

Phanerozoic record of plate tectonic control of seawater chemistry and carbonate sedimentation

Thomas Steuber* Institute of Geology, Mineralogy and Geophysics, Ruhr University, 44801 Bochum, Germany

Ján Veizer Institute of Geology, Mineralogy and Geophysics, Ruhr University, 44801 Bochum, Germany, and Ottawa-Carleton Geoscience Centre, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

ABSTRACT

Sr concentrations in Phanerozoic biological calcite suggest a close link between fluctuations in the Sr/Ca ratio of seawater, aragonite versus calcite sedimentation, and the Mg/Ca ratio of seawater, the entire chain being driven by the rate of production and hydrothermal alteration of the oceanic crust. Model simulations suggest that variations in hydrothermal and continental weathering fluxes cannot be the sole reason for the observed Phanerozoic seawater Sr/Ca trend. Changing Sr burial in marine carbonates is likely the most important mechanism that can explain the experimental data. During episodes of high seawater Mg/Ca ratios, aragonite was preferentially deposited, resulting in low seawater Sr/Ca ratios. At low Mg/Ca ratios, calcite was the dominant carbonate sediment, and the Sr/Ca ratio of seawater was high. The evidence for changing chemistry of seawater also has implications for the application of the Sr/Ca and Mg/Ca paleothermometers, in particular for pre-Quaternary samples, and for the assessment of diagenetic alteration of fossil skeletal carbonates by using Sr/Ca ratios.

Keywords: seawater, strontium, calcite, geochemical models, Phanerozoic.

INTRODUCTION

During the Phanerozoic Eon, the mineral composition of marine skeletal and inorganic carbonates oscillated between predominantly calcite, and aragonite plus high-Mg calcite. This oscillation was attributed to either the changing Mg/Ca ratio of seawater (Sandberg, 1975; Hardie, 1996; Stanley and Hardie, 1998) or to variations in atmospheric $p\text{CO}_2$ (Mackenzie and Pigott, 1981; Sandberg, 1983). Tectonics, specifically elemental fluxes related to the alteration of the newly formed oceanic crust, were postulated to be the ultimate cause (Wilkinson and Algeo, 1989; Hardie, 1996). Experimental evidence for the changing seawater chemistry is emerging (Kovalevich et al., 1998; Cicero and Lohmann, 2001; Lowenstein et al., 2001), and the attribution to tectonic causes is still tenuous. This contribution provides a compelling case for both the changing chemical composition of Phanerozoic seawater and the ultimate tectonic control.

Strontium is one of the major dissolved species in seawater (8 ppm), and marine carbonate sedimentation is its most important sink. Strontium may therefore respond strongly to perturbations in its input versus output fluxes. The molar distribution coefficient for Sr [$D_{\text{Sr}} = (M_{\text{Sr}}/M_{\text{Ca}})_{\text{carbonate}} / (M_{\text{Sr}}/M_{\text{Ca}})_{\text{seawater}}$] is close to 1 for aragonite of scleractinian corals and calcareous green algae, ranges from 0.13 to 0.28 for calcite of mollusks, calcareous nannofossils (coccoliths), and planktonic foraminifera (Morrison and Brand, 1986; Stoll et al., 1999; Elderfield et al., 2000), and varies from 0.05 to 0.20 for inorganic calcite (Morse and Bender, 1990). Biological aragonite formation is thus a much more effective sink for seawater Sr than is calcite precipitation, and shifts in the aragonite versus calcite production rates could be an important factor controlling the Sr/Ca ratio of seawater (Graham et al., 1982).

PHANEROZOIC Sr/Ca TREND

The database utilized for evaluation of the just-described propositions consists of a large number of low-Mg calcite shells¹. It includes 1116 Ordovician–Triassic brachiopods (Veizer et al., 1999), 278 Jurassic–Cretaceous belemnites (Podlaha et al., 1998), and 93 Cretaceous rudist bivalves. The latter are supplemented by 592 analyses of intrashell variations in 11 rudist shells (Steuber, 1999, 2002). Samples were screened for diagenetic alteration, and most are believed to have retained their near-original geochemical compositions (Veizer et al., 1999; Steuber, 1999).

