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INSTRUMENTS AND METHODS

A simple method for the rapid determination of biogenic opal in pelagic marine sediments

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Abstract—Biogenic opal in marine sediments is determined with a single extraction of silica into 2 M Na_2CO_3 solution at 85°C for 5 h. The method has been applied to sediments of varied opal contents (3–100% opal) and age (Recent to Pliocene). It is sufficiently simple, precise and rapid to be used routinely for high resolution spatial and temporal mapping of the biosiliceous component in deep-sea sediments. Evidence from timed dissolution experiments, germanium/silicon ratios, and comparisons with other methodologies demonstrates that systematic errors produced by leaching of silica from aluminosilicates or by incomplete dissolution of siliceous microfossils are small compared to the range of opal contents in biogenic sediments. When estimating mass accumulation rates, we report sedimentary biogenic opal both as $\%Si_{OPAL}$ (silicon content) and as %OPAL ($2.4 \times \%Si_{OPAL}$). This conversion accounts for the average water content of diatomaceous silica (about 10% water = $SiO_2 \cdot 0.4\ H_2O$).

INTRODUCTION

SILICEOUS microfossils constitute about one-half of the mass of biogenic sediments accumulating on the deep-sea floor (BROECKER and PENG, 1982); yet quantitative data necessary to map spatial and temporal distributions of sedimentary opal are limited. Global mass balances of the oceanic silica cycle rely heavily on a sparse covering of site-specific opal accumulation rates extrapolated regionally and globally (HEATH, 1974; DEMASTER, 1981; LEDFORD-HOFFMAN *et al.*, 1986). Recent compilations of percent biogenic opal in surface sediments have revealed a close link to biosiliceous productivity patterns in the overlying surface waters (LEINEN *et al.*, 1986), and regional time-slices of opal accumulation have demonstrated both secular and spatial variations related to shifts in productivity (MOLINA-CRUZ and PRICE, 1977; LEININ, 1979; BREWSTER, 1980; HEATH *et al.*, 1983; BANAHAN and GOERING, 1986; LYLE *et al.*, 1988). In addition, a few high resolution down-core traces of percent biogenic opal have linked local siliceous paleo-productivity to Milankovitch-type orbital rhythms (PISIAS, 1976; PISIAS and LEINEN, 1984). Thus it is clear that the opal content of marine sediments carries a valuable paleoceanographic record of changes in the strengths and locations of surface ocean productivity.

Many methods have been used to estimate percent biogenic opal: (1) X-ray diffraction after heated conversion of opal to cristobalite (ELLIS and MOORE, 1973); (2) direct X-ray

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diffraction of amorphous opal (EISMA and VAN DER GAAST, 1971); (3) direct infra-red spectroscopy of amorphous opal (CHESTER and ELDERFIELD, 1968); (4) elemental normative partitioning of bulk sediment chemistry (LEINEN, 1977; BREWSTER, 1983); (5) differential wet-alkaline extraction (EGGIMANN *et al.*, 1980; DEMASTER 1981); and (6) microfossil counts (e.g. POKRAS, 1986). Each of these procedures has inherent systematic problems or is analytically cumbersome. Consequently, none is widely accepted and only rarely have different techniques been compared on a sample-to-sample basis (e.g. as in CHESTER and ELDERFIELD, 1968; LEINEN, 1985; DEAN *et al.*, 1985) or evaluated in terms of the physical chemistry of biogenic opal (e.g. HURD, 1983).

The purpose of this paper is to report a rapid wet-alkaline extraction procedure to estimate biogenic opal in marine sediments. The procedure is similar to that described by EGGIMAN *et al.* (1980) but is simplified to offer an attractive conventional method for routine determinations in most sediments.

In the following treatment we will take the silicon content of pure biogenic opal as 42% silicon rather than the conventional method of calculating %OPAL as SiO_2 (47% silicon). Justification for this assumption will be presented later.

METHODS

The procedure described below involves extracting biogenic silica from a sediment sample with an alkaline solution and then measuring the dissolved silicon concentration in the extract by molybdate-blue spectrophotometry. We routinely extract 48 samples at the same time.

