The isotopic record of ocean chemistry and diagenesis preserved in non-luminescent brachiopods from Mississippian carbonate rocks, Illinois and Missouri

JAY L. BANNER   Department of Geological Sciences, University of Texas, Austin, Texas 78712
JONATHAN KAUFMAN   Exxon Production Research Company, P.O. Box 2189, Houston, Texas 77252-2189

ABSTRACT

Fossil brachiopod shells are commonly used as a faithful record of the chemical and isotopic composition of the ancient ocean water in which they grew, owing to their stable mineralogy and their presence in marine strata throughout Phanerozoic time. The utility of these fossils for preserving ocean-water compositions is evaluated through analyses of multiple specimens that grew in contemporaneous sea water at individual stratigraphic horizons in the Mississippian-age Burlington-Keokuk Formation of mid-continent North America. Significant variations in Sr, C, and O isotopic compositions are observed in contemporaneous, non-luminescent shells, indicating that apparently pristine brachiopod shell material has been altered by post-depositional processes of diagenesis. The least-altered compositions at each horizon are used to estimate secular variations of $^{87}Sr/^{86}Sr$ in Early Mississippian ocean water. The estimated rates of change of ocean-water $^{87}Sr/^{86}Sr$ are comparable in magnitude to the rapid Sr isotopic changes documented for Cenozoic ocean water, for which high-frequency glacial cycles are inferred as a driving mechanism. The rigorous assessment of diagenetic effects on the isotopic signatures of marine phases is requisite for the advancement of high-resolution reconstructions of paleo-ocean chemistry.

INTRODUCTION

Geochemical techniques are applied to the study of ancient marine carbonate rocks with the goals of (1) establishing the composition of ancient oceans through the analysis of fossils, marine cements, fluid inclusions, and whole-rock samples (for example, Burke and others, 1982; Holland, 1984; DePaolo and Ingram, 1985; Meyers and Lohmann, 1985; Shaw and Wasserburg, 1985; Popp and others, 1986a, 1986b; Veizer and others, 1986;

Hodell and others, 1989; Capo and DePaolo, 1990); and (2) understanding the nature of diagenetic processes (for example, Land, 1980; Meyers and Lohmann, 1985; Banner and Hanson, 1990). Diagenesis can obscure the original marine composition of all components of a carbonate rock, and if undetected can lead to erroneous conclusions regarding secular variations in ocean chemistry. Brachiopods are commonly used for establishing secular variations in ocean chemistry because they precipitate shells composed of low-Mg calcite, which is more stable during diagenesis than the more common high-Mg calcite and aragonite components of marine carbonate sediments (Veizer and others, 1986; Popp and others, 1986a). Furthermore, cathodoluminescence of carbonate minerals is used as an indicator of alteration, whereby the parts of fossil brachiopod shells that exhibit a lack of cathodoluminescence (that is, non-luminescence) are proposed to preserve the least-altered chemical signatures (Popp and others, 1986b; Cummins, 1992). Rigorous tests of the cathodoluminescence criteria are needed, however, as shown by Rush and Chafetz (1990) and Fouke and others (1993).

A fundamental criterion for any fossil or mineral phase that is proposed to preserve ancient sea-water compositions should be that multiple, contemporaneous samples yield the same isotopic composition. This criterion is particularly applicable to Sr isotopes, because (1) the world's oceans have a high degree of homogeneity of $^{87}Sr/^{86}Sr$ at a given time, as evinced by measurements on Holocene marine carbonate shells and modern sea water (DePaolo and Ingram, 1985; Capo and DePaolo, 1992), and (2) biologic fractionation of Sr isotopes is negligible (see "Sample Selection and Analytical Methods" section below).

The purpose of our study is to apply this criterion to test the utility of fossil brachiopod shells for preserving the isotopic composition

of Sr, C, and O in sea water during the Early Mississippian period (~350 Ma) in the Burlington-Keokuk Formation (BKF) in the mid-continent of North America (Fig. 1). The BKF is of Osagean age and is composed of fossiliferous limestone and fossil-poor dolostone representing subtidal deposition on a shallow shelf with open-marine circulation (Cander and others, 1988; Kaufman and others, 1988). This formation is well suited to the examination of marine components in ancient carbonate rocks because its diagenetic history is well understood. The diagenetic sequence includes multiple episodes of calcite cementation, dolomitization, chertification, and compaction that involved pervasive migration of both meteoric ground waters and warm basinal brines through these strata (Banner and others, 1988; Cander and others, 1988; Kaufman and others, 1988; Kohrt, 1988; Hoff and others, 1988). We have determined the Sr, C, and O isotopic variability in non-luminescent shell calcite from multiple, contemporaneous brachiopod specimens that were collected laterally along a single bedding plane, and from specimens collected from the vertical extent of the formation. These data are used to document measurable isotopic shifts due to diagenesis in apparently well-preserved brachiopods and to discuss implications for reconstructing temporal variations in the composition of Mississippian ocean water.

GEOLOGIC SETTING

Brachiopods were collected from road cuts and quarries in the Mississippian (Osagean) Burlington-Keokuk Formation, a regionally extensive marine carbonate sequence that crops out in the upper Mississippi Valley in Missouri, Illinois, and Iowa (Fig. 1). Biostratigraphic analysis using conodonts, foraminifera, and algae was used to assign a mid-Osagean age to the lower half of the BKF,
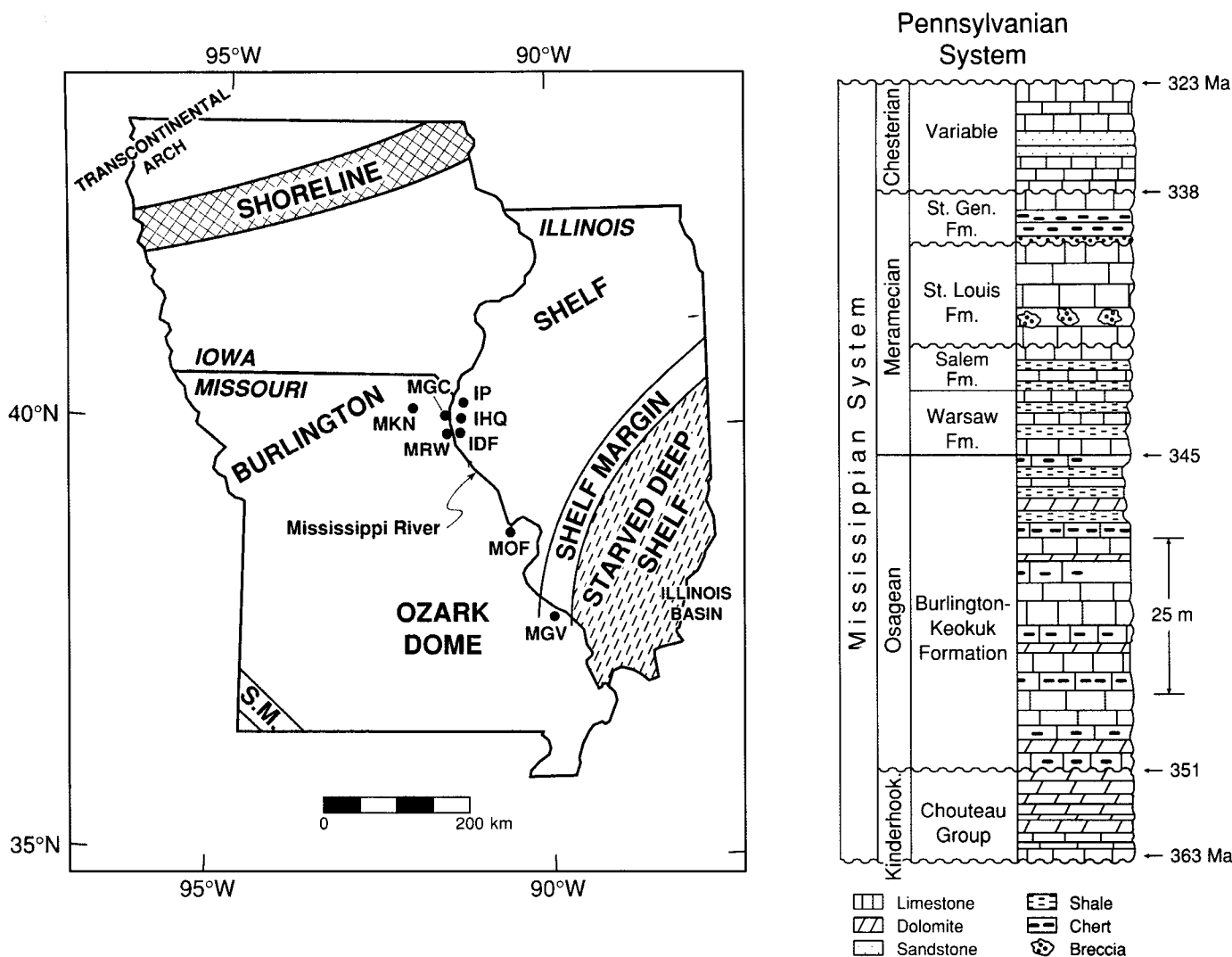
Figure 1. Brachiopod sample localities in the Burlington-Keokuk Formation. Facies interpretations are summarized in Kaufman and others (1988). S.M. = shelf margin. Absolute ages on series boundaries are from Harland and others (1990). Typical uncertainties for these age assignments are ±15 Ma.

