SUPPLEMENTAL ONLINE MATERIAL

Boron proxies record paleosalinity variation in the North American Midcontinent Sea in response to Carboniferous glacio-eustasy

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AUXILIARY FIGURES
Figure S1. B and Ga concentrations of Stark Shale from (A) IRC and (B) CC. BS = black shale (circles), GS = gray shale (squares), LS = limestone (triangles; CaCO₃ >40%), and “L” and “U” prefixes for BS and GS indicate “lower” and “upper”, respectively. mfs = maximum flooding surface; detr = detrital. Note that the difference between the total concentration and the detrital fraction (for either B or Ga) represents the seawater-sourced (hydrogenous) fraction. For calculation of detrital B and Ga concentrations, see below.
Figure S2. Crossplot of Rb/B versus $\delta^{11}$B for shale samples from IRC (blue) and CC (red), showing strong negative covariation ($r = -0.87$; $p < 0.001$). This relationship reflects mixing of Rb-rich illite (deposited more proximally) and Rb-poor smectite (deposited more distally) and is similar to that reported for modern marine shales (Ishikawa and Nakamura, 1993). B in the illitic component is mostly detrital in origin and exhibits $\delta^{11}$B closer to the detrital value ($-9.1\%$), whereas a large fraction of B in the smectitic component is in the form of B(OH)$_4^-$ adsorbed from seawater ($+19\%$ to $+24\%$), yielding higher bulk-shale $\delta^{11}$B. This relationship supports interpretation of bulk-shale $\delta^{11}$B as an effective paleosalinity proxy.
Figure S3. Crossplot of $\delta^{11}$B versus B/Ga for both shale and limestone samples from IRC (blue) and CC (red). The few limestone samples (LS, triangles; $n = 5$) analyzed in this study yield higher $\delta^{11}$B (to +27‰) and are non-collinear with the black shales (BS, circle) and gray shales (GS, squares) [note: shale data and dashed regression line are the same as those in Figure 3 of the main text]. Note that B/Ga values at CC are similar for both shale and limestone samples, suggesting that the B/Ga of both lithologies is a robust paleosalinity proxy; differences in their $\delta^{11}$B values may reflect lithology-dependent B species uptake or the lack of detrital B in the limestone samples.

**ROLE OF NORMALIZATION OF BORON TO GALLIUM**

The reason for using an elemental ratio (i.e., B/Ga) rather than a simple concentration (i.e., $[B]$) to evaluate paleosalinity is that concentrations are highly susceptible to lithologic influences—for example, $[B]$ is typically 15-20 ppm in shales but <1 ppm in limestones, so $[B]$ variation will be heavily influenced by lithology in mixed limestone-shale successions. The elements B, Al, and Ga all belong to Group 13 (“boron group”) of the periodic table. The advantages of Ga rather than Al as a normalizer for B are that, compared to Al, the concentration of Ga in the sediment is much closer to that of B, and its behavior in aqueous systems is opposite that of B (i.e., Ga concentrations are higher in freshwater systems), enhancing the effectiveness of B/Ga as a paleosalinity proxy (Wei and Algeo, 2020).
Figure S4. Covariation of B versus Ga for the IRC (blue) and CC (red) study cores. Both sections exhibit strong positive covariation: IRC ($r = +0.59$, $p < 0.01$) and CC ($r = +0.87$, $p < 0.01$), reflecting lithologic influence on raw [B] and [Ga] concentrations. The solid lines connect samples in stratigraphic order from the base to the top of each study core. The dashed lines represent salinity facies thresholds between marine (B/Ga > 6), brackish (3-6), and freshwater (< 3) samples (from Wei and Algeo, 2020). Higher B/Ga ratios signify higher salinities at IRC (mostly marine) relative to CC (mostly brackish), recording a pronounced lateral gradient in salinity across the NAMS from the Midcontinent Shelf (marine) to the Illinois Basin (brackish).

**CALCULATION OF SEAWATER-SOURCED BORON FRACTION**

In siliciclastic formations containing a significant clay mineral fraction, crossplots of Al versus B and Al versus Ga allow estimation of the abundances of the detrital and hydrogenous fractions of each element for each sample (Fig. S5). For Ga, strong positive covariation with Al demonstrates that most Ga is resident in the detrital fraction (Spivack et al., 1987; Wei and Algeo, 2020), yielding similar estimates of detrital Ga/Al (2.7 ppm/%) for both IRC and CC.
For B, a ratio fitting the base of the data field at CC provides the best estimate of detrital B/Al (9±1 ppm/%), and the same value was applied to IRC. For all plots, excess B and Ga above the dashed detrital lines represent the seawater-sourced (hydrogenous) fractions of each element. Computationally, \( B_{detr} = (B/Al)_{detr} \times Al \), and \( B_{sw} = B_{total} - B_{detr} \).

