

EFFECT OF DIAGENESIS ON THE Sr, O, AND C ISOTOPE COMPOSITION OF LATE CRETACEOUS MOLLUSKS FROM THE WESTERN INTERIOR SEAWAY OF NORTH AMERICA

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ABSTRACT. Evaluating the effects of diagenesis on the isotopic compositions of Sr, O, and C in marine carbonates is critical to their use as proxies in reconstructing information on the salinity, temperature and dissolved inorganic carbon of ancient oceans. We have analyzed a series of samples of mollusk shells from the *Baculites compressus* zone (late Campanian) of the Pierre Shale of South Dakota. Samples included outer shell material and septa of cephalopods collected inside and outside concretions. Preservation was evaluated using light microscopy, scanning electron microscopy (SEM), trace element analysis and X-ray diffraction. All of the material consists of aragonite based on X-ray diffraction. An SEM preservation index (PI) was established based on comparison of the microstructure of the fossil material with that of modern *Nautilus*. Excellent preservation (PI = 5) was characterized by well-defined nacreous plates with discrete, angular boundaries. In contrast, samples showing fused nacreous plates with indistinct boundaries were rated poor (PI = 1). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary with preservation and average $0.707648 \pm .000021$ (n = 10) for excellent preservation (PI \approx 5), $0.707615 \pm .000028$ (n = 5) for good preservation (PI \approx 3), $0.707404 \pm .000074$ (n=7) for fair preservation (PI \approx 2), and $0.707261 \pm .000053$ (n=8) for poor preservation (PI \approx 1). These data suggest that as the quality of the preservation declines, the mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio decreases and the standard error of the mean increases. Oxygen and carbon isotope analyses of the same specimens also show decreases with preservation, and $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ are well correlated, suggesting that these tracers are all altered as the PI decreases. The Sr/Ca ratio increases as preservation decreases, indicating that Sr is added to the shell material during diagenesis. In contrast, Mg/Ca shows no trend with preservation. If the increasing Sr concentration (and decreasing $^{87}\text{Sr}/^{86}\text{Sr}$) of the shell material with decreasing preservation represents the addition of Sr to the shell during diagenesis, we calculate that the added Sr had $^{87}\text{Sr}/^{86}\text{Sr}$ ranging from 0.707582 to 0.707032. Potential sources of the added Sr include older marine carbonates and weathering of volcanic ash layers present in the shale. The mechanisms of alteration likely include epitaxial growth of strontianite on the original shell aragonite and isotopic exchange of C and O between alteration fluids and shell carbonate. We conclude that SEM preservation criteria are effective in screening shell material that records original isotopic values and that variations in Sr, O and C isotope composition in well-preserved material can be used to assess paleoenvironmental parameters, such as salinity and temperature. Our results also indicate that assessing preservation is a critical prerequisite to the determination of numerical ages of shell material using strontium isotope stratigraphy.

INTRODUCTION

Measurements of the ratios of oxygen, carbon and strontium isotopes in marine carbonates and in the individual shells of fossil mollusks have been used extensively to

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reconstruct the conditions of temperature, salinity and dissolved inorganic carbon of the water in which the shells formed (for example, Tourtelot and Rye, 1969; Rye and Sommer, 1980; Wright, 1987; Whitaker and others, 1987; Ingram and Sloan, 1992; Ingram and DePaolo, 1993; Holmden and others, 1997; Pagani and Arthur, 1998; He and others, 2005; Knauth and Kennedy, 2009). A critical requirement for this approach is that the shell material be well preserved such that the original isotopic signal is retained, or that alteration during lithification and later alteration follows a predictable path (Knauth and Kennedy, 2009). For individual mollusk shells, Turekian and Armstrong (1961) showed that good visual preservation was not sufficient to insure that the trace element concentrations of late Cretaceous cephalopod shells accurately recorded those of the water in which the shells formed. Here we demonstrate that visually well-preserved shell material from fossil mollusks of the late Campanian (*B. compressus* zone) shows a range of values for $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr/Ca, but that screening by scanning electron microscopy (SEM) can be used to select material that records the initial values of these tracers as they were incorporated into the shell.

METHODS

Samples and Sample Localities

Samples were collected from the upper Cretaceous Pierre Shale (Meade County, South Dakota), all within the *Baculites compressus* zone (~73 Ma; table 1). Samples analyzed were derived from three different, approximately coeval collections: 1) samples (designated “WI”) obtained from multiple specimens preserved in a single concretion (AMNH loc 3274); 2) samples collected through the ontogeny of a single *B. compressus* specimen from the same concretion; 3) additional specimens, preserved both in concretions and in the shaley matrix outside of concretions, (designated “I”); and 4) samples representing ontogenetic series from specimens of the nautilid *Eutrephoceras dekayi* (YPM 45887, 201500 and 201480) from the same ammonite zone.

Initial Cleaning and Assessment of Preservation

Visually well-preserved material, as determined by the presence of iridescent luster, was selected from the outer shell and septa of the specimens for scanning electron microscopic (SEM) and isotopic analyses. Pieces of shell were removed with a probe and sonicated in deionized water to remove surficial material. A piece of intact shell from each sample was examined with SEM to assess surficial and internal shell structure. The surfaces of the specimens were examined at magnifications of 500 to 2,000X and the internal structure was examined at 5,000 to 15,000X. All specimens were assigned a “Preservation Index” (PI) based on the 15,000X internal SEM images. PIs were ranked from 5 (excellent preservation) to 1 (poor preservation) based on comparison of the shell structure with that of modern *Nautilus*, using SEM images of freshly fractured nacreous shell material of this cephalopod (fig. 1). Criteria for assigning PIs were as follows:

- PI = 5 (Excellent; fig. 1A,B): Surface clean and unetched; internal nacreous tablets distinct from adjacent layers and well-defined. Samples at this level of preservation are indistinguishable from nacreous shell structure in modern mollusks (for example, *Nautilus*).
- PI = 4 (Very Good; fig. 1C,D): Surface clean and unetched; nacreous tablets well defined, but their surfaces are slightly irregular and boundaries between adjacent tablets are slightly less distinct than in excellent preservation.
- PI = 3 (Good; fig. 1E,F): Surface good, but shows some signs of etching; nacreous tablets are visible, but show the onset of fusion with adjacent tablets. Specimens in

