

## Biogeochemical behavior and distribution of biogenic silica in marine sediments from Izmir Bay, Aegean Sea (Turkey)



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### ABSTRACT

The distribution of BSi (biogenic silica) in surface sediment and pore water from Izmir Bay was investigated using Si-only and Si/Al methods for determining the appropriate methods. Surface sediment samples were collected using a box core from 15 stations in the inner Izmir Bay from March to May 2008. The relationships between biogenic silica, heavy metals and geochemical data were investigated. Si/Al ratios (weight/weight) ranged between 0.88–1.39 for positive BSi values and 1.21–12.409 for negative BSi values.

The silica dissolution values showed a rapid increase in Al concentrations during the first 5 h of the experiment when the silica dissolved, followed by constant silica level at all stations. The dissolution curves in all stations have been stable in a maximum DSi (dissolved silica) value after 5 h. The linear curve of Al against the silica dissolution explained the biogenic silica content from intercept. The BSi measurements for this study give more accurate results according to the method of Si/Al. Factor analysis was used to determine the relationships between silica and geochemical data. BSi and Si<sub>pore</sub> have a strong association with manganese. The diatomae productivity in the water column has a significant importance on the stability of Mn in the sediment. Carbonate content of sediments controls the Mn anomalies from terrestrial sources in the bay. Maximum values of BSi at inner parts of the bay are due to the freshwater source at the deep.

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### 1. Introduction

The major source of dissolved silica to the marine environment is continental runoff, with minor amounts from hydrothermal influx, sea-floor weathering and from pore waters of marine sediment (Calvert, 1983; Pattan et al., 1992). Biogenic silica (BSi) plays an active role in marine biogeochemical cycles. It is an important mineral found in many marine sediments due to primarily produced by planktonic organisms living in the surface ocean. Also, BSi is a chemical determination on the amount of amorphous silica which can be comprised of different components mainly of biological origin such as diatoms, phytoliths, radiolarians, silicoflagellates and sponge spicules (Conley, 1998). Accumulation of biogenic silica continues as the biosiliceous debris through the water column. BSi has considerable effect on the physical properties of sediment (Pattan et al., 1992; Venkatratnam and Hays, 1974). Despite the active removal of dissolved silica by diatoms the content of dissolved silica in the oceans is believed to be in steady state, with a dynamic balance maintained between silica supplied to the ocean system from the rivers and weathering of marine sediments and that sinking from surface waters (Kamatani and Oku, 2000). The functioning of global silicon cycle is essential to understand the factors that control the

kinetics between dissolution and preservation of biogenic silica in the oceans. Because of this kinetic competition, BSi content in marine sediments is a valid indicator of high productivity in an overlying water.

Various techniques and modifications have been developed for the determination of BSi in marine sediments. They are: (1) X-ray diffraction of amorphous opal (Eisma and Van Der Gaast, 1971; Lapaquellerie, 1987; Bareille et al., 1990) or after heating and conversion of opal cristobalite (Goldberg, 1958; Ellis and Moore, 1973; Leinen, 1985; Bareille et al., 1990; Gehlen and Van Raaphorst, 1993) (2) infrared analysis (Froelich, 1989) (3) microfossil counts (Emelyanov and Shimkus, 1971) (4) normative calculation of mineral silicates (Leinen, 1977) and (5) wet alkaline digestion (Hurd, 1973; DeMaster, 1979, 1981; Eggimann et al., 1980; Mortlock and Froelich, 1989; Müller and Schneider, 1993).

All these procedures are based on different physical or chemical characteristics of amorphous biogenic silica. Besides the techniques mentioned above a number of alkaline leaching techniques have been applied (Hurd, 1973; Eggimann et al., 1980; DeMaster, 1981; Mortlock and Froelich, 1989; Gehlen and Van Raaphorst, 1993; Müller and Schneider, 1993; Ragueneau and Treguer, 1994; Konning et al., 1997; Krause et al., 1983; Kamatani and Oku, 2000; Ragueneau et al., 2005) which presently are considered to be superior for marine sediments of various composition (DeMaster, 1981; Conley, 1998; Konning, 2002). Marine scientists (Hurd, 1973; Kamatani, 1980; Kamatani and Takano, 1984; DeMaster, 1981, 1991; Mortlock and Froelich, 1989; Müller and

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Sneider, 1993; Kamatani and Oku, 2000) have successfully modified and applied the wet alkaline digestion methods.

The wet alkaline methods have been used to determine the biogenic silica content of samples. Although some modification of wet alkaline digestion techniques exist in literature, most of the methods follow either a timed sequential extraction (DeMaster, 1979, 1981) or a single step approach (Mortlock and Froelich, 1989). All of the wet alkaline digestion methods have measured the non-BSi as well as the BSi (Swann, 2010). These wet alkaline digestion methods have been applied by using either 0.05 M Na<sub>2</sub>CO<sub>3</sub> (Paasche, 1980), 0.5 M Na<sub>2</sub>CO<sub>3</sub> (Kamatani and Takano, 1984) or 0.2 M NaOH (Paasche, 1973) (Ragueneau and Treguer, 1994). Commonly, these hot solutions of NaOH or Na<sub>2</sub>CO<sub>3</sub> in different concentrations are used for the efficiency that biogenic silica can be leached selectively from sediment samples by treatment with an alkaline solution. NaOH digestion method has been developed for coastal (Krausse et al., 1983) as well as oceanic suspended matter samples (Brezeinski and Nelson, 1989; Treguer et al., 1992; Ragueneau and Treguer, 1994). Al is selected as a normalizing parameter because they are lithophilic elements mostly originating from the soil. The Si/Al ratios of samples can be applied to calculate the BSi in a single step digestion (Eggimann et al., 1980; Carter and Colman, 1994; Ohlendorf and Sturn, 2008; Swann, 2010).

