

## SILICA IN STREAMS AND GROUND WATER

STANLEY N. DAVIS

Department of Geology, Stanford University, Stanford, California

**ABSTRACT.** A survey of published chemical analyses shows that the silica content of natural water is less variable than any of the other major dissolved constituents. The median value of silica for ground water is 17 ppm and for stream water, about 14 ppm. Concentrations of less than 3 ppm are found only in lake and ocean water or water derived recently from rain or snow.

The most important factor controlling silica in ground water is the rock type in contact with the water. Salinity, pH, and relative percentage of various ions do not normally have a measurable influence on natural silica concentrations. Biological activity removes silica from some streams, particularly those passing through lakes.

The total quantity of silica exported in solution by streams is related directly to the amount of runoff. Rates of silica removal vary from less than 0.01 mg/cm<sup>2</sup>/yr in deserts to more than 2.0 mg/cm<sup>2</sup>/yr in humid mountainous regions. Vegetation and surface temperature show no discernible effects either on rates of removal or on absolute silica concentrations. Consequently, the common notion that moist tropical climates produce a more rapid removal of silica than do moist temperate and moist subarctic climates needs further scrutiny.

### INTRODUCTION

The silica content of natural water is of particular interest in geology inasmuch as it is related to such diverse problems as the origin of laterites, the diagenesis of sandstone, and the formation of chert. Recent geochemical work (Krauskopf, 1956; Lier, 1959; Morey, Fournier, and Rowe, 1962; Lewin, 1961; Pickering, 1962; and Siever, 1962) has outlined many of the physical and chemical factors that control the content of silica in water at low temperatures and pressures. Relations between field and laboratory data, however, are not well enough established to clarify many details connected with the hydrogeologic distribution of silica. For example, laboratory work suggests that temperature might be of prime importance in controlling silica concentrations in most natural water. Analyses of normal surface and ground water, nevertheless, do not appear to support this idea.

The purpose of this paper is to compare information from published analyses of natural water with the known laboratory behavior of silica. Although most analyses are of water from the United States, a wide variety of natural environments are represented, so a number of general conclusions are made. More data, nevertheless, are needed for certain regions, especially those having humid tropical and dry arctic climates.

### METHOD OF STUDY

Surveys of published water analyses commonly encounter at least five major difficulties. First, the total number of analyses is very large, probably numbering in the hundreds of thousands. Second, the accuracy of the work varies greatly according to the year and the laboratory in which the work was done. Third, the results are commonly contained in obscure publications. Fourth, important information concerning the geologic or hydrologic origin of the water is typically lacking. Fifth, the geographic distribution of samples is uneven. Some areas of several thousand square miles do not have a single water analysis whereas other areas may have more than one analysis per square mile.

To overcome some of these difficulties the following procedure was used. Publications containing large amounts of data from wide geographic regions were used when possible. Where a choice was possible, analyses in recent publications of the United States Geological Survey were chosen. If these were not available, analyses published by state agencies were used. Except for a few waters treated only with chlorine, analyses of water that had been treated chemically prior to sampling were not used. Where total numbers were too great, a sample of from 100 to 500 analyses was taken. An attempt was made to select samples that would be representative of a certain area or region. The following simple system was used where possible: If one analysis was to be chosen from a page or a list, the first in the page or list was taken. If two were to be chosen, the first and last were taken. If three were needed, the first, middle, and last were taken; and so forth. Inasmuch as data were listed alphabetically by towns and counties, no geographic bias is introduced by this system. It was modified, however, for some stream data which were arranged in chronological order. Commonly, a sample from a certain river station is taken on the same day other rivers in the region are sampled. Analyses made periodically were selected according to randomly chosen dates.

Cumulative frequency curves were constructed to facilitate visual comparison of data and to allow a direct reading of 5, 25, 50, 75, and 95 percent values (fig. 1). For areas represented by fewer than 25 analyses, only the median values have been tabulated, and for those represented by 25 to 91 analyses, only the 25, 50, and 75 percent values were tabulated (tables 1, 2, and 3).