and a late Osagean age to the upper half (Brenckle and others, 1974; Collinson and others, 1979). Lowermost Osagean strata are absent in the study area due to erosion or non-deposition. Correlation with European biostratigraphic zones (Rhodes and Austin, 1970) suggests that the middle part of the BKF corresponds to the Tournaisian-Visean boundary (Brenckle and others, 1974). The Osagean series ranges from 354 to 345 Ma on the Harland and others (1990) time scale, from which we estimate that BKF deposition occurred from 351 to 345 Ma.

The BKF was deposited in shallow sea water on a broad, stable, intracratonic shelf (Sable, 1979). This shelf was bordered to the southeast by the Illinois Basin, a large intracratonic depocenter that received more than

4 km of siliciclastic and carbonate sediments during Paleozoic time. The BKF contains a diverse fauna dominated by crinoids and bryozoans, with minor amounts of brachiopods and corals. This fauna is indicative of open-marine circulation. The formation is composed of skeletal packstone and grainstone interbedded with dolomitized mudstone and wackestone. Nodular and bedded chert are common; selective silicification of brachiopods is occasionally observed. The upper half of the BKF is more thinly bedded than the lower half, and it contains interbeds of shale, representing distal tongues of the westwardly advancing Borden Delta (Lineback, 1981). The thickness of the BKF ranges from ~50 m in eastern Missouri to >60 m in Illinois.

Based on extensive field and diagenetic studies, diagnostic evidence for intraformational subaerial exposure (for example, caliche or soil horizons) of the BKF has not been found. Rather, observations support a model of continuous subtidal deposition with minor periods of slow to negligible carbonate production, which are indicated by several horizons enriched in glauconite and fish apatite. The BKF is conformably overlain by Meramecian limestone, dolostone, and shale of the Warsaw and Salem Formations. The earliest post–BKF unconformity is between the Salem and St. Louis Formations (Fig. 1; Harris and Parker, 1964). Major periods of regional exposure and erosion include early Chesterian unconformities and a pre-Pennsylvanian unconformity that is characterized by local

paleokarst development (Daniels, 1986). Maximum burial depths determined from vitrinite reflectance and coal grade in Pennsylvanian strata that rest unconformably on the BKF are <1 km (O. Cox, unpublished data).

DIAGENETIC HISTORY OF THE BURLINGTON-KEOKUK FORMATION

Previous field, petrographic, geochemical, and numerical modeling studies (Banner and others, 1988; Cander and others, 1988; Hoff and others, 1988; Kaufman and others, 1988; Kohrt, 1988; Banner and Hanson, 1990) have been used to reconstruct the fluid-rock interaction history of the BKF, which includes multiple episodes of calcite cementation and dolomitization that occurred on a regional scale. This allows us to assess the potential effects of these diagenetic processes on brachiopod compositions. Following deposition of the BKF and prior to extensive calcite cementation, carbonate mud was selectively replaced by dolomite across the shelf. The near-marine C, O, and Sr isotopic compositions of this early dolomite generation support a dolomitization model involving predominantly Mississippian marine fluids (Banner and others, 1988). Petrographic relations determined using cathodoluminescence indicate that the early dolomite was extensively recrystallized at many localities. The recrystallized dolomite is a more stoichiometric, Fe- and Mn-rich phase characterized by lower $\delta^{18}O$ values, lower Sr concentrations, and higher $^{87}Sr/^{86}Sr$ values compared to its precursor. Model calculations that simulate isotopic exchange during fluid-rock interaction suggest that early dolomite was recrystallized by basinal brines, perhaps derived from the Illinois Basin. These brines migrated into, and extensively interacted with, BKF strata during regional fluid-flow events (Banner and others, 1988).

The first major episode of calcite cementation consists of syntaxial overgrowths on crinoids (Fig. 2) that precipitated prior to or at the pre-Pennsylvanian unconformity (Kaufman and others, 1988). The low $\delta^{13}C$ and $\delta^{18}O$ values of these first-generation cements relative to estimates of Osagean marine calcite compositions suggest that these cements precipitated in a shallow meteoric phreatic lens (Kohrt, 1988). Circulation of meteoric water in the BKF also drove extensive recrystallization of metastable, high-Mg calcite fossils such as crinoids. The convergence of the lowest $\delta^{18}O$ values for crinoids and first-generation calcite cements at −4.5‰ (Kohrt, 1988) is interpreted as an end-member mete-

oric calcite composition. Calcite cementation, compaction, and minor Mississippi Valley–type mineralization (gangue calcite and dolomite, pyrite, sphalerite, and barite) dominate the diagenetic history of the BKF following the pre-Pennsylvanian unconformity. The gangue carbonate minerals record late-stage alteration at relatively high fluid:rock ratios by basinal brines with high $^{87}Sr/^{86}Sr$ values (Banner and others, 1988). Thus, if brachiopods have been altered by any of the fluids represented by the various diagenetic phases in the BKF, then they should have lower $\delta^{18}O$ (and perhaps $\delta^{13}C$) values, lower Sr concentrations, and higher $^{87}Sr/^{86}Sr$ values and higher Fe and Mn concentrations than their original marine compositions.

SAMPLE SELECTION AND ANALYTICAL METHODS

Brachiopods from the suborders *Spiriferacea* and *Productacea* were collected from 12 stratigraphic levels in the BKF in Missouri and Illinois (Table 1). The specimens selected for study consisted of whole, unabraded shells that were interpreted not to have been transported far from their growth positions. These specimens were subject to petrographic selection criteria that required less than 10% luminescent calcite and silica, and the absence of Fe-rich calcite and dolomite. As a further test, five samples that met these criteria were examined by SEM. These samples were found to have well-preserved brachiopod ultrastructures (Popp and others, 1986a; Rush and Chafetz, 1990; Brand, 1991). Non-luminescent and luminescent parts (Fig. 2) of selected shells were sampled separately (0.1 to 5 mg) using a binocular microscope and dental drill. The high purity of the non-luminescent samples selected based on petrographic criteria was confirmed by their low insoluble residue content and their low Rb, Fe, and Mn concentrations and high Sr concentrations (Table 1). HCl-insoluble residue contents for the Sr-isotope sample suite are less than 5%, except for samples MRW2b (9%) and MGV1b (24%).

The inter- and intra-sample isotopic variability of contemporaneous, non-luminescent brachiopods was assessed through multiple analyses of samples from a given stratigraphic horizon by analyzing (1) multiple specimens taken from the same bedding-plane surface of a single hand sample (for example, MKN1a, b, c, d); (2) multiple specimens taken from the same bedding plane surface of two hand samples, spaced 10 m apart at the same stratigraphic horizon (MKN1, MKN3);

(3) different parts of a single specimen (MKN3e); and (4) splits of sample powder from one part of a shell (for example, MKN5d).

Locations of samples within the BKF stratigraphic interval were estimated by lithostratigraphic correlation, for which we conservatively assign an error of ±3 m. Due to the lack of a preserved contact with the underlying formation at three localities (MGC, MGV, and IP), the relative stratigraphic positions of several samples listed in Table 1 were estimated using a calcite cement microstratigraphy. This microstratigraphy is based on the Fe content and cathodoluminescence of zoned cements; some cement zones are restricted to specific vertical intervals of the BKF (Kaufman and others, 1988). This allows strata to be correlated between localities on the basis of cement zones. We estimate the error associated with the microstratigraphy to be ±10 m.

Strontium, Fe, and Mn concentrations were analyzed by inductively coupled plasma atomic emission spectroscopy at the University of Texas at Austin. For the sample sizes used in this study, the analytical precision is ±5% for Sr and ±20% for Fe and Mn. Carbon- and oxygen-isotope analyses were conducted at the University of Michigan following procedures given in Carpenter and others (1991). $\delta^{13}C$ and $\delta^{18}O$ values were determined with a precision of better than ±0.1‰ (1σ).

