

Reports

The Marine Geochemistry of Germanium: Ekasilicon

Abstract. *The geochemical behavior of dissolved germanium in rivers, estuaries, and the oceans is similar to that of silicon. It is chemically weathered from continental rocks and transported by rivers to the oceans, where it is taken up by siliceous organisms and deposited in biogenic opal. The ratio of germanium to silicon buried in siliceous oozes must reflect the oceanic input ratios from rivers (crustal weathering) and sea-floor vents (mid-ocean ridge hydrothermal weathering). The opal germanium/silicon ratio may thus monitor relative variations in these weathering processes and provide information about the geochemical history of seawater.*

The fate of germanium during weathering, transport to the oceans, and passage through the oceans is unknown (1). Since germanium is a trace element (0.5 to 3 ppm) in the earth's crust (replacing silicon within silicate lattices of minerals), it presumably exists in natural solutions at very low concentrations. An understanding of the marine geochemistry of germanium may help to unravel the history of variations in crustal weathering and in mid-ocean ridge hydrothermal circulation. These two processes control the fluxes of many ions into and out of the oceans and thus affect the chemical composition of seawater over geologic time.

We report here systematic and geochemically consistent determinations of germanium in seawater, river water, and estuaries. Previous analyses of germanium in natural waters are scarce. Values reported for fresh, estuarine, and ocean waters have ranged from 16 to 106 parts per trillion (200 to 1500 pM) (2). Our data demonstrate that dissolved germanium is present in natural waters at concentrations of less than 8 parts per trillion (120 pM). An oceanic depth profile and a river-estuary transect show that germanium is a tracer of the low-temperature biogeochemical cycle of silicon. We thus add germanium to the growing list of trace chemicals whose behavior in the oceans is nutrient-like (3), a result that Mendeleev might have guessed when he predicted the occurrence and properties of element number 32 (which he called ekasilicon) based on his newly discovered periodic law.

We determined germanium in all samples by a technique involving a combination of hydride generation, graphite furnace atomization, and atomic absorption detection (4). Calibration by peak height

results in an absolute detection limit (95 percent confidence) of 140 pg of germanium (for a 250-ml sample, this is 560 pg per liter or 7.7 pM). The sensitivity and precision of our technique are 430 pg (0.0044 absorbance unit) and ± 4 percent (about ± 5 pM), respectively. We investigated the possibility of a positive interference from silicon and found none (4).

Open ocean samples from the northwest Pacific Ocean were from GEOSECS station 227 (25°00'N, 170°05'E). These samples were collected for trace metal work during leg 4 of the Pacific GEOSECS cruises (5). They were acidified to pH 2 with HCl and stored in polyethylene bottles for 7 years before our analyses. River and estuarine samples were collected in the Ochlockonee River and Bay system south of Tallahassee, Florida (29°59'N, 84°25'W). Samples were filtered through pre-rinsed 0.4- μ m Millipore filters, acidified, and

stored refrigerated in polyethylene bottles for 2 weeks before analysis.

Depth profiles of germanium and silicon at GEOSECS station 227 are shown in Fig. 1, a and b. Germanium is depleted in surface ocean waters compared to the deep water. This vertical distribution is typical of nutrient behavior in the oceans, reflecting uptake from surface waters by organisms and release from sinking biological debris in the deep sea. Surface water concentrations are below the limit of detection (< 7 pM), while deep-sea values are about 115 pM, yielding a surface-to-deep enrichment factor of more than 15.

In detail, the germanium profile closely resembles that of silicon. Germanium plots linearly against silicon (Fig. 1c) (plots against phosphate or nitrate are not linear). This covariation with silica (and not phosphate or nitrate) suggests that germanium is taken up by, and regenerated from, the hard parts of organisms, which dissolve at greater depths in the oceans than do organic carbon-, nitrogen-, and phosphorus-containing soft tissues.

