

Carbon, oxygen and strontium isotopes in Paleozoic carbonate components: an evaluation of original seawater-chemistry proxies

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Abstract

Brachiopods, trilobites, cements and whole rock (= matrix) material were evaluated for their reliability as proxies of original seawater carbon, oxygen and strontium isotope chemistry. In this process, coeval material was evaluated from individual horizons of formations spanning the Permian to Cambrian.

Unaltered shells of low-Mg calcite articulated brachiopods, retain original seawater oxygen, carbon and strontium isotope compositions, as old as late Ordovician. Assessments of older specimens are hampered by a lack of suitable material (coeval brachiopod–whole rock sets). A definitive assessment of cement marine chemistry is difficult due to the paucity of material, but despite this caveat, cements hold some promise for retaining original carbon and possibly strontium isotope seawater values. In contrast, the potential of whole rock material as a proxy of original seawater chemistry is quite complex. In some, but not all instances, the carbon isotopic composition of whole rock, after detailed scrutiny and evaluation, appears to represent an original seawater chemistry signal. In a few instances, their oxygen isotope compositions reflect original seawater values. Unlike the stable isotope compositions, the strontium isotopes of all studied whole rock material (Permian to upper Cambrian) appear not to reflect original seawater chemistry values. Thus the potential for retaining original seawater isotope chemistry and serving as specific proxies, in order of decreasing reliability, are (1) unaltered low-Mg calcite brachiopods (C, O and Sr isotopes), (2) pristine marine cements (C and Sr isotopes), and (3) whole rock material (C isotopes?).

Carbon, oxygen and strontium isotope compositions of Ordovician trilobites mirror those of coeval unaltered brachiopods. Cambrian trilobites hold significant promise as an important proxy of original seawater isotope chemistry but further studies are needed to ascertain their full potential. The survey of isotopes in some Ordovician and Cambrian intermediate/low-Mg calcite trilobites demonstrates their potential as an important proxy of original seawater chemistry.

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1. Introduction

The quest for proxies of original seawater chemistry continues to be problematic despite some major

advances in defining the diagenetic history of carbonate and phosphate allochems and their host rocks. Brand and Veizer (1980) clearly demonstrated that geochemical differences exist between diagenetically affected fossils and whole rock (= matrix) carbonates. Their results are supported by the observations of, among them, Al-Aasm and Veizer (1982), Popp et al.

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(1986a,b), Marshall (1992), Cummins and Elderfield (1994), Grossman (1994), Diener et al. (1996), Veizer et al. (1999), Wenzel (2000), Wenzel et al. (2000), Brand and Brenckle (2001), Brand and Bruckschen (2002), and Brand and Gao (2003).

Preservation potential of original seawater carbon, oxygen and strontium isotope values should be high for pristine aragonite or low-Mg calcite fossils, grains and marine cements. Irrespectively, preservation potential is probably moderate with retention of only original carbon values in calcites (fossils, micrites and cements) altered in closed diagenetic systems with low water/rock ratio. Finally, preservation potential should be low with a significant shift in the carbon, oxygen and strontium isotope values in calcites altered in open diagenetic systems with high water/rock ratio (cf. Brand, 1991; Brand and Veizer, 1981; Marshall, 1992).

Another alternative, in the absence of pristine/unaltered material, is to use the geochemistry of least altered material or performing diagenetic backstripping of allochem chemistry (elemental and isotopic covariation) for determining ‘original’ seawater signals. Correction of data by extrapolation or covariation of isotopes should be avoided as much as possible due to the high possibility of extraneous results (Marshall, 1992).

Articulated brachiopods are considered an important proxy in identifying original seawater chemistry because of the high resistance of their low-Mg calcite shell to diagenesis (e.g., Brand and Veizer, 1980; Al-Aasm and Veizer, 1982; Popp et al., 1986a,b; Brand, 1991; Bates and Brand, 1991; Grossman, 1994; Veizer et al., 1999; Wenzel, 2000; Brand and Brenckle, 2001; Samtleben et al., 2001). The challenge is to identify material(s) that has indeed preserved original seawater signatures of some or all geochemical parameters (trace elements, stable and radiogenic isotopes). According to Cummins and Elderfield (1994, p. 255), “only pristine nonluminescent articulate brachiopod shell material can be used to gain reliable estimates of Carboniferous and by, deduction, Paleozoic ocean chemistries” (cf. Bates and Brand, 1991; Brand, 1991; Marshall, 1992; Samtleben et al., 2001). Unless the effects of diagenesis are fully understood and accounted for in the evaluation process of the studied material, geochemical results may not necessarily reflect original seawater compositions (Rush

and Chafetz, 1990; Grossman, 1994; Barbin and Gaspard, 1995; Land, 1995; Veizer, 1995; Veizer et al., 1997).

Conodonts found favour in the 1980s as original seawater chemistry proxies (e.g., Luz et al., 1984). Compelling evidence to the contrary during the past decade have decreased the utility of conodonts as a universal seawater proxy. Diagenetic alteration even at low intensities, measured by the conodont alteration index (CAI), shifts the original isotopic signals contained in these materials (e.g., Kürschner et al., 1993; Diener et al., 1996; Veizer et al., 1997). Specimens subjected to minimal burial temperatures may preserve original paleoseawater chemistry. Despite this claim, it appears that conodonts incorporate radiogenic strontium during their post-depositional history (Kürschner et al., 1993; Diener et al., 1996), and their Sr isotopic signal may at best reflect 3rd order oscillations in seawater chemistry variations. Recently, Wenzel et al. (2000) suggested that Silurian conodonts from Gotland record paleotemperature and seawater- ^{18}O more faithfully than coeval calcitic brachiopods. Despite this anomaly, the overwhelming evidence suggests that conodonts do not preserve original isotope values (especially $^{87}\text{Sr}/^{86}\text{Sr}$) when compared to coeval low-Mg calcite brachiopods.

Denison et al. (1994, p. 143) proposed a set of geochemical criteria, supplemented by judicious field selection and careful petrographic examination, to identify shelf limestone (=matrix-whole rock) with apparently preserved original seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. They proposed that Mn and Fe concentrations of less than 300 and 3000 ppm, respectively, in conjunction with an Sr/Mn ratio of greater than 2.0 identify limestone whole rock (=matrix) samples with original seawater strontium isotope values. These and other supplementary criteria (e.g., luminescence patterns) have been used to identify Phanerozoic (e.g., Brasier et al., 1992; Corfield et al., 1992; Long, 1993; Montanez et al., 1996; Saltzman et al., 2000) and Precambrian ‘primary’ matrix material (e.g., Veizer and Compston, 1976; Kaufman et al., 1993; Pelechaty et al., 1996). Contrary to this plethora of studies and their continued utilization, Grossman (1994, p. 207) stated that “...whole rock samples are the least reliable for isotopic study, providing only an approximation of marine $\delta^{13}\text{C}$ values and diagenetically

altered $\delta^{18}\text{O}$ values”, and possibly $^{87}\text{Sr}/^{86}\text{Sr}$ (cf. Brand and Brenckle, 2001).

Inarticulated phosphatic brachiopods, despite their long range, have not found favour as proxies of original seawater chemistry. Wenzel et al. (2000) demonstrated that the relative shift in isotopic compositions in inarticulated brachiopods was attributable to post-depositional alteration of the biogenic phosphate. In contrast, belemnites with relatively stable mineralogy are likely to have suffered less alteration than components with less stable mineralogies (magnesian calcites, aragonite). At one time belemnites were the material of choice for Mesozoic sequences/units, until an apparent fall from grace, followed by a recent resurgence and use as a seawater proxy. In contrast, the potential of trilobite cuticular calcite to preserve original seawater chemistry has not been rigorously tested by geochemists except for a few studies by McAllister and Brand (1989), Wilmot and Fallick (1989), Brasier et al. (1992), and Dalingwater et al. (1999). Trilobites occupy an important segment of the geologic record and, if acceptable as a proxy of original seawater chemistry, may resolve some important evolutionary issues for early Phanerozoic seawater and life.

This paper presents and evaluates material such as articulated low-Mg calcite brachiopods, low/intermediate-Mg calcite trilobites, cement, and whole rock (matrix) material from a number of formations covering a large portion of the Paleozoic. Stratigraphically coeval material (brachiopods, trilobites, cement, whole rock) will be rigorously tested for preservation of carbon, oxygen and strontium isotope values and range agreements. Finally, the various materials will be rated according to their potential in retaining original seawater chemistry compositions and thus serving as oceanographic proxies.

2. Sample selection and general geology

Brachiopods, trilobites, whole rock and cement samples were selected to cover the Paleozoic. Samples are from the Madera Formation of New Mexico (upper Pennsylvanian), Bird Spring Formation of Nevada (lower Pennsylvanian and upper Mississippian), Louisiana Limestone of Missouri (upper Devonian), Ludlowville Formation of New York State (mid-

Devonian), Rochester and Irondequoit Formations of southern Ontario and New York State (lower Silurian), Georgian Bay, Cobourg and Verulam Formations of eastern Ontario (mid-upper Ordovician), Sullivan Formation of Alberta (upper Cambrian) and Petit Jardin Formation of Newfoundland (upper Cambrian; Appendix A).

The various formations and diagenetic evaluations of the allochems and coeval whole rock are discussed in some detail in the following studies. The Madera is described in detail by Brand and Gao (2003) and the Bird Spring by Brand and Brenckle (2001, and references therein). Descriptions for the Ludlowville, Rochester, Irondequoit, Georgian Bay, Cobourg and Verulam are in Bates (1990) and McAllister (1989; and references therein). The Cambrian units are described by Chow and James (1987), Westrop (1989), and Brophy (1990), and the Louisiana is described by Koenig et al. (1961) and Brand et al. (in press). The reader is referred to these articles for further information on the lithology, general geology, and biostratigraphy of the studied units and their allochems.

3. Methodology

A total of 206 samples (122 brachiopods, 12 trilobites, 59 matrix (whole rock), and 13 cements) were analyzed for Ca, Mg, Fe, Mn and Sr, and for $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$. Preparation of samples (selection, cleaning, etc.) is of utmost importance in acquiring unaltered geochemical signatures (cf. Brand and Veizer, 1980; Brand, 1991; Denison et al., 1994; Reinhardt et al., 2000; Wenzel, 2000). All adhering material, including matrix and visibly altered exoskeletal layers, must be separated from shell/carapace fragments (e.g., primary layer from brachiopod fragments with dental tools). Subsequently, brachiopod and trilobite fragments were immersed and leached in 10% HCl (suprapure) for as long as needed, and rinsed in copious amounts of deionized water and left to air-dry. Conversely, matrix and cement samples were cleaned of fossil fragments and weathered rinds to obtain an as least cross-contaminated sample as possible. These too were etched in acid solution and rinsed with water to assure cleanliness of the samples. Macro- and microtextural preservation of brachiopods and trilobites was examined under binocular micro-

scope, by cathode luminescence and scanning electron microscope (SEM; Bates and Brand, 1991; McAllister and Brand, 1989; Brand and Brenckle, 2001; Brand and Gao, 2003). Cleaned fragments were sputter coated with gold/palladium, and microstructures were evaluated with an ISI scanning electron microscope. Luminescence of carbonates and allochems was investigated with a Nuclide ELM-2B Luminoscope. Microtextural preservation, luminescence patterns and trace element contents are the primary selection tools of unaltered brachiopods and trilobites (e.g., Brand and Veizer, 1980; Popp et al., 1986a,b; McAllister and Brand, 1989; Samtleben et al., 2001). Up to 60 mg of sample powder of each sample, weighed to four decimal places, was digested in 10 ml of 5% (v/v) of suprapure HNO_3 for about 1 h. After volumetric filtration of liquid, the weight of the non-carbonate portion was determined thermogravimetrically by incinerating the ashless filter paper (Whatman #40) at 400 °C for 1 h. Samples were tested for insoluble residue (I.R.), and Ca, Mg, Sr, Mn, and Fe analyses were carried out on a Varian 400P atomic

absorption spectrophotometer. Precision and accuracy of elemental analyses are better than $\pm 3\%$ (SRMs 636, 633; cf. Brand and Veizer, 1980; Bates, 1990; McAllister, 1989; Brophy, 1990).

