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**Strontium isotope geochemistry of modern and ancient archives:
tracer of secular change in ocean chemistry**

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Keywords

$^{87}\text{Sr}/^{86}\text{Sr}$, modern and ancient brachiopods, halite, whole rock, secular- ^{87}Sr seawater curve,
Phanerozoic, Precambrian

Research highlights

Sr isotope compositions of modern brachiopods and evaporites

No species-dependent effect and biological fractionation

Latitude and depth have no impact on the $^{87}\text{Sr}/^{86}\text{Sr}$ in modern brachiopods

Salinity and temperature have minor impacts on the $^{87}\text{Sr}/^{86}\text{Sr}$ in modern brachiopods

Intensive screening for diagenetic impact on fossil archives

High-resolution Phanerozoic and late Precambrian seawater- ^{87}Sr curves

Abstract

Strontium isotopes of marine archives provide a significant means for tracing physical and chemical processes operating over geologic time. Modern articulated brachiopods and halite samples were collected from all depths of the world's main water bodies. Material from the Arctic, North and South Atlantic, North and South Pacific, Indian and Southern Oceans as well as Caribbean and Mediterranean Seas provide baseline parameters for diagenetic screening and reconstruction of seawater curves.

The strontium isotopic ratio of modern brachiopods is unobscured by latitude, depth and biologic factors (Order, valves, and shell segment). However, there is a small but significant impact of external sources reflected by salinity and temperature on the strontium isotope ratio of modern brachiopods. We found a significant difference in $^{87}\text{Sr}/^{86}\text{Sr}$ of brachiopods from polar and temperate-tropical habitats ($p = 0.001$), which should be considered when working with deep-time archives. The average $^{87}\text{Sr}/^{86}\text{Sr}$ value of all our modern shells (0.709160 ± 0.000019 ; $N = 95$) and halite (0.709153) is similar to values measured for modern seawater (0.710167 ± 0.000009 ; $p = 0.118$). The radiogenic strontium content of present-day seawater does not vary significantly, and modern biogenic-calcite $^{87}\text{Sr}/^{86}\text{Sr}$ ranges from 0.709126 to 0.709233 with a fluctuation of about ± 0.000054 .

With the most rigorous diagenetic evaluations and stratigraphic assignment of deep-time samples, and applying the strontium isotope fluctuation recorded by modern biogenic calcite to ancient carbonates and a 1 Myr interval, reconstructions resulted in a seawater- ^{87}Sr curve with greater details during the Phanerozoic and Neoproterozoic.

1. Introduction

The interplay between Earth's continental and oceanic activities and climate processes controls the strontium isotopic composition of modern seawater, whereas their evolution through time changed the marine Sr isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) significantly with geologic history (e.g., Burke et al., 1982; Elderfield, 1986; Veizer, 1989). Defining these changes is of great importance not only for correlating marine sediments on regional and global scales, but also for understanding the processes of the past and their impacts on ecosystems, habitats, biological diversity and geochemical cycles (e.g., Palmer and Edmond, 1989; Capo and DePaolo, 1990; Hodell et al., 1990; Derry et al., 1994; Martin and Macdougall, 1995; Montañez et al., 1996; Denison et al., 1998; McArthur et al., 1998, 2012).

The main carriers of Sr into the oceans are fluvial discharge and hydrothermal flux, and perhaps coastal groundwater discharge. Their Sr isotope loads reflect the intensity of weathering processes, type of rocks subject to erosion and rate of sea floor spreading (Capo and DePaolo, 1990; Berner, 1991; Raymo and Ruddiman, 1992; Palmer and Edmond, 1992; Basu et al., 2001; Krabbenhöft et al., 2010). Although strontium is dissolved at high concentration in modern seawater (~7.8 ppm), it is unable to precipitate its own minerals because of its high atomic mass (Capo et al., 1998). Instead it is incorporated into the crystal lattice of chemical and biochemical marine precipitates (e.g., Veizer, 1983; Farrell et al., 1995). Furthermore, rubidium is a low-abundance element with large ionic radius (1.48 Å) compared to that of calcium (0.99 Å) that is unlikely to substitute for Ca^{+2} in carbonate minerals, and no significant addition of ^{87}Sr from ^{87}Rb decay happens after precipitation of carbonate archives (Veizer, 1983; Capo et al., 1998).

Assessing the $^{87}\text{Sr}/^{86}\text{Sr}$ variations in paleo-oceans and its evolution through time requires measuring the Sr composition of pristine marine archives that inherit a marine signature with minimal isotope fractionation and extraneous outside influences. This precondition has been

subject to intensive work aimed at evaluating the diagenetic state of ancient marine archives and thus their preservation. This study evaluates the Sr isotope composition of modern brachiopods and halite of the world's main water masses (Arctic, North and South Atlantic, North and South Pacific, Indian and Southern Oceans as well as Caribbean and Mediterranean Seas), they are either quite resistant or readily dissolve during diagenetic processes (e.g., Brand and Veizer, 1980; Schreiber and El Tabakh, 2000). Although resistant to alteration, brachiopods as archives for trace elements, stable isotopes have limitations that must be considered when analysing modern and ancient counterparts. For example, their primary layer incorporates stable isotopes in disequilibrium with ambient seawater, a similar observation has been made about their umbonal area (e.g., Carpenter and Lohman, 1995; Brand et al., 2003; 2015). Trace elemental contents, especially Mg and Sr show variation in their valves with growth stage, and the optimal area for geochemical investigation is the internal mid-section of both ventral and dorsal valves for modern and ancient brachiopods (Romanin et al., 2018). This gives us an opportunity to test the concept that the standard normalization procedure for $^{87}\text{Sr}/^{86}\text{Sr}$ removes any natural fractionation within marine archives (cf. McArthur et al., 2012). Since this remains unsubstantiated for may biogenic carbonates, it gives us an opportunity to test this on our database of modern brachiopods covering the world's oceans, and various biological parameters, oceanographic and environmental conditions. Furthermore, we aim to apply our findings for modern archives to ancient ones, and supplemented them by detailed diagenetic evaluations of select brachiopods, conodonts and whole rock to improve on the Sr isotope curves reconstructed for Phanerozoic and Neoproterozoic seawater.

The strontium isotope composition of whole rock presents a special problem, 1) the Precambrian is dominated by this material for analysis, which in turn 2) may be subject to

aluminosilicate contamination and diagenetic alteration. These two issues tend to make the Sr isotope compositions more radiogenic (e.g., Shields and Veizer, 2002), although in special circumstances may make them less radiogenic (cf. Brand et al., 2010). The degree of diagenetic alteration can be assessed by rigorous screening of other proxies and petrographic means (i.e. cathodoluminescence), but contamination remains an on-going concern because of the bulk digestion method and selecting limited amounts of acid or strengths may not be sufficient to obviate this concern. Some authors (e.g., Banner et al., 1988; Bailey et al., 2000; Li et al., 2011; Liu et al., 2013) have suggested that sequential leaching of carbonate and simultaneous analysis of strontium isotopes and trace elements, among them Al and Rb, may help select the sequentially leached fraction of sample with the ‘closest’ to a primary or near-primary Sr isotope value. Most recently, Bellefroid et al. (2018) presented a procedure that may come close to achieving this goal in obtaining ‘primary’ Sr isotope values from whole rock that correspond to those of best-preserved coeval brachiopods. The observations of that study may help in revamping whole rock analyses especially when it comes to reconstructing deep-time seawater Sr-isotope curves that lack biogenic archives.

2. Sample localities

The study includes 96 modern brachiopods and one halite sample recovered from different bathymetric zones of the world’s main water bodies (Fig. 1), which includes results of Brand et al. (2003) and Vollstaedt et al. (2014) (Appendix 1). Their ambient oceanographic parameters cover the natural range of environmental variation of cold to warm zones, of low to high salinity and of clastic-detrital to carbonate substrates (Appendix 1).

In addition, the study is supplemented by Holocene brachiopods from Hudson Bay, Canada (N = 3), and fossil brachiopod shells from the La Meseta Formation (Eocene) of

Seymour Island, Antarctica (N = 14), the lower Ely Limestone (Mississippian to Pennsylvanian) of Granite Mountain, west-central Utah (N = 7) and the Snake Canyon Formation (Pennsylvanian) at Arco, east-central Idaho (N = 2), as well as Ediacaran Doushantuo Formation cap dolomicrite (N = 2) and Tonian Browne Formation halite (N = 2; Appendices 2, 3; Fig. 1).

3. Methodology

3.1 Sample Preparation

Live or recently dead brachiopods were obtained from their natural habitat by dredging or by scuba diver. The shells were cleaned of pedicles, periostracum, organic tissue and adhered inorganic matter with acid-washed stainless-steel tools. Organic nano-particulates in the shell punctae, encrusting epibionts and other organic remnants were removed with 2.5 % hydrogen peroxide. Subsequently, the primary layer and remaining surface contaminants were removed by leaching the shells in 10 % hydrochloric acid (v/v) for 10–30 seconds, or longer if necessary, until considered visually clean.

Fossil brachiopods were released from the enclosing rock using a sharp blade, and immersed in 10 % hydrochloric acid (v/v) for 10-30 seconds to remove their primary layer and surface contaminants. Shell fragments were examined by cathodoluminescence and scanning electron microscope for preservation of the shell's microstructure. Specimens with any sign of alteration were eliminated from further consideration, including those with slight surface discolouration.

Clean halite samples, after removal of weathered surfaces were crushed in an agate mortar and pestle. Fresh material was cleaned with isopropanol alcohol, air dried and optically examined for signs of alteration and discolouration. The diagenetic state of the fossil brachiopods, deep-time dolomicrite and halite were screened and assessed by Azmy et al. (2011), Spear et al. (2014) and Blamey et al. (2016). Elemental and stable isotope analyses of the modern brachiopods were described by Brand et al. (2013).

3.2 Strontium Isotope Geochemistry

Prior to strontium isotope analysis, the specimens (brachiopods and halite) were powdered in an agate mortar for analysis in the 'clean lab' at Ruhr University, Bochum. About 200 to 300 ng of each brachiopod sample was digested for 24 h in 6 M suprapure HCl at room temperature in closed PFA beakers and afterwards evaporated until dry. Dry samples were re-dissolved in 0.4 mL of 3 M HNO₃, and strontium was recovered using ion exchange complexing resin (Sr-resin TRISKEM) conditioned with 0.05 M and 3 M HNO₃ and 2 mL of distilled water. Subsequently, dried samples were treated with 0.5 mL of 1:1 of concentrated HNO₃:H₂O₂ to remove organic matter and remnants of TRISKEM resin. Finally, samples were converted to chloride-form with 0.4 mL of 6 M HCl. An alternate method was used for halite samples, with required sample size exceeding 15 to 25 mg. The first step involved application of TRISKEM_Sr-resin to isolate the strontium fraction, and the second step involved purifying the Sr fraction with BioRad AG 50W-X8 resin in a quartz glass column.