Alkaline extraction

The sediment sample is freeze-dried overnight, crushed (but not powdered) and then allowed to re-equilibrate with the atmosphere at room temperature for at least 24 h. An aliquot ranging from 25 to 200 mg is weighed into a 50 ml polypropylene centrifuge tube (Nalgene no. 3110; caps no. 3111 with pin-holes to allow gas expansion). Sample masses must be adjusted so that no sample contains more than 25 mg of pure biogenic opal. Five ml of a 10% H_2O_2 solution (technical or pharmaceutical grade) is added to the tube, and after about 30 min, 5 ml of a ~1 N HCl solution (a 1:9 dilution of concentrated HCl with water) is added. The tube is sonified, capped and placed in a rack for about 30 min. Addition of acid and peroxide removes diluting phases such as carbonate and organics, and assists in disaggregating the sediment, exposing opal surfaces to dissolution. About 20 ml of deionized water is added to the tube and then centrifuged at 4300 ***g*** for about 5 min (we use a Sorval SS-3 centrifuge with an SS-34 rotor at 6000 rpm). The supernatant is decanted to remove residual acid and peroxide. The tube is then placed in an oven to dry overnight (60°C). Samples containing large quantities of clay should not be dried to hardness but should remain moist to allow for disaggregation during opal extraction.

Exactly 40.0 ml of a 2 M Na_2CO_3 solution (Baker reagent grade) is added with a Repipet to the tube, which is then capped, mixed well (Vortex-Genie, Scientific Industries), sonified and placed in a covered constant-temperature bath pre-heated to 85°C (we use a Blue M Model MW-1130A-1). After about 2 h, and again at 4 h, the sample is removed and mixed vigorously (with a Vortex-Genie) to resuspend the solids and quickly returned to the water bath. After a total of 5 h, the tube is removed and immediately centrifuged for 5 min at 4200 ***g***. About 20 ml of the clear supernatant is then

quickly transferred to a polyethylene scintillation vial with linerless caps (Wheaton no. 986704) and stored for subsequent analysis. All steps after removing the tube from the hot bath must be done quickly (before cooling) to minimize irreversible loss of dissolved silica to solid surfaces.

Visual microscopic inspection of the residual solids after alkaline extraction generally reveals that although all diatoms have dissolved, some radiolarians and radiolarian fragments may still be present. If radiolarians represent a significant fraction of the initial opal (>25%) or if the residual solids appear to contain significant quantities of radiolarians, we recommend washing the residual solids through a 38 or 63 μm sieve and dissolving the >38 or >63 μm fraction in 10–30 ml of a 2 N NaOH solution for 5–8 h at 85°C to ensure complete dissolution. The measured silicon content of this extraction is then added to that resulting from the initial Na_2CO_3 extraction.

Work in progress in our lab suggests that up to 20–50% of the radiolarians can escape dissolution in 2 M Na_2CO_3. However, radiolarians generally represent only 2–4% of the mass of biogenic opal in Antarctic siliceous oozes and in eastern equatorial Pacific sediments (C. CHARLES and J. ALEXANDROVICH, unpublished data). This evidence suggests that in most sediments, solution-resistant radiolarians are not a significant portion (<2%) of total sedimentary biogenic opal mass.

Determination of dissolved silica

Dissolved silica is determined by modified molybdate-blue spectrophotometry (STRICKLAND and PARSONS, 1968; FANNING and PILSON, 1973; Appendix, this work). The solid to solution ratio of the alkaline extraction is designed to produce a supernatant containing <10 mM dissolved silica. Higher concentrations can produce erratic results and poor recovery in opal-rich samples due to loss of silica to solid surfaces remaining in the extraction tube, or possibly due to irreversible formation of unreactive silica gels or polymers that are not molybdate reactive. The extraction scheme reported here should produce supernatant silica concentrations in the range between 700 and 9000 μM. Dilution of the supernatant (by a factor of about 100) is accomplished by pre-diluting the molybdate working solution (FANNING and PILSON, 1973). All determinations are thus diluted equally and treated in the same run. The analytical method should result in absorbances between about 0.07 and 0.9 in 1 cm cells. Any sample exceeding 0.9 absorbance units must be redetermined by repeating the alkaline extraction using less sample mass.

Procedure

The volumes given here are sufficient for filling a 1 cm spectrophotometer cell. Reaction vessels can be any low density polyethylene container of appropriate volume that can be capped. All pipetting should be with high precision equipment since imprecision in the analytical method (0.2–1.0%) is entirely due to volume errors. We routinely analyse all samples, standards and blanks in duplicate. All working solutions (see Appendix) and samples should be at room temperature before beginning the procedure.

Dispense 17.5 ml (Repipet) of the molybdate working solution into each of the dry, clean reaction vessels (numbered sequentially) to be used. At 30 s intervals, pipette (Finnpipet) 125 μl of sample, standard or blank into each vessel and immediately mix by swirling. Cap the vessels and allow each to react for exactly 20 min.

Again working at 30 s intervals, pipette 7.5 ml of reducing working solution into each vessel, cap tightly and mix thoroughly by swirling. Do not permit the solution to touch the inside of the cap. Allow the solutions to stand overnight (minimum of 12 h) to complete the reduction of the silicomolybdate complex.

