thermometers based on the equilibrium crystal-liquid distribution of elements assume a melt phase that is chemically well mixed by diffusion. In small regions adjacent to growing crystals, the validity of this assumption depends to a large degree upon crystal growth rates (*5, 13*), but in any case the probability of attaining a true equilibrium distribution of elements between crystals and melt is improved by high mobility of ions in the melt. In light of the data presented here, it is clear that any assumptions regarding crystal-melt equilibrium are more likely to be valid for H_2O-bearing granitic magmas than for their dry counterparts (*5*).

The reasons for high ionic mobilities in H_2O-bearing silicate melts are not obvious. Earlier studies have revealed other melt composition parameters that affect diffusion rates and activation energies for diffusion (*14*), but in no case have the observed effects been as great as that of H_2O. One explanation may be the effectiveness of H_2O as a "depolymerizing" agent with respect to large silicate anions in the melt (*15*). A reduction in the size of silicate anions is equivalent to the creation of nonbridging oxygens; if the widespread occurrence of this process is viewed as a proliferation of atomic sites suitable for occupation by Cs^+ ions, then considerable reduction in the average diffusive jump distance would result from solution of H_2O in a melt. In view of the fact that 6 percent (by weight) of dissolved H_2O is roughly equal to 23 mole percent (calculated on a simple oxide basis), this proliferation of Cs sites could well account for the observed increase in diffusivity and the decrease in activation energy for Cs diffusion. If this general conception of diffusion in hydrous silicate melts is correct, then I would anticipate high mobilities for many ionic constituents in addition to Cs.

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References and Notes

1. F. Albarede and Y. Bottinga, *Geochim. Cosmochim. Acta* **36**, 141 (1972).
2. N. L. Bowen, *J. Geol.* **29**, 295 (1921); *The Evolution of the Igneous Rocks* (Princeton Univ. Press, Princeton, N.J., 1928).
3. J.-P. Carron, *C. R. Acad. Sci. Ser. D* **266**, 854 (1968).
4. A. Jambon and J.-P. Carron, *ibid.* **276**, 3069 (1973).
5. M. Magaritz and A. W. Hofmann, *Geochim. Cosmochim. Acta* **42**, 595 (1978).
6. H. R. Shaw, *J. Geophys. Res.* **68**, 6337 (1963).
7. P. E. Long, *Geochim. Cosmochim. Acta* **42**, 833 (1978); P. M. Fenn, *Can. Mineral.* **15**, 135 (1977).
8. O. F. Tuttle, *Geol. Soc. Am. Bull.* **60**, 1727 (1949).
9. H. R. Shaw, in *Geochemical Transport and Kinetics*, A. W. Hofmann, B. J. Giletti, H. S. Yoder, Jr., R. A. Yund, Eds. (Carnegie Institution of Washington, Washington, D.C., 1974), p. 139.
10. J. Crank, *The Mathematics of Diffusion* (Oxford Univ. Press, London, ed. 2, 1975).
11. O. F. Tuttle and N. L. Bowen, *Geol. Soc. Am. Mem. 74* (1958).
12. A. Jambon, J.-P. Carron, F. Delbove, *C. R. Acad. Sci. Ser. D* **287**, 403 (1978).
13. C. J. Allegre and J. F. Minster, *Earth Planet. Sci. Lett.* **38**, 1 (1978).
14. E. L. Williams and R. W. Heckman, *Phys. Chem. Glasses* **5**, 166 (1964); P. Winchell, *High Temp. Sci.* **1**, 200 (1969).
15. C. W. Burham, *Geochim. Cosmochim. Acta* **39**, 1077 (1975).
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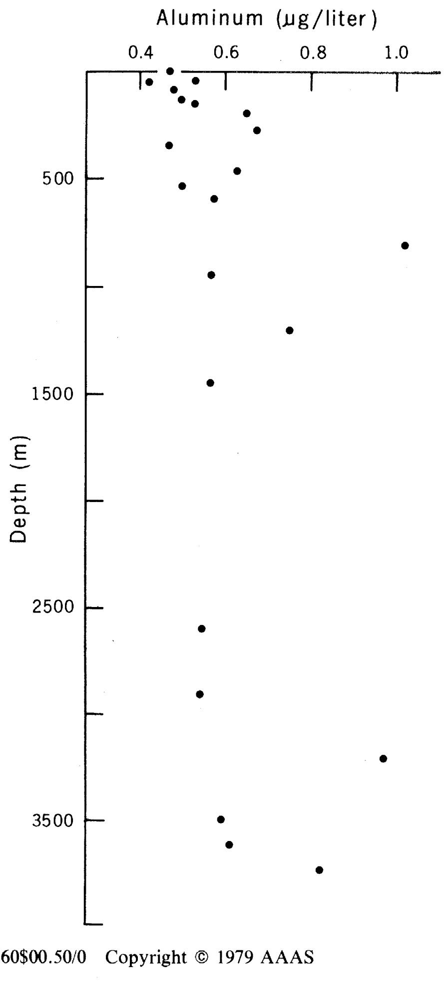
Aluminum in Seawater: Control by Inorganic Processes