For mass-spectrometry samples were re-dissolved in an ionization-enhancing solution (cf. Birck, 1986). This was followed by TIMS mass spectrometry analysis using a TiBox Spectromat Bremen 7-collector solid-source instrument with single Re filament in peak-hopping (dynamic) measurement mode. Applying 1 µL of ionization enhancing solution the loading, column and

reagent blanks were < 5 pg, < 1 ng, and < 0.01 ppb, respectively. Thermal fractionation is corrected by normalization to a $^{88}\text{Sr}/^{86}\text{Sr}$ ratio of 8.375209. The cut-off limit for a Sr run is generally at an error of ± 2 s.e. $< 5 \times 10^{-6}$ for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measured with a minimum of 100 acquisitions and a maximum of 200. The typical duration of a strontium run is 110 acquisitions and 2 hours and 15 min plus filament heating time.

No Rb correction was applied, since for an element with two isotopes and spectral interference on one of them makes reliable correction near impossible. Instead, Rb was monitored during the complete run and the signal must be below the detection limit, otherwise the result was discarded and the measurement repeated after chemical separation of a new sample.

The Ruhr University Bochum (Germany) laboratory means (long-term) for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the USGS EN-1 and the NIST NBS 987 standards were 0.709159 ($N = 348$; standard error: 0.000002 [± 2 s.e. mean], standard deviation: 0.000032 [± 2 s.d.]), and 0.710241 ($N = 394$; standard error: 0.000002 [± 2 s.e. mean], standard deviation: 0.000030 [± 2 s.d.]), respectively.

The reference sample results, bracketing our brachiopod-halite sample set, of 34 analyses of NBS 987 was 0.710240 with standard error of 0.000004 (± 2 s.e.) and standard deviation of 0.000023 (± 2 s.d.), and of 24 analyses of USGS EN-1 was 0.709153 with standard error of 0.000004 (± 2 s.e.) and standard deviation of 0.000019 (± 2 s.d.)

The ratios are within the range of average measurements of corresponding standard material published by others (Fig. 2). To limit inter-laboratory confusion, all reported strontium isotope results in Appendices 1 – 4 were adjusted to a value of 0.710247 for NBS 987 (cf., McArthur et al., 2001; Brand et al., 2003).

3.3 Statistical Analyses

A band width of ± 0.000054 was used for secular curve re-constructions, based on the total $^{87}\text{Sr}/^{86}\text{Sr}$ variation observed in modern brachiopods ($N=95$, Appendix 1). The residence time for Sr in seawater is assumed to range from 5 to 1 Myr (Broecker and Peng, 1982; Elderfield, 1986; Veizer, 1989; Hodell et al., 1990; Henderson et al., 1994; Krabbenhöft et al., 2010; McArthur et al., 2012), and according to McArthur et al. (2012, p. 127) “The degree to which this was true in past times is not known”. We adopted a temporal resolution of 1 Myr for the Sr residence time in seawater in our reconstructions, and with mixing times ranging from 10,000 to 1000 years, the world’s ocean is assumed homogenous with respect to $^{87}\text{Sr}/^{86}\text{Sr}$.

We calculated the summary statistics of our modern brachiopod database with one exception (sample MB-1407, Appendix 1). For the evaluation of Order, valves and shell segments, we employed the t-test (parametric) and Mann-Whitney U (non-parametric) tests (Tables 1, 2), and for the correlation between brachiopod shell $^{87}\text{Sr}/^{86}\text{Sr}$ and environmental parameters (latitude, depth salinity and temperature) we used the Pearson and Spearman’s rs correlation tests and coefficients. The free software program Paleontological Statistics (PAST3, v3.14) by Hammer et al. (2001) was used for all statistical calculations and evaluations.

4. Strontium isotope results

The Sr isotope compositions of the 99 modern and Holocene brachiopod samples are listed, in addition to their Order, species, and shell compartments, including co-ordinates, latitude, depth, salinity and temperature in Appendix 1.

4.1 Modern Brachiopods - Shell components

The umbo region is the oldest and the most prominent part of a brachiopod’s valve, and it is a fragment commonly found in rocks (James et al., 1992). However, it yields slightly to significantly different elemental contents (e.g., Mg and rare earth element) and stable isotope

compositions than the rest of the shell (Carpenter and Lohmann, 1995; Brand et al., 2003, 2013, 2015; Cusack et al., 2007; Pérez–Huerta et al., 2008; Zaky et al, 2015, 2016 a, b). Therefore, it has been recommended by authors not to include geochemical results of umbo material in paleoenvironmental and paleoclimatic studies (e.g., Carpenter and Lohmann, 1995; Parkinson et al., 2005; Brand et al., 2003, 2011, Azmy et al., 2011; Zaky et al 2016 a,b).

Assessing the Sr isotope composition of the brachiopod umbo region was conducted on thirteen different specimens representing the Rhynchonellida and Terebratulida. Although, the umbo area is slightly more radiogenic (mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio = 0.709164) than the other shell parts (mean= 0.709159), the difference is not significant at the 95 % confidence level ($p=0.442$, or 0.192, Table 1). Although the umbo area should be avoided for their stable isotopes and REE contents, this caution does not apply to their strontium isotopes.

4.2 Modern Brachiopods - Shell compartments

The valves of articulated brachiopod shells are bilaterally symmetrical, but dissimilar in size with the dorsal (brachial) valve generally smaller than the ventral one (pedicle; MacFarlan et al., 2009). They are hinged by a series of teeth and sockets, and simple opening and closing muscles, while their front end opens and closes for feeding and protection (James et al., 1992). The ventral valves of all brachiopods have a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.709157 which is comparable to that of their corresponding dorsal valves of 0.709159. Thus, there is no significant difference in $^{87}\text{Sr}/^{86}\text{Sr}$ between ventral and dorsal valves ($p=0.779$ and 0.702, Table 1), they may be lumped together or geochemically tested without special consideration as to valve, which will be of great benefit when sampling fossil material.

4.3 Modern brachiopods - Order

The modern articulated brachiopods belong to three different Orders, the Rhynchonellida, Terebratulida and Thecideida. They are all sessile benthic marine invertebrates of epifaunal microhabitats and precipitate low Mg-calcite shells, except the Thecideida are significantly different in their shell structure (James et al., 1992). The virtual suppression of the Thecideida's secondary layer leaves the shell structure with a relatively thick ($>100\text{ }\mu\text{m}$; Cusack and Williams, 2003) granular laminae to blocky rhombohedra 'primary' layer (cf. Williams, 1966, 1968). However, traces of secondary fibers occur sporadically on cardinalia and valve floors of adult specimens (Williams, 1973).

Although, the Rhynchonellida have a slightly higher average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.709164, it is not significantly different of the 0.709160 from that of the Terebratulida ($p = 0.368$ and 0.183, Table 1) collectively to that of the Thecideida ($p = 0.159$ and 0.158, Table 1). Thus, our statistical analysis suggests that the three Orders of modern brachiopods incorporate similar strontium isotope compositions.

4.4 Modern brachiopods – Water mass

The ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ is utilized as climatic and tectonic proxies for understanding the Earth's history and geochemical cycles (e.g., Veizer et al., 1999; McArthur et al., 2012). River water has a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio ranging from 0.7119 to 0.7136, which results from the chemical weathering and eroding of continental rocks (Wadleigh et al., 1985; Palmer and Edmond, 1989; Capo et al., 1998; Allègre et al., 2010; Peucker-Ehrenbrink et al., 2010). The discharge of the riverine load or seepage of groundwater into coastal seas and bays tends to elevate the corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the ambient seawater (DePaolo, 1986; Hodell et al., 1990; Blum et al., 1993; Basu et al., 2001). In contrast, low and high temperature exchange between mid-oceanic spreading systems and seawater releases mantle-derived ^{86}Sr and consequently lowers

the marine $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (Brass, 1976; Spooner, 1976; Capo and DePaolo, 1990; Capo et al., 1998; Rad et al., 2007). In general, the magmatic related flux is estimated to have a mean Sr isotopic composition of about 0.7035, with values as low as 0.7032 in hydrothermal systems and as high as 0.7058 in Atlantic and Pacific rift valleys (Albarede et al., 1981; Clauer and Olafsson, 1981; Elderfield and Greaves, 1981; Palmer and Edmond, 1989; Bach and Humphris, 1999; Krabbenhöft et al., 2010). The continental flux of about 2.21×10^{12} g to 2.7×10^{12} g per annum is distinctly higher than the magmatic-related input of about 0.38×10^{12} g to 1.27×10^{12} g per annum, and thus dominates the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of modern seawater (Chaudhuri and Clauer, 1986; Hodell et al., 1989; Veizer, 1989; Kuznetsov et al., 2012).

Modern brachiopods from all seas and oceans have a collective Sr isotope value of 0.709160 similar to that of seawater of the Atlantic, Pacific and Indian Oceans, Labrador and Black Seas, and Persian Gulf (Muller et al., 1990; Peckmann et al., 2001; Mokadem et al., 2015). There is no statistical difference in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of modern brachiopods and ambient seawater (Table 1). However, we noted some variation in brachiopod $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from polar and temperate-tropical zones. Polar brachiopods (Arctic and Antarctic) have a summary mean of 0.709171 compared to that of tropical-temperate brachiopods of 0.709156 which are significantly different at the 99 % confidence level (Table 2). Interestingly, no significant correlation was noted within these specific water masses with salinity and temperature (Table 2). River discharge and groundwater leakage linked to the weathered hinterland may be the cause for the apparent difference (more radiogenic) in the isotope ratios of brachiopods from the two regions. No other associations (differences) was noted in brachiopods from polar and temperate-tropical zones.

4.5 Modern brachiopods - Latitude & water depth

Most of our brachiopod shells are from shallow-water environments (<250 m), with a few from deep (1000 – 4000 m) and even fewer from abyssal depths (>4000 m; Fig. 3, Appendix 1). They represent the main geographical zones of the northern and southern hemispheres; the north and south Frigid (polar regions), Temperate (from the tropics to the Cancer and Capricorn), and Torrid (tropics) zones. Statistical analysis of the strontium isotope results shows no significant difference between the brachiopod population and latitude (Fig. 3, Table 2).

