Diffusion of Cesium Ions in H_2O-Saturated Granitic Melt

Abstract. *The intrinsic self-diffusion coefficient* (D) *for cesium-134 in a granitic melt containing 6.1 to 6.3 percent (by weight) of dissolved* H_2O *is three to four orders of magnitude higher than the values reported for chemically similar but dry granitic glass. For the temperature interval 700° to 800°C and a confining pressure of 2 kilobars, cesium diffusivity is given by* $D = 7.19 \times 10^{-5} \exp(-19.52 \times 10^3/RT)$, *where* R *is the gas constant and* T *is the absolute temperature; the activation energy of about 20 kilocalories per mole is less than half the value for* H_2O*-free glass. The observed increase in ionic mobility that accompanies solution of* H_2O *implies sharply reduced equilibration times for chemical processes that occur in* H_2O*-bearing silicate melts.*

The importance of many chemical reactions or processes that involve molten silicate (magma) at depth in the earth is determined by the rate at which they take place. This is true of small-scale processes such as the growth of crystals from the melt (*1*) and also of larger scale phenomena such as chemical exchange between magma and surrounding or included rock. Geologists have long recognized that knowledge of diffusion rates in silicate melts is fundamental to understanding magmatic processes (*2*). Recently, several workers have used high-temperature experimental data on the diffusion rates of Sr, Ba, Na, K, Rb, and Cs in water-free granitic obsidian to place constraints on the extent of diffusion control in processes such as those noted above (*3-5*). These constraints are invaluable to models of granite formation and evolution, but they cannot be considered to hold rigorously for all magmatic conditions. In view of the pronounced reduction in the viscosity of silicate melt that results from the presence of dissolved water (*6*), for example, existing data on diffusion in dry, essentially solid obsidian can be applied only tentatively to situations in the earth's crust where water is available for solution in magmas. The experimental results reported here for the diffusion of Cs in a water-saturated granitic melt confirm the common suspicion (*7*) that some ions at least are highly mobile in water-bearing silicate melts.

I prepared the diffusion medium for these experiments by artificial hydration of a homogeneous, crystal- and bubble-free obsidian from Lake County, Oregon (oxide analysis in percent by weight: SiO_2, 76.01; TiO_2, 0.11; Al_2O_3, 13.00; iron as FeO, 0.70; MgO, 0.09; CaO, 0.52; Na_2O, 3.65; K_2O, 4.81; MnO, 0.08; and H_2O, 0.17). Cylinders of this obsidian (3 mm in diameter) were cored and milled to fit tightly inside Pt tubing 1.8 mm in inside diameter. The cylinders were inserted into 2- and 3-cm lengths of the Pt tubing, and 10 percent of the glass weight in water was added. The tubes were then welded shut and held for 10 days at prescribed conditions (2 kbar, 700° or 800°C) in cold-seal, hydrothermal pressure vessels (*8*). [I based my choice of 10-day measurement times upon a preliminary time study in which I found that dissolved H_2O reached a maximum value in 5 to 6 days and then remained constant for longer durations. This saturation time is consistent with measured H_2O diffusion rates in obsidian (*9*).] Upon quenching and depressurization, the Pt tubes containing hydrated glass were cut into sections 6 to 10 mm long. The dissolved H_2O content of one section from each tube was estimated by weight loss from the glass upon heating at 1100°C. The average H_2O contents in glasses saturated at 700° and 800°C are 6.3 and 6.1 percent (by weight), respectively, in agreement with previous estimates of H_2O solubility in similar obsidian (*9*). I prepared the remaining sections of glass-filled Pt tubes for Cs diffusion measurements by drilling out the exposed glass at each end to a depth of ~ 1.5 mm. Cesium-134 (~ 0.05 μCi in 0.5*M* HCl) was placed as a thin source at one end of the hydrated obsidian cylinders. The samples were then heated overnight at 120°C to drive off water introduced with the tracer or adsorbed on the glass surface. For final sealing of the tubes I welded Au or Pt plugs in the recessed ends. I then proceeded with the actual Cs diffusion experiments by annealing the tracer-doped samples at the temperature of original hydration and a pressure of 2.1 kbar (that is, just above the original pressure of saturation) for periods ranging between 2 and 8 days. The Cs diffusion profiles in the quenched samples were recorded by longitudinal sectioning of the glass cylinders and exposure of the surface to nuclear emulsion plates suitable for recording beta particles emitted by the ^{134}Cs tracer. I determined the beta-track density on the developed emulsions by scanning with a recording microdensitometer. Values for Cs diffusivity (*D*) were obtained by fitting the densitometer scans to the thin-source solution to the nonsteady-state diffusion equation (*10*).

