Particle alignment analyses provide additional information on long-term bottom-water activity. The net alignment direction of all magnetic particles is represented in the AMS analysis by the χ_a direction, corresponding to the orientation of the long axis of the magnetic grains. This orientation is meaningless, however, unless the cores can be realigned within geographic coordinates. We accomplished this by using the stable remanent magnetic declination measured in the cores (*3*). It is assumed that the mean remanent magnetic declination recorded in the cores represents an axial dipole magnetic field with secular variation averaged out. After the core is rotated until the remanent magnetic declination is coincident with geographic direction 0° (due north), the χ_a declination represents the geographically realigned orientation of the long axis of the magnetic grains.

Realignment values for cores 60PG and 61 are reported elsewhere (*3*). Because of the lack of Brunhes age sediments, the stable but reversed remanent magnetic direction obtained within reversed polarity segments (0.2 to 3.7 m in depth; Fig. 4) in core 62 was used to realign the core. Current directions for the three cores are shown in Fig. 1, along with the mean AABW direction determined from current meter data obtained near the core 60PG site (*9*).

The long axes of the magnetic grains from all three cores are aligned within a few degrees of an east-west azimuth, and there is excellent agreement between the inferred AMS current azimuth for core 60PG and the mean current meter direction near the site. Since the flow direction of bottom water is constrained by the bathymetry of the Vema Channel to be northerly, the long axes of the magnetic grains are aligned normal to the flow direction; this was a surprising result since we expected the long axis of the magnetic grains to be aligned parallel to the bottom current flow direction. This unexpected alignment is, however, consistent with a traction transport mechanism of sedimentation. If elongated grains are moved along the sea floor by high-velocity bottom currents, the long axes may align normal to the flow (*17*). (By analogy, the long axis of a barrel rolling down a hill aligns normal to the direction in which the barrel is rolling; a parallel alignment would produce a tumbling pattern.) The consistency of the alignment data in all three cores and the excellent agreement with modern flow directions determined by current meter (Fig. 1) suggest that grain movement by traction transport best explains our results.

Combined particle alignment and particle size data may be used to determine fluctuations in both relative magnitude and azimuth of bottom current flow recorded by abyssal sedimentary fabric. The alignment efficiency of long magnetic grains together with the mean silt particle size of abyssal sediment may be used to infer relative current speed. The method may be applied to sedimentary sections with a suspected hiatus to delineate zones of high bottom current activity. Since both relative speed and azimuth of bottom currents may be inferred from our measurements, we suggest that abyssal sedimentary fabric may be considered as a long-term fossil bottom current indicator. Although it is not possible at present to determine absolute paleocurrent speeds by any method, temporal changes in the relative speed may be determined. The excellent agreement between our magnetically determined current azimuth and current meter data supports the reliability of paleocurrent direction analysis.

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18. We thank D. A. Johnson for providing samples and much encouragement. Cores were collected by D.A.J. under NSF grant OCE74-01744. M.T.L. received support from NSF grants DES72-01568 and DPP77-09491. We are very indebted to N. D. Watkins, who, before his death in 1977, instilled in us a sense of excitement about research in bottom current processes.

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Geologic Migration Potentials of Technetium-99 and Neptunium-237

Abstract. *Relatively mobile TcO_4^- and NpO_2^+ can be chemically reduced to less soluble oxidation states in the presence of igneous rocks, as predicted by oxidation-reduction measurements. Current risk assessments, which consider technetium and neptunium as potentially capable of migrating from high-level radioactive waste repositories, may be overestimating their potential hazard to the public since the Fe(II) content of many subsurface waters may maintain these elements in less soluble oxidation states.*

The permanent disposal of high-level radioactive wastes in geologic media is under active consideration by many nations facing the problem of isolating long-lived radionuclides from the biosphere. Geologic disposal is attractive for many reasons, one of which is the retardation of radionuclide migration if water enters the disposal formation. In assessing the risks of geologic disposal, one must have a thorough understanding of the interactions between the geologic media and the long-lived radionuclides which might migrate.

We believe that the migration potentials of at least two of the longest lived radionuclides, ^{99}Tc and ^{237}Np, are possibly being overestimated. Technetium has been considered to be poorly "sorbed" by deep geologic media (*1*), apparently on the basis of experimental data obtained with the pertechnetate oxyanion (TcO_4^-) under oxidizing conditions (*2*). The migration potential of Tc

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has therefore been equated with that of another long-lived fission product, ^{129}I (*1*). The conclusion that Np is a relatively mobile element by comparison with Pu (*3*) was based on data obtained with the oxycation NpO_2^+, also under oxidizing conditions (*2*).

