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Alkaline leaching characteristics of biogenic opal in IODP drilled cores from the Bering Sea

Shinya Iwasaki, Kozo Takahashi and Yoshiyuki Kanematsu

Abstract

Leaching characteristics of biogenic opal in alkaline solutions were studied for Bering Sea sediment samples from the cores obtained during Integrated Ocean Drilling Program (IODP) Expedition 323. Generally, biogenic opal content is measured after alkaline leaching using Na_2CO_3 solution. Biogenic opal in some sediment samples could not be completely leached by Na_2CO_3 solutions, particularly in the deeper sections depending on sites: below the depth of ca. 122 m (CCSF-A) with 1.1 Ma at Site U1341 and ca. 211 m (CCSF-A) with 0.8 Ma at Site U1343. Strong alkaline 2M and 4M NaOH solutions were used instead of the standard Na_2CO_3 solution. As a result of the time-series leaching analysis, silicon contribution rates from clay minerals and other detrital grains were estimated in each of the methods employing two different concentrations of NaOH solutions. This made possible to correct for silicon contribution of clay minerals and other detrital grains.

Keywords: Biogenic opal, alkaline leaching, IODP Expedition 323, Bering Sea, diagenesis, Sites U1341 and U1343

1. Introduction

The Bering Sea is known as one of the North Pacific marginal seas with a high biological productivity and high biogenic opal fluxes with its key location between the Pacific Ocean and the Arctic Ocean for the surface water circulation (Fig. 1). The changes in biological productivity and consequent biogenic opal fluxes are considered to be well governed by the change in sea surface conditions. From these points of views, the Bering Sea is a suitable region to study the evolution of paleoceanographic changes that are relevant to the global context during the Pliocene to Peistocene (Takahashi et al., 2011a, b).

The primary objectives of IODP Expedition 323 were to characterize changes that occurred in the Bering Sea around the times of: (1) the onset of the Northern Hemisphere Glaciation (NHG, ca. 2.7 Ma); (2) the Mid Pleistocene Transition (MPT, ca. 1 Ma); and (3) glacial-interglacial cycles (<1 Ma). During IODP Expedition 323, a total of seven sites were drilled in the Bering Sea. Among them four sites were drilled in the area of the Bering slope, and three sites were drilled on Bowers Ridge. The cores from these sites are mostly obtained by advanced piston coring (APC) with triple holes in the upper section in order to fill core-to-core gaps by splicing pertinent cores. Hence they allow us to study high resolution reconstruction of the Pliocene-Pleistocene record.

Biogenic opal is one of the most important and useful indicators that depict productivity capacity in the oceans (e.g., Leinen et al., 1986). Diatoms, radiolarians, silicoflagellates and sponge spicules are the primary constituents of biogenic opal. In the subarctic Pacific and its northern marginal seas, it is known that the export of diatoms is especially high (Takahashi et al., 2000, 2002; Honjo et al., 2010). Thus, it is anticipated that in the Bering Sea, diatom frustules make up the main component of biogenic opal, which can also shed light on past changes in primary productivity. Because that diatom productivity is influenced by surface water structure, water circulation and sea-ice cover, such conditions can be reconstructed in part by measuring biogenic opal content.