For carbon and oxygen isotope analyses, aliquots of about 5 mg of each sample were reacted with 100% phosphoric acid at 25 °C for the appropriate time. The carbon and oxygen isotope analyses were performed on a VG SIRA-12 triple collector mass spectrometer (University of Ottawa) with soft seat micro-inlet, results calibrated to PDB, and reported in the standard δ notation (Appendix A). Precision and accuracy of the isotopic analyses are better than 0.05‰ and 0.02‰ for carbon, and 0.10‰ and 0.05‰ for oxygen, respectively (NBS 19-IAEA; Brand and Veizer, 1981).

For strontium isotope analyses, about 1 mg of each sample was digested in 2.5 N suprapure HCl for about 24 h at room temperature. This was followed by separation with 4.5 ml of AGW 50 \times 8 (Biorad) cation exchange resin in quartz glass columns to obtain purified Sr. Samples were analyzed at Ruhr University

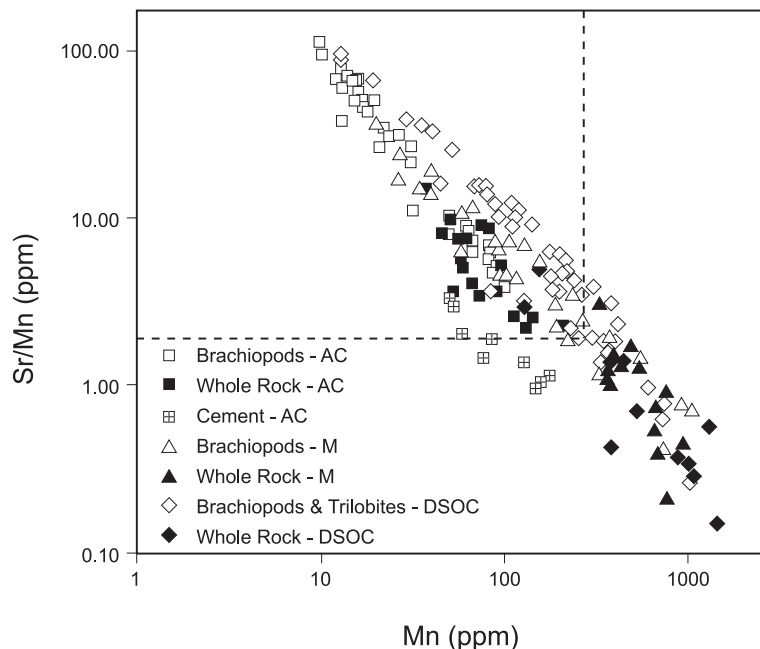


Fig. 1. Sr/Mn ratios and Mn contents of coeval brachiopods, trilobites and corresponding matrix (whole rock) and cement from Carboniferous, Devonian, Silurian, Ordovician and Cambrian formations of North America. The limits for limestones (whole rock) retaining original seawater Sr isotopes are ≥ 2.0 Sr/Mn and ≤ 300 mg/kg for Mn from Denison et al. (1994). Symbols: AC—Arrow Canyon/Bird Spring Formation, M—Madera Formation, DSOC—brachiopods/trilobites—whole rock from Devonian, Silurian, Ordovician and Cambrian formations.

(Bochum) on a Finnigan MAT 262 5-collector solid-source mass spectrometer with single Ta filament (Brand, 1991). Loading blank was below 5 pg, column blank was less than 1 ng, and reagent blank was below 0.01 ppb. The mean of 71 analyses of NBS 987 was 0.710238 ± 0.000008 (2σ), and the mean of 20 analyses of ocean water off Norway and France was 0.709149 ± 0.000020 (2σ). Precision of duplicate analyses was better than 0.000008 (Brand, 1991). Strontium isotope values of this study were all corrected to a nominal NBS 987 value of 0.710240 (Appendix A).

4. C, O, Sr seawater proxy evaluation

Isotope geochemists are divided into two camps, those that use exclusively whole rock material and those that use mostly brachiopod material for proxies of original seawater chemistry in their chemostrati-

graphic/paleoceanographic studies. Those who use whole rock material evaluate it by a number of means such as textural integrity, trace chemistry and/or luminescence characteristics, to identify an ‘original’ signal. Most fine-grained whole rock is deemed to preserve the original seawater isotope value, and in conjunction with fossils their $^{87}\text{Sr}/^{86}\text{Sr}$ has been used to construct seawater curves for the Phanerozoic (e.g., Peterman et al., 1970; Burke et al., 1982; Denison et al., 1997, 1998). To improve on the evaluation and selection of suitable material, Denison et al. (1994) promulgated criteria to specifically identify whole rock material with original seawater- ^{87}Sr .

Data of this study show that many brachiopods and trilobites, whole rock samples and cements from the various units satisfy the abovementioned criteria (Fig. 1). In that case, compliant coeval brachiopod, whole rock and cement material from a bed should retain original seawater chemistries (strontium and by inference carbon and oxygen isotope values). In the case of

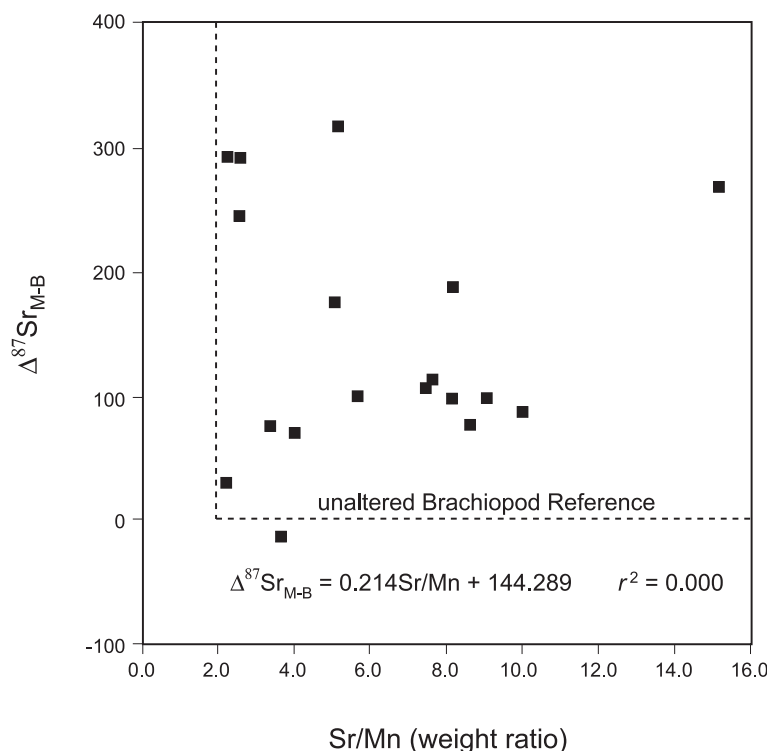


Fig. 2. $\Delta^{87}\text{Sr}_{\text{M-B}}$ and Sr/Mn of matrix (whole rock) samples from the Bird Spring Formation, Arrow Canyon, Nevada. The Sr/Mn limit (≥ 2.0) is from Denison et al. (1994), and the $\Delta^{87}\text{Sr}_{\text{M-B}}$ limit of 0 (zero) is based on enrichment/depletion of coeval whole rock values relative to unaltered brachiopods.

the Bird Spring Formation, all brachiopods (42) satisfy the chemical criteria for preservation as set out by Denison et al. (1994). In contrast, 21 of 23 whole rock samples satisfy the ‘criteria’, and for the cement it is 3 of 9 samples (Fig. 2; Appendix A). For the Pennsylvanian–Devonian material, compliance with the criteria drops to 32 out of 40 brachiopod, to 2 out of 17 whole rock, and to 0 out of 2 for cement samples. Compliance is slightly better for the Silurian–Ordovician–Cambrian with 31 out of 34 for brachiopods, 6 out of 11 for trilobites, and 0 out of 7 for whole rock samples (Fig. 1). A detailed evaluation of the various components/allochems follows in reverse stratigraphic order.

4.1. Carboniferous material

Samples from the Bird Spring (BS) and Madera Formations (M) were subjected to detailed comparative analysis to determine original isotopic signals within the various samples (cf. Brand and Brenckle,

2001; Brand and Gao, 2003). Further tests involve an examination of the potential impact of insoluble residue (IR: noncarbonate fraction of clay, quartz, etc.) on Sr isotopic composition of whole rock and brachiopods. Whole rock samples (BS and M, were divided into four groups; Fig. 3), and insoluble residue (mostly quartz) of unaltered brachiopods (BS) was also evaluated for potential impact on their Sr isotopic composition (inset, Fig. 3). The data suggest that for Group 1 whole rock samples with $\leq 10\%$ IR the impact on $^{87}\text{Sr}/^{86}\text{Sr}$ is minimal ($r^2=0.017$), similarly for Group 2 samples with $\leq 20\%$ IR ($r^2=0.036$). Some minor concern is raised by Group 3 samples with $\leq 30\%$ IR, ($r^2=0.133$), and a definite concern for Group 4 samples with $\geq 30\%$ IR, ($r^2=0.495$). This confirms the observation of Denison et al. (1994) that insoluble residue (probably clay) does not impact on the strontium isotope composition for whole rock samples with $< 20\%$, but is a concern for samples with $\text{IR} > 30\%$. The correlation between unaltered brachiopods and their insoluble

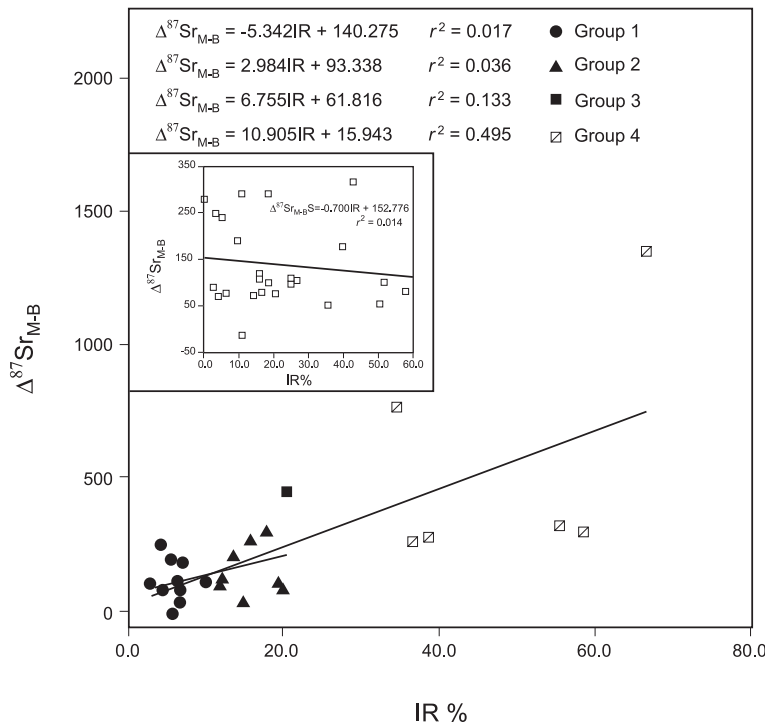


Fig. 3. $\Delta^{87}\text{Sr}_{\text{M-B}}$ and IR (insoluble residue) of matrix (whole rock) samples from the Bird Spring and Madera Formations. Group 1: IR $\leq 10\%$, Group 2: IR $\leq 20\%$, Group 3: IR $\leq 30\%$, and Group 4: IR = 0–60%. Inset is $\Delta^{87}\text{Sr}_{\text{M-B}}$ and IR of unaltered brachiopods from the Bird Spring Formation.