TABLE 1
Isotopic data for *B. compressus* zone shell material

Specimen	Sample ID	SEM PI	$^{87}\text{Sr}/^{86}\text{Sr}^*$	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	Comment	
<i>Pocillopora domicotris</i> (coral)	Modern Coral	na	0.709176 ± .000035				
WESTERN INTERIOR SEAWAY CONCRETION (WI SERIES)							
<i>Jeletzkytes nodosus</i> (ammonite)	WI-3	4.5	0.707502 ± .000019	-1.1	0.2	All samples recovered from single concretion	
<i>Baculites compressus</i> (ammonite)	WI-8	4.0	0.707513 ± .000020	-1.4	-1.7		
<i>Baculites compressus</i> (ammonite)	WI-9	4.5	0.707597 ± .000004	-1.4	-0.2		
<i>Baculites compressus</i> (ammonite)	WI-18	4.0	0.707600 ± .000011	-1.7	-1.1		
<i>Eutrephoceras deKayi</i> (nautilid)	WI-10	2.5	0.707563 ± .000002	-1.1	-1.7		
<i>Eutrephoceras deKayi</i> (nautilid)	WI-6	2.0	0.707431 ± .000014	-2.9	-4.3		
<i>Placenticerus meeki</i> (ammonite)	WI-12	1.0	0.707088 ± .000034	-8.4	-11.8		
<i>Hoploscaphites brevis</i> (ammonite)	WI-29	2.0	0.707208 ± .000016	-5.6	-7.2		
<i>Pteria</i> sp. (bivalve)	WI-32	4.0	0.707600 ± .000021	-1.6	4.0		
CONCRETION ONTOGENETIC SERIES							
<i>Baculites compressus</i>	WI-40a	4.0	0.707579 ± .000014	nd	nd		outer shell, dorsal
<i>Baculites compressus</i>	40b	4.0	0.707583 ± .000017	nd	nd		outer shell, left flank
<i>Baculites compressus</i>	41	4.0	0.707508 ± .000012	nd	nd		septum, early ontogeny
<i>Baculites compressus</i>	42	4.5	0.707629 ± .000078	nd	nd	septum	
<i>Baculites compressus</i>	43	4.5	0.707648 ± .000066	nd	nd	septum	
<i>Baculites compressus</i>	44	4.5	0.707657 ± .000004	nd	nd	septum	
<i>Baculites compressus</i>	45	5.0	0.707671 ± .000045	nd	nd	septum	
<i>Baculites compressus</i>	46	5.0	0.707697 ± .000021	nd	nd	septum, late ontogeny	
	CaCO ₃ , WI-42	na	0.707674 ± .000040	nd	nd		
	Matrix	na	0.707631 ± .000026	nd	nd		

TABLE 1
(Continued)

Specimen	Sample ID	SEM PI	$^{87}\text{Sr}/^{86}\text{Sr}^*$	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	Comment
WESTERN INTERIOR SEAWAY (I-SERIES)						
<i>Baculites compressus</i>	I-62	5.0	0.707667 ± .000013	nd	nd	sample from concretion
<i>Jeletzkytes nodosus</i>	I-36	3.5	0.707699 ± .000013	nd	nd	
<i>Jeletzkytes nodosus</i>	I-39	3.5	0.707554 ± .000005	nd	nd	
<i>Eutrophoceras dekayi</i>	I-63	2.0	0.707646 ± .000015	nd	nd	
<i>Placenticerus meeki</i>	I-60	3.0	0.707580 ± .000010	nd	nd	sample from concretion
<i>Baculites compressus</i>	Harries	5.0	0.707720 ± .000011	nd	nd	
<i>Inoceramus</i>	I-61	4.5	0.707689 ± .000003	nd	nd	
<i>Inoceramu</i>	KRM-2002	nd	0.707716 ± .000010	nd	nd	
<i>Opertochasma</i> sp. (bivalve)	I-52	nd	0.707182 ± .000012	nd	nd	
Specimen number						
<i>Eutrophoceras dekayi</i> SEPTA/SHELL	Septum #	SEM PI	$^{87}\text{Sr}/^{86}\text{Sr}^*$	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	Comment
45887	8	2.0	0.707116 ± .000010	-5.4	-7.9	
45887	10	1.0	0.707222 ± .000043	-5.5	-8.0	
45887	11	1.0	0.707033 ± .000014	-5.9	-8.3	
45887	16	1.5	0.707263 ± .000014	-4.9	-7.0	
45887	27	2.0	0.707333 ± .000013	-3.8	-5.1	
45887	28	3.5	0.707566 ± .000032	-1.5	-2.4	
201500	15	3.5	0.707678 ± .000010	-0.5	-0.7	
201500	23	3.5	0.707873 ± .000031	-0.4	-0.2	

TABLE 1
(Continued)

Specimen number	Septum #	SEM PI	$^{87}\text{Sr}/^{86}\text{Sr}^*$	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	Comment
<i>Eutrophoceras dekayi</i> SEPTA/SHELL						
201480	19	1.0	0.707378 ± .000012	-3.9	-6.6	
201480	21	2.0	0.707532 ± .000015	-3.6	-3.8	
201480	26	1.5	0.707349 ± .000017	-4.5	-6.9	
201480	29	1.0	0.707257 ± .000028	-4.4	-4.8	
201480	32	1.5	0.707494 ± .000017	-3.2	-3.6	
201480	20	nd	0.707383 ± .000007	-4.0	-4.9	
201480	30	nd	0.707292 ± .000022	-4.2	-4.8	
201482	4	nd	0.707652 ± .000009	-2.1	-1.3	
201482	6	nd	0.707670 ± .000007	-3.2	-2.5	
201483	outer shell	nd	0.707388 ± .000010	-2.4	-0.5	
201492	outer shell	nd	0.707674 ± .000007	-2.9	-3.4	
201494	outer shell	nd	0.707693 ± .000009	-0.8	-1.8	
201484	outer shell	nd	0.707756 ± .000011	-0.9	1.7	
201484	outer shell	nd	0.707660 ± .000010	-1.6	-3.1	
201496	outer shell	nd	0.707505 ± .000007	-2.9	-2.4	
201496	septum	nd	0.707378 ± .000006	-4.4	-3.8	
201496	chamber calcite	na	0.707722 ± .000013	-1.2	-7.7	
201489	outer shell	nd	0.707439 ± .000023	-2.3	-3.8	
201491	outer shell	nd	0.707617 ± .000013	-1.6	-3.7	