The strontium isotope ratios of the brachiopods are consistent among the shallow and total depth intervals with values of 0.709159 and 0.709160, respectively (Fig. 4). The low correlation coefficient values between shells and water depth ($p = 0.463$ and 0.653 , Table 2), support the observation that strontium isotopes in brachiopods are similar irrespective of latitude and water depth.

4.6 Modern brachiopods - Seawater temperature & salinity

Temperature and salinity may exercise some influence on the natural fractionation of strontium isotopes between modern biogenic carbonate and seawater by association with sources linked to the weathering of continental hinterlands (Ingram and Sloan, 1992; Ingram and DePaolo, 1993; Fietzke and Eisenhauer, 2006). Our modern brachiopods cover a wide range of temperatures (-1.8° to 29.5° C) and represent three different salinity regimes. Shells from cold-water temperatures ($\leq 5^{\circ}$ C) have a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.709161 which is comparable to those from temperate and tropical-water settings of 0.709159 and 0.709151, respectively. Moreover, the correlation between modern brachiopods and temperature of their ambient water masses are relatively low, but are statistically significant (Fig. 5, Table 2). However, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized to 0.1194 for $^{88}\text{Sr}/^{86}\text{Sr}$ in order to eliminate mass spectrometer-related

mass bias. Consequently, only variations of radiogenic ^{87}Sr relative to stable isotopes are not affected by the normalization.

Salinity may impact the radiogenic Sr isotope ratio of marine biogenic carbonates, but at a salinity of 20 and above, the local riverine effect is negligible on the marine $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and the Sr composition of biogenic carbonates (DePaolo and Ingram, 1985; Andersson et al., 1992; Paytan et al., 1993; Bryant et al., 1995; McArthur et al., 2012). But what about a long-term effect on the isotopic composition of polar waters or other restricted bodies of water such as the Mediterranean (cf. McArthur et al., 2012)? Statistically there is a weak anticorrelation between salinity and brachiopod Sr isotope ratios which is slightly significant with non-parametric testing (Fig. 6, Table 2). Instead of a direct impact by salinity and temperature, we suggest that these oceanographic parameters are proxies of weathering and the influx of more radiogenic strontium into restricted environments as the ultimate cause for the observations in modern brachiopods.

4.7 Modern halite

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio incorporated into the modern halite obtained from the Bahamas (0.709153) is indistinguishable from that in modern biogenic calcite of brachiopods. Such similarity validates the potential of the radiogenic Sr isotope ratio in halite sediments as a proxy for paleo-oceanic investigations and stratigraphic correlation. However, caution is required in interpreting the origin of the evaporites for only those sourced from open seas and seawater are reliable archives for paleo-oceanographic studies as well as those that preserved their primary fabric and compositions (cf. Blamey et al., 2016).

5. Evaluation of archives

Elemental and isotopic compositions of marine archives such as brachiopods, conodonts, whole rock and halite have been used as proxies of ancient seawater chemistry (e.g., Kaufman and Knoll, 1995; Veizer et al., 1999; McArthur, 2010; Brand et al., 2012; Blamey et al., 2016). Because the original chemistry of archives may be overprinted during diagenesis, preservation of the original composition needs to be verified by screening tests prior to their application, for example, to reconstructing seawater curves (e.g., Brand and Veizer, 1980, 1981; Kaufman and Knoll, 1995; Brand, 2004; Brand et al., 2010).

5.1 Brachiopods

Low-Mg calcite shells of articulated brachiopods are relatively resistant to diagenetic alteration (cf. Brand and Veizer, 1980; Brand et al., 2003). Also, they have a long geological record extending back to the Cambrian (Curry and Brunton, 2007), and are widespread and abundant in Phanerozoic sediments (Brand et al., 2011). Consequently, they are considered a primary paleo-oceanic archive to study the geochemical evolution of ancient oceans (Veizer et al., 1999; Brand, 2004; Azmy et al., 2009, 2011, 2012; Brand et al., 2010). However, their resistance to diagenetic alteration is not perfect, sometimes fossil brachiopods may suffer significant diagenetic changes. The degree of alteration may vary from dissolution pits and other superficial features in shells stabilized in low to medium fluid/rock ratio diagenetic environments, to complete dissolution and replacement by other minerals in a high fluid/rock ratio system (cf. Brand, 2004; Casella et al., 2018).

Several screening tests have been introduced to evaluate the preservation of brachiopod calcite. Petrographic examination is a popular technique for identifying visual signs of alteration like powdery appearance, inconsistent colouration, lack of structural cohesion (Denison et al. 1994; Brand et al., 2012). Scanning electron microscopy (SEM) is another test used to assess the

degree of diagenetic alteration as it provides visual evidence for preservation of microstructural features such as fibres and columns in shell layers (Gaspard and Nouet, 2016; Ye et al., 2018). Cathode Luminescence (CL) is another method for identifying alteration in brachiopods, other biogenic and abiogenic allochems and whole rock (Tomasovych and Farkas, 2005). However, CL may be unduly influenced by the luminescing or quenching potential of their respective Mn and Fe contents (Machel and Burton, 1972).

The geochemistry of brachiopods serves as an additional screening tool to evaluate their preservation state (Brand and Veizer, 1980). The trace element (Mg, Sr, Mn, Fe and Na) contents and stable isotope ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) compositions and distribution within the calcite lattice of carbonates are governed primarily by their original mineralogy, seawater composition, partition coefficients and the fluid/rock ratio of the diagenetic system (Brand and Veizer, 1980, 1981). During meteoric-water diagenesis marine carbonates incorporate more Mn and Fe, discriminate against Sr and Na, and more of the light stable isotopes ^{12}C and ^{16}O (Brand and Veizer, 1980, 1981). Changes in contents and compositions allows us to differentiate between original and altered contents and thus assess the fidelity of the archive.

A sample of four groups of brachiopods from the Carboniferous Bird Spring Formation of Nevada, show some typical and atypical geochemical trends with increasing diagenetic alteration. Group I brachiopods (from horizon A55) with Mn/Sr ratios of less than 0.06 retained their original radiogenic strontium isotope signatures, whereas those with Mn/Sr ratios of greater than 0.06 are altered and their values are outside the realm of natural variation based on observations in modern brachiopods (Fig. 7). In Group II brachiopods (A56), the change in strontium isotopes is more subtle with change in Mn/Sr. Within a sediment column thickness of 1.5 m, we noticed extensive to subtle change in strontium isotopes with diagenesis in the

respective brachiopods (cf. Brand et al., 2012). Group III brachiopods (A312) are from a sublithographic unit with exceptionally constant strontium isotope values (Fig. 7). In contrast, the Group IV brachiopods (A408) are unique in that two samples are deemed altered with Mn/Sr greater than 0.06 and one with less than 0.06 has a most radiogenic value (Fig. 7). Partial dolomitization of these brachiopod shells may have played a role in the odd Mn/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ relationship. This demonstrates that a fixed Mn/Sr ratio is not a suitable indicator of detecting or deciding between alteration/preservation in carbonates, instead a flexible Mn/Sr ratio and other screening tools should be consulted prior to final assessment and assignment of a degree of preservation of carbonates (cf. Brand et al., 2011; Ullmann and Korte, 2015).

The 'cut-off' point in Mn/Sr between preservation and alteration of strontium isotope values is variable and considerably lower than the level suggested by Kaufman and Knoll (1995) for tracking diagenetic change. Instead, we suggest that carbonates altered in oxic fluids should be deemed altered with Mn/Sr ratios greater than 0.06 or at best 0.1 (Fig. 7). However, as a note of caution, much of the original parameter depends on the original depositional water conditions (Groups I, II, III <0.06 and Group IV <0.02 ; cf. Brand, 2004). Thus, instead of a fixed numerical value for Mn/Sr as proposed by Kaufman and Knoll (1995) for the 'preservation' cut-off point, we suggest it should be dynamic, on a horizon basis and determined for each individual population whether brachiopods or whole rock (cf. Brand, 2004; Ullmann and Korte, 2015).

5.2 Conodonts

Conodonts first appeared in the Tommotian (Cambrian), and were widespread during the Paleozoic and Mesozoic, but became extinct by the end of the Triassic (Azmi and Pancholi, 1983). They possess high stratigraphic acuity and their distribution characteristics make them ideal environmental archives (Brand et al., 2011). Conodonts consist of carbonate fluorapatite

(francolite), and based on its heavier oxygen isotopes relative to other archives was judged a superior archive most resistant to diagenesis (Wenzel et al. 2000; Joachimski et al. 2009). Others argue that francolite is not an original mineralogical phase, but an end-product of early diagenetic substitution (dissolution-reprecipitation) of primary hydroxylapatite, which takes place under natural low-temperature conditions with enhancements by microbial enzymatic activity (Soudry and Champetier, 1983; McArthur et al., 1987; Schuffert et al. 1990; Iacumin et al. 1996; Blake et al., 1997; Sharp et al., 2000; Trotter and Eggins, 2006). The uncertainty with the mineralogy and the preservation potential of conodonts are due to a lack of modern representatives, and having to use fish bone, teeth and scales as modern analogues does not acquiesce the issue (Brand et al., 2011).

In the absence of robust diagenetic evaluation techniques and screening tests, the colour alteration index (CAI) has been utilized to assess the degree of alteration in conodonts (Nowland and Barnes, 1987). Francolite is susceptible to thermal alteration and its colour changes with increasing maturation (Epstein et al. 1977). Conodonts buried at temperatures of less than 80°C attain a CAI of less than 2 are deemed least altered, and potentially should yield an original seawater chemistry (Joachimski et al. 2002). However, recent studies argue that the least post-depositional chemical exchange applies only to the densest, least permeable conodont histologies such as their albid crowns, hyaline crowns, and basal plate (Trotter and Eggins, 2006; Trotter et al., 2007; Bright et al., 2009; Zhao et al., 2013; Song et al., 2015; Li et al., 2017). Thus, the reliability of the geochemical contents of conodont archives is seriously challenged by these observations.

