A major drop in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during the Middle Ordovician (Darriwilian): Links to volcanism and climate?

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A major drop in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during the Middle Ordovician (Darriwilian): Links to volcanism and climate?

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ABSTRACT

A large drop in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during the Middle Ordovician was among the most rapid in the entire Phanerozoic. New $^{87}\text{Sr}/^{86}\text{Sr}$ measurements from Nevada indicate that the rapid shift began in the Pygodus serra conodont zone of the upper Darriwilian Stage. We use a numerical model to explore the hypothesis that volcanic weathering provided the flux of non-radiogenic Sr to the oceans. A close balance between volcanic outgassing and CO2 consumption from weathering produced steady $p\text{CO}_2$ levels and climate through the middle Katian, consistent with recent Ordovician paleotemperature estimates. In the late Katian, outgassing was reduced while volcanic weathering continued, and resulted in a cooling episode leading into the well-known end-Ordovician glaciation.

INTRODUCTION

A large drop in Phanerozoic seawater $^{87}\text{Sr}/^{86}\text{Sr}$, from ~0.7090 to ~0.7078, has long been documented for the Ordovician (e.g., Burke et al., 1982; Qing et al., 1998). The magnitude of this change is comparable to the rise in $^{87}\text{Sr}/^{86}\text{Sr}$ over the past ~35 m.y. of the Cenozoic (Fig. DR1 in the GSA Data Repository1). Shields et al. (2003) compiled new Ordovician $^{87}\text{Sr}/^{86}\text{Sr}$ data from biostatigraphically constrained successions and showed that most of this drop was concentrated in an ~3–6 m.y. time interval spanning the Middle-Late Ordovician boundary (late Darriwilian–early Sandbian), making it the most rapid change of this magnitude in the Phanerozoic.

The cause of the Ordovician $^{87}\text{Sr}/^{86}\text{Sr}$ drop may have implications for carbon cycling and global climate. Berner (2006) used the marine $^{87}\text{Sr}/^{86}\text{Sr}$ record as a proxy for the proportion of the global silicate weathering flux that is due to volcanic rock weathering. Basaltic weathering may account for ~35% of total silicate weathering today (Dessert et al., 2003) and provides relatively nonradiogenic Sr to the global oceans. Because basaltic rocks are rich in Ca and Mg silicate minerals that weather rapidly and consume $p\text{CO}_2$, incorporation of Ordovician $^{87}\text{Sr}/^{86}\text{Sr}$ as a proxy for organic carbon burial does not help to resolve these climate paradoxes.

Here we present a new $^{87}\text{Sr}/^{86}\text{Sr}$ curve from a biostatigraphically significant Ordovician reference section in central Nevada that was previously analyzed for $\delta^{13}C$ (Qing et al., 1998). Crossplots of $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr isotope compositions were measured using dynamic multicollection with a MAT-261A thermal ionization mass spectrometer (see Table DR1 for laboratory standards used, external reproducibility, and 2σ uncertainties).

The $^{87}\text{Sr}/^{86}\text{Sr}$ values in the Lower and Middle Antelope Valley Limestone range between ~0.7089 and 0.7090 (Fig. 1). Values then fall in the uppermost Antelope Valley Limestone to ~0.7086 and continue to drop from 0.7085 to 0.7080 in the Copenhagen Formation. This timing and magnitude of the shift is in good agreement with previous studies (Qing et al., 1998; Shields et al., 2003). We do, however, note differences in absolute $^{87}\text{Sr}/^{86}\text{Sr}$ values for some intervals that could be related to secondary alteration, which typically produces more radiogenic values, or to errors in age assignments of individual sample sets. For example, Qing et al.’s (1998) $^{87}\text{Sr}/^{86}\text{Sr}$ values in the late Darriwilian–early Sandbian are less radiogenic than our data, but this is apparently due to incorrect age assignments for the Gull River and Shadow Lake formations that correlate to the uppermost Sandbian (e.g., Kolata et al., 1996). The degree of diagenetic alteration of our micritic limestone $^{87}\text{Sr}/^{86}\text{Sr}$ values may potentially be addressed by associated Sr concentrations and $\delta^{13}C$ values (e.g., Gao et al., 1996; Qing et al., 1998). Crossplots of $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr ($ppm$) and $\delta^{18}O$ from our sections (Figs. DR3 and DR4) show no apparent covariance, although...
that horizontal error bars for 87Sr/86Sr correspond to 2 complete biostratigraphy, see Harris et al., 1979; Finney et al., 1999; Sweet et al., 2005). Note (Webby et al., 2004) and key biostratigraphic zonal boundaries and/or occurrences (for composite section. Also plotted and italicized are important geochronologic dates