nd- Not determined

na- Not applicable

* Values are mean ±1σ of replicate analysis of each sample

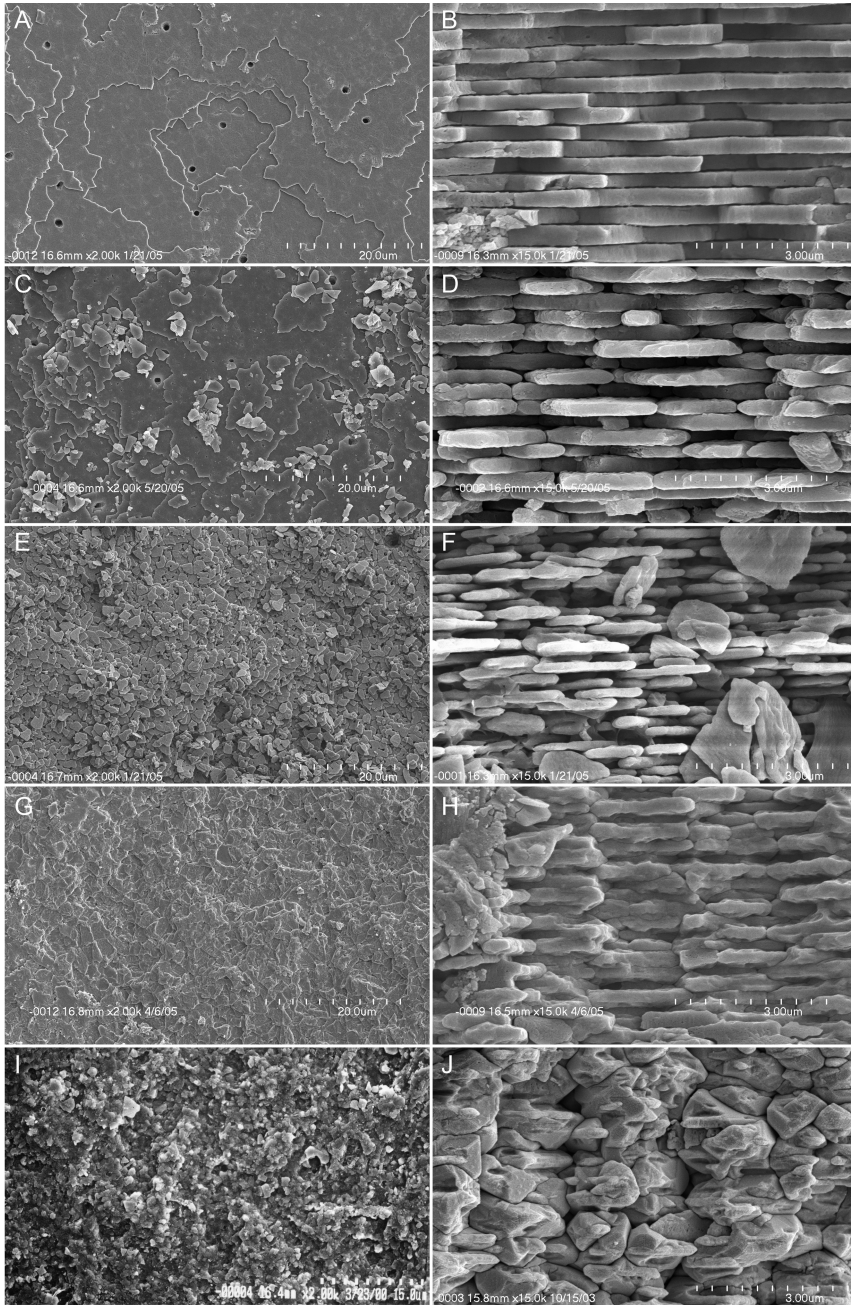


Fig. 1. Scanning electron microscopy images representative of different degrees of preservation (expressed as a Preservation Index, PI) in aragonite shell material of the late Cretaceous Western Interior Seaway of North America (*B. compressus* zone). A, B—“Excellent” preservation (PI = 5) in *Baculites compressus* (specimen I-62): A, surface 2000X; B, cross-section 15000X. C, D—“Very Good” preservation (PI = 4) in *Baculites compressus* (specimen WI-40a): C, 2000X; D, cross-section 15000X. E, F—“Good” preservation (PI = 3) in *Placenticerus meeki* (specimen I-60): E, surface 2000X; F, cross-section 15000X. G, H—“Fair” preservation (PI = 2) in *Hoploscaphites brevis* (specimen WI-29): G, surface 2000X; H, cross-section 15000X. I, J—“Poor” preservation (PI = 1) in *Placenticerus meeki* (specimen WI-12): I, surface 2000X; J, cross-section 15000X.

this group may show a range of preservation, such that SEM images from different parts of the shell show variation in preservation.

- PI = 2 (Fair; fig. 1G,H): Surface shows etching; nacreous tablets are discernible, but show fusion with adjacent layers.
- PI = 1 (Poor; fig. 1I,J): Surface is significantly etched; nacreous tablets are indistinct and fused with adjacent layers.

All SEM photographs were independently examined and ranked for preservation by at least two of the authors (JKC, KK or NHL). Where differences in rankings existed, values were averaged and rounded to the nearest 0.5 PI value.

Isotopic Analyses

For Sr isotopes, sonicated shell fragments (2-6 mg) were ground and dissolved in 1N HCl, and any undissolved residue (largely organic) was separated by centrifugation. Sr was separated by loading the sample on a column with SrSpec™ resin. Strontium was loaded with tantalum oxide (Birk, 1986) onto a single rhenium filament and analyzed in the dynamic mode on a Finnigan MAT 262 mass spectrometer (Department of Geosciences, Stony Brook University). The static mode was used for the matrix samples. Repeated analyses of NBS 987 during the time of sample analyses provided a mean $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.710238 ± 0.000011 (16 runs) in the dynamic mode and 0.710271 ± 0.000012 (10 runs) in the static mode. The $^{87}\text{Sr}/^{86}\text{Sr}$ values in all samples were normalized to a $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.1194. An internal standard consisting of powdered Modern coral (*Pocillopora domicotris*) also was analyzed with each set of samples. The $^{87}\text{Sr}/^{86}\text{Sr}$ of the coral analyses was 0.709176 ± 0.000035 , comparable to that of modern seawater (~ 0.70916 ; DePaolo and Ingram, 1985; Elderfield, 1986; Palmer and Edmond, 1989; Dia and others, 1995).

Oxygen and carbon isotopic analyses were undertaken at the University of Michigan Stable Isotope Laboratory. Samples weighing a minimum of 10 μg were placed in stainless steel boats. Calcite samples were roasted at 380°C in a vacuum for one hour to remove volatile contaminants. Aragonite was roasted at a lower temperature of 200°C to minimize effects of thermal decarboxylation that can alter the isotopic composition of the carbonate. Samples were then placed in individual borosilicate reaction vessels and reacted at $76^\circ \pm 2^\circ\text{C}$ with 3 drops of anhydrous phosphoric acid for 8 minutes in a Finnigan Kiel preparation device coupled directly to the inlet of a Finnigan MAT 251 triple collector isotope ratio mass spectrometer. Isotopic enrichments were corrected for acid fractionation and oxygen-17 contribution by calibration to a best-fit regression line defined by two standards, NBS-18 and NBS-19. Precision of data was monitored through daily analysis of a variety of powdered carbonate standards. At least six standards were reacted and analyzed daily, bracketing the sample suite at the beginning, middle, and end of the day's run. Measured precision was maintained at better than 0.1 permil for both carbon and oxygen isotope compositions. Data are reported in permil notation relative to VPDB.

Elemental Analyses

Samples of cleaned shell material (0.5-16 mg) from the WI and I series were dissolved in 200 μL concentrated HNO_3 . Sample digests were diluted 11-fold with ultrapure 1N HNO_3 , and analyzed for Sr, Mg, Ba, Mn and Fe by ICP-MS (Thermo-Fisher Element2) at Stony Brook University. Instrument drift and random variability associated with the sample-introduction system during direct-injection analyses were corrected using indium as an internal standard. Calibration curves were constructed with CertiSpec multi-element standard solutions diluted in the same 1N HNO_3 as samples. Instrument response was checked by analysis of Certified Reference Material NIST 1643d (Trace Elements in Water), and measured values were within 10 percent

of those certified. Element/Ca ratios were calculated assuming that Ca is ~40 weight percent. All samples were run in duplicate.

RESULTS AND DISCUSSION

Preservation

Based on the SEM criteria established above, the preservation index for the shell material analyzed ranged from 1 to 5 (table 1). All of the shell material assayed for PI was from ammonites, nautilids, pteriites and the nacreous layer of inoceramids and thus showed nacreous microstructure with different levels of preservation (fig. 1). There was no clear species-specific link with PI, although all the samples analyzed from specimens of the nautilid *Eutrephoceras dekayi* had PI values <3.5. The *E. dekayi* samples were all determined to be aragonite on the basis of X-ray diffraction, despite the relatively poor preservation as indicated by SEM. The consistently best-preserved shell material was found in specimens of *Baculites compressus*, with PI values of 3.5 to 5. There is also no clear link between SEM-based PI determination and the occurrence of the fossils in concretions. For example, samples of *B. compressus* exhibited high values of PI whether collected in concretions or as isolated fossils. Slight differences in preservation may occur within a single specimen, as seen in the samples from the single *B. compressus* specimen taken from the WI concretion (specimens WI-40 to WI-46). Although all samples in this specimen were assessed to be “very good-to-excellent” preservation, the phragmocone samples (WI-40a, b) were slightly less well preserved (PI = 4) than samples from the septa (WI-41 to 46; PI = 4.5-5).