Recently, Woodard et al. (2013) published strontium isotope results of some conodonts from the Carboniferous Bird Spring Formation sequence in Arrow Canyon. A sequence also

studied for their brachiopod and whole rock geochemistry (Brand et al., 2012). The separated conodonts were extensively cleaned of attached sediment, surface contaminants, organic material and pyrite (Woodard et al., 2013). A compilation of strontium isotope results from the respective databases (conodonts and brachiopods) shows that most of the strontium isotope values of the conodonts are more radiogenic than those of brachiopods from the same stratigraphic interval (Fig. 8). Only 6 of 15 strontium isotope results of the conodonts are within the range deemed acceptable, and represent original values (A50, A62, A112, A312, A373, A438; Fig. 8). All others are slightly (Δ of 0.000116) to significantly more (0.000948; Appendix 2) radiogenic than the best-preserved coeval brachiopod calcite. Our observation questions the superior fidelity of conodonts, suggested by some, to carry a primary strontium isotope proxy value. Since the preservation status of conodonts obtained from the literature cannot be confirmed, consequently, in our Phanerozoic and Precambrian seawater curves strontium values of conodont archives will not be used in the seawater reconstruction.

5.3 Whole rock

Whole rock represents a mixture of carbonate components, plus clay and aluminosilicate fractions (=insoluble residue, Brand and Veizer, 1980), ranging in texture from fine- to coarse-grained that were stabilized through solution-reprecipitation processes in marine and/or meteoric derivative fluids into diagenetic low-Mg calcite (Brand et al., 2011). Preservation of the original fine-grained texture infers mineralogical stabilization in a closed diagenetic system with low water/fluid ratio, and is assumed to be a 'solid' indicator of an original seawater signature retained by the carbonate archive (Veizer, 1983). Consequently, detailed petrographic, including cathodoluminescence, investigation is a key step for identifying the degree of diagenetic alteration in whole rock (e.g., Brand and Veizer, 1980; Kaufman and Knoll, 1995)

Low temperature reaction with silicate rocks elevates the Mn, Fe and radiogenic ^{87}Sr , while it reduces the Na and Sr contents of diagenetic fluids (Drever, 1988; Chaudhuri and Clauer, 1993). The resulting chemical differences between the diagenetic fluid and the precursor carbonate causes lower $\delta^{18}\text{O}$ values, Sr and Na contents, and higher Mn and Fe contents of the fine-grained diagenetic carbonate (Pingitore, 1978; Brand and Veizer, 1980, 1981; James and Choquette, 1983; Denison et al., 1994; Jones et al., 1994a; Gorokhov, 1996; Brand, 2004). In contrast, carbon isotopes may be preserved in what is deemed to be an 'original' composition, but CO_2 -charged marine pore water or meteoric water might increase or decrease it during post-depositional diagenesis (Brand and Veizer, 1981; Walter et al., 1993, 2007; Patterson and Walter, 1994; Hover et al. 2001; Hu and Burdige, 2007). Based on these observations, the Mn/Sr ratio was adopted as a screening parameter for evaluating the degree of diagenetic alteration in whole rock carbonates (Kaufman et al., 1992). Whole rock carbonates with a Mn/Sr ratio of $<2-3$ were deemed to retain reliable strontium isotope compositions, whereas those with $\text{Mn/Sr} < 10$ were deemed to store near-primary carbon isotope compositions (Kaufman and Knoll, 1995).

Our Bird Spring whole-rock samples have Mn/Sr ratios of less than 1.05 (Fig. 9), and according to the cut-off parameters put forth, they all should retain near primary $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Kaufman and Knoll, 1995). The diagenetic state of the brachiopods based on multiple textural, fabric, and geochemical screening parameters disclosed that except for the samples from horizon A91 (Fig. 9), most shells are preserved near original conditions (cf. Brand et al., 2012). In addition, their Mn/Sr ratios are consistently less than 0.1 (Fig. 9). A one-on-one comparison of brachiopods and whole rock from the Bird Spring Formation show that only three whole rock sample results (A91: 0.000032, A312: 0.000001, A373: 0.000066) are comparable to 'pristine' values recorded by the best-preserved brachiopods (Fig. 9). Thus, the universally accepted 'cut-

off level for Mn/Sr of less than 2-3 is less than satisfactory in identifying the least altered whole rock carbonate material from the Carboniferous Bird Spring Formation of southern Nevada. Therefore, caution is strongly advised when using this cut-off parameter, and more than one sample should be evaluated for any horizon and followed by detailed petrographic information (cf. Brand, 2004).

In addition to diagenetic alteration, carbonates digested in bulk may be subject to Sr isotope contamination from the aluminosilicate fraction of the whole rock (e.g., Banner et al., 1988; Liu et al., 2013). This ‘leaching’ during acid digestion may lead to more radiogenic values in most instances, which may be countered by the sequential leaching of whole rock carbonates and tracing the process with trace element contents (cf. Bellefroid et al., 2018). Similar to the diagenetic evaluation above, comparison of results obtained from sequentially and selectively leached whole rock from the Bird Spring Formation show that the majority of Sr isotope values fall within the range of primary values garnered from coeval best-preserved brachiopods (Brand et al., 2012a; Bellefroid et al., 2018). Thus, it is proposed that sequential leaching of whole rock carbonates be made the preferred method for obtaining Sr isotopes with near-primary values of seawater-⁸⁷Sr.

5.4 Halite

Halite is a chemical sedimentary rock, it may precipitate in marginal marine subaerial-subaqueous hypersaline settings (Melvin, 1991), in water bodies partially cut-off from the free circulation of the open sea. Progressive evaporation of standing brines leads to the accumulation of halite as subaqueous cumulate, subaqueous bottom precipitate and intra-sediment precipitate (Hovorka, 1987). Cumulate forms at the brine-air interface during the initial stage of halite precipitation, and are dominated by four-sided inverted pyramidal crystals that form weakly

coalesced rafts (Lowenstein and Hardie, 1985). Secondary halite consists of large and clear, but occasionally distorted, interlocking mosaic crystals (Schreiber and El Tabakh, 2000). Petrographic inspection for preservation of the main components like crystal fabric, texture and bedding is, thus, a crucial step to evaluating the degree of alteration in halite (e.g., Spear et al., 2014). If preserved in their original mineralogy marine halite should be an excellent archive for storing primary seawater strontium isotope compositions.

6. Secular seawater- ^{87}Sr curves

Regardless of local climate, oceanographic parameters, latitude and water depth, the marine $^{87}\text{Sr}/^{86}\text{Sr}$ ratio should be globally uniform at any point in geologic time (e.g., Burke et al., 1982; Elderfield, 1986; Veizer et al., 1999; McArthur et al., 2012). However, it has not remained invariant with time, but fluctuated over millions of years in response to changes in Earth's tectonic activity and strontium cycle (Armstrong, 1971; Brass, 1976; Palmer and Edmond, 1989; Capo and DePaolo, 1990; Hodell et al., 1990). Strontium isotope compositions in high fidelity marine archives are utilized to define time-dependent variations and reconstruct a secular seawater trend that tracks the fate of strontium isotopes with geologic time-and provides a method for correlating marine deposits (e.g., Peterman et al., 1970; Veizer and Compston, 1974; Burke et al., 1982; Veizer et al., 1999; McArthur et al., 2001, 2006, 2012). Plus, we will be examining a number of time periods exemplary of icehouse (i.e. Sturtian and Marinoan glaciations, end Ordovician, mid Carboniferous) and greenhouse (end Permian, Paleogene) events.

6.1. Phanerozoic Eon

Modern investigations, including the current study, prove the capability of some chemically/biochemically precipitated marine archives (e.g., brachiopods, molluscs, corals,

foraminifera and evaporites) to inherit the $^{87}\text{Sr}/^{86}\text{Sr}$ signature of seawater at the time of their formation (Koepnick et al., 1985; DePaolo and Ingram, 1985; Hodell et al., 1990; Andersson et al., 1992; Paytan et al., 1993; Henderson et al., 1994; Brand et al., 2003; Ando et al., 2009; Kuznetsov et al., 2012). In contrast, some other archival minerals such as phosphate suffer a certain degree of alteration during early and/or late burial that overprints their original elemental and isotopic compositions, and raises their radiogenic ^{87}Sr content (e.g., McArthur and Walsh, 1984; Elderfield and Pagett, 1986; Tuross et al., 1989; Reynard et al., 1999; Trueman and Tuross, 2002; Trueman et al., 2002, 2004, 2006, 2008a, 2008b; Smith et al., 2005; Bright et al., 2009; Kocsis et al., 2010; Roberts et al., 2012).

Numerous secular trends have been published tracking the evolution of marine $^{87}\text{Sr}/^{86}\text{Sr}$ during the Phanerozoic (e.g., Peterman et al., 1970; Burke et al., 1982; Veizer et al., 1999; McArthur et al., 2012). We aim to streamline the existing ones, one of them is available online under the name “Ottawa-Bochum dataset”, by including up-to date results and a comprehensive modern dataset (Appendix 1). Refinement is achieved by excluding results of archives that, 1) lack modern representatives (see Evaluation of Archives section) such as conodonts, 2) are unable to retain their original compositions to the present day due to syn- or post-depositional alteration like biogenic phosphate (e.g., Trueman and Tuross, 2002), and 3) lack sufficient stratigraphic resolution. Furthermore, we aim to apply the natural variation in strontium isotopes observed in modern marine biogenic carbonates (± 0.000054) to the fossil record. Thus, the modified Phanerozoic trend (Fig. 10) relies only on the biogenic carbonate archives of either calcite or aragonite that were evaluated thoroughly for the preservation of the original structure, mineralogy and chemistry. It involves the work of most of the major contributors in the field of Sr isotopes (Appendix 3).

Numeric age assignment of the latest Sr isotope results, other than those of Veizer et al., 1999, and the age adjustment to the measurements published in Veizer study “Ottawa-Bochum dataset” were based on the latest version of the International Chronostratigraphic Chart (Cohen et al., 2013; updated). However, uncertainty in age estimates remains a problem that may exclude some accurate results (Appendices 3 and 4). Therefore, to minimize the effect of age-assigned error, the $^{87}\text{Sr}/^{86}\text{Sr}$ measurements were grouped into 1 Ma intervals. The mean ratio of each interval was calculated (Appendix 3) and plotted (Fig. 10) to reconstruct an average trend line based on a 2-period moving average of measurements for the Phanerozoic. Further, the observed value for the magnitude of Sr isotope fluctuation in modern marine calcite (± 0.000054) was added to and subtracted from the mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of each group to calculate the upper and lower limit of natural variation for the proposed 1 Ma intervals and consequently the band reflects natural fluctuation (Fig. 10).

