Integrated Sr isotope variations and sea-level history of Middle to Upper Cambrian platform carbonates: Implications for the evolution of Cambrian seawater $^{87}Sr/^{86}Sr$

Isabel P. Montañez Department of Earth Sciences, University of California, Riverside, California 92521
Jay L. Banner Department of Geological Sciences, University of Texas, Austin, Texas 78712
David A. Osleger Department of Earth Sciences, University of California, Riverside, California, 92521
Lars E. Borg Department of Geological Sciences, University of Texas, Austin, Texas 78712
Paula J. Bosserman Department of Soil and Environmental Sciences, University of California, Riverside, California 92521

ABSTRACT

A high-resolution Sr isotope study of Middle to Upper Cambrian platform carbonates of the southern Great Basin significantly refines the structure of the existing seawater Sr isotope curve. Samples were selected using rigorous stratigraphic, petrographic, and geochemical criteria in order to minimize the effects of diagenetic alteration and contamination from noncarbonate components. Highest seawater $^{87}Sr/^{86}Sr$ values over the past 2 b.y. are constrained to <0.7093 and occurred during the latest Middle Cambrian to earliest Late Cambrian. Integrated with published Cambrian seawater $^{87}Sr/^{86}Sr$ values, these new data record the culmination of an increasing trend in seawater $^{87}Sr/^{86}Sr$ beginning in Early Cambrian time. This trend is interpreted to reflect increasing flux and/or isotopic ratio of riverine Sr delivered to Cambrian oceans in response to Pan-African orogenesis and attendant enhanced chemical weathering. High-resolution changes in seawater $^{87}Sr/^{86}Sr$ values are superimposed on the longer-term trend. Correlation between $^{87}Sr/^{86}Sr$ values and sea level leads us to propose a model that links changes in weathering rates and riverine Sr flux with variations in exposed continental surface area related to short-term (1–5 m.y.) sea-level events during greenhouse times.

INTRODUCTION

Secular variations in late Paleozoic through Cenozoic seawater $^{87}Sr/^{86}Sr$ values at the scale of 10^6 to 10^8 yr have proven to be a powerful chronostratigraphic tool for post-middle-Paleozoic stratigraphic successions and provide information on the hydrologic cycle of Sr and on the rates of large-scale processes (e.g., orogenesis, climatic variations, eustasy, weathering) that controlled the isotopic evolution of ancient oceans. In contrast, seawater $^{87}Sr/^{86}Sr$ variations during the early Paleozoic, and especially the Cambrian, remain poorly documented. The recent construction of a detailed seawater $^{87}Sr/^{86}Sr$ database for pre-Middle Cambrian time (Derry et al., 1989, 1994; Kaufman et al., 1993) highlights the large degree of scatter in published Middle to Late Cambrian $^{87}Sr/^{86}Sr$ values (0.7089 to 0.7104) and delineates a significant gap in a portion of the seawater secular Sr isotope curve for the Middle Cambrian. This scatter reflects limitations commonly associated with extracting a seawater Sr isotope signal from ancient carbonates, including (1) diagenetic alteration of samples, (2) contamination by radiogenic ^{87}Sr leached from detrital siliciclastics during sample dissolution, and (3) incorporating data from geographically separate, partial sections with limited chronostratigraphic resolution.

We present the results of a high-resolution Sr isotope study of Middle to Upper Cambrian carbonates of the Bonanza King Formation of the southern Great Basin. These strata provide a unique opportunity to test the Sr isotope evolution of Middle Cambrian seawater given their excellent lateral (0.5 to >1 km), vertical (400 to 1100 m), and temporal (5 to 10 m.y.) continuity, along with a well-defined relative sea-level history. These results significantly refine the structure of the existing Sr isotope curve throughout Middle to earliest Late Cambrian time. When integrated with other Cambrian data, our results may enhance chronostratigraphic resolution and provide important clues regarding the timing and magnitude of Cambrian orogenic events. Integration of our high-resolution Sr isotope data with the Middle to Late Cambrian accommodation history suggests that eustatic changes during greenhouse times may be a viable mechanism for producing short-term variations in the Sr isotopic composition of paleooceans.