$^{87}\text{Sr}/^{86}\text{Sr}$ and Preservation

The $^{87}\text{Sr}/^{86}\text{Sr}$ values range from 0.707033 to 0.707720 (table 1). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio co-varies with PI (table 2), such that samples with poor preservation (PI = 1-1.5; n = 8) have mean ratios (± 1 standard error) of $0.707261 \pm .000053$, significantly less than that of samples with excellent preservation (PI = 4.5-5; $0.707648 \pm .000021$; n = 10). The $^{87}\text{Sr}/^{86}\text{Sr}$ of samples with fair (PI ≈ 2) and good (PI ≈ 3) preservation are intermediate, $0.707404 \pm .000074$ and $0.707615 \pm .000028$, respectively (table 2). In comparison, McArthur and others (1994) reconstructed the $^{87}\text{Sr}/^{86}\text{Sr}$ of water in the Western Interior Seaway in the late Cretaceous, and the average of their values for samples from the *B. compressus* ammonite zone (n = 3) is 0.707674 ± 0.000013 , within the uncertainty of our value for material with PI = 4.5-5.

Additional detail on the variation of $^{87}\text{Sr}/^{86}\text{Sr}$ with preservation is shown by plotting all the data as a function of PI (fig. 2). $^{87}\text{Sr}/^{86}\text{Sr}$ is relatively constant above PI = 3, but scatter increases below PI = 3, and $^{87}\text{Sr}/^{86}\text{Sr}$ decreases markedly in most cases. *B. compressus* samples with intermediate PI (for example, 2-2.5), have normal to low $^{87}\text{Sr}/^{86}\text{Sr}$ values, which may arise from varying degrees of preservation within a single sample. Several SEM photos from the same sample occasionally show variation in preservation. In such samples, it is possible that the portion of shell analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$ came from a slightly different level of preservation than the average obtained from the SEM photographs. Because sample sizes and treatments differ for SEM and isotopic measurement, it is not possible to determine the PI on precisely the same sample that is analyzed isotopically. At the extremes of preservation (1 and 5), the preservation in a specimen is uniformly poor or excellent, respectively, and the PI and isotopic results tend to be more consistent. Further research may help to document better the variation in preservation and isotopic signatures within a single specimen. Although there is some subjectivity in determining the SEM PI rankings, excellent-to-very good preservation (PI = 4-5; fig. 1A-D) may be likened to Justice Potter Stewart’s definition of pornography—to paraphrase, “One knows it when one sees it.” In future studies, it is this material that should, in general, be selected for further analysis.

TABLE 2
 $^{87}\text{Sr}/^{86}\text{Sr}$, $[\text{Sr}]$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in PI groupings and calculated "adsorbed" $^{87}\text{Sr}/^{86}\text{Sr}$ and exchanged fraction of O and C

PI	$^{87}\text{Sr}/^{86}\text{Sr}^*$	$[\text{Sr}]^*$ (ppm)	Calculated $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{ads}}$	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	Fraction O exchanged** (%)	Fraction C exchanged** (%)
4.5 - 5	0.707648 ± 0.000021 (n=10)	1680 ± 190 (n=6)	-	-1.3 (n=2)	0.0 (n=2)	-	-
4	0.707564 ± 0.000017 (n=6)	1560 ± 295 (n=4)	-	-1.6 (n=3)	0.4 (n=3)	-	-
3 - 3.5	$0.707615 \pm 0.000028^\ddagger$ (n=5)	3320 ± 160 (n=2)	0.707582	-0.8 (n=3)	0.4 (n=3)	-	-
2 - 2.5	0.707404 ± 0.000074 (n=7)	3240 ± 400 (n=4)	0.707142	-3.7 (n=6)	-5.0 (n=6)	14	20
1 - 1.5	0.707261 ± 0.000053 (n=8)	4530 (n=1)	0.707032	-5.5 (n=8)	-6.5 (n=8)	23	26

* Mean ± 1 standard error

** Based on fluid $\delta^{18}\text{O} = -19\text{‰}$ and $\delta^{13}\text{C} = -25\text{‰}$ (see text for discussion)

‡ One high value (0.707873) excluded from average

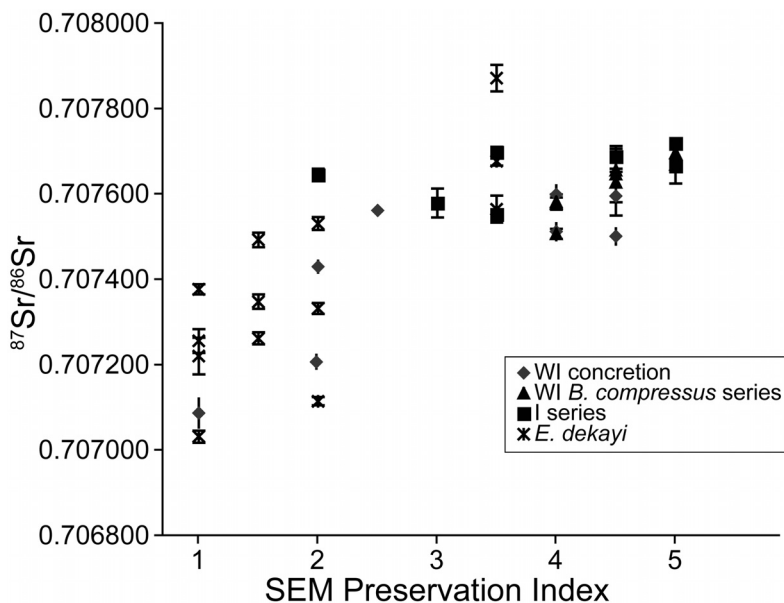


Fig. 2. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Preservation Index in samples from *Baculites compressus* ammonite zone (table 1).

The agreement of $^{87}\text{Sr}/^{86}\text{Sr}$ in our well-preserved specimens with that of McArthur and others (1994) is encouraging. Yet some of the variation in $^{87}\text{Sr}/^{86}\text{Sr}$ at the high PI values may be real and reflect paleoceanographic variations in salinity, for example. Cochran and others (2003) analyzed samples from different paleoecologic settings in the *Jeletzkytes nebrascensis* ammonite zone (~67 Ma BP) and found lower $^{87}\text{Sr}/^{86}\text{Sr}$ values in specimens collected in brackish environments relative to those from more fully marine settings. For reasonable values of salinity within the WIS, it was difficult to explain this variation with simple dilution of seawater with freshwater riverine input, and Cochran and others (2003) concluded that the brackish environment was affected by submarine groundwater discharge (for example, Moore, 1996, 1999). The preservation of the samples analyzed by Cochran and others (2003) was assessed by X-ray diffraction and by SEM, although the latter was not performed at the higher magnifications used in the present study. We have redone the SEM imaging of the samples analyzed by Cochran and others (2003) at higher magnifications and evaluated their PI according to the protocols used in the present study. All of these samples display PI values >3 (fig. 3). The pattern of $^{87}\text{Sr}/^{86}\text{Sr}$ with PI in these specimens is distinctly different from those in the *B. compressus* zone (fig. 2); for all the *J. nebrascensis* PI groupings, there is a clear trend from lower values in the brackish environment to those in the fully marine. This is especially well demonstrated for PI = 5, in which values range from 0.707815 ± 0.000007 (fully marine) to 0.707699 ± 0.000014 (brackish). We reassert the conclusion of Cochran and others (2003) that the variation in $^{87}\text{Sr}/^{86}\text{Sr}$ of material collected in different paleoenvironmental settings reflects real differences in $^{87}\text{Sr}/^{86}\text{Sr}$ in the WIS at that time. For the well-preserved samples from the *B. compressus* zone analyzed in the present study, we lack the control on paleoenvironmental setting available for the *J. nebrascensis* zone, and thus can not easily apply the same approach as Cochran and others (2003) to this time slice of the WIS.

