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87 Sr/ 86 Sr, δ^{13} C and δ^{18} O evolution of Phanerozoic seawater

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Abstract

A total of 2128 calcitic and phosphatic shells, mainly brachiopods with some conodonts and belemnites, were measured for their δ^{18} O, δ^{13} C and 87 Sr/ 86 Sr values. The dataset covers the Cambrian to Cretaceous time interval. Where possible, these samples were collected at high temporal resolution, up to 0.7 Ma (one biozone), from the stratotype sections of all continents but Antarctica and from many sedimentary basins. Paleogeographically, the samples are mostly from paleotropical domains. The scanning electron microscopy (SEM), petrography, cathodoluminescence and trace element results of the studied calcitic shells and the conodont alteration index (CAI) data of the phosphatic shells are consistent with an excellent preservation of the ultrastructure of the analyzed material. These datasets are complemented by extensive literature compilations of Phanerozoic low-Mg calcitic, aragonitic and phosphatic isotope data for analogous skeletons. The oxygen isotope signal exhibits a long-term increase of δ^{18} O from a mean value of about -8% (PDB) in the Cambrian to a present mean value of about 0% (PDB). Superimposed on the general trend are shorter-term oscillations with their apexes coincident with cold episodes and glaciations. The carbon isotope signal shows a similar climb during the Paleozoic, an inflexion in the Permian, followed by an abrupt drop and subsequent fluctuations around the modern value. The ⁸⁷Sr/⁸⁶Sr ratios differ from the earlier published curves in their greater detail and in less dispersion of the data. The means of the observed isotope signals for 87 Sr/ 86 Sr, δ^{18} O, δ^{13} C and the less complete δ^{34} S (sulfate) are strongly interrelated at any geologically reasonable (1 to 40 Ma) time resolution. All correlations are valid at the 95% level of confidence, with the most valid at the 99% level. Factor analysis indicates that the 87 Sr, δ^{18} O, δ^{13} C and δ^{34} S isotope systems are driven by three factors.

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The first factor links oxygen and strontium isotopic evolution, the second ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and $\delta^{34}\text{S}$, and the third one the $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$. These three factors explain up to 79% of the total variance. We tentatively identify the first two factors as tectonic, and the third one as a (biologically mediated) redox linkage of the sulfur and carbon cycles. On geological timescales (≥ 1 Ma), we are therefore dealing with a unified exogenic (litho-, hydro-, atmo-, biosphere) system driven by tectonics via its control of (bio)geochemical cycles. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The Sr isotopic composition of past seawater, as monitored by marine carbonate shells and rocks, can be utilized as a proxy parameter for tectonic evolution of the Earth System, because the 87 Sr/ 86 Sr variations reflect principally the waxing and waning of Sr input from rivers ('continental' flux) vs. the input from the submarine hydrothermal systems ('mantle' flux) (Faure, 1986; Taylor and Lasaga, this issue). The general trends of 87 Sr/ 86 Sr variations for Phanerozoic seawater have been sketched already in the pioneering studies of Peterman et al. (1970), Veizer and Compston (1974) and Burke et al. (1982). The published 'curve' of the last authors served subsequently as a baseline for all follow-up studies. The last decade, however, witnessed a considerable advance in instrumental precision, sample preparation and in better geological constraints, particularly in stratigraphic assignment of samples. This resulted in a considerably tighter delineation of the secular marine isotope trend and opened the stage for utilization of Sr isotopes as a correlation and dating tool, 'isotope stratigraphy'. This stage of research has been summarized in DePaolo and Ingram (1985), Elderfield (1986), Veizer (1989), McArthur (1994) and Smalley et al. (1994). Nevertheless, the utility of this new tool has been restricted mostly to the Cenozoic, because of the steep and well-defined rise in marine ⁸⁷Sr/⁸⁶Sr ratio. Apart from the steep slope, the major reason for delineation of such a well-defined trend has been the fact that this young portion of the geologic record has a relatively well-resolved and detailed stratigraphy and that sediments of this age contain shells that were only marginally affected by the vicissitudes of diagenesis.

In theory, it should be possible to define similar well-constrained trends also for other Phanerozoic intervals with equally steep slopes and thus extend the utility of the 'isotope stratigraphy' into the Mesozoic and Paleozoic (Veizer et al., 1997a). The constraining factors in achieving this goal are not so much the instrumental capabilities, because for many laboratories intra- and interlaboratory reproducibility routinely falls within $\pm 25 \times 10^{-6}$ limits (Thirwall, 1991; McArthur, 1994), but the preservation and resolution of the geologic record.

The $\delta^{13}C$ of ancient oceans (e.g., Clayton and Degens, 1959: Schidlowski et al., 1975: Veizer and Hoefs, 1976) was for a long time regarded as essentially invariant, but with a considerable noise, around 0% PDB. Only in the 1980s was it realized that this noise contains a real oscillating secular signal (Scholle and Arthur, 1980; Veizer et al., 1980; Arthur et al., 1985; Shackleton, 1985). In contrast to the below-discussed oxygen isotopes, the primary nature of the $\delta^{13}C_{carbonate}$ secular trend has not been seriously challenged. The reason is that diagenetic recrystallization of carbonates is accomplished in a system with a low water /rock ratio for carbon, and a high ratio for oxygen (Banner and Hanson, 1990; Banner, 1995; Jacobsen and Kaufman, this issue). Diagenetic stabilization of carbonates therefore results in transposition of carbon from a precursor to a successor mineral phase.

The above oscillations in the $\delta^{13}C_{carbonate}$ trend are being increasingly utilized for correlation and isotope stratigraphy (e.g., Knoll et al., 1986; Derry et al., 1992). This tool, however, is subject to additional limitations if compared to Sr isotopes. The major difference arises from the fact that $\delta^{13}C_{carbonate}$ at any given time shows a considerable spread of values due to spatial variability of oceanic $\delta^{13}C_{\Sigma CO_2}$ (e.g., Kroopnick, 1985) and due to biological factors of shell formation (McConnaughey and Whelan, 1997). The complications arise not so much during logging of a single well or a profile, but can become considerable if unrelated sequences or wells are compared. Nonetheless, large peaks can serve as correlation markers, particularly in the Precambrian (Kaufman et al., 1992). In addition, the secular $\delta^{13}C_{carbonate}$ trend is increasingly utilized as a proxy for determining oceanic paleoproductivity/preservation patterns, ancient pCO_2 and pO_2 states, and similar paleoenvironmental phenomena (Berner et al., 1983; Berner, 1994; Kump and Arthur, this issue).

The ${}^{18}O/{}^{16}O$ composition of ancient oceans is one of the perennial and most controversial issues of isotope geochemistry. Commencing with the nascent stages of isotope geochemistry, it has been realized (Baertschi, 1957; Clavton and Degens, 1959) that oxygen isotopic composition of carbonates becomes progressively more depleted in ¹⁸O with increasing age of the rocks. This trend for carbonates (and other chemical marine sediments) has been confirmed by many studies (e.g., Veizer and Hoefs, 1976) and its validity is not disputed. It is the implications of such observations that result in a sharp division within the scientific community. If essentially a primary feature, the implications could be one or all of the following: (1) seawater δ^{18} O must have changed in the course of the Phanerozoic (e.g., Weber, 1965; Perry and Tan, 1972; Hudson and Anderson, 1989); (2) the early oceans must have been much warmer than today, up to $\sim 70^{\circ}$ C (Knauth and Epstein, 1976; Kolodny and Epstein, 1976; Karhu and Epstein, 1986); or (3) they were stratified, with deep waters being generated by sinking of salty brines from extensive evaporation at low latitudes (Brass et al., 1982; Railsback, 1990). Objections to alternative (1) arise from studies of the oceanic crust and its ancient counterparts (Gregory and Taylor, 1981) and from model considerations (Muehlenbachs and Clavton, 1976; Gregory, 1991; Muehlenbachs, 1998), both claiming that the δ^{18} O of ocean water is, and has been, buffered at ~ 0% SMOW by rock/water interactions in hydrothermal cells at oceanic ridges. For alternative (2), the persistence of essentially the same faunal assemblages and the recurrence of ice ages throughout the Phanerozoic are difficult to reconcile with the advocated warm temperatures (Veizer et al., 1986). Finally, for alternative (3), the implied permanent saline stratification would be difficult to

sustain and, even if sustainable, it could account for no more than $\sim 1.5\%^{-18}$ O depletion in the near-surface oceanic layer (Railsback, 1990).