Under the oxidation-reduction conditions expected for groundwater not in contact with the atmosphere (*4*), TcO_4^- and NpO_2^+ are not the stable oxidation states for these elements. Rather, insoluble TcO_2 and NpO_2 or related hydrated forms should be the solubility-controlling phases. This conclusion is based on available thermodynamic data (*5*) and is supported by the experiments on TcO_4^- and NpO_2^+ reduction reported here.

The rock materials and radioisotopes used in this work (three igneous rocks and three shales) were supplied as part of a Department of Energy program on radionuclide-rock sorption evaluation (*6*). In this procedure, 10 g of an igneous rock or 2 g of a shale were added to a stirred cell (65 cm^3) fitted with a shiny Pt "button" electrode (0.3 cm^2), a miniature glass electrode, and a remote junction containing saturated KCl and a saturated calomel electrode. After the addition of freshly ground rock, the cell was continuously purged with research-grade N_2 (< 1 part per million O_2). Before it entered the cell, the N_2 was passed through two oxygen-sensitive solutions, alkaline dithionite containing 1,2-dihydroxyanthraquinone-3-sulfonate and alkaline pyrogallol. Deoxygenated water (60 ml) was added after the cell and sample had been purged for 15 minutes. Equilibrium was assumed to have been established when the measured potentials remained constant (± 5 mV) for 24 hours. In several instances where the *p*H was adjusted to test the slope of the *Eh* (oxidation-reduction potential) response, oxidation-reduction equilibrium was assumed when the *Eh* drift with time could be attributed solely to a slow *p*H drift. All equilibrations and measurements were conducted at 25°C.