The results of one estuarine transect (6) analyzed for germanium are presented in Fig. 2. Germanium concentrations in the Ochlockonee River average about 50 pM. The Ge/Si mole ratio in this river is about 0.6×10^{-6} , close to that expected for congruent dissolution of crustal rock with the average Ge/Si ratio [about 10^{-6} (1)]. Concentrations in offshore surface seawater are undetectable (< 7 pM). Both the silica and germanium profiles display curvatures below the linear mixing line characteristic of estuarine removal (7). Nitrate and phosphate (not shown) also display nonconservative curves. A simple removal model (7) of

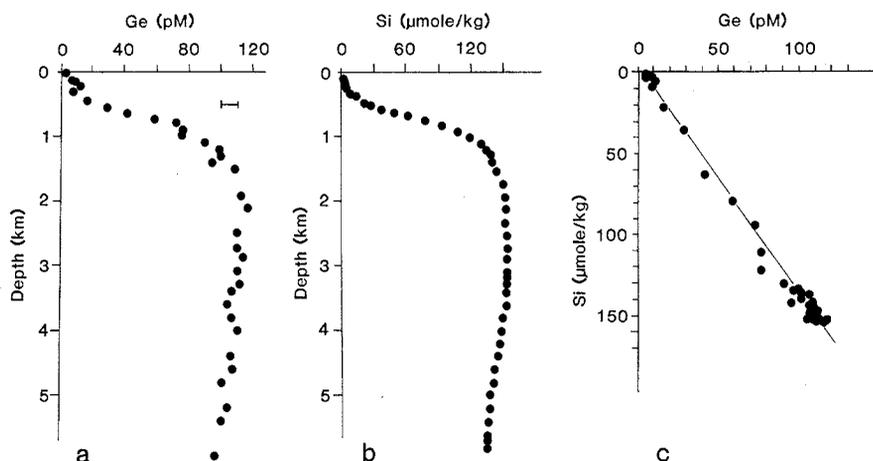


Fig. 1. (a) Germanium versus depth at GEOSECS station 227 in the northwest Pacific. Precision of the analytical method is indicated by a short horizontal bar (± 5 pM). (b) Silicon versus depth at GEOSECS station 227. (c) Germanium versus silicon at GEOSECS station 227. The best-fit straight line is given by: $\text{Ge}(M) = (0.7 \times 10^{-6}) \times \text{Si}(M)$.

these data suggests that nitrate, phosphate, silica, and germanium are extracted from the estuary in the ratios $\Delta N:\Delta P:\Delta Si:\Delta Ge = 16:1:23:(16 \times 10^{-6})$. These N:P:Si ratios are rather typical of uptake by mixed marine phytoplankton (3). Most of the removal occurs between 0 and 50 mM Cl where the river enters the head of the estuary. Chlorophyll a data demonstrate a high standing crop of phytoplankton in the estuary over this salinity range (Fig. 2d). The ratio of Ge to Si extracted by this estuarine bloom (0.6×10^{-6}) is similar to the extraction ratio observed in the open ocean (0.7×10^{-6}). Since the Ge/Si fluvial input ratio and the removal ratio are indistinguishable, germanium plots linearly against silicon over the entire estuarine mixing length (Fig. 2c).

It is likely that the biological activity of germanium is due to uptake by one or several of a variety of siliceous organisms (diatoms, radiolarians, and silicoflagellates) that incorporate germanium into their opal tests. There are a number of independent lines of evidence in support of this proposition.

Germanic acid and silicic acid (the dissolved forms in water) are chemically very similar. Silicon and germanium have similar atomic radii (1.17 and 1.22 Å, respectively), and germanium is known to replace silicon within silicate lattices of minerals (8). A long list of

isostructural germanates with typical silicate structures have been prepared artificially (1). Thus it is not difficult to suppose that germanium could be easily accommodated in amorphous opal, nor is it difficult to suppose that siliceous organisms might fortuitously incorporate 1 germanium atom into their tests with every 1.4 million silicon atoms, as the Ge/Si ratio of Figs. 1 and 2 would indicate. The germanium in biogenic opal presumably exists in solid solution, replacing silicon. The germanium concentration in siliceous debris predicted from this interpretation would be about 0.35 ppm. Observed values in siliceous tests separated from netted plankton and siliceous oozes are 0.3 and 0.5 ppm, respectively (2). By comparison, biogenic calcite contains no detectable germanium, nor does bulk plankton (< 0.05 ppm) (2).