The curve of Sr concentrations in Ordovician to Cretaceous biological low-Mg calcite (Fig. 1) shows high concentrations for the early and middle Paleozoic samples, decreasing values from the Silurian to the Carboniferous, low concentrations from the Carboniferous to the Jurassic, and an increase from the Late Jurassic to the Cretaceous. No data are available for the Tertiary, but modern biological low-Mg calcites have concentrations that are lower than those in the Late Cretaceous samples. A few published Sr concentrations for Tertiary low-Mg calcite of brachiopods (see footnote 1) support the declining seawater

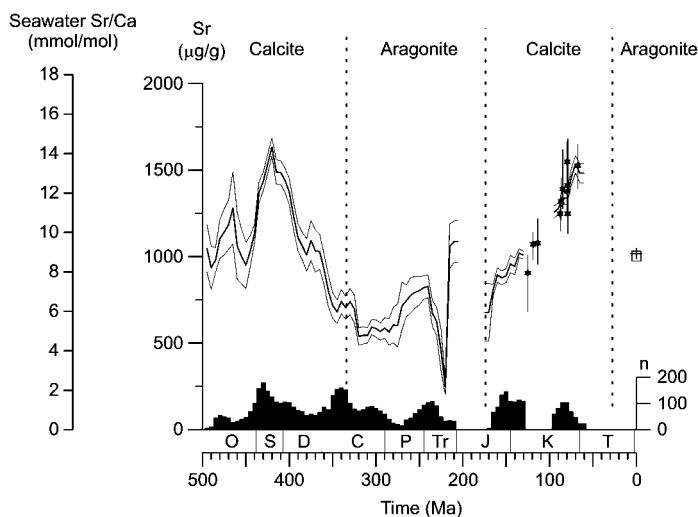


Figure 1. Sr concentrations in biological low-Mg calcite (see text footnote 1). Mean values (bold curve) and two standard errors (thin curves) were calculated by moving 20 m.y. window in 5 m.y. intervals across data set. Bar chart at bottom shows number of data falling into each 5 m.y. step. Ranges (vertical lines) and mean values (stars) of intrashell variations for concentrations in single rudist shells are also shown, but are not used in calculation of running means. Brachiopod and belemnite data have stratigraphic resolution on level of biozones. Stratigraphic positions of rudist shells were assigned by strontium isotope stratigraphy (Steuber, 2001). Cross and box on right show mean values for Sr concentrations in modern brachiopods (Carpenter and Lohmann, 1992) and bivalves (Al-Aasm and Veizer, 1986), respectively. Episodes of aragonite and calcite seas are from Stanley and Hardie (1998). Sr/Ca ratio of seawater is calculated by assuming mean distribution coefficient ($D_{\text{Sr}} = 0.13$), as observed in modern brachiopods and bivalves.

*E-mail: thomas.steuber@ruhr-uni-bochum.de.

¹GSA Data Repository item 2002132. Sr concentrations in Phanerozoic biological low-Mg calcite, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA, editing@geosociety.org, or at www.geosociety.org/pubs/ft2002.htm.

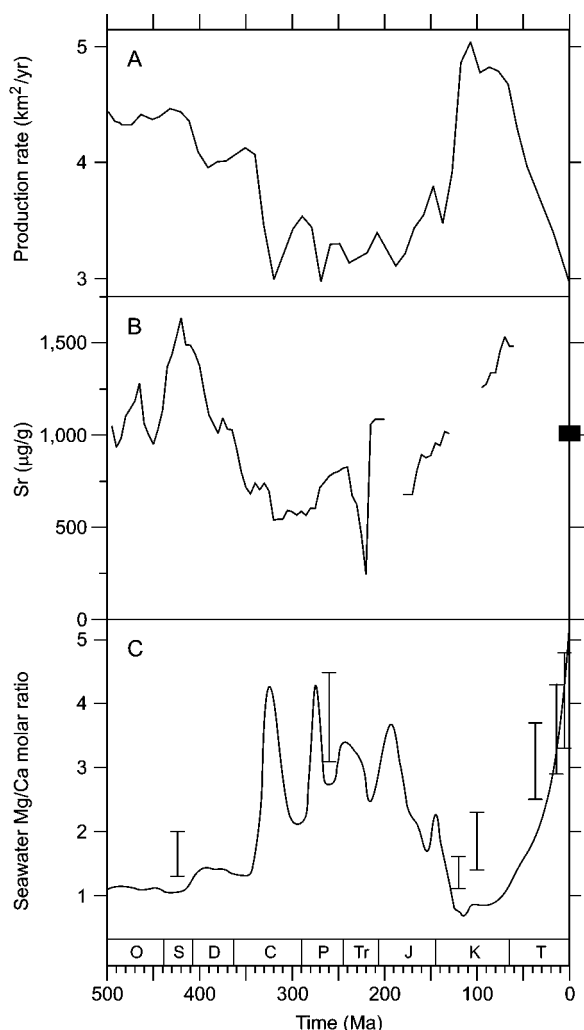


Figure 2. Production rate of oceanic crust and Phanerozoic trends in seawater chemistry. A: Production rate of oceanic crust (Gaffin, 1987). B: Sr concentrations in biological low-Mg calcite; box represents average Sr concentration of modern brachiopods and bivalves (cf. Fig. 1). C: Mg/Ca ratio of seawater; vertical bars are based on experimental data from fluid inclusions in halite (Lowenstein et al., 2001), whereas trend line results from model calculations (Stanley and Hardie, 1998).

