



# Authigenic carbonate formation rates in marine sediments and implications for the marine $\delta^{13}\text{C}$ record



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## ABSTRACT

Carbon isotope ( $\delta^{13}\text{C}$ ) variations measured in carbonates have been attributed to large-scale phenomena throughout Earth history, such as changes in atmospheric oxygen or global glaciations. These interpretations follow from a model wherein the  $\delta^{13}\text{C}$  of marine dissolved inorganic carbon (DIC) is controlled by the relative sedimentary burial rates of biogenic carbonate (BC) and organic carbon (OC). A new model proposes authigenic carbonate (AC) as a third major sedimentary C pool, implying that  $\delta^{13}\text{C}$  anomalies are not necessarily indicative of extreme changes in the global carbon cycle and/or atmospheric oxygen. Two conditions are required for AC formation to significantly alter bulk carbonate  $\delta^{13}\text{C}$ : the AC isotopic composition must be at least  $\sim 3\%$  different from that of BC and the AC/BC ratio must be  $>0.1$ . We use pore fluid Ca and Sr concentrations to estimate rates of AC formation in Late Cenozoic marine sediments, then calculate relative fractions of AC, OC, and BC. Today AC is not expected to constitute a significant fraction of total sedimentary carbon (AC+OC+BC) globally; however, there are modern sites where local conditions promote elevated AC/BC and anaerobic metabolisms can alter the  $\delta^{13}\text{C}$  of pore fluids. We investigate these sites to determine what conditions might enable AC to alter  $\delta^{13}\text{C}$  of marine DIC. We find there is very little net addition of AC relative to BC, but large quantities of AC form today across many settings via recrystallization. In settings where remineralization of organic matter causes recrystallized carbonate to form with modified  $\delta^{13}\text{C}$ , AC/BC is generally too low for this recrystallization to significantly shift the  $\delta^{13}\text{C}$  of the bulk carbonate. However, exceptions are found in sites with very low BC and extensive methane oxidation, suggesting that this environment type would need to be globally extensive in the past in order for AC formation to change the  $\delta^{13}\text{C}$  of marine DIC.

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## 1. Introduction

### 1.1. Overview

A longstanding problem in the study of paleoclimate lies in explaining carbon isotope ( $\delta^{13}\text{C}$ ) variation in the geologic record, thought to reflect changes in the  $\delta^{13}\text{C}$  of marine dissolved inorganic carbon (M-DIC) through Earth history (Fig. 1). In this record, there are both long-term ( $>10^7$  yr) and transient variations ( $\pm 3\%$  or larger) that persist for periods extending beyond the 0.1 My residence time of M-DIC (e.g., Halverson et al., 2005; Kump and Arthur, 1999; Payne et al., 2004; Saltzman, 2005;

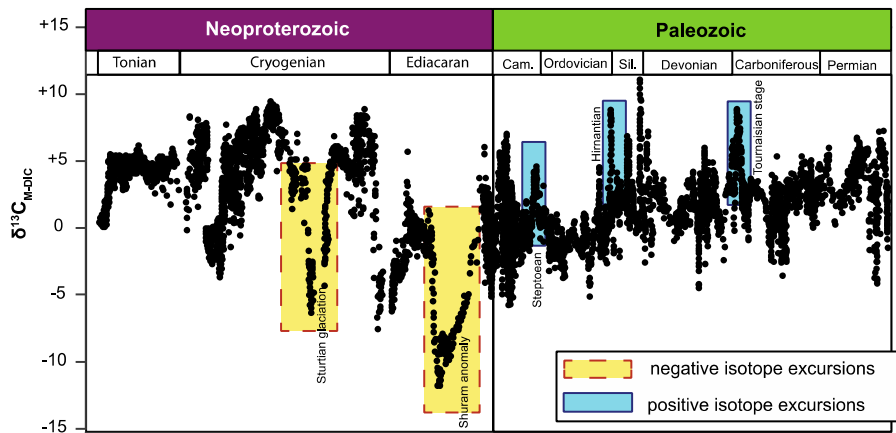
Saltzman and Thomas, 2012; Sephton et al., 2002; Shields and Veizer, 2002). The traditional interpretation of the  $\delta^{13}\text{C}_{\text{M-DIC}}$  record is based on a steady-state mass balance between carbon inputs ( $\delta^{13}\text{C}_{\text{in}}$ ) to the M-DIC reservoir and the relative sedimentary burial rates of carbonate carbon and organic carbon (e.g., Arthur et al., 1988; Canfield and Kump, 2013), written as:

$$\delta^{13}\text{C}_{\text{in}} = \delta^{13}\text{C}_{\text{out}} = (1 - f_{\text{org}})\delta^{13}\text{C}_{\text{carb}} + f_{\text{org}}\delta^{13}\text{C}_{\text{org}} \quad (1)$$

where  $f$  represents the fraction of total sedimentary carbon that is either carbonate (*carb*) or organic carbon (*org*). Organic carbon has a much lower  $\delta^{13}\text{C}$  relative to that of M-DIC due to fractionation during photosynthesis and other carbon fixation pathways. The  $\delta^{13}\text{C}_{\text{M-DIC}}$  is assumed to be roughly equal to  $\delta^{13}\text{C}_{\text{carb}}$ , as there is only a small fractionation between M-DIC and carbonate. There are spatial variations in  $\delta^{13}\text{C}_{\text{M-DIC}}$  (up to  $\sim 3\%$ ) due

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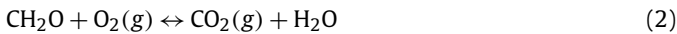


**Fig. 1.** Neoproterozoic and Paleozoic marine carbon isotope record. Some examples of isotope excursions highlighted in yellow with dashed line (negative excursions) and blue with solid line (positive excursions). Data from Halverson et al. (2005) and Saltzman and Thomas (2012). For color version of figure, the reader is referred to the web version of this article.

to temperature-dependent circulation effects as well as biological productivity, fluxes of organic matter to the deep ocean, and remineralization rates (e.g., Raven and Falkowski, 1999), although deep water values average 0‰, with modern mean  $\delta^{13}\text{C}_{\text{M-DIC}}$  equal to  $0 \pm 1$  (Saltzman and Thomas, 2012).

### 1.2. Use of the $\delta^{13}\text{C}$ record as a paleoproxy for oxygenation state

The  $\delta^{13}\text{C}$  record has been used in the context of equation (1) as a proxy for atmospheric oxygen production and removal due to burial or consumption of organic carbon. This proxy is based on the relationship between organic carbon and oxygen during aerobic respiration (Eq. (2); Berner and Canfield, 1989; Berner and Maasch, 1996) according to the reaction,



Following this relationship, if  $f_{\text{org}}$ , the organic carbon burial fraction, increases for an extended period of time, atmospheric oxygen is expected to build up. Similarly, atmospheric oxygen levels should decrease if the organic carbon burial rate decreases for an extended period of time (e.g., Berner and Petsch, 1998).

There exists a substantial body of work that attempts to constrain atmospheric oxygen levels in the past, based on evidence including distribution of redox-sensitive elements such as molybdenum, uranium, and iron, as well as sulfur isotopes and phylogenetic clues (Berner and Canfield, 1989; Canfield and Teske, 1996; Farquar et al., 2001; Lowenstein et al., 2014 and references therein). However, there are places in the record, some of which are summarized by Schrag et al. (2013), where the  $\text{O}_2$ -interpretation of the  $\delta^{13}\text{C}$  signal is at odds with other proxies and observations, lacks independent evidence, or implies much larger changes than are likely. Consequently, other explanations for patterns in  $\delta^{13}\text{C}$  have been proposed.