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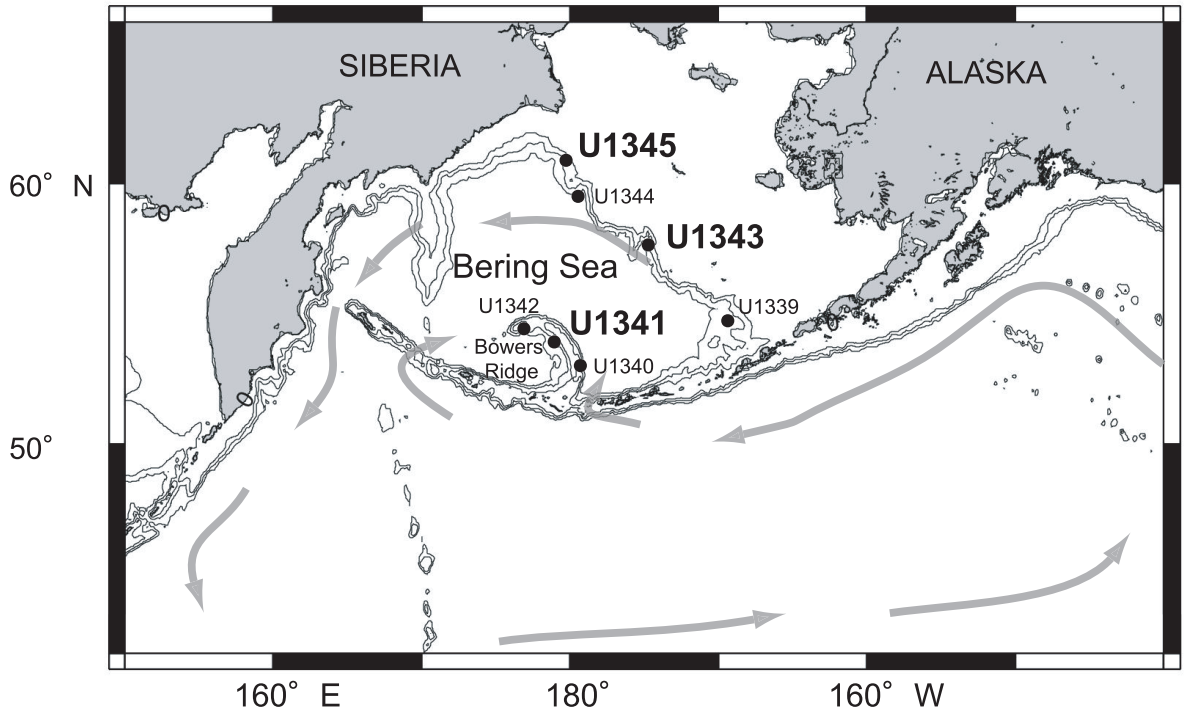

Fig. 1. Topographic map showing the locations of Site U1341, U1343 and U1345 together with all other sites of IODP Expedition 323 in the Bering Sea. Arrows show the direction of the major surface currents (Map drawn by "Online Map Creation").

To measure biogenic opal contents in the Bering Sea sediments the leaching characteristics of the sediment was investigated. Two molar Na_2CO_3 solution has been conventionally employed to dissolve biogenic opal in sediments (e.g., Okazaki et al., 2005; Iwasaki et al., 2012). In our study, however, as the depth in the sediment section goes deeper with increasing ages, we encountered the situations in which it was not possible to dissolve biogenic opal matter sufficiently by the standard method with the Na_2CO_3 solution. This is considered to be due to diagenesis of the biogenic opal transformation from opal-A into opal-CT (e.g., Hein et al., 1978). Therefore, in this paper we employed two solutions of different concentrations of NaOH to see how sufficiently biogenic opal was leached.

2. Materials and Methods

2.1. Drilled cores

Among the seven sites drilled in the Bering Sea during IODP Expedition 323, Sites U1340, U1341 and U1342 were drilled on Bowers Ridge. In particular, Site U1341 is located at 2,177 m water depth in the western slope of Bowers Ridge, and this site was drilled to 600 meters below sea-floor (mbsf) with a more or less complete record of the last 4.3 Myrs (Takahashi et al., 2011b). On the other hand, Sites U1339, U1343, U1344 and U1345 are located in the area of high biological productivity called the "Green Belt". The Green Belt is formed along the Bering Slope, whose water mass originates from the Alaskan Stream water that flows into the Bering Sea. Among the four sites which were drilled in the Bering Slope, the bottom cored depth of drilled Site U1343, with water depth of 1,986 m, is 745 mbsf with the bottom age of approximately 2.4 Ma. Site U1345 is the most northerly located one of all sites and its water depth is 1,020 m. This site was drilled to 150 mbsf with its bottom age of 0.5 Ma (Takahashi, 2011a). In this study, we used these three drilled sites (U1341, U1343 and U1345) to discuss the leaching of biogenic opal in the drilled cores from IODP Expedition 323.

2.2. Leaching methods

A sediment sample was crushed into fine powder in a mortar with a pestle after being freeze-dried at −45 ºC for 24 h. After the sample was dried, solutions of 10% H_2O_2 and 1 N HCl were added to 10 mg of the sample in a polypropylene centrifuge tube to remove organic material and calcium carbonate. Biogenic opal was leached

using two types of 10.0 ml alkaline solutions (2M or 4M NaOH, depending of the depth of the samples) at 85 ºC for 5 h, followed by molybdate-yellow spectrophotometry with a Shimazu UV Mini-1240 Spectrophotometer. The measured values were expressed in weight percent (wt%) biogenic opal. First, weight percent silicon (%Si) was calculated by equation (1), based on measured silicon concentration (C_{Si}). Next, the values were converted to weight percent biogenic opal (%biogenic opal) using the equation (2) (Mortlock and Froelich, 1989).

