

Kinetic and thermodynamic properties of the biogenic silica-sea water system: From laboratory-based experiments to the oceanic silica cycle

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There have been numerous studies of the production, dissolution and preservation of biogenic silica in the oceans. Nonetheless, a complete mechanistic and quantitative understanding of the dissolution process is still lacking. This interferes with our ability to systematically predict silica dissolution fluxes under variable conditions and, hence, it represents a major obstacle to the use of the accumulation rate of biogenic silica as a palaeoproductivity index, and to the reconstruction of the silica cycle through geological time.

Using stirred flow-through reactors, we have measured the effects of a number of critical physical and geochemical parameters on the solubility and dissolution kinetics of biogenic silica in sediments from the Southern Ocean. In this paper, we analyse whether the data set obtained can explain the reactivity and solubility of biogenic silica in a range of marine environments.

Samples

Surficial sediments (upper 0–30 cm) were retrieved with a multicorer in the Antarctic Ocean and the Sub-Antarctic zone of the Indian Ocean during the Antares I cruise (France JGOFS). Sampling was performed along a N-S transect which ran between the basaltic plateaus of Kerguelen and Crozet, from 55°S to 43°S. The southernmost sites are dominated by biogenic silica (= 75 wt.%), with minor detrital fractions (9–10 wt.%). The silica fraction consists of broken diatom frustules with a few silicoflagellate remains. Moving northward, the biosiliceous component is diluted by increasing concentrations of lithogenic (detrital) material.

Solubility

The detrital material acts as a source of soluble Al(III), which can then be incorporated in the surface layer of the biosiliceous fragments. Therefore, the

ratio of wt.% detrital material to wt.% biogenic silica, the pore water Al(III) level, and the Al/Si ratio of frustule surfaces all correlate positively with each other. Even in the biosiliceous oozes (> 70 wt.% SiO₂) the Al/Si ratio of frustule surfaces is an order of magnitude higher than observed in fresh plankton.

The results of the reactor experiments show that the uptake of Al by biogenic silica significantly alters the silica solubility. Variable Al incorporation therefore explains, in part, the reported solubility differences between living siliceous assemblages (lower Al/Si) and biogenic silica recovered in sediments (higher Al/Si), as well as between open ocean (lower Al/Si) and coastal (higher Al/Si) environments. However, inter-comparison of silica solubilities must take into account differences in temperature, pressure (water depth) and specific surface area. For example, the specific surface area of biosiliceous fragments in Southern Ocean sediments is on the order of $25 \pm 5 \text{ m}^2/\text{g}$, while typical values for living assemblages are 50 to 150 m²/g, with individuals having values up to 300 m²/g. A decrease of the specific surface area from 200 to 25 m²/g brings about a solubility decrease on the order of 16%.

When corrected for *in situ* temperature and pressure, the silica solubilities measured experimentally on samples from Southern Ocean sediments containing more than 36 wt.% SiO₂ agree well with silicic acid concentrations measured in sediments cores. This observation shows that the pore waters in these sediments reach equilibrium with the biogenic silica, but it also confirms that the flow-through reactor technique produces meaningful silica solubilities that can be extrapolated to the natural environment. For sediments with high detrital to biogenic opal ratios, however, the pore waters remain undersaturated with respect to the experimental solubilities. This indicates that additional kinetic factors (e.g. aging) or processes (e.g. authigenic clay formation) affect the build-up of pore water silicic acid concentrations.

Kinetics

The dissolution kinetics follow a distinctly non-linear rate law. With increasing distance from equilibrium, the dissolution rate switches from a linear dependence on the degree of undersaturation to an exponential one (Van Cappellen and Qiu, 1997). The rate measurements further show that the reactivity of biogenic silica decreases substantially with depth in the sediments. The decrease in reactivity is explained by a progressive reduction of the defect density of the silica surfaces (aging) through dissolution and reprecipitation of silica. The Al content of the biogenic silica does not affect the dissolution kinetics, other than through the effect on the solubility (see above).

Rates predicted from the experimental kinetics were compared to rates of silicic acid production obtained by fitting a reactive transport model to pore water profiles of H_4SiO_4 . The experimental rates were corrected for *in situ* temperature, pressure, pH and aging effects. The analysis shows that the laboratory based rates agree within a factor of two with those observed in the sediments. Overall, the results demonstrate that early diagenetic processes are the principal cause for the observed variability of the solubility and reactivity of biogenic silica. Differences in solubility and reactivity inherited from the biomineralization process in the water column are of minor importance in the sediments studied.

Oceanographic studies have shown that a large fraction of the biogenic silica produced in the photic zone of the oceans redissolves within the upper 100 m of the water column (e.g. Nelson and Gordon, 1982). In order to determine whether our kinetic data can explain the high recycling efficiency of silica in

the surface ocean waters, we extrapolated the dissolution rates measured on the topmost centimeters of biosiliceous oozes to conditions found in the surface waters of the Southern Ocean. The calculations show that the observed fraction of biogenic silica dissolving in the upper 100 m of the water column is 4 to 10 times higher than predicted from the experimental kinetics. This is true even after correcting for differences in temperature, solubility (Al content) and specific surface area. Hence, there must exist in the surface waters a silica fraction with an intrinsically higher reactivity. This fraction does not reach the seafloor. Ongoing work with fresh siliceous plankton intends to characterize this highly reactive silica fraction.

Conclusion

We have coupled our laboratory-based investigation of the kinetics and thermodynamics of the biogenic silica-sea water system to a continuous assessment of the capability of the experimental data to explain and reproduce actual field observations. Agreement between predicted and observed properties and dissolution fluxes indicates that the critical environmental parameters have been identified and their effects properly quantified. Equally important, however, is to recognize areas of disagreement between laboratory results and field observables, as they help us focus future experimental research.

References

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