Values of isotopic Sr contents in ancient marine evaporites were also plotted (Fig. 10), but not included in the trend or the band calculation, but emphasise their importance as a valuable archive provided they have a marine origin and were screened properly for their preservation (see Evaluation of Archives section). The whole rock measurements of D'Arcy et al. (2017) facilitate connection between the Phanerozoic and Neoproterozoic curves, but were not included in the trend or the band construction. The full set of results, accepted and rejected $^{87}\text{Sr}/^{86}\text{Sr}$ values of biogenic calcite, aragonite and evaporites, in addition to phosphate archives are plotted on figure 10A3 in Appendix 3.

6.1.1 Hirnantian (end Ordovician)

The Ordovician-Silurian seawater curve defines a secular trend of gradual decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from the maximum values of the early Late Cambrian through the Ordovician,

followed by a Middle-Late Ordovician transition, and then a progressive increase with time during the Silurian (Fig. 11; Veizer and Compston, 1974; Burke et al., 1982; Veizer et al., 1986; Denison et al., 1998; Qing et al., 1998; Azmy et al., 1999; Ebner et al., 2001; Shields et al., 2003; Brand et al., 2006). During the Late Ordovician to the Early Silurian, the Earth witnessed the first glaciation in the Paleozoic, the Hirnantian (Andean-Saharan) glaciation (~445 Ma) that lasted for 1-2 Ma (e.g., Holmden et al., 2012; Ravier et al., 2014) or up to 30 Ma (450–420 Ma; e.g., Pinti, 2011).

Weathering of the “Pan-African” mountain chains, that were uplifted during the terminal Proterozoic and Cambrian periods, was attributed as the primary source for the Late Cambrian $^{87}\text{Sr}/^{86}\text{Sr}$ maximum (Montañez et al., 1996, 2000). The waning of mountain building is probably the main reason for the progressive drop in the values through the Ordovician (Qing et al., 1998), whereas the explosive volcanism in the Ordovician (Ronov et al., 1980; Nikitin et al., 1990; Huff et al., 2010) and subduction of the Laurentian margin (Ettensohn, 1990; Wright et al., 2002) most likely sped up the rate of decrease across the Middle-Late Ordovician transition (Shields et al., 2003). Furthermore, the gradual increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio that started in the Early Silurian is probably due to the Salinic Orogeny, which impacted the eastern parts of Laurentia (Brand et al., 2006), or a gradual warming in climate (Azmy et al., 1999).

6.1.2 Mid-Carboniferous

The Sr isotopic trend of the Carboniferous (Fig. 10) displays continuous depletion in the Lower and Middle Mississippian (Tournaisian- Early Visean), progressive rise during the Middle Mississippian (Mid Visean) continuing through the Upper Mississippian (Serpukhovian) and Lower Pennsylvanian (Bashkirian), a uniform plateau in the Middle Pennsylvanian (Moscovian), then a slight decline in the Upper Pennsylvanian (Kasimovian and Gzhelian; Nishioka et al.,

1991; Bruckschen et al., 1999; Mii et al., 1999; Brand and Bruckschen, 2002; Azmy et al., 2009; Brand et al., 2007; 2012a; Woodard et al., 2013). The Early Carboniferous depletions were attributed to the waning of the Acadian orogeny and the subsequent decrease in continental weathering rates, whereas the Mid-Mississippian shift (Fig. 12) is probably due to the increase in the riverine flux rate accompanying the Hercynian orogenic uplift (Bruckschen et al., 1999; Woodard et al., 2013).

Strontium isotope ratios in well-preserved Mid-Carboniferous brachiopods from the Askyn River section (Southern Urals, Russia; Brand and Bruckschen, 2002), Bird Spring Formation (Lane et al., 1999) exposed at Arrow Canyon (Brand et al., 2012a), Apex and Kane Springs Wash East (Brand et al., 2007) in Nevada, Snake Canyon Formation at Arco in east-central Idaho, and lower Ely Limestone of Granite Mountain section in west-central Utah define a sharp positive excursion on the Mid-Carboniferous $^{87}\text{Sr}/^{86}\text{Sr}$ curve (Fig. 12). It coincides with onset of the second phase of the Permo-Carboniferous Glaciation (Glacial II; Isbell et al., 2003; Fielding et al., 2008) and probably represents some enhancements in the physical and chemical weathering of silicates.

6.1.3 Permian - Triassic

The $^{87}\text{Sr}/^{86}\text{Sr}$ trend of Late Paleozoic seawater (Fig. 10) documents a continual drop during the early and middle Permian (Asselian to Capitanian), followed by a slight increase in the upper stages (Dzhulfian and Dorashamian) and then a sharp rise to the Triassic boundary (Fig. 13; Martin and Macdougall, 1995; Korte et al., 2003; Brand et al., 2012b; Korte and Ullmann, 2016). Significant reduction in the continental weathering rate due to the deglaciation of Gondwanaland and the increasing aridity in Pangaea caused the notable depletions in the Sr ratio during the Early Permian (Martin and Macdougall, 1995; Korte et al., 2006). Widespread

basaltic volcanism associated with the opening of the Neotethys in the Artinskian assured the perpetuation of the established pattern, whereas its cessation in the Capitanian allowed slight recovery of radiogenic Sr isotope of seawater (Kani et al., 2013; Korte and Ullmann, 2016). The Early Triassic rise (Fig. 13), on the other hand, seemed to be of non-orogenic origin as it was initiated most likely due to the lack of protective vegetation cover, which led to an increase in the rate of continental weathering (Martin and Macdougall, 1995; Korte et al., 2003; Huang et al., 2008).

6.1.4 Paleogene

The Upper Cretaceous progressive rise in the Mesozoic $^{87}\text{Sr}/^{86}\text{Sr}$ curve (Fig. 10) ceased with the Tertiary (Fig. 14; e.g., McArthur et al., 1992, 1994, 1998; 2016; Jones et al., 1994a; Pardo et al., 1999; MacLeod et al., 2001; Vonhof et al., 2011). Strontium isotope ratios decreased slightly during the Paleocene and remained constant during most of the Eocene, reflected in the measurements of the Seymour Island brachiopods from the La Meseta Formation, Antarctica (Appendix 3). Of special interest, is the non-impact of the Paleocene-Eocene Thermal Maximum event on the seawater- ^{87}Sr curve (Fig. 14)

The Paleogene ‘depletion’ was probably initiated due to increases in the hydrothermal flux of less radiogenic Sr that accompanied the formation of the North Atlantic province and explosive volcanism in the Caribbean (Thomas and Shackleton, 1996; Bralower et al., 1997; Hodell et al., 2007). It is generally accepted that the weathering and unroofing of radiogenic rocks of the Himalayan-Tibetan uplift is the main reason for the Miocene to Recent increase in $^{87}\text{Sr}/^{86}\text{Sr}$ (Harris, 1995; McArthur et al., 2001, 2004; McArthur, 2010). In contrast, the main cause for the Late Eocene and Oligocene rise remains unresolved (McArthur et al., 2001). However, Zachos et al. (1999) argued that changes in climate and the formation of the Antarctica

ice sheet, either temporarily in the Late Eocene or permanently in the Oligocene, enhanced continental weathering thus contributed to the rise in radiogenic strontium.

6.2 Neoproterozoic Era

In contrast to the Phanerozoic curve, the pre-Ordovician $^{87}\text{Sr}/^{86}\text{Sr}$ seawater curve and trend is poorly constrained in the literature. It is composed either of sporadic data points (Halverson et al., 2007b), or a discontinuous curve (McArthur et al., 2012). Although our Ediacaran Doushantuo dolomicrite and Tonian Browne Formation halite measurements (Table 3) are in the range of counterparts of similar ages (Halverson et al., 2007a, b; Cox et al., 2016), they do not seem to fit on the reconstructed curve. Therefore, we reconstructed the secular trend for the Neoproterozoic Era using the Shields and Veizer (2002) data, which is available online under the Ottawa-Bochum dataset and the Halverson et al. (2007b) one as guidelines. The amount of work published in the last seven to eight years is sufficient to aid in the reconstruction of an enhanced Neoproterozoic seawater- ^{87}Sr curve (e.g., Kouchinsky et al., 2008; Miller et al., 2009; Maloof et al., 2010; Sawaki et al., 2010; Li et al., 2013; Rooney et al., 2014; Bold et al., 2016; Cox et al., 2016).

Similar to the Paleozoic, the proposed average trend line for the pre-Ordovician is constructed by grouping archival material of whole rock carbonate and evaporites into 1 Ma intervals (e.g., Frimmel and Jiang, 2000; Kah et al., 2001; Mazumdar and Strauss, 2006; Halverson et al., 2010). The mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of each interval was calculated (Appendix 4), calibrated based on a 2-period moving average of measurements (Fig. 15). Furthermore, the upper and lower limit of the variation were based on the magnitude of the radiogenic Sr isotope fluctuation in modern biogenic carbonates (± 0.000054). Generally, the average trend line displays an increasing curve from ~ 0.706267 during the Late Tonian to ~ 0.709206 by the early

Ordovician punctuated by excursions (Fig. 15). All results, accepted and rejected are included in figure 15A4 in Appendix 4. More than ever, more Sr isotope results of whole rock were rejected in light of the observations and conclusion based on the sequential leaching process of whole rock carbonates (Banner et al., 1988; Bailey et al., 2000; Li et al., 2011; Liu et al., 2013).

The Neoproterozoic Era (1000-541 Ma) witnessed some of the most extreme climate events in Earth's geologic record, and encompasses three major glaciations; the Sturtian, Marinoan and Gaskiers (Kaufman et al., 1997; Kennedy et al., 1998; Hoffman et al., 1998a, 1998b; Walter et al., 2000; Halverson et al., 2009). During the Cryogenian glaciations (Sturtian and Marinoan) severe cold prevailed over Earth's surface for millions of years, and the whole planet was almost completely frozen over with ice sheets reaching the equator (Snowball Earth; Hoffman et al., 1998a; Hoffman and Schrag, 2002; Miller et al., 2009; Rooney et al., 2014, 2015; Cox et al., 2016).

6.2.1 Mid Tonian

The low strontium isotope ratios of the Tonian halites from the Australian Browne Formation (0.706696 and 0.706767; Table 3) are similar to those of other coeval results (Fig. 15) of Halverson et al. (2007a, b) and Cox et al. (2016). These unusually low ratios constitute the base of a steady rising $^{87}\text{Sr}/^{86}\text{Sr}$ secular trend during the Neoproterozoic that started with the break-up of the Late Mesoproterozoic Rodinia supercontinent during the Tonian (Halverson et al., 2007b, 2009).

