Strontium isotope (^{87}Sr/^{86}Sr) stratigraphy of Ordovician bulk carbonate: Implications for preservation of primary seawater values

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ABSTRACT

The present study on bulk carbonate ^{87}Sr/^{86}Sr stratigraphy represents a companion work to earlier research that presented a conodont apatite-based Ordovician seawater ^{87}Sr/^{86}Sr curve for the Tremadocian–Katian Stages (485–445 Ma). Here, we directly compare the curve based on conodont apatite (including some new data not published in earlier work) with a new curve based on ^{87}Sr/^{86}Sr results from bulk carbonate from the Tremadocian–Sandbian Stages. We sampled eight Lower to Upper Ordovician carbonate successions in North America to assess the reliability of bulk carbonate to preserve seawater ^{87}Sr/^{86}Sr and its utility for ^{87}Sr/^{86}Sr chemostratigraphy. A high-resolution ^{87}Sr/^{86}Sr curve based on 137 measurements of bulk conodont apatite is used as a proxy for seawater ^{87}Sr/^{86}Sr (^{87}Sr/^{86}Sr$_{seawater}$). In total, 230 bulk carbonate samples that are paired to conodont samples were measured for ^{87}Sr/^{86}Sr in order to determine the conditions under which ^{87}Sr/^{86}Sr$_{seawater}$ is preserved in bulk carbonate. Results indicate that well-preserved bulk carbonate can faithfully record the ^{87}Sr/^{86}Sr$_{seawater}$ trend, but that its ^{87}Sr/^{86}Sr values are commonly more variable than those of conodont apatite. On average, bulk carbonate samples of the same age vary by $10–20 \times 10^{-5}$, compared to $5–10 \times 10^{-5}$ for conodont apatite. The amount of isotopic alteration of bulk carbonate from seawater ^{87}Sr/^{86}Sr (Δ^{87}Sr/^{86}Sr) was determined by taking the difference between ^{87}Sr/^{86}Sr values of bulk carbonate and the approximated seawater trend based on the least radiogenic conodont ^{87}Sr/^{86}Sr values. Cross plots comparing Δ^{87}Sr/^{86}Sr values to bulk carbonate Sr concentration ([Sr]) and conodont color alteration indices (CAI; an estimate of the thermal history of a rock body) indicate that bulk carbonate is most likely to preserve ^{87}Sr/^{86}Sr$_{seawater}$ (minimally altered) when either: (1) bulk carbonate [Sr] is greater than 300 ppm, or (2) carbonate rocks experienced minimal thermal alteration, with burial temperatures less than ~150 °C. Carbonates with intermediate [Sr] (e.g., between 130 and 300 ppm) can also yield ^{87}Sr/^{86}Sr$_{seawater}$ values, but results are less predictable, and local diagenetic conditions may play a greater role. Modeling results support the argument that seawater ^{87}Sr/^{86}Sr can be preserved in bulk carbonates with low [Sr] if pore water:rock ratios are low (<10–100) or if pore fluid ^{87}Sr/^{86}Sr is similar to the seawater ^{87}Sr/^{86}Sr value preserved in limestone. Bulk carbonate samples that meet these criteria can be useful for high-resolution measurements of ^{87}Sr/^{86}Sr$_{seawater}$, with a sample variation on par with fossil materials ($<10 \times 10^{-5}$), particularly for successions where well-preserved fossil material (i.e., conodonts or brachiopods) is not available, such as Precambrian strata, sequences recording mass extinction events, or otherwise fossil-barren facies. These criteria and model predictions based on bulk carbonate [Sr] must be considered in the context of whether a limestone accumulated under calcite seas (e.g., Ordovician), with relatively high seawater Sr/Ca, or aragonite seas, in which case the diagenetic transformation of aragonite to calcite may result in incorporation of non-seawater Sr.

INTRODUCTION

Strontium isotope (^{87}Sr/^{86}Sr) stratigraphy is a useful chemostratigraphic technique that can be used to correlate strata during times in Earth's history when there were rapid changes in the ^{87}Sr/^{86}Sr record, particularly when biostratigraphic data are limited or unavailable. In the present study, we compare the utility of a new Ordovician curve based on bulk carbonate with a conodont apatite-based seawater ^{87}Sr/^{86}Sr curve (^{87}Sr/^{86}Sr$_{seawater}$) recently published in a companion work by Saltzman et al. (2014). The application of strontium isotope stratigraphy over geologic time is possible because the oceans are regarded as having a homogeneous ^{87}Sr/^{86}Sr value reflecting a residence time of Sr (~10^6 yr) that is several orders of magnitude greater than the mixing time of the oceans today (~10^3 yr; Veizer, 1989). In general, the ideal materials to use for reconstruction of secular ^{87}Sr/^{86}Sr seawater variations are well-preserved fossils made of authigenic calcite or apatite, such as belemnites in the Mesozoic or brachiopods and conodonts in the Paleozoic (McArthur et al., 2012, and references therein). However, in stratigraphic successions where well-preserved fossil material is lacking or absent, particularly during the Precambrian or across mass extinction intervals such as the Permian-Triassic boundary (Veizer et al., 1983; Derry et al., 1989, 1992; Kaufman et al., 1993; Jacobsen and Kaufman, 1999; Halverson et al., 2007; Saltzman and Sedlacek, 2013; Sedlacek et al., 2014), bulk carbonate rock represents the only practical option for continuous sampling in seawater ^{87}Sr/^{86}Sr studies.

Whereas stringent documentation of the degree of diagenetic alteration of bulk carbonate (marine limestone) is required in order to confi-

dently interpret $^{87}Sr/^{86}Sr$ as representing ancient ocean chemistry, the methods and criteria used to assess alteration vary (e.g., Burke et al., 1982; Derry et al., 1992; Kaufman et al., 1993; Denison et al., 1994a, 1994b, 1997, 1998; Gao and Land, 1991; Gao et al., 1996; Montañez et al., 1996; Halverson et al., 2007; Young et al., 2009; Maloof et al., 2010; Li et al., 2011). General criteria used to screen samples most likely to retain a primary $^{87}Sr/^{86}Sr$ signal in bulk carbonate are similar to those used for fossil material and may include petrographic and cathodoluminescent microscopy, and trace-element and stable isotope ($\delta^{13}C$, $\delta^{18}O$) analysis (Popp et al., 1986; Veizer, 1989; Gao and Land, 1991; Derry et al., 1992; Ebneth et al., 1997; Shields et al., 2003; Korte et al., 2003, 2006; van Geldern et al., 2006; Azmy et al., 2009). Additionally, because pore fluids that migrate through sediment generally have less Sr than marine carbonate and act to lower Sr concentrations ([Sr]) in limestone until equilibrium is reached during diagenesis (Brand and Veizer, 1980; Banner and Hanson, 1990), some research groups have used thresholds in [Sr] to screen bulk rock samples prior to isotopic analysis (Burke et al., 1982; Denison et al., 1994a, 1994b, 1998; Halverson et al., 2007). Similarly, because pore fluids contain significantly more Mn than marine carbonates, some authors also used Sr/Mn ratios to delineate fields of least-altered samples (e.g., Derry et al., 1992; Montañez et al., 1996).

Although efforts to screen samples based on petrographic and geochemical criteria are well established, studies that have focused on refining the methods used to extract and measure only Sr derived from seawater in bulk rock have also improved the reliability of bulk carbonate to approximate primary $^{87}Sr/^{86}Sr$ trends. Methods include treating carbonate powders in ammonium acetate to strip away contaminant radiogenic Sr (likely sorbed to insoluble clay minerals) prior to dissolution in a weak acetic acid (Montañez et al., 1996; Bailey et al., 2000; Young et al., 2009). Some workers also advocate for the partial dissolution or a step-wise leaching procedure of carbonate powder in weak acid to remove any acid-soluble Sr in nontarget mineral phases (e.g., diagenetic calcitic cements) prior to a second dissolution step, which is then used for $^{87}Sr/^{86}Sr$ analysis (Bailey et al., 2000; Li et al., 2011; Liu et al., 2013). Petrographic screening can be effective at avoiding carbonate lithologies with clear evidence for diagenetic alteration (e.g., recrystallization, postburial cements), but these features may not be easily recognized in targeted very fine-grained carbonate lithologies (i.e., micrite) where grain sizes are <62 μm wide (mud-sized). Use of diagenetic screening criteria and carefully thought-out methods for Sr extraction

from bulk carbonate is essential but ultimately cannot guarantee that measurement of primary seawater values has been achieved without independent knowledge of the seawater trend. Currently, the best way to demonstrate that a seawater signal is preserved in bulk carbonate is to compare those values with an accepted seawater curve generated from well-preserved fossil materials. Although this is not possible for the Precambrian and parts of the Cambrian, it can be done in the rest of the Phanerozoic stratigraphic record. Few studies have been devoted to direct comparisons between both $^{87}Sr/^{86}Sr$ from bulk carbonate and $^{87}Sr/^{86}Sr$ from well-preserved fossil materials in the same rock samples. More commonly, general comparisons are made between $^{87}Sr/^{86}Sr$ from bulk carbonate in one stratigraphic section with the $^{87}Sr/^{86}Sr$ trend measured from well-preserved fossil materials from a previously studied, roughly age-equivalent section (e.g., Martin and Macdougall, 1995; Marenco et al., 2008; Young et al., 2009).

The purpose of this study is to assess the reliability and variability of bulk carbonate for reconstructing Ordovician $^{87}Sr/^{86}Sr_{seawater}$ through direct comparison to well-preserved conodont apatite, which forms the basis of the seawater $^{87}Sr/^{86}Sr$ curve recently published in a companion paper by Saltzman et al. (2014). We compare $^{87}Sr/^{86}Sr$ values from paired bulk carbonate (micrite) and conodont apatite (phosphate), which we use as a proxy for $^{87}Sr/^{86}Sr_{seawater}$ in each locality in eight Ordovician carbonate successions throughout North America (Fig. 1), from Nevada (Shingle Pass, Antelope Range, and Meiklejohn Peak), Oklahoma, and the Appalachian region (Clear Spring, Maryland; Rocky Gap, Virginia; Roaring Spring–Union Furnace, Pennsylvania; and a road cut along Interstate-81 in Virginia; see supplementary material for a description of the general geology [GSA Data Repository][1]). Micrite is ideal to use as an $^{87}Sr/^{86}Sr_{seawater}$ proxy for strontium isotope stratigraphy using bulk carbonate because fine-grained rocks typically have low porosity and permeability, which decrease the likelihood of recrystallization and isotopic exchange with pore fluids after burial. Stratigraphic sections with a range of lithologies (limestone and dolomite), varying [Sr] of bulk carbonate, and differing thermal histories (estimated from their conodont alteration index [CAI]; Epstein et al., 1977) were selected to constrain the range of conditions when bulk carbonate is most likely to preserve $^{87}Sr/^{86}Sr_{seawater}$. Some dolomite

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[1] GSA Data Repository item 2015123, data tables, figures, and method variation results, is available at http://www.geosociety.org/pubs/ft2015.htm or by request to editing@geosociety.org.

samples that meet certain criteria after careful diagenetic study appear capable of preserving $^{87}Sr/^{86}Sr_{seawater}$ (e.g., Li et al., 2011; Liu et al., 2013), despite having low [Sr], and we further evaluate this with comparisons of dolomite to $^{87}Sr/^{86}Sr_{seawater}$ using fossil components.

