Method improvement to separate and quantify SiO_2 phases in marine sediments: Testing wet-chemical sequential leaching on sediments with modified bSi contents

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Introduction

The silicon (Si) phases found in marine sediments, such as biogenic silica (bSi), lithogenic silicate (LSi), and amorphous secondary Si phases (ASSi) provide insights into past and present silicon deposition and cycling. DeMaster (1981) was the first one to use Na_2CO_3 leaching to extract diatoms from surficial marine sediments. This protocol has since then been widely used and modified. As recent studies have shown, it is especially difficult separating bSi and LSi phases from deeply-buried and diagenetically-modified sediments, where longer digestion times are needed to extract bSi via Na_2CO_3 leaching. Hence, there is a need for a robust protocol that allows both for isolation and quantification of the individual phases.

To test how much bSi can be extracted with the wet-chemical sequential leaching method (modified after Huang et al. 2023) we perform systematic experiments where PACS-3, a marine sediment certified reference material, is mixed with known amounts of bSi (0, 10, 20 wt%). Here, we present the results of the elemental analysis of the extracted leachates, and we use the Si/Al molar ratio in the leachate as an indication for the leached Si phases.

Material and Methods

bSi extraction

To be able to use pure diatoms as a reference material for bSi, we extracted these from a diatom culture (LPB™ Frozen Shellfish Diet®). To clean the silica skeletons from the organic material, we followed this protocol:

- Rinse+centrifuge the algae samples (~15 ml) with Milli-Q water 3 times
- Add in consecutive order 15% HNO_3, 30% HNO_3, 15% H_2O_2, and 30% H_2O_2: let each react for 8 hours in a water bath at 65 °C
- Centrifuge and remove supernatant after every step
- Rinse with Milli-Q water to remove H_2O_2, freeze dry until further use
- Quantify TOC content though EA → to be measured

Sequential leaching

PACS-3, a marine sediment certified reference material, is mixed with 10 and 20 wt%, respectively, of the extracted diatom bSi. Of these mixtures, duplicates of 0.5 g sample size are treated with H_2O_2 to remove organic matter before the leaching. In between steps, the samples are rinsed with Milli-Q water (Fig. 1).

To separate the different Si phases, the sediment+bSi samples are (sequentially) mixed with

- HCl: to dissolve amorphous secondary Si phase (ASSi)
- Na_2CO_3: to dissolve diatoms (bSi)
- NaOH: to dissolve lithogenic silicate (LSi)

