Supplementary Information

S.1 Method

S.1.1 Flow-through column experiments

Ten flow-through sediment reactors (12 cm in length) were constructed following modifications to designs reported by Pallud and Van Cappellen (2006), Ridenour (2017), and Sabur (2019). Each reactor was sealed at both ends with O-ring-lined caps to prevent leakage. A 47-mm, 0.2-µm polypropylene membrane filter was placed at the base to ensure even distribution of influent flow and to prevent clogging. The upper cap contained two 2-cm openings to permit gas exchange. Caps were secured tightly with threaded rods and nuts. Prior to loading, sediments were sieved (<500 µm) to remove coarse material and benthic fauna, then thoroughly homogenized to minimize variability among replicates. The prepared sediment was added to each reactor to form a 10-cm sediment layer overlain by ~1 cm of water. Reactors were pre-equilibrated overnight in the dark at 25°C ± 1°C. A schematic of the experimental setup is shown in Fig. S1.

Influent solutions consisted of deoxygenated artificial porewater (APW), formulated from in situ porewater chemistry measured at 5 cm depth using peepers (Ridenour, 2017; Parsons, unpublished). Six treatments with different combinations of dissolved Fe(II), DP, and DSi were prepared (Table 1): Bromide, Br^- added as KBr was used as non-reactive tracer, Ca^{2+} ($CaCl_2.2H_2O$) and Mg^{2+} ($MgCl_2$) concentrations were chosen to match the chemical composition of porewater. 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES, Sigma, Germany, purity ≥99.5%) was used as pH buffer instead of $NaHCO_3$ to avoid the precipitation of Fe(II) carbonate, acetate was used to avoid the depletion of organic carbon substance during the incubations, Si ($Na_2O_3Si.9H_2O$) concentration was chosen to enable co-precipitation with Fe(II) and to minimize the effects of amorphous silica dissolution in sediment on the DSi release, Fe(II) ($FeCl_2.4H_2O$) concentration was designed to enable the retention of DSi, and P (NaH_2PO_4) was added in some columns to assess its effects on the release of DSi. All influent solutions were buffered to pH 7.00 ± 0.02 with HEPES to inhibit Fe(II) oxidation and prevent precipitation of ferrous phosphate or carbonate minerals. A non-carbonate buffer was selected specifically to avoid formation of Fe(II) carbonate phases. Oxic and anoxic conditions refer to the status of the 1-cm overlying water layer. During oxic phases, purified air was continuously bubbled into the overlying water through one of the openings in the top cap. Influent solutions were introduced at ~5 mL/h through a bottom side port using peristaltic pumps, and effluent was withdrawn from a port positioned 1 cm below the upper cap at the same rate. For anoxic phases, both cap openings were tightly sealed with rubber stoppers and silicone to prevent gas exchange. Effluent samples were collected manually with syringes to avoid oxygen intrusion, rather than using peristaltic pumps.

Artificial porewater (APW) was circulated through the reactors for the first 24 hours to saturate the sediment columns and ensure consistent initial porewater conditions across treatments. Beginning on the following day, the different influent solutions were applied according to the durations and oxygenation regimes summarized in Table 1 and Fig. 1. Sampling frequency was highest at the onset of each new stage (three times daily) and reduced toward the end of the stage (one to two times daily).

After the flow-through experiments were completed, sediments were removed from the reactors, frozen at -20°C, and sectioned into six depth intervals (0–0.5, 0.5–1, 1–2, 2–4, 4–6, and 6–10 cm) using a bandsaw. Following freeze-drying, all sections from columns 1–9 were subjected to buffered ascorbate-citrate (BAC) extraction, while sections from columns 1, 2, 4, and 5 were also treated with 1 mol/L NaOH. The BAC extractant (pH ~7.5) consisted of 10 g L^{-1} ascorbic acid, 50 g L^{-1} sodium citrate, and 50 g L^{-1} sodium bicarbonate, and selectively dissolves highly reactive Fe(III) phases (Hyacinthe and Van Cappellen, 2004; Kostka and Luther, 1994). For each extraction, 50 mL of BAC solution was added to 25 mg of sediment in 60-mL serum bottles inside an anaerobic chamber. Bottles were sealed, placed in an environmental chamber, and shaken at 30 r/min at 25°C ± 1°C for 24 hours. Extracts were filtered through 0.2-µm syringe filters, acidified with HCl to $\text{pH} < 2$, and stored at 4°C until analysis.

