

Origin of cap carbonates: An experimental approach



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ABSTRACT

An experimental study was carried out to assess the abiotic natural reactions associated with carbonate precipitation leading to the formation of Neoproterozoic cap carbonate sequences. For this purpose, synthetic seawater solutions were prepared reflecting the presumed composition of Neoproterozoic seawater. These solutions were heated to 40 °C, undergoing degassing and/or evaporation, while monitoring their chemical composition (sulphate concentration, Mg/Ca molar ratio) and identifying the precipitated minerals. The experimental results are in good agreement with previous studies, allowing us to constrain the type of carbonate precipitates formed in the ocean during the Snowball Earth aftermath. Among the phases precipitated during heating of the solutions, Mg-bearing carbonate minerals (i.e. Mg-calcite, magnesite and dolomite) remain of minor importance compared to Ca-carbonates (especially aragonite). Consequently, the basal dolostone units of the cap carbonates (i.e. cap carbonates s.s.) were originally in the form of CaCO₃, and evolved spontaneously toward dolomite.

Cap carbonates s.l. (i.e. cap limestones) containing aragonitic cement could result from the degassing of the whole ocean and the concomitant precipitation of aragonite. The calculated thicknesses of carbonates formed in this way are of the order of several metres, in line with the field observations. Although this process of abiotic carbonate precipitation does not rule out biologically-mediated carbonate formation, it may represent an alternate route to produce carbonate, particularly in environments which are not yet colonized by bacteria after the global ice melting.

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1. Introduction

The strict definition of the term “cap carbonates” is initially applied to draping dolostone units that lie in sharp contact above periglacial marine to terrestrial facies ranging in age from 730 to 580 My (e.g. Shields, 2005). A general consensus has arisen to classify these formations as cap dolostones, while limestone units locally overlying cap dolostones are referred to as post-glacial limestones. The worldwide distribution of cap carbonates s.l. on platforms, shelves and slopes, and their unusual features – such as giant wave ripples or primary barite (Kennedy et al., 2001; Jiang et al., 2003), common stromatolitic laminations and, especially, an atypical negative C isotopic excursion (e.g. Hoffman et al., 2007) – have led to numerous models for their formation. According to different models, the deposition of cap carbonates could result from (1) an overturn of an anoxic deep ocean (Grotzinger and Knoll, 1995; Knoll et al., 1996; James et al., 2001), (2) catastrophically accelerated rates of chemical weathering because of super greenhouse conditions (Snowball Earth hypothesis) (Kirshvink, 1992; Hoffman et al., 1998; Hoffman and Schrag, 2002), (3) a massive release of carbonate alkalinity from destabilized methane clathrates on shelves (Kennedy et al., 2001; Jiang et al., 2003), (4) a microbially mediated precipitation during algal blooms within a low-salinity plumeworld or a re-initiation of global

ocean circulation leading to degassing of CO₂ into the atmosphere, triggering localized abiotic CaCO₃ precipitation (Shields, 2005).

Numerous field and modelling studies have been carried out over the last few years. However, many questions remain about cap carbonate formation, for example, their ubiquitous worldwide deposition and the lithological contrasts between cap dolostone and cap limestones.

Several authors have argued that the main factors conditioning the type of precipitated carbonates are Mg²⁺/Ca²⁺ concentration ratio in solution (e.g. Berner, 1975; Mucci and Morse, 1983; Zhong and Mucci, 1989), the presence of dissolved orthophosphate ions (e.g. Berner and Morse, 1974; Walter and Morse, 1979; Mucci, 1986), sulphate concentration of the fluids (e.g. Reddy et al., 1981; Mucci and Morse, 1983; Mucci, 1986; Folk, 1974; Morse, 1997; Loste et al., 2003; Bots et al., 2011) and temperature of the environment (Mucci, 1987; Burton and Walter, 1988).

This present study presents an experimental approach to address these issues, rather than a naturalistic approach. The experiments involved heating, degassing and evaporating synthetic sea water under high CO₂ partial pressure. The value of CO₂ partial pressure chosen in these experiments, namely 0.1 bars, is derived from the amount of greenhouse gases needed to initiate the melting of the Snowball Earth. Several authors have proposed high values ranging from 0.12 bars (Caldeira and Kasting, 1992) to 0.29 bars (Pierrehumbert, 2004). These physical conditions are all able to trigger carbonate precipitation (generally aragonite, calcite and magnesian calcite, as well as dolomite

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and magnesite in particular cases). The seawater chemical composition was monitored throughout the experiments, as well as the precipitated mineral assemblages characterized by XRD scans and SEM images; all carried out by point sampling. A simple numerical model, constrained by the experimental data, is used to upscale the results to the whole ocean. Except where otherwise stated, all the examples included in the study refer to Marinoan cap carbonates, which clearly exhibit the succession from dolostone to limestone.

2. Materials and methods

“Neoproterozoic Seawater” was prepared by placing synthetic seawater together with carbonates (calcite and dolomite) in sealed containers, and allowing the solution to equilibrate with $p\text{CO}_2 = 0.1$ bars at 6 °C. This solution was either (1) warmed to 40 °C or (2) degassed to 1 bar or (3) evaporated at 40 °C (as shown in Fig. 1).

2.1. Experimental procedure

Solutions of “Neoproterozoic seawater” (ca. 36 g of salt per kg) were prepared using analytical grade reagents of salts and double-distilled water according a simplified protocol drawn from Kester et al. (1967) (see Table 1). In particular, hygrometric salts were dried overnight before being dissolved in 850 g of MQ water, then made up to 1000 g. To assess the impact of the sulphate on carbonate precipitation, Neoproterozoic seawater with (SSW) and without sulphate (USW) were also prepared (Table 1).

