Lyle, M., Wilson, P.A., Janecek, T.R., et al., 2002
Proceedings of the Ocean Drilling Program, Initial Reports Volume 199

6. Determination of Biogenic Opal in Pelagic Marine Sediments: a Simple Method Revisited[1]

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ABSTRACT

A laboratory study was conducted to determine the adequacy of using a 2-M sodium carbonate (Na_2CO_3) solution to digest radiolarian-rich Eocene and Miocene samples to find their total opal content. In general, this commonly used method is not sufficient for complete digestion, even when digestion times are nearly tripled. However, digestion does proceed to completion when a 2-M potassium hydroxide (KOH) solution is substituted for the Na_2CO_3 reagent and digestion proceeds for 8.5–10 hr. Except when volcanic ash is present, a 2-M KOH digestion produced more accurate biogenic silica results for Paleogene samples with a high opal content than did a Na_2CO_3 leach. This conclusion is based on biogenic silica results obtained by an independent method of analysis (normative analysis) for Paleogene radiolarian-rich samples. More importantly, the KOH treatment does not appear to leach "excess silica" from the matrix components (such as clay minerals and other siliciclastics) in sufficient concentrations to compromise the relative accuracy of the results. In contrast, the Na_2CO_3 leach greatly underestimates the amount of biogenic silica in the Paleogene samples. For samples containing volcanic ash, both treatments overestimate the amount of biogenic silica present, with the KOH treatment producing values two to three times greater than the Na_2CO_3 leach. The commonly used 2-M Na_2CO_3 leach is inadequate for the rapid digestion of biogenic opal for radiolarians (e.g., Leg 199 sediments), but a 2-M KOH solution will produce reasonably accurate results.

[1] **Examples of how to reference the whole or part of this volume.**
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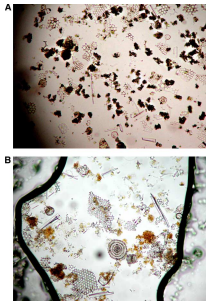
Ms 199IR-106

INTRODUCTION

A primary objective of Ocean Drilling Program (ODP) Leg 199 is to determine the position and strength of upwelling zones and the extent of primary production in the equatorial zones of the Pacific Ocean during the Paleogene. Calculating mass accumulation rates of the biogenic components in the sediments (specifically opal, calcium carbonate, and organic carbon) is essential for determining the locations and migrations of paleoupwelling zones. Our laboratory planned to generate the opal data for Leg 199 cores by employing a commonly used wet-digestion method, but we were concerned about the feasibility of obtaining good opal measurements using a sodium carbonate (Na_2CO_3) leach in light of previous studies that suggested the robust tests of Eocene radiolarians would be solution resistant. For example, Moore (1969) recognized that opaline assemblages of Eocene and Miocene surface sediments are more resistant to dissolution in seawater relative to Quaternary assemblages. The reasons that explain this observation have not been fully elucidated but may reflect possibilities such as bond changes in the opaline skeletons upon aging (Heath, 1974) and/or morphologically dissimilar shell remains between the two age groups. That is, Eocene fossil assemblages contain proportionately more opaline skeletons, which are larger and thicker compared to late Neogene opal assemblages, whose individuals exhibit thinner more delicate structures. Hence, the relatively low surface area per unit mass ratio of Eocene fossils might explain their slower dissolution rate under natural conditions. Therefore, we anticipated that the Leg 199 sediments will present special problems with regard to accurately measuring the biogenic silica fraction and, consequently, challenge our ability to achieve a primary objective of the cruise.

A commonly used method for rapidly measuring biogenic silica is the wet-digestion technique described by Mortlock and Froelich (1989). They successfully employed a 2-M Na_2CO_3 solution to efficiently digest sediments with a wide range of opal content (3%–100%). However, the samples used in their study span a relatively short geologic time interval (Pliocene–Holocene), ~5 m.y. The relatively young age of those sediments is contrasted to Leg 199 samples, where drilling recovered a sedimentary record spanning the Miocene–Paleocene, a span of geologic time nearly an order of magnitude older than the samples used in the Mortlock and Froelich (1989) study. Also, the opaline fossil assemblages differ between the two studies. Preliminary work during Leg 199 site survey samples (EW9709) indicates that the sediments are dominated by radiolarian oozes, which contrasts to Mortlock and Froelich's (1989) diatom-rich samples. The problem of dissolution-resistant radiolarians when using a Na_2CO_3 treatment is convincingly illustrated in Figure **F1A** and **F1B,** which show photographs of the smear slides with solid sediment residue that remained after 9- and 14-hr 2-M Na_2CO_3 digestions of two samples of Eocene radiolarian ooze (collected on the site survey cruise). Abundant radiolarian fossils remained undissolved, even after nearly doubling and tripling the recommended digestion time of 5 hr by Mortlock and Froelich (1989). Hence, their method's efficiency for rapidly determining biogenic opal in marine sediments may be limited to "young" diatom-rich, radiolarian-poor sediments. In this study, we employed a harsher alkaline treatment to dissolve the opaline fraction of site survey samples from Core EW9709 to determine this methods robustness for providing reasonable measurements of biogenic sil-

F1. Residue remaining after 2-M Na_2CO_3 digestions, p. 11.



ica for radiolarian-rich sediments. Site survey cores were recovered during the September 1997 cruise of the *Maurice Ewing*. Samples from three EW9709 cores and other sites used in this study (see **"Results for Site Survey Samples,"** p. 5) were digested in a 2-M potassium hydroxide (KOH) solution, and aliquots of the supernatant were analyzed by spectrophotometry for SiO_2. The sediment residue remaining after the digestion was recovered and mounted on a smear slide for microscopic analysis. Both the analytical and smear slide results, after the KOH digestion, were compared to an independent leach, supernatant analysis, and smear slide inspection of the residue after a 2-M Na_2CO_3 extraction. (A second aliquot of undigested sediment sample was used in the Na_2CO_3 leach). This analytical regimen (two independent leaches of the sampled interval: one sediment sample digested in Na_2CO_3, a second sediment sample in KOH, followed by recovery of the undigested residues for microscopic inspection) was applied to Pacific Ocean sediments comprising different opal assemblages (diatom-rich samples vs. radiolarian-rich samples) and spanning the Eocene–Holocene.

METHODS

The biogenic silica extraction method we employ for both the Na_2CO_3 and the KOH treatments generally follows Mortlock and Froelich (1989) with some important differences. Before analysis, samples are freeze dried for 3–4 days under vacuum (~2 Torr), ground with an aluminum oxide mortar and pestle, stored in glass-shell vials with Tightseal caps (Kimble 60965-D), and placed in air-tight plastic containers lined with indicating Drierite to minimize rehydration. Approximately 20–50 mg of dried sample is weighed and placed in a 50-mL Nalgene (No. 3110-0500) centrifuge tube (with the exception of Site 1098 Consistency Standard: 10–15 mg was used because of high biogenic silica content). Samples are not "equilibrated" with ambient atmosphere before weighing, as recommended by Mortlock and Froelich (1989). Significant errors can result in the final weight percent calculation of components when samples are rehydrated with "ambient" moisture before weighing, especially for samples with significant clay contents. Seven to ten milliliters of a 10% H_2O_2 solution (reagent grade) is added to each tube (including standards and blanks), sonified, and allowed to effervesce for 24–48 hr. Two and a half milliliter of 10% HCl is added to each tube, sonified, and allowed to stand for several hours. Tubes are filled with distilled water to dilute the reagents, centrifuged at 4300 rpm for 20 min (IEC Centra GP8), and very carefully decanted with a 10-mL single-channel pipette down to the last 3–4 mL of solution. Sample tubes with remaining sediment are lightly covered with polyvinyl chloride film, placed in constant-temperature gravity oven at 60°C (Precision Model 25EG) until dry, then stored at room temperature until ready for analysis, which is typically a few days.