Read the absorbances of the solutions in a 1 cm cell against doubly deionized water (DDW) in a spectrophotometer peaked at 812 nm. We use a Beckman DU spectrophotometer modified with a Gilford 1 cm pathlength sipper cell, power supply and photocell attachments.

Standards

Primary fused quartz silica standards (20,000 μM) are prepared as described in FANNING and PILSON (1973). Working silica standards (0, 2, 4, 6 and 8 mM silica) are prepared by diluting the primary standard with the appropriate volumes of 3 M Na_2CO_3 (or 3 N NaOH) and deionized water to produce solutions that are matrix-matched to the molarity of the alkaline extraction solutions (2 M Na_2CO_3 or 2 N NaOH). These working standards are stored in polyethylene bottles and are stable for months. We discard them when the volume remaining in the bottle is less than one-fourth of the initial volume to minimize evaporative concentration effects.

Blanks

We routinely run two types of blanks: a reagent blank and an operational blank. The reagent blank is composed of deionized water plus reagents and is analysed in duplicate with every batch of silica determinations to ensure the absence of contamination of water or reagents. Provided that high quality reagent grade chemicals and silica-free water are used, reagent blanks should display absorbances near zero (<0.001).

The operational blank is simply alkaline extraction solution that is carried through the extraction and analytical scheme without added sediment sample. Two or three blanks are analysed in duplicate to provide replicate values. The operational blank should be less than 0.003 absorbance units higher than that of zero standard. The average value of the operational blank is used to correct the sample absorbances.

The zero standard acts both as a standard and as a check on operational blanks, and should display absorbances less than 0.002 higher than the reagent blank. This absorbance results from silica in the Na_2CO_3 and NaOH. This quantity of silica represents about 30% of the sample absorbance expected for a 200 mg sample containing 1% opal. For samples containing <1% opal, this technique is therefore effectively blank-limited. However, for reasons discussed below, this procedure is not an accurate measure of biogenic opal in samples containing less than about 3% opal.

Extraction solutions (2 M Na_2CO_3 and 2 N NaOH) spiked with dissolved silica and carried through the 85°C 5 h procedure yield 99 ± 2% recovery. There are no apparent matrix interferences nor is there effective vapor loss.

Calculations

We use the following algorithms to calculate the opal content of samples:

- C_{STD} Silica concentration of the working standard (mM).
- C_S Silica concentration of the sample (mM).
- A_{STD} Absorbance of the standard (average of duplicates; absorbance units).
- A_S Absorbance of the sample (average of duplicates; absorbance units).
- A_O Absorbance of the operational blank (average of two pairs of duplicates; absorbance units).
- F F-factor (mM/Abs). $F = 1/S$, where S is the slope of a linear regression through the standard curve: a plot of A_{STD} vs C_{STD} for all standards. The linear regression should yield a correlation coefficient (r^2) greater than 0.99.
- M Sample mass (mg).

The concentration of dissolved silica in each sample is determined by the equation

$$C_S = F \times (A_S - A_O).$$

Typical values of F based on 38 runs are 9.20 ± 0.2 mM/Abs. An 8 mM standard should therefore produce an absorbance of 0.87 Abs units. Values of the slope "S" expected from the standard curve are 0.109 ± 0.002 Abs/mM. This response is near that of the theoretical molar absorptivity (sensitivity) for the silicomolybdate-blue method in deionized water standards, since the 2 M Na_2CO_3 and NaOH alkaline "salt" solutions, when diluted by a factor of 100, are too dilute to cause a significant salt or pH effect in the formation of the silicomolybdate complex.

Weight percent silicon is calculated by the equation $\%Si_{OPAL} = 100 \times (C_S/M) \times (28.09\ g\ mol^{-1}) \times (0.04\ l) \times (1000\ mg\ g^{-1}) \times (mol\ 1000\ mmol^{-1})$ or more simply

$$\%Si_{OPAL} = 112.4 \times (C_S/M).$$

For example, our "FI-STD" diatomaceous pure opal standard (SHEMESH *et al.*, 1988) contains 40.17% Si_{OPAL}, 25.0 mg of which will produce $C_S = 8.935$ mM.

There is a widespread tendency in the literature to report sedimentary opal contents as $\%SiO_2$ ($2.139 \times \%Si_{OPAL}$) or as %OPAL, often without an indication of how this result was calculated. In order to clarify the measurement of a biogenic mineral whose formula weight is uncertain and probably not constant, we recommend that values always be reported as $\%Si_{OPAL}$, an unambiguous measure resulting directly from the procedure.