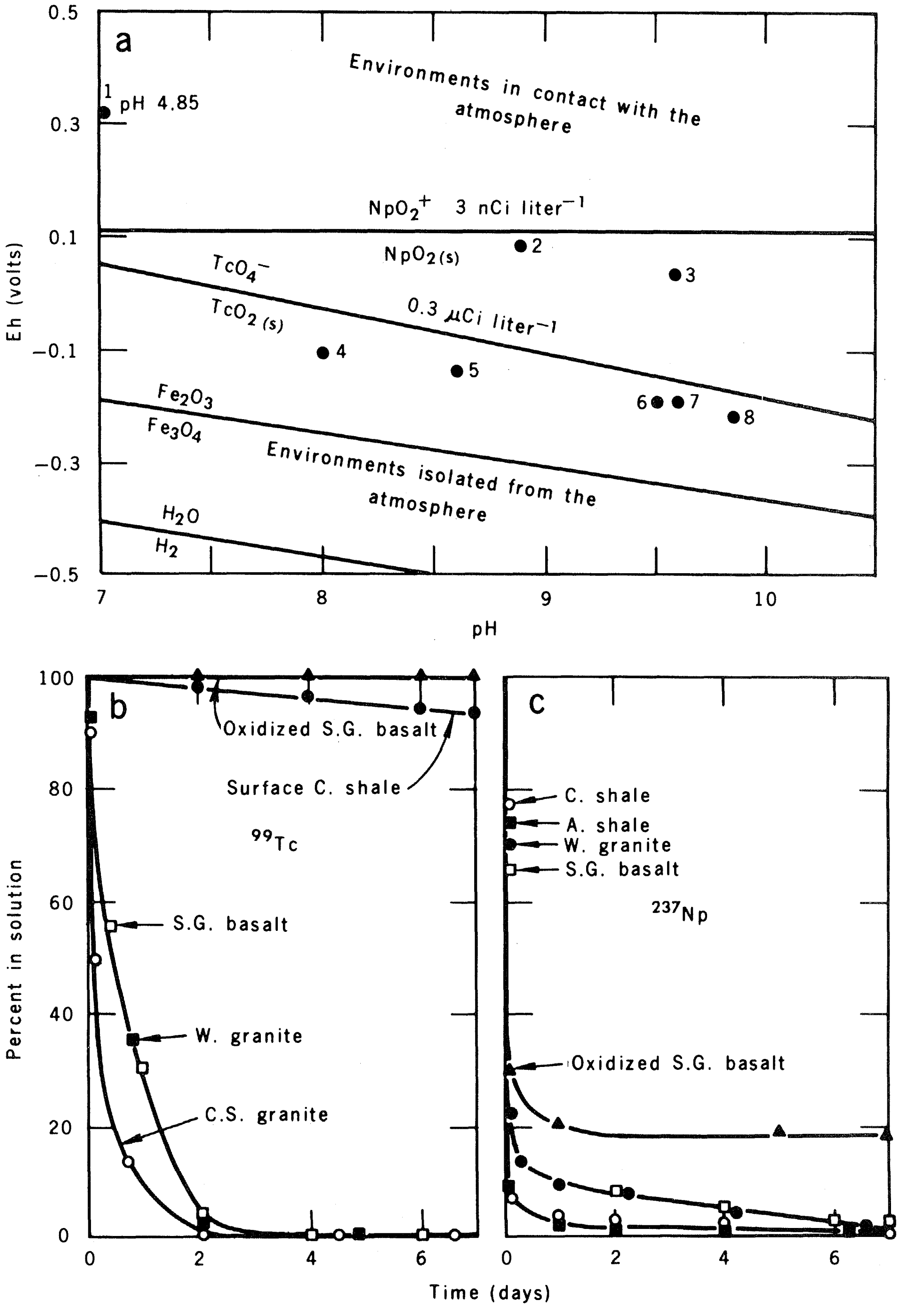

Fig. 1. Measured rock-water *Eh* values and resultant sorption behavior of Tc and Np. (a) *Eh* values of *1*, surface (weathered) Conasauga (*C.*) shale; *2*, subsurface Conasauga shale; *3*, argillaceous (*A.*) shale; *4*, *p*H-adjusted Westerly (*W.*) granite; *5*, Sentinel Gap (*S.G.*) basalt; *6*, Climax Stock (*C.S.*) granite; *7*, Westerly granite; and *8*, *p*H-adjusted Sentinel Gap basalt. The equilibrium lines for both Np and Tc were calculated on the basis of the ICRP recommendations for maximum permissible concentrations in drinking water (*8*). (b) Behavior of ^{99}Tc (initially TcO_4^-) in rock-water systems. (c) Behavior of ^{237}Np (initially NpO_2^+) in rock-water systems.

Calculated *Eh*-*p*H relationships of the radionuclide species and experimental measurements (*7*) of the *Eh* values exhibited by the rocks are illustrated in Fig. 1a. We calculated the $TcO_4^-/TcO_{2(s)}$ and $NpO_2^+/NpO_{2(s)}$ equilibrium lines from appropriate standard chemical potentials (*5*), using the International Commission on Radiological Protection recommendations for the maximum permissible drinking-water concentrations of the soluble species (*8*). The hematite/magnetite (Fe_2O_3/Fe_3O_4) and H_2O/H_2 equilibrium lines are included for reference. The three igneous rocks exhibited *Eh* values below the Tc line but above the Fe_2O_3/Fe_3O_4 line. Magnetite was present in all three igneous rocks. Shales, on the other hand, exhibited *Eh* values above the Tc line but below the Np line. Surface (weathered) Conasauga shale (+0.32 V, *p*H 4.85) was not different from subsurface (unweathered) argillaceous shale (+0.038 V, *p*H 9.6) when the effect of *p*H on electrode response (−0.0591 V per *p*H unit at 25°C) was considered. In fact, the presence of the shales resulted in only slightly lower potentials than observed in *p*H buffers under the same N_2 atmosphere.

Figure 1a indicates that TcO_4^- should be unstable with respect to reduction to $TcO_{2(s)}$ in the presence of the igneous rocks. This prediction was verified experimentally (Fig. 1b). In less than 3 days, 99 percent of the ^{99}Tc (initially TcO_4^-, 0.11 *μM*) added to the stirred cell containing one of the three igneous rocks was lost from solution (three separate experiments). In contrast, when the Sentinel Gap basalt was pretreated with NaOCl, no loss of Tc occurred (this experiment was conducted in the presence of air); these results demonstrate that the rocks do not have an inherent ability to remove the oxyanion TcO_4^-. A solution of $2M$ NaCl did not displace the rock-associated Tc. However, if the NaCl solution contained $0.1M$ BrO_3^-, 6 percent (25°C, 30 minutes) and 22 percent (100°C, 30 minutes) of the rock-associated Tc was released. This result indicated that oxidizing conditions regenerate TcO_4^-. A slow but significant rate of Tc removal by the surface Conasauga shale (which had a pH of 4.85 as a result of weathering) was also noted. The measured Eh of +0.32 V is not sufficient to reduce TcO_4^-. The low pH of the weathered rock suggests anion sorption by positively charged iron sesquioxides. Neither the subsurface Conasauga nor the argillaceous shales removed Tc (data not shown) at a concentration of 0.11 μM over a 7-day period.