To each tube, 20 mL of a 2-M Na_2CO_3 or 2-M KOH (reagent grade) solution is added using a Repipet Jr. (Barnstead/Thermolyne No. 7010; 10 mL ± 0.1 mL) or a single-channel pipette (Fisher brand Finnpipette; 2–10 mL ± 0.10%), capped, sonified to disperse sediment, and weighed. Sample racks (Nalgene 5970) of 24 tubes are placed in a covered, shaking water bath (Precision Model 25) containing room-temperature distilled water that just covers the reagent in the sample tubes. A programmed timer is set to turn on 6–24 hr later to heat to a constant tem-

perature of 85°C (±0.05°C) and constantly agitated at 70 rpm. After 8.5–10 hr at 85°C, sample tubes are removed from the bath and reweighed to monitor potential loss of reagent from evaporation or potential gain of bath water through the pinhole in the cap while in the shaking water bath. Samples are then centrifuged for 20 min at 4300 rpm, and before analysis, all samples will have cooled for ~1 hr. Sample cooling is preferable to taking aliquots while hot. We noticed significant pipetting errors when low-volume aliquots (50 µL) are taken from hot samples.

Dissolved silica is measured by the heteropoly blue method using a Hach Company DR/4000 spectrophotometer with a detection range from 0 to 1.600 mg/L SiO_2 ±0.01 mg/L at a wavelength set to 815 nm. An aliquot of 50 µL of digested sample is pipetted (Fisher Finnpipette 40–200 µL ± 1.1%) using sterile tips into a precleaned polypropylene reaction vessel containing 9.95 mL deionized distilled water (ASTM Type II, VWR 3234-7, also used to prepare reagents). Additional reagents (molybdate 3, citric acid, and amino acid F) are added following a standard procedure for low-range silica ("Method 8186" [Hach, 1997]). Sample aliquots larger than 500 µL failed to develop a colored solution and results were erratic, suggesting that the alkaline Na_2CO_3 or KOH matrix interferes with the complexation process. Because silica reacts with molybdate under acidic conditions to form the unreduced (yellow) form of silicomolybdic acid, matrix interferences, which significantly raise the pH, can be avoided by drawing aliquots no larger than 100 µL.

DISCUSSION

Accuracy and Precision of Analytical Method

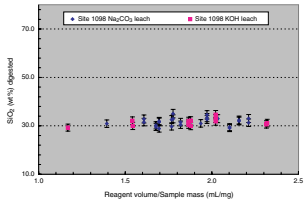
To gauge our accuracy and precision for the analytical method, at least one sample of an "in-house standard" was included in each run. This in-house standard, "ODP Site 1098 Consistency Standard," is a composite sample of Site 1098, a finely-ground, diatom-rich sediment from the Palmer Deep (provided by Linda Anderson at the University of California, Santa Cruz). The lithology of Site 1098 ranges from diatom ooze to diatom-bearing silts and clays (Barker, Camerlenghi, Acton, et al., 1999). Core descriptions (Barker, Camerlenghi, Acton, et al., 1999) indicate that Site 1098 sediments are essentially a two-component mixture of diatoms and siliciclastics (primarily quartz and clays). The volcanic glass component, based on 100 smear slide analyses, is zero (see **"Results for Site Survey Samples,"** p. 5). Summary statistics for repeated runs of the in-house standard are given in Table **T1** and show no significant difference in the SiO_2 weight percent content of the Consistency Standard for the two extractions (Na_2CO_3 and KOH). From these results, it is suggested that the harsher KOH treatment, relative to the Na_2CO_3 digestion, does not dissolve significant amounts of SiO_2 from the nonbiogenous sources, which are primarily clay minerals and quartz.

T1. Analytical results of an in-house Composite Standard, Site 1098, p. 18.

A second question regarding the analytical method is whether or not digestion proceeds to completion. Several parameters may affect the efficiency of digestion, including digestion time, bath temperature, molar strength of reagent, and the weighed sample mass to reagent volume ratio. One indicator of incomplete digestion, aside from visual proof, would be a positive correlation between the amount of digested SiO_2 as a function of sample mass:reagent volume. First, no visual proof of undigested fossils was found in the recovered residue after either of the al-

kaline extractions. Second, there is no correlation between the amount of digested silica as a function of the weighed sample mass to reagent volume ratio (Fig. F2). Digestion times of 8.5–10 hr were determined based on the offsets in the amount of SiO_2 leached from the Consistency Standard when digestion times were <8 hr. The average SiO_2 values increased for both extractions and corresponded to a lower standard error when digestion times were increased to 8.5–10 hr. Although this digestion time at 85°C should produce good results (complete extraction) for samples containing up to 31 wt% SiO_2, several factors, as discussed below, will affect the outcome of unknown samples.

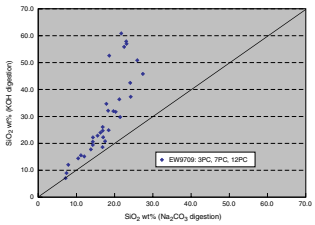
F2. Reagent volume to sample mass vs. SiO_2 extracted from Site 1098, p. 13.



RESULTS FOR SITE SURVEY SAMPLES

Leg 199 site survey samples were cored in December 1997–January 1998 aboard the *Ewing* and are labeled as EW9709. Thirty-three samples from three cores, representing ages spanning from 9 to 50 Ma, were analyzed twice: (1) in a 2-M Na_2CO_3 solution and (2) in an independently weighed sample digested in a 2-M KOH solution. Thirteen samples (39%) were run as replicate analyses to quantify the precision of the analytical method. Note that we do not correct our data for an assumed water content of the biogenous opal fraction. The water content of opal can range between 2 and 15 wt% and depends upon many factors including age, species, and sample handling. Our data is reported simply as SiO_2 or $SiO_{2\ biogenous}$ and probably underrepresents the total amount of hydrated biogenous opal in a given sample. However, correcting the reported silica data using an assumed scalar value for water content does not change the general conclusions drawn from this study. A comparison of the measured SiO_2 for the two digestion methods is illustrated in Figure F3. Two striking facts are noted. In most cases, the amount (weight percent) of digested silica for a given sample is higher after the KOH leach vs. the Na_2CO_3 leach, and in some cases, this amount exceeds the Na_2CO_3 value by more than a factor of two. The discrepancy in measured SiO_2 for the two methods increases with increasing SiO_2 in the sample. This is in contrast to the results of the composite standard (Fig. F2) whose SiO_2 value of 30 wt% is relatively constant for both alkaline extractions. Assuming both extractions produce accurate results for samples containing up to 30 wt% SiO_2 (based on the Site 1098 standard), one would expect no difference in dissolved SiO_2 for the site survey samples based on opal content alone. Yet, the KOH digestion consistently results in higher SiO_2 values, by a factor of 1.2–1.8, relative to the Na_2CO_3 extraction of identical samples.