Abstract. *The distribution of dissolved aluminum in open ocean waters is probably controlled by the solution of aluminum from atmospherically derived particles and bottom sediments balanced against scavenging by siliceous shells of dead organisms. Variations in the aluminum concentration within vertical hydrographic profiles are small as compared to those for other trace metals. Aluminum concentrations in the Atlantic and Pacific are inversely related to the silica contents of these oceans.*

Recent measurements of trace metals in deep ocean waters have shown that the dominant control on the distributions of Ni, Cd, and Zn (*1*) is biological. The metals are taken up from near-surface waters by microorganisms during growth and are then returned to solution as dead organisms decay and sink through the water column. The distribution profiles observed correlate closely with those of the micronutrients silicate or phosphate whose chemistries are similarly controlled in ocean waters. In contrast, Boyle *et al.* (*2*) have shown that, in the case of Cu, inorganic processes dictate the distribution pattern. Inputs of Cu across the surface and bottom boundaries of the ocean coupled with scavenging by particulate matter tend to produce profiles which display a concentration minimum at intermediate depths. Because of its importance in mineral forma-



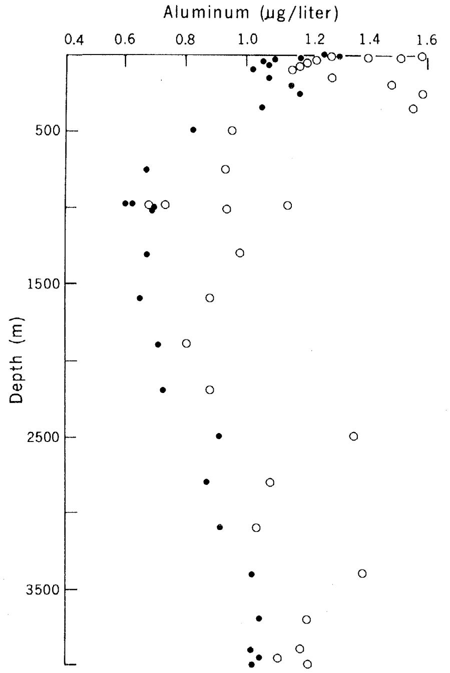


Fig. 1 (left). Profile of Al collected (October 1973) at GEOSECS station 219. Fig. 2 (right). Profiles of Al in acidified samples measured in (●) November 1977 and (○) May 1978 at station K69/10.

tion, Al is of interest in such studies of trace metal cycling. Mackenzie *et al.* (*3*) and Caschetto and Wollast (*4*) have reported results from the Mediterranean which show the covariance of Al and Si, and thus it may be said that Al behaves similarly to Ni and Zn. However, I report here results which show that in the open ocean the behavior of Al is more similar to that of Cu, which suggests that the situation in the Mediterranean, a confined marine basin, is anomalous.