One consequence of our demonstration of the change in $^{87}\text{Sr}/^{86}\text{Sr}$ with preservation is that the use of strontium isotope stratigraphy to determine numerical geological

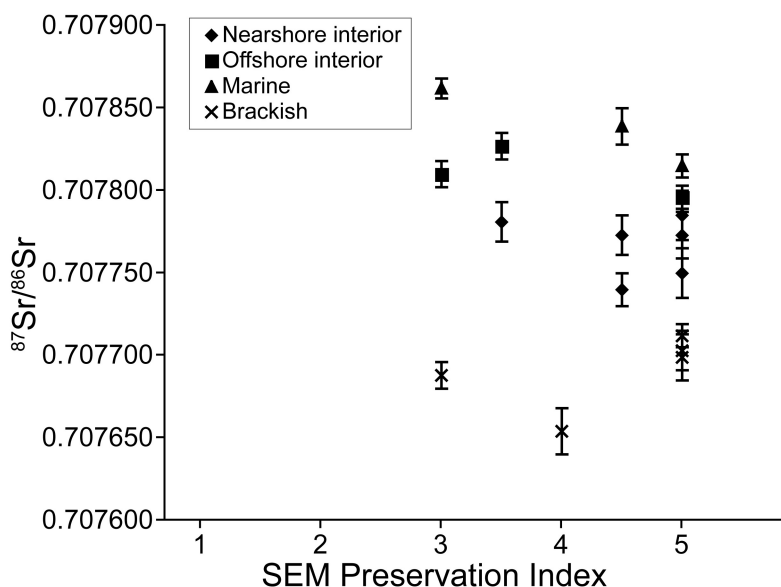


Fig. 3. $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Preservation Index in samples from *Jeletzkytes nebrascensis* ammonite zone (Sr isotope data from Cochran and others, 2003). The paleoenvironments listed are from the reconstruction by Waage (1968).

age of a specimen must be approached with caution. Applying the strontium isotope stratigraphy documented by McArthur and others (1994, 2001) for the late Cretaceous to the range of $^{87}\text{Sr}/^{86}\text{Sr}$ observed as a function of preservation in the present study would imply ages spanning approximately 17 Ma, extending from the mid-Cretaceous Turonian to the late Campanian.

Oxygen and Carbon Isotopes

As with $^{87}\text{Sr}/^{86}\text{Sr}$, values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ range widely from -0.35 to -8.4 permil and -0.16 to -8.3 permil, respectively (table 1, fig. 4). The ammonites and nautilids analyzed secreted aragonite shells, and for $\delta^{18}\text{O}$ values of ~ -1 permil for seawater in the late Cretaceous (Fatherree and others, 1998), the range in $\delta^{18}\text{O}$ values in the samples corresponds to a range in temperature of 18 to 55°C (Eqn. 1; Grossman and Ku, 1986). Clearly, the higher temperatures (corresponding to the lighter $\delta^{18}\text{O}$ values) are spurious. As well, there are good correlations between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ ($R^2 = 0.79$; fig. 4) and between $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ ($R^2 = 0.81$; fig. 5) in the specimens of *Eutrephoceras dekayi*, suggesting that the range in values of all three isotopic indices is coupled with preservation. A sample of chamber calcite infilling also was analyzed (table 1), and its isotopic values are consistent with its formation from marine porewater during early diagenesis, with $^{87}\text{Sr}/^{86}\text{Sr}$ (0.707722; table 1) slightly greater than that of seawater in *B. compressus* time, a $\delta^{18}\text{O}$ value reflecting precipitation at $\sim 21^\circ\text{C}$ and an isotopically light $\delta^{13}\text{C}$ value consistent with an imprint of C released from organic matter decomposition into the pore water dissolved inorganic carbon reservoir.

In contrast to the chamber calcite, alteration of the aragonite as seen in the crossplots of $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ versus $\delta^{18}\text{O}$ (figs. 4-5) suggests that the fluid involved in the alteration had low $^{87}\text{Sr}/^{86}\text{Sr}$ and isotopically light $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. The shoreline in the *B. compressus* zone was shoreward of its position in

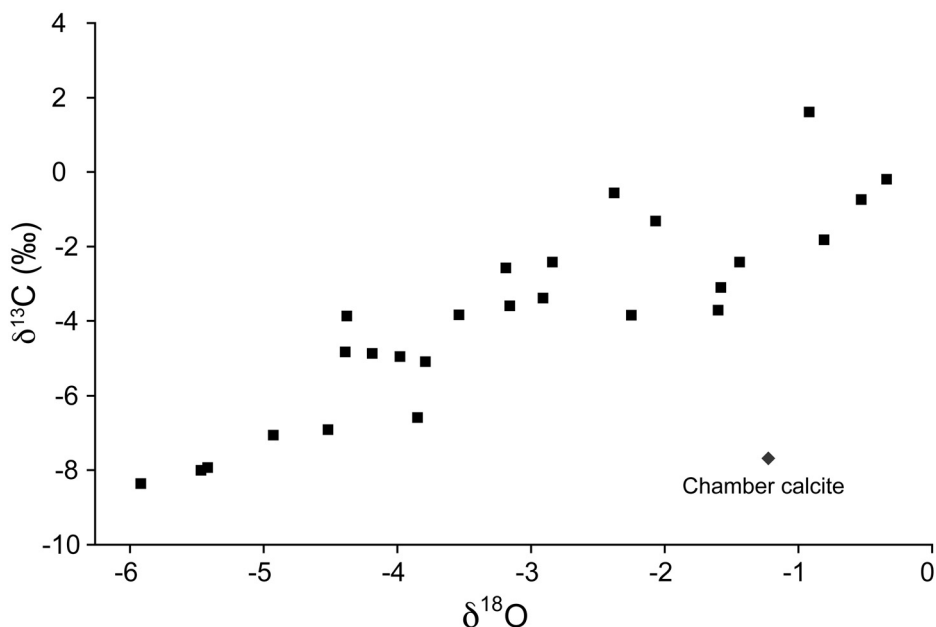


Fig. 4. $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ (‰ relative to VPDB) in septa and outer shell of *Eutrephoceras dekeyi*; $R^2 = 0.79$. Point labeled “Chamber calcite” represents C and O isotopic composition of secondary calcite precipitated in the chambers of the shell.

underlying zones (Cobban and others, 1994), and one possibility is that alteration occurred relatively early in diagenesis (although later than the stage of chamber calcite formation). Groundwater (meteoric water) involved in the alteration would have been isotopically light with respect to $\delta^{18}\text{O}$. It could also have been imprinted with lower $^{87}\text{Sr}/^{86}\text{Sr}$ derived from the older carbonate-containing sediments (or weathering of volcanic ash layers), and with light $\delta^{13}\text{C}$ values as a result of organic matter diagenesis. Indeed, Carpenter and others (1988) and Landman and others (2010) have argued that concretion formation in the Fox Hills Formation happened relatively early in diagenesis, and it is possible that the alteration we observe was contemporaneous with concretion formation.