F3. SiO_2 resulting from independent KOH and Na_2CO_3 digestions, p. 14.



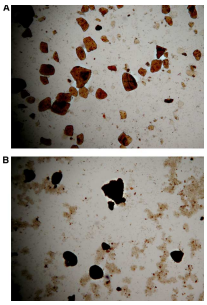
This discrepancy is explained by examining smear slides made of the solid residue after digestion with Na_2CO_3 and KOH. Fourteen smear slide pairs were made, providing a direct comparison of the microscopic examination of the residue with the SiO_2 previously measured in the supernatant. Figure F1A and F1C illustrate a typical visual comparison between the two residue types. For nearly all EW9709 samples, a common feature of the solid residue remaining after a 9-hr Na_2CO_3 digestion (Fig. F1A) is a high abundance of undigested radiolarians and other opal fragments. In contrast, such fragments are generally absent after the KOH digestion (Fig. F1C). However, in several cases, we noted the presence of rare to occasional highly resistant opal fragments, which remained even after a 9-hr KOH digestion at 85°C. Generally, the amount

of undigested siliceous fossils was essentially 0- after 9-hr KOH treatment.

To underscore the inefficiency of using Na_2CO_3 digestion, data are presented in Table T2 for six test samples from EW9709-3PC, which were allowed to digest for up to 14 hr at 85°C. Measurements were made at 6.5 and 14 hr, and the residue was examined afterward. Three of the six samples contained abundant undissolved radiolarians even after the 14-hr digestion (750, 800, and 850 cm), and all samples resulted in very low opal contents when compared to a 9-hr KOH extraction (Table T2). Generally, the KOH extraction residue contained very few opal fragments, indicating complete digestion of the biogenous opal. We caution against assuming that higher SiO_2 values resulting from a KOH leach relative to the Na_2CO_3 leach is simply the result of undigested silica fossils remaining after the Na_2CO_3 treatment. For example, Figure F4 illustrates this point when volcanic glass is present. The measured SiO_2 in this sample (EW9709-7PC; 122–124 cm) is 9.9% and 17.7 wt% SiO_2 for the Na_2CO_3 and KOH leach, respectively. However, the difference between the two values cannot be accounted for by the presence of biogenous silica remaining after the Na_2CO_3 leach. No opaline fossils were found upon a smear slide examination of the sediment residue remaining after the Na_2CO_3 leach (Fig. F4A). However, we did notice abundant glass in this residue and proportionally less glass after the KOH leach (Fig. F4B), which suggests that the near twofold difference in SiO_2 reflects a greater dissolution of the glass in the KOH solution relative to Na_2CO_3 solution. We tested whether the alkaline digestions attack amorphous volcanic glass by leaching a young volcanic ash from the eastern Pacific (ME0005-24JC; 981–982 cm, Ash Layer D; ~84.2 k.y.). The SiO_2 leached by the KOH digestion was 2.5× the measured result for the Na_2CO_3 extraction (25 vs. 10 wt% SiO_2, respectively) (Table T3). Nevertheless, both treatments strongly but incompletely dissolved the volcanic ash as well as the small amount of biogenic silica in the initial sample. An interesting result is the difference in the SiO_2 weight percent (of the weighed sediment sample) between the results from an initial extraction that is the "the opal-bearing ash," and the results from a second extraction of the recovered residue, the "the opal-free ash." For both the Na_2CO_3 and the KOH treatments, this difference yields a calculated biogenic opal content of 4 wt%, a value consistent with smear slide estimates of the amount of opal fragments in the undigested sample (<5 wt%). The potential for obtaining accurate opal values for ash samples using this double-extraction technique deserves further investigation.

T2. Amount of $SiO_{2\ biogenic}$ extracted from selected samples, p. 19.

F4. Residue remaining after Na_2CO_3 and KOH digestions, p. 15.



T3. Comparison of $SiO_{2\ biogenic}$ values, p. 20.

Comparison with Normative Opal Analysis Technique

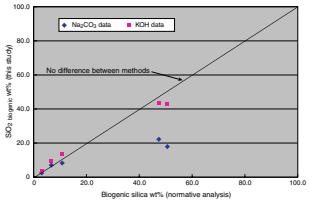
An obvious limitation of our results is the lack of independent analyses of the EW9709 samples, including the biogenic silica, calcium carbonate, and clay mineral components. Such data would provide a better gauge of the accuracy of the two extraction methods, including the amount of presumed clay dissolution, which occurs during digestion. (We are the first to measure biogenic opal for EW9709 cores. Other laboratories are not using KOH to digest the opal fraction of marine sediments, and there is a widespread belief that even the less harsh Na_2CO_3 treatment leaches excess silica from clay minerals.) Alternatively, we approached the problem by focusing on sediments that are similar to those from Leg 199 site survey sites where biogenic opal data are avail-

able and measured by an independent method. A total of 16 samples were provided by ODP's West Coast Repository for this part of the study (Deep Sea Drilling Project [DSDP] Leg 16 Site 162) and analyzed for SiO_2 and calcium carbonate. Site 162 samples are from the central equatorial Pacific Ocean, are Eocene in age, and the biogenic opal fraction is dominated by radiolarians. The 16 samples we analyzed are from a group of 116 composite samples studied by Leinen (1976, 1979), who estimated the amount of biogenous silica in each sample using a normative calculation calibrated to an X-ray determination of the opal in the sediment. The robustness of the normative method is based upon accurately measuring the relative proportions of the four clay mineral groups (montmorillonite, illite, chlorite, and kaolinite) such that one can estimate a bulk SiO_2:Al_2O_3 ratio for the sample. Leinen's SiO_2:Al_2O_3 ratio was obtained by employing X-ray diffraction (XRD) analysis for a subset of representative samples. This ratio is subsequently used to calculate the nonbiogenous silica fraction in each sample, which is finally subtracted from the bulk sediment to yield the biogenous silica fraction. The 16 samples we requested and analyzed correspond to the same 16 sampled intervals in Leinen's (1976, 1979) study. She organized these samples by age into five groups, each spanning a 1-m.y. interval between 30 and 50 Ma.