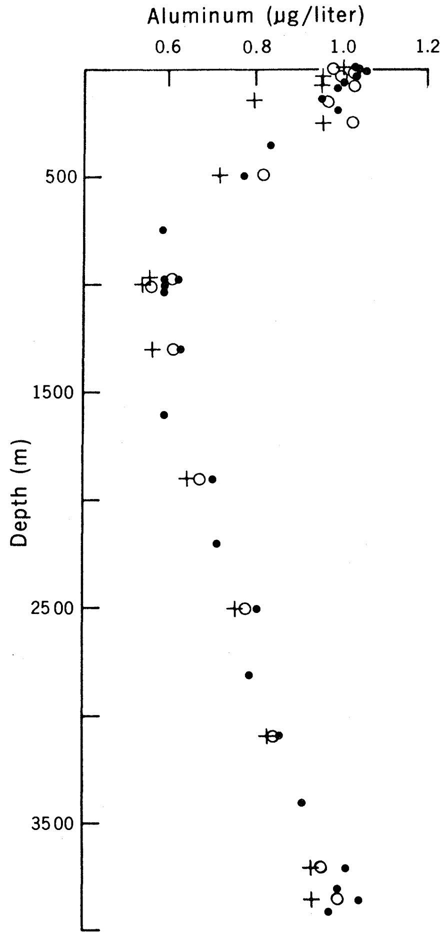


Fig. 3. Profiles of Al at station K69/10 in unacidified samples measured in (●) October 1977, (○) November 1977, and (+) May 1978.

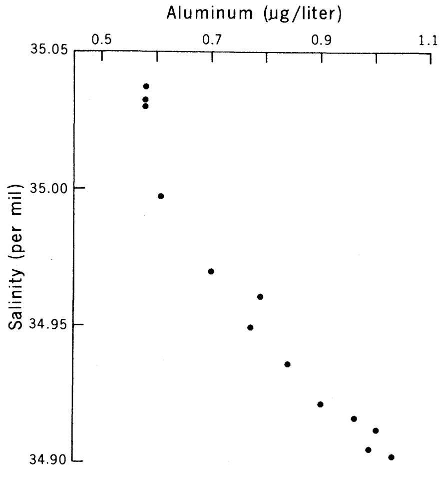


Fig. 4. Plot of Al versus salinity at station K69/10, below 990 m.

The Al analyses reported here were carried out in two stages. First, samples from the Geochemical Ocean Section Study (GEOSECS) library of water samples (*5*) were analyzed by the method of Hydes and Liss (*6*) at GEOSECS Central Atlantic station 37 and Pacific stations 204 off Hawaii and 219 in the Bering Sea. All three stations showed Al distributions similar to that shown in Fig. 1 for station 219. There is no detectable change in the Al concentration with depth, and there is considerable scatter of the data points as compared to data from other recent high-quality trace metal analyses (*1*). Earlier work on Al suggested that much of the scatter in these analyses may have resulted from the storage of samples in an acidified condition (*7*). The second stage was to collect a fresh suite of samples from the North Atlantic at station K69/10 (*8*); these samples were stored both unacidified and acidified, to study the influence of acidification and duration of storage. Comparison of the results (Figs. 2 and 3) shows that Al contamination does occur progressively with time in acidified samples, and that it varies from sample to sample. The average contamination over 8 months was 6.0 µg of Al per square meter of bottle surface. This finding is not unexpected in light of the recent results of Moody and Lindstrom (*9*) for acid leaching from linear polyethylene. It is thus highly probable that much of the scatter in the Al data from the GEOSECS stations is due to contamination during storage.