Table 1

One-way ANOVA of isotopic compositions between unaltered brachiopod and matrix (whole rock) samples from the Bird Spring Formation

Parameter	Brachiopods			Matrix			<i>p</i>
	<i>N</i>	Mean	S.D.	<i>N</i>	Mean	S.D.	
$\delta^{18}\text{O}$ (‰)	19	−2.36	0.87	19	−3.80	0.47	0.0000
$\delta^{13}\text{C}$ (‰)	19	+2.07	0.90	19	+0.26	1.49	0.0001
$^{87}\text{Sr}/^{86}\text{Sr}$	17	0.708194	0.000040	18	0.708344	0.000096	0.0000

Significance is at the 95% confidence level ($p < 0.050$) or better.*N* = number of horizon data, S.D.—standard deviation.

residue (up to 60%) is extremely low and considered insignificant ($r^2 = 0.015$; Fig. 3). This suggests that the insoluble residue material (i.e., quartz, chert) is not a contributing factor on Sr isotopes for the studied brachiopods.

Since most of the whole rock material from the Bird Spring passes the geochemical and petrographic test parameters of Denison et al. (1994), these samples would be considered to carry ‘original’ seawater- ^{87}Sr . An evaluation of the $^{87}\text{Sr}/^{86}\text{Sr}$ of the whole rock samples shows that most have more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ than their coeval unaltered brachiopods. This difference is statistically significant at the better than 99.9% confidence level for the coeval brachiopod–matrix pairs ($\Delta^{87}\text{Sr}_{\text{B-M}} = -0.000150$),

and supports the suggestion that for the most part these whole rock samples do not contain an original seawater Sr isotope-chemistry (Table 1). Differences are not as pronounced but still statistically significant for the carbon ($\Delta^{13}\text{C}_{\text{B-M}} = +1.44$ ‰) and oxygen ($\Delta^{18}\text{O}_{\text{B-M}} = +1.81$ ‰) isotopes between the coeval brachiopods and whole rock samples (Fig. 4, Table 1). These ranges well exceed those generally observed in modern brachiopods at any particular locality (Brand et al., 2003). This demonstrates, at least in this instance, that whole rock material from the Bird Spring Formation despite the fact that it satisfies the Denison et al. (1994) criteria does not contain original seawater isotopic values and are not suitable original seawater chemistry proxies.

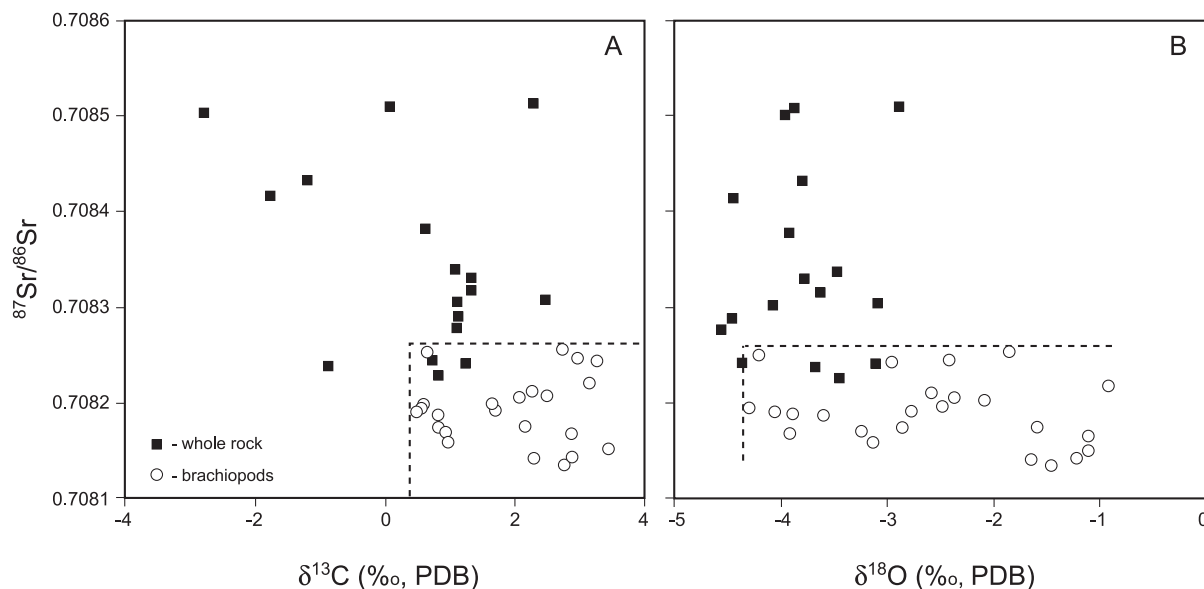


Fig. 4. Variation in $^{87}\text{Sr}/^{86}\text{Sr}$ with $\delta^{13}\text{C}$ (A) and $\delta^{18}\text{O}$ (B) of coeval matrix (whole rock) and unaltered brachiopods from the Bird Spring Formation. The $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ limits (dashed field) are of unaltered brachiopods (Brand and Brenckle, 2001).

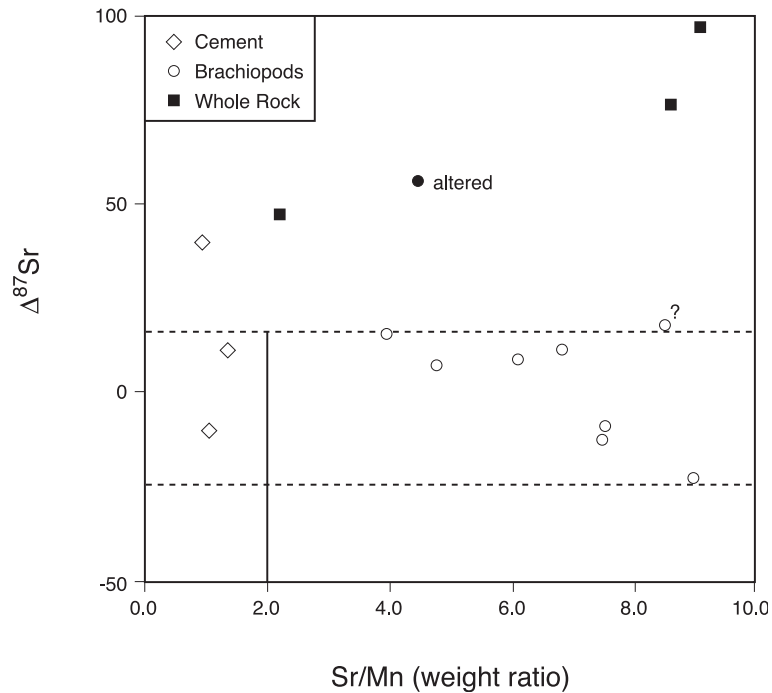


Fig. 5. Variation in $\Delta^{87}\text{Sr}$ with Sr/Mn of brachiopods, matrix (whole rock), and cement from horizon A44 (sample sets AC1 and A44; Appendix A) of the Bird Spring Formation. The Sr/Mn limit of ≥ 2.0 is from Denison et al. (1994). The $\Delta^{87}\text{Sr}$ is based on the mean $^{87}\text{Sr}/^{86}\text{Sr}$ of unaltered brachiopods from this horizon (Table 2; Brand and Brenckle, 2001), and the $\Delta^{87}\text{Sr}$ upper and lower ranges for the unaltered brachiopods from this horizon is based on variation exhibited by modern counterparts (Brand et al., 2003).

Evaluation of coeval brachiopod, whole rock and cement material from just one horizon of the Bird Spring Formation shows complicated trends and results. In this instance, nine brachiopods were compared with four whole rock and four cement samples. The cements were obtained from within the brachiopod valves. Unaltered brachiopods are different from their altered counterparts as well as from the whole rock and cement samples (Fig. 5). Statistical analysis shows that brachiopod- ^{87}Sr is not

different from cement- ^{87}Sr , but different from whole rock- ^{87}Sr at the 95% confidence level (Table 2). For the carbon isotope distribution, the three coeval materials are not different at the 95% confidence level (Table 2). A different scenario is observed for the oxygen isotope data, where unaltered brachiopods are significantly different from their coeval cements but not their whole rock samples (albeit it is not a very big difference) at the 95% confidence level (Table 2). Other horizons may present totally

Table 2

One-way ANOVA of isotopic compositions between unaltered brachiopod, matrix (whole rock) and cement samples from horizon A44 of the Bird Spring Formation

Parameter	Brachiopods			Matrix			<i>p</i>	Cement			<i>p</i>
	<i>N</i>	Mean	S.D.	<i>N</i>	Mean	S.D.		<i>N</i>	Mean	S.D.	
$\delta^{18}\text{O}$ (‰)	7	-3.48	0.56	3	-4.13	0.60	0.135	4	-4.87	0.28	0.000
$\delta^{13}\text{C}$ (‰)	7	+0.89	0.38	3	+0.94	0.14	0.816	4	+0.78	0.12	0.615
$^{87}\text{Sr}/^{86}\text{Sr}$	7	0.708180	0.000014	3	0.708253	0.000025	0.000	3	0.708194	0.000025	0.301

Significance is at the 95% confidence level ($p < 0.050$) or better.

N = number of samples, S.D. = standard deviation.

different scenarios than the one discussed above, and thus all material from all horizons should be evaluated for each and every horizon. This clearly supports the purported approach of chemically evaluating all available material from individual horizons, and by doing so, one should be able to determine what material is pristine and thus carries an original seawater chemistry signal (cf. Marshall, 1992; Wenzel, 2000; Brand and Brenckle, 2001; Brand and Gao, 2003).