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Figure 1. Plots of 87Sr/86Sr, δ13C, and simplified stratigraphic column for Antelope-Monitor Range composite section. Also plotted and italicized are important geochronologic dates (Webby et al., 2004) and key biostratigraphic zonal boundaries and/or occurrences (for complete biostratigraphy, see Harris et al., 1979; Finney et al., 1999; Sweet et al., 2005). Note that horizontal error bars for 87Sr/86Sr correspond to 2σ uncertainties reported in Table DR1 (see footnote 1). VPDB—Vienna PeeDee belemnite. Genera of important graptolites: N.—Normograpthus, P.—Paraorthograptus, D.—Dicellograptus; conodonts: Pl.—Plectodina, Ph.—Phragmodus, B.—Baltoniodus, H.—Histiodella, M.—Microzarkodina.
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this may not completely rule out some degree of alteration. More generally, our Sr concentrations (100–700 ppm) are similar to carbonates previously reported to preserve a record of primary Late Cambrian seawater 87Sr/86Sr variations (e.g., Montañez et al., 1996).

**DISCUSSION**

**Controls on Middle to Late Ordovician Seawater 87Sr/86Sr**

Seawater 87Sr/86Sr is determined by fluxes from rivers and seafloor hydrothermal exchange at mid-ocean ridges (e.g., Burke et al., 1982; Davis et al., 2003). The riverine flux includes Sr derived from old continental crust that is relatively radiogenic with highly variable 87Sr/86Sr (~0.711 or higher), juvenile volcanic rocks with relatively nonradiogenic 87Sr/86Sr values similar to the hydrothermal exchange flux (~0.704), and weathered carbonates that are closest to the oceanic value (e.g., Davis et al., 2003). To balance the marine Sr cycle, Berner (2006) argued that basaltic volcanic weathering on land may represent a flux that is ~3 times that of basaltic seawater exchange.

Shields et al. (2003) proposed that the Ordovician drop in 87Sr/86Sr resulted from a combination of factors. One factor was lowered rates of tectonism during the waning Pan-African orogeny, which had produced highly radiogenic Middle to Late Cambrian 87Sr/86Sr values (Montañez et al., 1996). The more rapid drop in the late Darriwilian may have been related to increased seafloor spreading rates and eustatic rise that flooded radiogenic source areas, or to input of nonradiogenic Sr from weathering of volcanic rocks in island-arc settings in eastern Laurentia (Taconic orogeny) and Kazakhstan (Shields et al., 2003). Ultimately, these changes could relate to a mantle superplume (e.g., Qing et al., 1998).

The timing of the 87Sr/86Sr drop in Nevada (Fig. 1) supports the notion that volcanic weathering played a critical role. A significant increase in the rate of 87Sr/86Sr decline occurs within the *Pygodus serra* North Atlantic conodont zone (Fig. 1; late Darriwilian; time slice 4c of Webby et al., 2004; stage slice Dw3 of Bergström et al., 2008), which also correlates to the *Cabunagatus friendswillensis* Midcontinent conodont zone in the McLish Formation in Oklahoma (Shields et al., 2003). Initiation of subsidence associated with the Taconic orogeny in eastern North America correlates to the *Pygodus serra* zone based on graptolitic shales of the Didymograptus murchisoni and Glyptograptus teretiusculus graptolite zones (Finney et al., 1996). Analysis of εNd values in these graptolitic shales at the base of the Taconic foreland basin sequence indicates a source rock consisting of relatively young igneous rocks (D. murchisoni zone; Gleason et al., 2002). Similar εNd shifts are not observed in other ocean basins at this time (Wright et al., 2002), pointing to the potential importance of eastern Laurentian source rocks on 87Sr/86Sr. Numerous altered volcanic ash beds also occur in the Argentine Precordillerá in upper Floian–mid-Darriwilian strata (Oepikodas evae through P. suecicus conodont zones) (Huff et al., 1998). Weathering of the associated Famatinian arc may have produced the smaller, more gradual drop in seawater 87Sr/86Sr observed in the Floian portion of the Shields et al. (2003) compilation.

However, in contrast to the evidence for enhanced volcanic weathering in Laurentia during the Ordovician 87Sr/86Sr drop, the timing of Middle Ordovician eustatic events is complicated in our Nevada section and elsewhere in North America by regional tectonic events and locally variable sediment supply (e.g., Mussman and Read, 1986; Knight et al., 1991; Finney, 2007). Moreover, links between seafloor spreading and changes in sea level or ocean chemistry are uncertain (e.g., Kump, 2008).