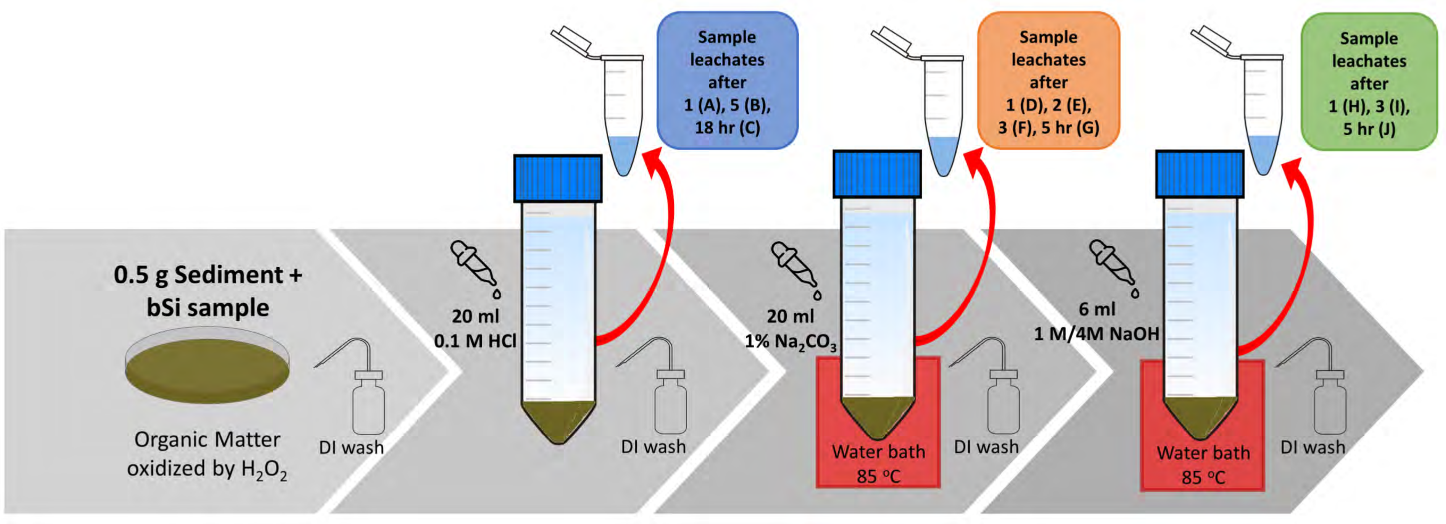

Fig. 1: Step-by-step procedure of the wet-chemical sequential leaching (modified after Huang et al. 2023)

In total, we sample the supernatant (leachate) ten times. The reagent is renewed after every sampling.

Geochemical analysis

The leachate samples are analysed regarding their elemental abundance using ICP-OES (ICAP 6000 series, Thermo Scientific) at the Department of Geological Sciences, Stockholm University. Samples were acidified and diluted with HNO_3 (2 vol%) before analysis.

My PhD Project:

Export of weathering products to the Baltic Sea – natural and anthropogenic interferences

Starting from January 2024, the overall goal of my PhD project will be to investigate the past and present export of weathering products to the Baltic Sea. Overall, weathering intensities vary as a function of climatic pattern, bedrock composition, topography, and potentially human activities. One prominent activity, especially in the coastal regions of the Northern Baltic Sea, is the damming of rivers.

The separating of Si phases, as presented here, can therefore be used to study the composition of the suspended particles in the rivers and to investigate how later the exported Si is potentially affected by early diagenetic processes in the marine sediments of the Baltic Sea.

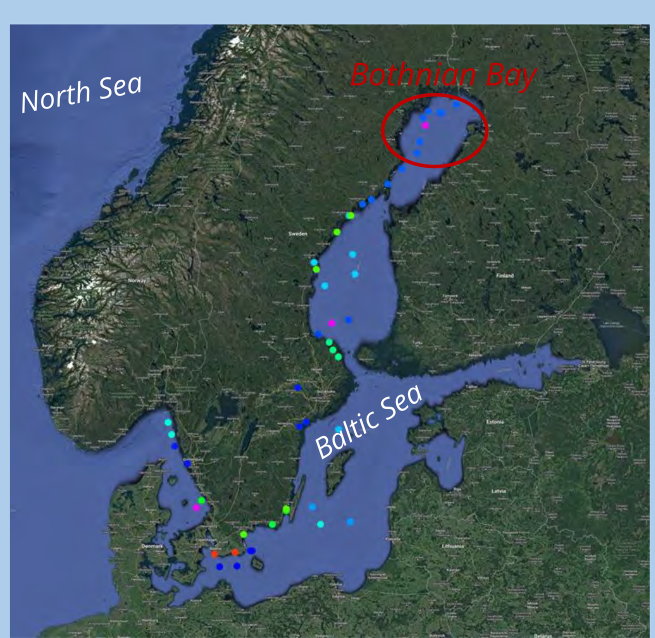

Fig. 2: Map of the Baltic Sea showing the locations of sediment cores and the study area in the Bothnian Bay

Results and Discussion

HCl leaching

- Lowest Si conc. (0.03 to 0.06 wt%), lowest Si/Al ratios (1.5 to 3 mol mol^{-1}) (Fig. 3), and lowest Si/Fe ratios (0.4 to 0.7 mol mol^{-1}) in the leachates
- Indicates the dissolution of Fe oxide and clay-like material (Childs 1992, Michalopoulos & Aller, 2004)

Na_2CO_3 leaching

- Highest SiO_2 conc. (0.3 to 9.5 wt%) and highest Si/Al ratios (7.1 to 884 mol mol^{-1}) in the leachates (Fig. 3) → indicates the dissolution of diatoms
- Si/Al ratio increases in the second hour for 20%-samples: higher release of Al in the first hour can potentially be attributed to dissolution of residual ASSi (Huang et al. 2023)

NaOH leaching

- Low Si conc. (0.5 to 3.2 wt%) and low Si/Al ratios (3.5 to 3.8 mol mol^{-1}) in the leachates (Fig. 3)
- During the first hour of NaOH leaching, the 20%-samples show higher Si/Al ratios: remaining diatoms are potentially dissolved

