

Precambrian marine carbonate isotope database: Version 1.1

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[1] We present a compilation of strontium, carbon, and oxygen isotope compositions of roughly 10,000 marine carbonate rocks of Archean - Ordovician age (3800 Ma – 450 Ma). The Precambrian Marine Carbonate Isotope Database (PMCID) has been compiled from 152 published and 3 unpublished articles and books of the past 40 years. Also included are 30 categories of relevant “metadata” that allow detailed comparisons and quality assessments of the isotope data to be made. The PMCID will be updated periodically as new data and better age constraints come to light. Here we outline the structure of the first published version of the database and its inherent merits and limitations.

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1. Introduction

[2] Temporal trends in the isotopic compositions (Sr, C, O, and S) of marine sedimentary rocks have been used to hypothesize tectonic, chemical, and biological change during the Precambrian. Fluctuations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$, which can be retained in

well-preserved marine carbonate rocks, reflect changes in the relative contributions of the continental versus mantle chemical reservoirs to ocean composition [Veizer, 1989]. By contrast, the stable isotopes of C and S have generally been used to recognize changes in the biogeochemical cycling of these elements, which may be related to tectonic

events, biological innovations, and the oxidation state at the Earth's surface [Schidlowski *et al.*, 1975; DesMarais *et al.*, 1992; Canfield and Teske, 1996; Farquhar *et al.*, 2000; Godd ris and Veizer, 2000]. Recently, attention has also been paid to the potential of Sr and C isotopes in the global stratigraphic correlation of Paleoproterozoic [Melezhik *et al.*, 1999] and Neoproterozoic rock successions [Kaufman and Knoll, 1995; Shields, 1999; Walter *et al.*, 2000].

[3] Here we outline the Precambrian marine carbonate isotope database or PMCID (http://www.science.uottawa.ca/geology/isotope_data/), which complements the published Phanerozoic isotope database [Veizer *et al.*, 1999] that is freely available at http://www.science.uottawa.ca/geology/isotope_data/. Both current and future versions of these databases will be available from the Global Earth Reference Model (GERM) site under [http://earthref.org/cgi-bin/erda.cgi?n = 48](http://earthref.org/cgi-bin/erda.cgi?n=48). The PMCID was conceived in the light of increasing amounts of isotope data that were rapidly invalidating published isotope compilations. In addition to ever larger and more numerous isotope studies, there have been continual improvements to the dating and correlation of Precambrian strata, which make necessary a flexible, electronic database that can be periodically updated. It is hoped that the current use of electronic data processing and the international standardization of analytical techniques will make the task of updating the database increasingly less work-intensive. The generosity of those who have so far given of their time and expertise is gratefully acknowledged.

2. Merits of the PMCID

[4] The Precambrian marine carbonate isotope database (PMCID) is believed to contain all relevant, published isotope data. This has been achieved through an exhaustive 2 year literature search and by directing requests for suggestions and contributions to members of the geochemical community. Despite this effort, some published data have almost certainly been overlooked, and these will be incorporated in future versions. The

capacity for expansion is an important feature of the PMCID as is its flexibility, which will allow it to evolve in response to feedback from users and contributors.

[5] In addition to compiling Sr, C, and O isotope data from marine carbonates, we have attempted to include as many categories of "metadata" as possible (Table 1), for example, original sample identification, geographic and stratigraphic details, mineralogy, age, trace element contents, and other isotopic data as available. Such metadata provide a context for the isotope data and help toward their interpretation. Metadata can be updated with time as age constraints or palaeoenvironmental interpretations improve or change. It is also hoped that some categories of nonisotopic metadata will prove to be useful in their own rights, for example, when assessing changes in the abundance of carbonate rocks or in the chemical composition of marine carbonates and seawater through time.

3. Limitations of the PMCID

3.1. General Limitations

[6] The usefulness of any database is limited not only by the quantity, i.e., the statistical significance, of the data, but also by the quality. The PMCID comprises isotope data of highly variable degrees of usefulness due to the following:

3.1.1. Poor quality of metadata

[7] Some isotope data cannot be assigned specific geographic locations or stratigraphic positions. This may be due to the intentions of the original authors, which may have been quite different from those of isotope stratigraphers or may be due to tectonic complications. In either case, assigned ages may be poorly constrained and are unlikely to improve with time, thus severely restricting the usefulness of the isotope data. In some studies, the mineralogy or paleoenvironmental setting (e.g., marine versus nonmarine setting) of the measured samples is unclear, in which case, depending on the importance of this information, some isotope data may need to be disregarded for the purposes of interpretation.

Table 1. Structure of the PMCID – Version 1.1(a)