An alternate explanation that would account for isotopically light $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values in the altered aragonite is that alteration occurred during late diagenesis at higher temperatures (for example, Winter and Knauth, 1992). Alteration of carbonate at high temperatures would have produced carbonate with isotopically light $\delta^{18}\text{O}$ values, and decarboxylation would produce isotopically light dissolved inorganic carbon (Winter and Knauth, 1992). We think that this explanation is unlikely, however, because of the nature of the alteration seen in the SEM images (see below for further discussion). As well, Gupta and others (2008) showed that the molecular structure of organic components of the jaws of ammonites in the *B. compressus*-*B. cuneatus* zones of the Pierre Shale were “nearly original” and had not been subjected to elevated temperatures or pressures.

The pattern of isotopic variation with preservation documented here suggests that earlier studies using oxygen isotope ratios to discern paleohabitats of mollusks need reexamination. For example, Tsujita and Westermann (1998) found ranges of $\delta^{18}\text{O}$ similar to those of the present study in ammonoid species from the Bearpaw Formation (late Campanian-early Maastrichtian). Their criteria for assessing preservation relied

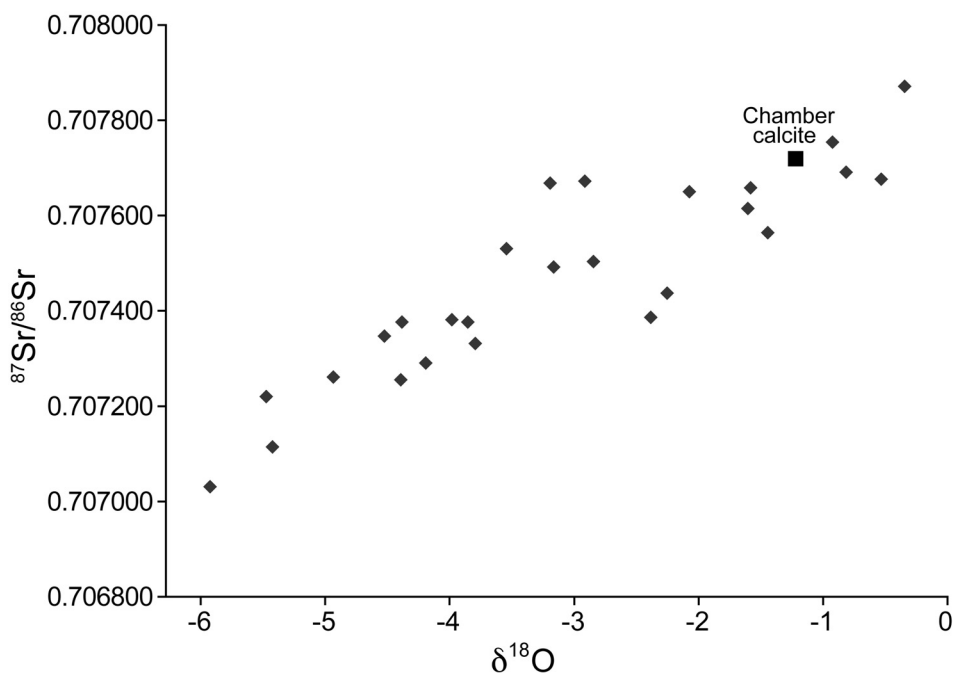


Fig. 5. $^{87}\text{Sr}/^{86}\text{Sr}$ vs $\delta^{18}\text{O}$ (‰ relative to VPDB) in septa and outer shell of *Eutrephoceras dekeyi*; $R^2 = 0.81$. Point labeled “Chamber calcite” represents Sr and O isotopic composition of secondary calcite precipitated in the chambers of the shell.

on visual examination (well-preserved nacre) and X-ray diffraction (“... minimal degree of alteration of aragonite to calcite”, p. 138). They interpreted light $\delta^{18}\text{O}$ values, especially in the ammonite *Placentoceras meeki*, to indicate that this ammonite lived in subsaline conditions, possibly in the upper water column. Our results suggest that this interpretation may have been biased by preservation. For example, specimens of *Placentoceras meeki* analyzed by Tsujita and Westermann (1998) displayed $\delta^{18}\text{O}$ values as light as ~ -9 permil. We measured a similarly light $\delta^{18}\text{O}$ value (-8.4 ‰) in a specimen of *P. meeki* (WI-12, table 1; fig. 11J) with poor preservation (PI = 1).

Variation of Elemental Concentrations with Preservation: Diagenetic Addition of Sr and the Mechanism of Alteration

Prior studies involving isotopic analyses of fossil material have used elemental concentrations and element/Ca ratios to screen samples for preservation (for example, Morrison and Brand, 1986; Brand and Morrison, 1987; McArthur and others, 1994; Holmden and others, 1997; Pagani and Arthur, 1998). Elemental analyses of fossil shell material are compared with those of modern mollusks to develop screening criteria. Indeed, ratios such as Mg/Ca and Sr/Ca are often used in their own right as indicators of environmental parameters such as temperature and salinity, although growth rate of the organism is often a complicating factor (Pilkey and Goodell, 1963; Kinsman and Holland, 1969; de Villiers and others, 1995; Klein and others, 1996a, 1996b; Elderfield and Gansen, 2000; Purton-Hildebrand and others, 2001; Anand and others, 2003; Takesue and van Geen, 2004; Wanamaker and others, 2008; Foster and others, 2008, 2009). The Mg/Ca ratio of modern mollusks ranges from ~ 1 –13 mmol/mol, while that of Sr/Ca spans a smaller range, ~ 1 –2 mmol/mol (Chave, 1954;

Thompson and Chow, 1955; Turekian and Armstrong, 1960; Klein and others, 1996a, 1996b; Takesue and van Geen, 2004; Wanamaker and others, 2008). Most of our samples are from ammonites and nautilids, and perhaps the best point of comparison is modern *Nautilus*. Crick and others (1987) reported Sr and Mg concentrations ranging from ~1600 to ~2400 ppm (Sr/Ca ~ 1.8-2.6) and ~200 to 1300 ppm (Mg/Ca ~ 0.8-5.3), respectively, in four species of *Nautilus*. Our analysis of a single sample of *Nautilus pompilius* is at the low end of these ranges (Sr/Ca = 1.2 and Mg/Ca = 0.5; table 3).

Based on the suite of trace elements measured in the present study, there is no clear trend of element/Ca ratios with preservation, except for Sr/Ca. As shown in figure 6, the Sr/Ca ratio increases as the Preservation Index decreases. For good-to-excellent preservation, the Sr/Ca ratio is in the range of modern mollusks (~2), and at low preservation, it exceeds 3 (fig. 6). This pattern suggests that Sr is added to the carbonate during diagenesis. In general, Sr/Ca decreases as biogenic aragonite is replaced with calcite (Turekian and Armstrong, 1961; Brand and Morrison, 1987). However, Turekian and Armstrong (1961), in a careful study of fossil mollusks (mostly ammonites) from the Fox Hills Formation (South Dakota), noted that Sr concentrations increased from the values observed in pristine shell material (0% calcite) to higher values at low calcite percentages (<~5%) before decreasing as the aragonite recrystallized to calcite on a large scale. Turekian and Armstrong (1961) argued that the increase was due to the addition of Sr to the shell through adsorption in a “reaction layer”. They suggested that reaction layer sites might be located in interstices formed by decomposition of organic material originally incorporated in the shell. Indeed, the interspaces between the nacreous tablets originally had organic matter and are possibilities for such reaction layer sites. They are also the zones in which SEM photographs show fusion of the nacreous tablets as PI decreases (for example, PI = 1-2, fig. 1HJ).