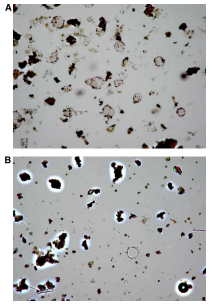
Two sediment samples from each of the 16 samples were weighed and digested separately: the first in a 2-M Na_2CO_3 solution and the second using a 2-M KOH solution. The solid residue remaining after the extractions was saved for later smear slide analysis. A summary of results for both the wet-digestion methods and the normative analysis calculations are given in Table **T4** and illustrated in Figure **F5.** In general, the Na_2CO_3 extractions underestimate the amount of biogenous silica as predicted from the normative calculation. Samples whose normative biogenic opal is <10 wt% are in the best agreement, but above this value, the Na_2CO_3 treatment underestimates, by one-third to one-half, the normative opal values. Conversely, results from the KOH extractions are very good overall. They are slightly higher than the normative calculation for values <10 wt% biogenic opal, and beyond this division, the measurements from the KOH treatment are within 80%–90% of the normative value. This discrepancy between the two treatments for samples with opal >10% is significant because Leg 199 recovered many stratigraphic intervals with very high opal contents (>50 wt%). Smear slide examination of the postdissolution residues further supports using a KOH extraction for opal measurements of Leg 199 sites. In general, opal fragments were common to abundant in the residue after the Na_2CO_3 extraction but rare to occasional in the KOH residue. Many were very small rod-shaped spicules, frustules, and fragments, which are nearly impossible to physically separate from the residue matrix (e.g., to do a simple mass balance to compare the two techniques). Figure **F6A** and **F6B** illustrates the differences in the dissolution residue for Sample 162-14-4: 80–81 cm (~46 Ma). Note the abundance of silica fossils in the Na_2CO_3 digestion residue (Fig. **F6A**) compared with the occasional fragments remaining after the KOH leach (Fig. **F6B**). Corresponding opal values are consistent with the assertion that the KOH extraction is a better estimator of this component over Na_2CO_3. This yields 37.1 wt% vs. 19.2 wt%, respectively (Table **T4**), which indicates that half of the fossil opal remains undigested in the Na_2CO_3 treatment.

T4. Comparison of measured $SiO_{2\ biogenic}$ and weight percent $CaCO_3$, p. 21.

F5. Normative analysis vs. wet-alkaline $SiO_{2\ biogenic}$ results, p. 16.



F6. Residue remaining after Na_2CO_3 and KOH digestions, p. 17.



The clay mineral fraction of samples used in the normative study is generally dominated by smectite (60%–80% smectite) (Leinen, 1976; Heath, 1969). Leinen (1976) selected one sample from Site 162 and determined the clay mineral content by XRD analysis (162-17-4: 125–126 cm). This sample, which we also obtained and analyzed, contains 30 wt% nonbiogenic components, of which 93 wt% is smectite, based on replicate analyses (Leinen, 1976). For both extractions, our digested silica values for this sample are in very good agreement with her normative calculation (~3.5% biogenic silica) (Table T4). The fact that both extractions did not produce excess silica from a matrix containing ~30 wt% smectite indicates that the presence of clay minerals does not obviate accurate measurements of biogenic silica, and that widely-held beliefs about clay mineral solubility during alkaline digestions required reexamination. Although the KOH extraction produced better biogenic silica results overall when compared to the normative analysis, the differences between our samples limits our ability to refine the comparisons. First, Leinen's samples (1976) represent 2-cm-thick intervals, whereas our sampled intervals are 1 cm thick, due to sample availability from the repository. Thus, we are missing up to 50% of her sampled interval. Second, Leinen (1976) mixed her samples together and did one analysis for each million-year time interval. We analyzed all samples individually within each million-year time interval. Therefore, we can compare results only for the average of the interval, rather than by a sample-by-sample comparison of the opal results. In addition to missing half of her sampled interval, one of our samples from the time interval 37–38 Ma (162-4-6: 60–61 cm) is 40 cm below the sample she used for her composite value for this time interval (Table T4). These differences, along with the inherent errors associated with each of the two types of analyses (normative vs. wet alkaline), probably account for some of the observed discrepancies in our respective results.

Comparison Using Younger Sediments

Finally, we report SiO_2 results for relatively young sediments from the Pacific to test whether or not the harsher KOH extractions can produce acceptable biogenic opal values compared to the Na_2CO_3 digestion. A total of 40 analyses, including replicates, were performed for 9 samples ranging in age from 0 to 84 ka. The results of these analyses are summarized in Table T3 for the samples taken from cores W8709A-5BC, ME0005-24JC and K7905-42BC. For all samples except two, there is little difference between the measured SiO_2 weight percent of the two alkaline techniques. Additionally, smear slide analyses show no evidence of residual opaline fossil fragments after both digestions. As was the case for the Site 1098 Composite Standard discussed previously, this result is significant because dissolution of aluminosilicates does not appear to be a significant source of excess SiO_2, particularly for the KOH extraction. The two exceptions to these results are samples which contain volcanic ash and glass: W8709A-5BC, 5–20 cm, and Ash Layer D from Site ME0005A-24 JC, discussed previously. The first sample shows a twofold difference in SiO_2 weight percent for the KOH digestion relative to the Na_2CO_3 digestion. However, smear slide analysis shows no evidence of undigested silica shells remaining in the residue after the Na_2CO_3 extractions, again suggesting that the source of the excess silica is volcanic, not biogenic. We did observe occasional volcanic glass fragments in the residue, but a quantitative estimate of the glass was not

adequately determined for this sample. The presence of volcanic ash and glass will likely result in erroneously high estimates of the biogenic silica for both digestions, but the KOH digestion will produce a much greater error. In summary, these results suggest that there is no disadvantage to routinely using a 2-M KOH solution to estimate the biogenic opal in pelagic sediments of both young sediments and others spanning the Cenozoic.

CONCLUSIONS

For sediments with a significant radiolarian content, the commonly used Na_2CO_3 method is not adequate to efficiently digest the opaline shells. The KOH digestions produced much better results overall. Complete digestion normally did occur with a 2-M KOH solution and the operating conditions we used (85°C for 8.5–10 hr in a shaking water bath). In some cases, rare opal fossil fragments were still visible on smear slides even after this harsher treatment. Except for the case where volcanic glass is present, the KOH treatment does not seem to result in the leaching of excess silica from the matrix material (e.g., aluminosilicates and quartz). For samples containing volcanic ash and glass, significant discrepancies in the measured silica were found for the two treatments; the KOH digestion resulted in a twofold difference in dissolved SiO_2 relative to the Na_2CO_3 treatment. However, both the Na_2CO_3 and the KOH extractions dissolved a significant fraction of the volcanic ash and overestimate biogenic opal in ash-bearing samples. A possible method for measuring opal in ash-bearing samples utilizes a double extraction treatment. The biogenic opal is calculated as the difference between the SiO_2 value obtained from the opal-bearing sediment and the value obtained on the opal-free residue, which is recovered and digested a second time using the same operating conditions of the first extraction. In summary, our study suggests that the commonly used Na_2CO_3 method is inadequate and that KOH digestions will give more accurate biogenic silica values for Eocene and Miocene sediments, primarily because Na_2CO_3 is not nearly as effective at dissolving radiolarians. More generally, our results indicate that using a 2-M KOH solution to measure biogenic silica is an acceptable treatment for marine sediments throughout the Cenozoic.

ACKNOWLEDGMENTS

We wish to thank the following reviewers as well as persons and repositories who provided samples used in this study: two anonymous reviewers, the Core Laboratory at Oregon State University, Corvallis, Linda Anderson at the University of California, Santa Cruz, and the West Coast Repository of the Ocean Drilling Program (ODP), La Jolla, California.

This research used samples and/or data provided by ODP. ODP is sponsored by the U.S. National Science Foundation (NSF) and participating countries under management of Joint Oceanographic Institutions (JOI), Inc. Funding for this research was partially provided by NSF grants OCE99-07292 and EPS-0132626.