Reactive particulate silica was quantified using a modified single-point alkaline extraction (Koning et al., 2002; Ohlendorf and Sturm, 2008). In this procedure, 10 mL of 1 mol/L NaOH was added to 10 mg of freeze-dried sediment in Teflon liners, which were then placed into metal digestion vessels and heated at 100°C for 3 hours. Extracts were filtered (0.2 µm), acidified with HNO_3, and analyzed by ICP-OES for major elements and DSi. To estimate amorphous silica (ASi), the NaOH-extractable Si was corrected for contributions from aluminosilicate dissolution using a Si:Al ratio of 2:1.

S.1.2 Mass balances

To compare the elemental masses supplied to the sediment columns to those released to the overlying water, the following cumulative masses were calculated (Eqs. (S1) and (S2)):

$$Mass_D^{Outflow}(t) = \sum_{i=1}^{n} Mass_D(t_i) \tag{S1}$$

$$Mass_D^{Inflow}(t) = C_D \cdot Q \cdot t \tag{S2}$$

where $Mass_D^{\mathrm{Outflow}}$ (t) is the cumulative mass of dissolved Fe, DSi or DP (µmol) released to the overlying water at time *t*, $Mass_{\mathrm{D}}(t_i)$ is the mass of dissolved Fe, DSi or DP (µmol) accumulated in the overlying water sample collected at time t_i ($\leq t$), and *n* is the number of samples collected over the time interval *t*, $Mass_D^{\mathrm{Inflow}}$ (t) is the cumulative mass of dissolved Fe, DSi or DP supplied to the sediment columns up to time *t*, C_D is the concentration of dissolved Fe, DSi or DP in the influent solutions (µmol/L), *Q* is the flow rate at which the influent solution is supplied (5 mL/h).

Equations (S1) and (S2) were integrated over the oxic and anoxic time intervals. However, because these intervals had different durations, the cumulative inflow and outflow masses were normalized to the corresponding durations. The net release or retention rate (R_D^{Net}) during a given interval was then computed by subtracting the normalized cumulative inflow masses from the corresponding outflow masses (Eq. (S3)):

$$R_D^{Net} = (Mass_D^{Outflow}(\Delta t) - Mass_D^{Inflow}(\Delta t))/\Delta t \tag{S3}$$

where Δt is the duration of oxic or anoxic period, with $t = 0$ corresponding to the start of the period. Positive values of R_D^{Net} indicate net retention of the dissolved element supplied to the sediment column, negative values imply net release. The latter implies production of dissolved Fe, DSi or DP within the sediment.

When an experiment with a given column was terminated, the concentrations of BAC extractable Fe, Si, P, and NaOH-extractable reactive Si were determined at different depths along the column. The final depth distributions were then compared to the initial (homogeneous) concentration distributions in order to identify depth intervals of accumulation or depletion of the extractable element pools. Furthermore, by integrating the concentrations over the entire length of the column, the total masses of the extractable elements were calculated to quantify whole-column accumulation or loss of solid-bound Fe, P and Si.

