Silicates: Reactivity with Sea Water

Abstract. *Silicate minerals rapidly release silica to sea water. Fine-grained, 1-gram samples were placed in 200 milliliters of sea water, and the silica content of the water was measured intermittently for 6 months. At the end of 10 days and of 6 months the silica concentrations with various minerals, in parts per million, were, respectively: kaolinite, 0.6, 2.2; chlorite, 2.5, 2.4; illite, 1.8, 2.6; muscovite, 1.8, 3.9; montmorillonite A, 7, 10.5; montmorillonite B, 10, 21. Except for ion exchange phenomena, it generally has been assumed that these minerals do not react significantly with sea water, or, if they do, they react at geologically slow rates. The rates observed indicate that the ocean must be looked upon as a chemical system with a rapid response to added detrital silicates.*

In a study of the controls of sea water composition, it is necessary to know the solids that interact significantly with the aqueous phase. Detrital minerals, mainly silicates, dumped into the ocean basins by streams, constitute a major possible source or sink of dissolved materials; however, little is known about the rates at which these silicates react with aqueous solutions. To test structural breakdown rates directly, we decided to determine the rate of release of silica to sea water from a number of minerals common in the detrital load of streams.

One-gram ($< 62\text{-}\mu$) samples of kaolinite, illite, chlorite, muscovite, and two montmorillonites were placed separately in polyethylene vessels containing 200 ml of sea water low in silica (0.03 part per million), freshly collected from Ferry Reach, Bermuda. X-ray examination showed that the mineral samples, except for muscovite and chlorite, were not single phases. The montmorillonites contained accessory feldspar and small amounts of quartz and illite; the kaolinite contained about 5 percent illite; and the illite contained about 5 percent quartz and a trace of poorly crystalline chlorite or mixed-layer material. The silica content of the filtered supernatant sea water and the *p*H of the supernatant water, as well as that of the stirred suspensions, were monitored with time. A glass–saturated calomel pair of electrodes was used to measure *p*H; the *p*H suspension effect (*1*) is minimal at these suspension concentrations. Dissolved silica was determined by the colorimetric method of Mullin and Riley (*2*). For each experiment, a sea water sample with no added minerals was monitored as a control, to assess the effects that plankton and suspended material might have on the system. The dissolved silica found in the sea water control was subtracted from that determined in the mineral-containing samples. Silica in the control never exceeded 0.4 ppm, and was usually much less. Resultant data are presented in Figs. 1–3.

The minerals rapidly released silica to sea water in measurable amounts, and, except for kaolinite, within 10 days they released more than 50 percent or about 50 percent of the amount found at 6 months (Fig. 1). At the end of 6 months, illite, chlorite, and kaolinite had produced between 2 and 3 ppm of silica (SiO_2) and, to judge from the shape of the silica release curves, had nearly ceased to react. The curve for muscovite is similar to that for illite, but the silica concentration achieved was about 4 ppm, with a suggestion that it might rise a little higher with longer exposure.

The montmorillonites behaved quite differently from the other silicates. Montmorillonite A apparently reached a nearly constant silica concentration of 10.5 ppm at the end of 6 months, whereas montmorillonite B produced 21 ppm and clearly had not stopped reacting.

The results shown in Fig. 1 were obtained from samples stirred originally and again only at the time of analysis, so they represent minimum rates of reaction. Figure 2 shows the results of experiments on kaolinite samples that were stirred vigorously twice a day for 8 days. The silica concentrations reached (1 to 2 ppm) are apparently independent of surface area exposed, and are reasonably consistent with the 6-month value for the unstirred sample (2.2 ppm).

