

Compilation and time-series analysis of a marine carbonate $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ database through Earth history

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Abstract

The Sr, S, O and C isotope database of marine carbonates contains over 55,000 published isotope values of low-Mg calcite from diagenetically little altered Phanerozoic fossil shells as well as samples of whole rocks and calcite cements of Ordovician to Archean age. Carbon and oxygen isotope data for the shell material are divided into habitat subsets (high-, mid-, low-latitude and deep sea), and whole rock data are separated by mineralogy into calcite/dolomite subsets. Trend, correlation, wavelet, and spectral analyses on Gaussian-filtered isotope records were applied to detect and quantify similarities and patterns in temporal records with the following results:

- (1) Oxygen isotope trends from the “high-latitude” and “deep-sea” habitats are almost indistinguishable through the last 115 Ma, consistent with the existence of the “oceanic conveyor belt” throughout this interval;
- (2) All oxygen isotope habitat records show a strong, coherent 30–45 Ma (~38 Ma) cyclicity throughout the Cretaceous and the Cenozoic
- (3) Up to 70% of the multi-million year variability in the $\delta^{18}\text{O}$ record of the last 115 Ma can be simulated by the following equation:

$$\delta^{18}\text{O}(\text{‰}) = 0.64\sin(2\pi t/120 \text{ Ma} + 0.9) + X\sin(2\pi t/38.3 \text{ Ma} + 1.1)$$

with X ranging from 0.4–0.6‰ for the “low-”, “high-latitude” and “deep-sea” habitats, to 0.8‰ for the “mid-latitude” realm.

- (1) A $\sim 120 \pm 20$ Ma cycle occurs in the Paleozoic and Neoproterozoic $\delta^{18}\text{O}$ record, consistent with paleoclimate variability as interpreted from sedimentological and faunal records.
- (2) The offset of $\delta^{13}\text{C}$ values between “deep water” and “high-latitude” vs. surficial habitats at lower latitudes is consistent with the operation of a biological pump in the oceans since at least the Cretaceous.
- (3) Sr and S isotope records exhibit a ~ 60 –70 Ma cyclicity throughout the Phanerozoic.

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1. Introduction

Over recent decades some hundred thousand isotope analyses of C, O, S, and Sr have been carried out for geologic studies. Their purposes varied, as did the rock and fossil material used, the accuracy and resolution of the stratigraphy, and the care taken during sample selection. Commencing with Keith and Weber (1964) and Veizer and Compston (1974) and Veizer and Hoefs (1976), several such isotope databases have been compiled in an attempt to reconstruct global multi-million-year records of

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seawater isotope variability. At that time, the primary challenge was to detect and overcome diagenetic alteration of original isotope signals as well as advancing the limits of analytical precision. Subsequently, in order to avoid as much as possible the problems of diagenesis, effort has been mainly concentrated on unaltered low-Mg calcite shell material, preferably from articulate brachiopods, belemnites and foraminifera (e.g. [Veizer et al., 1999](#); [Lisiecki and Raymo, 2005](#)). More recently, the oxygen isotope ratios of phosphatic shells of conodonts or fish teeth enamel, and of aragonitic shells (e.g. ammonites), have also been used as paleoenvironmental tracers (e.g., [Picard et al., 1998](#)).

The Phanerozoic marine $^{87}\text{Sr}/^{86}\text{Sr}$ trend has remained without significant change for about three decades because this ratio is relatively insensitive to habitat variability or to the fossil material used ([Veizer et al., 1999](#)). In contrast, oxygen and carbon isotope ratios are highly sensitive to environmental and biological factors. For example, the application of oxygen isotopes to the reconstruction of seawater temperature has to concern itself with water depth, salinity, pH and the mode of shell growth. Moreover, the species-specific physiological (“vital”) factors may reflect additional variables, such as coral photosymbiosis with algae that, in turn, can modify the isotope fractionation of carbon ([Abramovitch et al., 2003](#)). As a consequence, with an improved understanding of isotopic proxies for reconstruction of past environments, there has emerged a need to address not only the temporal variability of the signal but also the variability due to habitat and organism-specific isotope fractionation parameters (e.g., [Spero and DeNiro, 1987](#)).