A mass balance approach was used to calculate the net release from, or retention by, the sediment columns of dissolved Fe, DSi, and DP. Total amounts of dissolved Fe, Si and P released from columns were calculated as the integration of mass over time (Eqs. (S4) and (S5)):

$$Mass_D^{Cum}(t) = \sum_{i=0}^{n} Mass_D(t_i) \qquad \text{(S4)}$$

$$Mass_D^{Influent}(t) = C_D \cdot Q \cdot t \qquad \text{(S5)}$$

$Mass_D^{Cum}$(t) is the cumulative release of dissolved Fe, DSi or DP (µmol) from sediment columns to overlying water at time t, $Mass_D(t_i)$ is the amount of dissolved Fe, Si or P released (µmol) at time t_i, n is the number of samples collected, $Mass_D^{Influent}$(t) is the total amount of dissolved Fe, DSi or DP supplied to the sediment columns at time t, C_D is the concentration of dissolved elements in influent solutions (µmol/L). Q is the flow rate of influent solution (5 mL/h). The net released or retained elements masses were calculated as the total amounts of dissolved Fe, DSi, and DP collected in the effluents minus the total amounts of Fe, DSi, and DP supplied by the influents. The masses were normalized by the duration of the oxic or anoxic periods to represent the budgets of dissolved Fe, DSi, and DP of the flow-through sediment columns per unit time (Eq. (S6)):

$$\frac{dMass_D}{dt} = (Mass_D^{Cum}(t) - Mass_D^{Influent}(t))/\Delta t \qquad \text{(S6)}$$

where $Mass_D$ is the net released or retained mass of dissolved Fe, Si or P, and Δt is the duration of either the oxic or anoxic periods.

The concentrations of BAC extractable Fe, Si, P, and NaOH-extractable ASi in the solid phase were determined for specific depth intervals of the sediment columns. Therefore, the total amounts of BAC extractable Fe, Si, P and NaOH extractable ASi in the sediment columns were calculated as the integration of mass over depth (Eq. (S7)):

$$Mass_S = \sum_{j=0} C_S(j) \cdot m_j \qquad \text{(S7)}$$

where $Mass_D$ is the total amounts of BAC extractable Fe, Si, P or NaOH-extractable ASi in the sediment columns, $C_S(j)$ is the concentration of BAC extractable Fe, Si, P or NaOH-extractable ASi (µmol/g) at depth j, m_j is the mass of sediment (g) at depth j. The budgets of solid phases, *i.e.*, BAC extractable Fe, Si, P and NaOH-extractable ASi were also calculated (Eqs. (S8) and (S9)):

$$\frac{dMass_S^I}{dt} = (Mass_S^{tI} - Mass_S^0)/(t_I) \tag{S8}$$

$$\frac{dMass_S^{II}}{dt} = (Mass_{S,i}^{tII} - Mass_S^{tI})/(t_{II} - t_I) \tag{S9}$$

where $Mass_S^0$, $Mass_S^{tI}$, and $Mass_S^{tII}$ are the total amount of BAC extractable Fe, Si, P or NaOH-extractable ASi of initial sediment columns (at time zero), sediment columns after oxic incubation periods, and sediment columns after the whole incubation experiments (include both oxic and anoxic periods), t_I is the duration of oxic incubation, t_{II} is the duration of the whole incubation.

S.1.3 Analytical methods

Water samples and solid extraction samples were filtered using 0.2 µm polypropylene syringe filters. They were then acidified with trace-metal grade hydrochloric acid to a pH below 2 and kept at 4°C until testing. Major elements and DSi were measured with an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Thermo Scientific iCAP 6300, USA). Standards were made from Fisher Scientific stock solutions. Reference solutions were made from multi-element standards (Delta Scientific Laboratory Products Ltd., Canada) and tested with all samples to check accuracy. The precision of these tests was better than 10%, and the relative standard deviation stayed within 5%.

Two milliliters of water samples were also filtered through 0.2 µm polyethersulfone (PES) syringe filters for major anion analysis (Br^-, NO_2^-, NO_3^-, and SO_4^{2-}) using Ion Chromatography (Dionex ICS-5000, Thermo Scientific, USA). Detection limits in

μmol/L were: Br$^-$ (1.2), NO$_2^-$ (2.1), NO$_3^-$ (1.5), and SO$_4^{2-}$ (0.8). Precision was usually better than 5%, and standard values stayed within 10% of certified results.

