



## In vitro, batch-dissolution of biogenic silica in seawater – the application of recent modelling to real data

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Received 16 January 2004; received in revised form 1 December 2004; accepted 22 February 2005

Available online 18 April 2005

### Abstract

Both for straight-forward oceanographic needs as well as application to climate-change amelioration, there is a need for quantitative description of the spatial and temporal variability in the recycled flux of silicic acid in the ocean water column in terms of governing processes. As part of that, the need for a fuller chemical kinetics treatment of biogenic silica dissolution, involving laboratory rate measurements, rate equations and mechanisms, is stressed. Advantage is taken of recent modelling of batch reactor dissolutions, which relies upon simple and sum of exponentials models. This is applied to archived data, and to some new data for *Cyclotella cryptica*, to stiffen an earlier four-point classification of dissolution behaviour which relies upon plots of  $\ln\{(C_\infty - C_t)/C_\infty\}$  versus time. The models are also used to demonstrate the potential for serious errors in the earlier rate constants derived from the batch approach. By extending recent modelling of non-linearity in the back reaction of the O'Connor and Greenberg equation, it is shown how simple exponential behaviour during dissolution might still be approximated, even though a net reaction is involved. The earlier approach is further extended to introduce non-linearity in the forward term of the O'Connor and Greenberg equation, caused by adsorption of silicic acid on the silica surface. The study of marine biogenic silica dissolution is reviewed in the wider context of general mineral dissolution, with an explanation of the relative merits of Transition State Theory used generally in mineral dissolution, and the more pragmatic approach to kinetics used here. The relative strength of chemo-stat (flow-through) and batch reactors is discussed.

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**Keywords:** Silica dissolution; Biogenic silica; In vitro dissolution; Chemical kinetics; Batch dissolutions; Mineral dissolution

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## 1. Introduction

Silicon, as ortho-silicic acid, is a major plant nutrient in marine ecosystems and its uptake into phytoplankton and its re-generation are important in understanding silicon biogeochemistry. Silicon biogeochemistry is also finding importance in the international quest to counter global warming. Thus, about 45% of marine primary productivity involves diatoms (Mann, 1999), and the extent to which they sink to the bottom or re-cycle in the water column has a considerable bearing upon carbon burial. Finally, the biogenic silica buried in ocean sediment has much to tell us about past environments and climate change (Van Cappellen & Qiu, 1997).

Given the importance of diatoms in the transport of carbon and nutrients to the deep ocean, silica dynamics are an important component of ocean process models. Unfortunately, recent attempts to include them have been hampered by a lack of understanding of how best to couch the dissolution and settling terms. This has led to the adoption of simple exponential relationships for the decay of biogenic silica with depth, based on sediment trap data (Heinze, Maier-reimer, Winguth, & Archer, 1999) or Arrhenius type relationships (Gnanadesikan, 1999; Jiang et al., 2003) that focus on temperature as the primary control. In other simpler treatments constant dissolution rates representative of different water column or sediment conditions have been imposed (Heinze, 2002; Yool & Tyrell, 2003). Ultimately though, if the spatial and temporal variability in the recycled flux of silicic acid is to be evaluated in both the water column and in the sediment, it will be desirable to describe the dissolution process explicitly in terms of its governing processes.

Study of the chemical kinetics of *in vitro* biogenic-silica dissolution (Greenwood, Truesdale, & Rendell, 2001) is a relatively small but potentially important part of the overall investigation of the silicon cycle. Its objective is to reduce the process of biogenic dissolution to a simple physico-chemical mechanism from which can be derived mathematical equations linking the key variables such as the surface area of frustules, ambient dissolved silicic acid concentration, temperature, etc. It is envisaged that these equations will eventually be embedded in biogeochemical models to predict the rate of production of dissolved silicic acid arising from biogenic silica dissolution in any water column. A complete chemical kinetics study requires three elements: the measurement of rates of reactions, the identification of appropriate rate equations, and the selection of a mechanism, all of which have to be consistent with each other (Bunnett, 1974a, 1974b). Until recently, the study of biogenic-silica dissolution has involved mainly the former, with little headway with rate equations and mechanisms. Rates have been measured in batch (Hubbard & Riley, 1984; Kamatani, 1982; Kamatani & Riley, 1979; Kamatani, Riley, & Skirrow, 1980; Tréguer, Kamatani, Gueneley, & Quéguiner, 1989; Greenwood, Truesdale, & Rendell, 2005; Truesdale, Greenwood, & Rendell, 2005) and in flow-through reactors (Rickert, Schulters, & Wallmann, 2002; Van Cappellen & Qiu, 1997).

In the “full reaction curve” approach to the *in vitro* kinetics of biogenic silica dissolution in batch, the dissolution is observed as an increase in the dissolved silicic acid concentration with time. The approach is relatively simple, requiring only suitable reaction vessels in which the dissolution can take place, and an analytical method based upon the very reliable molybdosilicic acid-blue chemistry for silicic acid (Truesdale & Smith, 1975, 1976). Nevertheless, its use has been limited by the lack of a mathematical model with which to parameterise the reaction curve. Kamatani and Riley (1979) and Kamatani (1982) tried to do this by plotting the logarithm of the degree of reaction versus time, with the expectation of a linear plot. Instead, more often than not they found marked curvature which they interpreted as two separate straight lines, the gradients of which provided separate rate constants. To involve a proper physical mechanism, Kamatani et al. (1980) derived an advanced version of the “shrinking core model” in which the biogenic silica is considered as a sphere which shrinks as it dissolves. This led to a somewhat fearsome equation which has not been fitted routinely to data. The work carried out by Kamatani and others in the late part of the 20th century did map out some of the major practical aspects of biogenic dissolution, particularly in respect to realistic conditions. Greenwood et al. (2005) have stressed that despite the problems with parameterising

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