GEOLOGIC SETTING AND TIME CONTROL

Middle to Upper Cambrian carbonates of the Banded Mountain Member of the Bonanza King Formation range from 400 m in thickness at the craton margin near Las Vegas, Nevada, to 1100 m on the outer shelf, located 250 km to the northwest in eastern California. Banded Mountain Member carbonates exhibit several superimposed scales of shallowing-upward cyclicity ranging from individual metre-scale peritidal and subtidal cycles to depositional sequences that are tens to hundreds of metres thick. Cycle stacking patterns defined by systematic lithofacies and thickness variations define five depositional sequences, each recording relative sea-level events of 1 to 3 m.y. duration (Montañez and Osleger, 1993). Biostratigraphic control is based on trilobite zonation but has limited temporal resolution (Fig. 1).

SAMPLE SELECTION AND ANALYTICAL METHODS[1]

More than 150 carbonate samples were collected from a continuous (830 m) stratigraphic section of the Banded Mountain Member at Indian Ridge, in the Spring Mountains, southern Nevada. Samples were collected at 0.1 to 10 m vertical intervals. Contemporaneous samples were collected at 1 to 500 m spacings from the same stratigraphic bed. Petrographic and geochemical criteria were applied prior to $^{87}Sr/^{86}Sr$ analysis in order to identify the least diagenetically altered samples and to minimize contamination from noncarbonate minerals. Originally marine components (marine-cemented micrite of microbial origin, marine cements, trilobites) were considered the least altered on the basis of the following petrographic criteria: (1) minimal amounts (<10%) of the luminescent calcite that typifies late-diagenetic calcite in Banded Mountain Member carbonates; (2) lack of significant recrystallization or oblit-

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[1] GSA Data Repository item 9654, sample data, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301. E-mail: editing@geosociety.org.

Data Repository item 9654 contains additional material related to this article.

erative fabrics; (3) lack of two-phase fluid inclusions; and (4) negligible secondary microporosity. Microsamples (0.5–10 mg) of least-altered marine components were drilled from thick petrographic sections using a microscope-mounted dental drill.

Sr, Mn, Rb, and Al contents and $\delta^{18}O$ values of microsamples were analyzed in order to further assess their preservation state and to check for contamination from noncarbonate minerals. Samples with Rb contents >0.5 ppm, Sr contents <150 ppm, Mn contents >300 ppm, Al contents >10 ppm, Sr/Mn ratios ≤2, and Rb/Sr ratios >0.001 were not further analyzed. The limits for Sr, Mn, and Sr/Mn were chosen based on trace element contents of Precambrian to Paleozoic marine calcites interpreted by others as retaining primary seawater $^{87}Sr/^{86}Sr$ values (Derry et al., 1992, 1994; Kaufman et al., 1993; Denison et al., 1994). The limits for Rb contents and Rb/Sr ratios reflect those values that necessitate an age correction to the measured $^{87}Sr/^{86}Sr$ value that is greater than the analytical uncertainty (±0.000 024). There is no correspondence between the $\delta^{18}O$ values and $^{87}Sr/^{86}Sr$ values of Banded Mountain Member marine components, suggesting that $\delta^{18}O$ values are sensitive indicators of even minimal diagenetic alteration of marine carbonate $^{87}Sr/^{86}Sr$ values and thus are not always useful criteria for screening Sr isotope samples (cf. Jones et al., 1994).

It has been suggested that treatment of insoluble-residue–rich marine carbonates with ammonium acetate (a cation-exchange solution) prior to weak acid dissolution may minimize leaching of exchangeable Sr from noncarbonate minerals (Kupecz and Land, 1991). We experimentally determined the contribution of Rb, Sr, and $^{87}Sr/^{86}Sr$ from noncarbonate phases to sample leachates. The results indicate that (1) ^{87}Sr may be leached from even presumably pure carbonates (<0.5% insoluble residue) during sample dissolution and (2) treatment of carbonate microsamples with ammonium acetate typically results in significant decreases in Rb/Sr ratios and $^{87}Sr/^{86}Sr$ values of samples. All samples for trace element and Sr isotope analysis were (1) treated three times in 0.2 M ultrapure ammonium acetate buffered to a pH of 8.2 and (2) leached in acetic acid (4% for calcites; 8% for dolomites) for 10 min.