4.2. Carboniferous–Devonian–Silurian–Ordovician material

The above discussion suggests that the studied unaltered low-Mg calcite brachiopods are better proxies of original seawater chemistry than either their coeval marine cement or matrix-whole rock materials (cf. Brand, 1991; Marshall, 1992; Grossman, 1994; Azmy et al., 1998; Table 1). It also supports the assertion that brachiopods, cements and whole rock, for at least some horizons of the Mid-Carboniferous Bird Spring Formation, are equally good proxies of original seawater carbon-isotope chemistry (Table 2).

Evaluation of Paleozoic material shows that brachiopods are different in their strontium isotope compositions relative to coeval whole rock samples (Fig. 6). A total of 59 coeval brachiopod–whole rock pairs

representing 40 horizons from nine formations were evaluated for their $\Delta^{87}\text{Sr}_{\text{B-M}}$. Modern brachiopod counterparts from the global oceans exhibit an $^{87}\text{Sr}/^{86}\text{Sr}$ range of ± 0.000023 (Brand et al., 2003), and only two brachiopod data exhibit this range overlap with coeval matrix (whole rock) material (Fig. 6). Otherwise, $\Delta^{87}\text{Sr}_{\text{B-M}}$ between coeval brachiopod–whole rock samples range from a high of -25 to a low of -4803 (Fig. 6). Thus whole rock (matrix) in 57 out of 59 cases is more radiogenic than their coeval brachiopods. These strontium isotope ratio differences of coeval brachiopod–whole rock samples from horizons of Carboniferous, Devonian, Silurian and Ordovician formations are significant with p equal to 0.001, 0.033, 0.024 and 0.004, respectively (Table 3; excludes -4803 and -4797 values, Fig. 6).

The table also includes comparisons between coeval brachiopods and whole rock from other studies. Brachiopods from the mid-Devonian of Europe have $\Delta^{87}\text{Sr}_{\text{B-M}}$ less radiogenic by about -327 than their coeval whole rock material (Table 3; Diener et al., 1996). The overall evidence and presented data suggest that unaltered low-Mg calcite articulated brachiopods as old as Ordovician are superior proxies to whole rock for retaining original seawater-Sr isotope chemistry (cf. Brand, 1991; Lavoie, 1993).

A large degree of scatter characterizes the distribution of oxygen isotopes of unaltered brachiopods and

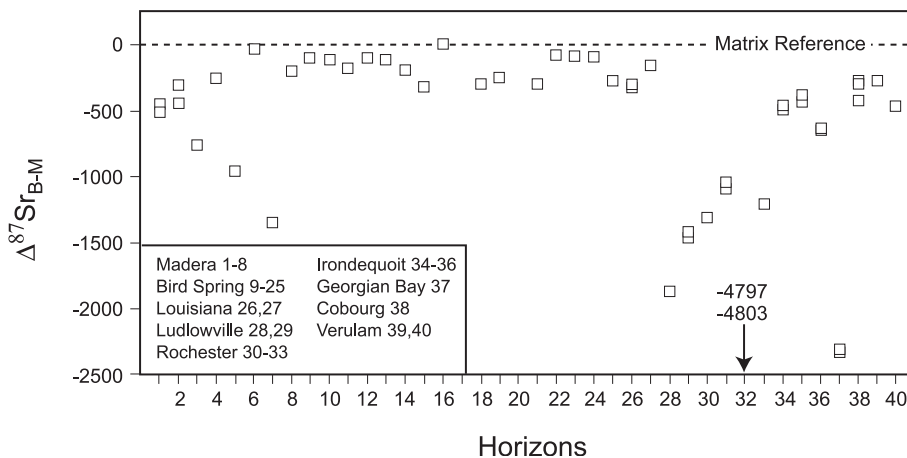


Fig. 6. Variation in $\Delta^{87}\text{Sr}_{\text{B-M}}$ of coeval brachiopods and enclosing matrix (whole rock; set to 0 for $\Delta^{87}\text{Sr}_{\text{B-M}}$) representing the Pennsylvanian Madera, Pennsylvanian–Mississippian Bird Spring, Devonian Louisiana and Ludlowville, Silurian Rochester and Irondequoit, and Ordovician Georgian Bay, Cobourg and Verulam Formations. Relative position of data sets reflects order of evaluation of specific horizons within formations.

Table 3

One-way ANOVA of isotopic compositions between Carboniferous, Devonian (¹material from Diener et al., 1996), Silurian (²includes samples from Sweden; Wenzel, 2000) and Ordovician unaltered brachiopod and matrix (whole rock) samples (Appendix A)

Parameter	Brachiopods			Matrix			<i>p</i>
	<i>N</i>	Mean	S.D.	<i>N</i>	Mean	S.D.	
$\delta^{18}\text{O}$ (‰) _C	27	-2.93	1.15	27	-4.40	1.19	0.000
$\delta^{13}\text{C}$ (‰) _C	27	2.11	0.96	27	-0.39	2.02	0.000
$^{87}\text{Sr}/^{86}\text{Sr}$ _C	25	0.708244	0.000103	25	0.708522	0.000368	0.001
$\delta^{18}\text{O}$ (‰) _D	4	-2.34	1.40	4	-5.86	2.56	0.052
$\delta^{13}\text{C}$ (‰) _D	4	4.66	1.99	4	1.73	2.57	0.122
$^{87}\text{Sr}/^{86}\text{Sr}$ _D	4	0.707770	0.000198	4	0.708913	0.000654	0.033
$^{87}\text{Sr}/^{86}\text{Sr}$ _D ¹	6	0.707834	0.000016	6	0.708161	0.000315	0.029
$\delta^{18}\text{O}$ (‰) _S	7	-3.33	0.59	7	-5.87	1.03	0.000
$\delta^{13}\text{C}$ (‰) _S	7	+4.98	0.20	7	+4.40	0.54	0.021
$^{87}\text{Sr}/^{86}\text{Sr}$ _S	7	0.708340	0.00001	6	0.709920	0.00161	0.024
$\delta^{18}\text{O}$ (‰) _S ²	21	-3.47	1.07	21	-5.63	1.29	0.000
$\delta^{13}\text{C}$ (‰) _S ²	21	+4.89	2.59	21	+5.03	2.78	0.863
$\delta^{18}\text{O}$ (‰) _O	13	-5.69	0.78	5	-6.08	1.43	0.460
$\delta^{13}\text{C}$ (‰) _O	13	+0.53	0.57	5	+0.10	0.85	0.224
$^{87}\text{Sr}/^{86}\text{Sr}$ _O	13	0.707997	0.000089	5	0.708739	0.000812	0.004

The values are from coeval stratigraphic horizons/formations. Significance is at the 95% confidence level ($p < 0.050$) or better.

N = number of sample horizon data, S.D.—standard deviation; subscripts: C—Carboniferous, D—Devonian, S—Silurian, O—Ordovician.

whole rock samples (Fig. 7). A total of 98 coeval brachiopod–whole rock pairs representing 40 horizons from nine formations were evaluated for their $\Delta^{18}\text{O}_{\text{B-M}}$. Based on ranges in isotope values from modern brachiopods from individual locations, about 24 $\Delta^{18}\text{O}_{\text{B-M}}$ pairs exhibit values within ± 1.0 ‰ of the whole rock reference, whereas the majority of brachiopods exhibit $\delta^{18}\text{O}$ values that are heavier by

up to 5‰ (Fig. 7). Statistically, the Carboniferous, Devonian and Silurian (including the coeval material studied by Wenzel, 2000 from Gotland, Sweden) whole rock material $\Delta^{18}\text{O}_{\text{B-M}}$ values are significantly different from those retained by the coeval unaltered brachiopod samples (Table 3). In contrast, there appears to be no significant difference between the Ordovician data sets of brachiopod and whole rock

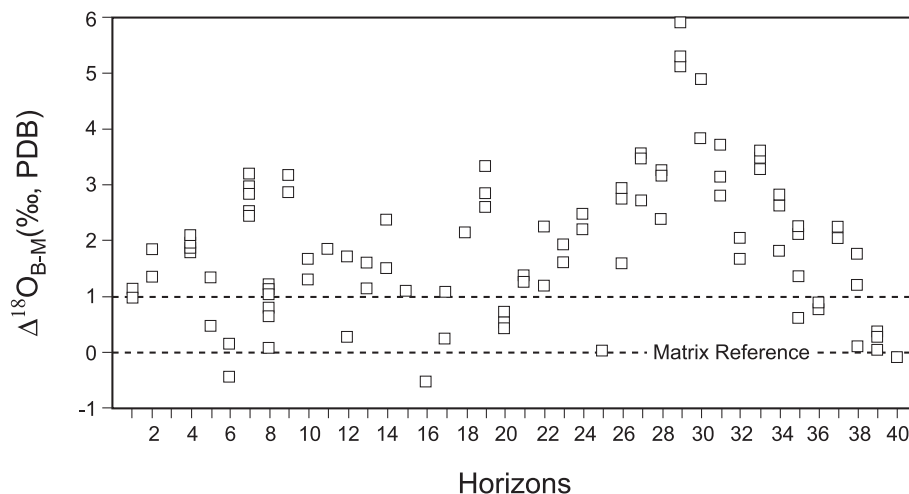


Fig. 7. Variation in $\Delta^{18}\text{O}_{\text{B-M}}$ of coeval brachiopods and enclosing matrix (whole rock, set to 0 for $\Delta^{18}\text{O}_{\text{B-M}}$) representing the Madera, Bird Spring, Louisiana, Ludlowville, Rochester, Irondequoit, Georgian Bay, Cobourg and Verulam Formations. Explanations as in Fig. 6.

samples. The small size of the data sets or an unknown factor may be contributing in skewing these results.

A total of 98 coeval brachiopod–whole rock pairs representing 40 horizons from nine formations were evaluated for their $\Delta^{13}\text{C}_{\text{B-M}}$ differences between unaltered brachiopods and their enclosing whole rock material. Of the carbon-isotope coeval pairs, about 30 samples of brachiopods fall within the $\pm 1\%$ envelope representative of variation expected at any particular location/horizon (cf. Brand et al., 2003; Fig. 8). For the most part, though, brachiopods carry a heavier $\delta^{13}\text{C}$ signal than their contemporaneous whole rock, this seems to be especially pronounced for material younger than Mid-Devonian. In contrast, there seems to be a much greater degree of overlap (20 of 30 pairs) between brachiopod and whole rock $\delta^{13}\text{C}$ values older than Mid-Silurian (Fig. 8, Table 3 includes the material studied by Wenzel, 2000). This ‘anomaly’, if it is real, deserves more attention and research.

In summary, there appears to be a significant difference between the Carboniferous and Devonian plus older age groups. This supports the assertion that carefully selected and appraised for composition and diagenetic impact, whole rock material may possibly carry original carbon-isotope seawater chemistry (Brasier et al., 1992; Corfield et al., 1992; Long, 1993; Kaufman et al., 1993; Pelechaty et al., 1996; Saltzman, 2001).