The data in Fig. 3 show much less scatter than the analyses from GEOSECS stations, and a steady variation of Al concentration with depth can be seen. The distribution is similar in form, but the change is smaller in magnitude than that observed by Boyle *et al.* (*2*) in several of their Cu profiles. They suggested that such a profile could be generated by atmospheric input to the surface layer, scavenging at mid-depth, and input from bottom sediments. Such an explanation is consistent with our knowledge of Al chemistry. Hodge *et al.* (*10*) have shown that airborne particulate matter acts as a source of Al on entering seawater. This may give rise to some of the patchiness in the Al distribution in surface waters. I measured surface concentrations of 0.6, 0.5, and 2.25 µg/liter at GEOSECS stations 204, 219, and 37; 1.0 µg/liter at station K69/10; and values between 0.5 and 5.5 µg/liter in the North Sea (*7*). For conditions at the benthic boundary, clay mineral solubility studies (*11*) predict that, at the dissolved Si concentrations found in pore waters of nonsiliceous sediments, the solubility of Al will be sufficiently high that the sediment will act as a source of Al to the overlying seawater. Plots of potential temperature versus salinity at stations 219 and K69/10

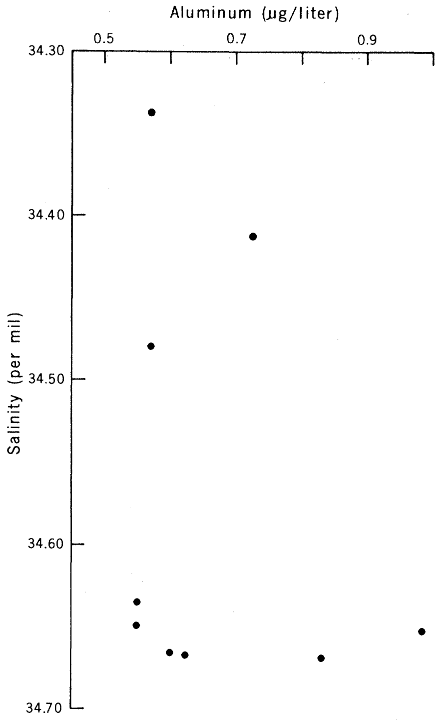


Fig. 5. Plot of Al versus salinity at GEOSECS station 219, below 943 m.

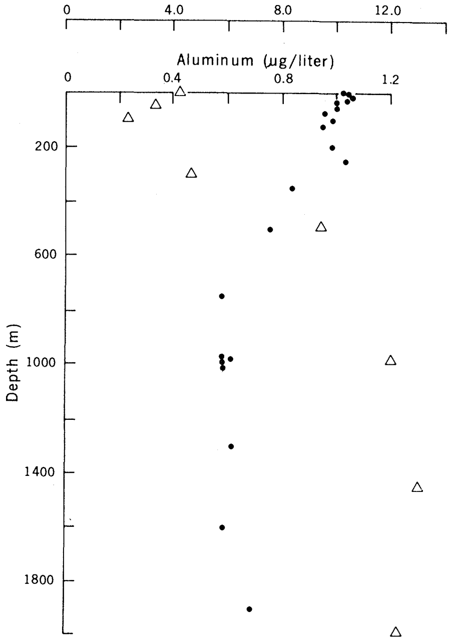


Fig. 6. Profiles of Al (●) and Si as silica (△) at station K69/10.

are linear below 943 and 990 m, respectively, indicating an unstratified water mass (*12*). Corresponding plots of Al versus salinity (Figs. 4 and 5) display curvature, an indication that scavenging of Al from solution (*13*) dominates any solution of Al from aluminosilicate particles that is taking place. I suggest that, when the organic coatings of diatoms and radiolaria are degraded after the death of the organisms, the silica shells become the most likely active site for Al scavenging. Lewin (*14*) found that leached diatom shells adsorb Al (up to 1.9 percent as Al_2O_3), and Hurd (*15*) observed mineral overgrowths on siliceous shells containing 0.8 percent Al_2O_3. In addition, Al concentrations up to 1.8 percent Al_2O_3 in diatoms have been reported; however, the origin of this Al is uncertain, and much of it may be due to contamination of samples caused by clay minerals (*16*).