BACKGROUND

The two main sources of Sr in the oceans are riverine influxes of radiogenic Sr derived from the weathering of continental crust ($^{87}Sr/^{86}Sr >$ 0.710) and input of mantle-derived Sr via hydrothermal circulation through basaltic ocean crust along mid-ocean ridges ($^{87}Sr/^{86}Sr = $ ~0.703; Veizer, 1989). Diagenetic recrystallization of carbonate rocks and groundwater flow to the oceans are other sources of Sr, but their effect on changing seawater $^{87}Sr/^{86}Sr$ is considered to be minimal (Chaudhuri and Clauer, 1986; Veizer, 1989). Alteration of primary $^{87}Sr/^{86}Sr$ in rocks and fossils increases their $^{87}Sr/^{86}Sr$ value as a result of isotopic exchange with pore fluids and clay minerals derived from weathered radiogenic continental crust, and thus the least radiogenic $^{87}Sr/^{86}Sr$ values throughout a stratigraphic sequence are considered to be the best approximation of seawater $^{87}Sr/^{86}Sr$ (Veizer and Compston, 1974).

The most recent Phanerozoic $^{87}Sr/^{86}Sr$ curve is a compilation of numerous studies using a variety of well-preserved materials (McArthur et al., 2012). Cenozoic studies have primarily measured foraminiferal calcite recovered from deep-sea drilling programs for seawater $^{87}Sr/^{86}Sr$ (e.g., Palmer and Elderfield, 1985; Hodell and Woodruff, 1994; Farrell et al., 1995). Sr isotopes from the Mesozoic have largely been sampled from calcitic and aragonitic belemnite and ammonite skeletal material (Jones et al., 1994a, 1994b; McArthur et al., 1994, 2000, 2004) and are supported by measurements made on bulk carbonate (e.g., Veizer and Compston, 1974; Burke et al., 1982; Marenco et al., 2008; Saltzman and Sedlacek, 2013; Sedlacek et al., 2014) and nannoplankton oozes (McArthur et al., 1993). For the Paleozoic, low-Mg brachiopod calcite has commonly been used to estimate seawater $^{87}Sr/^{86}Sr$ (Popp et al., 1986; Keto and Jacobsen, 1987; Bertram et al., 1992; Kürschner et al., 1992; Gruszczynski et al., 1992; Cummins and Elderfield, 1994; Diener et al., 1996; Ebneth et al., 1997; Azmy et al., 1999, 2009; Veizer et al., 1999; Korte et al., 2003, 2006; Shields et al., 2003; Brand, 2004; van Geldern et al., 2006; Cramer et al., 2011). However, because well-preserved brachiopods are not always present throughout a stratigraphic section, other studies have estimated Paleozoic seawater $^{87}Sr/^{86}Sr$ using the apatite of conodont

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Figure 1. Locality map of stratigraphic sections sampled in this study. AR—Antelope Range, Nevada; SP—Shingle Pass, Nevada; MP—Meiklejohn Peak, Nevada; OK—Oklahoma; PA—central Pennsylvania; CS—Clear Spring, Maryland; RG—Rocky Gap, Virginia; I-81—Interstate-81, Virginia.

elements (Kovach, 1980, 1981; Keto and Jacobsen, 1987; Kürschner et al., 1992; Cummins and Elderfield, 1994; Ruppel et al., 1996; Holmden et al., 1996; Ebneth et al., 1997; Qing et al., 1998; Armstrong et al., 2001; John et al., 2008; Saltzman et al., 2014) or bulk carbonate (Burke et al., 1982; Gao and Land, 1991; Denison et al., 1994a, 1994b, 1998; Bailey et al., 2000; Young et al., 2009). Precambrian and Early to Middle Cambrian studies are based only on carbonate carefully screened to exclude diagenetic phases (e.g., Derry et al., 1992; Kaufman et al., 1993; Saltzman et al., 1995; Montañez et al., 1996; Halverson et al., 2007; Maloof et al., 2010; Li et al., 2011; Liu et al., 2013).

A major drop in seawater $^{87}Sr/^{86}Sr$ has been observed in Middle–Upper Ordovician strata reported from studies using brachiopod calcite (Veizer et al., 1999; Shields et al., 2003), bulk rock (Burke et al., 1982; Young et al., 2009), and conodont apatite (Saltzman et al., 2014). The major decrease started during the Darriwilian Stage and ended during the Sandbian Stage, when seawater $^{87}Sr/^{86}Sr$ decreased from roughly 0.70865 to 0.70795 (Fig. 2), representing ~10 m.y. (Saltzman et al., 2014). Poten-

tial causes of this $^{87}Sr/^{86}Sr$ decrease include: (1) increased rates of seafloor spreading and hydrothermal activity that provided a higher input of nonradiogenic Sr to the ocean, (2) a eustatic sea-level rise that flooded radiogenic source areas (diminishing the radiogenic Sr riverine input), (3) increased weathering rates of juvenile (nonradiogenic) volcanic rocks associated with the Taconic or coeval orogenic events, or (4) ocean ventilation and introduction of a nonradiogenic Sr reservoir from the deep ocean (Shields et al., 2003; Young et al., 2009; Kah and Thompson, 2011). Young et al. (2009) predicted that enhanced weathering of young volcanics would also draw down atmospheric CO_2, but this was balanced by CO_2 output from coeval volcanism. An apparent stabilization of sea-surface temperatures in the middle Darriwilian (Trotter et al., 2008) at the onset of the sharp $^{87}Sr/^{86}Sr$ decrease supports the argument that atmospheric CO_2 levels were balanced until the end-Ordovician glaciation. Future studies that utilize new advances in paleothermometry (e.g., clumped isotopes; Finnegan et al., 2011) may better constrain the Ordovician climate and the relationship to seawater $^{87}Sr/^{86}Sr$.

METHODS AND MATERIALS

Collections and Defining the Seawater Trend

Conodont and rock samples were obtained from collections by Wilson (1988) and Sweet and Tolbert (1997) for the lower-middle portion the Shingle Pass section, and the remainder of the section was supplemented by new field work (Edwards and Saltzman, 2014; Saltzman et al., 2014; Fig. 3). Conodont samples from the Antelope Range were obtained from the work by Spencer (1984; see Saltzman et al., 2014), and bulk carbonate $^{87}Sr/^{86}Sr$ values are from data published by Young et al. (2009) from the Hill 8308 section (Fig. 4). Conodonts from the Meiklejohn Peak section were from Harris et al. (1979) study collections, and bulk rock samples were collected during recent field work (Fig. DR1 [see footnote 1]). Conodonts and bulk rock samples from the Oklahoma section (Fig. 5) were obtained from the collections of Bauer (1987, 1994, 2010). Conodont and bulk rock samples from the Roaring Spring–Union Furnace, Rocky Gap, Clear Spring, and I-81
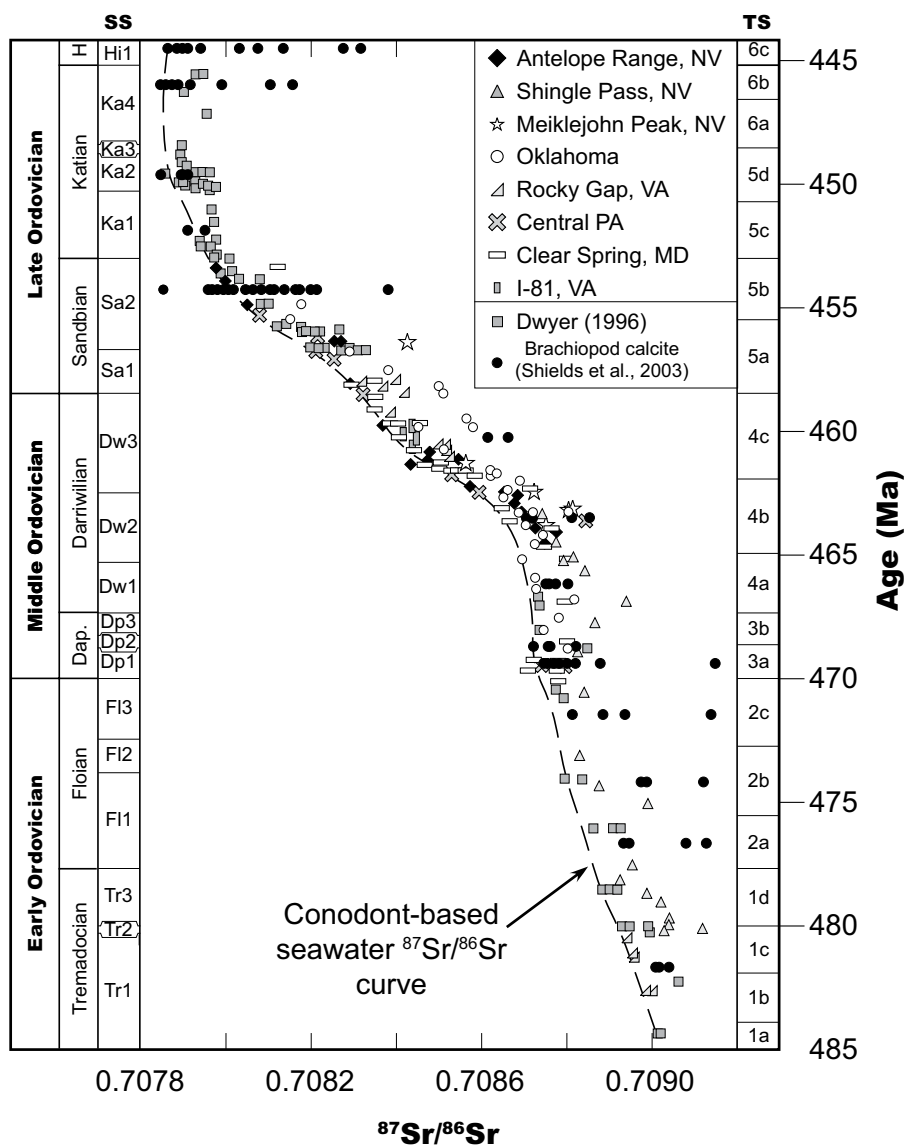
Figure 2. Compilation of brachiopod $^{87}Sr/^{86}Sr$ data from Shields et al. (2003), replotted using the *2012 Geologic Time Scale* (Cooper and Sadler, 2012), plotted along with conodont $^{87}Sr/^{86}Sr$ data (Saltzman et al., 2014). Overlap between brachiopod and conodont $^{87}Sr/^{86}Sr$ values suggests that $^{87}Sr/^{86}Sr_{seawater}$ trends are preserved in conodont apatite. Seawater $^{87}Sr/^{86}Sr$ curve (dashed line) connects least radiogenic conodont samples and provides improved age control relative to brachiopod data up to time slice 5d (Katian Stage). Age information for brachiopod collections is only resolved to time slices (TS; from Webby et al., 2004). This likely accounts for the some of the $^{87}Sr/^{86}Sr$ variability within individual time slices (up to 50×10^{-5} in 5b) and low resolution of $^{87}Sr/^{86}Sr$ data throughout the Darriwilian-Sandbian Stage interval when seawater $^{87}Sr/^{86}Sr$ drops at the fastest rate during the Ordovician. Dap.—Dapingian; H—Hirnantian; SS — Stage Slice; NV—Nevada; PA— Pennsylvania; VA—Virginia; MD—Maryland.

sections were collected during multiple field excursions (Figs. 6 and 7; Figs. DR2 and DR3 [see footnote 1]).