$$\%Si = 100\times(CSi\times V\times 10^{-3}\times 28.09/M) \quad \ldots (1)$$

%Si (wt%)…Weight percent silicon
C_{Si} (mM)…Silicon concentration
V (ml)…Volume of solution
M (mg)…Sample mass

$$\%Biogenic\ opal=2.4\times(\%Si - \%Lsi\times T) \quad \ldots (2)$$

%Bogenic opal (wt%)…Weight percent biogenic opal
%Si (wt%)…Weight percent silicon
%Lsi (wt%/h)…Dissolution rate of silicon derived from clay and other detrital grains
T (h)…Dissolution time

3. Discussion

3.1. Diagenesis of biogenic opal and leaching with NaOH

It is known that biogenic opal in the deep-sea is often transformed from opal-A to opal-CT by the effect of diagenesis (caused by e.g., temperature and pressure) in the deeper part of sedimentary record (e.g., Hein et al., 1978). The effect of diagenesis is thought to cause dissolution and reprecipitation of biogenic opal. In fact, such a diagenesis has already been recognized during IODP Expedition 323 (Takahashi et al., 2011a). We initially attempted to leach biogenic opal with 2 M Na_2CO_3 solution of the standard leaching method (Mortlock and Froelich, 1989) for the samples from both Sites U1341 and U1343. However, it turned out that substantial amount of biogenic opal had been left unleached with the Na_2CO_3 solution in many samples, which were determined by microscopic examinations. In particular, we found that some sponge spicules in samples near the bottom of the holes at Sites U1341 and U1343 were sometimes hard to completely dissolve with the Na_2CO_3 solution and hence they were still present in residues after leaching. In the case of the samples from Site U1341 we found that the opal-diagenesis was apparent below the depth of ~122 m (CCSF-A), whose age is 1.1 Ma.

In order to overcome of the problematic situation with the Na_2CO_3 leaching we employed NaOH solutions for the leaching process. For the samples from Site U1341, 10 ml of 2M NaOH solution was used for leaching biogenic opal in the samples from relatively shallow depths (0-122 m CCSF-A, 1.1 Ma) and 10 ml of 4M NaOH solution was used for the samples from deeper depths (below 122 m CCSF-A). At Site U1343 on the other hand, 10ml of 2M NaOH solution was used for the samples from shallower depths (0-210.6 m CCSF-A, 0.8 Ma) and 10 ml of 4M NaOH solution was used for the deeper samples (below 210.6 m CCSF-A). For the samples from Site U1345, 2M NaOH solution was used (0-162 m CCSF-A, 0.5 Ma). Reproducibility of the measurements was assessed based on replicated measurements of the representative samples without further correction for lithogenic matter for both the methods (2M and 4M NaOH), precision average was generally better than ±4 wt% for the method with the 2M NaOH solution, and ±6 wt% for the 4M NaOH solution.

Based on the analyses employing 2 M Na_2CO_3 solution and 2M and 4M NaOH solutions it was possible to determine the shallowest depths at which biogenic opal diagenisis began to occur at IODP Expedition 323 sites. For example, %biogenic opal values for identical samples from Site U1341 employing the two different extraction procedures showed substantial difference in biogenic opal values depending on the depths of samples (Fig. 2). Such a piece of information on the opal diagenetic front is quite important for geochemistry of sediments.

3.2. Correction for dissolved silicon derived from lithogenic matter

Generally, NaOH solutions are reported to dissolve a greater amount of silicon from lithogenic matter than the method with Na_2CO_3 solution (e.g., Eggimann et al., 1980; Paasche, 1980). The correction for the dissolved silicon released from the lithogenic matter during the extraction process of biogenic opal is necessary. Thus, we determined the dissolution of silica from clay minerals and other lithogenic matter using time-series extractions. The separation of biogenic opal from lithogenic silica is based on the different leaching characteristics of the two phases: relatively fast dissolution of biogenic opal and rather continuous and constant dissolution of silica in

lithogenic matter (DeMaster, 1981). Therefore, it is anticipated that only small amount of dissolved silicon from lithogenic matter is included in the measured %biogenic opal values (wt%) at 85 ºC for 5 h. To confirm this, we measured the dissolved silicon in several batches of alkaline extraction with varying in duration (1-8 h). The results showed the dissolution rates of silica from lithogenic matter in the specific samples based on each of the leaching procedures (2M and 4M NaOH: Fig. 3). According to the visual microscopic examination, leaching of biogenic opal was completed during the 5 h alkaline extraction with 2M and 4M NaOH solutions. Thus, it is considered that the leached dissolved silicon after the 5 h alkaline extraction is derived mostly from lithogenic matter. Based on this consideration, we estimated dissolution rate of silica from lithogenic matter as follows: 0.38 (wt% h^{-1}) for 2M NaOH solution and 0.78 (wt% h^{-1}) for 4M NaOH solution. These values are useful in correcting for the influence by lithogenic matter.