If we assume that Sr is added to the shell as PI decreases, we can estimate the $^{87}\text{Sr}/^{86}\text{Sr}$ associated with the diagenetically-added Sr. The Sr mass balance for the shell is:

$$[\text{Sr}]_m = [\text{Sr}]_s + [\text{Sr}]_{ads} \quad (1)$$

and the isotope balance is:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_m [\text{Sr}]_m = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_s [\text{Sr}]_s + \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{ads} [\text{Sr}]_{ads} \quad (2)$$

where $[\text{Sr}]_{m,s,ads}$ are the Sr concentrations as measured (m) in the sample, in unaltered pristine shell material (s) and that added in reaction layer sites (ads), and $(^{87}\text{Sr}/^{86}\text{Sr})_{m,s,ads}$ are the respective Sr isotope ratios as measured in the sample, in unaltered (pristine) shell and added in reaction layer sites. Combining equations 1 and 2 and solving for $(^{87}\text{Sr}/^{86}\text{Sr})_{ads}$ gives:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{ads} = \frac{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_m [\text{Sr}]_m - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_s [\text{Sr}]_s}{[\text{Sr}]_m - [\text{Sr}]_s} \quad (3)$$

We have applied equation 3 to the data using the average $^{87}\text{Sr}/^{86}\text{Sr}$ and $[\text{Sr}]$ measured in each PI grouping (table 2). For the values in pristine shell material, we use $(^{87}\text{Sr}/^{86}\text{Sr})_s = 0.707648$ (PI = 4.5-5) and $[\text{Sr}]_s = 1680$ ppm. The results give $(^{87}\text{Sr}/^{86}\text{Sr})_{ads}$ ranging from 0.707582 to 0.707032 for PI from ~3 to ~1, respectively (table 2). The calculated values of $(^{87}\text{Sr}/^{86}\text{Sr})_{ads}$ for PI 1 to 3 correspond to $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater

TABLE 3
Trace element data for fossil shell material from the Western Interior Seaway

Specimen	Sample ID	SEM PI	Mg (ppm)	Mn (ppm)	Fe (ppm)	Sr (ppm)	Ba (ppm)	Mg/Ca (mmol/mol)	Mn/Ca (mmol/mol)	Fe/Ca (mmol/mol)	Sr/Ca (mmol/mol)	Ba/Ca (mmol/mol)	Mg/Sr (mol/mol)
WI Series													
<i>J. nodosus</i>	WI-3	4.5	1220	3350	4010	1160	341	5.00	6.09	7.18	1.32	0.25	3.80
<i>B. compressus</i>	WI-8	4.0	820	60	545	2420	2690	3.37	0.11	0.98	2.76	1.96	1.22
<i>B. compressus</i>	WI-9	4.5	306	29	203	1140	164	1.26	0.05	0.36	1.30	0.12	0.95
<i>B. compressus</i>	WI-18	4.0	441	46	432	1100	313	1.81	0.08	0.77	1.26	0.23	1.44
<i>E. dektayi</i>	WI-10	2.5	478	168	143	2670	97	1.97	0.31	0.26	3.05	0.07	0.64
<i>E. dektayi</i>	WI-6	2.0	366	94	262	3030	166	1.51	0.17	0.47	3.46	0.12	0.43
<i>P. meeki</i>	WI-12	1.0	1090	205	300	4530	276	4.47	0.37	0.54	5.16	0.20	0.87
<i>H. brevis</i>	WI-29	2.0	1240	84	1340	4410	779	5.09	0.15	2.40	5.04	0.57	1.01
<i>B. compressus</i>	WI-40A	4.0	1280	29	2510	1410	3280	5.28	0.05	4.50	1.61	2.38	3.34
<i>series</i>	WI-40B	4.0	96	33	83	1300	39	0.39	0.06	0.15	1.48	0.03	0.27
	WI-43	4.5	1160	928	760	2100	193	4.77	1.69	1.36	2.39	0.14	1.98
	WI-44	4.5	462	361	527	1630	52	1.90	0.66	0.94	1.86	0.04	1.02
	WI-45	5.0	1060	134	576	2210	121	4.37	0.24	1.03	2.52	0.09	1.73
I Series													
<i>J. nodosus</i>	I-36	3.5	760	19	605	3160	2470	3.13	0.04	1.08	3.61	1.80	0.90
<i>E. dektayi</i>	I-63	2.0	437	86	373	2850	1300	1.80	0.16	0.67	3.25	0.94	0.55
<i>P. meeki</i>	I-60	3.0	440	207	416	3470	159	1.81	0.38	0.74	3.96	0.12	0.45
<i>Inoceramus</i>	I-61	4.5	466	71	231	1860	91	1.92	0.13	0.41	2.13	0.07	0.90
<i>Nautilus (modern)</i> ¹	5	156	11	28	1020	5	0.64	0.02	0.050	0.050	1.17	0.004	0.54
<i>Nautilus (modern)</i> ²	5	410	nd	nd	1840	nd	1.69	nd	nd	nd	2.12	nd	nd

¹ This study; ² Crick and others (1987); nd = not determined

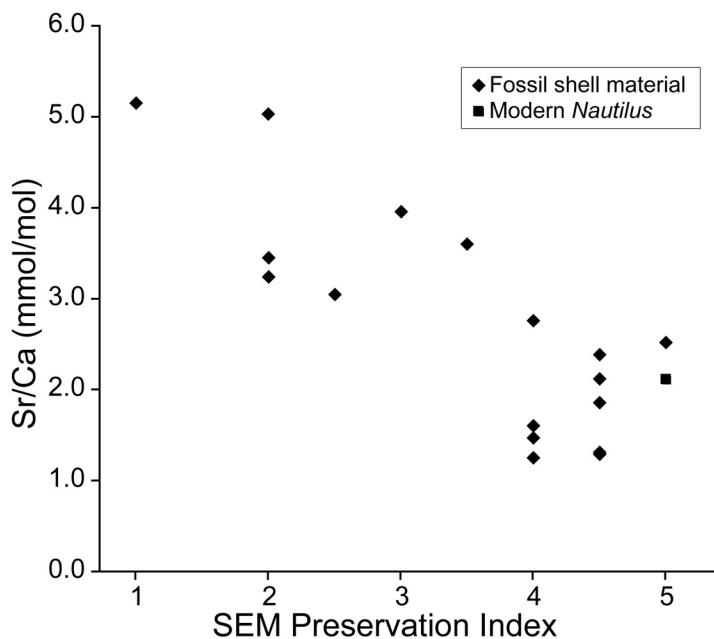


Fig. 6. Sr/Ca (mmol/mol) vs Preservation Index. Values from modern *Nautilus* are plotted at PI = 5 (excellent) for reference (data from this study and Crick and others, 1987).

from ~10 Ma to 80 Ma prior to that of *B. compressus* time (McArthur and others, 2001). Indeed, the different values of ($^{87}\text{Sr}/^{86}\text{Sr}$)_{ads} calculated for PI = 3 (0.707582) versus PI = 1–2 (0.707142–0.707032) may represent diagenetic alteration of the shell material at different times, with small decreases in preservation (to PI = 3) occurring in “early” diagenesis and larger decreases (PI = 1–2) occurring later via interactions of the fossil shell material with groundwater. Weathering of the extensive volcanic ash layers (bentonites) present in the late Cretaceous (Gill and Cobban, 1966) may serve as an additional source of the Sr that is added to the shell material during diagenesis. Such Sr would have a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, and the low calculated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios added to material with the poorest preservation may, in part, reflect this volcanogenic Sr.