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Figure F1. A. Smear slide of the residue remaining after a 9-hr 2-M Na_2CO_3 digestion of site survey Sample EW9709-3PC: 1192–1194 cm (#0937, slide 06R). **B.** Smear slide of the solid residue remaining after a 14-hr 2-M Na_2CO_3 digestion of site survey Sample EW9709-3PC: 750 cm (#C624, slide 23Y). (Continued on next page.)

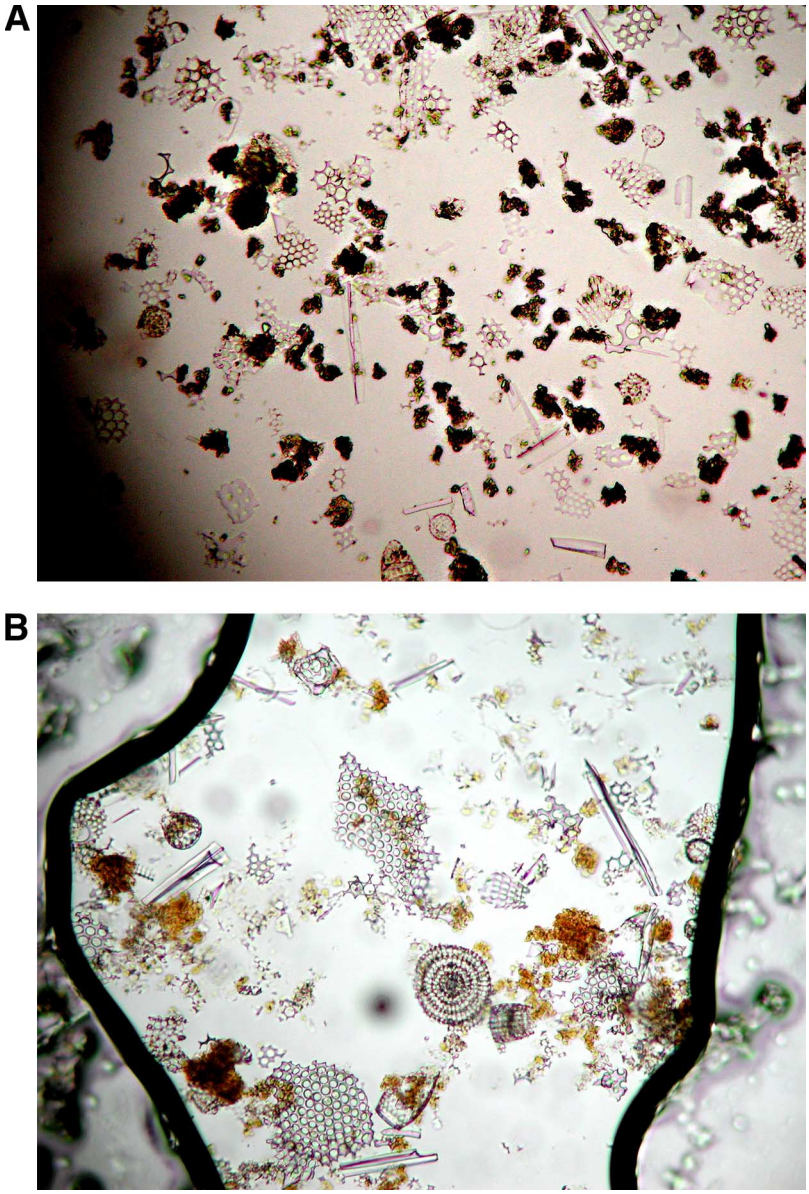

Figure F1 (continued). C. Solid residue remaining after a 9-hr KOH digestion of site survey Sample EW9709-3PC: 1192–194 cm. Note occasional biogenic opal fragments (#0940, slide 07R).

C

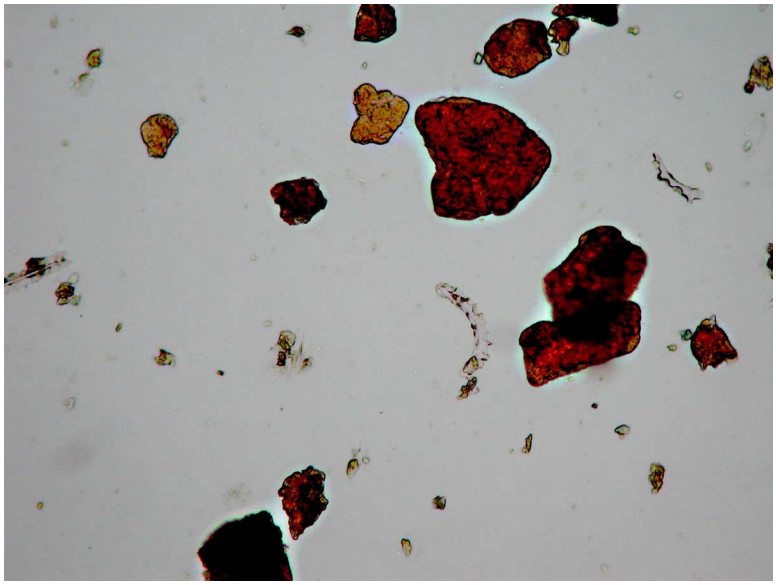

Figure F2. Reagent volume to sample mass ratio vs. SiO_2 extracted from Site 1098 Composite Standard sample.