An altered oxygenation state of the Earth's atmosphere and oceans is not the only interpretation of the  $\delta^{13}\text{C}_{\text{M-DIC}}$  record, although many proposed interpretations are at least indirectly tied to an altered global redox environment. There are large magnitude excursions associated with glaciations (e.g., Marshall et al., 1997), mass extinctions (e.g., Sephton et al., 2002), ocean anoxic events (e.g., Arthur et al., 1988), consequences of emplacement of large igneous provinces (e.g., Retallack and Jahren, 2008), as well as inferred events such as the catastrophic release of methane clathrates (e.g., Dickens et al., 1995). However, there are isotope excursions in the record, such as those identified by Schrag et al. (2013), that do not have other geochemical or stratigraphic indicators of global change, specifically changes in oxygenation state, and

these excursions therefore cannot be interpreted with any degree of confidence.

### 1.3. Considering authigenic carbonate in the carbon isotope mass balance

Motivated by inconsistencies between the  $\delta^{13}\text{C}$  record and evidence from other proxy records, alternative models have been proposed that would serve to decouple atmospheric  $\text{O}_2$  from seawater  $\delta^{13}\text{C}$ . One of these models posits that carbonate formed within marine sediments, called authigenic carbonate (AC), could take on values of  $\delta^{13}\text{C}$  and form at high enough rates relative to the organic C and biogenic carbonate burial fluxes, such that  $\delta^{13}\text{C}_{\text{M-DIC}}$  could shift without requiring a large change in atmospheric oxygen (Schrag et al., 2013). This mechanism could then cause variations in  $\delta^{13}\text{C}_{\text{M-DIC}}$  that are no longer directly tied to the  $\text{CO}_2$ - $\text{O}_2$  balance. In the marine environment, AC forms within sediments, either by (a) "recrystallization", which is dissolution of biogenic carbonates ("BC"; i.e., detrital tests of foraminifers or coccoliths) followed by reprecipitation as nonbiogenic carbonate, or (b) net precipitation from pore fluids due to an increase in carbonate alkalinity caused by microbial respiration of organic carbon or methane (Morse et al., 2007), or alternatively due to deepening of the carbonate compensation depth (CCD) to well below the sediment-water interface.

The steady-state  $\delta^{13}\text{C}$  mass balance described by Eq. (1) has been rewritten by Schrag et al. (2013) to include AC in addition to the original sedimentary C sinks, biogenic carbonate (BC) and organic carbon (OC):

$$\delta^{13}\text{C}_{\text{in}} = f_{\text{BC}}(\delta^{13}\text{C}_{\text{M-DIC}} + \varepsilon_{\text{BC}}) + f_{\text{AC}}(\delta^{13}\text{C}_{\text{M-DIC}} + \varepsilon_{\text{AC}}) + f_{\text{OC}}(\delta^{13}\text{C}_{\text{M-DIC}} + \varepsilon_{\text{OC}}) \quad (3)$$

$$\delta^{13}\text{C}_{\text{M-DIC}} = \delta^{13}\text{C}_{\text{in}} - f_{\text{BC}}\varepsilon_{\text{BC}} - f_{\text{AC}}\varepsilon_{\text{AC}} - f_{\text{OC}}\varepsilon_{\text{OC}} \quad (4)$$

where  $\varepsilon$  indicates the fractionation factor between M-DIC and the sedimentary carbon pool (e.g., if  $\varepsilon_{\text{OC}} = -25$ ,  $\delta^{13}\text{C}_{\text{OC}} = \delta^{13}\text{C}_{\text{M-DIC}} - 25$ ). According to these formulae, two conditions must be met for AC to be important to the overall isotopic mass balance and to cause changes to  $\delta^{13}\text{C}_{\text{M-DIC}}$ . First,  $f_{\text{AC}}$  must be similar in magnitude to  $f_{\text{BC}}$  and  $f_{\text{OC}}$ . Second,  $\varepsilon_{\text{AC}}$  must be different from  $\varepsilon_{\text{BC}}$ , or Eq. (3) reduces to Eq. (1). As written in Eq. (4), the value of  $\delta^{13}\text{C}_{\text{M-DIC}}$  depends on the sedimentary fractions and fractionation factors for AC, OC, and BC, as well as the isotopic inputs to the M-DIC pool.

For the AC term to be significant in equation (4), not only must  $f_{\text{AC}}$  be sufficiently large, but the AC isotopic composition must

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