The seawater $^{87}Sr/^{86}Sr$ trend ($^{87}Sr/^{86}Sr_{seawater}$) is defined herein as the least radiogenic values of the comp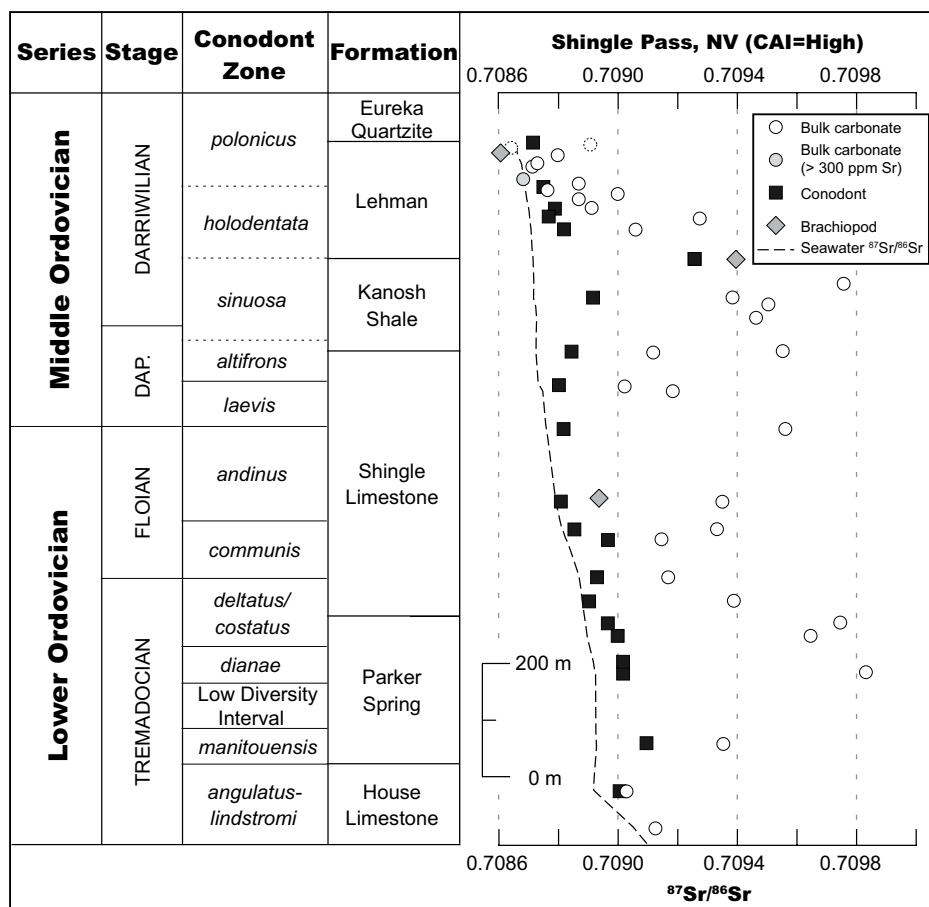ilation of conodont $^{87}Sr/^{86}Sr$ data reported here and in a companion paper by Saltzman et al. (2014; dashed line in Fig. 2). The rationale for using conodonts in place of brachiopods is that both fossils can yield nearly identical $^{87}Sr/^{86}Sr$ values within the range of sample heterogeneity (Saltzman et al., 2014)

and that conodonts are more continuously available throughout carbonate strata than brachiopods (Shields et al., 2003). The least radiogenic values are used as the best approximation of seawater $^{87}Sr/^{86}Sr$, reflecting the tendency of diagenesis to alter samples toward more radiogenic values (cf. Veizer and Compston, 1974; Shields et al., 2003). The seawater trend is drawn to accommodate most conodont samples and ignore outliers based on the assumption that seawater $^{87}Sr/^{86}Sr$ did not vary rapidly, because of the relatively long residence time of Sr in the oceans. Compared to use of the least radiogenic values, approaches that use a statistical best fit through the conodont data (e.g., LOWESS of McArthur et al., 2012) would have a relatively small effect on the value we use for $^{87}Sr/^{86}Sr_{seawater}$, because $^{87}Sr/^{86}Sr_{conodont}$ values show good precision based on replicate analyses (Saltzman et al., 2014).

Analytical Chemistry

Bulk carbonate samples were prepared for $^{87}Sr/^{86}Sr$ analysis using the methods of Montañez et al. (1996) and Young et al. (2009). Lime mudstone samples composed entirely of micrite were preferentially selected, but the micritic matrix of wackestone-packstone lithologies free of visible alteration was selectively microdrilled to produce ~40–60 mg of carbonate powder. Powders were treated with ultrapure 1 *M* ammonium acetate (buffered to a pH = 8) and leached in three rinses of acetic acid (4%). Li et al.'s (2011) recent study used a partial leach of bulk carbonate samples before isotopic analysis, but because much of our work was conducted prior to this publication and our preliminary efforts of preleaching were equivocal (see supplementary material [footnote 1]), we used the same methods conducted in previous studies for consistency (Young et al., 2009).

Conodonts were prepared for $^{87}Sr/^{86}Sr$ analysis using the methods of John et al. (2008) and Saltzman et al. (2014), briefly reviewed here. Conodonts were obtained from rock samples using traditional extraction techniques using acetic acid (10%–15%) for limestone lithologies and a formic acid solution (6%) buffered with $CaCO_3$ and $Ca(PO_4)_3$ for dolomitic lithologies. Whole and broken conodont elements were first rinsed with 1 mL Milli-Q water to remove surficial material or residues. Cleaned elements were leached using ultrapure 1 *M* ammonium acetate to remove altered surficial material and labile Sr sorbed onto minute clay minerals that may still have been attached to elements before being dissolved in ultrapure 6 *N* HCl. To test the effects of the way in which an acid preleach step might affect the measured

Figure 3. $^{87}Sr/^{86}Sr$ from bulk rock (this study), conodont apatite (see Saltzman et al., 2014), and brachiopods from the Shingle Pass section (Nevada). Gray circles indicate least-altered bulk carbonate samples with [Sr] >300 ppm. Conodont biostratigraphy is from Sweet and Tolbert (1997). The two uppermost bulk carbonate samples are dolomite (dashed symbol lines). CAI—conodont color alteration index.
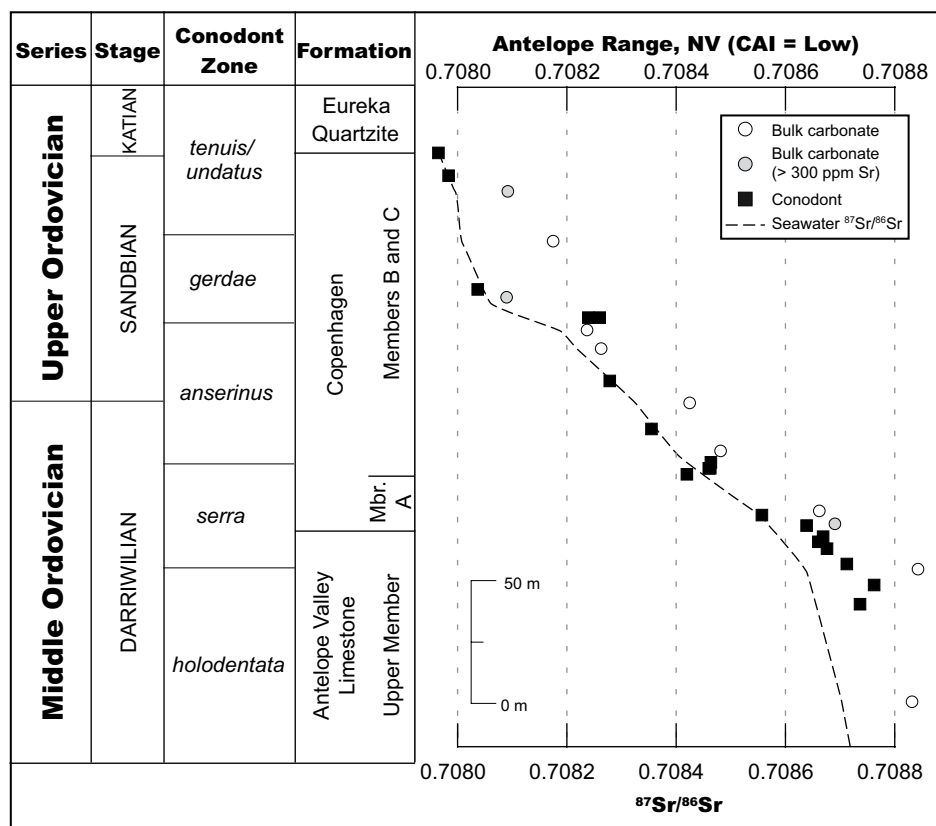
0.000013 (1σ). The laboratory value of 80 measurements of the SRM 987 standard over the duration of measurements of conodont apatite and brachiopod calcite (August 2012–December 2013) is $^{87}Sr/^{86}Sr$ = 0.710226 ± 0.000016 (1σ). Therefore, the $^{87}Sr/^{86}Sr$ values of conodont apatite and brachiopod calcite samples have been corrected to the long-term value of the bulk rock measurements by adding the difference between the two standard values (0.000013; Tables DR2 and DR3 [see footnote 1]).

RESULTS

In total, 230 bulk carbonate samples (11 from Young et al., 2009), 137 conodont samples (100 from Saltzman et al., 2014), and seven brachiopods were measured for $^{87}Sr/^{86}Sr$ (Tables DR1–DR3 [see footnote 1]). Thirty-seven pairs of bulk carbonate–conodont samples from the same stratigraphic beds were measured for $^{87}Sr/^{86}Sr$ to directly document the variability between the two materials.