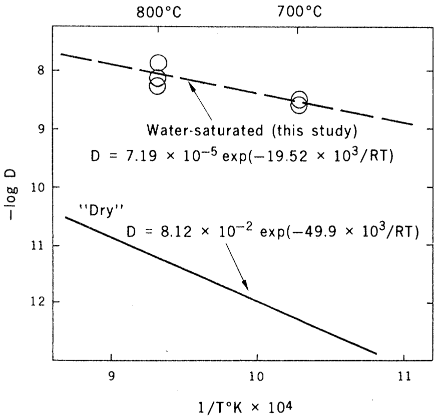

Fig. 1. Arrhenius plot of diffusion data for ^{134}Cs in H_2O-saturated granitic melt at 2 kbar (circles) compared with earlier data (solid line) for dry granitic glass (*4*); *D* has the dimensions square centimeters per second. The three data points at 800°C represent diffusion experiments of 2, 3, and 4 days; the experiment times at 700°C were 5 and 8 days.

My measurements of Cs diffusivity in H_2O-saturated obsidian are plotted on an Arrhenius diagram (Fig. 1) in comparison with previous values for Cs diffusion in dry obsidian of similar composition (*4*). The new data show that Cs^+ mobility is dramatically enhanced by the presence of dissolved H_2O in molten granite. At the temperatures appropriate for H_2O-saturated initial melting of granitic materials in the deep crust (650° to 700°C) (*11*), Cs diffusivity is three to four orders of magnitude faster than previously predicted from experimental data on dry glasses. This result is in qualitative agreement with preliminary estimates of Cs diffusion rates in wet granitic melts (*12*) and also provides a reasonable explanation for the observation that water promotes reaction between silicate melts and crystals.

If my results on Cs diffusion are to any extent general for other elements, then they have important consequences in several areas of geochemistry. In the realm of geochronology, for example, it seems clear that incipient or partial melting of crustal rocks may be far more effective in resetting radioisotope chronometers than previously supposed (*5*). During a given melting episode, the average diffusional transport distance [$x \sim (D \cdot \text{time})^{1/2}$] may be ten to a hundred times greater for H_2O-saturated conditions than for anhydrous melting. In radiometrically dating such an event, then, the necessary scale of bulk-rock sample collection may be critically dependent upon the actual conditions of melting.

The new diffusion data also bear upon problems related to chemical homogenization in silicic magma chambers. Many geochemical models and all geo-

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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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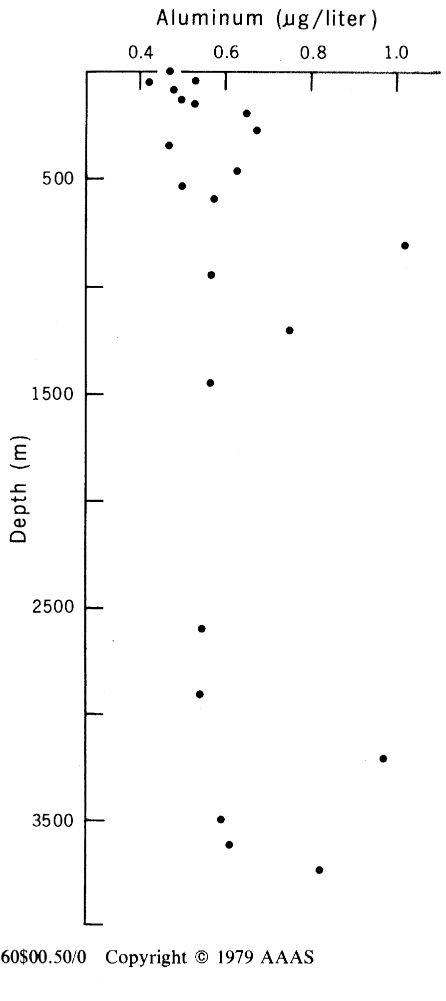
Aluminum in Seawater: Control by Inorganic Processes

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-



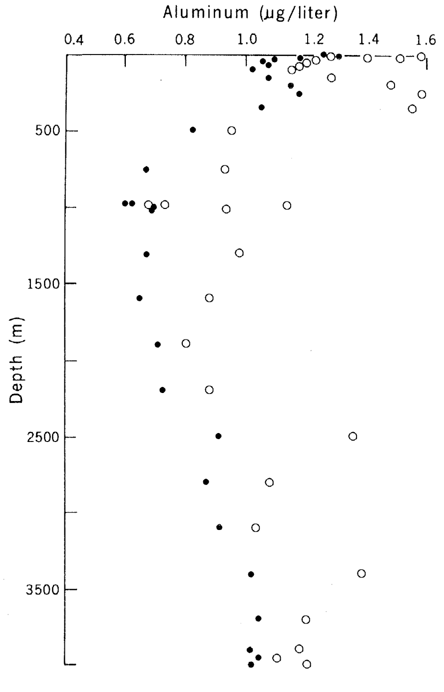


Fig. 1 (left). Profile of Al collected (October 1973) at GEOSECS station 219. Fig. 2 (right). Profiles of Al in acidified samples measured in (●) November 1977 and (○) May 1978 at station K69/10.