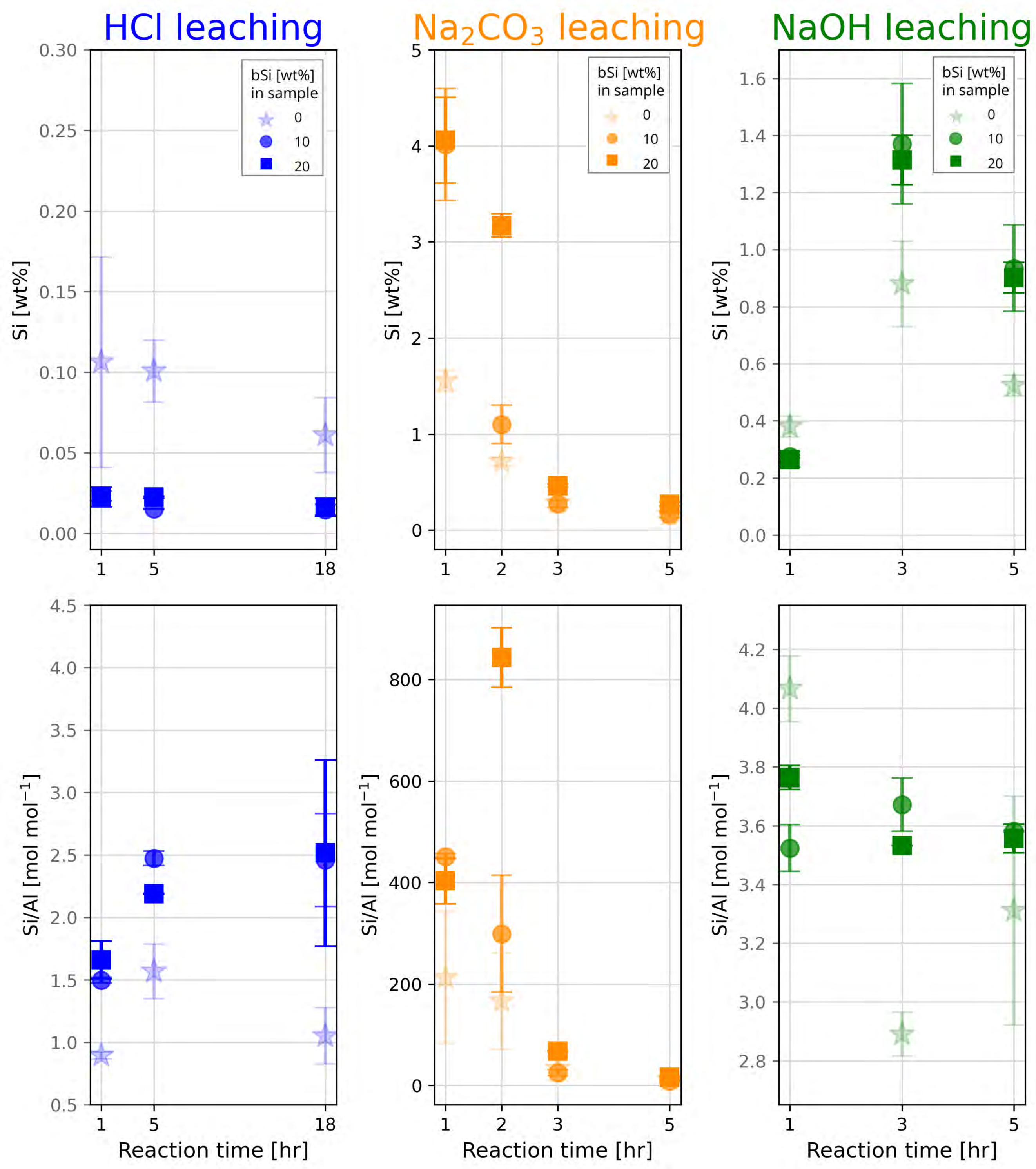

Fig. 3: Concentration of Si (upper plots) and measured molar ratios of Si/Al in the leachates (lower plots). Pay attention to the different ranges of values on the y-axes.

bSi recovery

- In samples with low bSi content (10 wt%), up to 79% of the added bSi could be dissolved.
- In samples with higher bSi content (20%), longer reaction times (>2 hrs) were needed to dissolve bSi. Overall, only 58 to 66% of the bSi in the 20%-samples could be dissolved.
- We might overestimate the bSi amount we added (remains of TOC after diatom cleaning).