Strontium Isotopes—Bulk Carbonate

The best approximation of $^{87}Sr/^{86}Sr_{seawater}$ is inferred from the least radiogenic bulk carbonate ($^{87}Sr/^{86}Sr_{carb}$) values (Veizer and Compston, 1974), and these values record an overall decreasing $^{87}Sr/^{86}Sr$ trend similar to other published Ordovician data. The $^{87}Sr/^{86}Sr_{carb}$ value decreases gradually from ~0.70910 at the base of the Ordovician to ~0.70870 by the mid-Darriwilian Stage (Middle Ordovician; Figs. 3 and 4). By the end of the Darriwilian Stage (*Pygodus serra* and *Cahabagnathus friendsvillensis* conodont zones), $^{87}Sr/^{86}Sr_{carb}$ decreases at a faster rate (~6–8 × 10^{-5} per m.y.; Saltzman et al., 2014), decreasing steadily from 0.70865 to 0.70810 by the end of the Sandbian Stage. This decrease is preserved in the Antelope Range, Oklahoma, Clear Spring, and Roaring Spring–Union Furnace sections (Figs. 4–6; Fig. DR2 [see footnote 1]). The Rocky Gap section preserves a portion of this mid-Ordovician $^{87}Sr/^{86}Sr$ drop, where $^{87}Sr/^{86}Sr_{carb}$ values just above the Knox unconformity (a major erosional surface present throughout much of the Appalachian region; Mussman and Read, 1986) sharply decrease from 0.70860 to 0.70820 throughout the Elway, Benbolt, and Witten Formations (Fig. 7). The $^{87}Sr/^{86}Sr_{carb}$ values measured from the dolomite lithologies of the Knox Dolomite and lower Blackford Formation are substantially more radiogenic (Fig. 7). Methods used to dissolve bulk carbonate confirm the results of Bailey et al. (2000), where an ammonium acetate rinse and leaching of bulk carbonate yielded the least radiogenic $^{87}Sr/^{86}Sr$ (Table DR4 [see footnote 1]).

radiogenic $^{87}Sr/^{86}Sr$ value (cf. Ruppel et al., 1996; John et al., 2008), a small subset of six conodonts from three localities was selected for preleaching tests (supplementary data [see footnote 1]).

Additionally, where available, small numbers of well-preserved calcitic brachiopods were sampled for $^{87}Sr/^{86}Sr$ to compare with conodont and bulk rock $^{87}Sr/^{86}Sr$ from the same sections. Brachiopod calcite was prepared using methods similar to Shields et al. (2003). Two brachiopods were imaged using scanning electron microscopy (Figs. DR4 and DR5 [see footnote 1]). The outer layer of brachiopod valves was removed with a stainless-steel needle to expose the optically present pearlescent inner fibrous layer. Samples were rinsed three times in 18 MΩ Milli-Q water in an ultrasonic bath to remove any remaining surficial material. Cleaned shells were drilled with a fine-tipped dental tool to produce 1–3 mg of powder. Brachiopod powders were rinsed in 1 *M* ammonium acetate before being dissolved in 4% acetic acid in the same procedure used for bulk rock samples. All samples were spiked with an ^{84}Sr tracer and purified using H$^+$ cation exchange resin via two elutions of 2 *N* HCl through silica glass columns (cf. Foland and Allen, 1991).

Mass Spectrometry

Isotopic data were measured using dynamic multicollection on a Finnigan MAT-261A thermal ionization mass spectrometer at the Radiogenic Isotope Laboratory at The Ohio State University. The $^{87}Sr/^{86}Sr$ values were normalized for instrumental fractionation using a normal Sr ratio of $^{86}Sr/^{88}Sr$ = 0.119400. The long-term laboratory value of 415 measurements for the NIST SRM 987 standard during the period when bulk rock samples were measured (May 2008–December 2013) is $^{87}Sr/^{86}Sr$ = 0.710239 ±

Figure 4. $^{87}Sr/^{86}Sr$ from bulk rock (Young et al., 2009) and conodont apatite (see Saltzman et al., 2014) from the Antelope Range section (Nevada). Conodonts recovered by Harris et al. (1979) have some the lowest conodont color alteration index (CAI) values measured in this study (1–2) and yield a narrow zone of sample variability ($\sim$5 $\times$ 10^{-5}). Gray circles indicate least-altered bulk carbonate samples with [Sr] >300 ppm.

Bulk carbonate $^{87}Sr/^{86}Sr$ can be highly variable throughout an entire stratigraphic section or even within a single formation of nearly uniform lithology. The average $^{87}Sr/^{86}Sr_{carb}$ variability (the width or spread of data throughout a section) may be as little as 5–10 $\times$ 10^{-5} (Fig. 4; Table DR1 [see footnote 1]), but it can be as much as 100 $\times$ 10^{-5}, as measured in the Shingle Pass section (Fig. 3). On average, $^{87}Sr/^{86}Sr_{carb}$ variability ranges between 15 and 20 $\times$ 10^{-5}. The $^{87}Sr/^{86}Sr_{carb}$ values in dolomitic lithologies with low [Sr], however, exhibit greater variability (on average ~40 $\times$ 10^{-5}), such as in the Bellefonte Formation in central Pennsylvania (Fig. 6) and the Knox Dolomite at the Rocky Gap section (Fig. 7).

Strontium concentrations measured from bulk carbonate vary considerably, from as low as 17 ppm (Shingle Pass) to 1296 ppm (Union Furnace section; Table DR1 [see footnote 1]). Most rock samples, however, have [Sr] between 100 and 300 ppm, with the exception of one outlier that has over 75,000 ppm Sr at Union Furnace (but still close to the inferred $^{87}Sr/^{86}Sr_{seawater}$

trend; Table DR1 [see footnote 1]) and likely represents a mixed $CaCO_3$-$SrCO_3$ composition, the cause of which remains unclear.

Strontium Isotopes—Conodont Apatite

Strontium isotopes measured from conodont apatite ($^{87}Sr/^{86}Sr_{conodont}$; Table DR2 [see footnote 1]) are consistently less radiogenic than corresponding $^{87}Sr/^{86}Sr_{carb}$ values, typically 10–80 $\times$ 10^{-5} (avg. 30 $\times$ 10^{-5}), and they generally record the same seawater trend defined by $^{87}Sr/^{86}Sr$ measured from brachiopod calcite (Shields et al., 2003; Fig. 2). The $^{87}Sr/^{86}Sr_{conodont}$ values generally have a small variability (based on 2σ of replicate or stratigraphically adjacent samples; see also Saltzman et al., 2014) between 5 and 10 $\times$ 10^{-5} throughout all of the measured sections, in spite of the large range of CAI values and host lithologies (i.e., limestone or dolomite). Strontium concentrations vary between 2000 and 25,000 ppm Sr, and [Sr] does not appear to show any correlation with the CAI value (Fig. DR6 [see footnote 1]).

Strontium Isotopes—Brachiopod Calcite

A preliminary selection of seven brachiopod shells ($^{87}Sr/^{86}Sr_{brach}$) has values consistent with the least radiogenic $^{87}Sr/^{86}Sr_{carb}$ and $^{87}Sr/^{86}Sr_{conodont}$ values (Figs. 3 and 5). Analysis of the brachiopod samples using scanning electron microscopy shows a range of preservation of microstructures and secondary shell layers (Figs. DR4 and DR5 [see footnote 1]). There is one outlier $^{87}Sr/^{86}Sr_{brach}$ value that was sampled from a red shaley limestone at the top of the Kanosh Shale (Fig. 3; [Sr] = 383 ppm). It is 57.5 $\times$ 10^{-5} more radiogenic than the inferred $^{87}Sr/^{86}Sr_{seawater}$ trend at Shingle Pass but only 13.7 $\times$ 10^{-5} more radiogenic when compared to the corresponding $^{87}Sr/^{86}Sr_{conodont}$ value (SP-165.5c, also an outlier in the context of other $^{87}Sr/^{86}Sr_{conodont}$ values at Shingle Pass). Sr concentrations of these brachiopods are similar to other reported data (e.g., Veizer et al., 1999; Shields et al., 2003), where [Sr] ranges between 383 and 744 ppm (average = 474 ppm; Table DR3 [see footnote 1]).

DISCUSSION

Relationship between Sr Concentrations and $^{87}Sr/^{86}Sr$ in Ordovician Bulk Carbonate

Although strontium concentrations in our bulk carbonate samples vary from 17 to 1296 ppm (Table DR1 [see footnote 1]), most are between 100 and 300 ppm. Preservation of primary $^{87}Sr/^{86}Sr$ in bulk carbonate is dependent on the ratio of primary seawater [Sr] to secondary [Sr] with a composition different from seawater. The incorporation of Sr into carbonate minerals that form in equilibrium with seawater is a complex process, but the most important factors include the original mineralogy, Sr/Ca and Mg/Ca ratios of seawater, precipitation rate, and temperature of the precipitating fluid (Table 1; Katz et al., 1972; Lorens, 1981; Mucci and Morse, 1983, 1990; Morse et al., 1997; Malone and Baker, 1999). The Sr content can be further modified during diagenesis (e.g., recrystallization or transformation of aragonite to calcite) via exchange with pore fluids and with large water:rock weight ratios (Banner and Hanson, 1990), which will typically reduce the Sr content when equilibrium is reached but not necessarily significantly change bulk carbonate $^{87}Sr/^{86}Sr$ (Fig. 8). Trace-element impurities, particularly Sr, are commonly excluded during the formation of more stable carbonate minerals (e.g., low-Mg calcite, dolomite; Brand and Veizer, 1980).

Because the [Sr] of carbonate rocks changes during diagenesis and is a function of the cumulative water:rock weight ratios (N) and the Sr/Ca ratio of the pore fluid (Banner and Hanson, 1990),
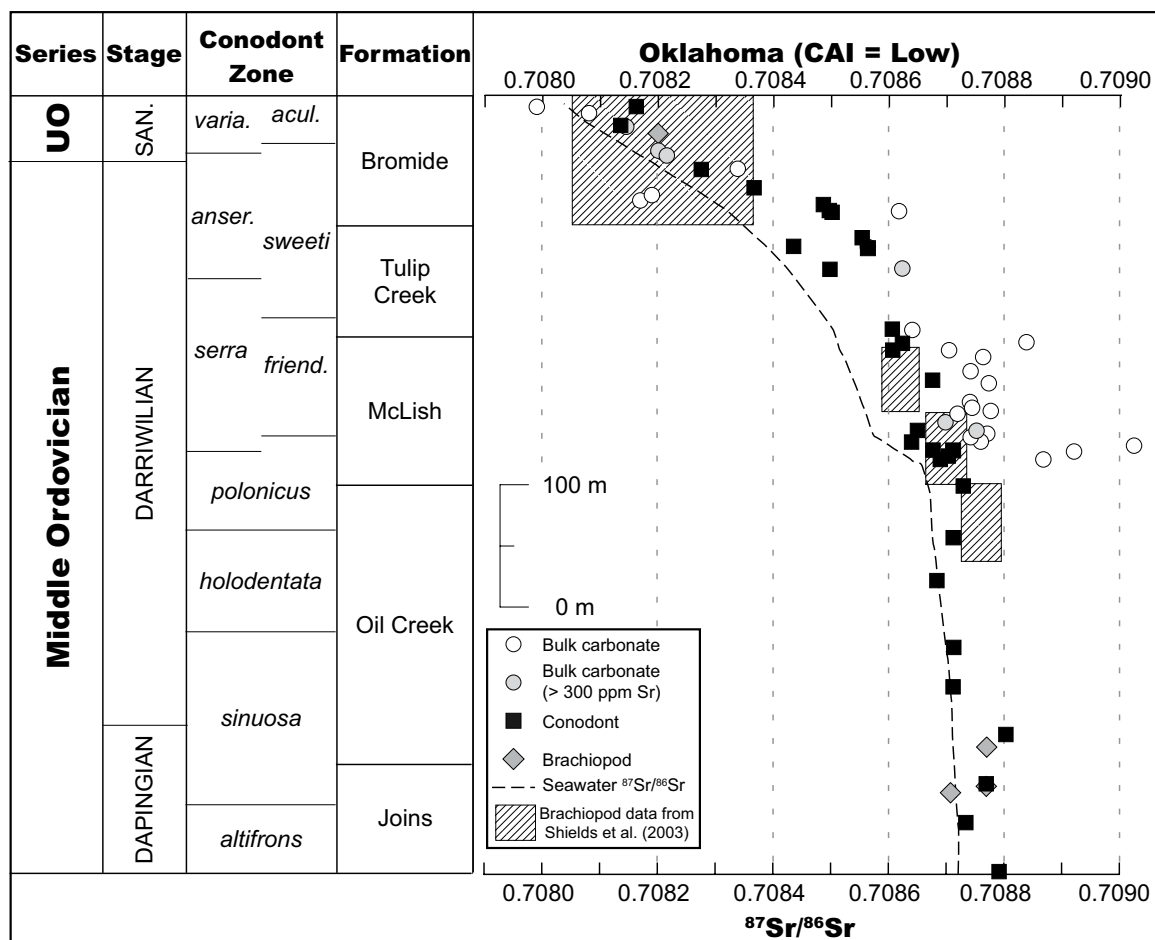
Figure 5. $^{87}Sr/^{86}Sr$ from bulk rock (this study), conodont apatite (see Saltzman et al., 2014), and brachiopods from the Arbuckle Mountains, Oklahoma. Hatched boxes depict the range of $^{87}Sr/^{86}Sr$ and stratigraphic uncertainty from several brachiopod calcite measurements reported by Shields et al. (2003). Overall, $^{87}Sr/^{86}Sr_{conodont}$ data are consistent with earlier brachiopod values in addition to brachiopods measured in this study (Table DR3 [see text footnote 1]). Conodont biostratigraphy is from Bauer (1987, 1990, 1994, 2010). CAI—conodont color alteration index; UO—Upper Ordovician; San.—Sandbian; *varia.*—*variablis*; *acul.*—*acuelata*; *anser.*—*anserinus*; *friend.*—*friendsvillensis*. Gray circles indicate least-altered bulk carbonate samples with [Sr] >300 ppm.