Mackenzie *et al.* (*3*) observed in a partial profile from the Mediterranean that the Al and Si concentrations covaried. They proposed that Al is removed from seawater during the growth of siliceous microorganisms and is regenerated below the productive zone. In comparison, the distributions of Al and Si in Fig. 6 show none of these correspondences. Similarly, if the distributions of Al and Si covary in the Pacific as claimed for the Mediterranean by Mackenzie *et al.*, then at station 219 the concentration of Al should increase sixfold in parallel to the Si increase from 32.2 μm of Si per kilogram of water to 190.1 μm at a depth of 1676 m (*3, 4*). The data in Fig. 1 show no indication of such a change.

The above evidence suggests that the situation observed by Mackenzie *et al.* in the Mediterranean is anomalous. Certainly, the Al concentration they report is five times higher than those reported here and in earlier studies (*7, 17*). Further, in spite of contamination, the mean Al concentration measured at both Pacific GEOSECS stations is 0.6 μg/liter, which is significantly below the mean of 0.85 μg/liter for the unacidified samples at station K69/10. The mean Al concentration at GEOSECS station 37 is 1.61 μg/liter. Atlantic stations show higher Al concentrations than Pacific ones whereas the reverse is true for Si, and so an inverse rather than a direct relation may apply to Al and Si concentrations on an oceanic scale. This inverse relationship between Al and Si may reflect the greater flux of Si through Pacific water, producing greater scavenging and probably a lower input of Al.

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References and Notes

1. E. A. Boyle, F. Sclater, J. M. Edmond, *Nature (London)* **263**, 42 (1976); F. Sclater, E. A. Boyle, J. M. Edmond, *Earth Planet. Sci. Lett.* **31**, 119 (1976); K. W. Bruland, G. A. Knauer, J. H. Martin, *Nature (London)* **271**, 741 (1978).
2. E. A. Boyle, F. Sclater, J. M. Edmond, *Earth Planet. Sci. Lett.* **37**, 38 (1977).
3. F. T. Mackenzie, M. Stoffyn, R. Wollast, *Science* **199**, 680 (1978).
4. S. Caschetto and R. Wollast, *Mar. Chem.* **7**, 141 (1979).
5. D. W. Spencer made the GEOSECS samples available and S. Kadar, C. L. Smith, and D. W. Spencer provided the Si analyses for station K69/10.
6. D. J. Hydes and P. S. Liss, *Analyst (London)* **101**, 922 (1976). This is the same method as that used by Mackenzie *et al.* (*3*).
7. ———, *Estuarine Coastal Mar. Sci.* **5**, 755 (1977).
8. Woods Hole *Knorr* cruise 69, station K69/10, September 1977; position, 40°51′N, 64°10′W; water depth, 4195 m.
9. J. B. Moody and R. M. Lindstrom, *Anal. Chem.* **49**, 2264 (1977).
10. V. Hodge, S. R. Johnson, E. D. Goldberg, *Geochem. J.* **12**, 7 (1978).
11. D. J. Hydes, *Nature (London)* **268**, 136 (1977).
12. North Atlantic deep water is a complex mixture of five different water masses. [L. V. Worthington and W. R. Wright, *North Atlantic Ocean Atlas* (Woods Hole Oceanographic Institution Atlas Series, Woods Hole, Mass., 1970), vol. 2]. It is possible that this apparent linearity is the fortuitous result of insufficient hydrographic data.
13. H. Craig, *Earth Planet. Sci. Lett.* **23**, 149 (1973).
14. J. C. Lewin, *Geochim. Cosmochim. Acta* **21**, 182 (1961).
15. D. C. Hurd, *ibid.* **37**, 2257 (1973).
16. A. J. van Bennekom and S. J. van der Gaast, *ibid.* **40**, 1149 (1976).
17. J. J. Alberts, D. F. Leyden, T. A. Paterson, *Mar. Chem.* **4**, 51 (1976); W. M. Sackett and G. O. S. Arrhenius, *Geochim. Cosmochim. Acta* **26**, 955 (1962).

