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# Dissolution kinetics of biogenic silica collected from the water column and sediments of three Southern California borderland basins

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#### ABSTRACT

Understanding biogenic silica (bSi) dissolution kinetics in margin environments is important in assessing the global silicon cycle, a cycle closely linked to the global carbon cycle. This understanding is also essential to answer the question of whether bSi content in marine sediment is a valid indicator of productivity in the overlying surface ocean. In this study, plankton tow, sediment trap, and sediment samples were collected at sites in three Southern California borderland basins. Batch dissolution experiments with plankton tow and sediment trap materials (conducted in the laboratory at 22 °C) showed linear dissolution kinetics, from which mean dissolution rate constants of 0.05 d<sup>-1</sup> for plankton tow samples and 0.07 d<sup>-1</sup> for sediment trap samples could be calculated. The dissolution rate constants for both types of samples showed seasonal variability but not the same seasonal patterns. Faster dissolution was observed with sediment trap samples collected at 800 m than at 550 m. With sediment multi-core samples, non-linear dissolution kinetics was observed, which complicates the direct comparison of dissolution rates. Nonetheless, dissolution appeared to be slower for the sediments samples than for samples collected from the water column and to decrease with depth in the sediments. Rate constants for surface sediment (0-0.5 cm) were at least 3-5 times less, and sediments at depths >2 cm had rate constants at least 6-13 times less than those for material sinking to the sediment surface at these sites. Dissolution experiments conducted with Santa Barbara Basin surface sediment samples amended with dissolved aluminum (Al) and San Pedro Basin trap samples amended with enriched detrital materials (obtained by leaching bSi from sediment samples) suggested that dissolution was inhibited by Al and that the sediments from the different basins varied in the extent of Al release.

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#### 1. Introduction

Silicic acid is a limiting nutrient for diatoms, an important group of phytoplankton that exports carbon from the photic zone to the deep ocean (Goldman, 1993; Dugdale et al., 1995; Ragueneau et al., 2006). To assess the global silicon cycle, which is closely linked to the global carbon cycle, it is essential to understand the factors that control dissolution kinetics of biogenic silica (i.e., bSi or opal) (Nelson et al., 1995). This understanding is also essential to answer the question of whether bSi content in marine sediment is a valid indicator of productivity in the overlying water. Much research on bSi dissolution has focused on open ocean environments. However, margin environments, especially the coastal upwelling systems, play an important role in the global silicon cycle (Nelson and Goering, 1977; Nelson et al.,

1981; Brzezinski et al., 1997a,2003; Bidle et al., 2003). About 40% of bSi burial in the ocean occurs in margin sediments (DeMaster, 2002), yet the factors controlling bSi dissolution in margin sediments are not well understood.

This study examined three California borderland basins: San Pedro Basin (SPB), Santa Monica Basin (SMB), and Santa Barbara Basin (SBB) (Fig. 1). Despite their geographic proximity, previous studies have shown very different patterns in the early diagenesis of bSi in sediments of the SBB site as compared with the SPB and SMB sites. For example, the maximum pore water Si concentration is 750-850 µM in the SBB, but only 380-480 µM in the SPB/SMB. Diffusive flux calculations and benthic chamber studies suggest that the benthic bSi dissolution rate is ~3-4 times higher in the SBB sediments than in the SPB and SMB sediments (Berelson et al., 1987; 2005). Previous studies have suggested that the reactivity of bSi (and hence the bSi dissolution rates) may vary in different locations; decreases in the bSi dissolution rate have also been observed as the material sinks through the water column (e.g., Rickert et al., 2002). It has also been suggested that benthic processes, for example, the dissolution of detrital matter, could significantly reduce bSi dissolution rate in the sediments (e.g., Dixit et al., 2001). Seasonal variation in bSi flux may also play a role

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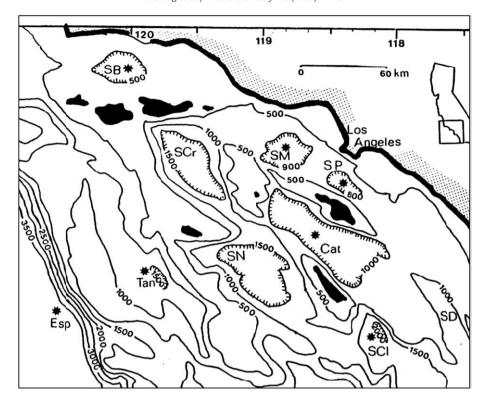


Fig. 1. Location of the three California borderland basins (SP: San Pedro Basin, SM: Santa Monica Basin, and SB: Santa Barbara Basin).