In this review, we constructed separate Phanerozoic oxygen and carbon isotope records for “deep water” and for “high-”, “mid-” and “low-latitude” surface water in an attempt to improve the reconstruction of paleoenvironmental conditions. We calibrated these datasets to an articulate brachiopod standard, in order to address the differences in habitat and physiology of the organisms. Brachiopods were chosen as a standard because they have been extant since the Cambrian and, except for the Cenozoic, the bulk of Phanerozoic O and C isotope measurements were carried out on their shells. The Precambrian records are based on calcitic or dolomitic components of whole rock carbonate samples.

The aims of this review are:

- (1) to provide the scientific community with an updated (up to February 2006) compilation of marine Sr, O, C, and S isotope data from published literature for the entire Earth history. The database is fully annotated, grouped into different habitats where deemed necessary, and consistently referenced to the new geologic time-scale GTS2004 ([Gradstein et al., 2004](#));

The storage of the database in a secure databank where it can be available to the community for their own retrieval and manipulation is the primary goal of this publication, because with Veizer’s retirement, its continuation and even survival cannot be guaranteed. The supplementary goals listed below are only tentative suggestions for future advances in development and interpolation of the database.

- (2) to carry out data processing that transforms the raw data into habitat-specific geologic records;
- (3) to determine long-term trends, periodic patterns and interrelationships within and between the isotope records using time-series analytical techniques;
- (4) to interpret the results of the time-series analysis in terms of paleoenvironmental reconstructions.

We particularly avoided any reconstruction of records through time intervals where no data are available. Differences in temporal data density are clearly highlighted. In this way, the reader can easily recognize for which time interval and at which resolution the suggested reconstructions and interpretations are robust or less so. All raw data used for record compilations associated with this article can be found at [doi:10.1016/j.earscirev.2007.12.003](https://doi.org/10.1016/j.earscirev.2007.12.003).

2. Phanerozoic fossil data

2.1. Data selection

This review is an update and restructuring of the Ottawa–Bochum O, C, S and Sr isotope database for marine carbonates ([Veizer et al., 1999](#); [Shields and Veizer, 2002](#); [Kampschulte and Strauss, 2004](#)). The updated database includes oxygen and carbon isotope data for fossil shells from 146 references, three references for sulfur isotope values from marine sulfates, and 43 references for strontium isotope ratios of fossil shells and micrite. In order to extend the fossil carbonate database to cover the entire Phanerozoic, it has been supplemented by Cambrian whole rock carbonate data (11 references for $^{87}\text{Sr}/^{86}\text{Sr}$ and 16 for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$).

The database includes over 39,000 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for the low-Mg calcite or aragonite of diagenetically little altered shells of ammonites, belemnites, brachiopods, inoceramids, trilobites, benthic and planktonic foraminifera, as well as micrite and conodont data for $^{87}\text{Sr}/^{86}\text{Sr}$ ([Table 1](#)). The 380 $\delta^{34}\text{S}_{\text{sulfate}}$ data are from marine barites and structurally substituted sulfate. A set of 2282 whole rock samples, mostly deriving from references up to 2002, has been included to fill the large stratigraphic gaps between shell samples in the Cambrian. For consistency, the deep-sea carbon and oxygen isotope data of the last 67 Ma were taken entirely from the benthic foraminifera dataset of [Zachos et al. \(2001\)](#). Isotope data for shell material with Mn concentrations >350 ppm, some duplicate data entries, and Holocene foraminifera data from the Ottawa–Bochum database ([Veizer et al., 1999](#)) have not been incorporated into the new database. In addition, the abundant Quaternary isotope data from the literature have not been utilized in this database. The only exceptions are the articulate brachiopod data because of their importance as a standard for the Phanerozoic isotope records.

The individual samples of the database represent discrete measurements that are subject to stratigraphic uncertainty as well as errors in both analytical and palaeoenvironmental interpretations. All sample ages were transformed from their original time scale into the GTS2004 time scale ([Gradstein et al., 2004](#)) and include also estimates of the $\pm 1\sigma$ stratigraphic uncertainty.

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