Fig. S1 Photo of the experimental set-up.

S.2 Results

Operating conditions of the sediment columns

The hydraulic behavior, pH evolution, and overlying water oxygenation of the sediment columns have been described in detail elsewhere (Sabur, 2019) and are briefly summarized here. The sediment porosity was approximately 0.81. At an influent flow rate of 5 mL/h, the conservative tracer bromide (Br^-) reached roughly 65% of its inlet concentration within one day. Breakthrough curves were nearly identical across all columns (Fig. S2), confirming comparable transport properties among the reactors. The overlying water initially had a pH of 8.50 in all columns, which decreased to 7.60 ± 0.10 within 12 hours after switching to pH-adjusted (7.0) APW. During oxic operation, pH remained stable, whereas sealing the top cap to establish anoxic conditions caused a further decrease to 7.25 ± 0.05. In the absence of active aeration during the first day of incubation (Stage II, Fig. 1), dissolved oxygen (DO) levels in the overlying water fell below 50% saturation at 25°C (Sabur, 2019). When continuous air sparging was applied during subsequent oxic stages, DO exceeded 70% saturation. Although porewater oxygen profiles were not directly measured, the appearance of a yellowish oxidized layer at the sediment surface suggested that the oxic front extended roughly 1 cm into the sediment.

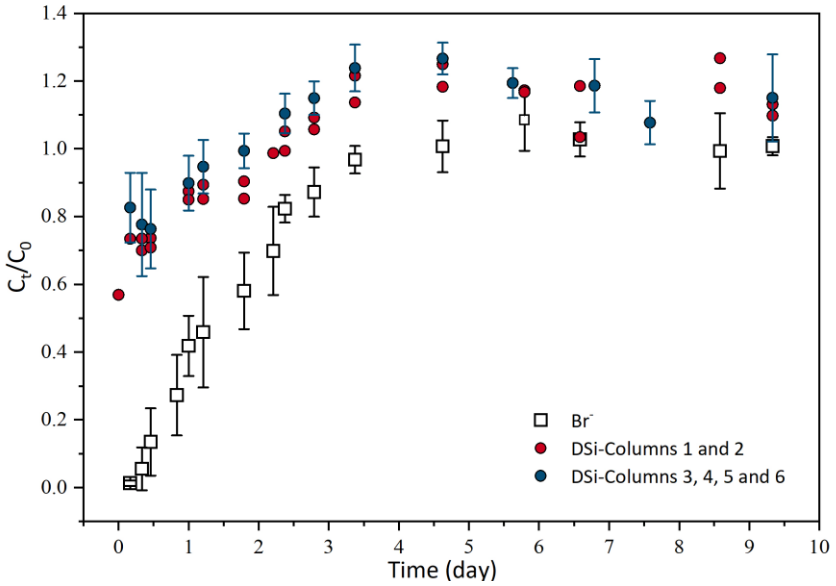

Fig. S2 The normalized concentration (C_t/C_0) of Br^- and DSi measured in the effluents from the columns over time (n = 10). C_t is the concentration of Br^- or DSi in the effluents at time t, C_0 is the (constant) concentration of Br^- or DSi in the influent. C_t of Br^- is the average of columns 1, 2, 3, 4, 5, and 6. Columns 1 and 2 were control columns supplied with "DSi", columns 3, 4, 5 and 6 were supplied with "Fe, DSi". Note that the greater than one C_t/C_0 values for DSi imply production of DSi in the sediment columns, likely through the dissolution of amorphous silica.