Strontium-isotope analyses were conducted at the University of Texas using a Finnigan-MAT 261 thermal ionization mass spectrometer in static multi-collection mode. $^{87}Sr/^{86}Sr$ data are corrected for fractionation to $^{86}Sr/^{88}Sr$ = 0.1194 using an exponential law. This correction procedure adjusts measured isotope ratios for mass-dependent fractionation that occurs during analysis and in nature. Therefore, the effects of mass-dependent, biologic isotope fractionation are negligible for the incorporation of Sr isotopes into brachiopods. During the course of this study, 17 analyses of NBS SRM 987 yielded a mean $^{87}Sr/^{86}Sr$ value of 0.710251, with a value for one standard deviation in the measurements (1σ) of ±0.9 × 10^{-5}. Replicate $^{87}Sr/^{86}Sr$ analyses on samples, which were performed on either the same sample powder or the same ion exchange solution typically yielded values for two standard deviations of the mean of ±(1.4 − 1.6) × 10^{-5} (Table 1). Procedural blanks for Sr ranged from 40 to 100 pg and were negligible for the samples analyzed. Rubidium concentrations were determined by isotope dilution. Corrections to the measured
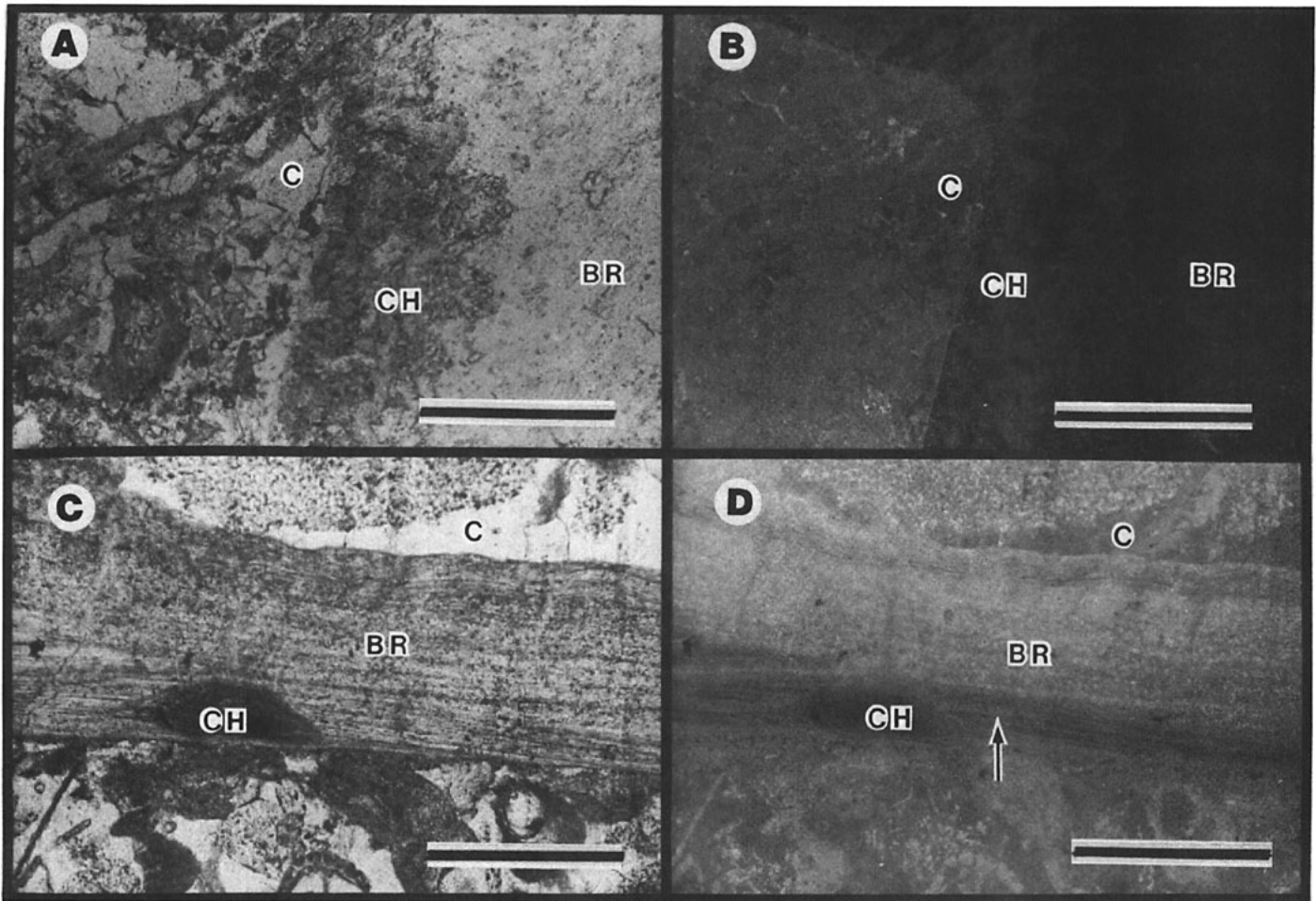
Figure 2. Thin-section photomicrographs of BKF brachiopods.

A. This view of a Spiriferid brachiopod (sample MKN3b) under plane-polarized light shows the selective replacement of calcite at the shell margin by chert (CH); the interior of the shell consists of coarse, prismatic calcite (BR). The matrix surrounding the brachiopod is composed of fine skeletal debris (crinoids, bryozoans) and calcite cements (C). The scale bar is 1 mm.

B. The same view as in A, under cathodoluminescent light. Note that the calcite within the shell interior (BR) is non-luminescent; the fossils and cement (C) in the matrix consist mainly of dull to moderately luminescent calcite. Chert (CH) has a very dull cathodoluminescence. The state of preservation of sample MKN3b is typical for the non-luminescent brachiopods sampled in this study (Table 1). The non-luminescent parts of such samples were selectively microsampled for geochemical analysis.

C. The brachiopod (sample MGC2) in this example is composed of fibrous calcite (BR) and shows partial, localized replacement by chert (CH). Clear syntaxial overgrowth cement (C) terminates against the upper margin of the brachiopod shell. View is under plane-polarized light; scale bar is 0.25 mm.

D. The same field of view as in C, under cathodoluminescent light. The brachiopod shell (BR) contains a mixture of luminescent and non-luminescent calcite that is similar in appearance to syntaxial overgrowth cement (C). The arrow indicates an area where luminescent and non-luminescent shell calcite alternates. The areas of mixed luminescence are representative of the luminescent parts of brachiopods sampled in this study (Table 1).

$^{87}Sr/^{86}Sr$ ratios for the *in situ* decay of ^{87}Rb ranged from 5×10^{-8} to 1×10^{-6}. These corrections were negligible and not applied.

RESULTS

The non-luminescent brachiopod shells have mean $\delta^{18}O$ and $\delta^{13}C$ compositions of $-2.12\%o$ and $4.30\%o$, respectively. These values are similar to those for brachiopods of equivalent age from other localities (Popp and others, 1986a; Brand and Veizer, 1980; Brand, 1982). The BKF brachiopods' C and O isotopic compositions are also similar to independent estimates for Osagean marine calcite compositions (Fig. 3). $\delta^{18}O$ values for non-luminescent brachiopods increase from the base to the top of the BKF (Fig. 4). In contrast, $\delta^{13}C$ values remain nearly constant throughout the vertical extent of the forma-tion (Fig. 4). For a given stratigraphic horizon, C and O isotopic compositions of brachiopods may vary by as much as $0.8\%o$. This variation is well outside of the analytical uncertainty. Regional trends in non-luminescent brachiopod C and O compositions are not observed. $^{87}Sr/^{86}Sr$ values for non-luminescent brachiopods range from 0.707645 to 0.707783, which are comparable to the lowest previously estimated values for Mississippian