Sr/Ca ratios commencing in the Late Cretaceous, but the general scarcity of such data precludes calculation of running means and these data are therefore not included in Figure 1. This macrofossil based Late Cretaceous and Tertiary decline in the Sr/Ca ratio is opposite to the trend reported for coeval pelagic carbonates (Renard, 1985). The latter trend, the progressive loss of Sr with age, likely reflects the long-term postdepositional stabilization of pelagic carbonate oozes (Veizer, 1989), a proposition partially at variance with model calculations (Richter and Liang, 1993). Note, however, that oozes younger than 10 Ma that are not yet strongly affected by diagenesis show a decline in Sr/Ca ratio similar to that based on macrofossils (Hampt Andreasen and Delaney, 2000). Our record is incomplete for the Early and Middle Jurassic, and this gap marks the transition between values obtained from brachiopods and belemnites, respectively. The concentration shift across this gap therefore may be due to a somewhat different D_{Sr} for brachiopods and belemnites, or may be a reflection of a short-term change in seawater composition. The Aptian data for the Cretaceous belemnites and rudists overlap, arguing for a similar D_{Sr} for both groups of the now extinct mollusks. Furthermore, recent brachiopods and mollusks have similar

TABLE 1. STEADY-STATE FLUXES OF Sr AND Ca USED IN SIMULATIONS

	Sr (10^{10} mol/yr)	Ca (10^{13} mol/yr)
Continental weathering flux	3.33*	2.0 [†]
Hydrothermal flux	1.05*	0.5 [§]
Uptake by authigenic minerals	0.70 [#]	0.5**
CaCO ₃ burial [¶]	3.68 ^{††}	2.0 [†]

*After Palmer and Edmond (1989).

[†]Mean value from various estimates, compiled in Stoll and Schrag (1998).

[§]After Berner and Berner (1996).

[#]Value within the range given by various sources, as compiled in Wallmann (2001) and adopted here to balance the modern assumed steady-state Sr budget.

**Value required to balance modern Ca budget of seawater; refers to uptake of Ca during low-temperature alteration of oceanic crust.

^{††}Sr burial in CaCO₃ depends upon the evolving Sr/Ca ratio of seawater in model runs.

D_{Sr} values (Fig. 1). It is therefore likely that all these fossil groups had similar Sr distribution coefficients.

MODEL SIMULATIONS OF THE SEAWATER Sr/Ca BUDGET

The curve of Sr concentrations in Phanerozoic biological low-Mg calcite is in phase with the previously advocated (Sandberg, 1983; Stanley and Hardie, 1998) calcite and aragonite "seas" (Fig. 1). The aragonite seas correspond to low Sr concentrations; the calcite ones correspond to high concentrations. This curve also mimics the production rates of the oceanic crust and is inversely correlated with the postulated, and partially experimentally confirmed, Mg/Ca ratio of Phanerozoic seawater (Fig. 2). This covariance suggests that we are dealing with coupled phenomena, and the most reasonable proposition is that all these variables are ultimately driven by tectonics, specifically the seafloor-spreading rates that, in turn, control the associated hydrothermal and low-temperature alteration processes. Can seafloor spreading alone account for the observed Sr/Ca variations in Phanerozoic seawater? Taking the Sr and Ca fluxes summarized in Table 1 as representative, a doubling or halving of the present-day hydrothermal Sr flux results in the new steady-state seawater Sr/Ca ratios of 11.3 and 7.6, respectively (Fig. 3). These scenarios are not sufficient to explain the amplitude of variations in the experimental data set (Fig. 1). Alternatively, one could argue that the Sr/Ca covariance with the curve for seafloor-production rate (Fig. 2) is a consequence of coupling between the rate of seafloor spreading and the intensity of orogenic activity, the latter controlling the continental weathering fluxes of Sr and Ca. A factor of two variability in the Sr/Ca ratio of the riverine input, e.g., due to differing proportions of silicates to carbonates in the catchments (Gaillardet et al., 1999; Gibbs et al., 1999), could generate the magnitude of changes observed in the experimental record (Fig. 3). However, the catchments of most large rivers contain enough carbonates for this lithology to dominate the composition of their dissolved load (Gaillardet et al., 1999). Evaluations based on paleogeographic inventories (Bluth and Kump, 1991) show that carbonates, and not the silicates with their high Sr/Ca ratios, were the dominant lithologies in the source areas at times of high seawater Sr/Ca ratios. It therefore appears that the Sr/Ca seawater secular trend cannot be due solely to variability in either the hydrothermal or weathering fluxes, and that other, tectonically related, factors are required to explain the trend.