18. I thank D. W. Spencer for providing GEOSECS samples. I am grateful to S. Kadar, C. L. Smith, and D. W. Spencer for supplying the Si analyses. This work was supported by National Science Foundation grant OCE 76-10277 and the Woods Hole Oceanographic Institution. Woods Hole Oceanographic Institution Contribution 4289.

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N-Nitrosamines in the Rubber and Tire Industry

Abstract. *Airborne* N-*nitrosomorpholine (0 to 27 micrograms per cubic meter) was found in two of four rubber industry factories.* N-*Nitrosodimethylamine was also found in two factories, but at lower levels. These findings may be relevant to the reported increased risk of certain types of cancer in rubber workers in some of the same areas where the* N-*nitrosomorpholine levels were highest.*

A number of studies have shown that workers in the American rubber industry have a significantly increased incidence of several types of cancer (*1*). It has been suggested that various chemicals used in the rubber industry are associated with this excess cancer risk. We now report the presence of an additional agent, *N*-nitrosomorpholine (NMOR), a well-known animal carcinogen (*2*), in rubber factory air and in bulk samples. Smaller amounts of a related carcinogen, *N*-nitrosodimethylamine (NDMA), were also found in two of the four factories sampled.

The laboratory apparatus, including gas and high-pressure liquid chromatographs, fume hood, and detectors, was located inside a fully equipped mobile laboratory, which was parked near each site (*3*). A TEA analyzer (Thermo Electron model 502LC) was used as a nitrosyl-specific detector for an isothermal gas chromatograph (GC) (*4*). The high-pressure liquid chromatograph (HPLC) was constructed (*5*) by combining a high-pressure pump (Altex model 110) with an injector (Rheodyne model 7120), a stainless steel column (4 by 39 mm) packed with 10-μm Lichrosorb Si60 (Merck), and a second TEA detector. Authentic samples of NMOR, NDMA, *N*-nitrosodipropylamine (NDPA), and *N*-nitrosodiphenylamine (NDPhA) were obtained from Thermo Electron. Solvents (distilled-in-glass grade) were supplied by Burdick & Jackson Laboratories.

Table 1 summarizes the findings at four rubber industry factories in Ohio visited in the spring of 1978. *N*-Nitrosodiphenylamine, which is used as a vulcanization retarder, was found at a tire chemical factory where it was being produced. Thus it was not unexpected to find it there in the air, in wastewater from the NDPhA reaction (730 μg/g), or in scrapings from the floor (up to 15,000 μg/g) (*6*). It was even found in the soil outside the building (47 μg/g). It was not found at the other three factories, although it is sometimes used in the manufacture of tires. *N*-Nitrosodiphenylamine is not generally considered to be carcinogenic (*7*), although a recent report casts some doubt on this conclusion (*8*).

N-Nitrosodimethylamine was found as an air pollutant at both the chemical factory and the industrial rubber products factory. In the chemical factory, the concentration ranged from 0.05 to 0.5 $\mu g/m^3$ close to a tank where dimethylamine (DMA) was being stored (Table 1). The DMA was found to be contaminated with NDMA (1.3 μg/g), and this may have contributed to the airborne NDMA. In the industrial rubber products factory, all four samples contained NDMA at levels between 0.07 and 0.14 $\mu g/m^3$. The source of the NDMA at this factory was not determined.

N-Nitrosomorpholine was found as an air pollutant inside both the chemical factory and the aircraft tire factory. In the chemical factory, it was found as an

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