The above considerations, and the observation that advancing diagenetic recrystallization of carbonate (and other) phases results in ¹⁸O depletion, either due to involvement of meteoric waters or to elevated temperatures, led one group of researchers to argue that the δ^{18} O secular trend is essentially a diagenetic feature (Degens and Epstein, 1962; Killingley, 1983; Land, 1995). Resolution of this secondary vs. primary dilemma is of utmost importance, because the δ^{18} O could potentially serve as a powerful paleoceanographic tracer for the entire Phanerozoic.

In this contribution, due to space restrictions, we concentrate solely on documentation of the trends in order to make the datasets available to the scientific community. Their interpretations and implications for the δ^{13} C are discussed by other authors in this volume (Hayes et al., this issue; Kump and Arthur, this issue). For the δ^{18} O, the resolution of the primary vs. secondary nature of the Phanerozoic trend is a precondition for any argumentation dealing with consequences. We shall therefore concentrate on this issue only, leaving the model implications for future consideration.

Because of the potential utility of 87 Sr/ 86 Sr, δ^{13} C and δ^{18} O secular trends for resolution of paleoceanographic, paleoecological and stratigraphic questions, it is essential to define these trends as tightly as possible. Here, we introduce a new set of paleoseawater curves for the Phanerozoic. In order to minimize the impact of diagenetic resetting of the signal, we have concentrated on material that is relatively resistant to diagenetic alteration. Similarly, in order to attain high resolution, we resampled 'complete' and well-dated sequences. Nevertheless, fulfillment of these two requirements, in particular the temporal assignment of samples, is a complex task that requires some introductory discussion.

2. Completeness of the sedimentary record and isotopic ages

Any given stratigraphic section only intermittently records the passage of geological time (Dingus, 1984). On a global scale, the volume of sedimentary rocks decreases with age because the record becomes progressively less complete with time. Within any sedimentary sequence, there are hiatuses which represent periods of non-deposition, erosion and/or diagenesis. Stratigraphic sections spanning greater temporal intervals have a greater opportunity of incorporating more hiatuses and hiatuses spanning longer periods of time (Sadler, 1981; Korvin, 1992). Determining the stratigraphic position and duration of a hiatus within a section is often problematic. The end result is a progressive decrease in the completeness of the stratigraphic record with increasing age.

In general, sequences often have erosional or non-depositional contacts which are difficult to identify from lithological parameters alone. In these situations, biostratigraphy, absolute dating and magnetostratigraphy are often utilized. Unfortunately, each method has its limitations. Presently, the highest resolution can be achieved with biostratigraphy, with a resolution limit rarely better than 0.5 Ma and more often on the order of 1 Ma or more. As a result, the upper limit for using this method for hiatus identification cannot be better than 0.5 Ma. In addition, bioturbation can effectively homogenize sediments in the upper 10-15 cm, rendering any stratigraphic method meaningless at scales less than 15 cm (Anders et al., 1987). If sediment accumulation is slow, then the effect of bioturbation on the resolution may become geologically significant.

Stratigraphers define a complete section as one which has no gaps larger than each time unit of a specific scale (Anders et al., 1987). As the resolution improves (corresponding to shorter time scales), there is a corresponding decrease in the perceived completeness of the section. Therefore, improved sampling accuracy will result in an overall decrease in the perceived completeness of the stratigraphic section (Schindel, 1982; Dingus, 1984). On average, it is estimated that only 1/30th of the elapsed time is represented by sediments (Algeo and Wilkinson, 1988; Miall, 1994).

The above constraints are compounded by problems with assignment of 'absolute', or more correctly 'isotopic', ages to particular samples. In order to enable comparison with other datasets, we consistently utilized the time scale of Harland et al. (1990), despite the fact that many of these 'ages', including the commencement of the Phanerozoic at 570 Ma ago (rather than 543 Ma; Bowring and Erwin, 1998), are today not accepted anymore. The uncertainties in 'age' estimates for epochs and stages are usually several million years, larger than the entire duration of many stages. For example, the estimated duration of the Eifelian of ~4 Ma is bracketed by isotopic ages of 386 ± 5 to 382 + 9/-14 Ma (Harland et al., 1990). This interval encompasses some five conodont biozones, each arbitrarily assigned an isotopic age by linear extrapolation between these two estimates that have large experimental errors.

Because of the above complications, we have concentrated on sedimentary sequences that were as complete as possible, preferably stratotypes, providing they contained suitable material (shells) for isotopic studies. The correlation of samples from different localities was based on biostratigraphy (biozones) and not on 'isotopic ages'. The relative 'age' within the same sequence and biozone was based on stratigraphic superposition. Unfortunately, when comparing distant Paleozoic and Mesozoic sequences, the best that we could accomplish was a correlation to a biozone resolution. This will be important when discussing higher level oscillations in the isotope signal.

3. Sample selection

In order to constrain as much as possible post-depositional alteration of the isotope signal, we have concentrated on samples that are relatively resistant to diagenesis. The preferred material is the low-Mg calcite of marine skeletons, such as brachiopods, belemnites and foraminifera. Keeping in mind that the Cenozoic portion of the isotope record has been extensively studied, chiefly due to DSDP, we have concentrated on the Paleozoic and Mesozoic. These left brachiopods and belemnites as the only abundant and stratigraphically widespread fossils with low-Mg calcitic skeletons. Furthermore, for brachiopods, we have utilized only the so called 'secondary' (i.e., interior) layer, because its elongated calcitic fibers showed the highest degree of preservation, up to sub-micron levels. The details of our approach and examples of the exceptional degree of preservation of many shells have been documented in Diener et

al. (1996), Veizer et al. (1997a,b), Azmy et al. (1998) and Bruckschen et al. (1999). For the Mesozoic belemnites, the approach has been similar, except that the samples were drilled within a single 'lamina' of the rostrum, parallel to its elongation (Podlaha et al., 1998).

For Sr isotopes, in the initial stages, we have concentrated also on conodonts, believing that because of their superior stratigraphic resolution and the high Sr content of their phosphatic skeletons, they may yield a 87 Sr/ 86 Sr curve for the Phanerozoic seawater with the highest temporal resolution attainable. Comparison with brachiopod data showed, however, that conodonts, even at a conodont alteration index (CAI) as low as 1.5, had 87 Sr/ 86 Sr ratios that were at best comparable to coeval brachiopods, but mostly the measurements were more radiogenic (Ebneth et al., 1997; Veizer et al., 1997a). These, and the textural and proton-induced X-ray emission (PIXE) trace element studies (Bruhn et al., 1997), showed that conodonts exchanged about 1/3 of their Sr with the surrounding rock matrix. In suitable matrix, such as pure carbonates, conodonts may still retain their near-original ⁸⁷Sr/⁸⁶Sr values, but mostly the values are ~ 5×10^{-5} more radiogenic (Ebneth et al., 1997). Because of these reasons, we have discontinued conodont studies, except for the time intervals where the low-Mg calcitic fossils were rare or absent, such as the Cambrian and the early Triassic.



