such as CaF_2, CdF_2, and BaF_2, there also exist transitions at high pressures (*15*) to the still denser (about 10 percent) orthorhombic $PbCl_2$-type structure. These might be even more dense than the phase of TiO_2 reached under shock compression, but no positive identification can be made at this time. Similar possibilities exist for the recovery of TiO_2 in the α-PbO_2 structure in the static experiments of Bendeliany *et al.* (*11*), or again this may be a metastable quench product. This seems characteristic of the occurrence of the α-PbO_2 structure in RX_2 compounds.

Another material in the rutile phase, the mineral stipoverite, has become of considerable geologic interest since it has been found at impact sites of meteorite craters, apparently produced by the impact shock. Hence it is possible that this new phase may be of interest because of the common occurrence of rutile as a constituent mineral of sedimentary rocks. Rocks of this type that have been subjected to impact may yield minor quantities of the new orthorhombic phase. The behavior of shocked rutile when considered along with that of quartz (*16*) should give additional evidence of shock conditions. As distances are traversed outward from the point of impact, the new phase should be found coexisting with stipoverite and silica glass (relict of stipoverite) until the shock pressure is decreased below that required for its transformation.

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Silica in Sea Water: Control by Silica Minerals

Abstract. *Silicate minerals typical of those carried in the suspended load of streams release silica to silica-deficient sea water and abstract silica from silica-enriched sea water. Experimental rates of release and uptake permit the conclusion that the suspended solids carried into the oceans by streams are a major control of the concentration of silica in the ocean.*

This report shows that silicates typical of those carried in the suspended load of streams release dissolved SiO_2 to silica-deficient sea water and take up dissolved SiO_2 from silica-enriched sea water. Experimental concentrations of dissolved SiO_2 in sea water after reaction with silicates are approximately the same as those in the oceans.

We have shown (*1*) that several common silicates rapidly released dissolved SiO_2 to silica-deficient [SiO_2 (aqueous) $\cong$ 0.03 ppm, initially] sea water, and that the final concentrations obtained were near the average concentration of dissolved silica of the ocean [SiO_2 (aqueous) $\cong$ 6 ppm]. We concluded that the ocean must be considered as a chemical system with a rapid response to the detrital silicates carried in by streams.

Our experiments were designed to see whether typical silicates extract dissolved silica from sea water "enriched" with silica. One-gram ($< 62\ \mu$) samples of the minerals kaolinite, montmorillonite, illite, chlorite, muscovite, and glauconite were added separately to 200 ml of silica-enriched [SiO_2 (aqueous) $\cong$ 25 ppm] sea water in polyethylene containers. The sea water was initially

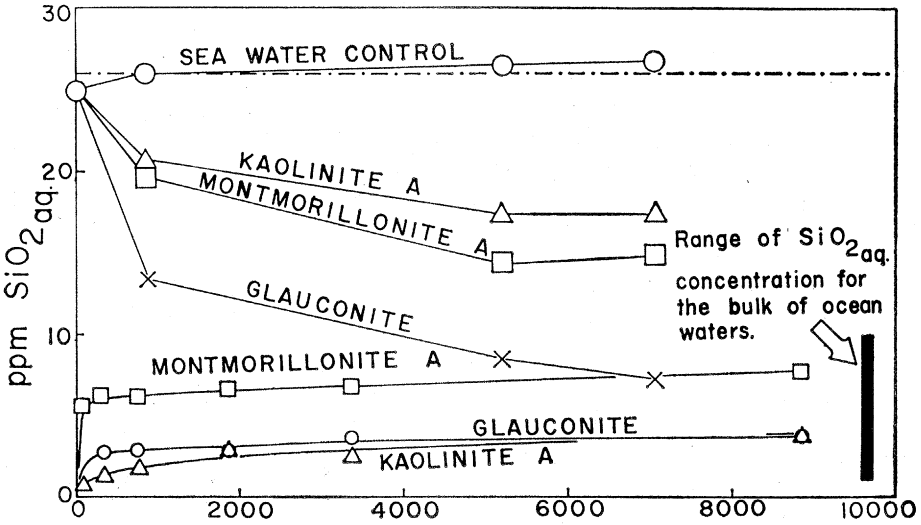

Fig. 1. Concentration of dissolved silica as a function of time for suspensions of silicate minerals in sea water. Curves are for 1-g ($< 62\ \mu$) mineral samples in 200 ml of silica-deficient (SiO_2 in water was initially 0.03 ppm) and silica-enriched (SiO_2 was initially 25 ppm) sea water at room temperature. Size of symbols indicates precision of SiO_2 determinations. Dash-dot line shows minimum SiO_2 concentration of sea water in equilibrium with a hydroxylated magnesium silicate at the *p*H's of our experiments.

Table 1. Final concentration of dissolved silica of sea water supernatants, change in concentration of dissolved SiO_2, weight (milligrams) of dissolved SiO_2 released and taken up, and final pH of 1-g (< 62 μ) mineral samples in 200 ml of silica-deficient and silica-enriched sea water at room temperature. Reaction time was 8850 hours for silica-deficient and 7050 hours for silica-enriched sea water experiments.