Trace element samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) at the University of California, Riverside. External error (1σ) based on standards was ±2% to ±3% for Mn, Sr, and Rb, and ±5% to ±7% for Al, Mg, and Fe. $^{87}Sr/^{86}Sr$ analyses were conducted at the University of Texas following procedures outlined in Banner and Kaufman (1994). During the course of this study 48 analyses of NBS-SRM 987 yielded a mean $^{87}Sr/^{86}Sr$ value of 0.710 254 with an external error (2σ) of ±24 × 10^{-6}. Replicate $^{87}Sr/^{86}Sr$ analyses (n = 13 sets) of samples from the same sample powder or ion-exchange solution yielded average values for two standard deviations of the mean of ±9 × 10^{-6}. Procedural blanks for Sr ranged from 14 to 90 pg, and were negligible for the samples analyzed.

RESULTS

The stratigraphic distribution of $^{87}Sr/^{86}Sr$ values of 66 samples and 6 pairs of contemporaneous samples are shown in Figure 1. Although all samples passed the petrographic and geochemical criteria, the $^{87}Sr/^{86}Sr$ values of some penecontemporaneous samples have a larger range than the analytical uncertainty, reflecting that even apparently well preserved marine components can show modification of their primary geochemical values (cf. Banner and Kaufman, 1994). Previous studies have demonstrated for individual sample sets that Sr/Mn ratios are a sensitive index of diagenetic alteration, and that Sr/Mn ratios of ≥0.5 to ≥2 are indicative of samples likely to record primary marine $^{87}Sr/^{86}Sr$ values (Derry et al., 1992, 1994; Kaufman et al., 1993; Denison et al., 1994; Jones et al., 1994). The $^{87}Sr/^{86}Sr$ values of marine components from Banded Mountain Member carbonates are presented in Figure 1 catagorized by their Sr/Mn ratios. Our data indicate that only samples with Sr/Mn ratios >15, values considerably higher than those previously suggested as indicative of pristine marine carbonates, are reliable indicators of seawater $^{87}Sr/^{86}Sr$ values. Samples with Sr/Mn ratios <5 have $^{87}Sr/^{86}Sr$ values that are indicative of diagenetic alteration; however, intermediate values (5 < Sr/Mn but <15) are not diagnostic.

Calcite marine components in Banded Mountain carbonates that have Sr/Mn ratios ≥15, and many samples with Sr/Mn ratios ≥5, yield $^{87}Sr/^{86}Sr$ values between 0.7091 to 0.7093 that define a nonlinear trend throughout Middle to earliest Late Cambrian time (Fig. 1). Two syndepositional dolomites that fall within the trend have Sr/Mn ratios >10. Calcite components with Sr/Mn ratios between 2 and 5 (and a few with Sr/Mn <15), and dolomites with Sr/Mn <10 have high $^{87}Sr/^{86}Sr$ values, are outliers to the overall trend, and are inferred to record diagenetic alteration of their $^{87}Sr/^{86}Sr$ values. Two samples with Sr/Mn ratios <5 have $^{87}Sr/^{86}Sr$ values <0.7091 but are interpreted to record late-diagenetic alteration indicated by overlap in their values with those of late-diagenetic calcites (not shown). The calcite marine components that define the Sr isotope trend typically have higher Sr (154 to 966 ppm) and lower
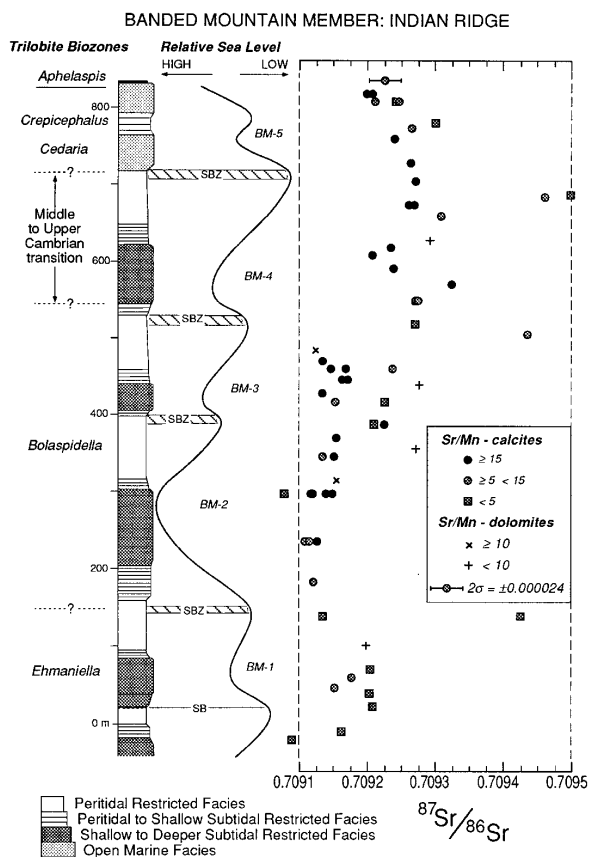