Comparisons of brachiopod data sets are usually hampered by a lack of/or difficulty with synchronicity. Comparison of Ordovician material from other sources would be an important consideration especially in light of the controversy (Land, 1995; Veizer, 1995) surrounding the results presented by Qing and Veizer (1994). The mid-Ordovician material from the Cobourg and part of the Verulam (Appendix A) lends itself for comparison to the mid-Ordovician data set from Ontario and Ohio of Qing and Veizer (1994) and Qing et al. (1998); several samples were deleted because their values are altered). Table 4 shows the statistical evaluation of C, O, and Sr isotopes for unaltered brachiopods/trilobites from the Cobourg/Verulam (Ontario) with those from the Trenton (Ontario and Tennessee). There are no significant differences between the coeval formational data sets for the three test parameters. Indeed the significance of similarity is high for both carbon and oxygen isotopes, whereas the slightly lower concurrence of the Sr isotope values may be related to temporal correlation problems of the two data sets. Furthermore, a comparison of the Spechts Ferry Formation (Shields et al., 2003) with the upper Verulam Formation (horizon 77iii) shows some similarity between the formational data sets (Table 4). However, the low significance of the p values suggests some temporal correlation difficulties between the studied units. Temporally better-resolved material, preferably from global stratotype

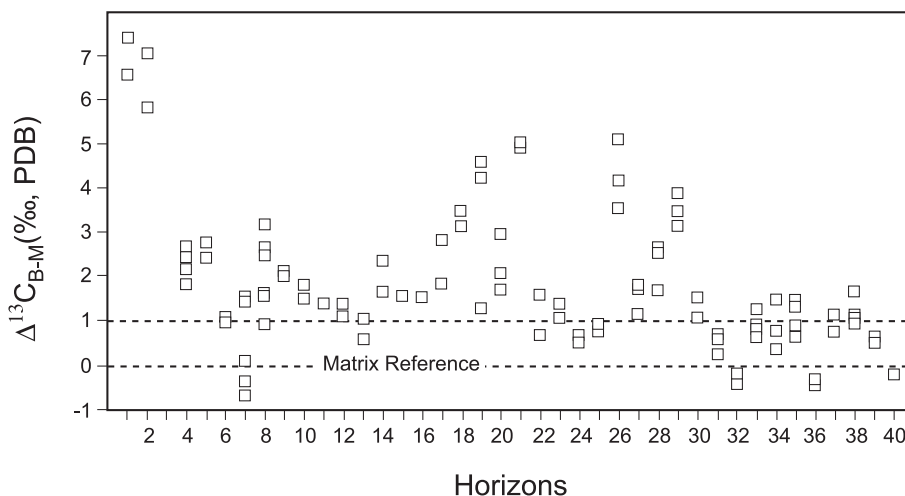


Fig. 8. Variation in $\Delta^{13}\text{C}_{\text{B-M}}$ of coeval brachiopods and enclosing matrix (whole rock, set to 0 for $\Delta^{13}\text{C}_{\text{B-M}}$) representing the Madera, Bird Spring, Louisiana, Ludlowville, Rochester, Irondequoit, Georgian Bay, Cobourg and Verulam Formations. Explanations as in Fig. 6.

Table 4

One-way ANOVA of isotopic compositions of Ordovician unaltered brachiopod/trilobite samples of this study (Cobourg [horizon 47] and Verulam Formations [horizons 77iii, 78i, 78ii]) and brachiopods of Qing and Veizer (1994) and Qing et al. (1998); Trenton Formation—Ontario and key to textures: Ohio¹

Parameter	Brachiopods/trilobites			Brachiopods			<i>p</i>
	<i>N</i>	Mean	S.D.	<i>N</i>	Mean	S.D.	
$\delta^{18}\text{O}$ (‰) ¹	9	-5.18	0.35	8	-5.19	0.18	0.956
$\delta^{13}\text{C}$ (‰) ¹	10	0.85	0.39	8	0.79	0.73	0.826
$^{87}\text{Sr}/^{86}\text{Sr}^1$	8	0.708013	0.000028	6	0.707992	0.000030	0.210
$\delta^{18}\text{O}$ (‰) ²	7	-5.20	0.32	6	-5.48	0.56	0.265
$\delta^{13}\text{C}$ (‰) ²	7	0.73	0.35	6	0.05	0.81	0.067
$^{87}\text{Sr}/^{86}\text{Sr}^2$	6	0.708045	0.000020	4	0.708061	0.000010	0.174

Another set are from the Verulam (horizon 77iii) and Spechts Ferry Formations (Shields et al., 2003)². Significance is at the 95% confidence level ($p < 0.050$).

N = number of data, S.D.—standard deviation.

sections and point (GSSPs), auxiliary stratotypes (ASs), or biostratigraphically well-defined sections greatly facilitates comparisons within and between continents (cf. Brand and Bruckschen, 2002).

4.3. Ordovician trilobite material

McAllister and Brand (1989) demonstrated that low/intermediate-Mg calcite carapaces of trilobites may contain original microstructures (cf. Wilmot and Fallick, 1989; Dalingwater et al., 1999) and chemical compositions. Despite this conclusion, they are a potentially important original seawater-chemistry proxy left unexplored by researchers (e.g., Brasier et al., 1992). The following is a succinct evaluation of isotope chemistry in some Ordovician coeval unaltered brachiopods (determined in Section 4.2 and Bates, 1990) and trilobites (some material from McAllister and Brand, 1989) in relation to their enclosing whole rock material. The Sr/Mn ratio of the coeval whole rock material ranges from 0.29 to 1.34 (Appendix A; several not tested for trace chemistry), which indicates significant diagenetic alteration and low potential of preservation of original seawater chemistry (cf. Denison et al., 1994). Coeval brachiopods and trilobites exhibit a small $\Delta^{87}\text{Sr}_{\text{B(T)-M}}$ range; definitely different from the values of their enclosing whole rock (Fig. 9). This suggests that brachiopods and trilobites probably contain original seawater-⁸⁷Sr values whereas their enclosing matrix does not.

Statistical analysis supports this interpretation in that there is no significant difference in the strontium

isotope ratios between Ordovician coeval unaltered brachiopods and trilobites ($p = 0.704$, Table 5). Just as important, their values are within the range of variation (23×10^{-6}) observed in modern articulated

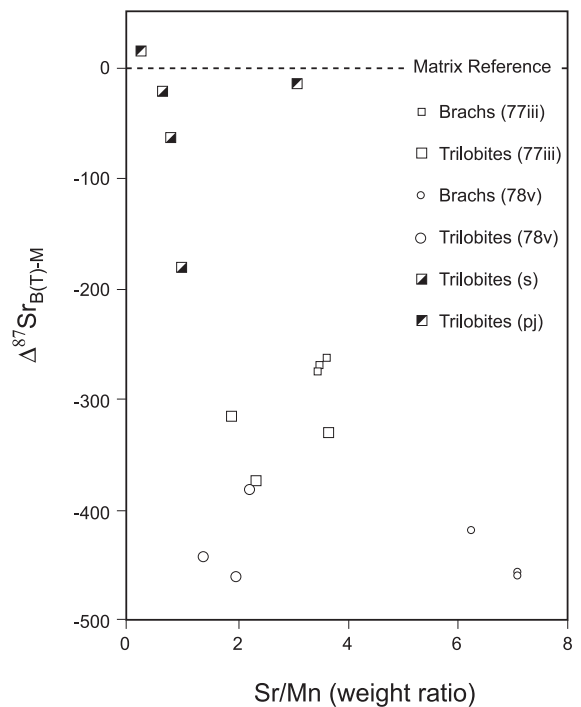


Fig. 9. Variation in $\Delta^{87}\text{Sr}_{\text{B(T)-M}}$ and Sr/Mn of coeval brachiopods and trilobites relative to enclosing matrix (whole rock) from the Ordovician Verulam Formation, eastern Ontario (horizons 77iii and 78v), and Cambrian Sullivan (s), Alberta and Petit Jardin Formations (pj), Newfoundland.

Table 5

One-way ANOVA of isotopic compositions between Ordovician (O) and Cambrian (C) unaltered brachiopods, trilobites and matrix (whole rock), and from Brasier et al. (1992)*

Parameter	Unaltered brachiopods			Trilobites			<i>p</i>	Matrix			<i>p</i>
	<i>N</i>	Mean	S.D.	<i>N</i>	Mean	S.D.		<i>N</i>	Mean	S.D.	
$\delta^{18}\text{O}$ (‰) _O	6	−5.51	0.66	6	−5.39	0.36	0.693	3	−5.35	0.13	0.867
$\delta^{13}\text{C}$ (‰) _O	6	+0.51	0.37	6	+0.75	0.30	0.248	3	+0.59	0.42	0.534
$^{87}\text{Sr}/^{86}\text{Sr}$ _O	6	0.708076	0.000040	6	0.708087	0.000055	0.704	3	0.708418	0.000125	0.000
$\delta^{18}\text{O}$ (‰) _C				4	−8.70	1.10		2	−8.61	1.10	0.923
$\delta^{13}\text{C}$ (‰) _C				4	−0.70	0.21		2	−0.66	0.34	0.870
$^{87}\text{Sr}/^{86}\text{Sr}$ _C				5	0.709392	0.000121		3	0.709465	0.000164	0.495
$\delta^{18}\text{O}$ (‰) _C *				2	−6.00	0.85		4	−7.13	0.68	0.147
$\delta^{13}\text{C}$ (‰) _C *				2	+0.35	0.50		4	−2.30	1.62	0.097

Sets of values are from coeval stratigraphic horizons. Significance is at the 95% confidence level ($p < 0.050$) or better.

N = number of samples, S.D. — standard deviation.

brachiopods for global seawater (Brand et al., 2003). Since the brachiopods are deemed unaltered and their chemistry reflects original seawater conditions, this suggests that the trilobite results, by analogy, also represent original seawater values. The Sr isotope value of the enclosing matrix is significantly different from the brachiopod and trilobite ones and well outside the range of natural seawater variation. Consequently, the matrix results reflect diagenetic signals.

Evaluation of the carbon and oxygen isotope results is more complex than the trends and values exhibited by the Sr isotopes. Carbon and oxygen isotope values are not significantly different between the coeval unaltered brachiopods and trilobites (Table 5). This suggests that brachiopods and trilobites may represent original seawater isotope values. In contrast to the above observations, a definite difference in Sr isotope values is noted between coeval trilobites and whole rock material ($\Delta^{87}\text{Sr}_{\text{B(T)-M}} = -0.000331$; $p = 0.0001$) at the 95% confidence level, but surprisingly not for their carbon and oxygen pairs (Table 5). This suggests that the whole rock material may have retained original seawater values for carbon and oxygen but not for Sr isotopes or the brachiopod and trilobite material has experienced selective diagenetic alteration. It is possible that the low/intermediate-Mg calcite of trilobite carapaces may contain original seawater values. But the limited database and the numerous canals/pores within the exoskeleton (McAllister and Brand, 1989) that may be filled by cement suggest caution in the interpretation of the results and its wider application to all trilobites. A comprehensive study is needed to

confirm the original seawater proxy potential for isotopes in Ordovician trilobites.

4.4. Cambrian trilobite material

A few Cambrian trilobites with coeval whole rock material were tested for their potential of retaining original seawater chemistry. The whole rock material is from horizons of upper Cambrian formations, and their low Sr/Mn ratios and bright luminescence attest to the diagenetic alteration of these specific samples (Appendix A; Brophy, 1990). Their carbon and oxygen isotopic values are similar to those of their coeval trilobites (Table 5). Since, the whole rock material is deemed diagenetically altered, the similarity in chemistry between the two allochems suggests that the carbon and oxygen isotope values of the trilobites must also be a product of diagenesis, and as such do not reflect original seawater conditions.