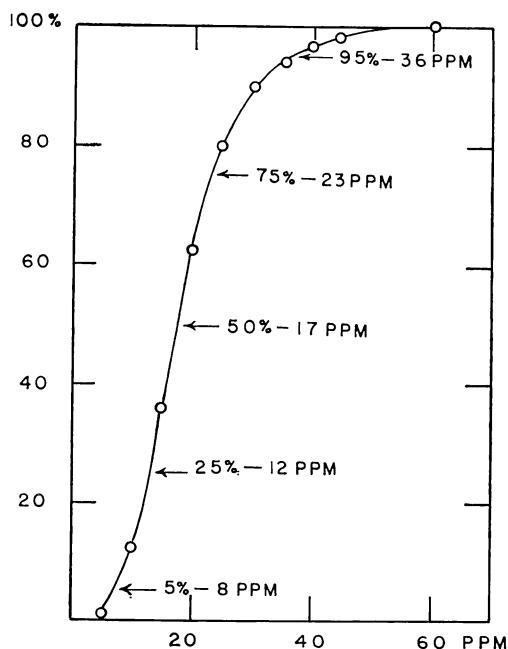


Fig. 1. Cumulative frequency curve of 545 analyses of silica from California streams. Data are from California Dept. Water Resources, Bulletin 65.

TABLE 1  
Silica in potable ground water

Location	Number of Analyses	Ppm silica at given percentile					Source of data
		5	25	50	75	95	
United States	99	7	12	17	26	43	U. S. Geol. Survey Water-Supply Papers 1299 and 1300.
Selected States							
Alaska	62	—	9	17	23	—	U. S. Geol. Survey Water-Supply Papers 1460-A and 1494.
California	132	11	19	28	43	68	California Dept. Water Resources Bull. 66.
Florida	137	4	9	15	21	31	Florida Board of Conserv., Water Research Paper No. 6.
Georgia	90	—	18	28	37	—	Georgia Geol. Survey Bulls. 49, 52, and 55.
Kansas	127	3	11	19	30	48	Kansas Geol. Survey V. 12 and Bulls. 85, 96 pt. 5, 98, 100, and 120.
Maryland	483	5	9	14	24	50	Maryland Dept. Geology and Mines, Water Resources Bulls. 13, 14, 15, 16, 17, 18, 21, 22.
North Dakota	107	7	15	23	27	42	North Dakota Geol. Survey Bull. 11.
Texas	512	8	13	17	27	57	U. S. Geol. Survey Water-Supply Papers 1047, 1069, 1070, and 1106.
Local Areas							
Oahu, Hawaii	63	—	17	27	39	—	Terr. Hawaii Div. Hydrography Bull. 1.
Puerto Rico	5	—	—	22	—	—	U. S. Geol. Survey Water-Supply Paper 1460-A.
Brazil, East central	4	—	—	12	—	—	see references (Kegel, 1955).
Virgin Islands	21	—	—	37	—	—	U. S. Geol. Survey Water-Supply Paper 1067.
Pagan Island, Marianas	11	—	—	51	—	—	see references (Corwin, Bonham, Terman, and Viele, 1957).
Saipan Island, Marianas	15	—	—	7	—	—	see references (Davis, D., 1959).
Okinawa Island, Ryukus	12	—	—	12	—	—	see references (Cameron, Flint, and Saplis, 1958).

TABLE 1 (Continued)