The isotopic composition of \( B_{sw} \) was calculated as \( \delta^{11}B_{sw} = \frac{\delta^{11}B_{meas} \times B_{total} - \delta^{11}B_{detr} \times B_{detr}}{B_{sw}} \), where \( \delta^{11}B_{meas} \) is the measured composition of bulk boron, and \( \delta^{11}B_{detr} \) was assumed to be –9.1±2.4‰ based on the B-isotopic composition of average continental crust (Lemarchand et al., 2012; Gaillardet and Lemarchand, 2018). Calculation of \( \delta^{11}B_{sw} \) for each sample yielded similar estimates for IRC (mean +5.5‰, range +4.4 to +6.6‰) and CC (mean +5.5‰, range +5.3 to +5.9‰). Modern marine shales on continental shelves exhibit relatively low bulk \( \delta^{11}B \) (median = –4.4‰, range = –6.6 to –1.8‰) due to the presence of large amounts of \( ^{11}B \)-depleted eolian dust (Spivack et al., 1987; Ishikawa and Nakamura, 1993), but open-ocean sediments contain a ‘marine smectite’ component with \( \delta^{11}B \) (+4 to +10‰; Ishikawa and Nakamura, 1993) similar to the \( \delta^{11}B_{sw} \) of the present study units.

Figure S5. Crossplots of Al versus B (a,c) and Al versus Ga (b,d) for IRC (blue) and CC (red).
The dashed line in each panel represents the estimated B/Al or G/Al ratio of the detrital component. CC shows well-defined detrital ratios of 9±1 ppm/% for B/Al and 2.5 ppm/% for Ga/Al. IRC shows greater data scatter, although the detrital Ga/Al is similar to that at CC; the detrital B/Al at IRC could not be determined graphically and was assumed to be the same as at CC, which is reasonable given the similar detrital Ga/Al ratios of the two study sites.

BORON ISOTOPE SYSTEMATICS

Boron isotopes exhibit substantial variation in natural systems. During weathering, B is adsorbed onto clay-mineral surfaces (Williams et al., 2001; Ercolani et al., 2019) or becomes structurally incorporated into secondary clay minerals (Voinot, et al., 2013; Gaillardet and Lemarchand, 2018). Both processes favor uptake of $^{10}$B in the solid phase by up to 30‰ (Rose et al., 2000; Noireaux et al., 2021), yielding lower $\delta^{11}$B values for weathered clays and aeolian dust (ca. –12 ± 6‰) and higher values for riverine (+2‰ to +20‰) and meteoric waters (+1 to +26‰; Rose-Koga et al., 2006; Mao et al., 2019). Seawater B, which is mainly (>90%) sourced from rivers (Spivack et al., 1987; Gaillardet and Lemarchand, 2018), has a homogeneous $\delta^{11}$B of +39.61 ± 0.04‰ (Ercolani et al., 2019; Mao et al., 2019) due to its long residence time (~29 Myr; Lemarchand et al., 2002).

Boron isotopic compositions are influenced by pH-controlled chemical speciation, with B(OH)$_3$ and B(OH)$_4$ being the dominant species at low pH and high pH, respectively. In predominantly low-pH freshwater systems, B is present only as B(OH)$_3$, resulting in a uniform B-isotopic composition, whereas in seawater, both B(OH)$_3$ ($\delta^{11}$B = +40.4 to +45.2‰) and B(OH)$_4$ ($\delta^{11}$B = +19.4 to +24.1‰) are present (Rose-Koga et al., 2006; Mao et al., 2019). Whereas carbonate minerals take up only the latter species, yielding marine carbonate $\delta^{11}$B of +22.1 ± 3‰ (Hemming and Hanson, 1992), clay minerals can take up either B species depending on mineral surface charge and fluid pH, with low pH (< 7) favoring B(OH)$_4$ uptake and high pH (> 7) favoring B(OH)$_3$ uptake (Williams et al., 2001; Kowalski and Wunder, 2018).

Modern marine carbonates faithfully record the $\delta^{11}$B of seawater B(OH)$_4$ (+19.4 to +24.1‰), and the $\delta^{11}$B of carbonate samples of the present study is consistent with this B source.
The similarity of δ\(^{11}\)B values of Pennsylvanian brachiopods (+12.4 to +15.8‰; Joachimski et al., 2005) to those of modern marine brachiopods (+16.8 to +19.7‰; Lécuyer et al., 2002) implies only minor differences in the δ\(^{11}\)B of Pennsylvanian and modern seawater.

REFERENCES CITED