Fig. 1. The SEM photos of representative brachiopods. Note the excellent preservation of the secondary shell layer (from Azmy, 1996). (a) *Isorthis amplificata* (B27; Wenlock, Much Wenlock, UK) shell, with punctae filled by secondary calcite. The punctae calcite has intensive yellowish cathodoluminescence, as opposed to no or only intrinsic blue luminescence of the shell. The isotopic and chemical characteristics of the shell are the following: $\delta^{18}O = -5.50\%$, $\delta^{13}C = +0.39\%$, Mn = 307 ppm, Sr = 1934 ppm. (b) As (3a) at higher magnification. (c) *Delthyris elevata* (EK 38-7; Pridoli, Ohesaare Cliff, Estonia): $\delta^{18}O = -5.50\%$, $\delta^{13}C = -0.50\%$, Mn = 104 ppm, Sr = 1328 ppm. (d) As (3c) at higher magnification.



Fig. 2. Histograms of Sr (n = 1370) and Mn (n = 1267) concentrations in the studied brachiopods and belemnites.

The samples were screened for their degree of preservation by optical (transmitted light, cathodoluminescence and scanning electron microscopy, SEM) techniques. These have been documented in Bruhn et al. (1995) and Bruckschen et al. (1995a,b). Fig. 1 demonstrates an example of excellent preservation of textures on sub-micron scale. This optical screening was complemented by trace element evaluation by

wet chemical techniques (inductively coupled plasma atomic emission spectroscopy [ICP-AES], atomic absorption spectroscopy [AAS]) on aliquots remaining after phosphoric acid liberation of CO₂ for stable isotope measurements (Coleman et al., 1989) and by PIXE spot analyses on thin sections. Based on the wet chemical approach, some 2/3 of all studied samples have Sr and Mn concentrations comparable to modern low-Mg calcitic shells (Fig. 2). The remaining 1/3, mostly with Sr content < 800 ppm, may or may not have suffered some diagenetic loss of Sr. since concentrations as low as 200 ppm have been reported for modern brachiopods (Morrison and Brand, 1986; Brand, 1989b). Note also that recrystallization, unless at exceptionally high water /rock ratios, does not necessarily result in resetting of 87 Sr / 86 Sr or δ^{13} C values. For carbon, this is because of the earlier-discussed low water /rock ratios of the respective diagenetic systems. For strontium, due to the fact that D_{sr} (calcite) is < 1, recrystallization happens in a partially open system buffered by the dissolving carbonate phase (Veizer, 1983). Alternatively, the lower Sr concentrations may be, in part, due to inclusion of distinct small domains of secondary calcites, and not to partial recrystallization, leaving the bulk of the shell unaltered. The presence of such secondary calcites can usually be detected by optical means (Fig. 3), particularly cathodoluminescence, and these calcites have also distinctive chemical (Table 1) and isotopic signatures (Bruckschen et al., 1995a; Bruhn et al., 1995).

4. Samples

The present study is based on several thousand samples of Cambrian to Cretaceous ages. These were collected in Canada (Anticosti Island, Ontario), USA (Utah, Oklahoma, Texas, Ohio, Kentucky, Missouri, New York), Ireland, England, Wales, Spain, Italy, Belgium, Germany, Poland, Norway (including

Fig. 3. (Top) Cathodoluminescence photomicrograph of a Carboniferous punctate brachiopod (sample PB 192a). Note the bright yellow luminescence of the punctae that are filled by diagenetic calcite. (Bottom) PIXE elemental map of the dark square in the top figure. Step size 10 μ m. Note that the punctae are typified by Sr depletions (light domains) and simultaneous Mn enrichments (dark domains). The trace element data are in Table 1. Punctate brachiopods, except for demonstration purposes, were avoided in the present study. Modified from Bruhn (1995) and Bruckschen et al. (1995a).



| | Mn | | Fe | | Sr | | |
|----------|-------|---------|-------|---------|-------|---------|--|
| | Shell | Punctae | Shell | Punctae | Shell | Punctae | |
| | 33 | 1810 | 40 | 733 | 1042 | 518 | |
| | 20 | 3699 | 35 | 9261 | 977 | 217 | |
| | 27 | 2043 | 36 | 722 | 969 | 379 | |
| | 36 | 5040 | 73 | 1069 | 953 | 223 | |
| Mean | 29 | 3148 | 48 | 2946 | 985 | 334 | |
| σ | 8 | 1501 | 22 | 4833 | 12 | 92 | |

Table 1 The PIXE trace element concentrations for a Carboniferous punctate brachiopod (sample PB 192a)

Svarlbad), Sweden (including Gotland), Estonia, Latvia, Lithuania, Ukraine (Donetsk basin, Podolia),

Austria, Slovakia, Hungary, Russia (Moscow basin, St. Petersburg area, Urals, western Siberia), Mo-



Fig. 4. ⁸⁷Sr/⁸⁶Sr variations for the Phanerozoic based on 4055 samples of brachiopods ('secondary' layer only for the new Bochum/Ottawa measurements), belemnites and conodonts, and nine samples of micritic matrix. Normalized to NBS 987 of 0.710240. The literature data (foraminifera, belemnites and conodonts) are from the following sources: Peterman et al. (1970), Dash and Biscaye (1971), Veizer and Compston (1974), Brass (1976), DePaolo and Ingram (1985), Koepnick et al. (1985), Hess et al. (1986, 1989), Popp et al. (1986c), McKenzie et al. (1988, 1993), Hodell et al. (1989, 1990, 1991), Brand (1991), Martin and McDougall (1991, 1995), Bertram et al. (1992), Dia et al. (1992), Barrera et al. (1993), Kürschner et al. (1993), Whittaker and Kyser (1993), Banner and Kaufman (1994), Cummins and Elderfield (1994), Denison et al. (1994), Hodell and Woodruff (1994), McArthur et al. (1994), Oslick et al. (1994), Quinn et al. (1994), Jones et al. (1994a,b), Chaisi and Schmitz (1995), Farrell et al. (1995), Ruppel et al. (1996), Wenzel (1997), Qing et al. (1998).

rocco, south China, Australia (Oueensland, Northern Territory) and New Zealand. They have been collected (assembled) and described by the following researchers and publications: Cambrian (S. Ebneth). Ordovician (G.A.F. Carden). Silurian (Azmv. 1996: Azmy et al., 1998, 1999), Devonian (Diener, 1991; Ebneth, 1991: Pawellek, 1991: Fauville, 1995: Golks, 1995: Ala, 1996: Diener et al., 1996: Ebneth et al., 1997). Carboniferous (Bruckschen et al., 1995b. 1999: Bruckschen and Veizer, 1997). Permian (Jasper, 1999), Triassic (Korte, 1999) and Jurassic / Cretaceous (Podlaha, 1995; Podlaha et al., 1998, Podlaha et al., this issue). Judging from paleogeographic reconstructions of Scotese et al. (1994), most of these samples originate from tropical regions (30°N to 30°S) of the paleoceans, with few from higher paleolatitudes. From this collection, some 1500 samples of brachiopods and belemnites (and additional conodonts) have been selected for further Sr. O and C isotope studies and the details of their descriptions, including chemistry, isotopes, geology and location, are available in the above publications or in the summary tables posted on the Web site: http://www-ep.es.llnl.gov/germ/evolution. html or http://www.science.uottawa.ca/geology/ isotope _ data/.