The main purposes of this paper are to obtain the distribution of the BSi using the appropriate methods in surficial sediments at the first time and to investigate the relationships between biogenic silica and other parameters.

## 2. Material and methods

### 2.1. Study area

Bay of Izmir which is one of the great natural bays of the Mediterranean is located at 38° 20' N–38° 40' N latitudes and 26° 30' E–27° 10' E longitudes. It is an important semi-enclosed basin and has been increasingly polluted with massive loads of contaminants discharge from extending to the Aegean Sea, on the west coast of Turkey. From the topographic and hydrographic points of view, the bay is divided into inner, middle and outer regions (Ozkan, 2012). Its average depth is 15

m and total area is 500 km<sup>2</sup>. The exponential growth of Izmir on both sides of inner Izmir Bay has led to severe pollution. The quality of water and sediment in the inner Izmir Bay is seriously affected by pollutants which enter through drains that bring domestic as well as industrial effluents and discharge into the river and also from the sewage system that pumps untreated effluent into it during its journey through the city.

### 2.2. Analytical procedure

Surface sediment samples were collected using a box core from 15 stations in the inner Izmir Bay from March to May 2008. Sampling stations were shown in Fig. 1. Surface sediment samples were frozen in a freezer (−20 °C) until analysis. Also, pore water was collected from each station in 20 ml polythene bottles and frozen until analysis. The biogenic silica concentrations at dry sediment were determined using the method which is modified from the methods of Ohlendorf and Sturn (2008) and DeMaster (1981). 10 sediment samples weighted for each station (between 10 and 50 mg) was transferred to 50 ml Teflon tubes and added with 10 ml 1 M NaOH. The tubes were homogenized with ultrasonic bath for 1 min and then placed in an oven. The leaching (100 °C for 24 h) method (Ohlendorf and Sturn, 2008) was used to overcome the difficulties of leaching BSi from the sediment. Samplings were made at 30 min, 1 h, 1.5 h, 3 h, 5 h, 6 h, 8 h, 12 h and 24 h. At least two replicates of each sediment sample and blank were treated in each leaching experiment. Then, 5 ml of the supernatant sample was pipetted from the hot solution (for preventing silica polymerization in samples) and added to 30 ml of deionized water in 50 ml PE-flasks and neutralized with HNO<sub>3</sub> to pH = 6. After cooling, the volume of the solution was adjusted to 50 ml. Dissolved silica (DSi) was measured in 24 h by ICP-MS (inductively coupled plasma-mass spectrometer). Based on simultaneous determination of Al, the ICP technique allows for the correction of Si derived from dissolution of silicate minerals (Teodoru et al., 2006; Eggimann et al., 1980). Biogenic silica was determined by plotting extracted silica against the time as intercept (Fig. 2a) (Ohlendorf and Sturn, 2008). BSi values of samples according to Kamatani and Oku (2000) were calculated by plotting extracted silica

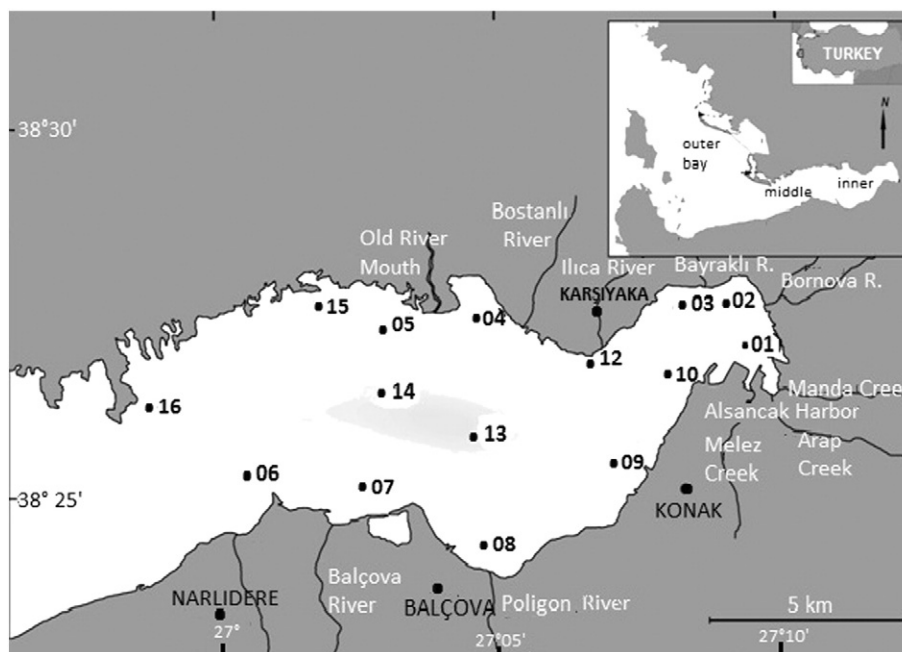


Fig. 1. Study area and location of the 15 sampling sites of sediments.

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