Large shifts in seawater Sr/Ca ratios, similar to those inferred from our data, can also result from varying the proportion of aragonite versus calcite in the carbonate deposits (Fig. 3). The high values, such as those in the Silurian and the middle Cretaceous (Fig. 1), can be generated at times of dominant calcite precipitation, because the relevant D_{Sr} is ~ 0.13 , thus partitioning the bulk of the input Sr into seawater. However, in order to generate a low Sr/Ca ratio, such as the one observed in the Carboniferous and Permian, the coeval carbonate sediments would have to contain an appreciable proportion of aragonite

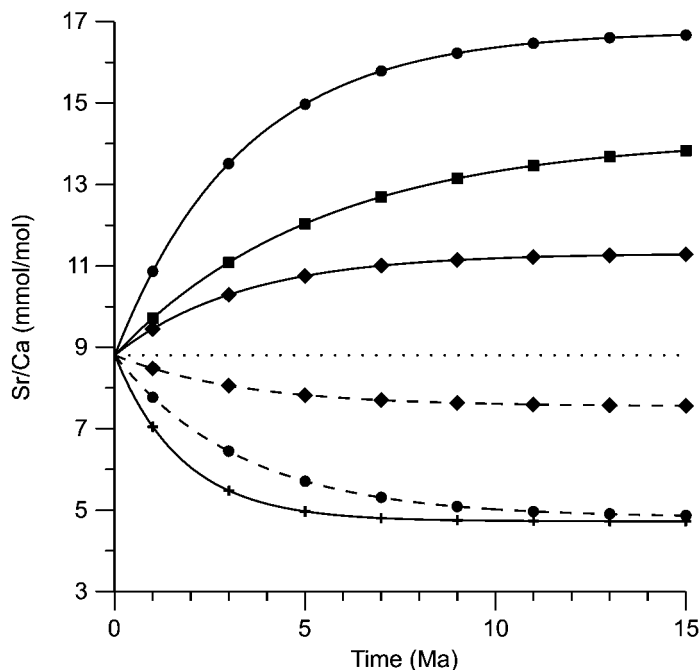


Figure 3. Response of seawater Sr/Ca molar ratio to changes in input vs. output fluxes. Considering that incorporation of Sr into carbonate mineral is linearly proportional to Sr/Ca ratio of seawater (Carpenter and Lohmann, 1992), Sr concentration in calcite or aragonite changes with changing seawater Sr/Ca ratio. As result, seawater Sr concentration is buffered and Sr/Ca ratio approaches new steady states only after 10–15 m.y. in model simulations. Dotted line—assumed modern steady state based on fluxes in Table 1. Diamonds—effect of doubling (solid curve) and halving (broken curve) modern steady-state fluxes of Sr for hydrothermal system (Table 1). Circles—doubling (solid curve) and halving (broken curve) of Sr flux from continental weathering. In all these simulations, Sr burial in carbonates is assumed to be controlled by $D_{Sr} = 0.21$ low-Mg calcite. Remaining two curves simulate variable calcite vs. aragonite sedimentation. Boxes—situation in which it is assumed that all carbonates formed as calcite ($D_{Sr} = 0.13$). Crosses—predominance of aragonite sedimentation, with assemblage composed of 23% calcite ($D_{Sr} = 0.13$) and 77% aragonite ($D_{Sr} = 0.47$). Justification for low D_{Sr} of aragonite is explained in text. Ca fluxes and Ca seawater concentrations are assumed to have been constant in all simulations.

(Fig. 3). The geologic record is consistent with such a proposition (Sandberg, 1975; Stanley and Hardie, 1998). For example, the Late Cretaceous tropical shelves, during times of high seawater Sr/Ca ratios, were dominated by calcitic rudist bivalves (Steuber, 2002), whereas the Early Cretaceous and modern shelves, during times of low seawater Sr/Ca ratios, were dominated by aragonitic coral-algal communities.