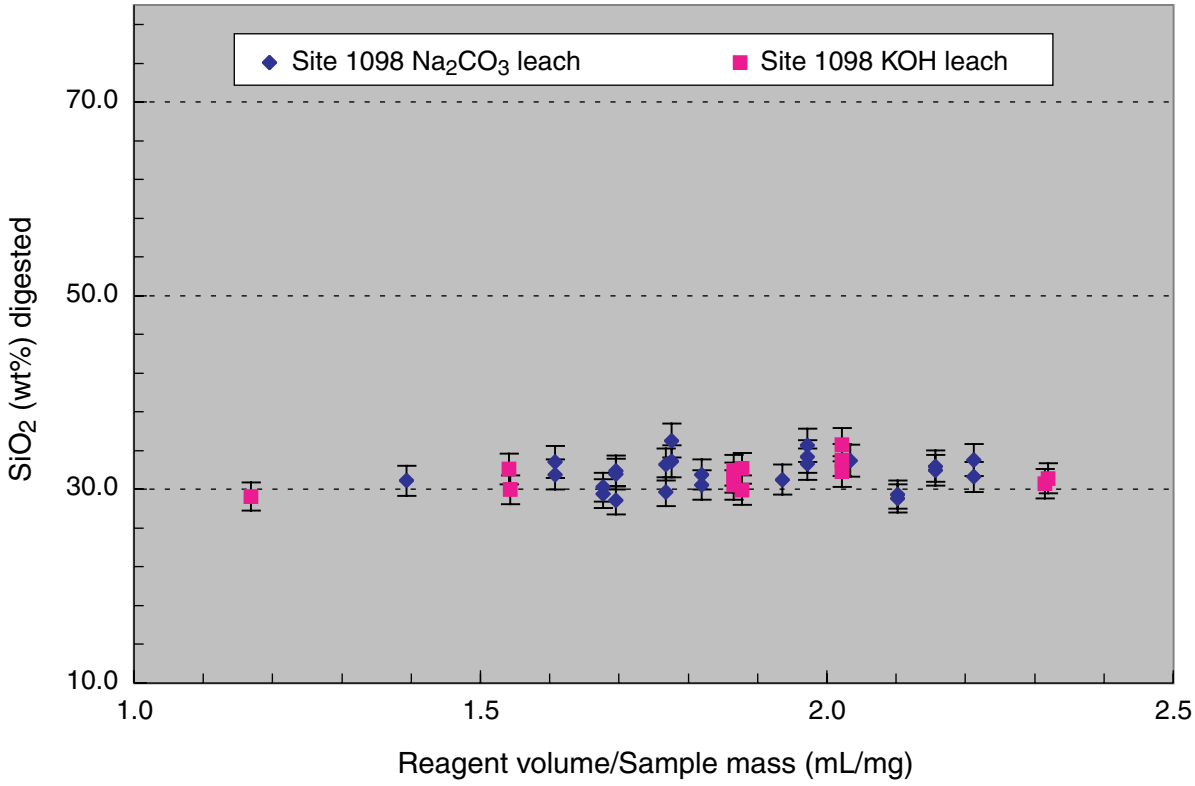

Figure F3. SiO_2 weight percent resulting from independent KOH and Na_2CO_3 digestions of site survey samples.

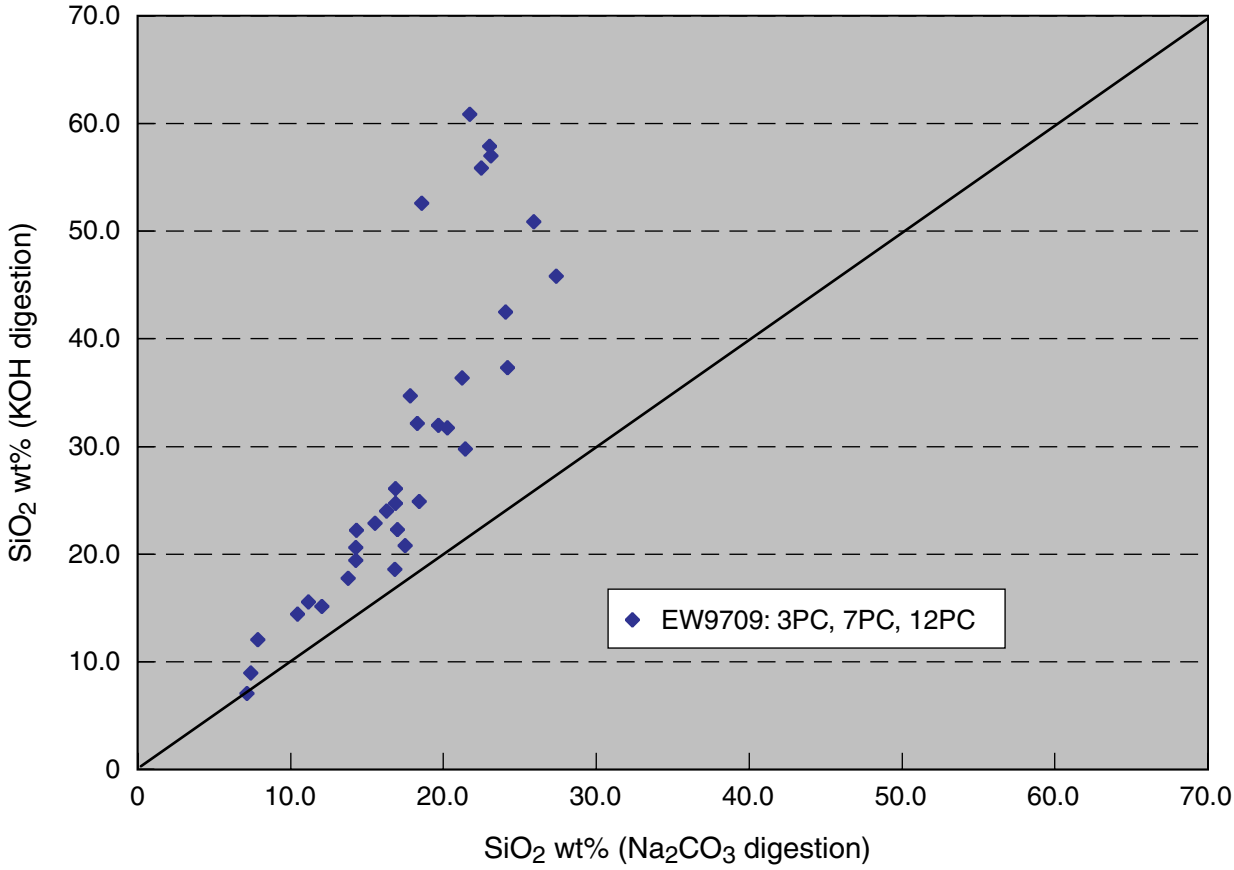

Figure F4. A. Smear slide of glass residue remaining after a 2-M Na_2CO_3 digestion of site survey Sample EW9709-7PC: 122–124 cm (#0945, slide 10). **B.** Smear slide of residue remaining after KOH digestion of site survey Sample EW9709-7PC: 122–124 cm. Note the lower abundance of glass remaining compared to amount in part A (#0947, slide 11).