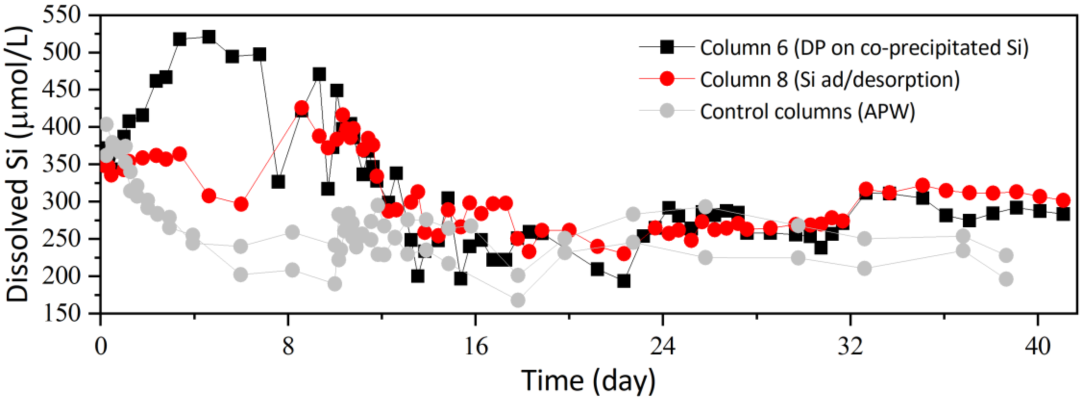

Fig. S3 Concentrations of DSi in the effluents of columns 6 and 8, and the two control columns, as a function of time. Column 6 was firstly supplied with "Fe, DSi" for 224 hours, and then with "P" for 280 hours under oxic conditions; column 8 was firstly supplied with "Fe" for 144 hours, then with "DSi" for 80 hours, and finally with "P" for 280 hours under oxic conditions. The influent to columns 4 and 5 was switched to "P" under anoxic conditions after 504 hours. Control columns were supplied with only APW throughout the incubation experiment, and the overlying water was switched to anoxic conditions after 224 hours of aeration.

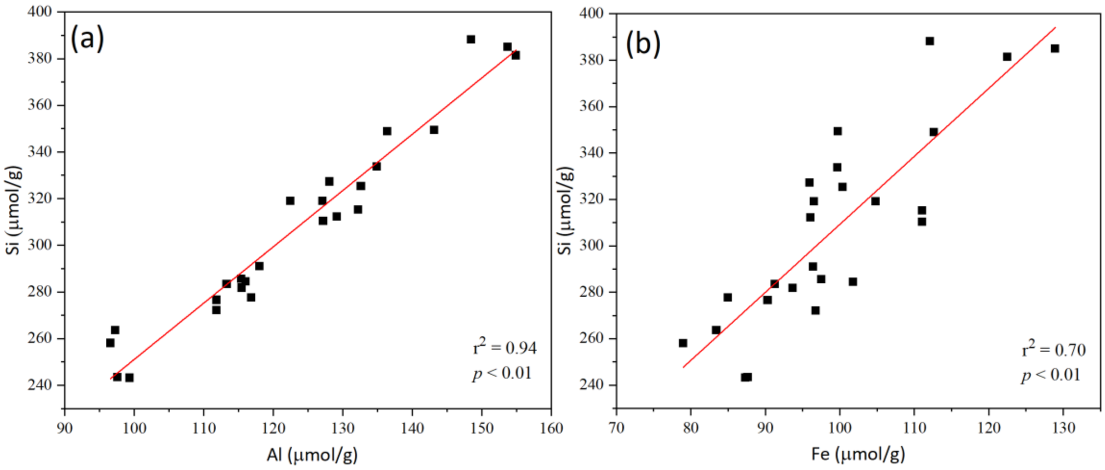

Fig. S4 Relationship between 1 mol/L NaOH extractable Al, Fe and Si in sediments from columns 1, 2, 4 and 5. Column 1 was flushed with "DSi" for 9 days under oxic conditions, column 2 was flushed with "DSi" for 9 days under oxic conditions, and then flushed with "DSi" for 32 days under anoxic conditions. Column 5 was flushed with "Fe, DSi" for 9 days under oxic conditions, column 4 was firstly flushed with "Fe, DSi" for 9 days under oxic conditions, then with "DSi" for 32 days under anoxic conditions.