increases of the Ca content in the fluid alone will decrease water:rock ratios (N) required for $^{87}Sr/^{86}Sr$ and [Sr] to equilibrate with pore fluids (Fig. 8). For example, a fluid with Sr/Ca = 0.01 and [Ca] = 100 ppm (a typical carbonate aquifer; Matthess, 1982) will begin to equilibrate when N > 10–100 (Fig. 8), but a fluid with Sr/Ca = 0.01 and [Ca] = 1000 ppm will begin to equilibrate with a limestone when N > 1 (Fig. DR8 [see footnote 1]). However, these theoretical trends apply to limestone rocks that maintain constant porosity *and* permeability. Fine-grained lime micrite that undergoes early compaction and cementation will reduce porosity and permeability, thus reducing the ability for water:rock ratios to be elevated. This may create more variable alteration of the rock in general, depending on which pathways are the most permeable for fluid flow. Ultimately, bulk carbonate samples are most

likely to preserve primary seawater $^{87}Sr/^{86}Sr$ if at least one of the following conditions is met: Pore fluids have sufficiently low [Ca] (<1000 ppm), water:rock ratios are <100, or pore fluid $^{87}Sr/^{86}Sr$ is similar to seawater.

Ordovician seawater is thought to have had higher [Sr] than found in the modern ocean (up to 46 ppm compared to 8 ppm; Table DR9 [see footnote 1]), based on [Sr] in well-preserved brachiopod calcite (fig. 1 *in* Steuber and Veizer, 2002). Calcite would have been the stable $CaCO_3$ carbonate mineral that formed in equilibrium with seawater based on observations of the mineralogy of ooids and marine cements (Sandberg, 1983), the predominance of organisms that biomineralized low-Mg calcite (e.g., Stanley and Hardie, 1998; Porter, 2010; Ries, 2010), and low Mg/Ca ratios (<2) observed in fluid inclusions (Lowenstein et al., 2001, 2003).

Variations in the molar distribution coefficient of Sr [$D_{Sr} = (M_{Sr}/M_{Ca})_{calcite}/(M_{Sr}/M_{Ca})_{seawater}$, where M = molar weight of that element] can range between 0.03 and 0.25 for abiotic calcite (Table 1), based on experimental study of seawater-like solutions with low Mg/Ca ratios (see references in Table 1). Calcite micrite that formed in equilibrium in Ordovician seas would have contained between 180 and 2800 ppm Sr (Table 1), an upper value that is twice as much as the bulk carbonate samples measured in this study. This indicates that a significant amount of Sr may have been removed through recrystallization during diagenesis, and $^{87}Sr/^{86}Sr_{carb}$ preserves the $^{87}Sr/^{86}Sr$ of the equilibrating pore fluid. However, only by comparison with $^{87}Sr/^{86}Sr_{seawater}$ is it possible to determine whether diagenesis resulted in alteration of the seawater value in $^{87}Sr/^{86}Sr_{carb}$.

Figure 6. $^{87}Sr/^{86}Sr$ from bulk rock (this study) and conodont apatite (this study) from the Roaring Spring and Union Furnace sections in central Pennsylvania. Bulk carbonate samples in the Bellefonte are dolomitic (dashed symbol lines) with one limestone exception. Gray circles indicate least-altered bulk carbonate samples with [Sr] >300 ppm. CAI—conodont color alteration index.
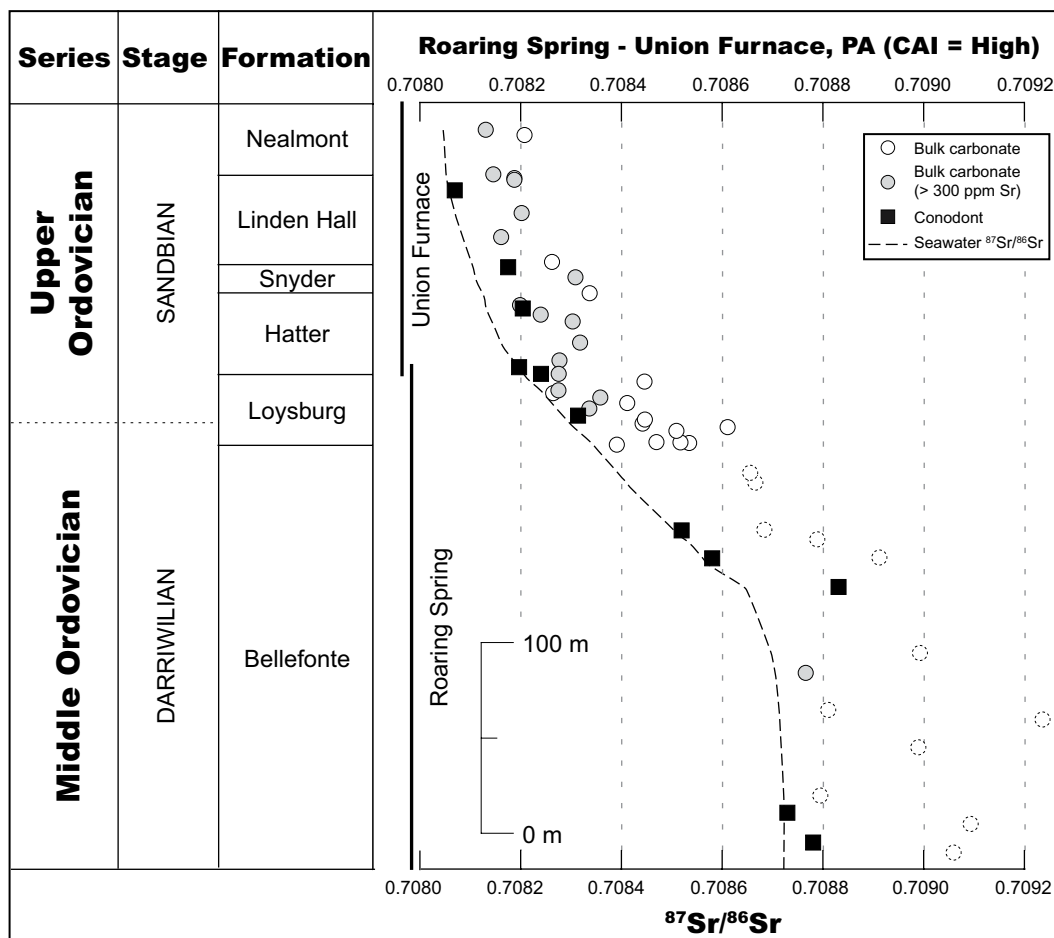
Bulk Carbonate as a Proxy for Seawater $^{87}Sr/^{86}Sr$

Use of conodont apatite as our inferred $^{87}Sr/^{86}Sr_{seawater}$ composition allows us to compare it with $^{87}Sr/^{86}Sr_{carb}$ as a means to assess variations in the degree of isotopic alteration of bulk carbonate. We define this alteration ($\Delta^{87}Sr/^{86}Sr$) as:

$$\Delta^{87}Sr/^{86}Sr = {}^{87}Sr/^{86}Sr_{carb} - {}^{87}Sr/^{86}Sr_{seawater},$$

where $^{87}Sr/^{86}Sr_{carb}$ represents the $^{87}Sr/^{86}Sr$ of bulk carbonate, and $^{87}Sr/^{86}Sr_{seawater}$ is the $^{87}Sr/^{86}Sr$ value of the least radiogenic $^{87}Sr/^{86}Sr$ trend approximated from $^{87}Sr/^{86}Sr_{conodont}$ values (Fig. 2). Smaller $\Delta^{87}Sr/^{86}Sr$ values therefore represent a relatively low degree of isotopic alteration of bulk carbonate. Use of $\Delta^{87}Sr/^{86}Sr$ values is needed because a more traditional plot of $^{87}Sr/^{86}Sr_{carb}$ versus other parameters (e.g., [Sr], CAI value) does not normalize for the effects caused by major drops in seawater $^{87}Sr/^{86}Sr$ such as those during the Darriwilian–Sandbian Stage interval of the Ordovician.

For 18 out of the 230 bulk carbonate samples analyzed in this study, $\Delta^{87}Sr/^{86}Sr$ values are near 0 within analytical error of 1.3×10^{-5} (based on external reproducibility of the SRM 987 standard). The $\Delta^{87}Sr/^{86}Sr$ values near 0 are measured in nearly every studied section, indicating that bulk carbonate has the potential to accurately preserve $^{87}Sr/^{86}Sr_{seawater}$ values in a range of geologic settings. For 146 out of the 230 bulk carbonate samples, $\Delta^{87}Sr/^{86}Sr$ values are $<20 \times 10^{-5}$ (Table DR1 [see footnote 1]), and 197 out of 230 have $\Delta^{87}Sr/^{86}Sr$ values $<40 \times 10^{-5}$ (Fig. 9). The acceptable upper limit determined by Li et al. (2011) in their strontium isotope stratigraphy study of Ediacaran–Cambrian bulk rock samples (limestone, dolostone, and phosphorite) was $^{87}Sr/^{86}Sr$ measurements that deviated from $^{87}Sr/^{86}Sr_{seawater}$ by less than 40×10^{-5} ($\Delta^{87}Sr/^{86}Sr$). This value may be practical for strontium isotope stratigraphy use in long time intervals when seawater varies slowly and by much greater than 100×10^{-5}, but it would not be helpful for intervals when there were rapid changes in seawater $^{87}Sr/^{86}Sr$. For example, Saltzman et al. (2014) calculated

that $^{87}Sr/^{86}Sr_{seawater}$ decreased by 43×10^{-5} over ~6.3 m.y. during the Middle–Late Ordovician (*P. serra–Baltoniodus variabilis* conodont zones). Therefore, strontium isotope stratigraphy during this interval using bulk carbonate requires the use of samples with $\Delta^{87}Sr/^{86}Sr$ values much less than 40×10^{-5}. Although some bulk carbonate $^{87}Sr/^{86}Sr$ samples closely approximate $^{87}Sr/^{86}Sr_{seawater}$, in the following section, we seek to better characterize the conditions under which $^{87}Sr/^{86}Sr_{carb}$ is likely to be the least altered. This will be used to establish criteria for determining when bulk carbonate closely approximates $^{87}Sr/^{86}Sr_{seawater}$ for future studies that use bulk carbonate strontium isotope stratigraphy during intervals where the $^{87}Sr/^{86}Sr_{seawater}$ is unknown or poorly constrained.