TABLE 1. GEOCHEMICAL AND ISOTOPIC DATA FOR BURLINGTON-KEOKUK FORMATION BRACHIOPODS

Sample no.	Species	Strat. ht. (m)	Rb (ppm)	Sr (ppm)	Fe (ppm)	Mn (ppm)	δ^{13}C (‰)	δ^{18}O (‰)	^{87}Sr/^{86}Sr
Non-luminescent									
MKN 1a	SIH	3.1	..	920	25	b.d.	4.45	-2.25	0.707774 ± 14 (2/6)
MKN 1b	SIH	3.1	..	870	33	27	4.95	-2.37	..
MKN 1c	SIH	3.1	..	850	230	b.d.	4.50	-2.72	0.707734 ± 16 (2/4)
MKN 1d	SIH	3.1	..	890	140	b.d.	4.44	-2.57	0.707762 ± 13
MKN 3a	S	3.1	0.021	830	140	b.d.	4.64	-2.39	0.707779 ± 13
MKN 3b	S	3.1	0.006	870	b.d.	b.d.	4.45	-2.28	0.707763 ± 12
MKN 3c	S	3.1	0.011	810	35	b.d.	4.32	-2.44	0.707780 ± 14 (1/2)
MKN 3d	S	3.1	0.003	810	52	34	4.05	-2.30	0.707776 ± 14
MKN 3e	S	3.1	0.005	850	37	b.d.	4.15	-2.13	0.707783 ± 15 (2/3)
MKN 4	S	3.1	..	930	b.d.	b.d.	4.25	-2.25	..
MKN 2	SIH	3.1	..	..	..	..	4.54	-2.61	
MKN 5a	BS	9.2	0.007	900	b.d.	b.d.	4.08	-2.30	0.707774 ± 10
MKN 5b	BS	9.2	0.032	880	b.d.	b.d.	4.44	-2.31	0.707743 ± 10
MKN 5d	BS	9.2	0.005	830	65	b.d.	4.25	-2.39	0.707747 ± 15 (2/5)
MKN 5e	BS	9.2	..	..	..	..	3.70	-2.95	..
MKN 5f	BS	9.2	0.024	830	55	b.d.	3.99	-2.13	0.707752 ± 25 (1/2)
IDF 1	DB	9.2	..	..	..	..	3.95	-2.03	..
MOF 2	BV	18.3	..	..	..	..	4.55	-2.20	..
MRW 5b	SLH	24.4	0.032	920	b.d.	b.d.	4.02	-2.07	0.707741 ± 12
MRW 6	SLH	24.4	0.012	720	b.d.	b.d.	4.48	-2.25	0.707742 ± 13
MRW 9	SLH	24.4	0.007	870	b.d.	b.d.	3.75	-2.32	0.707734 ± 11
MOF 7	S	26.4	..	..	..	..	4.45	-2.08	..
IP 1	SLH	≥27.6	..	..	..	..	4.98	-1.69	..
IHQ 1	AC	36.8	..	..	..	..	4.23	-1.65	..
MGC 1	SKH	-37	..	920	b.d.	b.d.	4.58	-1.59	0.707645 ± 14
MGC 3	SKH	-37	..	980	640	b.d.	4.25	-1.44	0.707673 ± 11
MGV 1a	S	-48	..	830	b.d.	b.d.	4.06	-1.28	0.707654 ± 10
MGV 1b	S	-48	0.116	1400	b.d.	b.d.	3.62	-1.16	0.707655 ± 11
MGV 2	S	-48	..	..	..	..	4.44	-1.45	..
Luminescent									
MRW 1	SF	3.1	..	..	..	..	3.09	-4.67	..
MRW 2a	SXH	3.1	..	..	..	..	3.12	-4.50	..
MRW 2b	SXH	3.1	0.025	440	83	120	2.49	-4.56	0.707986 ± 12
MRW 2c	SXH	3.1	..	330	150	95	3.37	-4.05	0.707953 ± 13
MRW 3a	SXH	3.1	..	..	..	..	2.68	-4.91	..
MKN 5g	BS	3.1	..	..	..	..	3.30	-3.52	..
MRW 15	S	5.5	..	..	..	..	2.84	-5.46	..
MRW 10	SGH	21.4	..	..	..	..	3.22	-4.13	..
MOF 4	S	21.4	..	..	..	..	3.08	-6.63	..
MGC 2	CI	-31	..	..	..	..	3.54	-3.26	..
Modern brachiopods				739-2150	80-276	10-47			
Permo-Carb. brachiopods				420-1800	<1-405	<1-65			

Key to column headings:

Sample no.: Locality information given in Kaufman and others (1988) and Cander and others (1988). Upper-case letters denote eight quarry and roadcut localities, numbers denote individual hand samples, and lower-case letters denote multiple brachiopod specimens within a given hand sample. Samples denoted as luminescent have >10% luminescent calcite. Range for modern and Permo-Carboniferous brachiopods from Popp and others (1986a).

Species as follows: SIH, *Spirifer incertus* Hall; S, *Spirifer* sp.; BS, *Brachthyris suborbicularis*; DB, *Dictyoclostus burlingtonensis*; BV, *Buxtonia viminalis*; SLH, *Spirifer logani* Hall; AC, *Avonia concentrica*; SKH, *Spirifer keokuk* Hall; SXH, *Spirifer imbrex* Hall; SGH, *Spirifer grimesi* Hall; CI, *Chonetes illinoisensis*.

Strat. ht.: Stratigraphic height in meters above base of the BKF. Hand samples MKN1 and MKN3 were spaced 10 m apart at the 3.1 m level. Samples in upper BKF, above 27 m height, are positioned using cathodoluminescent microstratigraphy, as discussed in text.

Detection limits are 20 ppm for Fe and Mn. b.d., below detection limit. ··, not analyzed. δ^{13}C and δ^{18}O values relative to PDB standard. Sr isotope values given as ^{87}Sr/^{86}Sr ± $2\sigma_m$ for the last two significant figures. Numbers in parentheses after $2\sigma_m$ value [for example, (2/4)] indicate the number of separate fractions of sample analyzed (= 2) and the number of mass spectrometer analyses of these fractions (= 4), the mean and $2\sigma_m$ of which are reported here. No parentheses indicates one analysis, for which within-run statistics for 65–80 ratios are given. Separate fractions for MKN3e are for different parts of the same shell; separate fractions for other samples are for splits of micro-sampled powder from one part of a shell.

sea water (Burke and others, 1982; Popp and others, 1986b). The non-luminescent brachiopod isotope data do not show any species dependence or marked intra-sample variability. Brachiopods from the uppermost beds of the formation (37- and 48-m intervals) have ^{87}Sr/^{86}Sr values that are up to 1.4 × 10^{-4} lower than values for those from lower BKF strata (Fig. 4). ^{87}Sr/^{86}Sr variations are also observed within individual stratigraphic horizons (Fig. 4). Most notably, nine non-luminescent brachiopod samples from the 3.1-m level have a range of 4.9 × 10^{-5} in ^{87}Sr/^{86}Sr. This range is larger than (1) the analytical uncertainty for a brachiopod analysis and (2) the range of ^{87}Sr/^{86}Sr values for Holocene marine carbonate shells (Fig. 4).

Luminescent brachiopods are characterized by lower δ^{18}O and δ^{13}C and higher ^{87}Sr/^{86}Sr values, and lower Sr and higher Mn concentrations, relative to non-luminescent shells (Table 1 and Figs. 3 and 5). Their C and O isotopic compositions overlap the range of values found in crinoids and syntaxial overgrowth cements from the BKF (Kohrt, 1988). Regional and stratigraphic trends in isotopic compositions are not observed.

EFFECTS OF SAMPLING AND DIAGENESIS ON BRACHIOPOD ISOTOPIC COMPOSITIONS

Microsampling of brachiopod shells may yield mixtures of original, non-luminescent

brachiopod-shell calcite and diagenetic calcite that precipitated as cement in fractures and pores within the shells. Such two-component mixing can potentially account for the isotopic variations observed in non-luminescent samples within and between stratigraphic horizons, but it would require 30% to 50% of the diagenetic end member to produce a (4 to 8) × 10^{-5} shift in a brachiopod's ^{87}Sr/^{86}Sr value (Fig. 5). This amount of luminescent diagenetic calcite is far greater than the <10% observed in the non-luminescent shells sampled. Furthermore, luminescent and non-luminescent cements in the BKF have low Sr contents (<150 ppm; Grams, 1987); therefore, mixing of diagenetic calcite and original shell calcite will produce samples with lower Sr contents and higher ^{87}Sr/^{86}Sr values than the original shell calcite. The non-luminescent brachiopod data (Table 1) are not consistent with this mixing model.