5. Phanerozoic ⁸⁷Sr /⁸⁶Sr trend

The summary of Sr isotope data for Phanerozoic seawater (Fig. 4) is based solely on measurements on fossils. The Cenozoic and late Cretaceous part is from the literature and based chiefly on foraminifera. The remaining literature data, and all of Bochum/ Ottawa measurements, are based on brachiopods, belemnites and conodonts. The sole exceptions are the matrix (micrite) samples for the early Cambrian that were incorporated because of the lack of suitable fossils. The 'curve' resembles the one by Burke et al. (1982), but it differs in detail and is more tightly constrained. Where larger spread of data exists, such as the radiogenic mid-Permian Chinese samples (Jasper, 1999), it is dealt with in the publication describing these particular periods. However, the



Fig. 5. ⁸⁷Sr/⁸⁶Sr variations during the Devonian (new Bochum/Ottawa data only).

clumping of data (cf. Devonian and Carboniferous) is mostly a reflection of a large number of measurements, with higher-order oscillations compressed along the temporal axis (cf. Bruckschen et al., 1995b, 1999; Bruckschen and Veizer, 1997).

Taking the Devonian as an example (Fig. 5), the higher-order oscillations, based on 384 samples, are well-illustrated. The secular trend shows a continuous decline through the Lower Devonian, a plateau in the Middle Devonian, a rise through the Frasnian and another plateau in the Upper Frasnian and Framenian. This figure also illustrates that conodonts are usually somewhat more radiogenic than coeval brachiopods. Furthermore, even at this resolution, some clumping still persists, such as at the Emsian/Eifelian and Frasnian/Famenian transitions. Again, the major culprit is the presence of still higher-order fluctuations in a compressed time scale. For the Middle Devonian, this was illustrated in Diener et al. (1996) (their Fig. 6), where it was also pointed out that the geological reproducibility of the Sr isotope pattern in profiles only several kilometers apart was no better than 5×10^{-5} . Thus, only the oscillations in excess of this range could be resolvable on regional to global scales.

Another constraining issue is the problem of correlations within a single biozone. As discussed in Veizer et al. (1997a) (their Fig. 8), the scatter of 87 Sr/ 86 Sr values at the Frasnian/Famenian transition, the Kellwasser 'event', results from real oscillations within one or two biozones. Yet, on larger regional or global scales, it is difficult to match these



Fig. 6. 87 Sr/ 86 Sr variations during the Devonian based on conodont biozones. Explanations: circle = mean; box = $\pm 1\sigma$; vertical line = minimum and maximum. The 2σ in the lower right corner is an average 2σ for the NBS 987 standard. Note that only brachiopods are included in this figure. The biozones are the following (Weddige, 1977, 1988; Carls, 1988; Sandberg et al., 1989; Ziegler and Sandberg, 1990): 1 — woschmidti, 2 — postwoschmidti, 3 — pesavis, 4 — sulcatus, 5 — kindleri, 6 — pirinea, 7 — deniscens, 8 — gronbergi, 9 — laticostatus, 10 — serotinus, 11 — patulus, 12 — partitus, 13 — costatus, 14 — australis, 15 — kockelianus, 16 — esensis (arkonensis, obliquimarginalus, bipecatus), 17 — hemiansatus, 18 — varcus, 19 — hermani — cristatus, 20 — disparitis, 21 — falsovialis, 22 — transitans, 23 — punctata, 24 — hassi, 25 — jamieae, 26 — rhenana, 27 — linguiformis, 28 — triangularis, 29 — crepida, 30 — rhomboidea, 31 — marginifera, 32 — trachytera, 33 — postera, 34 — expansa, 35 — presulcata.

wiggles in different profiles. In effect, one is limited by constraints of biostratigraphy and the matching is in the term of biozones. This is not to say that some of the observed 87 Sr / 86 Sr variations may not be a result of undetected post-depositional alteration, but a portion of these variations is real. It is therefore difficult to claim some specific 87 Sr / 86 Sr value for a given biozone. The alternatives can rely on either selecting the least radiogenic value or accepting all 'good' data as representative of that biozone. We prefer the second approach as more representative of the real situation. We therefore plot the mean, the 2σ range and the total range of values for each of the 35 Devonian conodont biozones (Fig. 6). The Phanerozoic 87 Sr / 86 Sr marine trend based on the above principles is, in our view, a more realistic reflection of the natural situation and as such should be constructed separately for each period, not only for the Devonian or Silurian (Azmy et al., 1999).

6. Correlation potential

Bearing in mind the above qualifications, Sr isotopes can serve as a useful complementary correlation tool, particularly for sequences where the biostratigraphic approach is of little value, due either to the dearth of fossils or to their limited stratigraphic utility. Nevertheless, the technique can lead to improved correlations even for sequences with good biostratigraphic control. Azmy et al. (1999) demonstrated that for the Silurian, the 87 Sr / 86 Sr ratio enables stratigraphic assignment of samples from independent sets to within +1 graptolite biozones. This is no minor accomplishment considering the difficulty of correlation for profiles with differing sedimentation rates and taking into account the uncertainty of the 'first and last appearance' of a given 'Leitfossil' in the sedimentary record. The issue can be illustrated by the present study of the Givetian / Frasnian transition in the Eifel Mountains of Germany. These well-studied sections, in close proximity to the Belgian stratotypes, have a well-established biostratigraphy (Weddige, 1977; Struve, 1982). Unfortunately, the Givetian/Frasnian transition is strongly dolomitized and it was necessary to sample the coeval sections at the Teerstrassenbau Wahlheim/Friesenrath quarry in Aachen and at the tunnel near Behringhausen, east of the Rhine (Ostsauerland). The measured 87 Sr / 86 Sr values (Fig. 7) define a rising trend of $\sim 3 \times 10^{-4}$ in about 4 Ma that spans the gap between the varcus (No. 18) and rhenana (No. 26) biozones in the Eifel. In detail, however, it appears that the steepest rise in the curve, of about



Fig. 7. ⁸⁷Sr/⁸⁶Sr trend at the Givetian/Frasnian transition. Conodont biozones as in Fig. 6.

 1×10^{-4} in ≤ 1 Ma, appears in the *falsiovalis* (No. 21) conodont biozone in Aachen and in the *transitans* (No. 22) biozone in Behringhausen. The critical portion of the profile in Aachen is at its top (Reissner, 1990) and it was assigned to the (lower) *assymetricus* biozone in the older stratigraphic assignment (Ziegler, 1962) that encompassed the present *falsiovalis* and *transitans* biozones. If so, that portion of the Aachen profile that contained the brachiopods measured for ⁸⁷Sr/⁸⁶Sr should perhaps be assigned to the *transitans* biozone (No. 22), and be correlative with the Behringhausen.

A third approach of utilizing Sr isotopes for correlation purposes is based on inflexions in the trend (McArthur, 1994; Azmy et al., 1999). The higherorder oscillations are not necessarily reproducible, particularly in their amplitude. This is because the sedimentary sequences are not an unbroken recorder of time and the 87 Sr/ 86 Sr evolutionary trend of seawater can thus be truncated at any time prior to reaching the apex of an oscillation. An inflexion, on the other hand, can be recognized even if some corresponding strata are missing. Note that unrecognized hiatuses may appear also as abrupt 'jumps' in the strontium isotope trend (cf. Diener et al., 1996, their Fig. 7).

7. Phanerozoic δ^{13} C trend

The secular Phanerozoic trends based on the new Bochum/Ottawa dataset (Fig. 8) or on the compilation of literature data (Fig. 9) resemble each other in terms of their overall shape and in the considerable spread of values. As for Sr isotopes, some of this scatter is due to higher-order natural oscillations clumped together by compressed time scale. This is particularly the case for the literature dataset with its much poorer temporal resolution. Additional scatter



Fig. 8. Phanerozoic δ^{13} C trend based on 1564 brachiopod (secondary layer) and belemnite (laminae pelucidae) measurements at Bochum and Ottawa. Three Triassic samples (two corals and one bivalve) from Cassian Beds and Kössener Schichten (Alps) are still preserved as aragonite.



