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Chemical Geology 217 (2005) 113–126

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

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# A model of Phanerozoic cycles of carbon and calcium in the global ocean: Evaluation and constraints on ocean chemistry and input fluxes

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Received 23 March 2004; received in revised form 16 December 2004; accepted 27 December 2004

## Abstract

The relationships between the global carbon cycle and paleo-climates on short and long time scales have been based on studies of accumulation rate of the two main components of the sedimentary carbon reservoir, organic carbon and carbonate carbon. Variations in the rate and proportion of carbonate burial through Phanerozoic time have been attributed to the effects of tectonics on eustasy, atmospheric $CO_2$ concentration, MOR (Mid-Ocean Ridge) hydrothermal flux, and weathering and riverine flux.

This study addresses the history of variations in the state of the surface ocean and its degree of saturation with respect to calcite and aragonite, based on a geochemical model that considers the Phanerozoic atmospheric $P_{CO_2}$ and surface ocean temperature reconstructions as the main forcings on the system. The results show that, using near-present-day values of ocean salinity and alkalinity, the Early Paleozoic and Middle Mesozoic oceans are calculated to be undersaturated (or nearly undersaturated) with respect to $CaCO_3$. For the near-present-day values of supersaturation ($\Omega$=ICP/$K_{sp}$) of 3–5 with respect to calcite, paleo-alkalinity of ocean water would have been up to 2.5 times greater than at present, although the pH values of surface ocean water would have been somewhat lower than the present values. This alkalinity factor is consistent with a higher calcium concentration (up to ×2.5) due to increased circulation at ocean spreading-zones and also higher salinity (up to ×1.5) attributed by other authors to segments of the geologic past. Our model results indicate that although $P_{CO_2}$ was a contributing factor to shifts between calcite and aragonite saturation of seawater, additional changes in alkalinity were needed to maintain supersaturation at the level of 3–5, comparable to the present. Continental weathering of crystalline and older carbonate rocks, in addition to MOR (Mid-Ocean Ridge) circulation, was likely an important mechanism for maintaining supersaturation of surface ocean water, particularly during times of increased carbonate storage.

*Keywords:* Phanerozoic; Calcium carbonate; Carbonate minerals saturation; Carbon cycle; Alkalinity

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doi:10.1016/j.chemgeo.2004.12.010

## 1. Introduction

Natural perturbations of the long-term carbon cycle and atmospheric $CO_2$ reservoir size have been suggested to impact global climate (e.g., Crowley and Berner, 2001). Variations in atmospheric $CO_2$ are likely linked to $CO_2$ variations within the oceanic reservoir because of its much greater carbon mass and relatively rapid exchange of $CO_2$ with the atmosphere. In the Earth surface environment, carbon exchange between atmospheric, biotic, soil, and oceanic reservoirs is generally rapid on a geologic time scale, with characteristic times from years to thousands of years, and it is referred to as the exogenic or short-term carbon cycle (e.g., Berner, 1999). The long-term carbon cycle, with characteristic times of $10^8$–$10^9$, years involves accumulation of oceanic sediments, their partial subduction and partial incorporation in the continental crust, volcanic and metamorphic degassing, continental uplift, erosion and chemical weathering (e.g., Rankama and Sahama, 1950).

The oceans are the largest short-term carbon cycle reservoir where mineral $CaCO_3$ and biologically produced organic matter form, that are the main sources of carbon to the sedimentary reservoir for long-term storage. Therefore, the oceanic reservoir of carbon and environmental conditions in that reservoir are important components of long-term carbon cycling.

The relationships between the global carbon cycle and paleo-climates on short and long time scales have largely been based on studies of accumulation rates of the two main components of the sedimentary carbon reservoir, organic carbon and carbonate carbon (Berner and Canfield, 1989; Wilkinson and Walker, 1989; Mackenzie and Morse, 1992; Bosscher and Schlager, 1993; Hayes et al., 1999; Walker et al., 2002). Variations in the rate and proportion of carbonate burial through Phanerozoic time have been variably attributed to the influence of eustasy, atmospheric $CO_2$ concentration, mid-ocean ridge (MOR) hydrothermal flux, and weathering and riverine flux (Mackenzie and Pigott, 1981; Sandberg, 1985; Hardie, 1996). However, the relative importance of these processes to carbon cycling, possible changes in surface ocean chemistry, and paleo-climate is not fully understood. For example, either the dynamics of MOR circulation, and corresponding changes in Mg/Ca ratios (Stanley and Hardie, 1998) or atmospheric $CO_2$ concentrations and associated changes in marine carbonate chemistry (Sandberg, 1985) were postulated as drivers of oscillations in preferential preservation of aragonite or calcite in sediments. These oscillations are due to the different solubilities of the two minerals: $K_{sp}(\text{calcite})=10^{-6.37}$ and $K_{sp}(\text{aragonite})=10^{-6.19}$ at the salinity of 35, 25 °C, and $P=1$ bar; at the same salinity, but at 5000 m depth where $P\approx510$ bar and the temperature is 1.5 °C, the two minerals are more soluble although the difference between their solubilities is essentially the same, $K_{sp}(\text{calcite})=10^{-5.93}$ and $K_{sp}(\text{aragonite})=10^{-5.76}$. The difference in the degree of saturation at ocean surface conditions is $\Omega_{\text{calcite}}\approx1.5\Omega_{\text{aragonite}}$, due to the higher solubility of aragonite. Such oscillations are noted in the record of inorganic precipitates of $CaCO_3$ in ooids and cements (Sandberg, 1985) are interpreted as reflecting changes in ocean chemistry or environmental conditions in calcification and depositional settings. As a better understanding of the input and burial fluxes of carbon and calcium within the oceanic reservoir would help to constrain their relative importance to the changes in the long-term carbon cycle, this study addresses the following specific questions:

- What would be the saturation state ($\Omega$) of calcite and aragonite in Phanerozoic surface waters at equilibrium with reconstructed $P_{CO_2}$ concentrations and temperatures?
- What other major parameters of the oceanic carbon cycle have likely changed through time and can such changes be constrained?
- Are resulting saturation states consistent with the hypothesis of $P_{CO_2}$ as a driver of calcitic–aragonitic oscillations in the marine record?
- What input fluxes of C and Ca were needed to maintain organic carbon and carbonate burial rates through the Phanerozoic?

## 2. Background relationships

The chemical relationships essential to our analysis are summarized below. The solubility of $CO_2$ and its