). See text for discussion.