Paleoceanography and Paleoclimatology

Supporting Information for

A sequential leaching protocol for δ^{11} B and trace element analyses of multi-phase carbonate rocks

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Text S1. The effect of re-adsorption to boron composition in the leachate during sequential acid treatment

To further examine possible effects of boron re-adsorption during leaching (as discussed in section 4.2 from main text), we modeled the expected changes in $\delta^{11}B$ if all changes in B concentrations are due to both the release of clay-adsorbed boron and carbonate dissolution from steps S1 to S4 under a pH of 5.5. We assume that, for a given HAc leaching step *n*, the initial solution $([B]_i^n \text{ and } \delta^{11}_{\square}B_i^n)$ contains boron from carbonate dissolution $([B]_{carb}^n \text{ and } \delta^{11}_{\square}B_{carb}^n)$ with additional boron desorbed from clay surface $([B]_{ads}^{\square} \text{ and } \delta^{11}_{\square}B_{ads}^{\square})$. Immediate re-adsorption of boron onto the clay minerals occurs and results in a lower B concentration but higher $\delta^{11}B$ in the final leachate $([B]_f \text{ and } \delta^{11}_{\square}B_f^{\square})$ which can be expressed as:

$$[B]_{f}^{n} = [B]_{i}^{n} - [B]_{ads}^{n} \qquad \text{Eq. (1)}$$

$$\delta_{\square}^{11}B_{f}^{n} = \frac{[B]_{i}^{n} \times \delta_{\square}^{11}B_{i}^{n} - [B]_{ads}^{n} \times \delta_{\square}^{11}B_{ads}^{n}}{[B]_{f}^{n}} \quad (n=\text{S2 to S4})$$

As we removed all solution produced from the previous step, the initial leachate boron composition can be expressed as:

$$[B]_{i}^{n} = [B]_{carb}^{\square} + [B]_{ads}^{n-1} \qquad \text{Eq. (2)}$$

$$\delta_{\square}^{11}B_{i}^{n} = \frac{[B]_{carb}^{\square} \times \delta_{\square}^{11}B_{carb}^{\square} + [B]_{ads}^{n-1} \times \delta_{\square}^{11}B_{ads}^{n-1}}{[B]_{i}^{n}} (n=\text{S2 to S4})$$

where $[B]_{carb}^{\square}$ and $\delta_{\square}^{11}B_{carb}^{\square}$ are genuine values from carbonate. These values are essentially unknow but we assumed they are equal to $[B]_{i}^{S1}$ and $\delta_{\square}^{11}B_{i}^{S1}$, respectively, or the boron composition in the leachate before clay-adsorption during acid treatment takes place (i.e., S1). This assumption is justified since we are only interested in how such readsorption process affects the boron composition during acid treatment.

The $[B]_{ads}^{n}$ was calculated with a K_D value of 0.1055 (pH = 5.5) as follow:

$$[B]_{ads}^{n} = K_{D} \times [B]_{f}^{n}$$
 (n=S1 to S4) Eq. (3)

The $\delta_{\square}^{11}B_{ads}^n$ was calculated by re-arranging the following expression for α which is 0.9597 at pH 5.5:

$$\alpha = \frac{R_{ads}}{R_f} = \frac{\delta^{11}_{\Box} B^n_{ads} + 1000}{\delta^{11}_{\Box} B^n_f + 100}$$
(n=S1 to S4) Eq. (4)

where *R* equals to $\frac{11}{10}B_{II}$. We chose a pH value of 5.5 so that it not only represents the conditions of our S1 to S4 leachates, the resulting K_D is also able to increase boron concentration to the level observed (Fig. 6). It is apparent that the calculation with Eqs. (1) to (4) requires initial input values of [B] and $\delta^{11}B$, which we assigned the measured values of step S1 from MDAC sample MC-M5 as [B]_f and $\delta^{11}B_{II}^{\square}$ (9.9 µg/g and +11.07‰, respectively). The values for [B]_{ads} and $\delta^{11}B_{ads}^{\square}$ for S1 of this sample were calculated with assumed K_D values for three different pH (5.41, 5.5, and 6) as derived from Palmer et al. (1987). Values of [B]_i and $\delta^{11}B_{II}^{\square}$ for the same step were calculated by re-arranging Eq. (1) (see Suppl. Table 1 for the values derived).