Column Name	Content of Column
Sample ID number	unique sample number taken from original publication
Sample description	additional relevant information - incomplete
Formation	formation name occasionally including groups, members, etc.
Location	name of section, borehole and/or region
Country	name of country
Depth, m	depth in borehole
Height, m	stratigraphic height in section
Mineral	C, calcite; D, dolomite; M, magnesite; S, siderite; A, ankerite; R, rhodocrosite; CH, chert
Era	A, Archean; PP, Paleoproterozoic; MP, Mesoproterozoic; NP, Neoproterozoic; Ph, Phanerozoic
Interval	era subdivision from Eoarchean to Cenozoic
Geon	100 Ma intervals or “Geons” from 0 to 37 [Hofmann, 1999]
Age, Ma	well-constrained ages (less than ± 50 Ma)
Age, Ma	poorly constrained ages (greater than ± 50 Ma)
Uncertainty, Ma	published age constraints
Source: data	literature reference for isotopic data (see appendix)
Source: age	literature references for age constraints (incomplete)
Dating technique	dating technique, e.g., U-Pb single zircon, biostratigraphy, etc.
Fe, ppm	iron concentration in carbonate phase, ppm
Mg/Ca	Mg/Ca ratio of carbonate phase
Mg, ppm	magnesium concentration in carbonate phase, ppm
Ca, wt %	calcium concentration in carbonate phase, weight%
Mn, ppm	manganese concentration in carbonate phase, ppm
Sr, ppm	strontium concentration in carbonate phase, ppm
$\delta^{13}\text{C}_{\text{calcite}}$ PDB	carbon isotope composition of calcite, ‰ PDB
$\delta^{13}\text{C}_{\text{dolomite}}$ PDB	carbon isotope composition of dolomite, ‰ PDB
$\delta^{13}\text{C}_{\text{others}}$ PDB	carbon isotope composition of other carbonate minerals, ‰ PDB
$\delta^{18}\text{O}_{\text{calcite}}$ PDB	oxygen isotope composition of calcite, ‰ PDB
$\delta^{18}\text{O}_{\text{dolomite}}$ PDB	oxygen isotope composition of dolomite, ‰ PDB
$\delta^{18}\text{O}_{\text{others}}$ PDB	oxygen isotope composition of other carbonate minerals, ‰ PDB
$^{87}\text{Sr}/^{86}\text{Sr}$	reported strontium isotope composition of carbonate phase
$^{87}\text{Sr}/^{86}\text{Sr}_{\text{norm.}}$	$^{87}\text{Sr}/^{86}\text{Sr}$ normalised to NBS 987 = 0.71025
$\delta^{13}\text{C}_{\text{organic}}$ PDB	carbon isotope composition of kerogen, ‰ PDB
Corg (wt.%)	total organic carbon content (TOC) of bulk rock, weight%
H/C	H/C ratio of kerogen
$\delta^{34}\text{S}_{\text{sulphate}}$ CDT	sulphur isotope composition of sulphate, ‰ CDT
$\delta^{34}\text{S}_{\text{sulphide}}$ CDT	sulphur isotope composition of sulphide, ‰ CDT
Rb (ppm)	rubidium concentration in carbonate phase, ppm
$\Delta\delta^{13}\text{C}$	$\delta^{13}\text{C}$ of carbonate phase - $\delta^{13}\text{C}$ of kerogen, ‰ PDB
Comments	problems with data, e.g. altered, poor age constraints, etc.

3.1.2. Poor age constraints

[8] Most Precambrian isotope data suffer from poor age resolution due to the scarcity of reliable radiometric ages coupled with the inherent difficulties in stratigraphic correlation in the Precambrian. This problem will undoubtedly improve with time as more ages are obtained for important sections. Substantial improvements have already been made during the last decade in the dating of entire rock successions, for example, the McArthur basin of Australia and the Belt/Purcell Supergroup of the USA/Canada, which have led to considerable changes in the age assignments of published isotope data.

3.1.3. Difficulties in stratigraphic correlation

[9] Although there has been a marked improvement in the number of radiometric age constraints on Precambrian successions, it is unlikely that there will ever be enough data to assign firm ages to most samples on this basis alone. Therefore other techniques of global stratigraphic correlation need to be applied. For the Neoproterozoic-Cambrian interval, schemes of global stratigraphic correlation have been consulted that use fossil, isotopic, and other information [e.g., Kaufman and Knoll, 1995; Shields, 1999; Walter et al., 2000]. However, in cases where age assignment has involved carbon or