Mineral	Deficient (SiO_2 initially 0.03 ppm; pH, 8.18)				Enriched (SiO_2 initially 25 ppm; pH, 8.10)			
	Concentration		Weight (mg)	Final pH	Concentration		Weight (mg)	Final pH
	Final (ppm)	Change (ppm)			Final (ppm)	Change (ppm)		
Glauconite	3.6	+ 3.6	+0.7	6.61	7.3	−17.7	−3.5	6.77
Muscovite	7.6	+ 7.6	+1.5	7.84	14.7	−10.3	−2.1	7.86
Montmorillonite A	7.8	+ 7.8	+1.6	7.92	14.8	−10.2	−2.0	7.83
Chlorite	4.2	+ 4.2	+0.8	7.85	16.2	− 8.8	−1.8	7.91
Kaolinite A	3.8	+ 3.8	+0.8	7.91	17.5	− 7.5	−1.5	7.75
Kaolinite B	5.0	+ 5.0	+1.0	7.86	17.8	− 7.2	−1.4	7.69
Illite	5.7	+ 5.7	+1.1	7.79	18.0	− 7.0	−1.4	7.80
Montmorillonite B	11.0	+11.0	+2.2	7.76	20.3	− 4.7	−0.9	7.65

filtered through a 0.45-μ Millipore filter, and several drops of Quatam "D" (*2*) were added to prevent further biologic activity. Solid sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) was added to the sea water so that the concentration of dissolved silica was 25 ppm, and the pH was adjusted to 8.1 with concentrated HCl. Special care was taken to prevent precipitation of a hydroxylated magnesium silicate from the sea water, which, according to results obtained so far, forms when the silica concentration exceeds 26 ppm at a pH of 8.1. A sample of sea water without added minerals was monitored as a control. The containers were continuously agitated on a shaker table for about 10 months; during this time samples were withdrawn and analyzed for dissolved silica (*3*). The final pH of the supernatants was also recorded.

All of the silicate minerals take up dissolved silica. Table 1 gives the amounts of dissolved SiO_2 abstracted by the various minerals and the final pH's of the supernatants. The results obtained with the same minerals in silica-deficient sea water also are presented in Table 1. These latter experiments differed from those reported (*1*) only by the fact that the containers were continuously agitated on a shaker table.

Three examples of reaction curves for the experiments on minerals in sea water are given in Figure 1. Apparently all of the minerals have nearly ceased to react. Most of the uptake or release of dissolved SiO_2 occurred in less than 6 months. The curves for silica release which are similar to our previous results (*1*), substantiate our earlier conclusions that (i) silicates rapidly release silica to silica-deficient sea water, and (ii) that this release is governed by the formation of an aluminous residue, either an aluminum oxide hydrate or an ill-defined aluminosilicate. In contrast, silica uptake by these same minerals involves the formation of more siliceous materials. Consequently, the curves for silica release and uptake for a specific mineral would not be expected to approach the same steady-state concentration of silica. Also, the uptake of silica by silicates involves the cations in sea water. To substantiate the conclusion that cations are involved in silica uptake, 1-g samples (< 62 μ) of these same minerals were suspended for 10 months in 200 ml of distilled water containing 25 ppm of dissolved SiO_2. Except for chlorite, the minerals abstracted at most only 0.4 mg of dissolved SiO_2 from solution.

The siliceous materials formed when aluminosilicate minerals take up dissolved silica are aluminosilicates rather than nonaluminous silicates. As indicated, titration of sea water with dissolved silica results in the precipitation of a hydroxylated magnesium silicate. No other silicates were detected in the titration experiments, and none would be expected. At a pH of 8.1, the concentration of dissolved silica in sea water at equilibrium with this solid is about 26 ppm, and it is higher at lower pH's. We conclude that aluminum must be involved in any reactions that lower dissolved SiO_2 below 26 ppm in the pH range of our experiment (6.7 to 8.1).

In conclusion, certain common silicates take up dissolved silica from silica-enriched sea water. This uptake involves the cations in sea water, and is governed by the formation of ill-defined aluminosilicates. The experimental concentrations of dissolved SiO_2 of silica-enriched or silica-deficient sea water after reaction with silicates are the same as, or very near, the concentrations of dissolved SiO_2 in the oceans. The duration of our experiments (about 10 months) is comparable to the average interval of exposure to sea water of suspended materials brought to the oceans by streams. We conclude that silicates are a major control of the silica concentration of the ocean, and other chemical species (*4*).

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Single Fallout Particles and Zirconium-95 from the Chinese Nuclear Explosion of 9 May 1966

Abstract. *Daily fluctuations of the number of single fallout particles and activity of zirconium-95 in the ground-level air were measured at Fayetteville (94°W, 36°N), Arkansas, for a period of about 3 months after the Chinese nuclear explosion of 9 May 1966. We found a cyclic pattern of variations for both zirconium-95 and fallout particles; this indicated that they were airborne for a long period and traveled far. Apparently, some of the particles circled the world more than once.*

The fallout of highly radioactive single particles has occurred in Japan for the past several years (*1*), and we have recently studied mass-yield distri-