Figure 1. Stratigraphy, relative sea-level curve, and $^{87}Sr/^{86}Sr$ values of Banded Mountain carbonates at Indian Ridge. Trilobite biozone boundaries are estimated by regional correlation of sections with good biostratigraphic control (data from Robison, 1976). Middle to Upper Cambrian boundary is not well constrained at Indian Ridge and is shown as transition interval. SB(Z) = sequence boundary (zone). Relative sea-level curve and sea-level events (BM-1 to BM-5) are interpreted from cycle stacking patterns and water depth estimates of lithofacies. $^{87}Sr/^{86}Sr$ values are shown relative to a value of 0.710 254 for NBS-SRM 987. Analytical uncertainty (2σ) shown by horizontal bar through stratigraphically highest $^{87}Sr/^{86}Sr$ value; no stratigraphic uncertainty is associated with samples. Sets of contemporaneous samples are shown at 141, 297, 386, 416, 445, and 669 m.

Mn (5 to 81 ppm) and Rb (0.0001 to 0.20 ppm) contents than those samples that plot outside the trend (Sr = 153 to 486 ppm; Mn = 16 to 258 ppm; Rb = 0.001 to 0.55 ppm).

On the basis of the above, we consider the $^{87}Sr/^{86}Sr$ values of samples with Sr/Mn ratios >15, and some samples with Sr/Mn ratios >5, to represent the best estimates of a primary marine $^{87}Sr/^{86}Sr$ signature. The stratigraphic distribution of these $^{87}Sr/^{86}Sr$ values defines an approximately sinusoidal trend, which we provisionally interpret to record secular variation in Cambrian seawater $^{87}Sr/^{86}Sr$. This interpretation is supported by four sets of contemporaneous samples that have Sr/Mn ratios ≥15 and $^{87}Sr/^{86}Sr$ values that differ by less than the analytical uncertainty (Fig. 1). Sr isotopes of contemporaneous samples should yield similar $^{87}Sr/^{86}Sr$ values given the homogeneity of seawater $^{87}Sr/^{86}Sr$ at any given time (DePaolo and Ingram, 1985), and the negligible biologic fractionation of Sr isotopes during growth of biotic carbonates (Banner and Kaufman, 1994). A future test of this interpretation will be the extent to which these variations are reproduced in coeval stratigraphic sections.
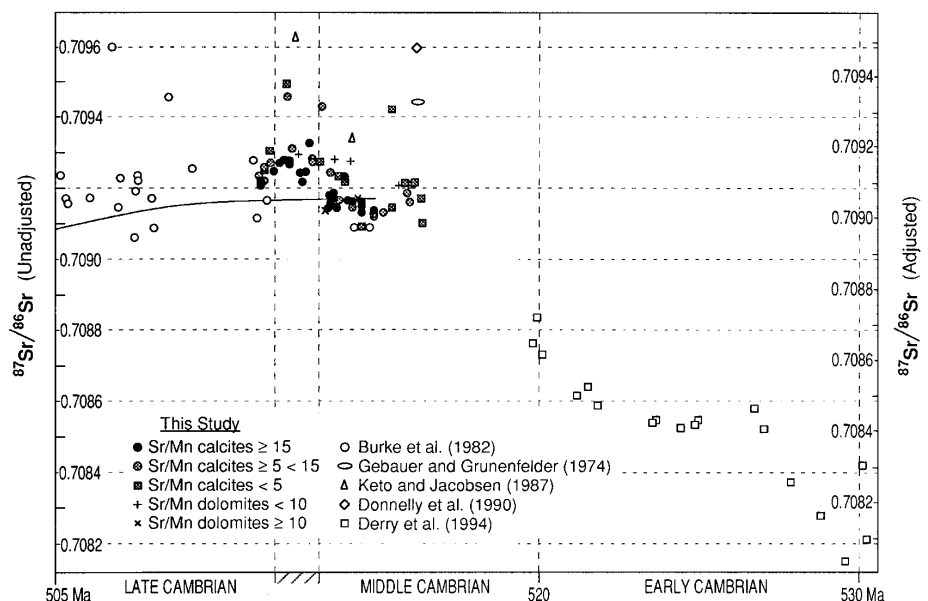
The Sr isotope trend in the lower 170 m of the stratigraphic interval is poorly constrained given that most samples have low Sr/Mn ratios. Two samples with intermediate Sr/Mn ratios, however, suggest a best estimate of marine $^{87}Sr/^{86}Sr$ values of ~0.709 15 to 0.709 18 for *Ehmaniella* time (Fig. 1). The $^{87}Sr/^{86}Sr$ values of samples between 170 and 500 m show a slight decrease to minimum values (~0.709 10 to 0.709 15), followed by a slight increase in values up to ~0.709 18. There are limited data from a dolomitic interval between 500 and 580 m. $^{87}Sr/^{86}Sr$ values progressively increase through