Location	Number of Analyses	Ppm silica at given percentile					Source of data
		5	25	50	75	95	
Salinas Valley, Calif.	90	—	39	41	46	—	California Dept. Water Resources Bull. 66.
Sacramento Valley, Calif.	31	—	52	64	70	—	California Dept. Water Resources Bull. 66.
Santa Ana, Calif.	101	6	9	14	19	25	U. S. Geol. Survey Water-Supply Paper 1136.
Santa Ynez, Calif.	32	—	28	38	43	—	U. S. Geol. Survey Water-Supply Paper 1107.
West Texas	132	10	19	30	44	60	U. S. Geol. Survey Water-Supply Paper 1106.
East Kansas	67	—	5	9	11	—	Kansas Geol. Survey V. 11 and 12.
West Kansas	59	—	32	41	47	—	Kansas Geol. Survey Bulls. 100, 116, and 117.
Owyhee Co., Idaho	36	—	78	85	93	—	U. S. Geol. Survey Water-Supply Paper 1460-D.
Matanuska Valley, Alaska	26	—	9	13	17	—	U. S. Geol. Survey Water-Supply Paper 1494.
Utah, Southeast	6	—	—	20	—	—	U. S. Geol. Survey Prof. Paper 424-C.
Atlanta, Ga.	41	—	15	18	26	—	Georgia Geol. Survey Bull. 55.
Coastal Plain, Ga.	37	—	35	38	46	—	Georgia Geol. Survey Bull. 52.
Maryland, water from various rocks, schist, phyllite marble granodiorite gabbro quartzite	50 9 22 12 9	— — — — —	8 — — — —	11 11 26 24 18	18 — — — —	— — — — —	Maryland Dept. Geology and Mines, Water Resources Bulls. 14, 17, 21, and 22.

In this table and those that follow complete bibliographic references are given only for obscure publications.

TABLE 2  
Silica in saline water and brine

Location	Number of analyses	Ppm silica at given percentile					Source of data
		5	25	50	75	95	
Illinois	482	3	7	13	18	33	Illinois Geol. Survey, Petroleum, v. 66.
North Dakota	504	6	13	21	28	36	U. S. Geol. Survey Water-Supply Paper 1428.
By Formations							
Hell Creek and Fort Union	226	6	10	15	22	35	"
Dakota	66	—	11	17	21	—	"
Pleistocene	212	13	21	26	31	38	"
Pennsylvania	37	—	7	9	15	—	Pennsylvania Geol. Survey Bull. M-47.
Texas	61	—	11	16	23	—	U. S. Geol. Survey Water-Supply Paper 1365.
New Mexico	130	8	14	20	26	55	U. S. Geol. Survey Water-Supply Paper 1601.
By Eras							
Paleozoic	44	—	15	19	23	—	"
Mesozoic	29	—	11	14	18	—	"
Cenozoic	57	—	18	23	37	—	"

TABLE 3  
Silica in stream water

Location	Number of analyses	Ppm silica at given percentiles					Source of data
		5	25	50	75	95	
United States	142	3	8	14	18	33	U. S. Geol. Survey Water-Supply Papers 1450, 1451, 1452, and 1453.
Western United States	82	—	11	15	23	—	U. S. Geol. Survey Water-Supply Paper 1575.
Alaska	63	—	4	7	10	—	U. S. Geol. Survey Water-Supply Paper 1500.
California	545	8	12	17	23	36	California Dept. Water Resources Bull. 65
Sierra Nevada, California	21	—	—	16	—	—	"
Puerto Rico	11	—	—	13	—	—	U. S. Geol. Survey Water-Supply Paper 1460-A.
Gabon	17	—	—	7	—	—	see table 4.
Glacial "milk" various localities	17	—	—	1.5	—	—	see references (Keller and Reesman, 1963).
Greenland	8	—	—	2.8	—	—	see references (Davis, S., 1961).
Africa	53	—	16	24	35	—	U. S. Geol. Survey Prof. Paper 404-G.
Venezuela	8	—	—	16	—	—	"

Water analyses generally give silica in parts per million as  $\text{SiO}_2$ , a convention followed in this report. Modern chemical work, however, indicates that most silica exists in natural water as an unionized silicic acid,  $\text{H}_4\text{SiO}_4$ , rather than a colloid or a silicate ion (Krauskopf, 1956).

#### NATURAL RANGE OF SILICA CONCENTRATION

Silica commonly accounts for 5 to 10 percent of the total dissolved solids in potable water (fig. 2) and less than 1 percent of the total dissolved solids in saline water and brine. Extreme ranges of silica in natural water are from a minimum of less than 0.1 parts per million by weight (ppm) in snow to almost 4000 ppm in a California mineral spring (Feth, Rogers, and Roberson, 1961). Although silica is one of the more common dissolved constituents of water, it is rarely the most abundant constituent. The highest concentration of silica relative to total dissolved solids has been reported from Reykjavik, Iceland. Here, a sample from a well fed by thermal water had a silica content of 172 ppm with a total dissolved solids content of only 333 ppm (White and Sigvaldason, 1963).