Fig. 9. Phanerozoic δ^{13} C trend compiled from 3918 measurements for LMC (brachiopods, belemnites, oysters, foraminifera) and 96 measurements for A (mollusc) shells. The sources of the data are the following: Compston (1960), Douglas and Savin (1971, 1973), Veizer and Hoefs (1976), Brand and Veizer (1981), Popp et al. (1986a,b), Veizer et al. (1986), Miller et al. (1987), Adlis et al. (1988), Brand (1989b), Delaney et al. (1989), Rush and Chafetz (1990), Grossman et al. (1991, 1993), Middleton et al. (1991), Jones (1992), Wadleigh and Veizer (1992), Brand and Legrand-Blain (1993), Lavoie (1993), Anderson et al. (1994), Qing and Veizer (1994), Carden (1995), Carpenter and Lohmann (1995), Mii (1996), Rao (1996), Samtleben et al. (1996), Wenzel and Joachimski (1996), James et al. (1997), Mii et al. (1997).

is due to oceanographic and biological factors, mentioned already in the introductory part, and well-preserved ancient aragonitic (Anderson et al., 1994) as well as modern calcitic representatives (Fig. 9) are no exception to this pattern. Both sets of data, as well as the secular $\delta^{13}C_{carbonate}$ curve based on whole rocks (Veizer et al., 1980; Lindh, 1983), show a general increase in $\delta^{13}C$ throughout the Paleozoic, followed by an abrupt decline and subsequent oscillations around the present-day value in the course of the Mesozoic and Cenozoic. Because of this coherence, we feel justified in pooling both datasets (Figs. 8 and 9) in order to generate a secular trend for the entire Phanerozoic (Fig. 10). The running mean based on this combined set was calculated for 5 Ma incremental shifts, because this is the realistic resolution for global biostratigraphic correlations and for our combined dataset. The bands around this mean incorporate 68 and 95% of all measured samples, respectively. Note also that superimposed on the overall trend are pronounced, but somewhat dampened due to the 20 Ma window, second- and higher-order oscillations. Considering the global nature of the database, with samples originating from five continents and a multitude of sedimentary basins, the observed peaks are likely of global significance. An exception may or may not be the Aptian peak at ~ 115 Ma that is based on a small number of measurements (cf. Podlaha et al., 1998). It is likely that even many of the shorter-term peaks may still be



Fig. 10. Phanerozoic δ^{13} C trend for combined Bochum/Ottawa and literature data for LMC shells. The running mean is based on 20 Ma window and 5 Ma forward step. The shaded areas around the running mean include the 68% ($\pm 1\sigma$ for a strictly Gaussian distribution) and 95% ($\pm 2\sigma$) of all data.

of global significance, as will be discussed later for the terminal Ordovician.

8. Phanerozoic δ^{18} O trend

In analogy to carbon isotopes, the δ^{18} O trends for the Bochum/Ottawa (Fig. 11) and the literature datasets (Fig. 12) overlap, including their similarities in the second-order structure (e.g., the Silurian/Devonian dip followed by Carboniferous rise). We therefore feel justified in combining them into a general Phanerozoic trend (Fig. 13). Several features are immediately apparent from this presentation.

(1) The data define a trend of increasing δ^{18} O values, from about -8% at the onset of the Phanerozoic to about 0% at present.

(2) As for the δ^{13} C, the trend is not a linear feature, but a band. Note, however, that the observed

 δ^{18} O variations in modern tropical brachiopods at shelf depths are $\sim 4\%$ (Carpenter and Lohmann, 1995: Bruckschen et al., 1999) and for the specimens from temperate climates they span about 8‰ (Fig. 12). A similar range of δ^{18} O values was observed by Anderson et al. (1994) for ancient belemnites and molluscs, the latter still preserved as pure aragonite (Fig. 13), within a single member of the Jurassic Oxford Clay Formation. From this perspective, it is indeed noteworthy that the collections of fossils from any one biozone, each representing populations with a much larger temporal and spatial range than the modern one, do not show a markedly larger dispersion of δ^{18} O values (Fig. 13). The existing 18 O depleted outliers in the Carboniferous and Permian (see Bruckschen et al., 1999 for further discussion) represent only $\sim 1\%$ of the total population, thus extending somewhat the lower range of the 95% limit. Such outliers have only a negligible impact on



Fig. 11. Phanerozoic δ^{18} O trend based on 1654 brachiopod (secondary layer) and belemnite (laminae pellucidae) measurements at Bochum and Ottawa. Three Triassic mollusc samples are still preserved as aragonite (see Fig. 8).

the mean, the 2σ range, or the upper 95% boundary of the band. The latter boundary is sharp, with almost no samples above it (Figs. 11 and 12). Consequently, even an arbitrary retention of only the 'heaviest' values would not invalidate the secular Phanerozoic trend.

(3) Statistical treatment of the data (Fig. 13) suggests an existence of second-order oscillations with a frequency of ~ 150 Ma, their apexes coincident with cold intervals and major glaciations. Advancing global cooling, intermittently compounded by generation of ice caps, could have been the principal reasons for the observed ¹⁸O enrichments.

(4) The three Carboniferous molluscs entombed in asphalt and still well-preserved as nacreous aragonite (Brand, 1989a), as well as the 122 Jurassic and Triassic aragonitic molluscs (Anderson et al., 1994; Korte, 1999), all plot well within the main trend (Fig. 13).

All the above points will be of importance for discussion of the primary vs. secondary nature of the δ^{18} O Phanerozoic trend.

9. Correlation of oxygen and carbon isotopes

The crossplots of all Phanerozoic data (Fig. 14) show the relationships of δ^{18} O and δ^{13} C for the entire Phanerozoic. Covariant δ^{18} O/ δ^{13} C trends, such as those of the Ordovician, Silurian, Permian or Triassic, are often interpreted as an indicator of diagenetic resetting due to ¹⁸O and ¹³C depletion in altered samples (e.g., Bathurst, 1975). While post-depositional resetting, particularly in diagenetic systems dominated by bicarbonate generated from soil CO₂, can indeed generate such trends, their existence is not an a priori proof of diagenetic alteration. Modern shells, almost as a rule, display such positive



Fig. 12. Phanerozoic δ^{18} O trend of compiled 3969 measurements for LMC shells (brachiopods, belemnites, oysters, foraminifera) and 122 Carboniferous and Jurassic aragonitic mollusc shells (Brand, 1989a; Anderson et al., 1994), the latter listed in literature as 100% aragonite. The sources of the data are as in Fig. 9 and Lowenstam (1961).

covariance, principally due to isotope fractionation effects in the process of shell secretion (McConnaughey and Whelan, 1997). The pattern in the diagenetically unaffected Quaternary cluster (Fig. 14) confirms this assertion.

Another reason for the covariance, particularly during the Paleozoic, is the fact that both isotopes show a general secular increase with decreasing age. The Paleozoic cluster represents, therefore, with large degrees of overlap, a trend from the isotopically depleted Cambrian to the enriched Permian. In detail, the covariance is particularly pronounced for periods of fast secular change, such as the Ordovician. Note, however, that the patterns of this $\delta^{18}O/\delta^{13}C$ covariance shift toward positive $\delta^{18}O$ values with decreasing age. The spread of $\delta^{13}C$ values, on the other hand, remains relatively invariant.