Assessment of Alteration of Bulk Carbonate $^{87}Sr/^{86}Sr$

The $^{87}Sr/^{86}Sr_{carb}$ values exhibit a wide range of variation, not only within stratigraphic sections, but also between sections with regard

Strontium isotope ($^{87}Sr/^{86}Sr$) stratigraphy of Ordovician bulk carbonate
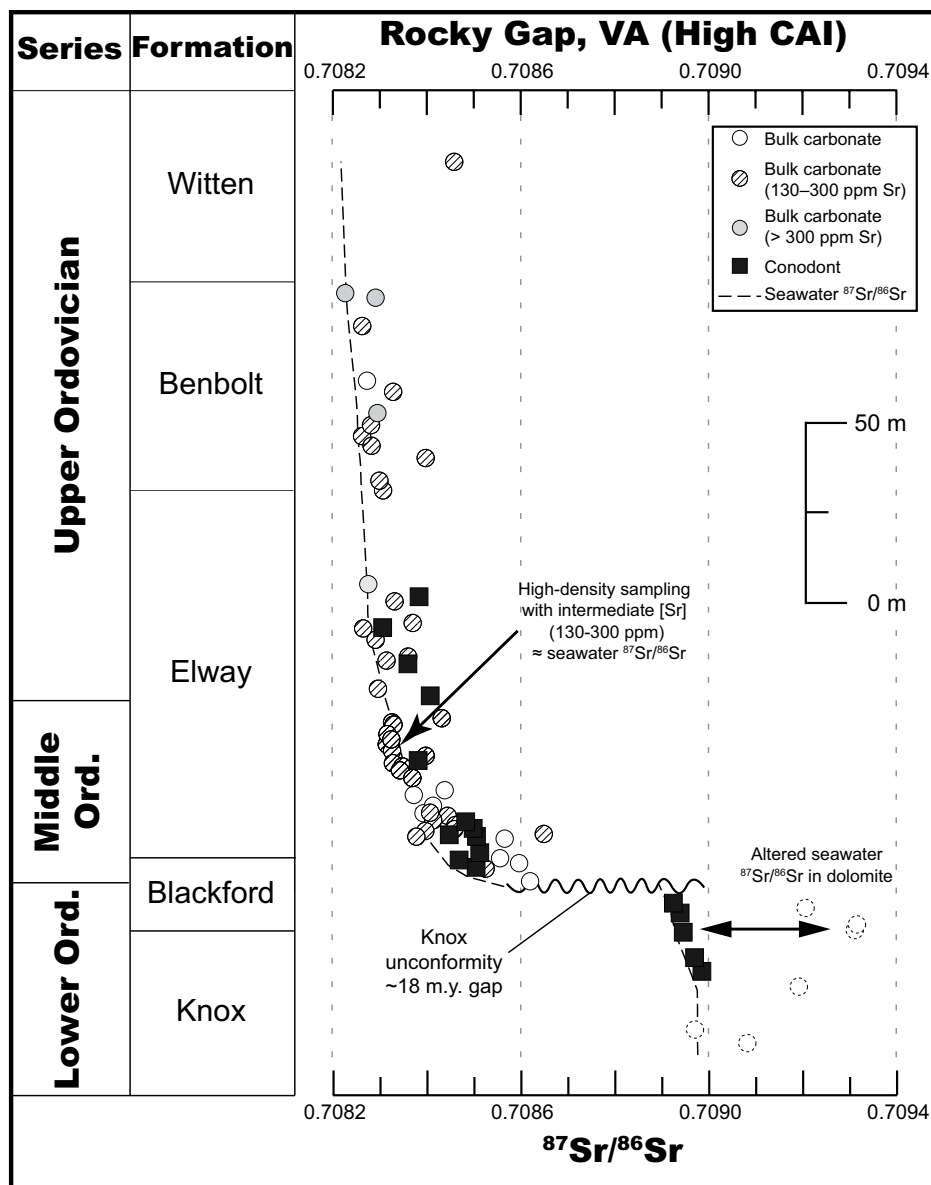
Figure 7. $^{87}Sr/^{86}Sr$ from bulk rock (this study) and conodont apatite (this study) from Rocky Gap (Virginia). Bulk carbonate samples in the Knox and Blackford formations are dolomite (dashed symbol lines). The $^{87}Sr/^{86}Sr$ in dolomite is altered from the seawater trend, but overlying limestone in the Elway Formation preserves a trend that is near the $^{87}Sr/^{86}Sr_{seawater}$ curve. Using conodont $^{87}Sr/^{86}Sr$ values, almost 18 m.y. of time appears to be missing across the Knox unconformity. Gray circles indicate least-altered bulk carbonate samples with [Sr] >300 ppm. Note: the seawater $^{87}Sr/^{86}Sr$ curve in the Elway-Witten Formations is estimated using the least-radiogenic $^{87}Sr/^{86}Sr_{carb}$ values due to a lack of conodont biostratigraphic data from this section. CAI—conodont color alteration index.

to $\Delta^{87}Sr/^{86}Sr$ values. Plots of $\Delta^{87}Sr/^{86}Sr$ versus bulk carbonate [Sr] and thermal history (CAI) can explain much of this variation. (See supplemental data for preliminary discussion on the inconclusive effect of variations in dissolution methods and insoluble residues on extracting an $^{87}Sr/^{86}Sr_{seawater}$ value from bulk carbonate [see footnote 1].)

Bulk Carbonate Sr Concentration

Because diagenesis often proceeds with loss of Sr (Fig. 8), the [Sr] of carbonate minerals is commonly used to assess the extent to which diagenesis of $^{87}Sr/^{86}Sr_{seawater}$ is likely to have occurred (e.g., Burke et al., 1982; Denison et al., 1994a, 1994b; Halverson et al., 2007; Maloof et al., 2010). Halverson et al. (2007) analyzed

bulk carbonate from three successions of Neoproterozoic strata and advocated that a lower [Sr] threshold was the most useful geochemical parameter to identify altered $^{87}Sr/^{86}Sr$ values. In each of their sections, these authors used a different lower threshold (250, 500, and 800 ppm), depending on variations in the burial and fluid-exchange histories of each section and the scatter in data in a cross plot of $^{87}Sr/^{86}Sr$ versus [Sr], in order to identify samples that likely approximate $^{87}Sr/^{86}Sr_{seawater}$. Maloof et al. (2010) also used a [Sr] threshold as the best parameter to identify diagenetic $^{87}Sr/^{86}Sr$ values, and their lower limit varied among each of their studied sections but was always <200 ppm Sr. These studies did not use high Mn/Sr ratios in their bulk carbonate samples as a criterion to screen for diagenetic alteration (cf. Banner and Hanson, 1990; Jacobsen and Kaufman, 1999) because high Mn concentrations may also result from precipitation under dysoxic conditions, which may have persisted throughout the early Paleozoic (Hurtgen et al., 2009; Gill et al., 2011; Thompson and Kah, 2012).

In our Ordovician study, a cross plot of $\Delta^{87}Sr/^{86}Sr$ and the [Sr] of bulk carbonate samples (Fig. 9) is used to establish a lower Sr threshold among all measured sections where bulk carbonate most closely approximates $^{87}Sr/^{86}Sr_{seawater}$. Figure 9 indicates that larger $\Delta^{87}Sr/^{86}Sr$ values (highly altered bulk carbonate) are associated with lowered bulk carbonate [Sr], less than 300 ppm, similar to other reported thresholds (Burke et al., 1982; Denison et al., 1994a, 1994b; Halverson et al., 2007). There are 43 bulk carbonate samples with [Sr] ≥300 ppm (and one outlier from Shingle Pass) and a maximum $\Delta^{87}Sr/^{86}Sr$ value of 27.3×10^{-5}, with an average $\Delta^{87}Sr/^{86}Sr$ value of 10.9×10^{-5}. A lower threshold of 300 ppm Sr appears to be optimal, as average $\Delta^{87}Sr/^{86}Sr$ values for higher [Sr] thresholds do not differ significantly (Table DR1 [see footnote 1]). However, 71 bulk carbonate samples with relatively small $\Delta^{87}Sr/^{86}Sr$ values ($<15 \times 10^{-5}$) have low [Sr], between 130 and 300 ppm (primarily from the Antelope Range, Oklahoma, Clear Spring, and Rocky Gap sections), so solely using [Sr] should not be the only criterion used to evaluate whether or not $^{87}Sr/^{86}Sr_{seawater}$ may be preserved.

Conodont Alteration Index

The conodont alteration index uses the color of conodont apatite to provide an estimate of the thermal history of a rock unit (Epstein et al., 1977), and it appears to explain some of the variation in $\Delta^{87}Sr/^{86}Sr$ that is not explained by [Sr]. Conodonts used in this study typically had a range in CAI values from a single locality (less than 1–2 units) and were classified as either

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Figure 8. Predicted changes in the Sr concentration: (A) Limestone with 50% porosity, pore-fluid Sr/Ca ratio of 0.01 ([Ca] = 100 ppm), and D_{Sr} = 0.05 (cf. Banner and Hanson, 1990) at increasing water:rock weight ratios (N). (B–C) Expected changes in the $^{87}Sr/^{86}Sr$ of (B) limestone with a fluid with a highly radiogenic $^{87}Sr/^{86}Sr$ value (0.7200) and (C) a fluid with a near-seawater $^{87}Sr/^{86}Sr$ value (0.7090). Symbols indicate how bulk carbonates are expected to alter given moderate water:rock ratios (N = 20–30) that yield low $\Delta^{87}Sr/^{86}Sr$ values (<10 × 10^{-5}) from Rocky Gap (white triangle) and central Pennsylvania (PA; gray X), and moderate $\Delta^{87}Sr/^{86}Sr$ values (50 × 10^{-5}) from Shingle Pass (gray triangle).

having low (1–2) or high (3–5) values. This grouping is similar to other studies that suggest only minimally altered conodonts (CAI <2.5) should be considered for geochemical analyses (Bertram et al., 1992; Ruppel et al., 1996; John et al., 2008). CAI values between 1 and 2 can have a range in burial temperatures between ~50 and 140 °C, and CAI values between 3 and 5 can have a greater range between 100 and 300 °C (Epstein et al., 1977). Unfortunately, these temperature estimates cannot always be confirmed with δ^{18}O measured from corresponding carbonates, assuming they still retain their primary mineralogy and isotopic composition, without knowing the δ^{18}O composition of the fluid within which they equilibrated.