A comparison of data for luminescent and non-luminescent brachiopod samples indicates that diagenetic alteration of shell calcite produces an increase in ^{87}Sr/^{86}Sr values and Mn concentrations and a decrease in δ^{18}O and δ^{13}C values and Sr concentrations (Table 1 and Figs. 3, 5). These isotopic and trace-element shifts are consistent with those found in regionally extensive diagenetic calcite and dolomite in the BKF (Banner and others, 1988; Kaufman and others, 1988; Kohrt, 1988). The most likely explanation for the Sr isotopic variability in non-luminescent shell material from the same bedding plane is the alteration of brachiopod-shell calcite by fine-scale, fabric-preserving, dissolution-reprecipitation (recrystallization) processes. In this case, diagenesis does not necessarily change the cathodoluminescent character of the shell and, moreover, apparently well-preserved brachiopod-shell calcite may not record a primary ocean-water Sr isotopic signature. This conclusion is consistent with C-O isotopic variations found in Devonian non-luminescent brachiopods (Rush and Chafetz, 1990). Minor diagenetic alteration of the BKF brachiopods could have produced the Sr isotopic heterogeneity observed *within* individual bedding planes. In this model, the lowest ^{87}Sr/^{86}Sr value at a given stratigraphic level represents the ^{87}Sr/^{86}Sr value of sea water at the time of deposition. The potential roles of three types of diagenetic fluids are evaluated below: basinal brines, sea water, and meteoric ground water. Limited extents of recrystallization of BKF brachiopods by basinal brines with high ^{87}Sr/^{86}Sr values, high Sr/Ca ratios, and high Sr and Ca contents (for example, 300 ppm Sr; 64,800 ppm Ca; δ^{18}O =
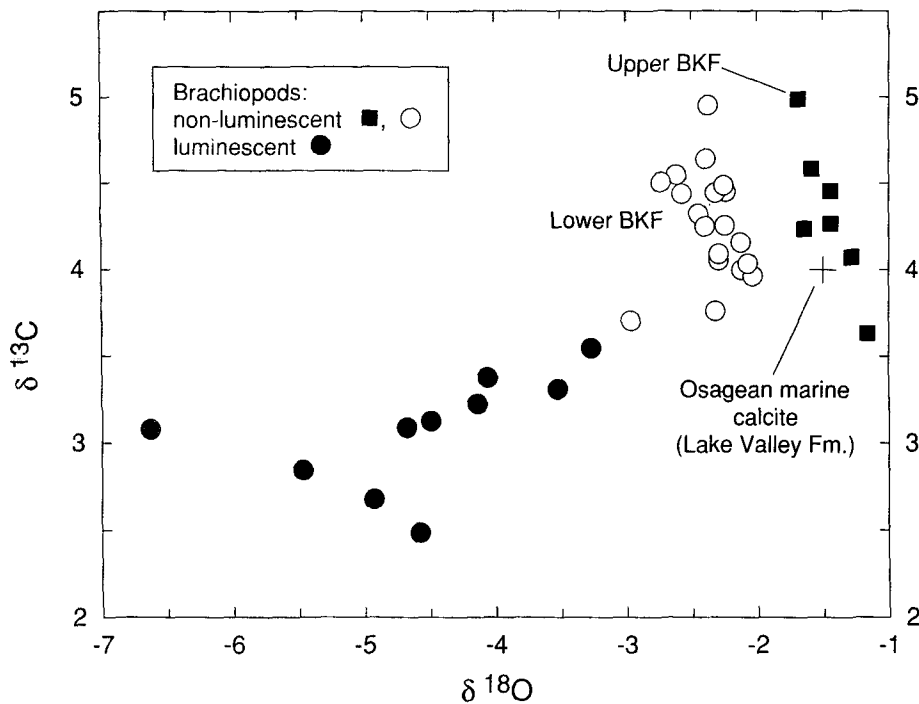
Figure 3. Carbon-oxygen isotopic covariations in non-luminescent and luminescent Burlington-Keokuk brachiopods. Osagean marine calcite isotopic compositions are based on isotopic trends for crinoids and marine and meteoric calcite cements from the Lake Valley Formation, New Mexico (Meyers and Lohmann, 1985). Upper BKF samples are those from above the 27-m interval.

$-2\%o$ SMOW; $^{87}Sr/^{86}Sr = 0.70950$; T = 60 °C) could produce a range of Sr isotopic compositions in the shell calcite without significantly altering $\delta^{18}O$ values or Sr, Fe, and Mn concentrations (Banner and Hanson, 1990). Diagenesis involving such a high-$^{87}Sr/$ ^{86}Sr brine has been shown to account for isotopic variations in regionally altered dolomite in the BKF (Banner and others, 1988). Alteration of the brachiopods by younger sea water with a high $^{87}Sr/^{86}Sr$ value (>0.7078) could also account for the brachiopod isotopic data, in a manner similar to that of the brine composition. Such a process would have had to have occurred at least 10 m.y. after deposition of the BKF, when sea water had an $^{87}Sr/^{86}Sr$ value of greater than 0.7078 (Burke and others, 1982). In contrast, water-rock interaction between meteoric ground water and brachiopods would shift all shell calcite to a common $\delta^{18}O$ value before any significant change in $^{87}Sr/^{86}Sr$ occurred (Banner and Hanson, 1990). This is clearly not the case for the BKF brachiopods (Fig. 5).

Diagenetic alteration must also be considered as an alternative to temporal variations in the composition of Osagean sea water as a means of accounting for the isotopic variations *between* stratigraphic horizons. For example, we may assume that the compositions
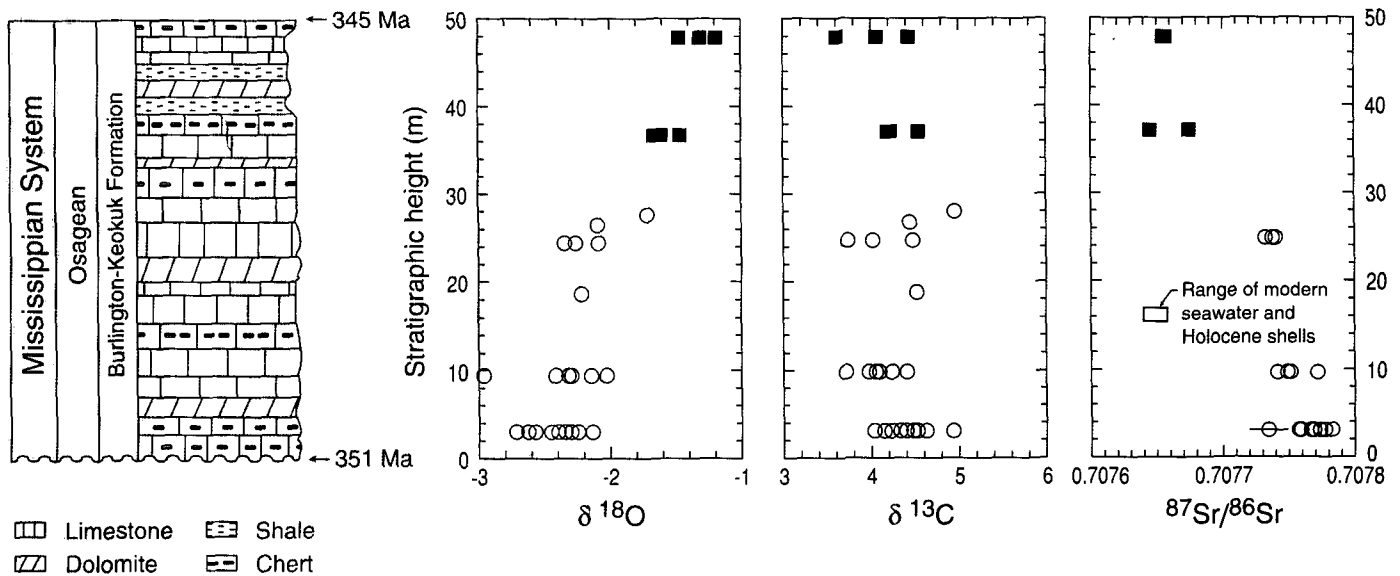