In the late Paleozoic clusters, a number of samples fall outside the general covariance domain due to excessively negative δ^{18} O values. These samples, mostly of Carboniferous age, are the same that plot as ¹⁸O depleted outliers in the δ^{18} O secular trend (Fig. 13). They originate mostly from the Donetsk Basin of the Ukraine and are further discussed in Bruckschen et al. (1999).

10. Primary or secondary trends

The primary nature of the δ^{13} C secular trend, at least in terms of its major features, is no longer disputed, but the issue is far from settled for the δ^{18} O (cf. Hoefs, 1997). Five lines of argumentation are pertinent to this issue: textural, geological, mineralogical, chemical and isotopic. We shall discuss them in this order.



Fig. 13. Phanerozoic δ^{18} O trend for Bochum/Ottawa and literature data for LMC shells. Aragonite specimens as in Figs. 11 and 12. Note that benthic foraminifera are excluded from this figure, because they may not represent ecological analogues to ancient brachiopods and belemnites. Glaciations and cold times after Frakes et al. (1992). Further explanations as in Fig. 10.

Starting with the textural considerations, the excellent textural preservation of the shells, even on a sub-micron scale, is illustrated in Fig. 1 (cf. also Bruckschen et al., 1999). Such excellent preservation is by no means a rarity in the present dataset. Documentation can be found, e.g., in Brand (1989a,b), Wadleigh and Veizer (1992), Grossman et al. (1993), Qing and Veizer (1994), Carden (1995), Copper (1995), Azmy (1996), Grossman et al. (1996), Samtleben et al. (1996), Wenzel and Joachimski (1996), Wenzel (1997), Azmy et al. (1998) and others. Note that the depicted samples (Fig. 1) have trace element, δ^{13} C and 87 Sr / 86 Sr values as expected for a Silurian marine calcite, yet their δ^{18} Os are around -5% PDB, well within the Phanerozoic trend (Fig. 13). For the sake of the argument, let us assume that the oxygen isotope values have been altered by meteoric waters with δ^{18} O of say -5 to -10% SMOW. In such a case, one-half to all of oxygens in these calcite structures, i.e., up to 60% of their building blocks, would have to be replaced by extraneous oxygen without leaving behind the slightest trace in the optical, mineralogical, chemical and isotopic make-up of the shells. This is difficult to conceive, irrespective of whether one invokes a solution/reprecipitation process or, the less likely, solid diffusion exchange.

The second line of argumentation is based on *geological consideration*. Let us assume that the trend of ¹⁸O depletion with age (Fig. 13) is in the first instance a result of post-depositional resetting due to interaction with meteoric and/or warm waters. Diagenetic stabilization of carbonate rocks indeed results in ¹⁸O depletion, but this depletion is mostly related to transformation of metastable polymorphs (aragonite, high-Mg calcite) into stable ones

(low-Mg calcite) and it usually happens very early in the post-depositional history of the rocks. Subsequently, and in deep sea environments, the alteration proceeds, at a slower rate, by pressure solution until complete lithification. Once lithified, the subsequent ¹⁸O depletions – if any – are much less pronounced. Note also that all ancient carbonate rocks have undergone this stabilization step, thus self-correcting for it for rocks older than about Cenozoic. As a result, such a post-depositional trend would have a steep slope during the Cenozoic, exponentially flattening out with increasing age. Furthermore, due to vagaries of post-depositional development of different sedimentary basins, the resetting towards ¹⁸O depleted values from the assumed modern day equilibrium would result in a fan-shaped pattern that broadens with age, with many outliers along the alteration pathway, i.e., between 0% PDB and the main Phanerozoic trend. Neither of these predictions is supported by experimental data (Figs. 11–13). Disregarding the second-order oscillations, the rate of decline is about linear, the band of about equal width, and there are essentially no outliers above the upper limit of this band. Whatever outliers do exist ($\sim 1\%$ of samples), they plot mostly below the main trend, i.e., any post-depositional ¹⁸O depletion advanced from (and not towards) the main trend. In order to sustain the diagenetic alternative, one would have to argue that the post-depositional alteration advances at roughly a constant rate, regardless of the age of the rocks, and that all basins throughout the world (see the distribution of our samples) have undergone alteration strictly proportional to their ages. Considering the plethora of geologic histories, with samples from all continents but Antarctica, and from a multitude of sedimentary basins, this is not a credible proposition.

As already pointed out, the apexes of the secondorder oscillations appear to have coincided with cold periods (Fig. 13), perhaps indicating that the δ^{18} O oscillations reflect global cooling trends. Leaving aside the issue of the origin of these second-order oscillations, let us concentrate on one of them, the Ordovician/Silurian transition. The δ^{18} O record of this transition (Fig. 15) shows the δ^{18} O pattern (Carden, 1995; Azmy, 1996; Azmy et al., 1998) where the positive δ^{18} O excursions coincide, within the resolution of a biozone, with glacial sediments, a pattern, except for the shift in the baseline, analogous to that of the Quaternary. Furthermore, the pronounced terminal Ordovician δ^{18} O peak is clearly a global feature within the *acuminatus* (No. 21) biozone, because this signal was detected in China (Carden, this project), the Baltic region, Canada and Argentina (Brenchley et al., 1995; Marshall et al., 1997). This pattern can be easily understood in terms of the primary signal, but is difficult to reconcile with a diagenetic interpretation.

The third line of argumentation is based on the *mineralogy of the shells*. Because of their exceptionally well-preserved textures (Fig. 1), we believe that low-Mg calcitic shells were relatively resistant to diagenetic alteration. Moreover, molluscs that are still preserved in their highly unstable original aragonitic mineralogy also plot within the general trend defined by the low-Mg calcitic shells (Fig. 13). In order to sustain the diagenetic alternative, it would again be necessary to claim that all these shells exchanged most of their oxygen, yet retained not only their original low-Mg calcitic, but also original *aragonitic* mineralogies.

The fourth line of argumentation is based on the *chemical composition* of the studied samples. As already demonstrated (Fig. 2), a minimum of 2/3 of the 1370 samples studied by us for trace elements have compositions directly comparable to modern low-Mg calcitic shells. Diagenetic alterations usually lead to decline in Sr (Na) and increase in Mn (Fe) contents (Brand and Veizer, 1980; Veizer, 1983; Banner, 1995). Based on such criteria, about 1/3 of the samples characterized by Sr contents of less than about 800 ppm may arguably be considered somewhat altered. Nonetheless, trace element criteria for at least 2/3 of the samples are not consistent with the proposition of diagenetic alteration.

The fifth line of argumentation is based on the *isotopic patterns* of the studied populations. The present Phanerozoic dataset is the first of such quantity and quality where the samples have been studied simultaneously for δ^{18} O, δ^{13} C, 87 Sr/ 86 Sr, trace elements, and optical parameters. In addition, some of the samples have been studied for δ^{34} S of structurally bound sulfur (Kampschulte and Strauss, 1996; Strauss, this issue). The possibility of a large stratigraphic mismatch for different isotopic systems is therefore mitigated. A crossplot of δ^{18} O vs. 87 Sr/ 86 Sr



Fig. 14. The δ^{18} O vs. δ^{13} C crossplots for the samples listed in Figs. 9–12. Explanations: circles — Bochum/Ottawa data; upright crosses — literature data (LMC brachiopods, belemnites, oysters, foraminifera); diagonal crosses — literature data (LMC Quaternary temperate brachiopods). P 103/4: Permian, 103 Bochum/Ottawa samples/four literature samples. Note that the Tertiary field contains only pelagic foraminifera.