Figure 10 indicates that sections with low CAI values (Antelope Range and Oklahoma) have low $\Delta^{87}Sr/^{86}Sr$ values (minimally altered bulk carbonate; note that some of the high $\Delta^{87}Sr/^{86}Sr$ values in the Antelope Range could be an artifact of uncertainty in direct comparison of conodont and bulk carbonate samples that were collected in separate field studies), whereas some of the largest $\Delta^{87}Sr/^{86}Sr$ values are present in sections with high CAI values. There are a total of 40 bulk carbonate values from sections with low CAI values (Oklahoma and Antelope Range) with a maximum $\Delta^{87}Sr/^{86}Sr$ value of 39.8 × 10^{-5} and an average value of 11.6 × 10^{-5}. Sections with high CAI values, however, do not always have large $\Delta^{87}Sr/^{86}Sr$ and may still have $^{87}Sr/^{86}Sr_{seawater}$ preserved in some bulk carbonate samples if they still retain >300 ppm Sr. For example, Meiklejohn Peak has among the highest CAI values (up to 5) but low $\Delta^{87}Sr/^{86}Sr$ values, suggesting $^{87}Sr/^{86}Sr_{carb}$ values have not been appreciably altered during burial diagenesis. It may be possible that thermal alteration has altered both conodont and bulk carbonate $^{87}Sr/^{86}Sr$ to give
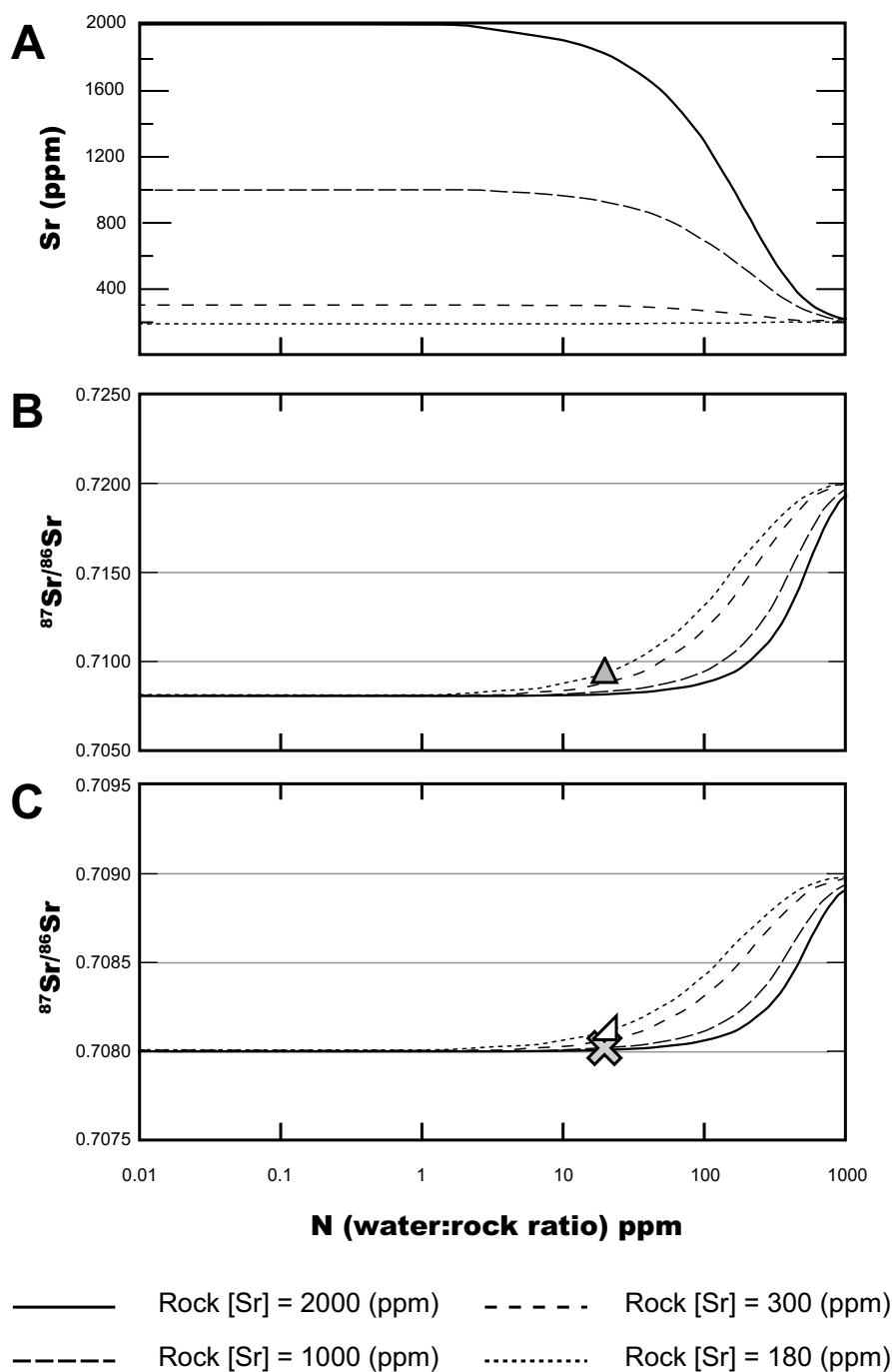
false low $\Delta^{87}Sr/^{86}Sr$ values, but this is unlikely because bulk carbonate samples from this section have some of the highest [Sr] measured in this study (Table DR1 [see footnote 1]), an indication that diagenesis was minimal (see earlier discussion and Fig. 8). Thus, $^{87}Sr/^{86}Sr_{carb}$ values from localities with the lowest CAI values consistently yield near-seawater $^{87}Sr/^{86}Sr$ trends, but high CAI values do not always indicate that $^{87}Sr/^{86}Sr_{seawater}$ in bulk carbonate is altered, especially when [Sr] values are >300 ppm. Samples

with intermediate values for [Sr] (130–300 ppm) or ones that come from sections with CAI values up to 3 also yield near-seawater $^{87}Sr/^{86}Sr$ (Fig. 11), but the results are less predictable and indicate that local conditions play a greater role in the preservation of $^{87}Sr/^{86}Sr_{seawater}$ (see "Relationship between Sr Concentrations and $^{87}Sr/^{86}Sr$ in Ordovician Bulk Carbonate" section). High-density sampling of these intermediate [Sr] values at the Rocky Gap section yielded a near-seawater $^{87}Sr/^{86}Sr$ trend (Fig. 7).

TABLE 1. MAJOR CONTROLS ON D_{Sr} VALUES AND INORGANIC CARBONATE Sr CONCENTRATIONS IN CALCITE AND ARAGONITE SEAS

Carbonate that formed in:	D_{Sr}	Sr/Ca of carbonate (mMol/Mol)	[Sr] in carbonate (ppm)#	Reference for D_{Sr} values
Ordovician (calcite sea I)*				
Precipitation rate				
0.5–2.0 nmol/mg/min	0.03–0.10	0.21–1.3	180–1100	Lorens (1981)
Mg content of solution				
[Mg]/[Ca]: 0 to 2.5	0.146–0.246	1.0–4.0	900–2800	Mucci and Morse (1983)
[Mg]/[Ca]: 0 to 10	0.05–0.21	0.35–2.7	310–2400	Morse and Bender (1990)
Temperature				
48 98 C	0.034–0.039	0.24–0.51	210–440	Katz et al. (1972)
Calcite sea II	0.05–0.21	0.22–2.9	190–2600	Morse and Bender (1990)
Aragonite sea II	1	1.8–7.9	1600–6900	Steuber and Veizer (2002)
Aragonite to calcite transformation during diagenesis	0.046–0.068	0.083–0.54	73–470	Malone and Ba er (1999)

*Sea ater Sr/Ca 7–13 mMol/Mol (Steuber and V eizer 2002).
Jurassic–Cretaceous Sr/Ca 4.4–14 mMol/Mol (Steuber and V eizer 2002).
Carboniferous–Triassic Sr/Ca 1.8–7.9 mMol/Mol (Steuber and V eizer 2002).
#Calculated using the molar eights of 87.62 g Sr/Mol Sr and 100.048 g CaCO $_3$/Mol CaCO$_3$.

Bulk Carbonate $^{87}Sr/^{86}Sr$ Study Elsewhere in the Rock Record: Calcite versus Aragonite Seas
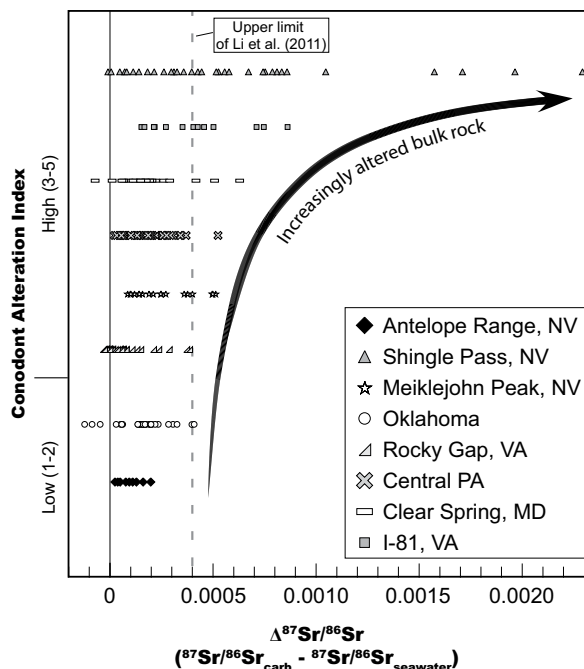
This study shows that bulk carbonate samples with >300 ppm Sr have the lowest $\Delta^{87}Sr/^{86}Sr$ values, and these are here considered to be the least altered; however, it is worth exploring how this lower [Sr] threshold applies to other times in Earth history, particularly when seawater [Sr] values were different compared to the calcite seas of the Ordovician. Calcite seas contained more dissolved Sr compared to aragonite seas because aragonite precipitation acts as a Sr sink compared to calcite precipitation, as a function of the higher rate of incorporation of Sr (D_{Sr} = 1 and 0.03–0.25, respectively). Aragonite that formed during the Carboniferous–Triassic (aragonite II seas) may have incorporated up to 6900 ppm Sr if it precipitated from seawater (Table 1). If during diagenesis, however, aragonite transforms to the more stable form of $CaCO_3$, low-Mg calcite, then bulk carbonate could contain less than 470 ppm Sr if all aragonite equilibrates with pore fluids (Table 1). In contrast, a limestone that accumulated during calcite seas (calcite sea I: Ordovician–Devonian or calcite sea II: Jurassic–Cretaceous) may contain up to 2800 ppm Sr if no equilibration with pore fluids occurred.