The reduction of TcO_4^- was also evaluated in columns of freshly fractured basalt particles (18 to 35 mesh) under unsaturated flow conditions (*9*). For an initial concentration of 4 μM $^{99}TcO_4^-$, 10 percent was reduced and lost from solution in 5 days. In a similar experiment with ^{95m}Tc at an initial concentration of $2 \times 10^{-11}M$, 80 percent was lost in 7 days. In both experiments, the rock-associated Tc could not be displaced by $2M$ NaCl but was partially removed by $0.2M$ $NaBrO_3$. These results, as well as the experiments in the stirred cell, demonstrated that TcO_4^- was not stable when equilibrated in the absence of air. The use of ^{95m}Tc in the column work (and also in the stirred cell) demonstrated that Tc was being reduced even at quite low concentrations ($\leq 4 \times 10^{-12}M$). If the column work was repeated under aerated conditions, Tc losses were negligible.

The Eh measurements in Fig. 1a indicate that Np(V) should be unstable in the presence of the igneous rocks and possibly in the presence of unweathered shales, depending on the choice of the Np(IV) phase used in the calculations (*5*). Figure 1c illustrates the rapid removal of Np [initially Np(V)] from solution during the equilibrations. The shales, because of their higher surface area, removed Np(V) faster than the igneous rocks. The NaOCl-oxidized basalt was less reactive toward Np(V) than the untreated basalt. The cationic sorption properties of NpO_2^+ makes changes of oxidation state more difficult to ascertain than in the Tc case. However, since Np(IV) is easily distinguished from Np(V) radiochemically, we attempted to determine if Np(IV) was present in solution and associated with the rocks (*10*).

Table 1. Oxidation-state determinations on solution and surface-associated Np in the igneous and shale-water systems after 7 days. Citric acid ($0.1M$) was used to remove Np(IV) and Np(V) from the igneous rocks; because citric acid–extracted Fe(II) reduced Np(V) in the Conasauga shale, $1M$ $(NH_4)_2CO_3$ was substituted in the shale extractions.

Np association	Np oxidation state (%)		Extracted (%)*
	(IV)	(V)	
	Sentinel Gap basalt		
Solution	66	34	NA
Surface	77	23	83
	Oxidized basalt†		
Solution	3	97	NA
Surface	3	97	95
	Westerly granite		
Solution	71	29	NA
Surface	82	18	96
	Climax Stock granite		
Solution	68	32	NA
Surface	75	25	94
	Conasauga shale		
Solution	3	97	NA
Surface	8, 18, 27‡	92, 82, 73	19, 15, 18
	Argillaceous shale		
Solution	3	97	NA
Surface	4, 5, 4‡	96, 95, 96	6, 6, 7

*The extraction percentage is based on the residual Np on the rock; NA = nonapplicable. †Pretreated with NaOCl. ‡Successive $(NH_4)_2CO_3$ extractions of shale and associated Np.

The data in Table 1 indicate that reduction indeed occurred. With the basalt and the granites, Np(IV) dominated the solution-phase species after an equilibration period of 7 days, indicating reduction. When $0.1M$ citric acid was used to extract the Np associated with the igneous rocks, more than 75 percent of the extracted Np was Np(IV). The pretreated basalt showed no Np reduction. No evidence for significant reduction during extraction or Np(IV) coprecipitation was obtained. This was deduced from the fact that, if the citric acid extract was allowed to stand for 5 or 15 minutes before the zirconium phenylarsonate precipitation was carried out, no changes in the oxidation state distribution were noted.