☐☐ Limestone   ▤ Shale
▨ Dolomite   ▱ Chert

Figure 4. Stratigraphic variations of oxygen, carbon, and strontium isotopic compositions of non-luminescent brachiopods within the Burlington-Keokuk Formation. Stratigraphic positions shown as meters above base of the formation. For Sr-isotope data, representative $2\sigma_m$ analytical uncertainty is illustrated for one sample. "Range of modern seawater and Holocene shells" box portrays narrow range of $^{87}Sr/^{86}Sr$ in 23 Holocene marine carbonate shells from six ocean basins (data from DePaolo and Ingram, 1985). The shells yield a mean $^{87}Sr/^{86}Sr$ value of 0.709172 and a standard deviation of 9 × 10^{-6} (adjusted to 0.710251 for SRM 987) and are plotted here at a value of 0.707650 ± 9 (and at an arbitrary stratigraphic height) for comparative purposes. The range of values for the Holocene shells also encompasses values for modern sea-water samples (Capo and DePaolo, 1992). The $^{87}Sr/^{86}Sr$ variations of up to 4.9 × 10^{-5} in non-luminescent brachiopods at a given stratigraphic horizon are therefore not likely to be the result of local Sr isotopic variations in Osagean sea water.
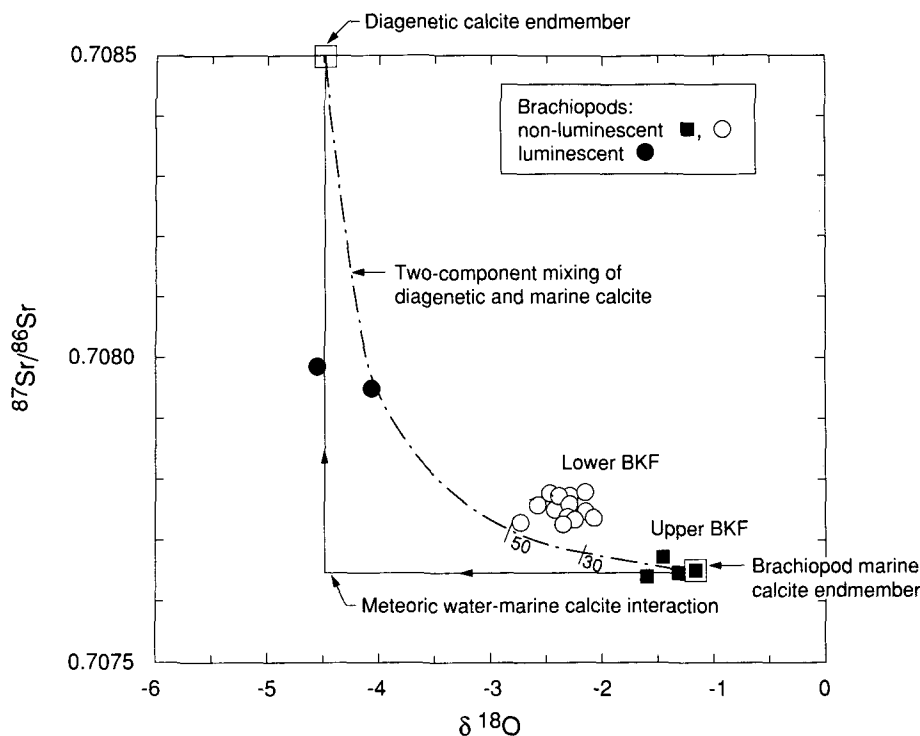
Figure 5. Oxygen-strontium isotopic covariations in Burlington-Keokuk brachiopods. Results of quantitative models (after Banner and Hanson, 1990) illustrate the effects of two different processes on brachiopod isotopic compositions: (1) sampling mixtures of original brachiopod calcite and luminescent diagenetic calcite, portrayed by a two-component mixing line, and (2) recrystallization of brachiopod calcite by meteoric ground waters (meteoric water-marine calcite interaction). Neither process can account for the isotopic variations in the non-luminescent brachiopod samples. The recrystallization process results in rapid oxygen isotopic equilibration between initial brachiopod marine calcite (900 ppm Sr, $\delta^{18}O = -1.2\%o$ PDB and $^{87}Sr/^{86}Sr = 0.70765$) and the meteoric water (0.5 ppm Sr, 20 ppm Ca, $\delta^{18}O = -2.2\%o$ SMOW, $^{87}Sr/^{86}Sr = 0.70850$, T = 25 °C; Kohrt, 1988). Measurable changes in the initial brachiopod's $^{87}Sr/^{86}Sr$ value begin only after oxygen-isotope equilibration with the diagenetic fluid. Recrystallization of brachiopod calcite by a basinal brine can account for the brachiopod isotopic variations, as discussed in text. The luminescent diagenetic calcite end member has 100 ppm Sr, $\delta^{18}O = -4.5\%o$ PDB, and $^{87}Sr/^{86}Sr = 0.70850$ (Kohrt, 1988). Numbers on mixing curve indicate percentage of luminescent end member in mixture.

of the non-luminescent brachiopods from the uppermost part of the formation, which have the highest $\delta^{18}O$ and lowest $^{87}Sr/^{86}Sr$ values (Fig. 4), represent the original isotopic composition of all BKF brachiopods. In this case, all of the non-luminescent brachiopods at the lower stratigraphic intervals, which have higher $^{87}Sr/^{86}Sr$ and lower $\delta^{18}O$ values, have been isotopically reset by varying extents of water-rock interaction. The constant minimum $^{87}Sr/^{86}Sr$ value measured at each of three intervals in the lower BKF (Fig. 4), however, suggests that this alteration mechanism is unlikely, because it would require the same minimum flux of diagenetic fluid at each horizon throughout the lower half of the formation to reset the shells' compositions in this manner.
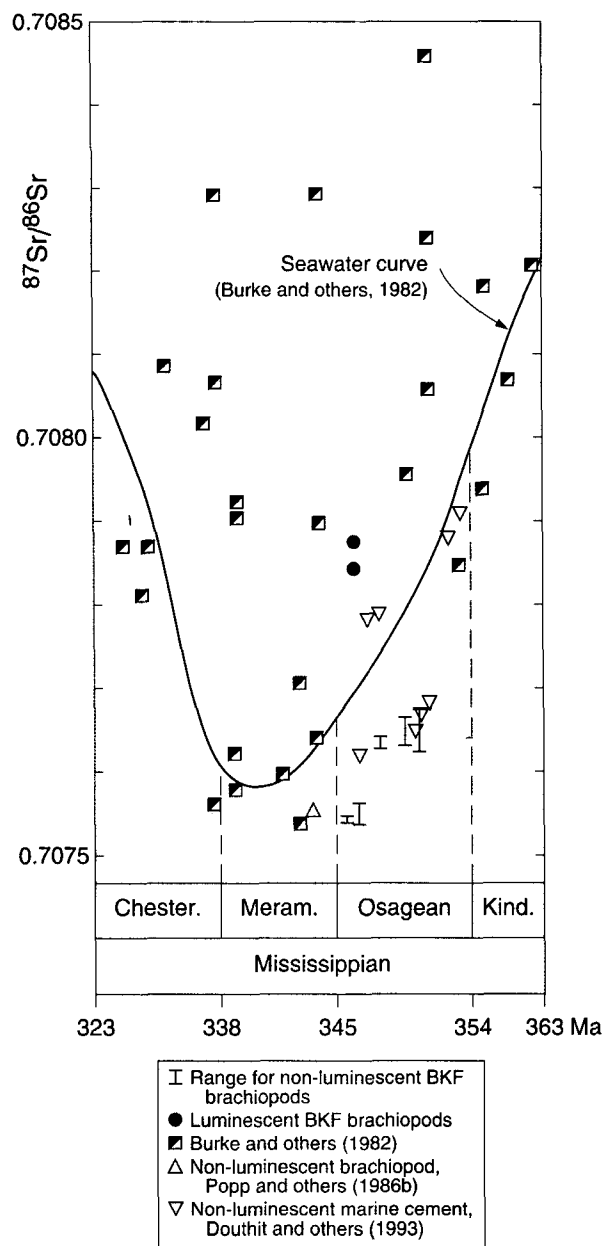
IMPLICATIONS FOR ISOTOPIC VARIATIONS IN MISSISSIPPIAN SEA WATER