Table 1. *Water content of biogenic silica*

H_2O Loss (%)	*n*	Age	ΔT (°C)	Procedure	Reference*
			Water content of diatoms		
2.0	1	Pleis.	25–60	Weight loss	1
8.1 ± 0.4	3	Pleis.	60–1000	Weight loss	1
†3.8 ± 0.7	10	Pleis.	25–200	6.2% ^{18}O xchng	2
3.4 – 6.7	75	Pleis.	110–1000	$H_2O \rightarrow H_2$; Vol.	3,4
4.6 – 5.1	3	Pleis.	110–1000	$H_2O \rightarrow H_2$; Vol.	5
9.7	1	?	20–1000	Weight loss	6
8.1	1	Mio.	25–1000	$H_2O \rightarrow H_2$; D/H	7
			Water content of Radiolaria		
14.5 ± 2.0	11	10 Ma	25–1000	Weight loss	8
11.0 ± 1.9	17	11–40 Ma	25–1000	Weight loss	8
13	?	Recent?	110–1000	$H_2O \rightarrow H_2$; Vol.	3,5

Formula weight conversions as a function of water content

H_2O Content (%)	Formula	Formula wt (g mol^{-1})	Theoretical $\%Si_{OPAL}$	Conversion OPAL/%Si
0	SiO_2	60.1	46.7	2.14
8	$SiO_2 \cdot 0.3\ H_2O$	65.5	42.9	2.33
10	$SiO_2 \cdot 0.4\ H_2O$	67.3	41.7	2.40
14	$SiO_2 \cdot 0.55\ H_2O$	70.0	40.2	2.49

* 1, FI-STD (this paper); 2, LECLERC *et al.* (1987); 3, WANG and YEH (1984a); 4, WANG and YEH (1985); 5, WANG and YEH (1984b); 6, LABEYRIE (1979); 7, KNAUTH and EPSTEIN (1982); 8, HURD and THEYER (1977).
† Calculated from exchangeable oxygen in Table 2 of LECLERC *et al.* (1987) assuming all O_{xch} is in $-OH_2$.

However, where mass fraction and mass accumulation rates of opal are required, it is necessary to make some estimate of the actual formula weight to convert $\%Si_{OPAL}$ to %OPAL. Determining the formula weight on all samples is impractical due to the difficulty in recovering pure opal from sediments. From the literature and our own analyses, it appears that most diatomaceous silica younger than 30 Ma displays a relatively constant water content of about 10% (see Table 1 and discussion below), which we will take as typical of "air-dried" diatomaceous opal. Thus we tentatively take weight percent opal as estimated from the equation

$$\%OPAL = 2.4 \times \%Si_{OPAL}.$$

Radiolarians typically display higher water contents (Table 1) requiring that a factor of about 2.5 be employed for these microfossils if they are a significant enough fraction of the opal to be analysed separately. Since the water content of radiolarians decreases with age (HURD and THEYER, 1977), the conversion factor we adopt here may not be applicable to biogenic opal of all ages.

Water content

Measurement of the water content of biogenic opal is dependent upon such factors as initial dehydration conditions and the final time and temperature of roasting (KNAUTH and EPSTEIN, 1982; HURD, 1983). Literature data on water contents in diatomaceous opal (Table 1) are consistent with a total water content of about 10%, provided one takes into consideration the temperature ranges of each treatment and the probable fraction of total water expelled. The silica content of purified and separated Holocene diatom and radiolarian samples is between 41 and 43% silica (SHEMESH *et al.*, 1988), suggesting that an "air-dried" water content of 10% is fairly representative of siliceous shells.

In order to systematically "standardize" the problem of water content and formula

weights in our lab, we routinely freeze-dry samples overnight and then let them re-equilibrate with the atmosphere in the belief that this treatment provides reproducible results. While our formula weight based on water content may not be the best estimator for all samples, we suggest that it is preferable to reporting opal as SiO_2, which not only ignores the problem but also systematically underestimates the mass fraction of opal in sediments by 10–20%. If the mass fraction of opal must be known more accurately than ±5%, there is probably no recourse other than separating the pure biogenic silica and determining water content (and other related factors such as density, refractive index, solubility, etc.) on selected samples. This is particularly true of older sediments.

DISCUSSION

Precision

Reproducibility of the overall method was estimated from both the short-term and long-term precision of replicate determinations of opal-poor and opal-rich samples. Short-term precision averages about ±6% for opal-poor samples (<15% OPAL). Long-term precision ranges from ±8% for opal-poor samples to ±4% for opal-rich samples (>50% OPAL). We suspect that some portion of this irreproducibility is caused by inhomogeneity, particularly for opal-poor samples.