Fig. 15. The δ^{18} O trend across the Ordovician/Silurian transition. The Ordovician biozones, based on graptolites, are the following: 17 – *Pleugograptus linearis*, 18 – *Dicelograptus complanatus*, 19 – *Dic. anceps*, 20 – *Climacograptus extraordinarius*, 21 – *Glyptograptus acuminatus*. The Silurian graptolite biozones are the following: 1 – *Parakidograptus acuminatus*, 2 – *Atavograptus atavus*, 3 – *Lagarograptus acinaces*, 4 – *Coronograptus cyphus*, 5 – *Monograptus triangulatus*, 6 – *Diplograptus magnus*, 7 – *Pribylograptus leptotheca*, 8 – *Monog. convolutus*, 9 – *Monog. sedgwickii*, 10 – *Monog. turriculatus*, 11 – *Monog. crispus*, 12 – *Monoclimacis griestoniensis*, 13 – *Monoc. crenulata*, 14 – *Cyrtograptus centrifugus*, 15 – *Cy. murchisoni*. Glacial episodes after Grahn and Caputo (1992). Patterns as in Fig. 6.

(Fig. 16) shows a very high degree of correlation. From a purely theoretical perspective, one could perhaps argue that this correlation is a result of diagenetic alteration. In that case, however, the Sr isotopic trend (Fig. 4) would have to be a secondary feature as well. In order to escape such a conclusion, it would be necessary to postulate that the 87 Sr/ 86 Sr of some 4000 samples remained almost perfectly preserved (Fig. 4) while their oxygens have been heavily reset. This is not a credible proposition in

view of the repeatedly documented reproducibility of the Sr isotope trend, even taking into account the differing water/rock ratios for these two elements in a diagenetic system.

Furthermore, all isotope pairs crosscorrelate (positively or negatively) at very high confidence levels (Fig. 17). We are not aware of any diagenetic scenario that would have been capable of producing such interrelationships. They can be, however, understood in terms of the primary signal that reflects



Fig. 16. Crossplot of mean 87 Sr/ 86 Sr vs. δ^{18} O values for 20 Ma intervals of the Phanerozoic. Mean values calculated from Figs. 4 and 13, respectively. The correlation coefficient is -0.57 for all points and -0.84 if the two Cenozoic points are excluded. Insert, based on the extension of the trend, suggests that seawater lies on a mixing line of two endmembers, primary magmatic water and meteoric water. The composition of endmembers from Hoefs (1997).

the operation of a unified and hierarchical exogenic system (litho-, hydro-, atmo-, biosphere) (Veizer, 1988), with tectonics driving it on geological time scales via its control of biogeochemical cycles, in this case the cycles of Sr, C, O and S. This proposition is supported by factor analysis (Table 2) which shows that the system is driven by three factors. The first factor links oxygen and strontium isotopic evolution (Fig. 16) and the second one 87 Sr/ 86 Sr and δ^{34} S (Fig. 18). These two factors explain up to 63% of the total variance. The last factor links the carbon and sulfur isotopic evolution (Fig. 19). Because of the high ⁸⁷Sr /⁸⁶Sr loadings, the tentative interpretation identifies the first two factors as tectonic, generated by the relative importance of the hydrothermal flux within the oceanic crust to its complementary meteoric component (riverine flux). The loading of sulfur and oxygen on two separate factors likely reflects the fact that the ${}^{18}O/{}^{16}O$ balance is temperature-dependent, with a crossover at ~ 300° C (e.g., Gregory, 1991), while the ${}^{34}S/{}^{32}S$ is only marginally dependent on this variable. The third factor is a biologically mediated redox linkage of sulfur and carbon cycles (Garrels and Perry, 1974; Veizer et al., 1980). Considering that the ultimate goal of this contribution is to tackle the primary vs. secondary



Fig. 17. Correlation coefficients for carbonate ${}^{87}\text{Sr}/{}^{86}\text{Sr}$, δ^{18} O, δ^{13} C and sulfate δ^{34} S mean values during the Phanerozoic. The Sr, O and C isotope data from Figs. 4, 10 and 13, respectively. The δ^{34} S data from Strauss (1997, this issue). The means and their correlation coefficients have been calculated for 1 to 40 Ma intervals. The shading encloses the 95% confidence level domain.

Table 2

Factor analysis of 87 Sr, 86 Sr, 13 C, 18 O and 34 S for Phanerozoic seawater

The input data are 5 Ma averages from Figs. 4, 10 and 13 and from Strauss (1997, this issue), respectively. This resolution was selected because it represents the realistic stratigraphic resolution of our database. Note, however, that other reasonable resolutions (1–40 Ma) yield similar outcomes (cf. Fig. 17). Calculated without and with (in parentheses) the anomalous 87 Sr/ 86 Sr data for the last 35 Ma.

| Variable | Factor 1 | Factor 2 | Factor 3 | |
|---|--------------|--------------------|--------------|--|
| ⁸⁷ Sr/ ⁸⁶ Sr ^{\$18} O | -0.83(-0.64) | 0.55 (0.63) | -0.06(-0.05) | |
| δ^{34} S | -0.15(-0.11) | 0.77 (0.73) | -0.37(-0.41) | |
| $\delta^{13}C$ | 0.17 (0.21) | -0.24 (-0.21) | 0.63 (0.65) | |
| Percent of variance explained | 38.9 (25.7) | 23.9 (24.8) | 15.9 (16.8) | |

controversy for the δ^{18} O record, we prefer to refrain from further discussion of the subject. At this stage, we only wish to reiterate that the isotope data are not consistent with the diagenetic scenario.

The pattern in Fig. 16 shows that the latest ~ 35 Ma deviate from the overall correlation, suggesting that either the δ^{18} O or the 87 Sr/ 86 Sr of modern cycles are not in a steady state. Since this departure is visible only for Sr isotope data, it is likely that the Sr cycle is the culprit in terms of its isotopic composition. This may have a bearing on the controversy regarding the role of the Himalayas in the steep rise in 87 Sr/ 86 Sr of the Cenozoic seawater (Fig. 4). If the unroofing of the Himalayas were indeed the cause, the rise in seawater 87 Sr/ 86 Sr could have been accomplished either by an enhanced riverine Sr flux (Raymo and Ruddiman, 1992) and/or by its more

radiogenic nature (Edmond, 1992). The isotopic relationships described in this contribution (Figs. 16–19) support the second alternative.

In the above discussion, we reviewed five lines of evidence for secondary vs. primary nature of the observed δ^{18} O secular trend. Our attempt to explain it as a secondary phenomenon failed, because it had to rely in all categories on a set of implausible and internally inconsistent special pleadings or could not be reconciled at all. The primary alternative, on the other hand, can be reconciled with all experimental observations. Note that we do not wish to claim that all samples are as well-preserved as those in Fig. 1. All screening techniques, singly or in concert, have their limitations and post-depositional alteration may indeed be partly responsible for some of the ¹⁸O depleted 'troughs' in Fig. 13, such as the mid-





Fig. 18. Crossplot of mean ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and $\delta^{34}\text{S}$ values for 20 Ma intervals of the Phanerozoic. Mean values were calculated from Fig. 4 and Strauss (1997, (this issue), respectively. Note that the $\delta^{34}\text{S}$ data are those of evaporitic sulfates with their relatively poor temporal resolution.

Fig. 19. Crossplot of mean δ^{13} C and δ^{34} S values for 20 Ma intervals of the Phanerozoic. Mean values were calculated from Fig. 10 and Strauss (1997, this issue), respectively. Note also that this factor is linked to the tectonic factor 2 via its sulfur and not the carbon cycle (Table 2).

Carboniferous. Nonetheless, except for these outliers, the cumulative optical, geological, mineralogical, chemical and isotopic evidence for the primary nature of the Phanerozoic secular δ^{18} O trend, at least in its major features, is compelling.

For the sake of a rounded discussion, we also consider two *objections* frequently raised against the primary nature of the δ^{18} O secular trend.