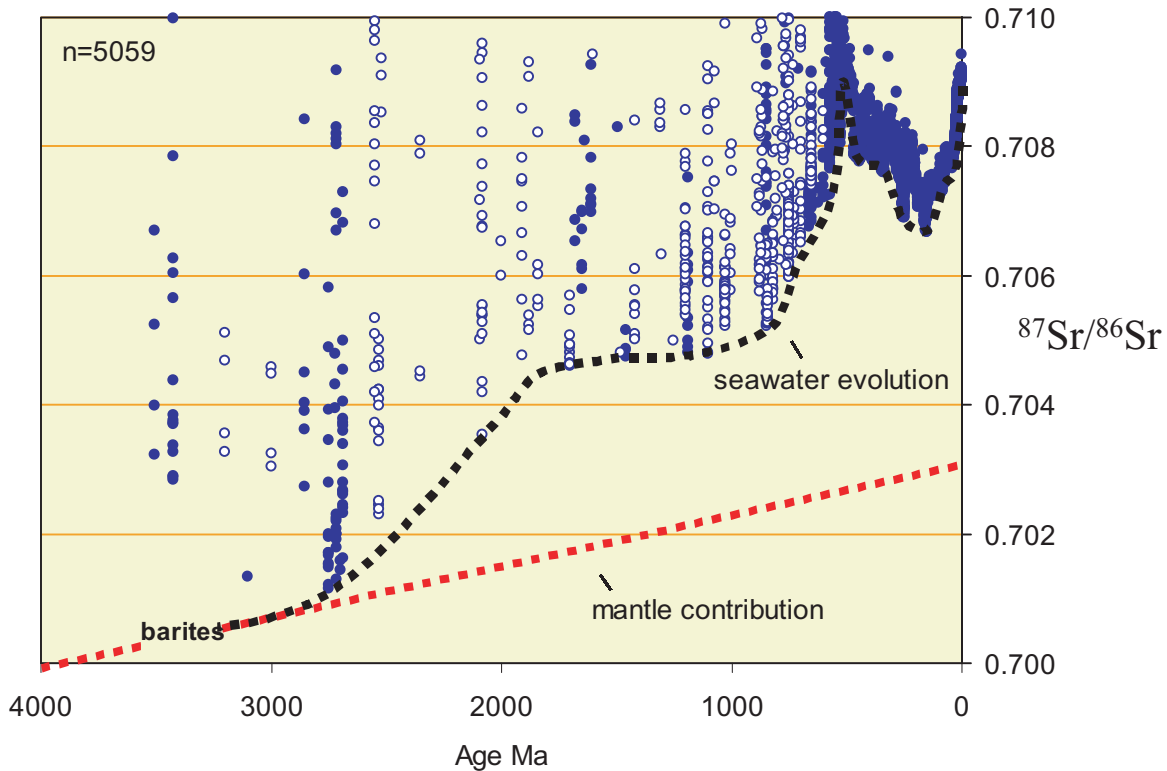


Figure 1. Strontium isotopic evolution of seawater based on published analyses of marine carbonate rocks and Phanerozoic calcitic fossils from *Veizer et al.* [1999]. Poorly time-constrained samples (greater than ± 50 Ma) are shown as open circles.

strontium isotope stratigraphy in isolation a generous margin of error has been chosen because of the potential dangers of circular reasoning.

3.2. Element Specific Limitations

3.2.1. Sr isotopes

[10] Published Sr isotope data (Figure 1) for carbonate rocks are generally reported relative to the NBS 987 standard or can, by means of reported standard values from the same laboratory of the Elmer Amend standard or modern ocean water, be recalculated against expected values of the NBS 987 standard. Today, the most commonly cited value for the standard NBS 987 is 0.71025 [*McArthur, 1994*], and this was used as the standard value for normalization of all reported Sr isotope ratios (Table 1, $^{87}\text{Sr}/^{86}\text{Sr}_{\text{norm}}$ column). Although laboratories may produce different systematic errors in their measurement of this standard, this only becomes a significant problem for high-resolution

Sr isotope stratigraphy in the late Phanerozoic [*McArthur, 1994*].

[11] The biggest problem in Precambrian Sr isotope stratigraphy is postdepositional alteration. Of the ~ 1000 Precambrian carbonate samples that have been analyzed for Sr isotopes, almost all have suffered alteration of their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to some degree. Alteration by a radiogenic source, by interaction with clay minerals, for example, will tend to increase $^{87}\text{Sr}/^{86}\text{Sr}$, while alteration by fluids affected by a juvenile volcanic source or by dissolution of older, less radiogenic authigenic minerals will tend to decrease $^{87}\text{Sr}/^{86}\text{Sr}$. In practice, postdepositional alteration nearly always causes an increase in $^{87}\text{Sr}/^{86}\text{Sr}$, which leads to the rule-of-thumb that lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios represent our best maximum estimate of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ at any particular time [*Veizer and Compston, 1974; Burke et al., 1982*]. This is certainly the case on the scale of the Precambrian (Figure 1) but should be demonstrated

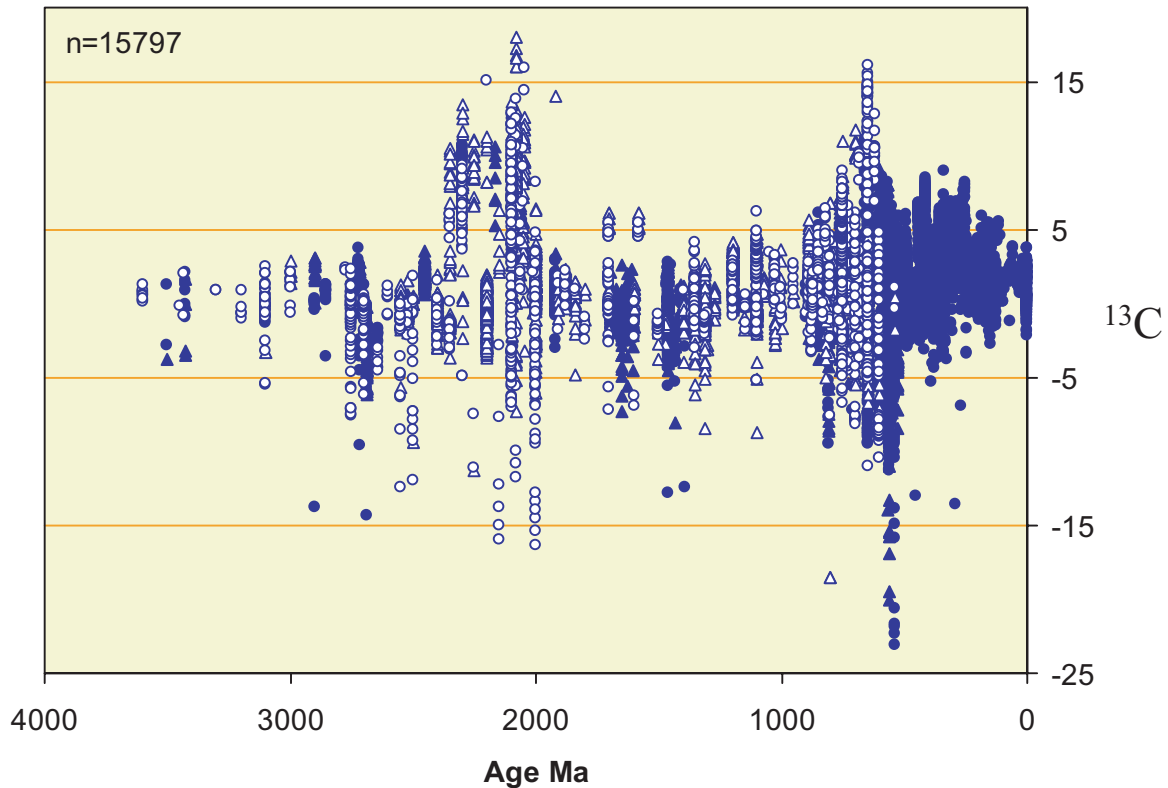


Figure 2. Carbon isotopic evolution of marine carbonate based on published analyses of limestones (circles), dolostones (triangles), and Phanerozoic calcitic fossils from *Veizer et al.* [1999]. Poorly time-constrained samples (greater than ± 50 Ma) are shown as open symbols.

