Reports

Silica: Role in the Buffering of Natural Waters

Abstract. *In the oceans, dissolved silica and degraded silicates appear to participate in a reaction which fixes silica and alkali metal cations and releases hydrogen ions, resulting in maintenance of the* pH.

Sillen (*1*) recently discussed the physical chemistry of sea water, concluding that reactions between silicate minerals and sea water are of greatest importance in controlling the *p*H as well as the concentrations of the chief cations in sea water. In his treatment of the problem he considered the reactions to be expected by successive additions of the constituents of rocks, as oxides, to an aqueous system.

The same conclusion can be reached from consideration of a simplified model of the water cycle, in which rain falls on rocks, descends to a basin in streams, and is concentrated there by evaporation, which returns water to the atmosphere to complete the cycle. If these rocks are limestones, the classical reaction for weathering of calcium carbonate applies:

$$\underset{\text{calcite}}{CaCO_3} + H_2O_l + CO_{2\,g} = Ca^{++}_{aq} + 2HCO^-_{3aq} \qquad (1)$$

If equilibrium with $CaCO_3$ and the CO_2 of the atmosphere is achieved, a dilute solution with a *p*H of about 8 would be formed. Such a solution, on removal to a basin and evaporation in equilibrium with the atmosphere, would maintain its *p*H, dissolved calcium, and bicarbonate constant, while precipitating $CaCO_3$ and releasing CO_2 to the atmosphere. This simplified model contains the essential characteristics of the commonly accepted calcium cycle, in which the $CaCO_3$ precipitated in the oceans as limestones by the agency of organisms is eventually reexposed to weathering. Also, before Sillen, reaction 1 was generally accepted as the chief buffering reaction in the oceans. The reaction is a simple "push-pull"; CO_2 removed from the atmosphere during solution of limestone is restored upon evaporation and deposition of $CaCO_3$.

However, another classical reaction of weathering, which is used to describe the essence of the decomposition of igneous rocks (*2*), is the breakdown of feldspar; albite is an example:

$$\underset{\text{feldspar}}{2NaAlSi_3O_8} + 2CO_{2g} + 3H_2O_l = 2Na^+_{aq} + 2HCO^-_{3aq} + \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 4SiO_{2aq} \qquad (2)$$

That this reaction is applicable in nature has been strikingly demonstrated in a study (*3*) of waters from igneous rocks of the Sierra Nevada. If the dilute aqueous solution (*p*H $\cong$ 6; Na^+ $\cong$ 6 ppm, SiO_2 $\cong$ 20 ppm) were removed from the solid kaolinite to a basin and evaporated, the result would be strikingly different from that of a water in equilibrium with a limestone. Silica would precipitate as amorphous silica after reaching about 120 ppm, CO_2 would be lost to the atmosphere, the water would become concentrated with respect to sodium, and the *p*H would rise above 9. Buffering would occur only when the solution became saturated with respect to a sodium carbonate mineral. In this case, so long as the water is isolated from the aluminosilicate decomposition product, there is no simple "push-pull." The initial water is not saturated with respect to a solid Na mineral, either carbonate or silicate, as weathering and evaporation are not complementary. Despite the oversimplification, the second model demonstrates the essence of what must happen to form many soda lakes.

Waters entering the oceans have complex sources, but carry components representing reactions 1 and 2. So long as some of the alkali metal cations and some of the silica are derived from decomposition of feldspars, and if the water is isolated from the aluminosilicate weathering residue, evaporation would yield $CaCO_3$ and amorphous SiO_2 as precipitates, but would have a higher *p*H and less dissolved calcium than a water derived entirely from a limestone terrain.

Thus, (i) silica in solution in streams is derived chiefly from the weathering of silicates and is initially accompanied largely by balancing alkali metals and bicarbonate. (ii) If silica is lost from the oceans as amorphous silica (eventually probably chert), the tendency is to raise the *p*H of the oceans. (iii) Deposition of silica implies synchronous deposition of a detrital aluminosilicate.

Because the sedimentary record contains little degraded aluminosilicate, such as kaolinite, and because the amount of chert in the record is far less than would be calculated from the rate at which dissolved silica is entering the oceans today, and because the oceans are only mildly alkaline, I conclude that there is a back-reaction in the oceans, or during early diagenesis, between dissolved silica and degraded silicates, which fixes silica and alkali metal cations while releasing hydrogen ions to sea water. Conversely, the great tonnages of kaolinite-type aluminosilicates carried into the oceans by streams each year represent "fixed acid" (or fixed CO_2); unless they are regenerated, the ocean water system would be much more alkaline than it is now.

The implication of the relations between silica, aluminosilicates, and alkali metal cations is far-reaching. Here, by a somewhat different analysis of the situation, the emphasis is on corroborating Sillen's conclusion of the importance of the silicate minerals in controlling oceanic chemistry.

ROBERT M. GARRELS
Department of Geology, Harvard University, Cambridge, Massachusetts

References and Notes

1. L. G. Sillen, in *Oceanography*, M. Sears, Ed. (AAAS, Washington, D.C., 1961), pp. 549–581.
2. L. D. Leet and Sheldon Judson, *Physical Geology* (Prentice-Hall, New York, ed. 2, 1958), p. 87.
3. J. H. Feth, C. E. Roberson, W. L. Polzer, *U.S. Geol. Surv. Water Supply Paper 1535 I* (1964), pp. 1–70.
4. Supported by grants from the Petroleum Research Fund of the American Chemical Society, the committee on experimental geology at Harvard University, and NSF.

21 January 1965