In contrast, the trilobite Sr-isotope values are either similar to or lower than those of their enclosing whole rock (Appendix A). The greatest level of Sr isotope deviation from the whole rock material is exhibited by a trilobite value (sample C-427: $\Delta^{87}\text{Sr}_{\text{B(T)-M}} = -0.000181$) from the Sullivan Formation. This is clearly outside the ‘natural’ range of ± 0.000023 observed in carbonates from modern oceans (Brand et al., 2003; Hodell et al., 1991), and as such suggests that the Sullivan trilobite sample is probably preferentially preserved relative to its enclosing whole rock material. The same trilobite sample exhibits carbon and oxygen isotope compositions similar to its enclosing whole

rock material (Appendix A). This suggests that differential preservation of the various isotopes is a strong possibility in the trilobite samples from the Sullivan Formation of Alberta. In contrast, no definitive conclusion, because of the overall similarity and paucity of material, may be reached about the isotopic compositions of the trilobites and whole rock material from the Petit Jardin Formation of Newfoundland (Table 5).

Trilobite–whole rock pairs from horizons Ac1 and Ac2 of the early Cambrian Comley Limestone show a distinct divergence between matrix and trilobite isotope results (Brasier et al., 1992; Fig. 4). Although the differences are not statistically significant (Table 5), their ranges are sufficiently large to draw attention to the probable better preservation of these early Cambrian trilobites. This observation supports the earlier assertion that trilobites may constitute an underutilized and invaluable proxy

of original seawater chemistry. Further comprehensive and comparative studies (trilobites–brachiopods–whole rock) are needed to unequivocally resolve the issue whether trilobite chemistry may serve as an important proxy for Ordovician and Cambrian seawater chemistry.

4.5. Summary trends of isotopes

The summary trends of Δ isotopes_(B–M) with geologic age appear to illustrate (a) the influence of detrital material on isotopic values, (b) some major implications on the reliability and usefulness of some original seawater proxies, and (c) secular trends in brachiopod–whole rock chemistry for the Paleozoic.

The presence of detrital material in whole rock samples significantly impacts on the deviation in Sr isotopes relative to coeval calcitic brachiopod-derived

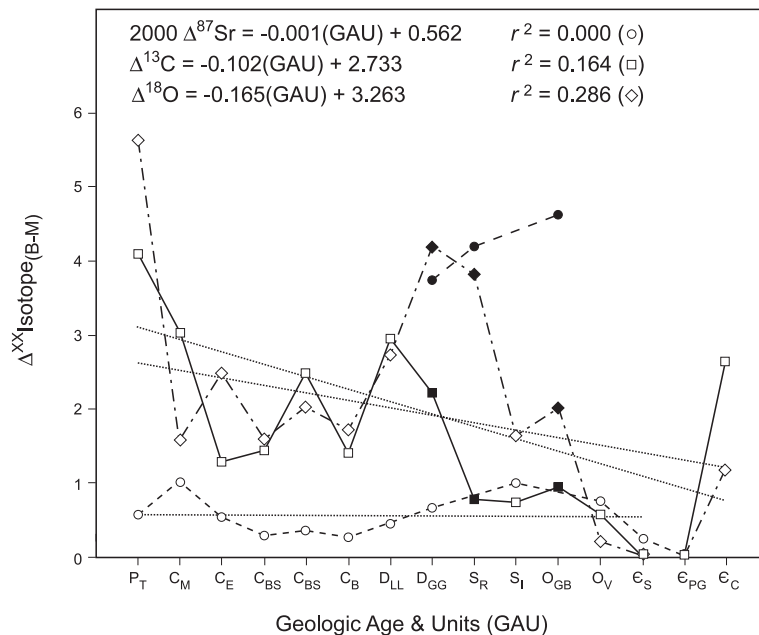


Fig. 10. Variation in isotopes ($\Delta^{13}\text{C}_{\text{B(T)–M}}$, $\Delta^{18}\text{O}_{\text{B(T)–M}}$, $\Delta^{87}\text{Sr}_{\text{B(T)–M}}$) of unaltered brachiopods and trilobites with respect to enclosing matrix per formation with geologic age [whole rock, [limestone (open symbols)] and calcareous shale [solid symbols]]. Formational samples are from the Permian (P_T—Timor), Pennsylvanian (C_M—Madera, C_E—Spain, C_{BS}—Bird Spring), Mississippian (C_{BS}—Bird Spring, C_B—Belgium), Devonian (D_{LL}—Louisiana Limestone, D_{GG}—Ludlowville Formation), Silurian (S_R—Rochester, S_I—Irondequoit), Ordovician (O_{GB}—Georgian Bay, O_V—Verulam), and Cambrian (ε_S—Sullivan, ε_{PJ}—Petit Jardin, ε_C—Comley). Supplementary material is from Popp et al. (1986a,b; P_T, C_E, C_B), Brasier et al. (1992; ε_C) and Diener et al. (1996; part of D_{GG}). Correlation curves and equations are based on unaltered brachiopod/trilobite samples from limestones with geologic age.

values (Fig. 10). Thus precautions are needed to advise of the impact on Sr isotope chemistry by argillaceous materials and their potential inclusion in brachiopods and trilobites and other biogenic material. This speaks directly to the need for careful sample preparation and the removal of all extraneous adhering material from biogenic samples.

In general, the brachiopod–trilobite data are heavier for both carbon and oxygen isotopes by about 3 ‰, this does not speak well for the use of whole rock material as a proxy for original seawater chemistry (Fig. 10). This is not unexpected since; the original mineralogy of the whole rock is different from its possible precursor believed to be aragonite lime-mud and lime sand and some admixture of high-Mg calcite (Brand and Veizer, 1981). The difference between Sr isotopes of biogenic material and whole rock seems relatively constant at an absolute value of about 0.000281, which is greater by a factor of about six than the natural variation observed in modern seawater (± 0.000023 ; Brand et al., 2003) at any particular time.

The low slopes of the isotope trends (ranging from -0.001 to -0.165) attest to the relative constancy of isotope differences between allochems and whole rock material with geologic time (Fig. 10). The perturbations within the trends may represent real oceanographic variations, or be simply a reflection of the limited database. More importantly, the databases and trends also reflect a secular constancy of the Δ isotope system_{B–M}. The degree of variation between biogenic and whole rock material for Sr isotopes is about -0.000284 ($\Delta^{87}\text{Sr} = -0.0000005 \text{ geologic age} + 0.000281$; $r^2 = 0.000$; Fig. 10). It is put forth that this value may be used as a general Sr isotope correction factor for whole rock material obtained from sequences that lack biogenic material to construct 1st order secular seawater-variation curves. A correction factor for the other two isotopes is unlikely in light of the greater perturbations and change in slope (drift) with geologic time (Fig. 10).

5. Conclusions

Permian to Cambrian brachiopods, trilobites, marine cements and whole rock (=matrix) material were assembled and evaluated from horizons of

several sedimentary formations and groups. The evaluation process demonstrated that in all instances unaltered articulated low-Mg calcite brachiopods, as old as mid Ordovician, retained original seawater carbon, oxygen and strontium isotope compositions. A definitive assessment of the nature of cement chemistry was difficult due to the paucity of material, but it showed some significant similarity with the data of the unaltered brachiopods. Despite this caveat, marine cement material holds promise for retaining original carbon and possibly strontium isotope seawater compositions. In contrast, the potential of whole rock material to serve, as a proxy of original seawater chemistry is more complicated. The oxygen isotopic composition of Carboniferous–Silurian whole rock material bears no semblance to that of coeval unaltered brachiopods, whereas for whole rock material older than Silurian the difference between the coeval pairs becomes less distinct. For carbon isotopes in whole rock, the discrepancy already starts in the Silurian, and continues into older material, with some coeval pairs being dissimilar whereas others being similar in composition. The distribution of Sr isotopes in whole rock is more unequivocal in that all Carboniferous to Ordovician material is significantly different from that of unaltered brachiopods.

Chemistry of some Ordovician–Cambrian low/intermediate-Mg calcite trilobites was compared to that of coeval unaltered brachiopods and enclosing whole rock. Trilobite carbon, oxygen and strontium isotope compositions are similar to coeval Ordovician unaltered brachiopods. The difference in the Sr isotope values suggests that brachiopods and trilobites are better preservers of original seawater chemistry for this specific parameter than coeval whole rock material. Upper Cambrian trilobites carry carbon and oxygen isotope compositions similar to those in the coeval whole rock. In contrast, Sr isotope compositions, although not significantly different, of the whole rock are outside the ‘natural’ range of seawater variation. Thus Cambrian trilobites may hold great potential of preserving original seawater Sr isotopes preferentially to their enclosing whole rock, but more comprehensive studies are needed.

Overall, the potential for retaining original seawater chemistry and serving as proxies, in decreasing order of importance and reliability, are (1) unaltered

brachiopods (C, O and Sr isotopes), (2) pristine cement (C and Sr isotopes), and (3) micritic whole rock material (C isotopes?).

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Appendix A

Geochemical data of brachiopods (altered and unaltered), trilobites, cement and matrix (whole rock) from Paleozoic formations of North America (all data adjusted to NIST SRM 987 = 0.710240; sample numbers in bold are from Brand and Brenckle, 2001; Brand and Gao, 2003; Brand et al., 2003; key to textures: m—micrite, ms—microspar, ps—pseudospar, s—sparite, ds—silicification, nc—noncarbonate).