on a case-by-case basis as postdepositional decreases in $^{87}\text{Sr}/^{86}\text{Sr}$ have been reported, although these are generally of a relatively minor magnitude. [12] Analytical techniques and reporting of Sr isotope data vary greatly. Sample dissolution techniques have generally become more carbonate-selective, while sampling techniques have become more component-selective, both of which have led to lower, more seawater-like $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Nowadays, carbonate samples are generally prepared by leaching with a weak acid, such as acetic acid, after initial washing in water or a buffer solution [McArthur, 1994]. Some research groups systematically carry out corrections of their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for radiogenic ^{87}Sr , which derives from the in situ decay of ^{87}Rb . However, well-preserved, pure carbonate components should not normally contain sufficient Rb to necessitate such correction, while Rb corrections usually involve unjustifiable assumptions that are likely to result in significant errors. For example, some leaching of clays during sample preparation is frequently inevi-

table and so measured Rb/Sr ratios could relate, in part, to clay minerals, which might have changed their trace element compositions during diagenesis. Clay minerals suffer preferential loss of radiogenic Sr from their lattices relative to the parent Rb, something which can occur during diagenesis or sample preparation, resulting in the overcorrection of initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Last the ages of most samples are not known with sufficient accuracy to carry out corrections for Rb decay, causing additional errors. Lastly, for these reasons, $^{87}\text{Sr}/^{86}\text{Sr}$ data in the PMCID have been left uncorrected for ^{87}Rb decay.

3.2.2. C isotopes

[13] Generally, analytical techniques, data reporting, and diagenetic alteration rarely present major problems for C isotope data (Figure 2) on the scale of the Precambrian. Nevertheless, some questions need to be asked of individual case studies, such as whether the presence of organic matter in C_{org} -rich

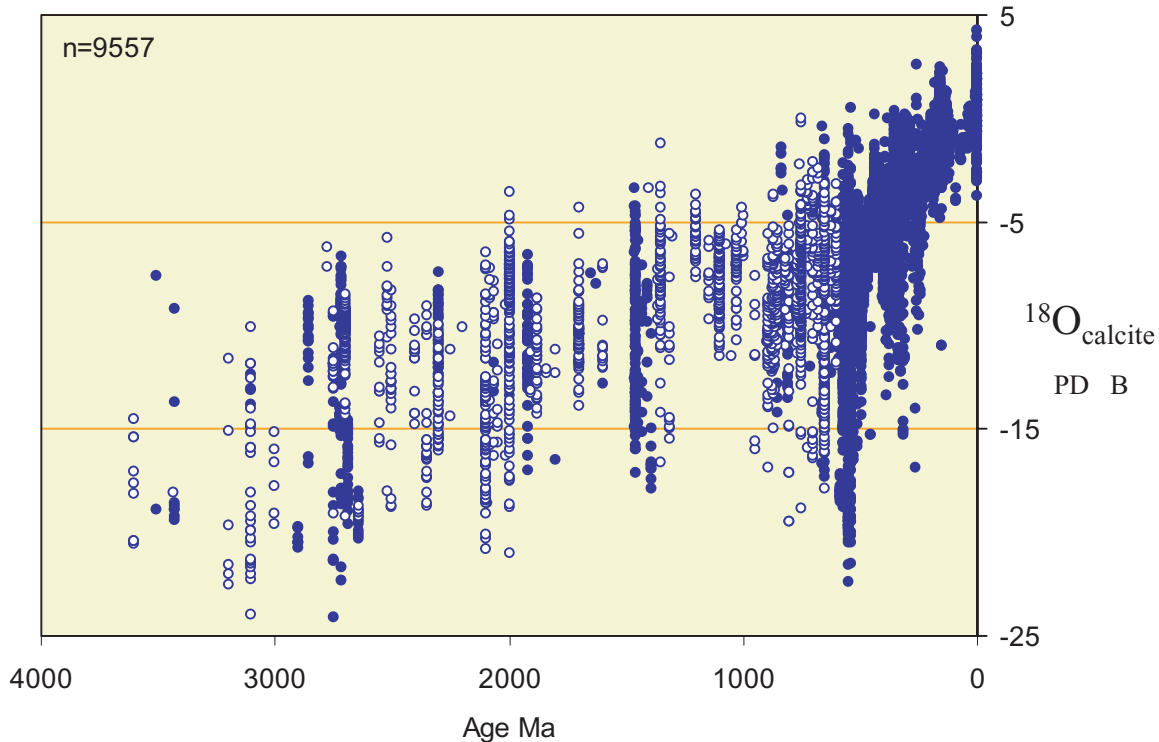


Figure 3. Oxygen isotopic evolution of marine calcite based on published analyses of limestones and Phanerozoic calcitic fossils from *Veizer et al.* [1999]. Poorly time-constrained samples (greater than ± 50 Ma) are shown as open circles.

samples has affected the analysis of $\delta^{13}\text{C}_{\text{carb}}$ and whether diagenetic or primary components were selected in the original study.

3.2.3. O isotopes

[14] O isotope data (Figure 3) suffer most from inconsistency and ambiguity. $\delta^{18}\text{O}$ data are often absent from data tables, especially where C isotope stratigraphy has been the authors' prime concern. This is generally because of the relative susceptibility of O isotopes to diagenetic alteration and subsequent difficulty in interpretation. For this reason, previous isotope compilations have not included O isotope data [e.g., *Schopf and Klein*, 1992] with the exception of the work of *Perry and Ahmad* [1983].