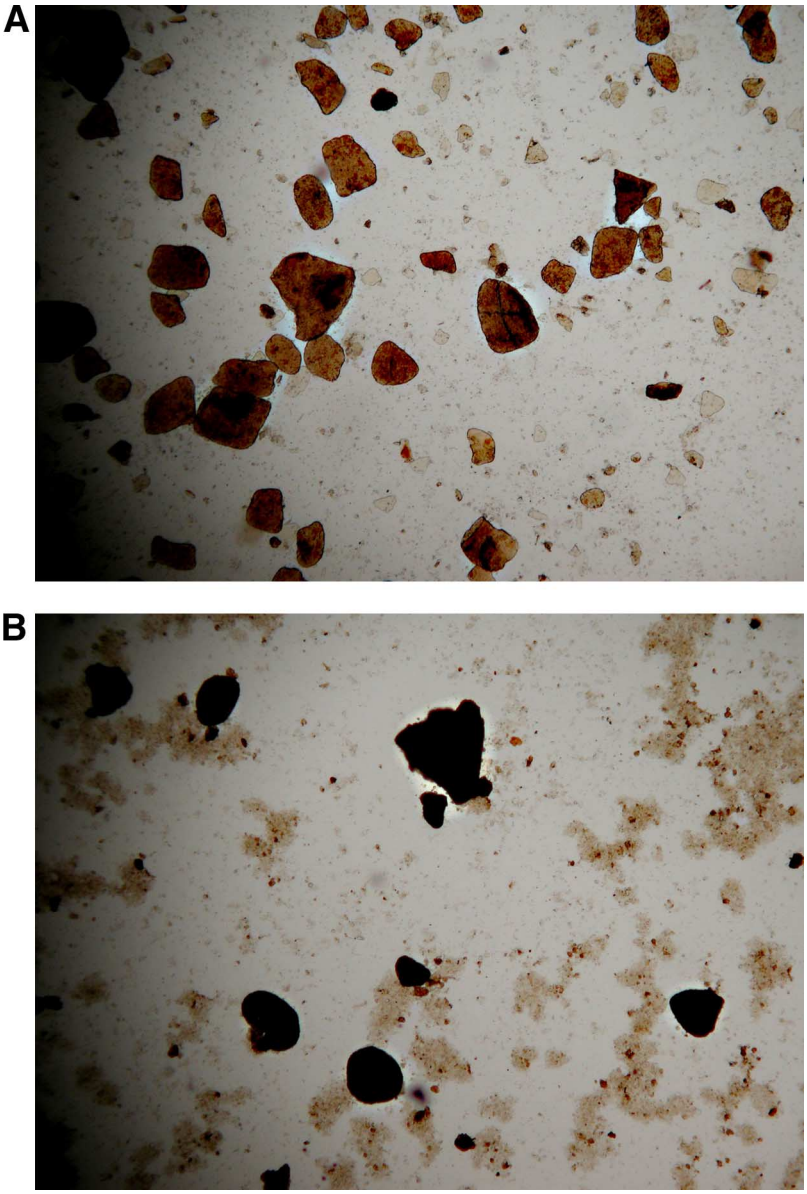

Figure F5. Normative analysis (Leinen, 1976) vs. wet-alkaline $SiO_{2\ biogenic}$ results of DSDP Site 162 samples.

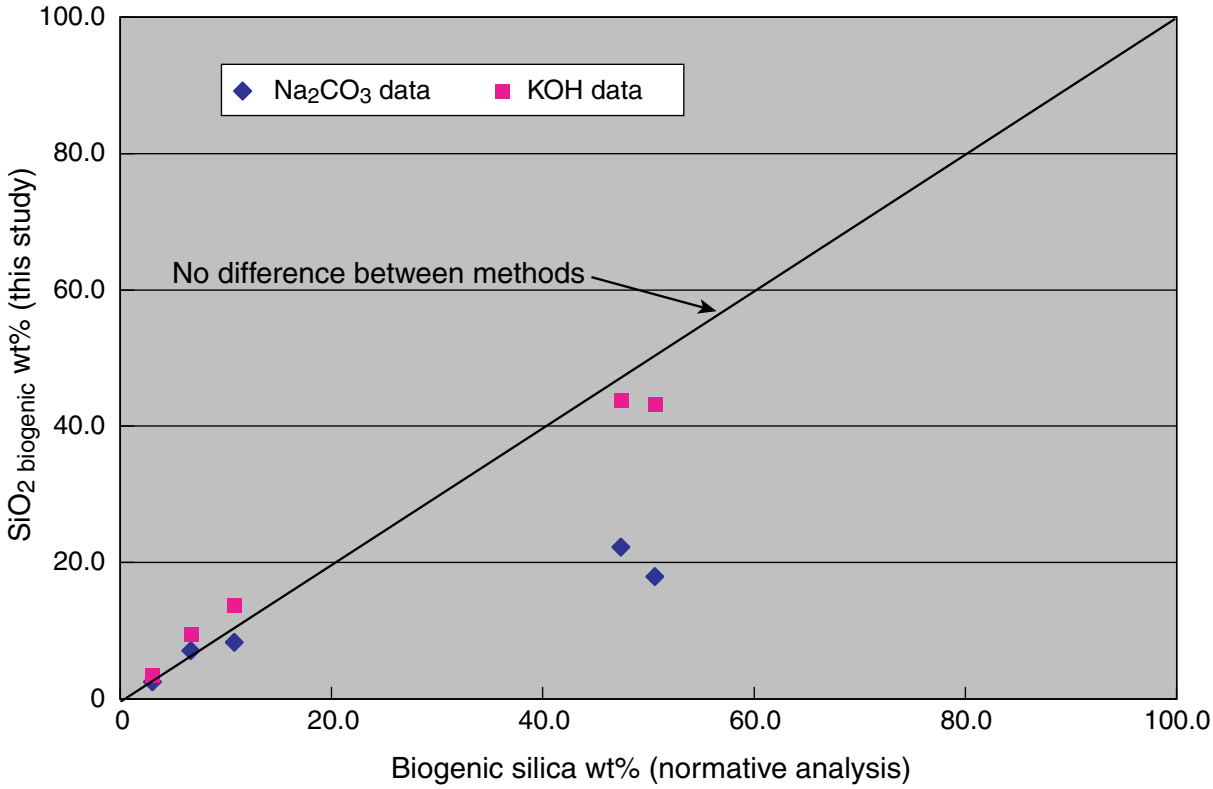

Figure F6. A. Smear slide of the solid residue remaining after a 9-hr 2-M Na_2CO_3 extraction of a 46-Ma sample from DSDP Site 162 (14-4: 80–81 cm). Dissolved SiO_2 = 19.2 wt% (#1576, slide 50). **B.** Residue remaining after a 9-hr 2-M KOH digestion of a 46-Ma sample from DSDP Site 162 (14-4: 80–81 cm). Note the dissolution-resistant opal fragments. Dissolved SiO_2 = 37.1 wt% (#1578, slide 51R).

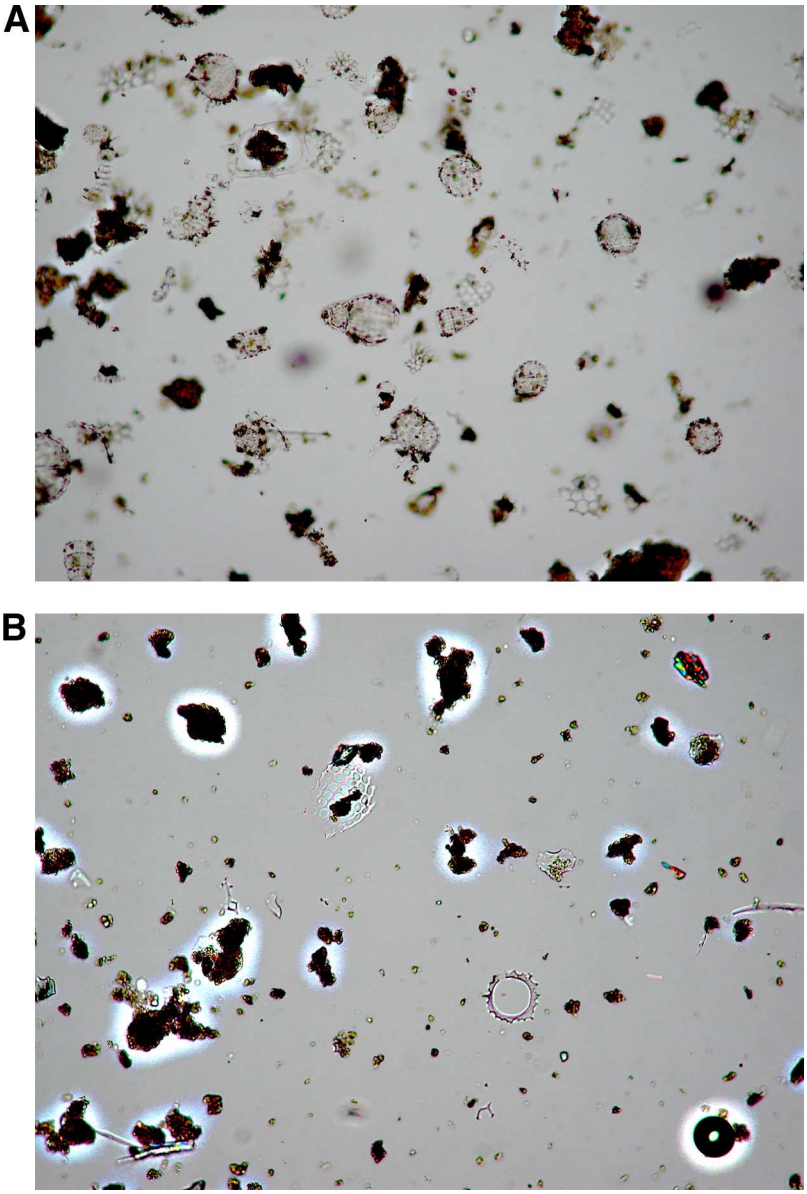

Table T1. Analytical results of an in-house Composite Standard, Site 1098. Standard was included in all sample runs.