**Modeling 87Sr/86Sr: Implications for Ordovician Climate**

We have adapted the model of Kump and Arthur (1997) to quantitatively explore possible causes of Sr isotopic and climate change during the Ordovician (see Table DR2). The slow decline of 87Sr/86Sr from the Early to Middle Ordovician (Fig. 2A) is driven by a reduction in the riverine isotope ratio, reflecting the decreasing importance of radiogenic source rocks associated with the Pan-African orogeny (Shields et al., 2003), or enhanced weathering of the Famatinian volcanic arc. A good fit is obtained when the riverine 87Sr/86Sr falls from 0.7106 (similar to today) to 0.7104. To drive the sharp decline in the late Darriwilian, we introduce a new flux from weathering of arc basalt of 0.7043 (Tables DR2 and DR3). The proportional contribution of volcanic arc materials to the total Sr weathering flux is tied to the specified increase in weatherability (from 1 to 1.25; see following). The new volcanic weathering flux, representing weathering of the Taconic arcs and possibly
The volcanic weathering flux is modeled to correspond to an increase in continental weatherability by ~25% compared to the pre-volcanic initial conditions equivalent to the modern (Fig. 2A; Table DR2). Weatherability refers collectively to all of the factors that affect silicate weathering other than climate (Kump and Arthur, 1997), and thus includes the proportion of continental basaltic rocks available to weather. Enhanced basaltic weathering beginning in the late Darriwilian and continuing through the end of the Ordovician is a major sink for \( p_{CO_2} \) (Fig. 2B). Because substantial volcanism began in eastern North America in the late Darriwilian, as seen in the abundant K-bentonite beds (Kolata et al., 1996), enhanced volcanic weathering was initially counterbalanced by volcanic outgassing. We used an outgassing rate that balances increased silicate weathering to maintain near constant \( p_{CO_2} \) (Fig. 2B) through the middle Katian, consistent with the paleotemperature curve of Trotter et al. (2008) (Fig. 3). In the late Katian, volcanic outgassing returned to baseline values but silicate weathering remained high due to continued volcanic weathering (Fig. 2B). This caused \( p_{CO_2} \) to fall and initiated cooling that led in the Hirnantian glacial episode (Fig. 3; Tremadocian Floian).

Figure 2. A: Model simulation of seawater \(^{87}\text{Sr}/^{86}\text{Sr} \) and the response to increase in weatherability (Kump and Arthur, 1997) caused by weathering of tectonically emplaced basaltic substrates beginning in late Darriwilian and continuing through Late Ordovician. See Table DR1 (see footnote 1) for magnitude and \(^{87}\text{Sr}/^{86}\text{Sr} \) of this excess volcanic weathering flux. B: Modeled \( p_{CO_2} \) response to weathering of volcanic arc terranes (i.e., silicate weathering flux; \( F_{\text{sil}} \)) and associated increase in volcanism. As volcanism ends and high \( F_{\text{sil}} \) continues in late Katian, \( p_{CO_2} \) falls sharply. Note that small rise in \( p_{CO_2} \) in late Darriwilian results from enhanced organic carbon weathered on land (\( F_{\text{org}} \); see Table DR3). See Figure 3 for Ordovician global stage abbreviations. Lland.—Llandovery.

Figure 3. Strontium and carbon isotopic variations in seawater through Ordovician. Gray dashed line represents best approximate seawater \(^{87}\text{Sr}/^{86}\text{Sr} \) trend. Also plotted are major volcanic ash falls from Argentine Precordillera terrane (APT; Huff et al., 1998), eastern North America and Baltica (ENA; Kolata et al., 1996), and tropical seawater temperature trend from Trotter et al. (2008). Ordovician \( \delta^{13}C \) data are replotted from Gao et al. (1996), Kump et al. (1999), Saltzman (2005), and Saltzman and Young (2005) (VPDB–Vienna Peedee belemnite). Time scale is from Webby et al. (2004) with new global stage names. H is Hirnantian.
Trotter et al., 2008). Several positive δ13C excursions, if used as a proxy for enhanced organic carbon burial, may also have contributed to lowering of CO2 (Figs. 1 and 3), but are not included in the current model. The specified volcanism and weatherability functions, together with the isotopic values of the various fluxes chosen, provide nonunique but internally consistent and geologically justifiable fits to the observed Sr isotope record (see Table DR2).

While the 87Sr/86Sr can be reconciled with the paleotemperature curve of Trotter et al. (2008) for the Late Ordovician, Early to Middle Ordovician cooling (Fig. 3) is more problematic. Low rates of organic carbon burial indicated by low δ13C in the Late Cambrian and Early through Middle Ordovician (Figs. 1 and 3; and Saltzman, 2005) could not have contributed to pCO2 drawdown. Volcanic weathering related to the Famatinian arc in the Argentine Precordillera may have lowered CO2, but cannot be the primary cause because cooling was already under way (Fig. 3). Perhaps the waning Pan-African orogeny and associated decrease in metamorphic degassing could have lowered CO2. Recent work on metamorphic degassing associated with the Himalayas (Evans et al., 2008) indicates that continental orogenic events may potentially be a net source of CO2.

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