[15] Some reported O isotope data may also be of limited usefulness due to a lack of background information (metadata) on original mineralogy and analytical technique. First, $\delta^{18}\text{O}$ data need to be mineral-specific to be of use as each carbonate mineral undergoes different degrees of fractionation

during its precipitation from solution. The $\delta^{18}\text{O}$ data are frequently reported without reference to the mineralogy of the carbonate phase analyzed and usually omit mention of whether the authors have determined the mineralogical purity of their samples. This problem is especially acute with older Precambrian sedimentary rocks, which are likely to contain iron, magnesium, and manganese carbonate minerals as well as dolomite and calcite. In cases, where a mixture of dolomite and calcite is known to have been analyzed, it is also desirable to know whether these mineral phases have been cleanly separated before analysis. Where doubts remain about the carbonate mineralogy, these data have been placed within the "other carbonate minerals" column.

[16] Research articles seldom clarify whether the respective corrections have been carried out according to the different equilibrium fractionations experienced during dolomite and calcite dissolution in phosphoric acid. Where dolomite has been analyzed without any correction at 25°C , this leads to a $\delta^{18}\text{O}_{\text{dol}}$ value that is roughly 0.8‰ higher than if the correction had been carried out.

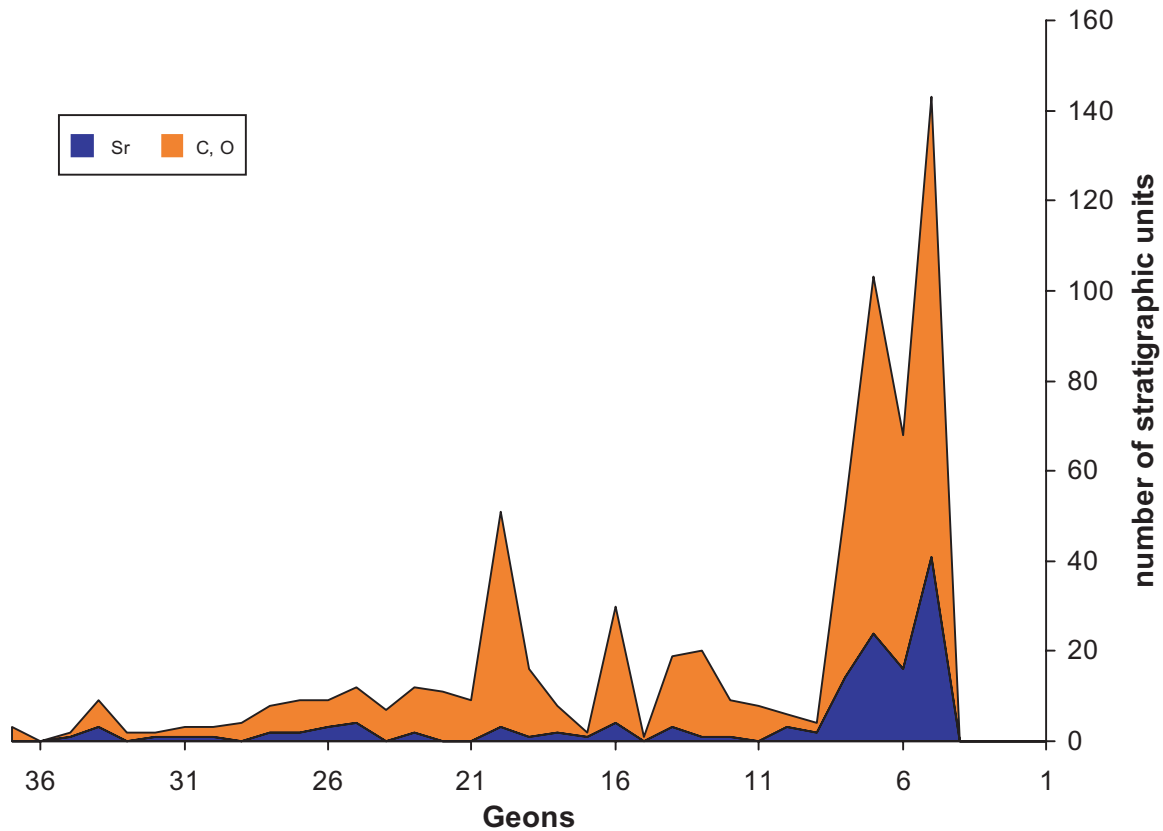


Figure 4. Number of identifiable stratigraphic units with published carbonate isotope data shown against 100 Ma intervals or geons [Hofmann, 1999].

3.3. Effects of Sampling Bias on the Precambrian Sr, C, and O Isotopic Records

3.3.1. Geographic bias

[17] Most sampling for isotope stratigraphy has been carried out in easily accessible areas of developed countries even though most Precambrian rocks derive from ancient cratons, which are frequently poorly exposed and relatively inaccessible. For these reasons, some sections in Australia, USA, and Canada have been resampled many times by different research groups, which may greatly exaggerate the importance of these sections.

3.3.2. Preservation bias

[18] Because of tectonic recycling and sedimentary burial, most potential marine carbonate samples of Precambrian age have been annihilated, either by uplift and erosion or by subduction, or are not exposed. In addition, many Precambrian rocks are highly metamorphosed. Metamorphism frequently

alters the chemical and isotopic compositions of carbonate rocks, rendering them of limited usefulness for isotope stratigraphy. Even in cases where metamorphic rocks have preserved their primary isotopic signatures, their tectonic settings can often be too complex to permit adequate dating and correlation.