In contrast, the two unweathered shales were not active in reducing Np(V), even though the measured Eh values suggested that reduction could occur. No significant amounts of Np(IV) were found in the aqueous phase. Citric acid extractions of the sorbed Np were inconclusive since coextracted Fe(II) reduced Np(V) during the oxidation-state determinations. Extractions with $1M$ $(NH_4)_2CO_3$ [to reduce the Fe(II) extraction] suggested the presence of Np(IV) on the Conasauga shale but not the argillaceous shale. Other work (data not shown) demonstrated that the Np associated with the unweathered Conasauga shale after an equilibration period of 7 days was more readily displaced by $CaCl_2$ if an oxidant such as BrO_3^- was present. The argillaceous shale, tested in a similar manner, did not give any indication that Np(IV) was being formed over the 7-day equilibration period.

Under similar experimental conditions, Pu(V) was reduced to Pu(IV) more rapidly than NpO_2^+ by the basalt, granites, and unweathered shales. This Pu oxidation state could be a migrating species since it can originate by the action of radiolytic decomposition products of water on Pu(IV) (*11*).

Because of the very long half-lives of ^{99}Tc and ^{237}Np (10^5 to 10^6 years), it is important to understand the chemical behavior of these radionuclides in the anoxic geologic regimes that they may encounter if a waste repository is breached by water. As this work illustrates, an evaluation of the migration potential for elements with multiple oxidation states must include more detailed investigations than simply measuring the partition coefficient K_d of the radioisotope. Although K_d values, which define the partitioning of the element between solid and solution, are convenient in chromatographic-type models of radionuclide migration through porous media, they do not necessarily reflect the nature of radionuclide-rock interactions. In fact, for many hydrolytic species including the reduced forms of Tc, Np, and Pu, their solubility-related characteristics may be more reflective of the true controls on maximum solution concentrations.

There are several examples of this idea which are important to consider since there is no geochemical history for Tc, Np, or Pu. At alkaline pH, MnO_2, which would be similar structurally to TcO_2, is geochemically insoluble. Likewise, tetravalent actinides show limited solubility in nature. Major deposits of U occur in reducing environments as a result of the reduction of mobile U(VI) to insoluble U(IV). Concentrations of "soluble" Th in groundwater have been found to be between $10^{-11}M$ and $10^{-10}M$ (*12*), whereas the solubility of the hydrolyzed Th species in equilibrium with crystalline ThO_2 is estimated at $2.5 \times 10^{-10}M$ (*13*). The geochemical behavior of these natural elements suggests that the concentrations of Np(IV) and Tc(IV) in migrating groundwater should be extremely low.

The degree to which geological media will influence the chemical state of the migrating elements will be determined by the reactivity of the rocks, the geologic contact time, and the degree of weathering (including oxidation) of the fracture surfaces through which migration occurs (*14*). In establishing geologic storage as an acceptable means of isolating long-lived radionuclides from people, it is important that all the factors that control solution concentrations be taken into consideration in assessing the risks.