(Ragueneau et al., 2001). However, it is not clear which factors cause the differences in the early diagenesis and dissolution rate of bSi at the SPB/SMB and SBB sites.

The objective of this study is to evaluate the change in bSi dissolution rate as biogenic material settles through the water column and is buried in near-surface sediments in these basins, and to investigate some of the factors that regulate bSi dissolution rates in margin environments. To achieve these objectives, we collected plankton tow, sediment trap, and sediment multi-core samples at three sites and conducted batch dissolution experiments to determine bSi dissolution rates. The plankton, trap and sediment provide us with material that captures the progression from productivity to sedimentation. Dissolution rates between sites were compared. The results of this study address: (i) the question of whether water column processes or benthic processes, or both have caused the observed difference in bSi dissolution rate in the sediment at the SPB/SMB and SBB sites, and (ii) the role of Al in controlling the difference in bSi dissolution rate between the sediment in SPB/SMB and SBB.

#### 2. Materials and methods

#### 2.1. Field sampling

A research cruise was carried out from May 19 to May 27, 2005 to three California borderland basins: San Pedro Basin (SPB), Santa Monica Basin (SMB), and Santa Barbara Basin (SBB). During this cruise and on subsequent dates, plankton samples were collected from seawater 15–20 m below sea surface using a plankton tow, and sediment cores were collected using a multi-core sampling device (Table 1). In addition, sediment trap (moored trap) samples were collected from SPB on a weekly basis using McLane traps deployed at depths of 550 m (trap A) and 800 m (trap B) and in SBB at a depth of 540 m. The bottom depths are ~900 m in SPB and SMB and ~590 m in SBB (Thunell et al., 1995).

The plankton tow and sectioned sediment multi-core samples were kept in a freezer until they were freeze-dried. The sediment trap

samples were filtered, rinsed with small amounts of distilled and deionized water, and air-dried. All the dry solid samples were gently fragmented and stored for subsequent experiments.

#### 2.2. Batch dissolution experiments

Batch dissolution experiments were conducted to determine bSi dissolution rates at room temperature (22±2 °C). In each batch experiment, solid sample was weighed into a 50 mL polypropylene centrifuge tube, 45 mL solution (0.7 M NaCl+2 mM NaHCO<sub>3</sub> solution with pH adjusted to 8.0±0.1) was added to suspend the solids, and the pH was re-adjusted when necessary to 8.0±0.1. The centrifuge tubes were placed on a shaker to gently mix the suspension. At time intervals of t=0, 1, 2, 4, 6, 8, 10, and 24 h, samples were taken from the reaction vessels and filtered through 0.25  $\mu$ m pore size Acrodisc nylon

 Table 1

 Sediment multi-core samples: Sampling date, location, and bottom depth

Sample ID	Sampling date	Sampling location		Bottom
		Latitude (N)	Longitude (W)	depth (m)
San Pedro Basin	!			
SP-MC1	05/18/05	33° 33′	118° 24′	900
SP-MC3	05/19/05	33° 33′	118° 23′	900
SP-MC4	05/20/05	33° 33′	118° 23′	900
Santa Monica B	asin			
SM-MC1	05/26/05	33° 41′	118° 47′	900
SM-MC2	05/26/05	33° 42′	118° 48′	900
SM-MC4	05/27/05	33° 41′	118° 47′	900
Santa Barbara E	Basin			
SB-MC4	05/21/05	33° 13′	118° 02′	590
SB-MC7	05/22/05	34° 14′	120° 02′	590
SB-MC8	05/22/05	34° 14′	120° 02′	590
SB-MC10	05/23/05	34° 13′	120° 01′	590
SB-MC11	05/24/05	34° 13′	120° 01′	590
SB-MC12	05/24/05	34° 13′	120° 01′	590

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