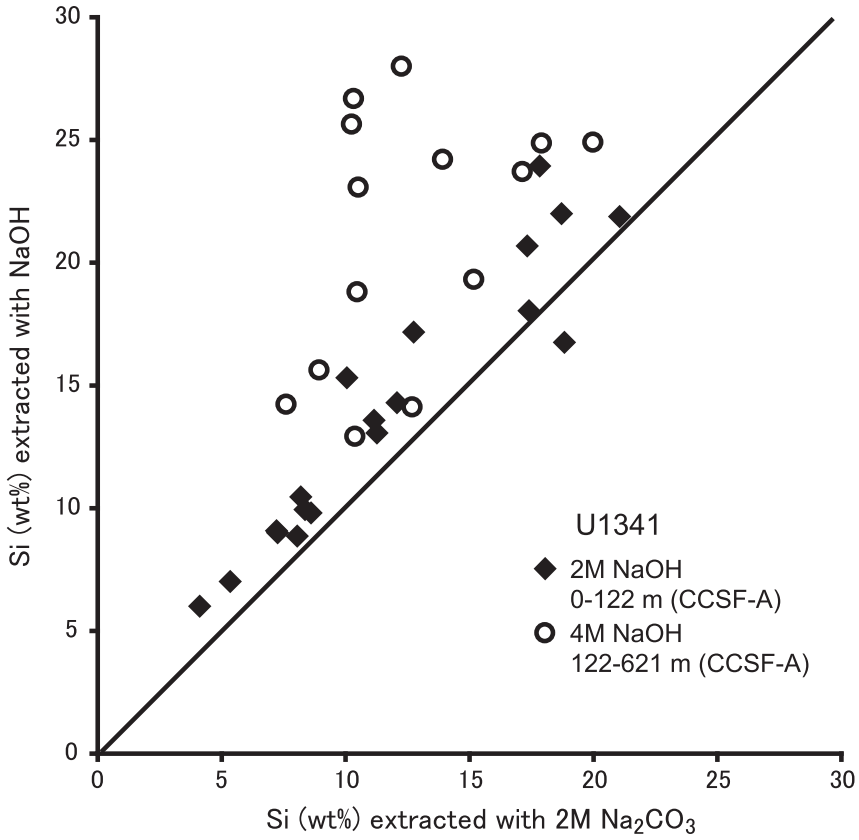

Fig. 2. Plot of silica extracted with NaOH solutions versus that with a Na_2CO_3 solution. Samples were selected at random from 0-122 m and 122-621 m (CCSF-A), respectively. The diagonal straight line represents the one to one correspondence between the two different methods employing the NaOH and Na_2CO_3 solutions.

4. Conclusions

In this study, leaching characteristics of biogenic opal in alkaline solutions were investigated for Bering Sea sediment samples. It was revealed that leaching characteristics of biogenic opal in sediment samples were different depending on depth/age due to diagenesis in the sediments. We reached the conclusion that it is necessary to employ the suitable alkaline solutions in order to measure biogenic opal content. Particularly, in the case of sample analysis of IODP Expedition 323 sediments, we suggest the use of two types of alkaline solutions depending on the depth of samples as follows. First, for the samples from Site U1341, 10 ml of 2M NaOH for shallower depths (0-122 m CCSF-A, 1.1 Ma) and 10 ml of 4M NaOH for deeper depths (below 122 m CCSF-A)