Changes in *p*H with time are shown in Fig. 3. There are initial minor differences and fluctuations in the *p*H values, but the changes are so small that they could be attributed to a variety of causes. The *p*H values of the 6-month samples are remarkably consistent at 7.8, about 0.4 *p*H unit below

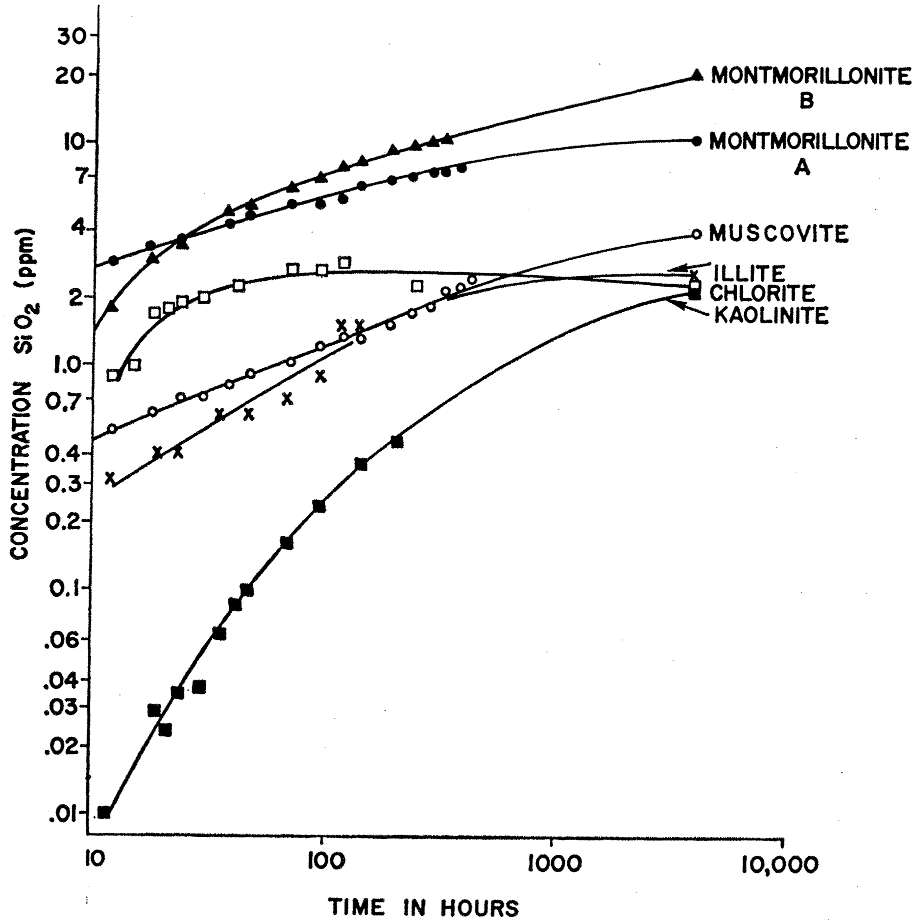

Fig. 1. Silica concentration as a function of time for silicate–sea water suspensions. Curves are for 1-g ($< 62\text{-}\mu$) samples in 200 ml of sea water at room temperature. Concentrations are corrected for silica content of control.

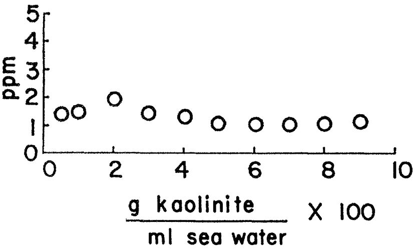

Fig. 2. Silica concentration in sea water supernatants of various weight-percent suspensions of < 62-μ kaolinite at room temperature after 196 hours. Concentrations are corrected for silica content of control. Suspensions were stirred vigorously twice daily to increase the rate of silica release.

the original sea water and the final reading on the sea-water control.