Based on the above discussion, we conclude that diagenesis has altered non-luminescent brachiopods and has raised their $^{87}Sr/^{86}Sr$ values to varying extents. Therefore, we use the least altered (lowest) Sr-isotope composition at each stratigraphic horizon to represent the best estimate of the Sr isotopic composition of sea water during deposition at that horizon. The data indicate that a significant decrease in the $^{87}Sr/^{86}Sr$ value of sea water occurred during Osagean time. The lower part of the section records a nearly constant minimum $^{87}Sr/^{86}Sr$ value of 0.70774, with a subsequent decrease in $^{87}Sr/^{86}Sr$ of

greater than 9×10^{-5} over the next 13 m (Fig. 4). If we assume a constant sedimentation rate during the estimated 6 m.y. of BKF deposition, then this 13-m interval was deposited over a period of ~1.5 m.y. This corresponds to a rate of change in sea-water $^{87}Sr/^{86}Sr$ of 6×10^{-5} per m.y. Although the uncertainties on absolute age assignments and sedimentation rates are large for Paleozoic strata (see Fig. 1), this rate of $^{87}Sr/^{86}Sr$ change is comparable to the highest rates observed for the Paleozoic era (Burke and others, 1982). Similar periods of rapid change in the $^{87}Sr/^{86}Sr$ value of sea water (~1×10^{-4} per m.y.) that occurred during the Cenozoic era are attributed to a change in the magnitude of the dissolved Sr flux delivered to the oceans by river water (Capo and DePaolo, 1990). Such results have been used to link increased riverine Sr fluxes to the onset of high-frequency glacioeustatic oscillations during Cenozoic time. A high-resolution record for the Pleistocene indicates that seawater $^{87}Sr/^{86}Sr$ changed at a very rapid rate of $7 \times 10^{-4}/m.y.$ during glacial-interglacial transitions (Clemens et al., 1993). For Phanerozoic time, major tectonic episodes are proposed to have caused (1) increased weathering and riverine Sr fluxes, (2) glacial climates, and (3) major Sr isotopic fluctuations in sea water (Raymo, 1991). The major temporal shift in $^{87}Sr/^{86}Sr$ found in BKF brachiopods corresponds with lithologic changes between the lower and upper BKF (see "Geologic Setting" section above), and with the proposed timing of the onset of a glacial episode during the Mississippian period (Veevers and Powell, 1987). Determining the cause(s) of these correspondences is limited by the short term of our $^{87}Sr/^{86}Sr$ record and by the greater obscurity in the eustatic record for the Mississippian period compared to the Cenozoic era.

The BKF brachiopod data also suggest a previously unrecognized temporal change in the oxygen isotopic composition of Osagean sea water, wherein marine waters attained higher $\delta^{18}O$ values with decreasing age (Fig. 4). Such stable isotopic variability, however, may also be due to the effects of seasonality, biologic isotope fractionation, or diagenesis (Lepzelter and others, 1983; Veizer and others, 1986; Hiebert and others, 1988; Romanek and Grossman, 1989; Grossman and others, 1993). Secular variations in seawater chemistry cannot explain the C and O isotopic heterogeneity found within stratigraphic horizons (Fig. 4); rather, diagenetic, seasonal, or biologic effects must be involved.

Figure 6. Estimated Sr isotopic evolution of Mississippian sea water based on several studies. In order to compare data from these studies, all $^{87}Sr/^{86}Sr$ values shown here have been adjusted to correspond to a value of 0.710140 for the NBS 987 standard. Therefore, the $^{87}Sr/^{86}Sr$ values for the BKF brachiopods are 0.000111 lower here than as presented in Table 1 and Figures 3–5. Individual analyses and the best-estimate sea-water curve are plotted from the study of Burke and others (1982). Ranges for non-luminescent BKF brachiopods from this study consist of multiple analyses at each stratigraphic interval (see Fig. 4).

ographically diverse localities. These uncertainties in age assignments underscore the potential utility of detailed Sr-isotope studies for improving stratigraphic correlations in the Paleozoic era. Additional uncertainties may arise when the relative age of the phase being used as a proxy for marine $^{87}Sr/^{86}Sr$ is not well known, as may be the case for marine calcite cements. Circulation of younger sea water through a carbonate platform may be facilitated by large interconnected pore systems such as neptunian fissures (Kerans and others, 1986; Ward, 1994) or stromatactoid cavities. Precipitation of marine cements in such a flow regime could produce erroneous estimates of sea water $^{87}Sr/^{86}Sr$, depending on the differences in age between the host sediment and the precipitating marine pore fluid, as demonstrated by Saller and Koepnick (1990).

SUMMARY

The results of this study indicate that the Sr isotopic composition of presumed pristine brachiopod-shell calcite has been altered by diagenetic fluids. Sampling multiple marine components along bedding planes, as well as diagenetic components, may be required to unravel the effects of diagenetic overprinting on original marine isotopic compositions. In this study, strontium isotopes are a more sensitive indicator of fine-scale diagenetic processes than are stable-isotope or trace-element parameters. Using the multiple-component approach, a higher degree of confidence may be applied to data used for high-resolution isotope chronostratigraphy. The Early Mississippian period appears to have been a time of rapid decrease in sea-water $^{87}Sr/^{86}Sr$ values, similar in magnitude to the rates of increase in sea-water $^{87}Sr/^{86}Sr$ for the Cenozoic era. Further study will determine how common such rapid fluctuations in the Sr isotopic composition of sea water were during other intervals of Paleozoic time.

ACKNOWLEDGMENTS

COMPARISONS WITH AGE-EQUIVALENT MARINE CARBONATES

We compare the Sr isotopic data for non-luminescent BKF brachiopods with (1) the Mississippian interval of the secular curve for Phanerozoic sea-water $^{87}Sr/^{86}Sr$ (Burke and others, 1982), which is based on data for marine carbonate and evaporite rocks; (2) data for non-luminescent, low-Mg calcite marine cements from Irish Waulsortian mud mounds; and (3) an analysis of a non-luminescent brachiopod from England (Fig. 6). The BKF data suggest two $^{87}Sr/^{86}Sr$ plateaus in sea water during the late Osagean series, as indicated by the clustering of Sr isotopic compositions in the lower and upper parts of the formation. A relatively rapid 0.00009 decrease in sea-water $^{87}Sr/^{86}Sr$ marks the transition between the plateau values. Burlington-Keokuk brachiopods record lower $^{87}Sr/^{86}Sr$ values than previously reported for the latter part of Osagean time. A sinusoidal variation in Osagean sea water $^{87}Sr/^{86}Sr$ values, as interpreted from measurements on marine cements (Douthit and others, 1993), is not found in the BKF data.

The lack of agreement among the different data sets stems in part from the uncertainty in assigning absolute ages to samples from ge-

the Geology Foundation of the University of Texas.

REFERENCES CITED

Banner, J. L., and Hanson, G. N., 1990, Calculation of simultaneous trace element and isotopic variations during water-rock interaction with applications to carbonate diagenesis: Geochimica et Cosmochimica Acta, v. 54, p. 3123–3137.

Banner, J. L., Hanson, G. N., and Meyers, W. J., 1988, Water-rock interaction history of regionally extensive dolomites of the Burlington-Keokuk Formation (Mississippian): Isotopic evidence, in Shukla, V., and Baker, P. A., eds., Sedimentology and geochemistry of dolostones: Society of Economic Paleontologists and Mineralogists Special Publication, v. 43, p. 97–113.

Brand, U., 1982, The oxygen and carbon isotope composition of Carboniferous fossil components: Sea-water effects: Sedimentology, v. 29, p. 139–147.

Brand, U., 1991, Strontium isotope diagenesis of biogenic aragonite and low-Mg calcite: Geochimica et Cosmochimica Acta, v. 55, p. 505–513.

Brand, U., and Veizer, J., 1980, Chemical diagenesis of a multicomponent carbonate system—1: Trace elements: Journal of Sedimentary Petrology, v. 50, p. 1219–1236.

Brenckle, P., Lane, R. H., and Collinson, C., 1974, Progress toward reconciliation of Lower Mississippian conodont and foraminiferal zonations: Geology, v. 2, p. 433–436.

Burke, W. H., Denison, R. E., Hetherington, E. A., Koepnick, R. B., Nelson, H. F., and Otto, J. B., 1982, Variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time: Geology, v. 10, p. 516–519.

Cander, H. S., Kaufman, J., Daniels, L. D., and Meyers, W. J., 1988, Regional dolomitization of shelf carbonates in the Burlington-Keokuk Formation (Mississippian), Illinois and Missouri: Constraints from cathodoluminescent zonal stratigraphy, in Shukla, V., and Baker, P. A., eds., Sedimentology and geochemistry of dolostones: Society of Economic Paleontologists and Mineralogists Special Publication, v. 43, p. 129–144.

Capo, R. C., and DePaolo, D. J., 1990, Seawater strontium isotope variations from 2.5 million years ago to the present: Science, v. 249, p. 51–55.

Capo, R. C., and DePaolo, D. J., 1992, Homogeneity of Sr isotopes in the oceans: Eos (American Geophysical Union Transactions), v. 73, no. 43, p. 272.

Carpenter, S. J., Lohmann, K. C., Holden, P., Walter, L. M., Huston, T. J., and Halliday, A. N., 1991, $\delta^{18}O$ values, $^{87}Sr/^{86}Sr$ and Sr/Mg ratios of Late Devonian abiotic marine calcite: Implications for the composition of ancient seawater: Geochimica et Cosmochimica Acta, v. 55, p. 1991–2010.