Sealed polypropylene containers with a capacity of 4 L, referred to here as “reactors”, were filled with 0.4 L seawater and a gas mixture of 90% N_2 /10% CO_2 . Special attention was paid to keeping a constant water–gas ratio to attain equilibrium for a gas composition of 10% CO_2 . The reactor was maintained at 6 °C for 24 h to achieve equilibrium between water and gases, which was ensured by measurement of the

initial pH at ca. 6.4. The experiments were carried out at conditions of pressure and temperature regulated to ± 2 °C. Solution aliquots were drawn off (each day during a week) into a *Low Density PolyEthylene* (LDPE) bottles without modifying the gas atmosphere in the reactor. As shown in Fig. 1, it was possible to sample the solutions without degassing the reactor. To keep a constant total volume, the reactor was replenished after each sampling. The total volume extracted during the course of each experiment represents less than 10% of the initial 0.4 L.

Three experimental cases were tested in this study (see Fig. 1).

- Heating: the sealed transparent reactor is heated from 6 °C to 40 °C in a thermostatically controlled oven. The final temperature (40 °C) is reached in a few minutes, and maintained constant for the entire experimental run duration.
- Degassing: the reactor is opened to the room and then heated to $T = 40$ °C. Complete degassing of the solution is attained in three days (see Table 2). Additional experiments were also performed: 1) complete degassing was achieved more slowly, by a carrying out a series of opening and closing of the reactor. In this case, equilibrium between solution and the atmosphere is only reached after 3 weeks; 2) Chemical composition of the Neoproterozoic seawater was modified by changing the Mg/Ca molar ratio (setting values of 10, 20 and 50), by increasing the Mg concentration and maintaining a constant Ca concentration. These values are chosen to encompass the various Mg/Ca values occurring in lagoonal environments. For example, the pioneering observations of Wells and Illing (1964) indicated that proto-dolomite can precipitate in waters with very high Mg/Ca ratios (from 10 to 35).
- Evaporation: the sealed reactor is connected to another little reactor containing 400 g of silica gel. Vaporised water from the first reactor is trapped in the silica gel. Final weighing of the silica gel and of the remaining solution allows us to calculate the amount of evaporation, ca. 17% in both cases.

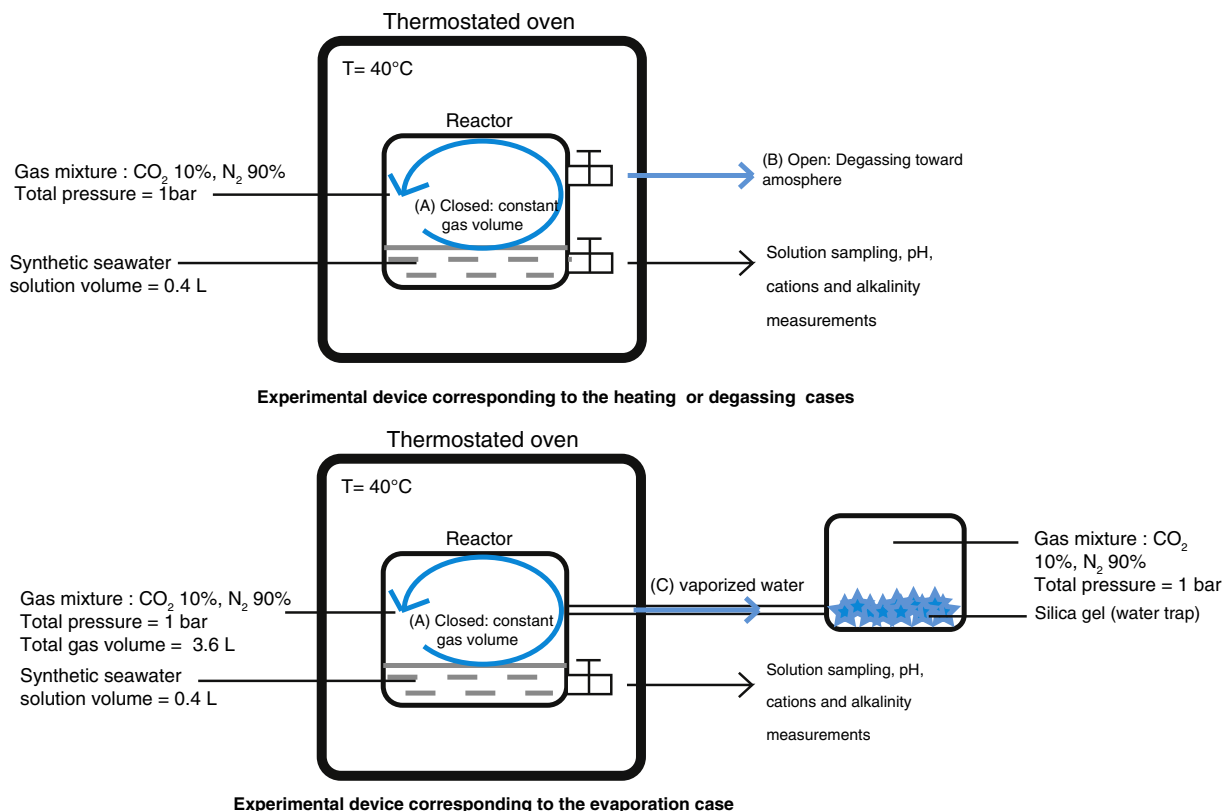


Fig. 1. Sketch of the experimental set-up used for processes involving (A) heating, (B) degassing and (C) evaporation.

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