6.2.2 Sturtian Glaciation

The post-glaciation trend in the seawater ^{87}Sr of the Sturtian Snowball is less developed compared to that of the Marinoan (Fig. 16). The abrupt upward kick of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from 0.706751 to 0.707364 after a long Snowball-Earth event is lower than anticipated, whereas the

subsequent drop in the ratio following the full meltdown of the low latitude ice sheets is insufficiently steep (0.706909; Fig. 16). In addition, the ratio of the established steady state that followed the post-glaciation fluctuation due to the re-dominance of the riverine flux with a value of 0.707270 was not significantly different from that of later post-glacial sediments (0.707221; Fig. 16). It suggests either discontinuous glaciation throughout the ~ 55 Ma of the Sturtian with short interglacials intersecting the main Snowball Earth event, or substantially less intense warming with weak snowmelt runoff of continental weathered material.

6.2.3 Marinoan Glaciation

A significant oscillation in the $^{87}\text{Sr}/^{86}\text{Sr}$ curve marks the post-Marinoan Glaciation (Fig. 17). The short glacial event of the Marinoan (lasted for ~4 Ma; 639?–635 Ma; Prave et al., 2016), and the long Sturtian one (lasted for ~55 Ma; 717–662.4 Ma; Rooney et al., 2014) were followed by worldwide precipitation of a thick cap carbonate layer of microbial origin at the base, then a chemogenic succession of limestone and/or evaporate (Kennedy et al., 1998; Macdonald et al., 2009). The Doushantuo microbial dolomicrite (Table 3) was obtained from the base of the cap carbonate layer just after the glaciation event. It yielded significantly higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.708421, 0.708570; Table 3) than those from well before and after the event (Fig. 17), but are similar to those of Kennedy et al. (1998) and Halverson et al. (2007a, b; Appendix 4). Shutdown of continental runoff due to the formation of a Snowball Earth in the Sturtian depleted the values from 0.707287 to 0.707200 during the Marinoan. Whereas extensive continental weathering accompanying the rapid melting of the low latitude ice-sheets and the consequent epic flooding at the end the Sturtian and Marinoan glaciations raised the ratio as high as 0.708797 during deposition of the base of the cap carbonates (Fig. 17). It explains the uncommonly high values of the Doushantuo microbialites (Table 3) and their world-wide

coevals (Kennedy et al., 1998, 2008; Halverson et al., 2007a, b). Furthermore, the sharp drop in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to a low of 0.707551 in the topmost diamictite deposits (Fig. 17) most likely reflects the dominance of the magmatic input of the nonradiogenic Sr isotopes over that of the riverine flux. However, as warming proceeded this state of balance could not last long, and fluvial discharge re-dominated the Sr flux into the oceans raising the ratio to a near steady-state value of 0.708116 (Fig. 17).

7. Conclusions

The establishment of a modern brachiopod-based database from a wide regime of oceanographic conditions allows for the introduction of baseline parameters, coupled with more rigorous diagenetic assessment and stratigraphic assignment, to a more refined deep-time reconstructed seawater ^{87}Sr curve.

- 1- No noticeable variation of strontium isotopes was recorded in the various brachiopod components (umbo, mid-, anterior sections; and ventral, dorsal valves).
- 2- The modern brachiopod Orders Rhynchonellida, Terebratulida, and Thecideida obtain their Sr exclusively from seawater essentially independent of locality, lithology and geochemistry of the seabed, which should apply to their ancient counterparts.
- 3-The strontium isotope compositions of modern articulated brachiopods and halite show no significant variation from that of modern seawater.
- 4-The strontium isotope compositions of brachiopods from polar seas are significantly different, by about +0.000015, from those of temperate-tropical seas ($p = 0.001$)
- 5- Oceanographic conditions of latitude and depth exert no control on the strontium isotope composition in brachiopod calcite and halite supporting the homogeneity of modern seawater

6-Oceanographic parameters of salinity and temperature exert small but significant controls on the strontium isotope composition in brachiopod calcite, with them acting as proxies for local input of Sr from isotopically different sources.

7- Phanerozoic and Neoproterozoic seawater- ^{87}Sr curves are greatly enhanced due to increased diagenetic screening, greater stratigraphic resolution, and limiting fluctuation in the Sr isotope composition equivalent to that observed in modern carbonates (± 0.000054).

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Figure captions

Fig. 1. Locality diagram of modern, Holocene and fossil brachiopods, modern halite, Ediacaran dolomicrite (Doushantuo Formation, China), and Tonian halite (Browne Formation, Australia; Appendix 1).

Fig. 2. Average long-term Sr isotope compositions in two standard reference materials, N.B.S. 987 ($N = 394$) and USGS EN-1 ($N = 348$) measured by the Ruhr University Bochum laboratory (red circle; A) relative to corresponding results of other laboratories (blue circles; (1) Burke et al., 1982, (2) Richter and DePaolo, 1988, (3) Hodell et al., 1989, (4) Müller and Mueller, 1991, (5) Denison et al., 1994, (6) McArthur et al., 2001, 2006, (7) Major et al., 2006, (8) Widerlund and Andersson, 2006, (9) Kuznetsov et al., 2012 [2005–2006 results], (10) Kuznetsov et al., 2012 [2009–2010 results], and (11) Dudas et al., 2017.

Fig. 3. Latitudinal distribution of modern brachiopods from all modern ocean bodies (Appendix 1).

Fig 4. Depth distribution of shallow-water modern brachiopods. Inset shows the total depth distribution of modern brachiopods. Legend as in figure 3 (Appendix 1).

Fig 5. Ambient seawater temperature of modern brachiopods from all modern ocean bodies (Appendix 1).

Fig 6. Ambient seawater salinity of modern brachiopods from all modern ocean bodies (Appendix 1).

Fig. 7. Mn/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of brachiopods and whole rock components from the Bird Spring Formation (Brand et al., 2012a). In Group I, some brachiopods are preserved (green field) while two are altered based on microstructural, CL and trace element screening (red field; Appendix 2). The whole rocks are deemed altered by their $^{87}\text{Sr}/^{86}\text{Sr}$ values being similar to those of coeval, altered brachiopods. In Group II, one brachiopod fails the screening test as depicted by its radiogenic strontium isotope composition. In Group III, brachiopods and whole rock have similar geochemistry, with the former passing the screening tests and the latter being of finest-grained micrite. In Group IV, although brachiopods passed the screening test one $^{87}\text{Sr}/^{86}\text{Sr}$ result is anomalous and similar to the coeval whole rock results.

Fig. 8. Strontium isotope evaluation of brachiopods and conodonts from coeval horizons of the Carboniferous Bird Spring Formation, Nevada (Brand et al., 2012a; Woodard et al., 2013). Most brachiopods, based on intensive screening, are preserved with exception of some samples from horizons A55 and A408. Horizons marked in bold font have conodont archives that carry presumed primary $^{87}\text{Sr}/^{86}\text{Sr}$ values.

Fig. 9. Strontium isotope evaluation of brachiopods and whole rock from coeval horizons of the Carboniferous Bird Spring Formation, Nevada (Brand et al., 2012a; Appendix 2). Most brachiopods, based on intensive screening, are preserved with exception of some samples from horizons A55 and A408. Horizons marked in bold fonts have whole rock (with the finest-grained lithology=lithographic limestone) $^{87}\text{Sr}/^{86}\text{Sr}$ values similar to coeval primary brachiopods.

Fig. 10. Secular ^{87}Sr seawater average trend line (black dashed line) and natural fluctuation band (solid lines) of 1 Ma intervals of measurements for the Phanerozoic Eon based only on biogenic calcite and aragonite material. The band width was based on the total Sr isotope fluctuation recorded in modern biogenic carbonates (± 0.000054 ; Appendix 1). All $^{87}\text{Sr}/^{86}\text{Sr}$ results were normalized to 0.710247 with respect to NBS 987. The biogenic calcite and aragonite and evaporite data are presented in Appendix 3. Whole rock measurements of D'Arcy and others (2017) are included to serve as anchor points for facilitating the connection between the Phanerozoic and the Neoproterozoic results. Excluded values (failed stratigraphic and diagenetic tests) along with those of phosphate archives are plotted on another version of this figure available in Appendix 3.

Fig. 11. Close-up of $^{87}\text{Sr}/^{86}\text{Sr}$ variation in carbonate archives from the upper Ordovician to Lower Silurian. Symbols and seawater- ^{87}Sr band width as in Fig. 10.

Fig. 12. Strontium isotope variation across the Mississippian-Pennsylvanian boundary. Close-up of the boundary based on $^{87}\text{Sr}/^{86}\text{Sr}$ results of unaltered biogenic carbonate components from Mid-Carboniferous Bird Spring Formation (GSSP; Lane et al., 1999) at Arrow Canyon (AC; Brand et al., 2012a), Apex (Apex; Brand et al., 2007) in Nevada, Snake Canyon Formation at Arco in east-central Idaho (Arco; this study), lower Ely Limestone of the Granite Mountain section in west-central Utah (GM; this study), Kane Springs Wash (KSW; Brand et al., 2007) and Askyn River section (Askyn; Brand and Bruckschen, 2002) in Southern Urals, Russia.

Fig. 13. Close-up of $^{87}\text{Sr}/^{86}\text{Sr}$ variation across the Permo-Triassic boundary (e.g., Brand et al., 2012b). Evaporite results are displayed, but not included in the average trend line or the band width. Other symbols and seawater- ^{87}Sr band width as in Fig. 10.

Fig. 14. Close-up of $^{87}\text{Sr}/^{86}\text{Sr}$ variation during the Paleogene. The investigated brachiopods of the Eocene La Meseta Formation in Seymour Island (Antarctica; Appendix 3) are represented by the green diamonds. Evaporite results are displayed, but not included in the average trend line or the band width. Red line represents the PETM (Paleocene-Eocene Thermal Maximum; Zachos et al., 2003; Frieling et al., 2016) and blue field is the initiation of the Antarctic glaciation (AIS – Antarctic Ice Shield; Zachos and Kump, 2005). Other symbols and seawater- ^{87}Sr band width as in Fig. 10.

Fig. 15. Secular ^{87}Sr seawater average trend line (black dashed line) and natural fluctuation band (solid lines) of 1 Ma intervals of measurements for the pre-Ordovician and Neoproterozoic. The band was calculated based on the magnitude of Sr isotope fluctuation in modern biogenic carbonates (± 0.000061). All $^{87}\text{Sr}/^{86}\text{Sr}$ results were normalized to a value of 0.710247 for NBS 987. The light blue vertical band represents the Sturtian (717–662.4 Ma; Rooney et al., 2014), Marinoan (639–635 Ma; Prave et al., 2016) and Gaskiers (~579.63 Ma; Pu et al., 2016) glaciations. Circle symbols are results in correct stratigraphic position, but deviate appreciably from the current mainstream trend. Thus, they are only displayed but not utilized in the average trend line or band width. Excluded values (fail stratigraphic, diagenetic tests) are plotted on another version of this figure available in Appendix 4.