Sample no.	Allochem	Texture	Strat Pos.	IR	Mg	Fe	Mn	Sr/Mn	Oxygen	Carbon	Sr isotopes
<i>Bird Spring Formation (latest Chesterian—earliest Morrowan, Nevada)</i>											
AC1-1	brachiopod	ds	0.30	16.10	3494	462	63	9.02	−3.13	0.97	0.708158
AC1-2	brachiopod		0.30	14.10	2957	367	99	3.95	−4.32	0.56	0.708195
AC1-22	brachiopod	ds	0.30	18.30	2870	248	92	4.50	−4.84	0.71	0.708236
AC1-3	brachiopod	ds	0.30	57.80	2973	281	87	4.79	−3.60	0.82	0.708187
AC1-32	brachiopod	ds	0.30	51.50	3125	290	65	7.46	−3.93	0.93	0.708168
AC1-4	brachiopod	ds	0.30	20.60	3416	569	82	6.85	−4.06	0.55	0.708191
AC1-42	brachiopod	ds	0.30	25.00	3145	424	64	7.55	−3.25	0.84	0.708171
AC1-43	brachiopod		0.30	16.50	3310	624	83	6.21	−3.90	0.46	0.708189
AC1-2C	cement	s-marine	0.30	0.00	1731	35	150	0.96	−4.56	0.84	0.708220
AC1-22C	cement	s-marine	0.30	0.00	1532	58	155	1.05	−4.73	0.64	0.708170
AC1-3C	cement	s-marine	0.30	0.00	2670	18	128	1.38	−4.96	0.92	0.708191
AC1-1M	matrix	m-ms	0.30	19.50	2246	1115	75	9.04	−4.55	1.10	0.708277
AC1-2M	matrix	m-ms	0.30	19.90	2144	1021	82	8.63			0.708256
A44-10	brachiopod	ds	0.33	35.80	3576	337	64	8.54	−2.49	1.64	0.708197
A44-11	brachiopod	ds	0.33	37.40	3714	446	67	7.34	−3.25	1.04	
A44-8M	matrix	m-ms	0.33	6.80	2513	402	135	2.22	−3.45	0.82	0.708227
A44-11M	matrix	ms-m	0.33	15.10	2519	679	104	5.77	−4.40	0.91	
A44-1c	cement	s-marine	0.33	1.20	1854	117	174	1.14	−5.21	0.73	
AC2-43	brachiopod	ds	4.55	26.50	714	186	15	50.12	−1.21	2.86	0.708142
AC2-42	brachiopod	ds	4.55	19.30	704	129	15	50.00	−1.51	2.76	
AC2-1M	matrix	ms-m	4.55	6.50	2644	452	58	5.68	−4.36	0.74	0.708242
AC2-1Md	matrix	ms-m	4.55	6.50							0.708242
AC3-3	brachiopod	ds	6.27	16.00	677	121	15	65.18	−1.45	2.74	0.708134
AC3-1	brachiopod		6.27	12.40	660	155	16	66.50	−1.80	3.05	
AC3-1M	matrix	m-ms	6.27	10.00	2791	666	56	7.51	−3.12	1.23	0.708241
AC4-2	brachiopod	ds	6.88	39.60	1125	339	31	21.47	−2.08	2.06	0.708204
AC4-1V	cement	s-vein/meteoric	6.88	0.00	850	37	5	28.08	−15.09	0.14	0.711099
AC4-1Vd	cement	s-vein/meteoric	6.88	0.00							0.711068
AC4-1C	cement	s-marine	6.88	0.00	916	375	78	1.46	−4.14	0.47	0.708287
AC4-1M	matrix	ms-m	6.88	7.10	2363	455	60	5.03	−3.92	0.66	0.708380
AC5-3	brachiopod	ds	10.18	18.50	837	192	13	79.01	−2.37	2.48	0.708205

Appendix A (continued)

Sample no.	Allochem	Texture	Strat Pos.	IR	Mg	Fe	Mn	Sr/Mn	Oxygen	Carbon	Sr isotopes
<i>Bird Spring Formation (latest Chesterian–earliest Morrowan, Nevada)</i>											
AC5-4	brachiopod	ds	10.18	29.50	1034	223	16	56.38	−3.80	2.20	
AC5-6C	cement	s-marine	10.18	0.00	1242	97	58	2.04	−3.72	0.82	0.708278
AC5-32M	matrix	m-ms	10.18	2.10	2694	405	47	8.13	−4.08	1.09	0.708303
A51-6	brachiopod	ds	10.25	25.00	2578	106	32	11.15	−2.85	2.15	0.708175
A51-7	brachiopod	ds	10.25	41.80	2784	271	49	8.00	−3.31	1.72	
A51-3M	matrix	m-ms	10.25	12.20	3062	526	62	7.67	−4.46	1.12	0.708278
A51-3Md	matrix	m-ms	10.25	12.20							0.708288
A51-3C	cement	s-marine	10.25	0.80	2329	104	86	1.88	−4.07	1.46	0.708204
AC6-6	brachiopod		11.26	9.80	1064	108	10	111.39	−1.11	3.43	0.708150
AC6-1	brachiopod		11.26	0.00	737	152	14	65.57	−1.96	2.74	
AC6-2M	matrix	m-ms	11.26	5.70	2868	514	48	8.26	−3.48	1.08	0.708338
AC7-13	brachiopod	ds	11.95	42.70	3080	467	50	10.37	−2.77	1.68	0.708191
AC7-12C	cement	s-marine	11.95	0.00	1071	150	53	2.88	−3.63	0.32	0.708232
AC7-3C	cement	s-marine	11.95	0.00	2758	96	51	3.36	−3.88	1.21	0.708195
AC7-2M	matrix	ms-nc	11.95	55.60	2420	1994	97	5.17	−3.88	0.11	0.708508
AC8-1	brachiopod		12.72	10.90	1902	201	21	26.80	−4.21	0.65	0.708251
AC8-1-2	brachiopod		12.72	7.00					−5.06	0.17	0.708366
AC8-1M	matrix	m-ms	12.72	5.80	1543	253	52	3.67	−3.69	−0.86	0.708238
AC9-3	brachiopod	ds	16.07	18.50	2414	164	17	45.45	−1.64	2.29	0.708141
AC9-1	brachiopod	ds	16.07	13.60	2604	110	17	46.06	−1.67	1.98	
AC9-2M	matrix	ms-nc	16.07	17.90	2553	754	142	2.58	−3.80	−1.19	0.708432
A56-4	brachiopod	ds? nc	17.27	51.30	1920	532	201	2.11	−3.26	0.94	0.708628
A56-5	brachiopod		17.27	10.90	1848	188	105	3.67	−2.44	0.15	
A56-3M	matrix	m-ms	17.27	5.10	1850	277	276	0.96	−3.28	−1.66	0.708357
A56-3Md	matrix	m-ms	17.27	5.10							0.708357
A56-5M	matrix	m-ms	17.27	4.90	2012	260	183	1.40	−3.76	−1.73	0.708345
AC13-1	brachiopod	ds	17.40	16.50	697	111	22	34.55	−1.84	2.51	
AC13-12	brachiopod		17.40	3.50	618	68	10	94.64	−1.12	2.84	0.708166
AC13-22	brachiopod		17.40	5.10	1565	83	13	38.30	−1.60	−0.45	0.708174
AC13-1M	matrix	ms-m	17.40	4.40	1976	253	113	2.59	−4.44	−1.76	0.708415
A56A-2	brachiopod	ds	17.73	65.60	2289	479	93	5.16	−2.98	0.18	
A56A-5	brachiopod	ds	17.73	62.70	1981	347	82	5.49	−3.03	−0.20	
A56A-7	brachiopod	ds	17.73	70.80	1887	355	67	6.23	−2.78	1.08	
A56A-1M	matrix	ms	17.73	8.90	2651	312	90	3.71	−3.51	−1.91	
AC15-1	brachiopod	ds	18.00	10.70	674	155	31	27.10	−2.58	2.25	0.708210
AC15-3	brachiopod		18.00	7.40	729	192	27	31.33	−2.67	2.18	
AC15-1M	matrix	nc-ms	18.00	58.70	2626	1059	211	2.26	−3.95	−2.78	0.708502
A58-2	brachiopod		21.25	6.90	774	91	14	69.07	−1.38	2.06	
A58-7	brachiopod		21.15	4.40	1116	65	19	50.63	−2.43	2.95	0.708245
A58-2M	matrix	ms-m	21.15	6.80	2272	230	67	3.98	−3.63	1.35	0.708316
A58A-1	brachiopod		21.35	13.20	1067	129	18	42.39	−2.16	2.39	
A58A-5	brachiopod		21.35	6.30	1032	112	16	51.45	−1.85	2.72	0.708254
A58A-1M	matrix	ms-m	21.35	4.60	2582	284	73	3.44	−3.78	1.31	0.708330
A64-4	brachiopod		30.42	3.00	868	44	17	50.20	−0.92	3.14	0.708218
A64-1	brachiopod		30.42	7.30	899	79	24	30.79	−0.65	3.00	
A64-1M	matrix	m-ms	30.42	13.50	4743	211	35	16.97	−3.10	1.89	
A64-4M	matrix	m-ms	30.42	11.90	4159	159	51	10.02	−3.12	2.45	0.708305
A67-4	brachiopod		34.65	1.60	3264	182	12	67.83	−2.91	3.09	
A67-6	brachiopod		34.65	0.00	2591	82	13	60.00	−2.96	3.24	0.708242
A67-1M	matrix	m-ms-nc	34.65	38.90	10,938	283	37	15.38	−2.89	2.29	0.708510
A67-1Md	matrix	m-ms-nc	34.65	38.90							0.708526

(continued on next page)

Appendix A (continued)

Sample no.	Allochem	Texture	Strat Pos.	IR	Mg	Fe	Mn	Sr/Mn	Oxygen	Carbon	Sr isotopes
<i>Madera Formation (late Vigilian, New Mexico)</i>											
JS-6	brachiopod		– 4.00		940	121	667	0.53	– 4.58	– 1.46	0.708621
JS-10	brachiopod		– 4.00		793	66	194	3.71	– 4.08	2.26	0.708334
JS-15	brachiopod		– 4.00		1343	87	330	1.17	– 4.24	3.10	0.708385
JS-10M	matrix	m-ms-nc	– 4.00	25.20	1333	161	684	0.39	– 5.20	– 4.32	0.708833
JS-7S	cement	s-marine	– 4.00		796	264	1407	0.19	– 6.56	– 4.52	
JS-16	brachiopod		– 4.50		948	31	58	10.69	– 3.91	3.41	0.708246
JS-25	brachiopod		– 4.50		900	77	193	2.24	– 3.43	2.18	0.708379
JS-18M	matrix	m-ms-nc	– 4.50		2900	259	377	1.22	– 5.17	– 3.57	
JS-24M	matrix	m-ms-nc	– 4.50	20.50	2544	362	677	0.55	– 5.33	– 3.72	0.708684
BR-5	brachiopod		– 2.40		1279	96	93	1.16	– 4.81	2.70	
BR-6	brachiopod		– 2.40		1385	80	58	6.41	– 4.52	3.57	
BR-7	brachiopod		– 2.40		1093	45	35	15.06	– 3.88	2.38	0.708244
BR-8M1	matrix	m-ms-nc	– 2.40	34.60	2887	409	778	0.21			0.709003
BR-29a	brachiopod		– 13.50		3062	385	946	0.78	– 4.56	– 0.21	
BR-29b	brachiopod		– 13.50		3022	316	1045	0.71	– 4.67	0.13	
BR-29c	brachiopod		– 13.50		3024	358	544	1.49	– 4.74	0.41	0.708597
BR-29d	brachiopod		– 13.50		2930	406	384	1.96	– 4.44	0.64	
BR-28M	matrix	ms-m-nc	– 13.50	36.60	3734	1292	766	0.90	– 6.93	– 1.10	0.708850
BR-29M	matrix	ms	– 13.50	14.10	3565	531	371	1.08	– 5.93	– 2.96	
BR-11b	brachiopod		– 3.40		1704	81	40	14.90	– 4.06	2.90	
BR-14b	brachiopod		– 3.40		1378	58	68	9.00	– 3.21	3.25	0.708277
BR-15M	matrix	m-ms-nc	– 3.40		4395	561	428	1.29	– 4.54	0.48	0.709237
BR-16S	cement	s-marine	– 3.40		2649	620	932	0.55	– 7.94	– 0.56	
BR-31	brachiopod		– 19.50		2088	216	170	4.46	– 5.04	– 2.11	
BR-33	brachiopod		– 19.50		4830	378	129	6.83	– 4.47	– 2.10	0.708392
BR-32M	matrix	m-ms-nc	– 19.50	14.90	17,959	1118	338	3.15	– 4.61	– 3.06	0.708417
BR-45	brachiopod		– 24.50		3082	509	105	7.32	– 5.06	1.55	
BR-46a	brachiopod		– 24.50		1050	165	20	36.65	– 4.60	3.02	0.708421
BR-46b	brachiopod		– 24.50		2277	380	65	11.62	– 5.01	2.88	
BR-47a	brachiopod		– 24.50		4138	226	283	3.66			
BR-47b	brachiopod		– 24.50		3255	367	159	5.42	– 4.73	1.11	
BR-47c	brachiopod		– 24.50		3732	221	235	3.47	– 4.36	0.79	
BR-46M	matrix	nc-ms	– 24.50	66.70	11,771	2307	536	1.27	– 8.68	1.21	0.709770
BR-48M	matrix	nc-ms	– 24.50		9579	1641	493	1.67	– 6.40	1.74	
BR-52a	brachiopod		– 25.50		1770	252	90	7.40	– 4.46	2.76	
BR-52b	brachiopod		– 25.50		1757	217	27	24.52	– 4.07	2.93	
BR-53a	brachiopod		– 25.50		3261	330	269	2.42	– 4.22	1.22	
BR-55a	brachiopod		– 25.50		2603	194	40	19.48	– 4.60	1.91	
BR-56	brachiopod		– 25.50		2997	819	319	2.33	– 5.16	1.85	
BR-57	brachiopod		– 25.50		889	137	26	17.35	– 4.16	3.46	0.708286
BR-55M	matrix	ms-m-nc	– 25.50		5974	1511	668	0.75	– 5.95	0.36	
BR-57M	matrix	ms-m-nc	– 25.50	13.70	5867	879	404	1.55	– 4.57	0.22	0.708484
BR-67	brachiopod		– 46.00		1370	204	117	4.36	– 4.45	0.62	
BR-68a	brachiopod		– 46.00		1632	250	106	4.44	– 4.44	1.15	0.708393
BR-68M	matrix	nc-ms	– 46.00	84.40	2541	1825	384	0.99	– 7.45	– 1.95	
<i>Louisiana Limestone (Fammanian, Missouri)</i>											
ULL-03	brachiopod		top of unit		545	89	51	25.60	– 1.03	6.80	0.708140
ULL-04	brachiopod		top						– 1.22	5.88	
ULL-05	brachiopod		top		1921	431	134	6.60	– 2.72	4.87	
ULL-05w	brachiopod		top		2580	298	113	8.81	– 2.37	5.24	0.708156
ULL-06M	matrix	m (lithographic)	top		1715	637	385	0.43	– 3.97	1.68	0.708458
MLL-01	brachiopod		1m below		1418	40	29	39.00	– 1.42	6.04	0.708137