Dissolution reagent	Digestion time (hr)	Avg. $SiO_{2\ biogenous}$ (wt%)	Standard deviation	n
2-M Na_2CO_3[1]	8.5–9	31.6	1.6	25
2-M KOH	9	31.4	1.4	14
2-M Na_2CO_3[2]	5	23	2	48

Note: 1 = this study, 2 = Anderson and Ravelo, 2001.

Table T2. Amount (weight percent of weighed sample) of $SiO_{2\ biogenic}$ extracted from selected samples from the site survey, Site EW9709-3PC.

	Na_2CO_3 leach		KOH leach
Digestion time:	6.5 hr	14 hr	9 hr
Sample ID (cm):	Undigested opal in residue	Undigested opal in residue	No opal in residue
EW9709-3PC: 50–51	5.4	7.8	14.3
EW9709-3PC: 150–151	5.8	8.7	14.4
EW9709-3PC: 300–301	3.0	9.6	17.8
EW9709-3PC: 750–751	13.6	32.4	41.3
EW9709-3PC: 800–801	16.5	27.2	44.9
EW9709-3PC: 850–851	19.4	36.8	60.4

Note: The 2-M Na_2CO_3 digestion was incomplete after 6.5 and 14 hr, as evidenced by abundant fossils in the undigested solid residue. Essentially, no opal remained after a 9-hr 2-M KOH digestion.

Table T3. Comparison of $SiO_{2\ biogenic}$ values resulting from the two extraction procedures used in this study on Leg 199 and other samples.

Sample ID (cm)	Age approx.	SiO_2 (average wt%) 2-M Na_2CO_3	2-M KOH	Notes
W8709A-5BC: 5–20	2 ka	5.0	10.1	Contains volcanic glass
K7905-42BC: 15–20	12 ka	2.0	2.3	
ME0005A-24JC:				
0–1	0.04 ka	14.0	12.7	
10–11	0.94 ka	14.4	13.5	
30–31	2.6 ka	13.4	13.1	
200–201	17 ka	17.1	16.0	
660–661	56 ka	26.7	26.1	
860–861	74 ka	18.1	18.3	
Ash layer D 981–982	84 ka	10.0	25.0	Opal-bearing ash layer
Ash layer D 981–982	84 ka	6.0	21.0	Opal-free ash layer
EW9709-7PC (Pat-8):				
122–124	9–21 Ma	13.8	17.7	Contains volcanic glass
335–337		16.9	24.7	
387–389		17.0	22.2	
518–520		14.3	20.6	
696–698		18.3	32.1	
804–806		10.5	14.4	
829–831		7.4	8.9	
982–984		17.9	34.6	
1163–1165		19.7	31.9	
1252–1254		21.4	29.7	
1317–1319		18.4	24.9	
1367–1369		20.3	31.7	
1436–1438		16.3	24.0	
1466–1468		14.3	22.2	
1518–1520		7.1	7.0	
EW9709-12PC (Pat-17):				
56–58	12–21 Ma	14.3	19.4	
258–260		21.3	36.3	
473–475		15.5	22.9	
593–595		16.9	26.1	
740–742		24.1	42.5	
833–835		25.9	50.8	
979–981		24.2	37.3	
1074–1076		27.4	45.8	
1261–1263		12.0	15.1	
EW9709-3PC (Pat-13):				
33–35	45–50 Ma	7.9	12.0	
314–316		11.2	15.5	
433–435		17.5	20.7	
633–635		16.8	18.5	
773–775		18.6	52.6	
830–832		21.7	60.9	
933–935		23.0	57.9	
1192–1194		22.5	55.9	
1337–1339		23.1	57.0	

Note: Approx = approximate.

Table T4. Comparison of measured SiO_2 and $CaCO_3$ weight percent from this study with results from a normative analysis for 16 samples, DSDP Site 162.

	This study						Normative analysis*			
					Percent nonbiogenic (wt%)					
Age interval (Ma)	Sample ID (cm)	SiO_2 wt% (Na_2CO_3 leach)	SiO_2 wt% (KOH leach)	$CaCO_3$ wt% (coulometry†)	Using Na_2CO_3 SiO_2 values	Using KOH SiO_2 values	Sample ID	Biogenic silica (%)	$CaCO_3$ (%)	Nonbiogenic silica (%)
30–31	1-1:91–92	8.1	15.1	51.7			1-1:90-92			
	1-2:61–62	9.5	18.4	46.9			1-2:60-62			
	1-3:80–81	7.3	7.8	60.0			1-3:80-82			
	Average:	8.3	13.8	52.9	38.9	33.4		10.8, 14.6	72.0	17.2,13.6
35–36	3-2:80–81	8.2	10.9	72.3			3-2:80-82			
	3-3:80–81	6.6	10.3	67.6			3-3:80-82			
	3-4:80–81	6.2	7.3	77.6			3-4:80-82			
	3-5:70–71	5.5	6.5	57.3			3-5:70-72			
	Average:	7.0	9.5	68.7	24.3	21.8		6.7, n/a	70.0	23.3,23.3
37–38	4-2:80–81	11.6	24.2	2.9			4-2:80-82			
	4-3:79–80	18.0	43.4	4.0			4-3:80-82			
	4-4:80–81	18.1	45.3	3.6			4-4:80-82			
	4-5:77–78	21.2	48.9	3.1			4-5:76-78			
	4-6:60–61	20.3	54.3	6.0			4-6:20-22			
	Average:	17.9	43.2	3.9	78.2	52.9		50.7, 56.0	3.3	46.0,40.5
46–47	14-2:80–81	26.6	52.0	16.0			14-2:80-82			
	14-3:81–82	20.8	42.2	28.7			14-3:80-82			
	14-4:80–81	19.2	37.1	35.3			14-4:80-82			
	Average:	22.2	43.8	26.6	51.1	29.6		47.4, 51.6	22.2	30.3,26.2
49–50	17-4:125–126	2.4	3.5	78.7			17-4:124-126			
	Average:	2.4	3.5	78.7	18.9	17.9		3.1, 4.0	68.0	28.9,27.9

Notes: * = data separated by commas from Leinen (1976, 1979), respectively. † = method described in Lyle, et al. (2000). $SiO_{2\ biogenic}$ values resulting from the KOH treatment are in good agreement with the normative calculation, especially for samples with opal contents >10 wt%.