Other evidence in support of germanium incorporation into siliceous tests is the work of Azam and co-workers (9), who used radioactive ^{68}Ge as a tracer of silicon uptake during studies of diatom nutrient kinetics. Lewin (10) originally suggested that ^{68}Ge might provide a convenient tool for measuring utilization rates of silicic acid in natural phytoplankton populations, since there is no appropriate silicon radioisotope. Azam (9) showed that in solutions with Ge/Si mole ratios of about 10^{-6} to 1, germanium

is taken up by a variety of diatom species and is incorporated into the siliceous tests. The germanium concentration range in his cultures was similar to what we observe in the Pacific (5 to 120 pM). In cultures with undetectable silica, diatoms take up germanium at a rate that increases linearly with concentration, showing no sign of approaching enzyme saturation up to 160 pM. This is the expected pattern if germanium is taken up, transported, and deposited as an accidental surrogate for silicon by the cellular silica mechanisms of these organisms. Diatoms perceive germanium as a superheavy stable isotope of silicon. Thus strong evidence exists that germanium is taken up by siliceous organisms and incorporated into biogenic opal. Azam, in fact, recognized the potential geochemical implications, which are borne out by our data.

These data are consistent with the following geochemical cycle for germanium. Germanium is chemically weathered from continental rocks and minerals congruently with silica and enters streams and rivers in a Ge/Si ratio reflecting that in the continental source rocks. Siliceous organisms in estuaries take up germanium and silicon in the ratios provided by rivers, so that the flux ratio to the oceans from estuaries is unaltered. Biogenic opal formation in surface ocean waters virtually depletes both germanium and silicon, producing a vertical particulate opal flux to the deep sea that carries the total (fluvial plus other) input flux ratio. If biogenic silica dissolves congruently in the deep sea, then the dissolution ratio and the burial flux ratio both reflect the input ratio.

The Ge/Si ratio buried in opal must reflect the weighted sum of all input flux ratios. Germanium is unlikely to enter the ocean by processes that do not transport silicon. About two-thirds of the global flux of silica to the oceans is carried by rivers; the other one-third enters via hydrothermal circulation of seawater through the global mid-ocean ridge crest system (11). There are no data on germanium concentrations in these hydrothermal effluents. The chalcophilic nature of germanium would suggest, however, that even though it may be mobile as a very soluble sulfide complex during high-temperature seawater-basalt reactions (1), it is probably also trapped in sulfide minerals forming within or around hydrothermal vents on the sea floor. We thus speculate that the Ge/Si flux ratio to seawater due to high-temperature hydrothermal weathering of sea-floor basalts (from sea-floor vents) may be very different from that due to

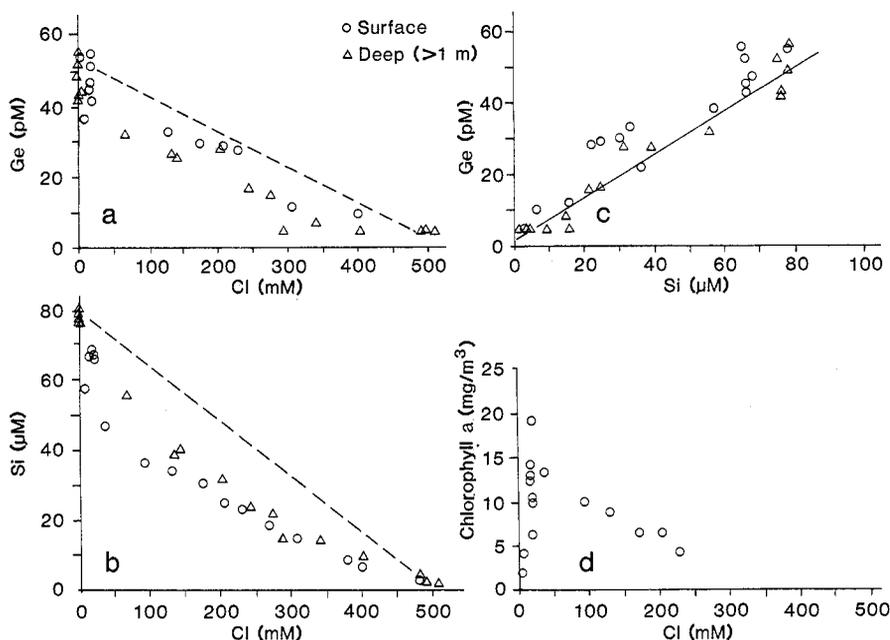


Fig. 2. (a) Germanium versus chloride in Ochlockonee Bay. The dashed lines indicate approximate linear mixing lines representing concentrations expected by conservative mixing of the freshwater ($\text{Cl} = 0$) and seawater ($\text{Cl} = 500$ mM) end members. (b) Silica versus chloride in the Ochlockonee Bay. (c) Germanium versus silica in the Ochlockonee Bay. The best-fit straight line is given by: $\text{Ge}(M) = (0.6 \times 10^{-6}) \times \text{Si}(M)$. (d) Chlorophyll a versus chloride in Ochlockonee Bay. The dramatic increase in chlorophyll a at a chloride concentration of about 25 mM (salinity ≈ 1.5 per mil) demonstrates active phytoplankton productivity at this salinity in the estuary.

low-temperature continental weathering (from rivers).

