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Retrodiction of secular variations in deep-sea $CaCO_3$ burial during the Cenozoic

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A B S T R A C T

Deep-sea sediments record changes in oceanic carbonate chemistry and $CaCO_3$ sedimentation rate through temporal variations in the total burial of $CaCO_3$ and the position of the carbonate snowline, i.e., the ocean depth at which $CaCO_3$-free sediments are first recorded. This paper links mathematically secular changes in snowline to those in the burial rate through a set of relatively simple equations. When the available Cenozoic deep-sea burial records are employed to predict secular variations in snowline, the process fails at some time in the past, indicating that these records are not consistent with each other. The burial records are more likely the source of this problem, as they involve far more uncertainties than the snowline records. As a consequence, we introduce a method for estimating carbonate burial through the use of a canonical $CaCO_3$-depth profile, which can respond dynamically to secular changes in carbonate sedimentation and the positions of both the snowline and the carbonate saturation horizon. The resulting synthetic $CaCO_3$ burial record is consistent with snowline records and indicates that the burial rates offered by Davies and Worsley (1981) are generally too high, with highly questionable maxima at 25 and 47 Ma BP. Our estimates of burial are more consistent with the range advanced by Mackenzie and Morse (1992); nevertheless, our results differ from the latter with respect to timing and magnitude of the variations. Our approach allows simultaneous calculation of the mean carbonate ion concentration of the deep sea. We find that carbonate-ion levels fell through the Cenozoic and are similar to those calculated by Tyrrell and Zeebe (2004), using a different model. Secular variations in $CaCO_3$ burial are found to be primarily driven by changes in the Ca^{2+}–${CO_3}^{2-}$ ion product within the bottom-waters, with an increase in the sedimentation rate of $CaCO_3$ of secondary importance over the Cenozoic.

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1. Introduction

Past changes in ocean carbonate saturation or rain of $CaCO_3$ to the seafloor can be recorded in preserved sediments as adjustments in the burial rate of $CaCO_3$ in pelagic sediments (Fig. 1) and/or the position of the carbonate "snowline" (Fig. 2), i.e., where the $CaCO_3$ content of ocean sediments falls to 0%, due to increasing dissolution with depth, or operationally $\lesssim$10% (Morse and Mackenzie, 1990; Zeebe and Westbroek, 2003).

The snowline (z_{snow}) position is the basis for our modern understanding of the effects of past global change on $CaCO_3$ dynamics of the oceans. Nevertheless, reconstruction of the position of the snowline over geological time, using cores from deep-sea drilling, is difficult. Early efforts were undertaken by Heath (1969), Berger (1973), van Andel and Moore (1974), and van Andel (1975), while Delaney and Boyle (1988) and Lyle et al. (2008) offered significant time-scale corrections to the van Andel results (Fig. 2A). These initial reconstructions were relatively coarse, but outlined significant long-term ($\geq$3 Ma) changes in the position of the snowline over Cenozoic time, i.e., 65 Ma BP until today. (All dates are BP hereafter and that designation is dropped for brevity.)

Pälike et al. (2012) have produced a vastly more detailed time-series of the snowline for the Equatorial Pacific, which highlights many "brief" ($\leq$1 Ma) preservational/dissolutive events – see Fig. 2B (blue dashed line). Much research has been focused on these short-term variations, and their causes have been addressed widely, if not entirely to everyone's satisfaction – see summaries by Zeebe (2012) and Pälike et al. (2012). The present paper does not further address that topic. Instead, we note that a time smoothing of the Pälike et al. (2012) reconstruction also exhibits large long-term (secular) variations (Fig. 2B – red solid line), and these variations and their implications to $CaCO_3$ burial that are

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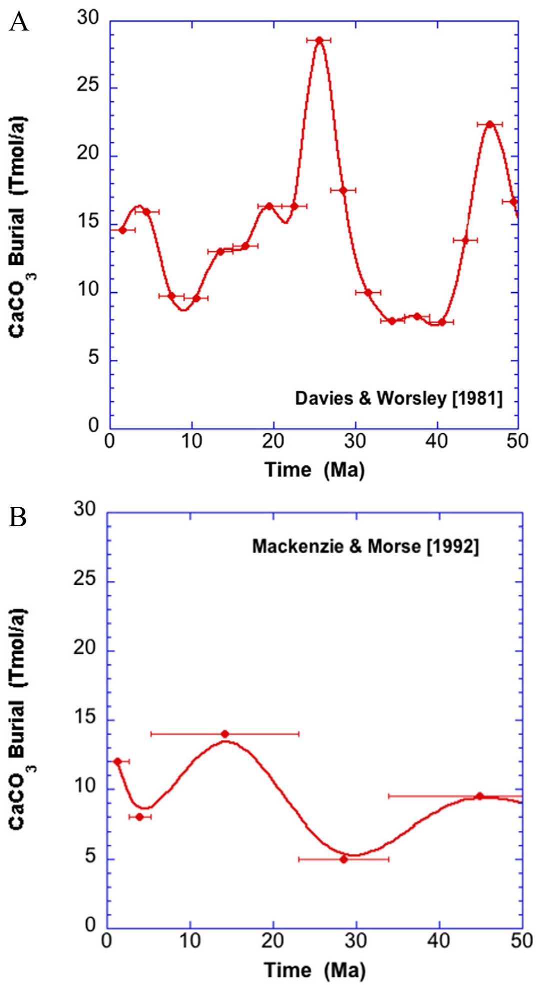