the end of Middle Cambrian time and perhaps into the earliest Late Cambrian to a maximum value of ~0.709 25 to 0.709 28 (Fig. 1). $^{87}Sr/^{86}Sr$ values gradually decrease to ~0.709 20 through earliest Late Cambrian time. Maximum seawater $^{87}Sr/^{86}Sr$ values from this record are between 0.709 25 to 0.709 28. These values contrast with previously published maximum Middle Cambrian $^{87}Sr/^{86}Sr$ values, most of which significantly exceed 0.709 30 (Fig. 2); this may reflect diagenetic alteration. Our data set thus constrains the highest $^{87}Sr/^{86}Sr$ values for paleo-oceans over the past 2 b.y. (~0.709 30) to latest Middle Cambrian to earliest Late Cambrian time, the precise timing being limited by available biostratigraphic resolution; these values are up to 1×10^{-4} higher than the present-day seawater value (0.709 18, adjusted to a value of 0.710 254 for NBS-SRM 987; DePaolo and Ingram, 1985).

IMPLICATIONS OF THE STRUCTURE OF THE CAMBRIAN $^{87}Sr/^{86}Sr$ CURVE

The Middle to earliest Late Cambrian data presented here record the culmination of an increasing trend in seawater $^{87}Sr/^{86}Sr$ values delineated by Derry et al. (1994) for Early Cambrian time, interpolating through a gap in earliest Middle Cambrian time (Fig. 2). The magnitude of the increase in seawater $^{87}Sr/^{86}Sr$ values during the Early Cambrian through earliest Late Cambrian (~0.7081 to 0.7093; 0.000 06/m.y. assuming 20 m.y. duration) is comparable to the rise in seawater $^{87}Sr/^{86}Sr$ values during the Tertiary (0.7077 to 0.7092; 0.000 04/m.y.; DePaolo and Ingram, 1985; Hess et al., 1986). A long-term increase in Vendian through Cambrian seawater $^{87}Sr/^{86}Sr$ values has been suggested previously (Jacobsen, 1988; Asmerom et al., 1991; Derry et al., 1994). This long-term increase in seawater $^{87}Sr/^{86}Sr$ values is interpreted to record increasing riverine strontium flux and/or its $^{87}Sr/^{86}Sr$ ratio due to high uplift rates and increased continental erosion rates during the Late Proterozoic–Cambrian Pan-African orogen (ca. 800–500 Ma; Miller, 1983). Peak seawater $^{87}Sr/^{86}Sr$ values constrained to the latest Middle to earliest Late Cambrian by this study (Fig. 2) may record isostatic rebound and associated unroofing and weathering of ^{87}Sr-rich high-grade metamorphic zones within the Pan-African Damara Belt (ca. 530–460 Ma; Miller, 1983), analogous to the effects of rapid exhumation and chemical weathering of Himalayan ^{87}Sr-rich metamorphic rocks on Neogene seawater $^{87}Sr/^{86}Sr$ (Richter et al., 1992; Harris, 1995). The gradual decrease in seawater $^{87}Sr/^{86}Sr$ values subsequent to the peak may record reduction in isostatic uplift and chemical weathering associated with the mature phases of orogenesis.