Appendix A (continued)

Sample no.	Allochem	Texture	Strat Pos.	IR	Mg	Fe	Mn	Sr/Mn	Oxygen	Carbon	Sr isotopes
<i>Louisiana Limestone (Famnenian, Missouri)</i>											
MLL-02	brachiopod		below		1061	10	13	94.50	− 0.68	6.67	0.708133
MLL-02d	brachiopod		below		1037	5	13	89.40	− 0.59	6.72	
MLL-07M	matrix	m (lithographic)	below		2207	488	130	2.93	− 4.15	4.88	0.708285
<i>Ludlowville Formation (Givetian, New York State)</i>											
Gen-289	brachiopod		be-20ii	6.50	1045	610	240	4.40	− 3.44	4.44	0.707799
Gen-287	brachiopod		be-20ii	9.20	1475	625	215	4.76	− 2.58	3.51	0.707812
Gen-288	brachiopod		be-20ii	10.40	1355	880	210	4.67	− 2.65	4.31	
Gen-291M	matrix	nc-ms	be-20ii	79.90	7495	8210	1340	0.56	− 5.82	1.78	0.709673
Gen-5	brachiopod		be-3ii	3.70	1185	380	150	5.30	− 4.36	2.46	0.707778
Gen-24	brachiopod		be-3ii	9.10	1060	475	140	6.90	− 3.53	2.08	0.707807
Gen-25	brachiopod		be-3ii	10.50	1260	1365	265	3.40	− 4.18	1.77	0.707798
Gen-15/16	matrix	nc-ms	be-3ii	89.90	7450	10,270	1130	0.30	− 9.49	− 1.41	0.709237
<i>Rochester Shale (Wenlockian, Ontario and New York State)</i>											
R-2100	brachiopod		40i	3.60	1090	30	19	66.31	− 1.74	5.15	0.708322
R-2101	brachiopod		40i	2.60	1735	175	75	15.93	− 2.84	5.64	0.708329
R-2103M	matrix	ms-nc	40i	36.20	30,650	5050	1450	0.15	− 6.67	4.09	0.709635
R-2377	brachiopod		41xix	5.30	1960	110	40	34.00	− 3.61	4.56	0.708320
R-2377	brachiopod		41xix	5.30					− 3.28	4.88	
R-2378	brachiopod		41xix	8.80	3220	235	140	9.17	− 2.71	5.02	0.708362
R-2379M	matrix	ms-nc	41xix						− 6.43	4.31	0.709406
R-2463	brachiopod		41x	9.60	1930	110	110	11.95	− 3.61	4.67	0.708331
R-2464	brachiopod		41x	3.90	2140	165	80	15.38	− 3.92	4.88	0.708337
R-2466M	matrix	ms-nc	41x						− 5.66	5.04	0.713134
R-2300	brachiopod		41xxiv	14.50	1670	90	35	36.00	− 3.25	5.32	
R-2301	brachiopod		41xxiv	4.60	3240	150	90	12.11	− 3.46	4.98	
R-2304	brachiopod		41xxiv	6.90	5225	330	205	6.05	− 3.16	4.82	0.708339
R-2308	brachiopod		41xxiv	5.70	3975	320	220	5.55	− 3.43	4.70	0.708347
R-2309M	matrix	ms-nc	41xxiv						− 6.74	4.03	0.709549
<i>Irondequoit Formation (Wenlockian, Ontario and New York State)</i>											
I-2195	brachiopod	ds	40ii	12.50	2860	210	120	10.75	− 3.61	5.65	
I-2191	brachiopod		40ii	6.70	6720	490	360	3.13	− 4.43	4.52	0.708351
I-2193	brachiopod		40ii	4.20	2970	225	115	10.26	− 3.42	4.95	0.708333
I-2192M	matrix	ms-ps	40ii						− 6.25	4.14	0.708819
I-2174	brachiopod	ds	40iii	15.00	5280	380	310	3.89	− 4.17	4.58	
I-2176	brachiopod		40iii	11.30	1880	135	140	9.11	− 3.29	5.36	
I-2173	brachiopod		40iii	8.70	1990	250	180	6.22	− 4.91	4.96	0.708328
I-2183	brachiopod		40iii	6.50	4850	400	375	3.15	− 3.40	4.81	0.708373
I-2178M	matrix	ms-ps	40iii						− 5.55	3.90	0.708745
I-2162	brachiopod		40v	5.30	1555	50	70	15.78	− 3.00	4.87	0.708350
I-2164	brachiopod		40v	4.70	2055	50	80	14.19	− 2.87	5.00	0.708335
I-2162M	matrix	ms-ps	40v						− 3.79	5.29	0.708982
<i>Georgian Bay Formation (Maysvillian, central Ontario)</i>											
O-703	brachiopod		51	2.60	3000	2610	405	1.83	− 6.56	− 0.47	0.707874
O-707	brachiopod		51	1.80	3440	2260	365	1.82	− 6.37	− 0.11	0.707861
O-707	brachiopod		51	1.80					− 6.85	− 0.32	
O-729	matrix	nc-m-ms	51						− 8.61	− 1.24	0.710177

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Appendix A (continued)

Sample no.	Allochem	Texture	Strat Pos.	IR	Mg	Fe	Mn	Sr/Mn	Oxygen	Carbon	Sr isotopes
<i>Cobourg Formation (Shermanian, eastern Ontario)</i>											
O-880	brachiopod		47	5.00	4260	755	465	2.56	−7.10	0.59	0.707847
O-890	brachiopod		47	6.20	4310	550	95	10.31	−4.53	1.74	0.707990
O-891	brachiopod		47	6.70	3930	695	180	4.47	−5.63	1.18	
O-891	brachiopod		47	6.70					−5.61	1.07	0.707972
O-897	matrix	m-ms	47						−5.75	−0.05	0.708264
<i>Verulam Formation (Shermanian, eastern Ontario)</i>											
O-765	brachiopod	ds	77iii	15.60	4270	680	205	3.51	−5.02	0.77	0.708042
O-767	brachiopod		77iii	8.30	4850	700	270	3.46	−4.94	0.85	0.708037
O-768	brachiopod		77iii	8.40	1510	220	85	3.64	−5.23	0.77	0.708048
O-769	matrix	m-ms-nc	77iii	11.40	18,015	6555	530	0.70	−5.31	0.18	0.708311
O-1186	trilobite		77iii	5.60	5060	160	425	2.32	−5.02	0.70	0.708012
O-11132	trilobite		77iii	8.40	5845	810	190	3.68	−5.72	1.34	0.708057
O-19133	trilobite		77iii	8.40	4405	820	260	1.90	−5.54	0.54	0.708072
O-11136	trilobite		77iii	6.70	4435	690	370	1.57	−4.91	0.17	
O-2087	matrix	m-ms-nc	77iii	26.20	4735	260	455	1.41	−5.24	1.01	0.708387
O-814	brachiopod		78i	3.10	3705	620	90	10.01	−5.39	0.46	0.707989
O-827	brachiopod		78ii	9.00	3945	430	255	2.23	−5.26	0.41	0.708010
O-801	brachiopod		78v	9.30	2980	790	115	6.26	−6.75	−0.13	0.708137
O-804	brachiopod	ds	78v	14.00	2825	610	100	7.10	−5.56	0.39	0.708097
O-804d	brachiopod		78v								0.708095
O-11630	trilobite		78v	7.90	4710	240	300	1.95	−5.31	0.66	0.708094
O-13642	trilobite		78v	12.10	4560	430	235	2.21	−5.79	0.66	0.708174
O-13633	trilobite		78v	8.00	4750	375	340	1.38	−4.93	0.57	0.708112
O-20631	matrix	m-ms-nc	78v	26.10	4060	890	370	1.34	−5.49	0.58	0.708555
<i>Sullivan Formation (Upper Marjumen, Alberta)</i>											
C-418	trilobite		SuM		8405	6410	730	0.64			0.709536
C-424	trilobite		SuM		6255	5340	740	0.77	−9.68	−0.40	0.709496
C-427	trilobite		SuM		4550	3020	620	0.97	−9.63	−0.72	0.709377
C-425M	matrix	m-ms-ooids	SuM		16,470	18,340	1010	0.35	−9.38	−0.42	0.709532
C-434M	matrix	m-ms-ooids	SuM		14,100	7775	880	0.38			0.709585
<i>Petit Jardin Formation (Dresbachian, Newfoundland)</i>											
C-472	trilobite		PJbc-D		8435	2400	130	3.08	−7.70	−0.78	0.709263
C-489	trilobite		PJbc-D		9970	6130	1040	0.27	−7.80	−0.89	0.709289
C-488M	matrix	ms-(ps)	PJbc-D		13,890	6050	1060	0.29	−7.83	−0.90	0.709278

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