(1) The brachiopods define a secular trend that overlaps with that of the whole rocks, the latter undoubtedly isotopically reset (Land, 1995).

(2) The studies of oceanic crust and of ophiolites (e.g., Muehlenbachs and Clayton, 1976; Gregory and Taylor, 1981) suggest that the magnitudes of highand low-temperature hydrothermal processes along their depth profile are about equal and thus cancel their opposing impact on the δ^{18} O of circulating water. As a result, the seawater δ^{18} O is, and has been, buffered around its present day value of about 0‰ SMOW (Gregory, 1991).

Concerning the first point, we already argued that diagenetic stabilization of *shelf carbonate facies* is mostly related to transformation of metastable polymorphs (aragonite, high-Mg calcite) into stable ones (low-Mg calcite) and usually happens very early in the post-depositional history of the rocks, at times when diagenetic solutions still retain partial memory of their seawater precursors (Choquette and James, 1990; James and Choquette, 1990). This often limits the whole rock shift to about -2% (Fig. 20). Once stabilized, the subsequent ¹⁸O depletions are much less pronounced. Such a shift can well be accommodated within the δ^{18} O secular band, particularly since the major rock components, the micritic matrix and the early, marine, cements, had initial δ^{18} O compositions around and above the top boundary (e.g., Milliman, 1974; Bathurst, 1975; Tucker and Wright, 1990) of the band based on skeletal precipitates.

Additional support for the claim that the bulk of diagenetic stabilization of shelf carbonates usually ceases at a rather early stage of diagenetic history is provided by sulfur isotope data. Kampschulte and Strauss (1998) studied the δ^{34} S of trace sulfate from brachiopods and their host rocks from this same Bochum/Ottawa collection. The δ^{34} S of the shells, as well as of the host rocks, all plot on the Phanerozoic δ^{34} S secular trend for evaporites. Such coherence can only be generated if the system 'shuts down' at a very early diagenetic stage, at times when pore waters still retain the memory of seawater composition.

Apart from the argument for the early diagenetic overprint, we wish to point out the misunderstandings that frequently arise from model images of



Fig. 20. The average formational δ^{13} C and δ^{18} O for the Silurian strata at Gotland. The brachiopod data are from Wenzel (1994) and the whole rock data from Jux and Steuber (1992). Note that except for the Burgsvik Formation that contains a disproportionate share of late meteoric cements, the δ^{13} C means are comparable, while the δ^{18} O's of whole rocks are depleted consistently by ~2‰ relative to brachiopods. Courtesy of W. Buggisch and B. Wenzel.

diagenesis. The reigning models of bulk rock solution/precipitation, diffusion/advection type (e.g., Richter and DePaolo, 1987; Schrag, this issue) have only limited applicability for diagenesis of multicomponent carbonate assemblages. These models, like their groundwater flow system precursors en vogue for the shelf facies in the 1960s and 1970s. predict well the chemical and isotopic gradients in pore waters, but not the chemistry of the diverse solid phases. The reason is that only a minuscule portion of the solids is required to generate the pore water gradients. Yet, it is not the millionth portion of every particle that reacts, at any instant, with the water, but only the most soluble millionth particle. This is repeated with the next most soluble particle. etc. As a result, the stabilized bulk rock consists of domains that may have been completely. even repeatedly, recrystallized, while neighbouring domains could have remained practically unscathed (cf. Brand and Veizer, 1980). This is the reason for the excellent textural, chemical and isotopic preservation of some components, such as the presently studied LMC shells.

Concerning the second argument, we concur that the oceanic ridge circulation (Muehlenbachs and Clayton, 1976; Gregory, 1991) is the, or one of several, controlling factor of δ^{18} O composition of seawater. Accepting this, the Phanerozoic trend can be reproduced, providing the magnitude of high-temperature alteration is kept consistently higher than that of its low-temperature analogue (Fig. 21). Modification of the 'balanced' model could therefore be a solution to the dilemma. Theoretically, the required imbalance could be created by either assigning a greater magnitude to the high-T flux or a lesser one to the low-T flux. The former may result from processes within the oceanic crust itself, such as those that generate the 18 O depleted gabbros (Lecuver and Reynard, 1996), or at magma chambers of subduction domains. Alternatively, the diminished low-T flux may be a consequence of a decline in continental weathering input.

A corollary to this argument is the claim that alteration trends in ophiolites 'prove' the buffering of δ^{18} O of ancient seawater at near modern values. In reality, these trends prove only that the waters were depleted in ¹⁸O relative to the mineral assemblages of the ophiolites. At this stage, considering



Fig. 21. Theoretical model of hydrothermal alteration required to produce the entire δ^{18} O secular trend in terms of changing sea water 18 O/ 16 O ratios. The model calculated evolution of the ratio *R* between the 18 O flux consumed by the weathering of seafloor basalts at low temperature and the 18 O flux produced by the high temperature weathering that is needed to reproduce an increase of about 8‰ in the δ^{18} O of seawater over the Phanerozoic. The curve was obtained by using a modified version of the ICM model (Goddéris and François, 1996), including the global alkalinity, carbon, δ^{18} O, δ^{13} C and 87 Sr/ 86 Sr budgets. The result indicates that the *R* should be about 40–50% in the course of the Phanerozoic. Continental contribution to the oxygen cycle was also taken into account.

the large scatter in the alteration patterns, we are neither in a position to demonstrate unequivocally the equality of the low- and high-temperature fluxes, nor to differentiate between alteration halos generated by water with δ^{18} O of 0‰ instead of say -5% SMOW.

We wish to emphasize that despite all the above argumentation, we do not suggest that the entire observed δ^{18} O secular trend would have to be accommodated by changes in isotopic composition of ancient seawater (cf. Azmy et al., 1998). At this stage, we only advocate a reassessment of discrepancies between theory and experimental data, an alternative far preferable to the wholesale dismissal of the latter.

11. Conclusions

Optical, mineralogical, chemical and isotopic studies of a large collection of newly sampled Phanerozoic low-Mg calcitic fossils (brachiopods and belemnites), complemented by geological considerations, demonstrate that the bulk of the shells are well-preserved and likely retained their primary isotope signals. The newly generated 87 Sr/ 86 Sr curve based on low-Mg fossils and conodonts resembles the one by Burke et al. (1982), but with greater detail and less dispersion.

The δ^{13} C curve for the Phanerozoic shows a general increase from about $-1 \pm 1\%$ to $+4 \pm 2\%$ PDB during the Paleozoic, an abrupt drop of 2‰ at the Permian/Triassic transition and oscillations around +2% in the course of the Mesozoic and Cenozoic. Superimposed on this general trend are higher-order oscillations, dominantly of global significance.

The δ^{18} O shows a general increase from about -8% to 0% PDB in the course of the Phanerozoic. Superimposed on this overall trend are second-order oscillations of ~ 150 Ma duration, their apexes coincident with cold intervals.

The means of Phanerozoic ⁸⁷Sr/⁸⁶Sr, δ^{13} C, δ^{18} O and δ^{34} S_{sulfate} correlate at any resolution in excess of 1 Ma, suggesting that we are dealing with a unified exogenic system (litho-, hydro-, atmo-, biosphere) driven by tectonic forces. Factor analysis shows that the above variables are controlled by three factors. The first factor is characterized by reciprocal loadings of ⁸⁷Sr/⁸⁶Sr and δ^{18} O, the second by positive loadings of ⁸⁷Sr/⁸⁶Sr and δ^{34} S and the third one by reciprocal loadings of δ^{37} Sr/⁸⁶Sr and δ^{34} S and δ^{13} C. We interpret the first two factors as tectonic and the third one as a biologically mediated redox balance of carbon and sulfur cycles.

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