Our Ordovician $^{87}Sr/^{86}Sr_{carb}$ study is consistent with previous work suggesting that samples with the highest [Sr] have the highest likelihood of preserving $^{87}Sr/^{86}Sr_{seawater}$ but that samples with low [Sr] and low sample-to-sample variability (based on high-density stratigraphic analysis) may also preserve $^{87}Sr/^{86}Sr_{seawater}$. For example, Sedlacek et al. (2014) measured Triassic bulk carbonate from Iran (aragonite seas) and interpreted their $^{87}Sr/^{86}Sr$ trend to represent seawater based in part on high [Sr] (some samples >1000 ppm, which is unexpected if inver-
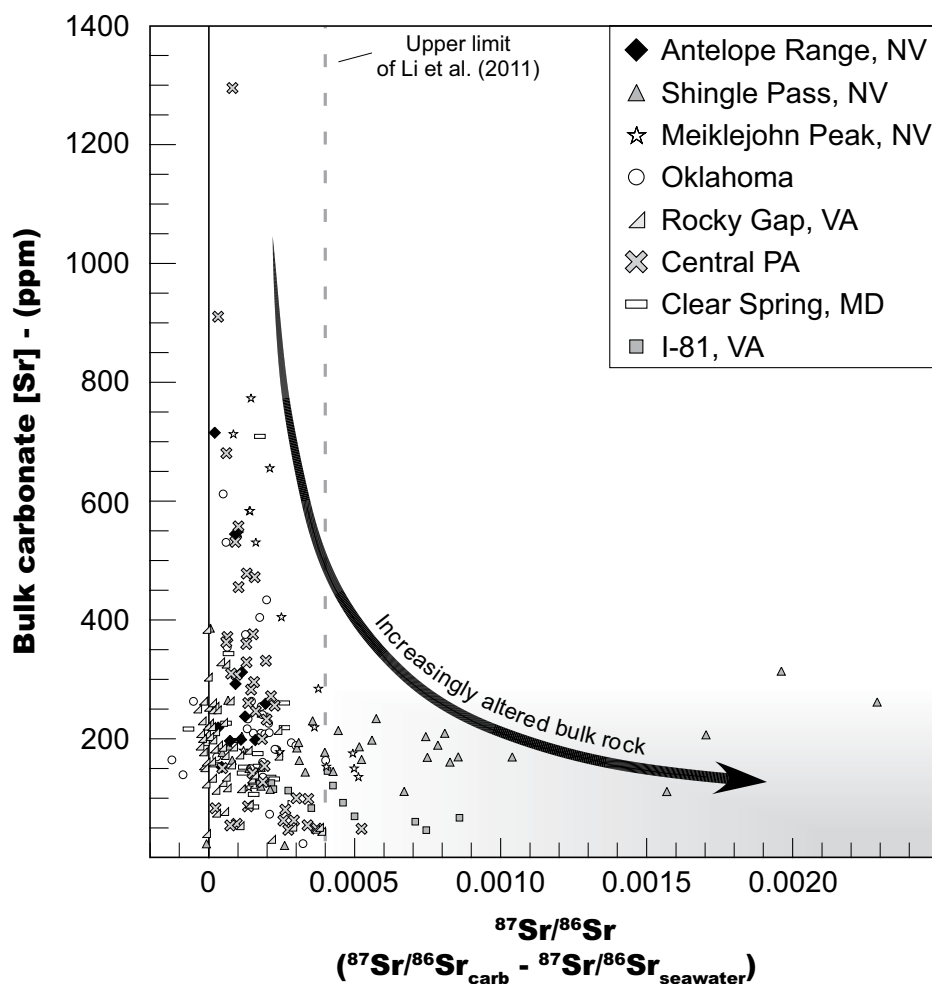
Figure 9. Cross plot of $\Delta^{87}Sr/^{86}Sr$ ($^{87}Sr/^{86}Sr_{carb} - ^{87}Sr/^{86}Sr_{seawater}$) vs. bulk rock [Sr]. Highly altered bulk rocks (i.e., high $\Delta^{87}Sr/^{86}Sr$ values) consistently have low [Sr] (<300 ppm), but many bulk rock samples with low [Sr] are not highly altered compared to corresponding $^{87}Sr/^{86}Sr_{conodont}$ values. Carbonates with high [Sr], however, consistently have low $\Delta^{87}Sr/^{86}Sr$ values and indicate that bulk carbonate with >300 ppm Sr likely preserves $^{87}Sr/^{86}Sr_{seawater}$. The $\Delta^{87}Sr/^{86}Sr$ values for the 43 samples with >300 ppm Sr are all less than the acceptable upper limit determined by Li et al. (2011) in their bulk rock $^{87}Sr/^{86}Sr$ study. NV—Nevada; PA—Pennsylvania; VA—Virginia; MD—Maryland.
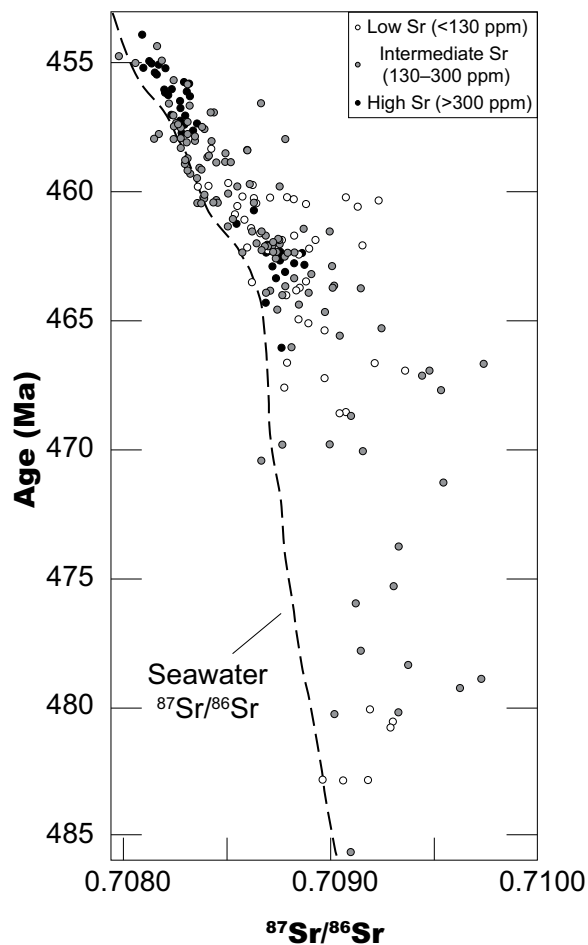
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Figure 10. Cross plot of $\Delta^{87}Sr/^{86}Sr$ values vs. the conodont alteration index (CAI) values of corresponding conodonts. Sections with low CAI values (1–2) show that bulk rock samples are not highly altered compared to conodonts, but highly altered bulk rocks are found in environments with high CAI values (3–5). The $\Delta^{87}Sr/^{86}Sr$ average of the 40 samples with low CAI values is less than the upper limit of 40×10^{-5} determined by Li et al. (2011) in their study of $^{87}Sr/^{86}Sr$ using bulk carbonate. NV—Nevada; PA—Pennsylvania; VA—Virginia; MD—Maryland.

Figure 11. Compilation of bulk carbonate $^{87}Sr/^{86}Sr$ compared with the $^{87}Sr/^{86}Sr_{seawater}$ trend. Bulk carbonate samples with >300 ppm Sr predominantly plot within ~20×10^{-5} of the seawater trend. Intermediate [Sr] samples with >130 ppm also plot within this range and can reliably represent a seawater trend (e.g., Rocky Gap), but their variability in comparison to high [Sr] bulk carbonate indicates that a greater uncertainty exists when used as a proxy for $^{87}Sr/^{86}Sr_{seawater}$.

sion to low-Mg calcite was complete; Table 1) and a low sample-to-sample $^{87}Sr/^{86}Sr$ variability. In a related study, Saltzman and Sedlacek (2013) reported Triassic bulk carbonate $^{87}Sr/^{86}Sr$ from Utah with much lower [Sr] (~100–250 ppm) and assumed significant alteration of $^{87}Sr/^{86}Sr_{seawater}$ ($\Delta^{87}Sr/^{86}Sr = 20–40 \times 10^{-5}$) related to loss of original Sr during diagenetic recrystallization to low-Mg calcite. However, the low sample-to-sample variability may indicate that pore fluids were buffered with a near-seawater $^{87}Sr/^{86}Sr$ value (see Fig. 8C) and that Saltzman and Sedlacek (2013) possibly overestimated the extent to which these rocks were altered from seawater (i.e., $\Delta^{87}Sr/^{86}Sr$ may be much lower than $20–40 \times 10^{-5}$). Future study of conodont apatite $^{87}Sr/^{86}Sr$ from these rocks could more accurately show the extent to which the seawater $^{87}Sr/^{86}Sr$ trend is still preserved. The lower [Sr] threshold for bulk carbonate that accumulated in aragonite seas requires further study where precise $\Delta^{87}Sr/^{86}Sr$ values of bulk carbonate can be determined.

CONCLUSIONS AND IMPLICATIONS

Although $^{87}Sr/^{86}Sr_{conodont}$ measurements represent the best estimate of Ordovician $^{87}Sr/^{86}Sr_{seawater}$, measurement of 230 bulk carbonate and 137 bulk samples of conodont apatite from eight Lower–Upper Ordovician carbonate successions indicates that bulk carbonate can faithfully record $^{87}Sr/^{86}Sr_{seawater}$ and provide a high-resolution record of seawater $^{87}Sr/^{86}Sr$ when either (1) Sr concentrations are >300 ppm, even at relatively high burial temperatures (e.g., CAI = 5 at Meiklejohn Peak), or (2) CAI values of associated conodonts are low (≤2), even at low [Sr] in bulk carbonate (e.g., Oklahoma). Bulk carbonate samples from rocks with intermediate CAI values (~1.5–3) or with intermediate [Sr] (130–300 ppm) can also yield $^{87}Sr/^{86}Sr_{seawater}$, but the results are less predictable and indicate that differential alteration or original [Sr] of bulk carbonate played a greater role in the preservation of $^{87}Sr/^{86}Sr_{seawater}$ postburial. Modeling results show that seawater $^{87}Sr/^{86}Sr$ can be preserved in bulk carbonates with low [Sr] if pore water:rock ratios are low (<10–100) or if pore fluid $^{87}Sr/^{86}Sr$ is similar to the seawater $^{87}Sr/^{86}Sr$ value preserved in limestone. Although the rocks of several of the studied sections appear to be well preserved based on petrographic analysis and $\delta^{13}C$ isotope data (Edwards and Saltzman, 2014), primary seawater $^{87}Sr/^{86}Sr$ is not necessarily preserved in bulk carbonate (e.g., Shingle Pass). Bulk carbonate can be very useful to document a high-resolution $^{87}Sr/^{86}Sr_{seawater}$ trend for chemostratigraphic correlation, particularly for rocks

where well-preserved fossil material is not available, but careful screening of the thermal and diagenetic history of a rock body should be undertaken. If these criteria can be combined with and pass other tests for diagenetic alteration (e.g., trace-element abundances and Sr/Ca ratios, which were not a part of this study), then it could be highly effective in identifying those bulk carbonate samples that will most reliably preserve $^{87}Sr/^{86}Sr_{seawater}$ and those samples with intermediate [Sr] that have the best potential to preserve $^{87}Sr/^{86}Sr_{seawater}$ values.

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