The model results and the co-variation of Sr, O and C isotope ratios as preservation decreases suggest a possible mechanism for the alteration of these aragonitic shells. The constraints are that the shell does not show appreciable calcite and the nacreous structure and shell luster remain evident even at the poorest preservation. As well, the SEM images show that interlayer sites between the nacreous tablets are the loci for alteration. We suggest that the “adsorbed” Sr represents the formation of strontianite by epitaxial growth on the shell aragonite. Addition of SrCO_3 to the aragonite shells accounts for the increase of Sr concentration with increasing alteration. The added Sr may be derived from weathering of older sediments enriched in marine carbonate debris (with a lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio). Alternatively, low ratios could be imprinted on groundwater by weathering of volcanic ash layers.

Although the Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ variations observed as preservation decreases can be explained by addition of strontianite, simple mass balance considerations preclude this mechanism as being responsible for most of the decreases in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Instead we suggest that isotopic exchange of O and C in the aragonite with alteration fluids produces the observed trends in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (table 2; fig. 4). We can calculate the fraction of O and C exchanged from:

$$\delta_{PI=5}(1 - f_{exch}) + \delta_{fluid}f_{exch} = \delta_{shell} \quad (4)$$

where $\delta_{PI=5}$ is the $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ in unaltered shell material (excellent preservation), δ_{fluid} is the $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ in the fluid involved in isotopic exchange, f_{exch} is the fraction of O or C exchanged, and δ_{shell} is the $\delta^{18}\text{O}$ or $\delta^{13}\text{C}$ observed in the altered shell. Table 2 shows that there is relatively little variation in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ from PI 5 to 3, but there are marked decreases in PI = 1–2.

We assume that the fluid involved in exchange is meteoric water imprinted with isotopically light C from the decomposition of terrestrial C. Cochran and others (2003) measured a mean $\delta^{18}\text{O}$ of -19 permil in samples of freshwater Unionid mussels from the *Jeletzkytes nebrascensis* ammonite zone of the WIS, and we use that value as δ_{fluid} for $\delta^{18}\text{O}$. The value of δ_{fluid} for C could be as light as -25 permil if the dissolved inorganic carbon reservoir is dominated by C released from terrestrial organic matter. Substituting these values (and the values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ for PI = 5, table 2) in equation 4 gives values of f_{exch} of 14 percent (PI = 2-2.5) and 23 percent (PI = 1-1.5) for O and 20 percent (PI = 2-2.5) and 26 percent (PI = 1-1.5) for C (table 2). Different $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for the fluid involved in alteration would produce different proportions for exchanged C and O. In particular, additions of C from marine carbonate dissolution and marine organic matter decomposition to the dissolved inorganic carbon (DIC) reservoir would produce a $\delta^{13}\text{C}$ for the DIC that is heavier than the value we have used, and the f_{exch} for C would be greater. Although the mechanisms of alteration of the isotope compositions of Sr on the one hand (growth of strontianite) and C and O on the other (isotope exchange) are not identical, the fact that the same fluid is involved can produce correlations between $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$, for example (fig. 5).

Paleoenvironmental Implications

Our results show that shell material with PI > 4 has Sr concentrations < 1700 ppm, and the SEM photographs of these samples suggest that they are minimally altered. These samples have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that range from 0.707502 to 0.707720. Is there paleoenvironmental significance to this range of values? Indeed, the range ($\Delta^{87}\text{Sr}/^{86}\text{Sr} \sim 200 \times 10^{-6}$) is similar to that seen in the *J. nebrascensis* zone (fig. 7). Cochran and others (2003) interpreted the *J. nebrascensis* data to represent paleosalinity variations, but in a setting in which the less-than-fully-marine environment was created by submarine groundwater discharge via a “subterranean estuary” (Moore, 1996, 1999). Such a process is different from surficial estuarine mixing and does not necessarily occur close to shore, although it would occur in near-bottom waters. Of the well preserved specimens analyzed (PI = 4-5), most are samples of *B. compressus*, and the $^{87}\text{Sr}/^{86}\text{Sr}$ values thus represent a range from fully marine to brackish environments. The septa of one specimen of *B. compressus* were sampled sequentially (samples WI-41 to WI-46). Although these represent the later ontogeny of the animal, the Sr isotope ratios suggest that the animal experienced a change from brackish to fully marine conditions. Similarly, the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the ammonite *J. nodosus* (WI-3) and the bivalve *Pteria* (WI-32) suggest that their shell material was formed under less than fully marine conditions. Samples of *Eutrephoceras dekayi* and *Placentoceras meeki* analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$ are rather poorly preserved (PI < 3) and thus no conclusions as to the paleoenvironmental habitats of these animals are possible from the present study. Further analyses of well-preserved samples from a diversity of mollusks are needed to test more fully the paleoenvironmental utility of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

CONCLUSIONS

High resolution scanning electron microscopy is an effective tool for assessing preservation of shell structure in fossil mollusks and predicting the likelihood that information obtained from analyses of $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in the material reflects

conditions in the water in which the shells formed. We have developed a Preservation Index (1 = poor preservation; 5 = excellent preservation) based on high-magnification SEM examination of a shell's outer surface and microstructure. Application of this approach to samples collected inside concretions and as single samples from the late Cretaceous *Baculites compressus* ammonite zone shows the full range of preservation (PI 1 to 5), with no strong links to occurrence of the fossil (that is within concretion or not). Samples from the baculite *B. compressus* tend to be well preserved (PI > 4) while those from the nautilus *Eutrephoceras dekayi* and ammonite *Placentoceras meeki* often display poorer preservation (PI < 3). $^{87}\text{Sr}/^{86}\text{Sr}$ values in the best-preserved material are comparable to independent estimates of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ in *B. compressus* time, but decrease markedly at PI < 3. Sr/Ca increases as preservation quality declines, suggesting that Sr is added to the shell during diagenetic alteration. Values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ also show a trend toward lighter values as PI decreases. Good correlations between strontium and oxygen isotope ratios and between oxygen and carbon isotope ratios suggest that the composition of all three isotopic systems are altered together. Interpretation of the isotope correlation plots as mixing curves shows that the fluids responsible for chamber calcite formation are not those controlling shell alteration. Instead, the process of alteration likely involves interaction of the shell material with groundwater imprinted with a lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and isotopically light O and C. We suggest that alteration involves both epitaxial growth of strontianite on aragonite and isotopic exchange of O and C isotopes between alteration fluids (meteoric water) and shell carbonate.

The range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios observed over different levels of preservation (mean $^{87}\text{Sr}/^{86}\text{Sr}$ 0.707648 to 0.707261 from excellent to poor preservation, respectively) corresponds to a time interval of ~20 Ma on the curve of $^{87}\text{Sr}/^{86}\text{Sr}$ versus time in seawater (McArthur and others, 1994; 2001). Because the evolution of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in seawater has been well documented, strontium isotope stratigraphy has become accepted as an approach to determining ages of fossil marine carbonate material (Smalley and others, 1994; McArthur and others, 2001). Our results indicate that it is imperative to assess textural preservation carefully even in aragonitic shell material before making any inferences on stratigraphic age based on $^{87}\text{Sr}/^{86}\text{Sr}$. As well, efforts to use $\delta^{18}\text{O}$ values to interpret paleohabitat in aragonitic shells must document carefully the shell material's state of preservation.

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