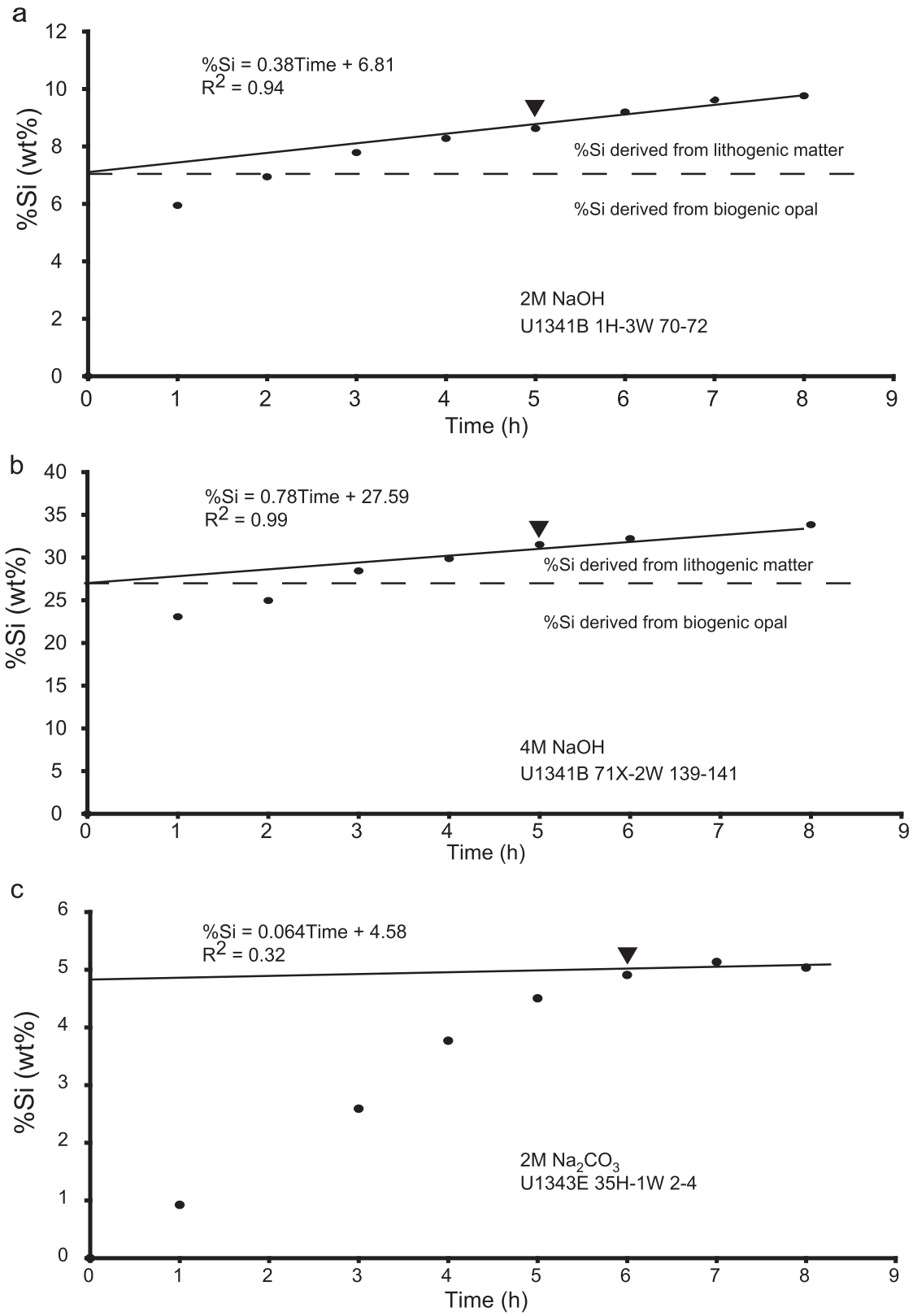

Fig. 3. Examples of the obtained %Si (wt%) versus time (h) plots for 85ºC with different concentrations of alkaline leaching of biogenic opal. (a) The leaching with 2M NaOH solution for Sample U1341B 1H-3W, 70-72 cm [0.03 Ma]; (b) The leaching with 4M NaOH solution for Sample U1341B 71X-2W, 139-141 cm [4.23 Ma]; (c) The leaching with 2M Na_2CO_3 solution for Sample U1343E 35H-1W, 2-4 cm [1.17 Ma]. The triangles show the earliest samples in the time-series leaching with absence of biogenic opal, based on visual microscopic examinations. The diagonal straight lines are the regression lines through the data obtained between; 5-8 h (a-b) and 6-8 h (c) of leaching, and the equations of the regression line are also shown. The level lines show the calculated %Si.

are recommended. Second, at Site U1343, 10 ml of 2M NaOH for shallower depths (0-210.6 m CCSF-A, 0.8 Ma) and 10 ml of 4M NaOH for deeper depths (below 210.6 m CCSF-A) are recommended. Finally, at Site U1345, 10 ml of 2M NaOH is recommended for the entire section (0-162 m CCSF-A, 0.5 Ma). However, a more detail examination is needed at each of the sites for the exact determination of the demarcation depths between with or without the diagenesis. Furthermore, because we employed NaOH solutions for alkaline leaching in this study, the dissolution rates of silica in lithogenic matter were calculated. This, enabled us to obtain most desirable values which we confidently defined as biogenic opal. The methods described here will be useful for the future measurements of other drilled cores in the region as well as others.

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