The amount of Sr that is recycled to seawater during diagenetic stabilization of carbonates is also an important variable for the Sr/Ca budget of seawater, particularly at times of high aragonite productivity on the shelves. Estimates of this diagenetic flux vary from 17% of the Sr originally incorporated into marine precipitates (François and Walker, 1992) to 70%–90% when shelf carbonates are subaerially exposed to meteoric diagenesis soon after deposition (Stoll and Schrag, 1998). The latter happens mostly during rapid, short-term (10 k.y. range) sea-level changes, such as those of the Pleistocene. While diagenetically stabilized carbonates typically have low Sr concentrations, it is nevertheless mostly the subsidence of continental margins and the burial of much of the original Sr in pore waters or authigenic minerals (Veizer, 1989) that controls the long-term diagenetic Sr flux. Celestite is a common diagenetic product in the Cenozoic deep-sea and periplatform sequences, and in fissures that crosscut such diagenetically stabilized carbonates (Melim et al., 2002). This mineral is estimated to hold a significant proportion of the total Sr in such sediments (Baker and

Bloomer, 1988; Swart and Guzikowski, 1988). Our model (Fig. 3) accounts for this long-term recycling flux by assuming that about one-half of the original Sr buried in shallow-water carbonates is recycled to seawater (Schlanger, 1988). This assumption is implicit in the low D_{Sr} (0.47) for model aragonite. Note that even small changes in the diagenetic recycling flux have considerable impact on the Sr/Ca ratio of seawater. For example, changing the D_{Sr} for aragonite from 0.47 to 0.4 or 0.6 results in seawater Sr/Ca ratios of 5.5 and 3.8, respectively. This underscores the importance of the original composition of carbonate sediments, and of the variable diagenetic recycling flux, on the overall chemistry of seawater.

The model estimates just discussed did not account for changes in the Ca concentration of seawater; however, changes in the Mg/Ca ratio of seawater were considered to have been the driving force for the calcite versus aragonite production (Stanley and Hardie, 1998). A rise from Mg/Ca ratio of one (e.g., the Upper Cretaceous) to five (modern seawater) was postulated to have been a result of either large variations in Mg concentrations coupled with minor Ca changes (7.5–15 mmol/L; Wilkinson and Algeo, 1989), or Ca concentration changes from 10 to 30 mmol/L coupled with minor Mg variations (Stanley and Hardie, 1998). Note, however, that Ca concentration of 30 mmol/L, such as during the Cretaceous, would require simultaneous doubling of the hydrothermal Sr flux and a low distribution coefficient of 0.10 for the average marine carbonate sedimentation in order to generate the observed Cretaceous Sr/Ca ratio, a scenario difficult to conceive.

IMPLICATIONS

The modeling considerations suggest that the variable proportions of aragonite to calcite deposition, if coupled with a diagenetic recycling flux, can generate the observed Sr/Ca ratios for Phanerozoic seawater (Fig. 1), regardless of the role that the complementary hydrothermal and weathering fluxes may have played. The preference for calcite or aragonite in marine carbonates has been attributed either to changing atmospheric pCO_2 or to a variable Mg/Ca ratio of seawater (Mackenzie and Pigott, 1981; Sandberg, 1983; Hardie, 1996; Stanley and Hardie, 1998). Carbonate saturation on time scales exceeding that of ocean mixing is buffered by the dynamics of the lysocline (Sundquist, 1991) and not by pCO_2 . Although this kind of buffering may or may not have been the case during the Paleozoic and early Mesozoic, when the accumulation of deep-sea carbonates was of minor importance and calcite compensation may have been less effective, the Mg/Ca ratio of seawater is the more likely controlling factor of carbonate mineral composition, because Mg inhibits the formation of calcite (Morse et al., 1997). Because the hydrothermal alteration of young oceanic crust effectively exchanges Mg for Ca, the production rate of the oceanic crust modulates the Mg/Ca ratio of seawater (Edmond et al., 1979). The low Mg/Ca ratio favors precipitation of calcite and, as a result, higher retention of Sr in seawater. At slow crustal production rates, the high Mg/Ca ratio favors aragonite precipitation and a higher rate of Sr removal from seawater.

The variations in Sr/Ca ratio of seawater also have important implications for utilization of Sr concentrations as a criterion of the degree of preservation of marine carbonates (Veizer et al., 1999). High Sr concentrations are generally considered to reflect minor alteration of biological carbonates, but our data show that different thresholds must be applied for skeletal carbonates that formed during episodes of aragonite and calcite seas, respectively. Improved knowledge about compositional changes in Phanerozoic seawater is also important for the derivation of paleotemperatures from Sr/Ca and Mg/Ca ratios in fossil skeletal carbonates, because the elemental ratios in seawater are needed as a starting point for the application of these paleothermometers, particularly for the pre-Quaternary samples (Stoll and Schrag, 1998; Lear et al., 2000).

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