3.3.3. Sedimentary bias

[19] Most samples represent marginal, shallow-water settings, which represent only a small proportion of the wide range of possible ocean sedimentary settings.

3.3.4. Temporal bias

[20] A disproportionately large number of the samples are of Neoproterozoic-Cambrian (800–500 Ma) and mid-Palaeoproterozoic age (2100–1900 Ma). This may partly be a true reflection of the marine carbonate record and partly a result of sampling bias. This temporal bias appears also when we consider

Table 2. Structure of the Alternative Version of the PMCID Database – Version 1.1(b)

Column Name	Content of Column
Formation	formation name occasionally including groups, members, etc.
Location	name of section, borehole and/or region
Country	name of country
Era	era subdivision from Eoarchean to Cenozoic
Geon	100 Ma intervals or “Geons” from 0 to 37 [<i>Hofmann, 1999</i>]
Age, Ma	relatively well constrained ages (less than ± 50 Ma)
Age, Ma max	assigned ages maximum age constraint
min	minimum age constraint
Duration	likely time equivalent of data range
Source: C,O data	literature references for stable isotope data (see appendix)
Source: age	literature references for age constraints (incomplete)
Dating technique	dating technique, e.g., U-Pb single zircon, biostratigraphy, etc.
$n^{\circ} C$	number of C isotope analyses on all carbonate minerals
$\delta^{13}C_{\text{mean}}$	mean of $\delta^{13}C$ values for all carbonate minerals, ‰ PDB
$\delta^{13}C_{\text{max}}$	maximum of $\delta^{13}C$ values for all carbonate minerals, ‰ PDB
$\delta^{13}C_{\text{min}}$	minimum of $\delta^{13}C$ values for all carbonate minerals, ‰ PDB
$\delta^{13}C_{\text{sd}}$	standard deviation of $\delta^{13}C$ values for all carbonate minerals
$n^{\circ} O_{\text{calcite}}$	number of O isotope analyses on calcite
$\delta^{18}O_{\text{mean calcite}}$	mean of $\delta^{18}O$ values for calcite, ‰ PDB
$\delta^{18}O_{\text{max. calcite}}$	maximum of $\delta^{18}O$ values for calcite, ‰ PDB
$\delta^{18}O_{\text{min. calcite}}$	minimum of $\delta^{18}O$ values for calcite, ‰ PDB
$\delta^{18}O_{\text{sd calcite}}$	standard deviation of $\delta^{18}O$ values for calcite
$n^{\circ} O_{\text{dolomite}}$	number of O isotope analyses on dolomite
$\delta^{18}O_{\text{mean dolomite}}$	mean of $\delta^{18}O$ values for dolomite, ‰ PDB
$\delta^{18}O_{\text{max dolomite}}$	maximum of $\delta^{18}O$ values for dolomite, ‰ PDB
$\delta^{18}O_{\text{min dolomite}}$	minimum of $\delta^{18}O$ values for dolomite, ‰ PDB
$\delta^{18}O_{\text{sd dolomite}}$	standard deviation of $\delta^{18}O$ values for dolomite
$n^{\circ} O_{\text{others}}$	number of O isotope analyses on other carbonate minerals
$\delta^{18}O_{\text{mean others}}$	mean of O isotope data on other carbonate minerals, ‰ PDB
$\delta^{18}O_{\text{max others}}$	maximum of $\delta^{18}O$ values for other carbonate minerals, ‰ PDB
$\delta^{18}O_{\text{min others}}$	minimum of $\delta^{18}O$ values for other carbonate minerals, ‰ PDB
$\delta^{18}O_{\text{sd others}}$	standard deviation of $\delta^{18}O$ values for other carbonates
$n^{\circ} C_{\text{org}}$	number of C isotope analyses on kerogen
$\delta^{13}C_{\text{mean org}}$	mean of $\delta^{13}C$ values for kerogen
$\delta^{13}C_{\text{max org}}$	maximum of $\delta^{13}C$ values for kerogen
$\delta^{13}C_{\text{min org}}$	minimum of $\delta^{13}C$ values for kerogen
$\delta^{13}C_{\text{sd org}}$	standard deviation of $\delta^{13}C$ values for kerogen
$\Delta\delta^{13}C$	$\delta^{13}C$ of carbonate minerals - $\delta^{13}C$ of kerogen
$\Delta\delta^{18}O$	$\delta^{18}O$ of dolomite - $\delta^{18}O$ of calcite
$n^{\circ} Sr$	number of Sr isotope analyses on carbonate minerals
$^{87}Sr/^{86}Sr$	lowermost or best preserved Sr isotope ratio
Source: Sr data	literature references for strontium isotope data - see appendix
Comments	comments (incomplete)

the number of individual studies or data sets (Figure 4) rather than individual samples. One obvious reason for this skewed distribution is that isotopic studies are more often carried out for these two intervals because of the large $\delta^{13}C$ excursions during these times (Figure 2).