This leads to the intriguing possibility that the ratio of germanium to silicon buried in siliceous oozes on the sea floor provides a continuous geologic record of variations in the relative rates of chemical weathering of the continents and hydrothermal weathering of the sea floor, processes which control the fluxes of the major cations and anions through the oceans (11). Since virtually all silicon and presumably all germanium brought to the oceans are removed with siliceous tests, changes in the Ge/Si ratio buried in opal would reflect contemporaneous changes in the fluxes of elements through the oceans. An understanding of such variations would help us to understand the geological history of seawater and the controls on its geochemical composition (12).

PHILIP N. FROELICH, JR.
MEINRAT O. ANDREAE

Department of Oceanography,
Florida State University,
Tallahassee 32306

References and Notes

1. A. Wittman and P. K. Hormann, in *Handbook of Geochemistry*, K. H. Wedepohl, Ed. (Springer, Berlin, 1970), vol. 2, part 2, p. 32.
2. S. A. El Wardani, *Geochim. Cosmochim. Acta* 13, 5 (1957); *ibid.* 15, 237 (1958); J. D. Burton, F. Culkun, J. P. Riley, *ibid.* 16, 151 (1959); F. Heide and D. Korner, *Naturwissenschaften* 49, 492 (1962); D. L. Johnson and R. S. Brame, *Deep-Sea Res.* 22, 503 (1975); R. S. Brame and M. A. Tompkins, *Anal. Chem.* 50, 1088 (1978).
3. W. S. Broecker, *Chemical Oceanography* (Harcourt Brace Jovanovich, New York, 1974); K. W. Bruland, *Earth Planet. Sci. Lett.* 47, 176 (1980).
4. M. O. Andreae and P. N. Froelich, *Anal. Chem.* 53, 287 (1981).
5. A. E. Bainbridge, *GEOSECS Pacific Final Hydrographic Data Report* (GEOSECS Operations Group Publ. 30, Scripps Institution of Oceanography, La Jolla, Calif., 1979).
6. Ochlockonee Bay is fairly well mixed: surface-to-deep salinity differences usually average only several parts per thousand. The bay is only 2 m deep except in one axial channel, which is 4 to 5 m deep. The river-bay system is essentially in a natural state. Population density is low, so there are no anthropogenic effects.
7. E. Boyle, R. Collier, A. T. Dengler, J. M. Edmond, A. C. Ng, R. F. Stallard, *Geochim. Cosmochim. Acta* 38, 1719 (1974); C. B. Officer, *Estuarine Coastal Mar. Sci.* 9, 91 (1979).
8. V. M. Goldschmidt, *Naturwissenschaften* 14, 295 (1926).
9. F. Azam, B. B. Hemmingsen, B. J. Volcani, *Arch. Mikrobiol.* 92, 11 (1973); F. Azam, *Planta* 121, 205 (1974); _____ and S. W. Chisholm, *Limnol. Oceanogr.* 21, 427 (1976).
10. J. C. Lewin, *Phycologia* 6, 1 (1966).
11. J. M. Edmond, C. Measures, R. E. McDuff, L. H. Chan, R. Collier, B. Grant, L. I. Gordon, J. B. Corliss, *Earth Planet. Sci. Lett.* 46, 1 (1979).
12. W. W. Rubey, *Geol. Soc. Am. Bull.* 62, 1111 (1951); W. S. Broecker, *Quat. Res. (N.Y.)* 1, 188 (1971); H. D. Holland, *Geochim. Cosmochim. Acta* 36, 637 (1972).
13. We thank the GEOSECS Operations Group, D. Spencer, P. Brewer, G. Klinkhammer, and M. Bender for collecting and handling the oceanic samples; F. Le Guillou, S. Glomb, J. Leon, K. Roe, J. Byrd, W. Barnard, and W. Watkins for assistance in collecting the estuarine data; the donors of the Petroleum Research Fund, administered by the American Chemical Society (grant PRF-12144-GZ); and the National Science Foundation (grants OCE 79-20183 and OCE 81-25223).