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6. Waste Isolation Safety Assessment Program (WISAP), managed by Battelle Pacific Northwest Laboratories, Richland, Wash. The rock samples were provided by R. J. Serne. The three igneous rocks were Sentinel Gap basalt (Mattawa, Wash.), Westerly granite (New Hampshire), and Climax Stock granite (Nevada). The three shales consisted of green argillaceous shale (New York, Wards Scientific Establishment 47W-7400) and Conasauga shales (surface and subsurface). These rocks and shales were crushed to ≤ 50 mesh with a ceramic mortar and pestle. The isotopes ^{99}Tc, ^{237}Np, and ^{239}Np were obtained from the Oak Ridge National Laboratory; ^{95m}Tc was obtained from Argonne National Laboratory, Argonne, Ill. The ^{95m}Tc was isotopically pure, having been made by the $^{93}Nb(\alpha, 2n)^{95m}Tc$ reaction.
7. After the *p*H of the rock-water slurries had been established, the cell was supplemented with a miniature Pt electrode (0.03 cm^2) in place of the glass electrode (there were now two Pt electrodes in the cell). The Pt electrode with the larger surface area consistently measured more negative potentials than the Pt electrode with the smaller surface area, although there was never more than a 40-mV difference. The *Eh* values recorded in Fig. 1a were based on measurements from the larger electrode. There is no certainty that the Pt electrode is really responsive to the true Fe^{2+}/Fe^{3+} activity in solution since the concentrations would be very low. Oxygen could also be limiting the attainment of potentials lower than observed.
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9. The basalt particles were packed into a glass column 23 by 1.5 cm. A dual-tagged (^3H and Tc) simulated basalt groundwater (*p*H 8.10) was made up containing the following ions (in milligrams per liter): Na^+, 30; K^+, 9; Ca^{2+}, 6.5; Mg^{2+}, 1.0; HCO_3^-, 58; SO_4^{2-}, 23; Cl^-, 16; and F^-, 0.7. This solution was slowly added to the column under anoxic conditions (9 ml to 57 g of 18- to 35-mesh basalt). Nontritiated water was used to displace portions of the surface-associated groundwater. The Tc recovery was referenced to the ^3H concentration.
10. The Np(IV) was distinguished from Np(V) by zirconium phenylarsonate precipitation [A. F. Voigt, N. R. Sleight, R. E. Hein, J. M. Wright, in *The Transuranium Elements*, G. T. Seaborg, J. J. Katz, W. M. Manning, Eds. (McGraw-Hill, New York, 1949) (part II), pp. 1119–1127]. Citric acid (0.1*M*) was used to extract Np from the igneous rocks, and 1*M* $(NH_4)_2CO_3$ was used for the Conasauga shale [citric acid extracted significant amounts of Fe(II), which reduced Np(V) during the precipitation procedure]. The carbonate extract was acidified to 0.5*M* HCl before precipitating zirconium phenylarsonate. Extractions of Np from the rocks were conducted for 1 minute. The precipitation procedure often results in some precipitation of Np even if Np(V) is the only oxidation state present. Thus a 1 to 3 percent Np(IV) value may not be significant evidence for the presence of Np(IV). Values greater than this are stronger evidence for the presence of Np(IV).
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14. Recent Swedish experiments on the in situ migration of ^{99m}Tc in fractured granite (80-m depth and residence times of several days) have not indicated the reduction of Tc (B. G. F. Carleson, AB Atomenergi Studsvik, Nykoping, Sweden, personal communication). However, it is anticipated that the Swedish radioactive waste repository will be located at 500 to 800 m in less weathered granite.
15. We thank J. N. Brantley and F. S. Brinkley for technical assistance and T. E. Cerling and S. Y. Lee for reading the manuscript and offering helpful suggestions. Research supported by the Office of Health and Environmental Research and the Waste Isolation Safety Assessment Program, U.S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corporation. Environmental Sciences Division Publication No. 1330.

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Variable Porosity in Siliceous Skeletons: Determination and Importance

Abstract. *Gas adsorption data were used to obtain the specific surface area and specific pore volume for a variety of biogenically precipitated silica samples. The results suggest that this material is finely divided and porous. This interpretation was corroborated by the use of transmission electron microscopy at magnifications up to 180,000.*

Box model calculations involving the geochemical cycle of silica in the oceans (*1*) suggest that at least ten times as much silica is annually precipitated by single-celled plants and animals (*2*) as is delivered to the oceans by rivers or preserved in sediments. Although the order in which a few species of organisms disappear with time or with depth in the water column has been observed in laboratory (*3*) and field (*4*) studies, the mechanism by which one species is better preserved than another under the same set of conditions is still poorly understood. In this report we present techniques for studying the porous ultrastructure of biogenically precipitated silica. Study of this structure will help to elucidate (i) mechanisms behind skeleton precipitation, (ii) recycling rates of silica in the water column, (iii) resistance of the skeleton to breakage during predation, (iv) settling rates of skeletons through the water column, (v) preservation of skeletons in the water column and sediments, and (vi) quantitative morphological and diagenetic structural changes in the skeletons.

We have begun to characterize the physical and chemical properties of the siliceous frustules, spicules, and skeletons of diatoms, sponges, and radiolarians. We studied changes with age in specific surface area, solubility, and dissolution rate (*5*) and density, refractive index, and water content (*6*). We now describe a methodology for the quantification of skeletal porosity and specific pore volume and discuss the importance of the relationship of specific pore volume to specific surface area.

Sample cleaning methods and the specific surface area measurement technique have been described elsewhere (*5*, *7*). A similar approach was used to estimate specific pore volumes (*8*) for each of the samples studied. It is important to note that surface area and pore volume measurements must be made on the same sample. Within one assemblage we have measured specific surface areas that differed from one another by a factor of 3 or more, depending on the species composition of one sample relative to the next. The data presented here are averages for well-mixed assemblages.

Sample ages range from present day to 40 million years ago and contain mostly radiolarians with lesser amounts of diatoms and sponge spicules. The overall dimensions of radiolarians vary from about 50 to 500 μm and the specific surface areas measured vary from about 2 to 130×10^4 cm^2/g, suggesting that the