Fig. 16. Close-up of $^{87}\text{Sr}/^{86}\text{Sr}$ variation about the Marinoan Glaciation period (639–635 Ma; Prave et al., 2016). The Sr isotope results of the Ediacaran dolomicrite of the Doushantuo Formation (China; Table 1; Appendix 4) are represented by dark green diamonds. Other symbols and seawater- ^{87}Sr band width as in Figs. 10 and 15.

Fig. 17. Close-up of $^{87}\text{Sr}/^{86}\text{Sr}$ variation about the Sturtian Glaciation (717–662.4 Ma; Rooney et al., 2014). Circle symbol value is displayed but not utilized in the average trend line or the natural fluctuation band calibrations (Appendix 4). Symbols and seawater- ^{87}Sr band width as in Figs. 10 and 15.

MB-SR 2018
Fig. 1

MB-SR 2018
Fig. 2

MB-SR 2018
Fig. 3

MB-SR 2018
Fig. 4

MB-SR 2018
Fig. 5

MB-SR 2018
Fig. 6

MB-SR 2018
Fig. 8

MB-SR 2018
Fig. 9

MB-SR 2018
Fig. 10

MB-SR 2018
Fig. 11

MB-SR 2018
Fig. 12

MB-SR 2018
Fig. 13

MB-SR 2018
Fig. 14

MB-SR 2018
Fig. 15

MB-SR 2018
Fig. 16

MB-SR 2018
Fig. 17

Table 1. Statistical analysis (t-test¹ and Mann-Whitney U test²) of modern brachiopod shell segments (umbo area, shell), valves (ventral, dorsal), Order (Terebratulida, Rhynchonellida, Thecideida) and equivalent modern seawater.

	<i>N</i>	<i>Mean</i>	<i>2s.d.</i>	<i>2s.e.</i>	<i>Max</i>	<i>Min</i>	<i>p</i> ¹	<i>p</i> ²
Umbo area	13	0.709164	0.000017	0.000005	0.709188	0.709126		
Shell segment	82	0.709159	0.000019	0.000002	0.709233	0.709126	0.442	0.192
Ventral valves	51	0.709157	0.000017	0.000002	0.709211	0.709126		
Dorsal valves	31	0.709159	0.000023	0.000004	0.709233	0.709126	0.779	0.702
Terebratulida	71	0.709160	0.000019	0.000002	0.709233	0.709130		
Rhynchonellida	17	0.709164	0.000018	0.000004	0.709188	0.709126	0.368	0.183
Thecideida	7	0.709150	0.000019	0.000007	0.709178	0.709126	0.159	0.158
Brachiopods*	95	0.709160	0.000018	0.000002	0.709233	0.709126		
Seawater**	20	0.709167	0.000009	0.000002	0.709174	0.709138	0.118	0.101

Note: Brachiopods*: this study (Appendix 1); Brand et al. (2003); Vollstaedt et al. (2014). Seawater**: Muller et al. (1990); Peckmann et al. (2001); Mokadem et al. (2015).

Table 2. Statistical analysis (t-test¹, Mann-Whitney², Pearson³ and Spearman’s rs⁴) of modern brachiopods (polar, temperate-tropical) and select ambient environmental (oceanographic) parameters.

	<i>N</i>	<i>Mean</i>	<i>2s.d.</i>	<i>2s.e.</i>	<i>Max</i>	<i>Min</i>	<i>stats</i> ³	<i>p</i> ^{1, 3}	<i>stats</i> ⁴	<i>p</i> ^{2, 4}
Polar	25	0.709171	0.000022	0.000005	0.709233	0.709126				
TT	70	0.709156	0.000015	0.000002	0.709211	0.709126		<0.001		<0.001
Polar										
Salinity	25	32.5	2.0	0.4	35.2	29.0	0.341	0.095	0.220	0.292
Temperature	25	3.1	3.3	0.7	7.7	-1.8	0.073	0.730	0.075	0.724
TT										
Salinity	61	35.4	1.9	0.2	38.6	31.0	-0.146	0.262	-0.248	0.054
Temperature	70	13.6	8.1	1.0	29.5	1.0	-0.036	0.767	-0.040	0.744
Latitude	95	18.5	43.5	4.5	70.9	-69.9	-0.076	0.463	0.047	0.653
Depth (<250)	69	67.7	69.9	8.4	250	1	-0.126	0.302	-0.182	0.135
Depth (all)	93	332.2	640.5	66.4	4029	1	0.040	0.703	-0.079	0.451
Salinity	86	34.5	2.3	0.3	38.6	29.0	-0.201	0.064	-0.270	0.012
Temperature	95	10.8	8.5	0.9	29.5	-1.8	-0.206	0.045	-0.187	0.070

Note: TT – Temperate & Tropical, Polar zones; stats³ – Pearson, stats⁴ – Shearman’s rs correlation coefficients.

Table 3. Supplementary $^{87}\text{Sr}/^{86}\text{Sr}$ results of modern and ancient halite (Bahamas and Australia) and dolomicrite (China).

Sample #	$^{87}\text{Sr}/^{86}\text{Sr}$	Formation	Mineralogy	Location	Age
B-2016	0.709153	-	Halite	Bahamas	Modern
E3-4 (1497)	0.706696	Browne	Halite	Australia	Tonian
466-25 (1466)	0.706767	Browne	Halite	Australia	Tonian
NT#1	0.708421	Doushantuo	Dolomicrite	China	Ediacaran
NT#1-D	0.708570	Doushantuo	Dolomicrite	China	Ediacaran

Draft

Table 2:

	T2	± 2σ St. error	± 2σ STD	N
NIST NBS 987	0.710241	0.000002	0.000032	394
USGS EN-1	0.709159	0.000002	0.00003	348

Draft

Appendix 1: Geochemical data of modern and Holocene articulated brachiopods, their classification and oceanographic parameters of

Sample #	Order	Species	Latitude	Longitude	Depth m	Salinity psu	Temperature °C	⁸⁷ Sr/ ⁸⁶ Sr	Shell*	collection year
ARCTIC OCEAN										
White Sea, Russia										
MB-1130	Rhynchonellida	<i>Hemithiris psittacea</i>	66°34' N	33°08' W	-15	29.0	2.0	0.709126	D/u	
MB-1133		"			-15	29.0	2.0	0.709143	V/2	
Norwegian Sea										
Pos391-542-1	Terebratulida	<i>Macandrevia cranium</i>	70°56.022' N	22°12.326' E	-193	35.0	7.2	0.709178		
Pos391-535-1		"	70°55.138' N	22°11.259' E	-201	35.0	7.2	0.709168		
ARK XXIIASt 70/3/2		<i>Terebratulina retusa</i>	67°31.9' N	9°30.3' E	-318	35.2	7.3	0.709175		
Pos391-563-1		"	64°5.916' N	8°5.494' E	-287	35.2	7.7	0.709175		
Beaufort Sea										
MB-963	Terebratulida	<i>Glaciarcula spitsbergensis</i>	70°42' N	134°45' W	-55	32.5	-1.8	0.709147	V/u	
Foxe Basin										
MB-1191	Rhynchonellida	<i>Hemithiris psittacea</i>	69°23' N	80°49' W	-45	32.0	-1.2	0.709188	D/1	
Mair Island, Frobisher Bay										
MB-960-3	Rhynchonellida	<i>Hemithiris psittacea</i>	63°40.2' N	68°26.3' W	-50	32.5	-1.8	0.709174	V/e	
Ungava Bay										
MB-1215	Rhynchonellida	<i>Hemithiris psittacea</i>	60°21' N	64°58' W	-20	30.0	5.0	0.709141	D/3	
off Churchill, Hudson Bay										
MB-783	Rhynchonellida	<i>Hemithiris psittacea</i> **	58°46.197' N	94°08.707' W	-15	31	5.5	0.709183	V/u	1929
MB-792		"			-15	31	5.5	0.709181	V/2-3	1929
MB-802		"			-15	31	5.5	0.709172	D/e	1929
MB-955-4	Rhynchonellida	<i>Hemithiris psittacea</i> **	58°46.197' N	94°08.707' W	-15	31	5.5	0.709175	V/u	1996
MB957-3		"			-15	31	5.5	0.709170	V/2	1996
MB957-4		"			-15	31	5.5	0.709179	V/u	1996
MB906-1	Rhynchonellida	<i>Hemithiris psittacea</i> **	58°46.197' N	94°08.707' W	-15	31	5.5	0.709171	V/u	2010
MB906-3		"			-15	31	5.5	0.709179	V/e	2010
Churchill, Hudson Bay										
MB-950-13	Rhynchonellida	<i>Hemithiris psittacea</i>	58°46.197' N	94°08.707' W	-20	30	4.8	0.709164		7800 BP

MB-951-5		"			-20	30	4.8	0.709180	"
MB-952-4		"			-20	30	4.8	0.709178	"
ATLANTIC OCEAN									
North Atlantic									
M61-3 ST 607	Terebratulida	<i>Macandrevia cranium</i>	56°29.98' N	17°18.63' W	-683		8.9	0.709170	
M61-3 ST 617	Terebratulida	<i>Terebratulina retusa</i>	56°29.84' N	17°18.30' W	-668		8.9	0.709175	
M61-1 ST 276	Terebratulida	<i>Dallina septigera</i>	51°27.16' N	11°43.61' W	-905		9.6	0.709169	
off Iceland									
MB-1941	Terebratulida	<i>Macandrevia cranium</i>	63°55.38' N	25°57.18' W	-220	35.2	7.4	0.709152	V/e
MB-1978		"	63°42.53' N	26°23.04' W	-680	35.1	6.2	0.709211	V/2
Smaholmarna, Sweden									
RB4-2A	Terebratulida	<i>Terebratulina retusa</i>	58°16' N	11°30' E	-28	34.5	5.0	0.709156	V/e
NW coast of Ireland									
RB25-1A	Terebratulida	<i>Macandrevia tenera</i>	57°25' N	11°03' W	-1295	35.0	2.6	0.709143	D/e
RB25-1A		"			-1295	35.0	2.6	0.709145	D/e
Bonne Bay, N.L.									
MB-1010	Rhynchonellida	<i>Hemithiris psittacea</i>	49°30.479' N	57°52.14' W	-30	32	5.6	0.709162	D/u
Bay of Fundy, N.B.									
RB18-1A	Terebratulida	<i>Terebratulina septentrionalis</i>	45°00.271' N	66°54.778' W	-15	32.2	6.2	0.709155	D/e
RB18-1A		"			-15	32.2	6.2	0.709148	D/e
RB18-1A		"			-15	32.2	6.2	0.709142	D/e
North Rock, Bermuda									
RB6-3	Terebratulida	<i>Argyrotheca bermudana</i>	32°28.423' N	64°46.2' W	-10	37.4	24.7	0.709150	V
RB6-3		"			-10	37.4	24.7	0.709139	V
RB6-3		"			-10	37.4	24.7	0.709150	V
Canary Islands									
RB58-1A	Rhynchonellida	<i>Hispanirhynchia cornea</i>	28°43' N	13°23' W	-1343	35.1	5.8	0.709146	D/e
RB58-1A		"			-1343	35.1	5.8	0.709146	D/e
Palma, Canary Islands									
RB7-1	Thecideida	<i>Pajaudina atlantica</i>	28°39' N	17°58' W	-100	36.6	18.4	0.709137	V
RB7-1		"			-100	36.6	18.4	0.709140	V
MB-571		"			-100	36.6	18.4	0.709126	V