2 February 1981; revised 6 April 1981

SCIENCE, VOL. 213, 10 JULY 1981

Lateral P-Velocity Gradients near Major Strike-Slip Faults in California

Abstract. *The P-wave velocity in shallow crystalline rock decreases systematically from a normal value of about 5.5 kilometers per second 20 kilometers or more from the Garlock and San Andreas faults to less than 3 kilometers per second at distances of less than 2 kilometers from these faults. This lateral velocity gradient closely resembles the shear stress profile. It is proposed that the velocity gradient results from increased fracturing nearer these major strike-slip faults and that this fracturing dominates the response of the shallow crust to tectonic stress.*

Granitic rocks in situ often exhibit compressional wave velocities (V_p) significantly different from velocities in laboratory specimens of otherwise identical rocks. Values of V_p in situ are often lower because of joints or fractures too large or pervasive (not appropriately modeled by a single saw-cut) to deal with in standard laboratory measurements (1, 2). Interpretation of crustal V_p in terms of stress, fluid saturation, or other rock properties related to earthquake prediction research is hampered by the low resolution of most surface refraction methods. Some authors (3) have recognized the difficulty in explaining the difference between their layered crustal models and the velocity structure predicted by laboratory measurements. Even when a vertical gradient similar to V_p dependence on pressure observed in the laboratory is used to fit surface refraction data, V_p rises (at least in the Gabilan Range of central California) more gradually with depth than is predicted by microcrack closure (4). Shear wave velocities (V_s), which could provide information regarding the mechanism (undersaturation or fracturing?) responsible for the low V_p in situ, are not routinely measured during most crustal velocity studies.

We measured travel times between a surface source and a three-component Geophone package lowered into boreholes in granitic rock of the Mojave Desert of southeastern California (Fig. 1). Boreholes allow good depth interrogation from modest source energy as well as relatively low ambiguity in resolving velocity as a function of depth. Also, V_s is more easily measured in boreholes than by refraction spreads. The nine boreholes, ranging in depth from 80 to 140 m, had been drilled as part of a U.S. Geological Survey (USGS) heat flow study (5).

We set up a weight-drop source for P waves 3 m from the borehole. The recording truck was parked on a railroad tie, also 3 m from the borehole. Hammer blows on opposite ends of this timber provided reversed polarity shear waves (6). Our Geophone package was lowered

in 5- or 10-m increments to detect waves generated by two to four weight drops and two or three hammer blows of each polarity. Reference Geophones placed near the center of the railroad tie and near the weight-drop impact point provided time breaks. Records were made at a paper speed of 40 cm/sec, with 10-msec timing lines. Our amplifier and camera were designed for exploration refraction studies, so high-frequency components were not recorded. Since the timing errors (± 1 to 2 msec) were too large for us to compute V_p from travel-time difference at such short (5 or 10 m) depth intervals, the travel time-depth data were fit with smooth functions and the time derivative taken to obtain a velocity-depth curve.

A variety of functions were tested for their ability both to fit our data and to predict reasonable velocities when extrapolated to greater depths. Linear regression (intervals of constant velocity) fit the travel time-depth data as well as functions involving a vertical velocity gradient (linear term with a decaying exponential), except for borehole GAR, where a gradient fit is better. Borehole GAR is the deepest but exhibits the lowest V_p of the nine holes studied. Longer travel times resulting from low V_p and greater depth lessen the relative influence of the timing errors. Future studies with better recorders and deeper boreholes should resolve the V_p gradient in shallow crystalline rocks.

Although we were unable to show statistically which of the functions tested provided a superior fit to our travel time-depth data (7), such details are not important for this report. The scatter in bottom-of-hole (BOH) V_p from well to well retains the general pattern shown in Table 1 for all functions tested, with a difference in V_p between the slowest and the fastest wells of at least 2.5 km/sec.

The V_p values ranged from about 5.5 km/sec, comparable to velocities reported for laboratory specimens of granitic rock, to 3.0 km/sec, with a scatter of intermediate values (Table 1). We ascribe V_p values lower than that typical of laboratory measurements to fracturing