The approximately sinusoidal shape of our proposed Middle to Late Cambrian seawater Sr isotope curve suggests that the Sr mass balance of Cambrian oceans was governed by more than just a gradual reduction in weathering rates of the Pan-African belt. An apparent short-term increase in seawater $^{87}Sr/^{86}Sr$ values during the Middle to Late Cambrian transition from low values of 0.709 15 to maximum values of 0.709 28 (450 to 700 m in Fig. 1) may record a rapid unroofing event and attendant increased erosion rates in the Damara Belt, analogous to the unroofing of southern Tibet interpreted to have driven the increase in seawater $^{87}Sr/^{86}Sr$ values from 15 to 20 Ma (Hodell et al., 1991; Richter et al., 1992). Alternatively, nonlinear variations in the seawater Sr isotope curve may record

Figure 2. $^{87}Sr/^{86}Sr$ values from this study and published Cambrian data. $^{87}Sr/^{86}Sr$ values are shown relative to value of 0.710 254 for NBS-SRM 987 (left scale), and relative to value of 0.710 140 for NBS-SRM 987 (right scale) reported by Burke et al. (1982). Relative age assignment of data from Donnelly et al. (1990) and Gebauer and Grünenfelder (1974) is arbitrarily shown as mid–Middle Cambrian. Previously published values >0.7096 are not shown. Solid curve is estimated Cambrian seawater secular Sr isotope trend (Burke et al., 1982). Cambrian dates were determined by Bowring et al. (1993), except for 505 Ma estimated Cambrian-Ordovician boundary (Palmer, 1983). Durations of Middle and Late Cambrian time are arbitrarily assumed to be equivalent. Middle and Late Cambrian transition is shown by diagonal line pattern; youngest boundary was used to tie in to data of Burke et al. (1982). Earliest Early Cambrian time (back to 544 Ma) is not shown. Data points do not directly correspond to an absolute time on the horizontal axis; rather they reflect stratigraphic position relative to available Cambrian absolute dates.

REGRESSION
- High $^{87}Sr/^{86}Sr$ Shelfal Siliciclastics Exposed
- Meteoric Diagenesis ⎫ Rapid Weathering
- Stream Incision ⎭
- Increased $^{87}Sr/^{86}Sr$ of Riverine Flux

SL—

TRANSGRESSION
- High $^{87}Sr/^{86}Sr$ Shelfal Siliciclastics Flooded
- Less Surface Area Exposed to Subaerial Erosion/Weathering
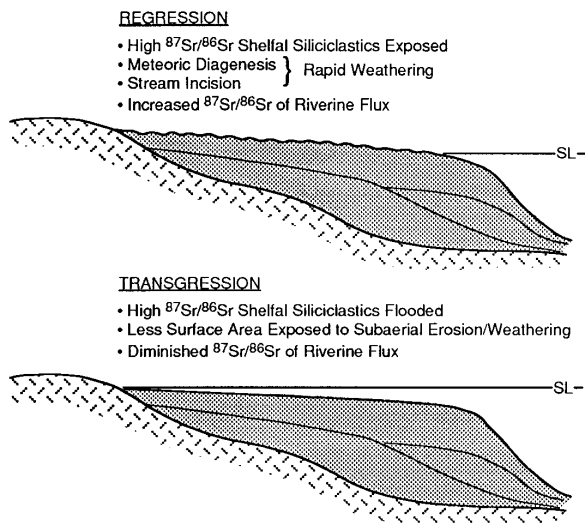- Diminished $^{87}Sr/^{86}Sr$ of Riverine Flux