Off Guyana

MB-51	Terebratulida	<i>Tichosina rotundovata</i>	7°39' N	56°57' W	-96	36.4	24.7	0.709152	D/u
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Sao Sebastiao, Brazil

RB29-1B	Terebratulida	<i>Bouchardia rosea</i>	27°33' S	47°32' W	-90	36.4	24.7	0.709147	V/1
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RB29-1B		"			-90	36.4	24.7	0.709160	V/1
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Falkland Islands

MB879-10	Terebratulida	<i>Terebratella dorsata</i>	53°00' S	60°00' W	-250	34.0	3.64	0.709142	D/e
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MEDITERRANEAN SEA**Golfe du Lion, France**

RB2-1B	Terebratulida	<i>Gryphus vitreus</i>	43°10' N	5°30' E	-200	38.45	12.95	0.709147	D
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RB2-1B		"			-200	38.45	12.95	0.709139	D
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RB52-1	Terebratulida	<i>Argyrotheca cuneata</i>	43°09' N	5°36' E	-30	38.45	12.9	0.709188	D
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RB60-2	Terebratulida	<i>Megathyris detruncata</i>	43°09' N	5°40' E	-7	38.45	12.9	0.709139	D
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RB12-2B	Terebratulida	<i>Megerlia truncata</i>	43°10' N	5°28' E	-150	38.5	12.9	0.709133	V
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RB12-2B		"			-150	38.5	12.9	0.709139	V
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CNY	Terebratulida	<i>Gryphus vitreus</i>	42° N	6° E	-400		13.3	0.709173	
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Tyrrhenian Sea, Italy

MB-1879	Terebratulida	<i>Gryphus vitreus</i>	42°22' N	10° 18' E	-145	38.6	14.0	0.709142	V/1
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MB-1890		"			-145	38.6	14.0	0.709158	V/12
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Ionian Sea, Italy

MB-1407	Terebratulida	<i>Megathiris detruncata</i>	37°32.21' N	15°08.14' E	-45	38.9	19.5	0.709110**	V
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CARIBBEAN SEA**Venezuela Basin**

MB-91	Terebratulida	<i>Chlidonophora incerta</i>	15°08.93' N	69°13.33' W	-4029	34.9	3.9	0.709174	V
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MB-111	Terebratulida	<i>Chlidonophora incerta</i>	13°26.9' N	64°42.7' W	-3443	34.9	3.9	0.709177	V
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Paynes Bay, Barbados

RB46-1A	Terebratulida	<i>Argyrotheca lutea</i>	13°09.48' N	59°38.808' W	-137	36.7	23.8	0.709154	V
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North of Caracas

MB-167	Terebratulida	<i>Tichosina obesa</i>	10°50' N	66°55' W	-95	36.8	22.3	0.709151	D/2
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MB-147		"	10°44' N	66°07' W	-67	36.8	22.3	0.709174	V/e	
MB-155		"	10°50' N	66°58' W	-97	36.8	22.3	0.709175	V/e	
Surinam										
MB-171	Terebratulida	<i>Tichosina obesa</i>	7°46' N	54°17' W	-46	36.4	24.7	0.709141	V/2	
PACIFIC OCEAN										
Haida Gwaii										
RB54-4	Terebratulida	<i>Terebratalia transversa</i>	51°45' N	131°00' W	-800	34.2	6.5	0.709143	V/4	
RB54-4D		"			-800	34.2	6.5	0.709149	V/4	
Juan de Fuca Strait										
SJ/1	Terebratulida	<i>Terebratalia transversa</i>	48.5° N	123° W			10	0.709167		
Elbow Point Saanich Inlet										
MB-870-3	Terebratulida	<i>Terebratulina</i> sp.	48°32' N	123°32.37' W	-65	31	9.3	0.709164	V/u	
Alice Arm, Saanich Inlet										
MB-874-11	Terebratulida	<i>Laqueus californica</i>	48°31' N	123°32.366' W	-350	31.1	8.6	0.709145	D/e	
Pudget Sound										
Hit 1	Terebratulida	<i>Terebratalia transversa</i>	47° N	122° W			10.5	0.709167		
Monterey Canyon										
MB-1902	Terebratulida	<i>Laqueus californianus</i>	36°43' N	122°00' W	-1500	34.2	4.0	0.709150	V/7	
Yokohama										
Yoko	Terebratulida	<i>Pictothyris</i> sp.	35.5° N	139.5° E	-20		21.6	0.709171		
Sagami Bay, Japan										
MB-2064	Terebratulida	<i>Laqueus rubellus</i>	35°04.8' N	139°21' E	-84	34.8	21.9	0.709144	D/5	
Aliguay Island										
MB-886-1	Terebratulida	<i>Campages asthenia</i>	8°44' N	123°00' E	-100	34.5	22.0	0.709161	V/u	
Palau										
MB-2090	Thecideida	<i>Thecidellina congregata</i>	7°16.33' N	134°22.84' E	-2	34.4	29.5	0.709147	D	
MB-894-1		"			-2	34.4	29.5	0.709172	D	2007
MB-904		"			-2	34.4	29.5	0.709178	V	2007
South Tonga										
RB72-1CB	Terebratulida	<i>Dallinid</i> , new genus, species	25°59' S	179°18' W	-660	34.5	7.6	0.709154	V	

off New Zealand										
MB-1839	Terebratulida	<i>Liothyrella neozelanica</i>	34°42.42' S	178°34.2' E	-1150	34.47	3.75	0.709158	V/14	
Huinay, Chile										
MB-1980	Terebratulida	<i>Magellania venosa</i>	42°22.484' S	72°25.686' W	-20	34.34	12.64	0.709172	V/e	2012
MB-2004		"			-20	34.34	12.64	0.709153	V/24	
off New Zealand										
CrRck	Terebratulida	<i>Calloria inconspicua</i>	43° S	180° E/W	-1		14	0.709171		
southwest off New Zealand										
So 168 St. 84	Terebratulida	<i>Liothyrella sp.</i>	44°30'24"S	175° 56'27.63" E	-700		5.57	0.709177		
Doubtful Sound, New Zealand										
MB-1504	Terebratulida	<i>Liothyrella neozelanica</i>	45°49.14' S	170°37.565' E	-24	34.0	15.0	0.709155	V/1	
MB-1512	Rhynchonellida	<i>Notosaria nigricans</i>			-24	34.0	15.0	0.709156	V/1	
Macquarie Island										
RB70-1	Terebratulida	<i>Aerothyris macquariensis</i>	54°36' S	158°57' E	-70	33.85	0.86	0.709148	D	
INDIAN OCEAN										
Expedition MIRIKY										
MB-1033	Terebratulida	<i>Nipponithyris afra</i>	15°22' S	45°58' E	-875	34.7	7.5	0.709156	D/u	
Expedition MAINBAZA										
MB-1041	Terebratulida	<i>Chlidonophora chuni</i>	21°47' S	36°24' E	-1405	34.7	3.8	0.709143	V/1	
Europa Is., Indian Ocean										
RB31-1	Thecideida	<i>Thecidellina blochmanni</i>	22°18' S	40°22' E	-55	35.0	25.5	0.709152	V	
Expedition ATIMO VATAE										
MB-1068	Terebratulida	<i>Megerlia truncata</i>	26°07' S	45°39' E	-270	35.0	11.6	0.709151	V/e	
off Durban, South Africa										
RB62-5A	Terebratulida	<i>Kraussina rubra</i>	32°57' S	28°02' E	-30	35.55	18.23	0.709132	V	
Kidds Beach, South Africa										
MB890-4	Terebratulida	<i>Megerlina pisum</i>	33°08.8486' S	27°42.2139' E	-1	35.47	21.03	0.709188	D/u	
Bass Strait, Australia										
RB71-3ap	Terebratulida	<i>Anakinetica cumingi</i>	39°06' S	143°07.4' E	-81	34.9	12.8	0.709155	V	
west of Tasman Sea										

RB73-1B	Terebratulida	<i>Abyssothyris wyvillei</i>	39°24' S	143°00' E	-1028	34.71	2.07	0.709167	D
SOUTHERN OCEAN									
Signy Island									
MB-557	Terebratulida	<i>Liothyrella uva</i>	60°43' S	45°38' W	-15	34.33	0.62	0.709162	D/u
MB-558		"			-15	34.33	0.62	0.709130	V/e
CEAMARC									
MB-1564	Terebratulida	<i>Magellania joubini</i>	66°20' S	141°20' W	-217	34.05	1.59	0.709198	D
Rothera Island									
MB-1801	Terebratulida	<i>Liothyrella uva</i>	67°34.11' S	68°07.88' W	-15	34.17	0.79	0.709183	V/1
MB-1817		"			-15	34.17	0.79	0.709233	D/4
Weddell Sea									
MB-876	Terebratulida	<i>Magellania fragilis</i>	69°57' S	11°49' W	-215	34.02	-1.69	0.709187	D
MB-877		"			-215	34.02	-1.69	0.709153	V

Note*: D, Dorsal valve; V, Ventral valve; U, Umbo; e. shell edge (anterior margin); number (mid section); ** result omitted from statistical evaluation

f ambient water mass

Salinity, Temperature, Source Reference

This study; Lukashin et al., 2003

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Stichel et al., 2012; Brand et al., 2013

Stichel et al., 2012

Draft