The pooled precision (1 sigma) for duplicate determinations of 27 samples (1.5–7.9% OPAL) was ±0.24% OPAL. Nine opal-poor samples (3–15% OPAL) analysed over a period of 1 year by three analysts yielded a pooled precision of ±0.77% OPAL. Finally, opal standards, reflecting the composition of opal-poor (4% OPAL) and opal-rich (70–100% OPAL) pelagic sediments, were analysed repeatedly over a period of 1 year and yielded a standard deviation of ±4–5% about the mean.

Accuracy

There are no certified methods or standards to characterize the accuracy of any biogenic silica technique. We thus estimated accuracy by three different methods: (1) comparisons with other techniques on the same samples; (2) analysis of an artificial sediment standard containing a known fraction of pure biogenic opal, and (3) assessment of potential systematic errors.

Comparisons

Fourteen marine sediment samples were extracted in 2 M Na_2CO_3 at Oregon State University (J. ROBBINS, written communication) and by us. The OSU technique is similar to ours (a single step 2 M Na_2CO_3 extraction) but differs in two important respects: (1) our solution to solid ratio in the extraction is 200–1600 ml g^{-1}, while theirs is about 80 ml g^{-1}; and (2) we extract at 85°C for 5 h in a water bath with only two mixing events, while they extract in an 80°C steam bath for 24 h with constant agitation on a mixing wheel. Comparison of the two sets of results (Table 2 and Fig. 1) suggests that for opal-poor samples (<7% Si), our values are systematically higher than the OSU values by an average of 0.85% Si, or 2% OPAL. The source of this discrepancy may be due to extraction of silica from marine clays and authigenic silicates in our technique or from differences in the solution to solid ratio between techniques. Until additional work can establish the systematics of the discrepancy we recommend that data from samples whose %Si contents (by our technique) fall below 2% be reported as <3% OPAL and that

Table 2. Comparisons of biogenic opal techniques

Sample	%Si_{OPAL}		Comments
	L-DGO*	OSU†	
SX20485	1.25 ± 0.24	0.43	Red clay, MANOP Site "R"
SX27548	2.96 ± 0.16	1.12	Metalliferous, MANOP "M"
SX27549	3.16 ± 0.29	2.98	Metalliferous, MANOP "M"
SX27550	3.05 ± 0.32	0.69	Metalliferous, MANOP "M"
SX27552	5.57 ± 0.69	6.22	Metalliferous, MANOP "H"
SX12280	6.24 ± 0.54	5.06	Siliceous clay, MANOP "S"
SX27553	5.21 ± 0.25	4.36	Carbonate ooze, MANOP "C"
SX21194	2.26 ± 0.17	1.92	Organic, Peru margin, 42RB
SX27547	6.13 ± 0.27	5.42	Anoxic, Gulf of Cal.
SX27551	28.53 ± 1.14	31.00	Siliceous ooze, KN7812-5
E49-17 (cm)			Biogenic ooze
310	15.41 ± 0.56	16.4	
350	19.11 ± 0.87	21.1	
500	17.78 ± 0.66	14.5	
880	15.67 ± 0.64	15.3	
	L-DGO	XRD‡	Sequential dissolution‡
RC14-105 (cm)			
310–312	8.93	8.13	7.95
329–330	6.45	5.33	7.25
510–512	5.89	6.12	5.61
1730–1732	2.99	2.95	3.97
2190–2192	2.34	2.38	0.93?
	L-DGO		Sequential dissolution	*K*§	Fig. 2
DSDP662A-18-2:100	1.47		1.36	0.02	A
DSDP662A-18-4:146	0.80		0.78	<0.01	B
E49-18:110	14.69		14.57	0.02	C
E49-18:1000	11.65		10.38	0.30	D
SX27551‖	29.81		28.69	0.30	E
E17-9:2000	39.94		40.01	<0.01	F

* Means and standard deviations of three values by three analysts with this method, or duplicate values by one or two analysts.

† Determined by J. Robbins at Oregon State University. The "SX" samples were also provided by J. Robbins.

‡ XRD and sequential dissolution data from LEINEN (1985). These values were reported as %opal. We converted them to %Si assuming that opal was reported as SiO_2 in LEINEN (1985).

§ *K* = linear rate of increase of dissolved silica between 5 and 8 h from linear regression in Fig. 2 (%Si h^{-1}) and presumably reflects clay dissolution.

‖ See above.

samples containing high clay contents and low opal (<5% OPAL) be regarded with suspicion.