3.3.5. Sample size bias

[21] Many studies, especially those before 1985, do not report many isotopic values per litholog-

ical unit, whereas some more recent studies report hundreds of values from a small part of one unit, which likely represents a much shorter period of time. This kind of bias exaggerates the effect of particular lithological units to the detriment of others and can be reduced by dividing the database into identifiable lithological units. We have carried this out in an alternative version (Table 2) of the PMCID (version 1). This version tends to overemphasise younger, more intensively studied parts of the geological record, while

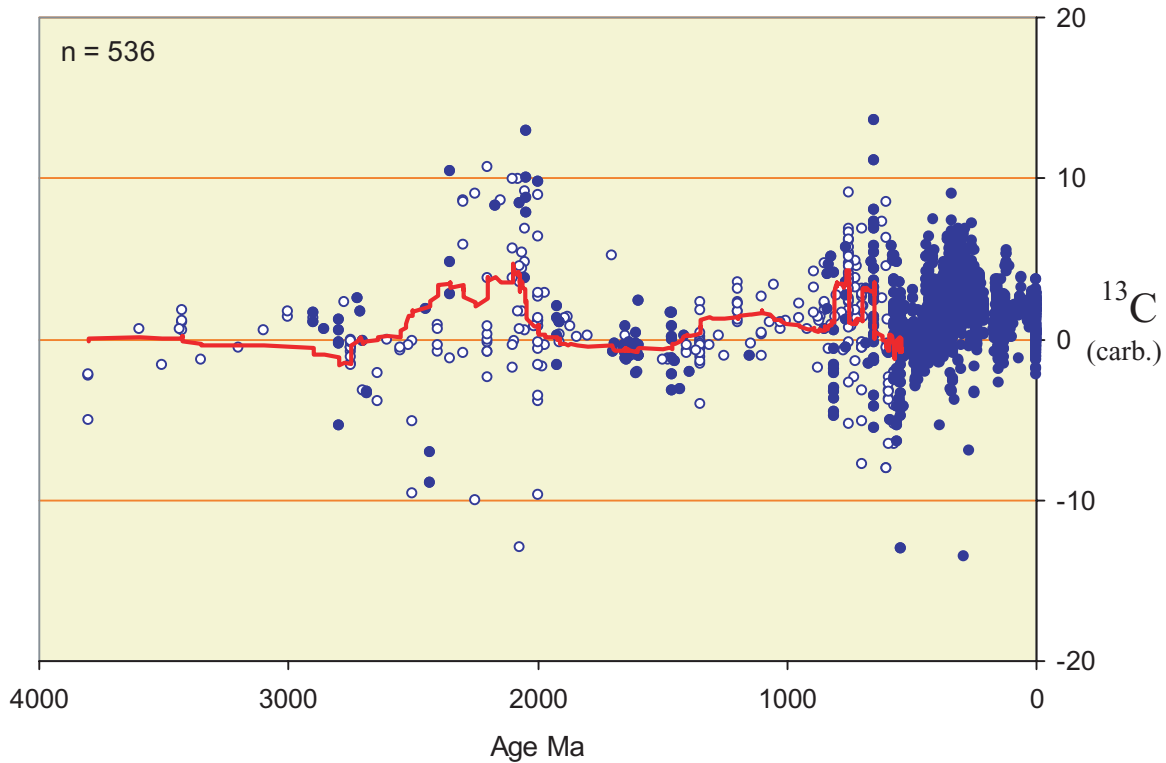


Figure 5. Carbon isotopic evolution of marine carbonate based on means of published analyses of carbonate rocks (including all carbonate minerals) from identifiable lithological units. Poorly time-constrained samples (greater than ± 50 Ma) are shown as open circles. Continuous line represents a running mean through all data points.

ignoring the obvious fact that not all, identifiable lithological units represent an equal duration. We consider, however, that the coupling of both kinds of database structure will lead to a more complete interpretation of the Precambrian isotopic record.

4. Interpretation

[22] It is not the purpose of the present article to interpret isotopic trends through the Precambrian in any depth. Nonetheless, we consider it necessary to describe the initial results of the PMCID compilation and to outline major similarities and differences between these results and those of previous compilations.

4.1. Sr Isotope Stratigraphy

[23] As discussed in section 3.2, the lower part of the $^{87}\text{Sr}/^{86}\text{Sr}$ band in Figure 1 is likely to represent a maximum constraint on seawater $^{87}\text{Sr}/^{86}\text{Sr}$.

These “best estimate” (least altered from seawater) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reveal a deflection away from mantle-like $^{87}\text{Sr}/^{86}\text{Sr}$ before ~ 2.5 Ga to more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ after ~ 2.5 Ga [Veizer and Compston, 1976]. This switch is consistent with a change from a “mantle”-buffered to a “river”-buffered global ocean around this time and is likely to result from a combination of (1) decreasing heat flux from the mantle and (2) intensified formation of continental crust [Veizer *et al.*, 1982]. A second major increase in $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.7052 to 0.7092 took place between ~ 1000 and 500 Ma, implying steadily increasing continental influence on ocean chemistry during this time. This is consistent with elevated rates of tectonic uplift and erosion of highly radiogenic crust, possibly related to the birth, break-up, and dispersal of the supercontinent Rodinia [Meert and Powell, 2000]. This second increase is also of potential importance in global stratigraphic correlation, especially