Clemens, S. C., Farrell, J. W., and Gromet, L. P., 1993, Synchronous changes in seawater strontium isotope composition and global climate: Nature, v. 363, p. 607–610.

Collinson, C., Norby, R. D., Thompson, T. L., and Baxter, J. W., 1979, Stratigraphy of the Mississippian stratotype—Upper Mississippi Valley, U.S.A.: International Congress of Carboniferous Stratigraphy and Geology, 9th, Field Trip 8 Guidebook: Urbana, Illinois, Illinois State Geological Survey, 109 p.

Cummins, D. I., 1992, The strontium isotopic composition of Lower Carboniferous seawater [Ph.D. dissert.]: Cambridge, U.K., Cambridge University, 232 p.

Daniels, L. D., 1986, Diagenesis and paleokarst of the Burlington-Keokuk Formation (Mississippian), central and southeast Missouri [M.S. thesis]: Stony Brook, New York, State University of New York, 403 p.

DePaolo, D. J., and Ingram, B. L., 1985, High-resolution stratigraphy with strontium isotopes: Science, v. 227, p. 938–941.

Douthit, T., Meyers, W. J., and Hanson, G. N., 1993, Non-monotonic variation of seawater $^{87}Sr/^{86}Sr$ across the Ivorian/Chadian boundary (Mississippian, Osagean): Evidence from marine cements within the Irish Waulsortian Limestone: Journal of Sedimentary Petrology, v. 63, p. 539–549.

Fouke, B. W., Beets, C. J., Meyers, W. J., and Hanson, G. N., 1993, Evaluation of $^{87}Sr/^{86}Sr$ chronostratigraphy with unaltered, partially altered and completely altered oyster and brachiopod shells, Seroe Domi Formation, Curacao, Netherlands Antilles: American Association of Petroleum Geologists Annual Convention Program, p. 103 [abs.], New Orleans, Louisiana.

Grams, J. C., 1987, Trace element geochemistry of calcite cement in the Burlington-Keokuk Formation, southeastern Iowa [M.S. thesis]: Stony Brook, New York, State University of New York, 193 p.

Grossman, E. L., Mii, H.-S., and Yancey, T. E., 1993, Stable isotopes in Late Pennsylvanian brachiopods from the United States: Implications for Carboniferous paleoceanography: Geological Society of America Bulletin, v. 105, p. 1284–1296.

Harland, W. B., Cox, A. B., Armstrong, R. L., Craig, L. E., Smith, A. G., and Smith, D. G., 1990, A geologic time scale: Cambridge, U.K., Cambridge University Press, 132 p.

Harris, S. E., and Parker, M. C., 1964, Stratigraphy of the Osage Series in southeastern Iowa: Iowa Geological Survey Report of Investigations I, 52 p.

Hiebert, R. N., Carpenter, S. J., and Lohmann, K. C., 1988, $\delta^{18}O$ and $\delta^{13}C$ variation in recent brachiopods: Implications for the use of brachiopods as indicators of paleo-ocean chemistry: Society of Economic Paleontologists and Mineralogists Annual Midyear Meeting, v. 5, p. 25 [abs.], Columbus, Ohio.

Hodell, D. A., Mueller, P. A., McKenzie, J. A., and Mead, G. A., 1989, Strontium isotope stratigraphy and geochemistry of the late Neogene ocean: Earth and Planetary Science Letters, v. 92, p. 165–178.

Hoff, J. A., Hanson, G. N., and Meyers, W. J., 1988, U-Th-Pb systematics in dolomites and whole-rock dolostones from Burlington-Keokuk Formation, Iowa, Illinois, and Missouri: American Association of Petroleum Geologists Bulletin, v. 72, p. 198.

Holland, H. D., 1984, The chemical evolution of the atmosphere and oceans: Princeton, New Jersey, Princeton University Press, 582 p.

Kaufman, J., Cander, H. S., Daniels, L. D., and Meyers, W. J., 1988, Calcite cement stratigraphy and cementation history of the Burlington-Keokuk Fm. (Mississippian), Illinois and Missouri: Journal of Sedimentary Petrology, v. 58, p. 312–326.

Kerans, C., Hurley, N. F., and Playford, P. E., 1986, Marine diagenesis in Devonian reef complexes of the Canning Basin, Western Australia, in Schroeder, J. H., and Purser, B. H., Reef diagenesis: Berlin, Germany, Springer-Verlag, p. 357–380.

Kohrt, K. A., 1988, Carbon and oxygen isotopic compositions of crinoids and calcite cements, Burlington-Keokuk Formation (Mississippian), southeastern Iowa and western Illinois [M.S. thesis]: Stony Brook, New York, State University of New York, 270 p.

Land, L. S., 1980, The isotopic and trace element geochemistry of dolomite: The state of the art, in Zenger, D. H., Dunham, J. B., and Ethington, R. L., eds., Concepts and models of dolomitization: Society of Economic Paleontologists and Mineralogists Special Publication, v. 28, p. 87–110.

Lepzelter, C. G., Anderson, T. F., and Sandberg, P. A., 1983, Stable isotope variations in modern articulate brachiopods [abs.]: American Association of Petroleum Geologists Bulletin, v. 67, p. 500–501.

Lineback, J., 1981, The eastern margin of the Burlington-Keokuk (Valmeyeran) carbonate bank in Illinois: Illinois Geological Survey Circular 520, 24 p.

Meyers, W. J., and Lohmann, K. C., 1985, Isotope geochemistry of regionally extensive calcite cement zones and marine components in Mississippian limestones, New Mexico, in Schneiderman, N., and Harris, P. M., eds., Carbonate cements: Society of Economic Paleontologists and Mineralogists Special Publication, v. 36, p. 223–240.

Popp, B. N., Anderson, T. F., and Sandberg, P. A., 1986a, Brachiopods as indicators of original isotopic compositions in some Paleozoic limestones: Geological Society of America Bulletin, v. 97, p. 1262–1269.

Popp, B. N., Podosek, F. A., Brannon, J. C., Anderson, T. F., and Pier, J., 1986b, $^{87}Sr/^{86}Sr$ ratios in Permo-Carboniferous sea water from analyses of well-preserved brachiopod shells: Geochimica et Cosmochimica Acta, v. 50, p. 1321–1328.

Raymo, M. E., 1991, Geochemical evidence supporting T. C. Chamberlin's theory of glaciation: Geology, v. 19, p. 344–347.

Rhodes, F.H.T., and Austin, R. L., 1970, Carboniferous conodont faunas of Europe, in Sweet, W. C., and Bergstrom, S. M., eds., Symposium on Conodont Biostratigraphy: Geological Society of America Memoir 127, p. 317–352.

Romanek, C. S., and Grossman, E. L., 1989, Stable isotope profiles of *Tridacna maxima* as environmental indicators: Palios, v. 4, p. 402–413.

Rush, P. F., and Chafetz, H. S., 1990, Fabric-retentive, non-luminescent brachiopods as indicators of original $\delta^{13}C$ and $\delta^{18}O$ composition: A test: Journal of Sedimentary Petrology, v. 60, p. 968–981.

Sable, E. G., 1979, Eastern Interior Basin, in Craig, L. C., and Connor, C. W., eds., Paleotectonic investigations of the Mississippian System in the United States, Part I: Introduction and regional analyses of the Mississippian System: U.S. Geological Survey Professional Paper 1010-E, p. 59–106.

Saller, A. H., and Koepnick, R. B., 1990, Eocene to early Miocene growth of Enewetak Atoll: Insight from strontium-isotope data: Geological Society of America Bulletin, v. 102, p. 381–390.

Shaw, H. F., and Wasserburg, G. J., 1985, Sm-Nd in marine carbonates and phosphates: Implications for Nd isotopes in seawater and crustal ages: Geochimica et Cosmochimica Acta, v. 49, p. 503–518.

Veevers, J. J., and Powell, C. McA., 1987, Late Paleozoic glacial episodes in Gondwanaland reflected in transgressive-regressive depositional sequences in Euramerica: Geological Society of America Bulletin, v. 98, p. 475–487.

Veizer, J., Fritz, P., and Jones, B., 1986, Geochemistry of brachiopods: Oxygen and carbon isotopic records of Paleozoic oceans: Geochimica et Cosmochimica Acta, v. 50, p. 1679–1696.

Ward, W. B., 1994, Platform evolution and diagenesis of Frasnian carbonate platforms, Napier Range, Canning Basin, Western Australia [Ph.D. dissert.]: Stony Brook, New York, State University of New York, 540 p.