%OPAL as determined by our technique compares favorably with the results reported for the same samples by other techniques (Table 2 and Fig. 1). Results from our method were also compared with those obtained by the timed sequential dissolution method of DEMASTER (1979; Table 2 and Fig. 2). Although some dissolution curves may appear linear after 2 h, dissolution of pure diatoms (Fig. 2F) indicates that a period of 4–5 h is required to extract 100% of the biogenic silica, and that the linear increase in dissolved silica is reached between 5 and 8 h. The linear increase in dissolved silica between 5 and 8 h (presumably representing clay dissolution), 0.02–0.3% Si h^{-1}, is typical of opal dissolution data presented in other studies (e.g. EGGIMANN *et al.*, 1980). Comparison of %Si_{OPAL} calculated from linear extrapolation of the timed dissolution plots vs %Si_{OPAL}

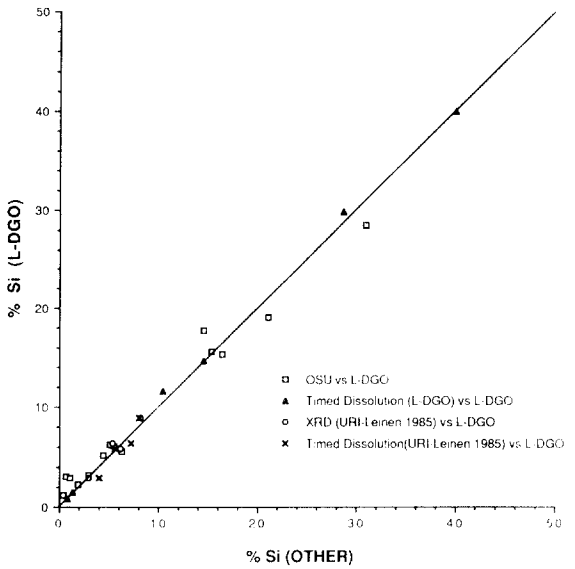

Fig. 1. Comparisons of percent silicon (opal) obtained by this technique (L-DGO) vs other techniques on the same samples (see Table 2). The straight line is the predicted 1:1 relationship for perfect agreement between methods.

calculated at 5 h for the same six samples (Table 2, Figs 1 and 2) demonstrates excellent agreement, even for opal-poor samples. Thus a single 5 h extraction with 2 M Na_2CO_3 is as accurate a measure of biogenic silica as the timed dissolution procedure and is much more rapid.

Artificial sediment standard (AS-STD)

An artificial sediment was manufactured to have a theoretical silica content of 1.50 ± 0.05% Si. The measured silica content of the standard (AS-STD, Table 3) by this technique is 1.58 ± 0.08% Si (n = 31 separate batches). The theoretical and observed means are not significantly different, suggesting the absence of large dilution artifacts or significant systematic errors due to clay dissolution in analysing opal-poor samples.

Clay contamination

In the following discussion, we evaluate the extent of clay contamination in our method by analyses of the trace element germanium extracted into the alkaline solutions. This method provides a unique tracer to separate dissolved opaline silica from that leached from detrital phases (SHEMESH *et al.*, 1988), regardless of whether "clays" are dissolving congruently or at a linear rate.

In the oceans, the geochemistry of inorganic germanium mimics that of silicon because siliceous organisms incorporate Ge as a trace replacement for silica in their silica shells (FROELICH *et al.*, 1985). The Ge/Si mass ratio in diatoms separated from high latitude Holocene siliceous oozes is very close to the present seawater ratio [FROELICH *et al.*, 1989: $(Ge/Si)_{diatoms} = 1.79 \pm 0.11 \times 10^{-6}$ g g^{-1}; $(Ge/Si)_{seawater} = 1.81 \pm 0.01 \times 10^{-6}$]. The $(Ge/Si)_{opal}$ ratio incorporated into siliceous microfossils and preserved into the sedimentary record has varied within narrow limits over the last four million years,

