

Mr R. French, Dartmouth '69, for the construction and calibration of the microwave cavity.

P. HOEKSTRA
G. SWINZOW
S. ACKLEY

*US Army Cold Regions Research and Engineering Laboratory,
Hanover,
New Hampshire 03755*

W. T. DOYLE

*Department of Physics and Astronomy,
Dartmouth College,
Hanover,
New Hampshire 03755*

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Diffusion Coefficient of Silica in Seawater

THE diffusion coefficient of dissolved monomeric silica in seawater of 36.1% salinity has been determined at 25° C by the diaphragm cell method. The value of the coefficient D is $1.0 \pm 0.05 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. The value at seafloor temperatures is probably about $0.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and is consistent with empirical diffusion coefficients of silica in pore water-sediment systems of the order of 0.1 to $0.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, when corrections for porosity are made.

The rate of transport of silica in sediments has been estimated to correspond to a diffusion coefficient for the sediment-water system of about $3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (ref. 1), but the coefficient for seawater alone has not been previously determined. We used the diaphragm cell method in which silica is permitted to diffuse across a porous membrane from stirred seawater of higher silica concentration into otherwise identical seawater of lower silica concentration. The membrane was a $0.45 \mu\text{m}$ 'Millipore' filter glued with silicone rubber cement to the end of a plastic tube of 3.8 cm diameter. The tube was suspended in the middle of an 800 ml. beaker so that 100 ml. of solution in the cell had the same level as 700 ml. in the beaker. The system was placed in a double-walled glass vessel and kept to a temperature of $25 \pm 0.1^\circ \text{C}$ by circulating water through the jacketed vessel. The solution in the beaker, or external solution, was stirred at a constant rate with a magnetic stirring bar. The internal solution was stirred mechanically from above with a rod. The top of the system was open but evaporation was negligible during any given run.

In the experiments, filtered seawater of 36.1% salinity spiked with 20 p.p.m. of dissolved silica was placed in the external container and 100 ml. of silica-free (less than 0.05 p.p.m.) seawater was placed in the central tube. Aliquots of 10 ml. were removed from the internal solution at intervals

of 1 to 4 h and were replaced by 10 ml. of fresh seawater to prevent mass transfer through the membrane. Silica was analysed by a method of Mullin and Riley², with an accuracy estimated at $\pm 5\%$. Concentration of the external solution was calculated at the end of each time interval and was measured again at the end of the experiment. There was no measurable increase in total silica during the experiments, showing that there was no contamination from the cement, nor absorption by the membrane.

The cell was calibrated by placing 0.1 N KCl solution in the external cell, and distilled water in the internal compartment. The external and internal solutions were analysed by titrating chloride content with a standard silver nitrate solution using a chloride sensitive electrode as an indicator. Precision was estimated at $\pm 3\%$.

The cell equation is³

$$\ln \frac{C_e - C_i}{C_e^0 - C_i^0} = \frac{DA}{l} \left(\frac{1}{V_e} + \frac{1}{V_i} \right)$$

in which C_e is the concentration in the external solution at the end of the run, C_e^0 is the concentration of the external solution at the beginning of the run, C_i and C_i^0 are concentrations of the internal solution corresponding to those of the external solution, D is the diffusion coefficient in $\text{cm}^2 \text{ s}^{-1}$, A/l is a constant characteristic of the membrane and V_e and V_i are the volumes of the external and internal solutions in cm^3 . The value of A/l as determined for the cell from six calibrations by KCl solution, four before and two after the silica experiments, was $2.4 \pm 0.1 \times 10^2 \text{ cm}$. Average values for the diffusion coefficient of KCl were obtained graphically from data in Robinson and Stokes⁴. Values for A/l before and after the run differed by 5%.

Two separate seawater samples were used and five individual determinations of the diffusion coefficients for silica were made on each sample. There was no significant difference between the average diffusion coefficient in the first run and that for the second run. The average deviation for the ten determinations was 2% and the average for all determinations is $1.0 \pm 0.05 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

We undoubtedly could have obtained a more accurate value of D by improving the constancy of our stirring, but the value obtained should be useful in many studies of seawater. The temperature coefficient was not determined but a good estimate can be made by assuming that D is inversely proportional to the viscosity of the seawater. If so, the value for sea bottom conditions would be approximately half of the one obtained, or about $0.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Recent marine sediments probably have a directional diffusional porosity of about 30%. Therefore the apparent diffusion coefficient for such systems should be about 0.3 times the value of the silica diffusion coefficient for pure seawater or about $0.15 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, in reasonable agreement with Anikouchine's estimate of $0.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. With the value given it should be possible to "calibrate" the membrane characteristics of such sediment-water systems.

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ROLAND WOLLAST

*Laboratory of Industrial Chemistry,
University of Brussels*

ROBERT M. GARRELS

*Scripps Institution of Oceanography,
La Jolla,
California*

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