Any detailed interpretation of our results is not warranted at this time, but some speculation and tentative conclusions may be useful. The similarity of the silica values obtained from kaolinite, illite, muscovite, and chlorite indicate incongruent solution, with the formation of an aluminous residue, perhaps an aluminum oxide hydrate. Carroll and Starkey (*3*) showed that silica is removed preferentially to alumina from silicates reacted with sea water, and aluminum oxide hydrates are virtually insoluble at the *p*H of our experiments. Waters draining a mixture of bauxitic and kaolinitic minerals in the Lower Congo (*4*) contain 2 to 4 ppm SiO_2, and Kittrick (*5*) determined the equilibrium silica concentration for coexistence of well-crystallized kaolinite and gibbsite at room temperature as 1 to 2 ppm. The independence of sample size and the silica values obtained by reaction of kaolinite (Fig. 2) also are suggestive of attainment of an equilibrium. On the other hand, the much higher silica values obtained from the montmorillonites suggest that their incongruent solution produces some substance other than an aluminum oxide hydrate—perhaps some ill-defined aluminosilicate. Whitehouse and McCarter (*6*) observed that montmorillonitic material was transformed to illitic and chloritic clay minerals after reacting with a limited volume of sea water for periods of up to 5 years. Perhaps the results we have obtained represent the first stages of a similar transformation, although our work is complicated by the presence of other phases in the montmorillonites used. We have no explanation for the consistent *p*H values at the end of 6 months; x-ray examination showed that no new crystalline phases were formed during immersion of the silicates in sea water.

The major conclusion we wish to draw is that oceanic chemistry is strongly influenced by the reactions of the great tonnages of detrital materials, primarily silicates, that are carried into the marine environment by streams. These same silicates rapidly release silica to sea water low in silica, and the concentrations reached are of the same order of magnitude as the average silica concentration of the oceans. Thus by releasing and, presumably, combining with silica, silicates exert a major control on the silica concentration in the oceans, and probably on other chemical species (*7*).

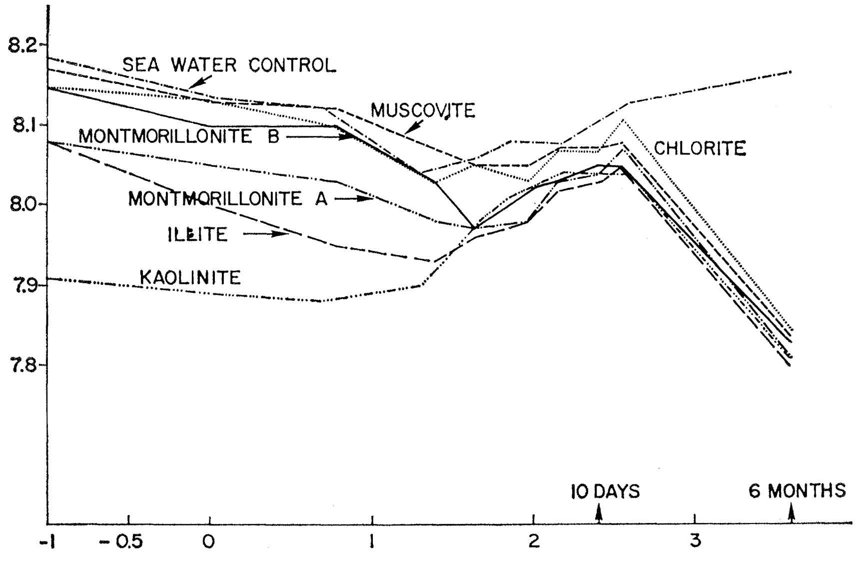

Fig. 3. Changes in *p*H as a function of time for suspensions of silicate minerals and for sea water control.

FRED T. MACKENZIE
Bermuda Biological Station for Research, St. George's West, Bermuda
ROBERT M. GARRELS
Department of Geological Sciences, Harvard University, Cambridge, Massachusetts

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Leukocyte Alkaline Phosphatase: Electrophoretic Variants Associated with Chronic Myelogenous Leukemia

Abstract. *Starch-gel electrophoresis of leukocyte alkaline phosphatases, rendered soluble by treating normal leukocytes with butanol, revealed three electrophoretic variants of the enzyme. The phosphatases in similarly prepared extracts of leukemia cells differed from the normal isozymes in electrophoretic mobility. A single variant was detected in one case of untreated leukemia; a similar component and three additional ones were seen in leukemia treated with 6-mercaptopurine.*

Much of the interest in the alkaline phosphatase activity of neutrophil granulocytes centers around the speculation that the locus of the gene which directs the formation of the enzyme is on chromosome 21 (*1*). This view has its primary support in observations made in chronic myelogenous leukemia and in Down's syndrome. Leukocyte alkaline phosphatase activity (*2*) is decreased in chronic myelogenous leukemia. Furthermore,