SL—

Figure 3. Schematic of potential effects of fluctuating sea level (SL) on Sr isotope composition of oceans. Tick mark pattern represents continental basement. The shaded area represents the pericratonic sedimentary wedge; the solid curves inside the wedge are schematic time lines and delineate stratal geometries. Depending on the hypsometric profile, the horizontal scale (and thus areal extent) may span several hundreds of kilometres.

changes in continental weathering rates governed by sea-level fluctuations of 10^6 yr. The Middle to Late Cambrian accommodation history delineated from Banded Mountain Member carbonates suggests that multiple sea-level events (BM-1 to BM-5 in Fig. 1) were superimposed on the longer-term high sea level that occurred during this time. The Sr isotope variations observed in our data set appear to be of comparable temporal scale to the 1–3 m.y. fluctuations in relative sea level (Fig. 1). The lowest $^{87}Sr/^{86}Sr$ values coincide with a time of progressively rising sea level (BM-2 rise) as recorded by deeper subtidal carbonates in the lower *Bolaspidella* biozone. This flooding event is correlative with that recorded by the deep-water Wheeler Shale in Nevada and Utah, and several other coeval deep-water units globally, suggesting a eustatic event (Robison, 1976).

Progressively increasing $^{87}Sr/^{86}Sr$ values coincide with a time of episodically falling sea level (BM-2 fall through BM-4 fall) as recorded by peritidal restricted carbonates and abundant evidence for subaerial exposure. The highest $^{87}Sr/^{86}Sr$ values correlate with the culmination of falling sea level, which may be time equivalent with a major relative sea-level fall observed elsewhere in North America (Read, 1989). The subsequent progressive decrease in $^{87}Sr/^{86}Sr$ values during the early Late Cambrian corresponds with a gradual rise in relative sea level recorded by noncyclic, open-marine carbonates in the uppermost Banded Mountain Member. The coincidence of decreasing $^{87}Sr/^{86}Sr$ values with a major eustatic flooding event and increasing $^{87}Sr/^{86}Sr$ values with a major sea-level fall leads us to suggest that weathering rates may also change in response to changes in continental surface area governed by major marine transgressions and regressions.

It has been suggested that short-term variations in the flux and isotopic ratio of riverine Sr delivered to Neogene oceans were governed primarily by the effects of glaciation on weathering rates (Capo and DePaolo, 1990; Hodell et al., 1991). This model, however, is not applicable to greenhouse times such as the Middle to Late Cambrian. We propose that, during greenhouse times, changes in the surface area of continents, governed by sea-level fluctuations, contribute to short-term variations in seawater $^{87}Sr/^{86}Sr$ values (Fig. 3). During sea-level falls, the exposure of shelfal, fine-grained siliciclastic sediments would introduce ^{87}Sr-rich phyllosilicates to

increased physical and chemical weathering. The effect of sea-level falls on weathering rates of radiogenic continental shields would be minimal given that they are typically continuously exposed in continental interiors. Chemical weathering of ^{87}Sr-rich phyllosilicates in pericratonic sediments would be enhanced by the replacement of marine pore waters by more acidic meteoric waters, whereas physical weathering would increase due to incision of rivers driven by lowered base level, thus expediting transport of dissolved Sr to the ocean. Conversely, the riverine $^{87}Sr/^{86}Sr$ ratio would decrease during marine flooding of ^{87}Sr-rich pericratonic sediments due to a reduction in their chemical and physical weathering, and possibly due to a suppressed riverine Sr flux to the oceans (Fig. 3).

The Sr isotope data presented here, combined with published data, supports a tectonic model of mountain building and associated increased weathering rates as the primary control on long-term (10–100 m.y.) variations in Cambrian seawater $^{87}Sr/^{86}Sr$ values. The integrated Sr isotope data and accommodation history suggest that eustatic changes may be a viable mechanism for producing short-term (1–5 m.y.) variations in the Sr isotopic composition of the oceans.

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