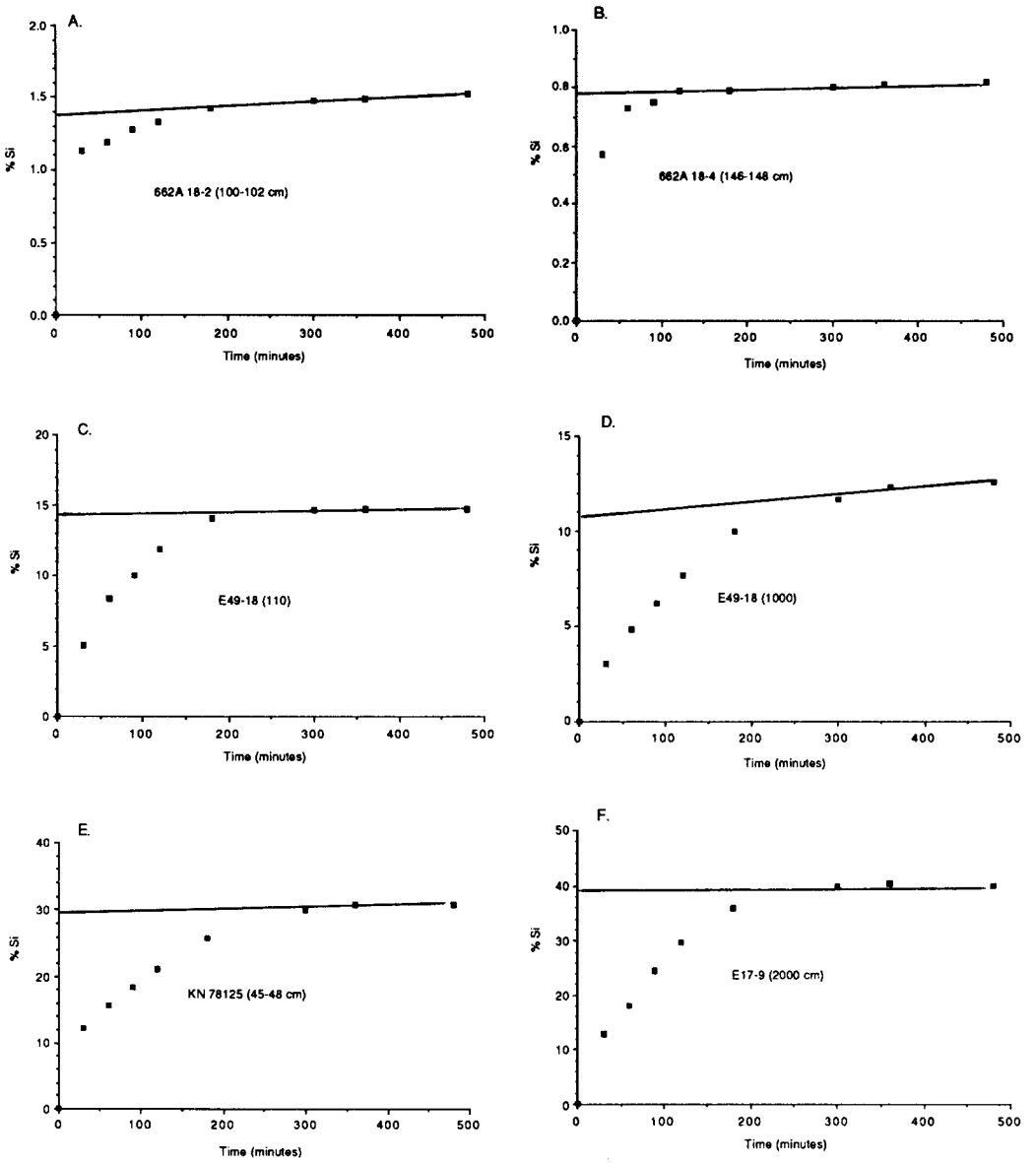

Fig. 2. Percent silicon vs time plots for 85°C 2 M Na_2CO_3 sequential timed extractions of six sediment samples. ODP-662A is in the equatorial Atlantic Ocean; E49-18 is in the Antarctic sector of the southeast Indian Ocean; KN78125 is in the southeast Pacific Ocean; and E17-9 (FI-STD) is from the Antarctic sector of the southeast Pacific Ocean and contains diatoms separated from the bulk sediment (SHEMESH *et al.*, 1988). The straight line is a "best fit" line through the data between 5 and 8 h.

Table 3. Clay contamination: (Ge/Si)

E49-18 (cm)	Si %	Ge/Si (10^{-6})	ΔSi %	OPAL %	$OPAL_{cor}$%	Clay %	Clay/Opal (g g^{-1})	$CaCO_3$ %
80	3.94	3.80	0.87	9.5	7.4	35.5	3.7	55.1
450	5.76	2.38	0.45	13.8	12.7	10.5	0.8	75.7
1120	2.16	3.72	0.46	5.2	4.1	37.9	7.3	56.9
1270	13.20	1.96	0.48	31.7	30.5	17.0	0.5	51.3
1330	0.92	2.02	0.04	2.2	2.1	8.3	3.8	89.5
1510	10.01	3.36	1.76	24.0	19.8	28.6	1.2	47.4
AS-STD	1.58	1.96	0.06	3.8	3.7	16.2	4.3	80.0
Quartz	0.06	3.10	(.01)	(0.1)	–	–	–	–