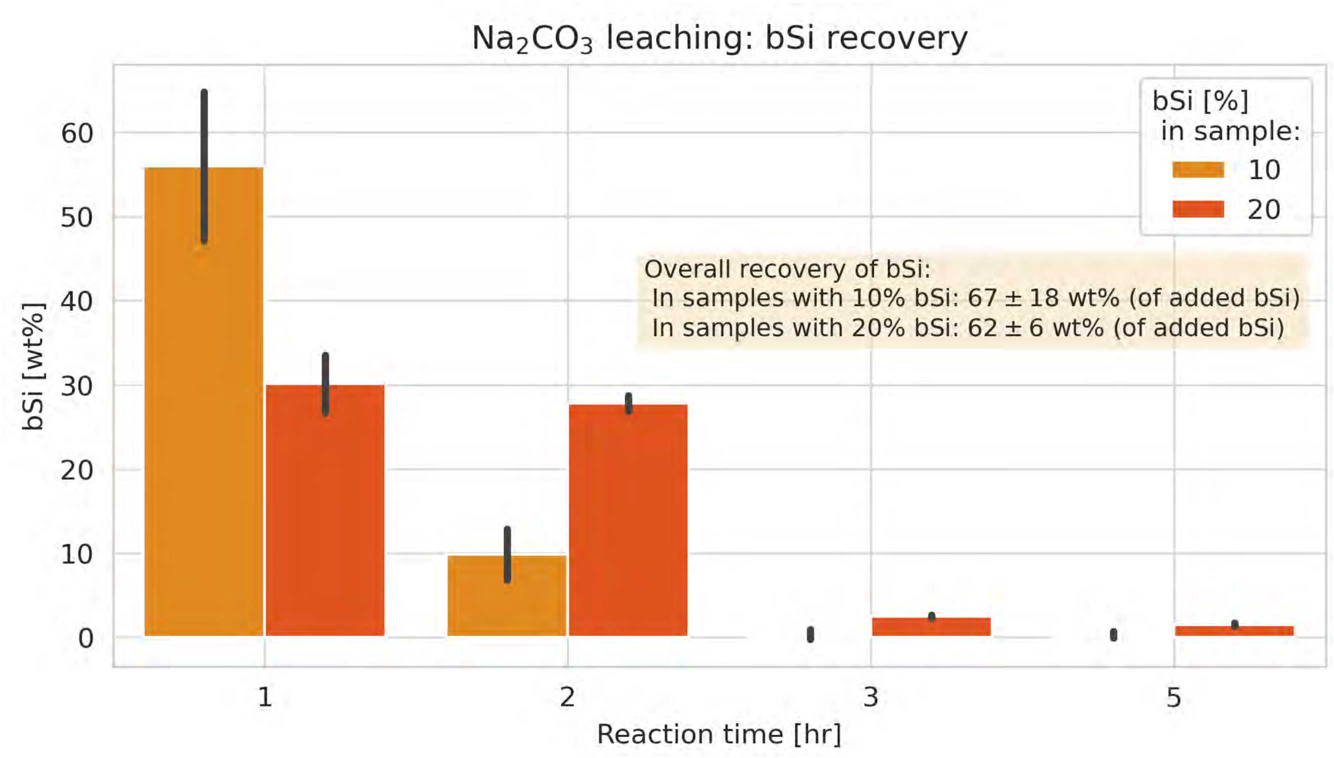

Fig. 4: Calculated recovery of the added diatom bSi based on the measured SiO_2 conc. in the Na_2CO_3 leachates.

Conclusions

- For samples with high diatom bSi contents, longer digestion times and frequent changes of the reagent are needed during Na_2CO_3 leaching to dissolve all diatoms.
- Depending on the amount and type of bSi in a marine sediment and its diagenetic modification, the bSi recovery during Na_2CO_3 leaching can vary strongly. Performing small-step sequential leaching (HCl, Na_2CO_3, NaOH), therefore, is important to separate and identify the individual Si phases.

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