Fig. 1. Time series of the total pelagic burial rate of $CaCO_3$, as calculated and reported by Davies and Worsley (1981) – Panel A and Mackenzie and Morse (1992) – Panel B. The lines in each diagram are smoothed curves (splines) through the data, which are used in driving the initial solutions to our model.

the central interest of our paper. Recently, Slotnick et al. (2015) have introduced a detailed reconstruction of the global snowline record for the time period of 48 to 62 Ma – blue dashed line in Fig. 2C, which also exhibits secular variations – red solid curve. Over secular time scales the snowline coincides with the carbonate compensation depth, a.k.a., the CCD, where secular will be defined quantitatively below. The CCD is the depth where the rate of $CaCO_3$ (calcite) dissolution is balanced by the rate of deposition of calcitic tests to the sediment–water interface (Morse and Mackenzie, 1990).

The effects and causes of the secular variations of the snowline/CCD and $CaCO_3$ burial during the Cenozoic have been examined with various types of "forward" geochemical models, e.g., Delaney and Boyle (1988), Merico et al. (2008), Zeebe (2012), and Pälike et al. (2012). These models account for the changing carbonate chemistry of the oceans, as driven by various known or hypothesized internal or external processes, e.g., changes in atmospheric temperature and CO_2 (Zeebe, 2012), alterations in continental weathering rates and alkalinity input to the oceans (Delaney and Boyle, 1988), variations in sea-level and resulting changes in the partitioning of shallow-versus-deep-water deposition (Delaney and Boyle, 1988), and modifications to the reactivity of organic matter (Lyle et al., 2008; Pälike et al., 2012).

We take a different approach here. From a cause-and-effect point of view, sediments record the effects of processes, e.g., the snowline and burial rate, and generally not the causes, with dissolved calcium as an exception. The pertinent question then becomes: is there not a way to derive information about direct cause(s) from the effects record, rather than the trial-and-error approach of the forward method? Inverse models do this, and this paper presents a simple inverse model that aims to identify the direct, i.e., within ocean, drivers of snowline and burial secular variations.

Specifically, the model given here can mathematically link deep-sea burial and snowline records; thus, we can evaluate the consistency of such burial records, i.e., Davies and Worsley (1981) and Mackenzie and Morse (1992), against snowline records, i.e., Lyle et al. (2008), Pälike et al. (2012) and Slotnick et al. (2015). Shallow-water $CaCO_3$ burial is explicitly excluded from our consideration and modeling; we are focused on directly correlating deep-sea burial to the CCD, and shallow water carbonates play no direct role in this relationship. In addition, our model can be extended to also make retrodictions ("predictions" of the past) about the sedimentation rate of $CaCO_3$ onto the deep-sea sediment–water interface and the carbonate ion concentration in the deep ocean through the Cenozoic. Our paper provides paleoceanographers and geochemists with relatively simple equations for important aspects of the carbonate system, alleviating the need to use complex geochemical models to answer some germane questions.

2. The burial-CCD model

2.1. Defining the secular time scale

Before relating burial (Fig. 1) and snowline (Fig. 2) records, a quantitative meaning of secular is needed. The term secular refers in our case to time scales greater than the time needed for the snowline to adjust to a major upward change in the position of the CCD; conversely, a deepening of the CCD does not raise this question (Boudreau et al., 2010a). The maximum time scale for such adjustments (τ) is given by dividing the maximum standing stock of $CaCO_3$ that can be dissolved (S_{CaCO_3}) by the rate of dissolution at the CCD, R_{cc}. The maximum standing stock of $CaCO_3$ is the product of the maximum $CaCO_3$ content of sediments above the saturation horizon (b_{max}), which is observed to be ~0.9 (volume fraction) presently, the maximum depth (ℓ) for chemical erosion of $CaCO_3$, which is approximately 1 m (Archer, 1996), the $CaCO_3$ molar density ($\rho_{CaCO_3} = 2.6 \times 10^4$ mol m^{-3}) and one minus the typical porosity (φ) of marine sediments (~0.7), i.e.

$$S_{CaCO_3} \approx (1-\varphi) b_{max} \rho_{CaCO_3} \ell \approx 7 \times 10^3 \text{ mol m}^{-2} \quad (1)$$

Boudreau (2013) has shown that R_{cc} is (largely) controlled by the linear rate of boundary-layer mass-transfer of the carbonate (or calcium) ion, so that it is given by:

$$R_{cc} = k_c\left(C_{sat} - [CO_3]_D\right) \quad (2)$$

where C_{sat} is the carbonate ion concentration that would be in equilibrium with $CaCO_3$ (calcite). To a reasonable degree of accuracy:

$$C_{sat} = \frac{K^c_{sp}(z_{cc})}{[Ca]_D} \quad (3)$$

where $K^c_{sp}(z_{cc})$ is the solubility product at the depth z_{cc}. With $k_c \approx 10$ m a^{-1} (Boudreau and Jørgensen, 2001; Boudreau, 2013) and $(C_{sat} - [CO_3]_D) \approx 10 \times 10^{-3}$ mol m^{-3}, based on present-day conditions, as given in Boudreau et al. (2010b) and Boudreau (2013), then

$$R_{cc} \approx 0.1 \text{ mol m}^{-2} \text{ a}^{-1} \quad (4)$$

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