All samples from E49-18 are less than 400 ka old. AS-STD is the artificially manufactured sediment standard: 80% calcite + 15% USGS SRM shale SDO-1 +5% siliceous ooze (E17-9:2000 cm = 30 ± 1% Si). Quartz is a pure powder quartz (SPEX). "Clay" is estimated by mass difference (i.e. 100 – [%OPAL + $\%CaCO_3$]). Ge/Si ratios in the Na_2CO_3 extractions are expressed as mass ratios (g g^{-1}). %Opal = 2.4 × $\%Opal_{cor}$ = 2.4 × (%Si – %ΔSi). %ΔSi is the silica derived from "clay" dissolution. It was estimated by mass balance from the equations: %ΔSi = %Si – $\%Si_{cor}$, where $\%Si_{cor}$ = %Si $[1 - (R_1 - R_2)/R_3]$, $\%Si_{cor}$ = silica derived from opal dissolution only, $R_1 = (Ge/Si)_M$ = the measured ratio (2 M Na_2CO_3), $R_2 = (Ge/Si)_{OPAL}$ = the intrinsic opal ratio = 1.6×10^{-6}, $R_3 = (Ge/Si)_{CLAY}$ = the ratio extracted from marine clays by 2 M Na_2CO_3 = 10×10^{-6}.

averaging about $1.6 \pm 0.3 \times 10^{-6}$ in diatoms and $1.0 \pm 0.4 \times 10^{-6}$ in radiolarians (SHEMESH *et al.*, 1989). In contrast, the Ge/Si ratio of marine clays extracted with 2 M Na_2CO_3 is about 10×10^{-6} (SHEMESH *et al.*, 1988), some 7–10 times the opal ratio. Thus the Ge/Si ratio of bulk marine sediments is a sensitive indicator of the amount of silica extracted from opal vs clay during alkaline dissolution.

Ge/Si was analysed in seven sediment extraction solutions to correct the silica contribution due to dissolution of detrital clays (Table 3). The measured values are on average 1.4% OPAL higher than the corrected opal contents (after subtracting the clay-derived silicon contribution). Thus, this procedure has a clay contamination of the order of 2–3% OPAL on a carbonate-free basis. However, the extent of Si clay contamination is not a function of clay content or of the clay/opal ratio, (SHEMESH *et al.*, 1988): silica extraction from clays by 2 M Na_2CO_3 in the first 5 h of the dissolution is suppressed by the presence of biogenic opal and the resulting high dissolved silica concentrations of alkaline solution.

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APPENDIX

Stock reagents

Molybdate reagent. Dissolve 16.0 g of analytical reagent quality ammonium paramolybdate—$(NH_4)_6Mo_7O_{24} \cdot H_2O$—in 1000 ml of silica-free distilled and doubly deionized water (DDW). Store the solution in a tightly capped polyethylene bottle out of direct sunlight. The solution is stable indefinitely, but should be discarded if it forms a white precipitate or turns faintly blue and gives a high reagent blank.

Metol-sulfite reagent. Dissolve 12 g of anhydrous sodium sulfite (Na_2SO_3) in 1000 ml of DDW, then add 20 g of metol (paramethylaminophenol sulfate) and stir until dissolved. Filter the solution through a no. 1 Whatman filter paper, and store in an amber ground-glass stoppered bottle in a refrigerator. This solution is stable for 1–2 months provided the bottle is tightly capped. Discard if the solution develops a faint brown color.

Oxalic acid reagent. Dissolve 60 g of analytical reagent quality oxalic acid dihydrate—$(COOH)_2 \cdot 2H_2O$—in 1000 ml of DDW and store in polyethylene. This solution is stable indefinitely.

Sulfuric acid reagent. Slowly add 300 ml of concentrated (sp.gr. 1.82) analytical reagent quality sulfuric acid into 770 ml of DDW. Cool to room temperature and store in polyethylene.

Hydrochloric acid reagent. Add 48 ml of concentrated (12 N) HCl to 952 ml of DDW and store in polyethylene.

Working reagents

Molybdate working solution. Mix molybdate stock reagent, HCl stock reagent and DDW in volume proportions of 1:1:5. Prepare this mixture for immediate use. It is stable for at least 6–12 h. Store in polyethylene out of direct sunlight.

Reducing working solution. Mix equal volumes of metol-sulfite stock reagent, oxalic acid stock reagent and sulfuric acid stock reagent, adding the sulfuric acid last. It is stable for 4–6 h, but should be prepared immediately before use.