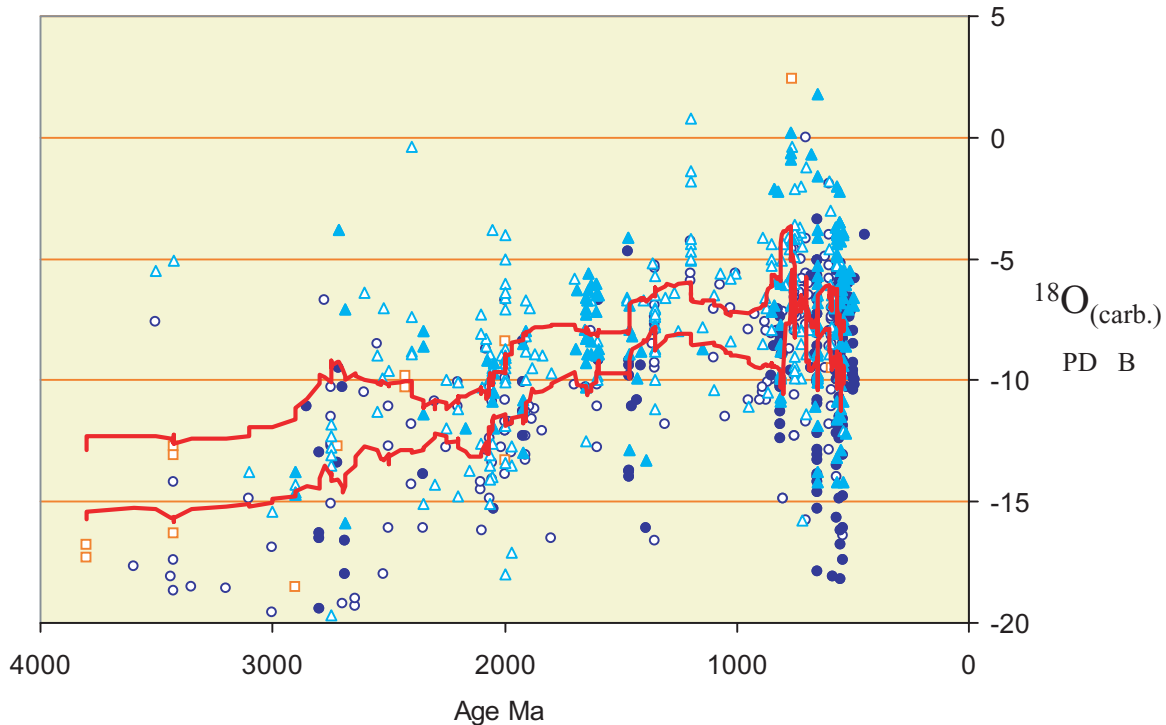


Figure 6. Oxygen isotopic evolution of Precambrian and Cambrian marine calcite (circles, $n = 318$), dolomite (triangles, $n = 349$) and other carbonate minerals (squares) based on means of published analyses of carbonate rocks from identifiable lithological units. Poorly time-constrained samples (greater than ± 50 Ma) are shown as open symbols. Continuous lines represent running means through the dolomite (top line) and calcite (bottom line) data, respectively.

when combined with C isotopes [Shields, 1999; Walter *et al.*, 2000].

4.2. C Isotope Stratigraphy

[24] The $\delta^{13}\text{C}$ values reflect changes in the biogeochemical redox cycling of carbon, with long-term trends (>100 Ma) likely reflecting real shifts in the proportion of carbonate versus organic carbon burial [Schidlowski, 1993]. Published Precambrian $\delta^{13}\text{C}$ data are relatively numerous with over 10,000 samples measured from 536 distinct lithological units. The compilations shown in Figures 2 and 5 confirm that marine bicarbonate $\delta^{13}\text{C}$ remained close to 0‰ during much of Precambrian time [Schidlowski *et al.*, 1975]. Two prolonged intervals of anomalously high (greater than +10‰) and variable (range up to 20‰) $\delta^{13}\text{C}$ can be identified: the mid-Paleoproterozoic (2.3–1.9 Ga) and the mid-Neoproterozoic (0.8–0.6 Ga). The extent to which high marine carbonate $\delta^{13}\text{C}$ represents truly elevated rates of

organic burial is difficult to prove for either period [Melezhik *et al.*, 1999; Shields *et al.*, 2002]. Mean $\delta^{13}\text{C}$ values reveal a sustained rise over some 10^8 years during both these times, which is consistent with a real increase in organic carbon burial and storage rates. Atmospheric oxygen concentrations seem likely to have risen as a consequence [DesMarais *et al.*, 1992].

4.3. O Isotope Stratigraphy

[25] Despite considerable scatter due to postdepositional alteration, primary variation and analytical inconsistencies, calcite $\delta^{18}\text{O}$ values are generally depleted throughout the Precambrian relative to most of the Phanerozoic (Figures 3 and 6). Mean $\delta^{18}\text{O}$ values from both calcite and dolomite increase in parallel through the Precambrian with a roughly constant isotopic discrimination (Figure 6) that probably reflects differences in their equilibrium isotopic fractionations [Land, 1980], either during precipitation from seawater or, more

likely, from near-marine, early diagenetic fluids. The low $\delta^{18}\text{O}$ values of most Precambrian carbonates are consistent with the well-documented increase in marine calcite $\delta^{18}\text{O}$ during the Phanerozoic, which has been interpreted as resulting from a tectonically controlled, first-order increase in seawater $\delta^{18}\text{O}$ with higher-order, climate-related fluctuations superimposed [Veizer *et al.*, 2000]. The extent to which seawater $\delta^{18}\text{O}$ has changed over geological history is still a matter of controversy [Muehlenbachs, 1998; Godd ris and Veizer, 2000], but the observed Precambrian O isotope record is consistent with recent modeling [Wallmann, 2001].

5. Future Work

[26] The Precambrian Marine Carbonate Isotope Database is still unfinished. At the moment of writing, a further 50 recently published articles await incorporation. Also, Precambrian isotope data need to be combined seamlessly with the Phanerozoic isotope record, which is based largely on data from fossil brachiopods and foraminifera [Veizer *et al.*, 1999]. At present, the PMCID contains a large proportion of the published carbonate isotope data for the Cambrian System, and it is hoped that this can be extended to include much of the lower Paleozoic, which will allow direct comparison between the carbonate rock-based data and fossil limestone-based data. Meanwhile, we await feedback from users, so that the PMCID can evolve into a useful tool for the geochemical community at large.

Appendix (Representative Sample).

PMCID Version 1.1 Database

References

[27] The full Appendix is available in the HTML version of the article at <http://www.g-cubed.org>.

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