We compared the results derived from this calculation with the values obtained from steps S1 and S4 for sample MC-M5 in Suppl. Fig. 4. The clay-adsorbed boron has δ^{11} B values ranging from -29.7 to -33.4‰ (B_{ads} in Suppl. Fig. 4 and Suppl. Table 1) and thus even a small fraction of boron being adsorbed to clay, 10.6 wt% in this case (i.e., K_D; Suppl. Table 1), will significantly increase the δ^{11} B values in the residual leachate (i.e., compare B_i and B_f for each step in Suppl. Fig. 4b that represent the δ^{11} B before and after clay adsorption, respectively). However, the release of clay-adsorbed boron in the following leaching steps should decrease δ^{11} B from 11.1‰ to 7.2‰ in our calculation (B_f in Suppl. Fig. 4), which was not observed in S1 to S4 (Suppl. Fig. 4a) in our samples. We therefore conclude that the re-adsorption of boron during our sequential leaching treatment.



Figure S1. Cross plots of elements released during oxidative cleaning.

1



Figure S2. Cross plots of elements released during buffer cleaning.

2





Figure S4. Modeling of boron re-adsorption. A calculation assuming immediate readsorption of boron onto clay surfaces during acid leaching suggests this process is not significant under these conditions. We assumed a solution pH of 5.5 for this calculation and used the partition coefficient and isotopic fractionation factor for such a condition from Palmer et al. (1987). (a) The calculated boron systematics in the final leachate (B_f) show a progressively decreasing trend in δ^{11} B signatures that is not observed in the measured data. (b) Changes in δ^{11} B signatures in the leachate before re-adsorption (B_i), after adsorption (B_i) and the boron adsorbed (B_{ads}). See Suppl. Table 1 for the calculation results.

	[B] _{carb}	δ ¹¹ B _{car} b	[B]i	δ ¹¹ Β i	[B] _f	δ ¹¹ B f	[B] ads b	$\delta^{11} \mathbf{B}_{ads}$ c
uni t	μM	%0	μM	‰	μM	%0	μM	%0
S1			1009.5 d	7.2 ^e	913.2ª	11.1 a	96.3	-29.7
S2	1009. 5 ^f	7.2 ^f	1105.8 g	4.0 ^g	1000.3 ^h	7.84 ^h	105.5	-32.8
S3	1009. 5 ^f	7.2 ^f	1114.9 g	3.4 ^g	1008.6 ^h	7.3 ^h	106.4	-33.3
S4	1009. 5 ^f	7.2 ^f	1115.8 g	3.3 ^g	1009.4 ^h	7.2 ^h	106.4	-33.4

^a measured values of sample MC-M5 (Suppl. Dataset. 2)

^b calculated by $[B]_f \times K_D$ (=0.10545 g/g for pH = 5.5; Palmer et al., 1987)

^c calculated by $\alpha \times (\delta^{11}B_f + 1000) - 1000 \ (\alpha = 0.9597 \ \text{for pH} = 5.5; \text{ Palmer et al., 1987})$ ^d [B]_i = [B]_f + [B]_{ads}

$${}^{e} \delta {}^{11}_{\square} B_i^{S1} = \frac{{}^{[B]}_{f}^{S1} \times \delta {}^{11}_{\square} B_{f}^{S1} + {}^{[B]}_{ads}^{S1} \times \delta {}^{11}_{\square} B_{ads}^{S1}}{{}^{[B]}_{i}^{S1}}$$

 $^{\rm f}$ assuming equals to [B]_i and $\delta^{11}B_i$ in S1.

^g calculated by assuming [B]_i equals [B]_{carb} in the same step and [B]_{ads} from the previous step (e.g., 1105.8=1009.5+96.3). $\delta^{11}B_i$ is calculated from the mass balance of the two. ^h [B]_f = [B]_i – [B]_{ads} and $\delta^{11}B_f$ calculated from the mass balance.

Table S1. Calculated • 11B signatures for S1-S4 in MDAC sample MC-M5 with clay readsorption assumed to be significant.

Data Set S1. XRD results for the 12 MDAC samples and their corresponding acid leaching residual materials. Data produced in this paper can be accessed at the Interdisciplinary Earth Data Alliance (Hong et al., 2024).

Data Set S2. Elemental composition and boron isotopic signatures for oxidative cleaning, buffer cleaning, and acid leaching steps. Data produced in this paper can be accessed at the Interdisciplinary Earth Data Alliance (Hong et al., 2024).