Despite the rather wide range found in nature, silica concentrations are notable by their lack of variation in comparison with other major constituents. For example, 90 percent of the public ground-water supplies in the United States have silica concentrations ranging from 7 to 43 ppm (table 1 and fig. 2) while 90 percent have sulfate concentrations ranging from 1 to 300 ppm (fig. 2), or a variation of almost 8 times that of silica. The steepness of the cumulative frequency curve of silica in figure 2 compared with the other curves

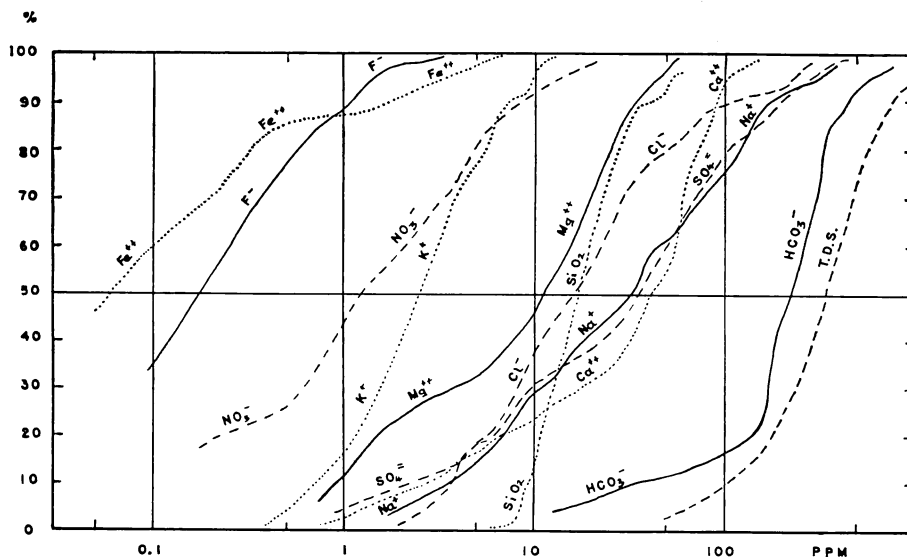


Fig. 2. Cumulative frequency curve of 99 analyses of various dissolved constituents in potable ground water from the United States. Data are from U. S. Geological Survey Water Supply Papers, 1299 and 1300.

indicates that silica is the least variable of the major constituents in ground water. This is also probably true of river and lake waters although the matter was not studied in detail.

Median values of silica in potable ground water from different areas and regions vary from 9 to 85 ppm (table 1). Medians for saline water and brines vary from 9 to 26 ppm (table 2). The median for all ground water in the United States is close to 17 ppm and for all streams is about 14 ppm (table 3). If the median value for streams were based on total water discharged by the stream and not on aerial distribution of sampling, it would be roughly 10 ppm. Livingstone (1963) has estimated the weighted mean concentration of silica in all rivers of the world to be 13.1 ppm which is close to the values calculated for the United States.

#### GEOCHEMICAL CONTROLS

*Relative Ion Concentrations.*—The relative concentration of various ions has been thought to influence the amount of silica in natural waters (Hem, 1959; Lovering, 1962). As a rough test of this hypothesis, 121 analyses of water having 40 ppm or more of silica and 128 analyses having 15 ppm or less of silica were plotted on trilinear diagrams of the type described by Piper (1944) (figs. 3 and 4). Although waters from certain geographical areas have similar proportions of dissolved constituents, no clear cut distinction is apparent between waters high in silica and those low in silica. There is a suggestion in the diagrams, however, that water low in silica tends to contain a greater proportion of calcium than does water high in silica. Also, water high in silica is most commonly high in relative percentage of bicarbonate.

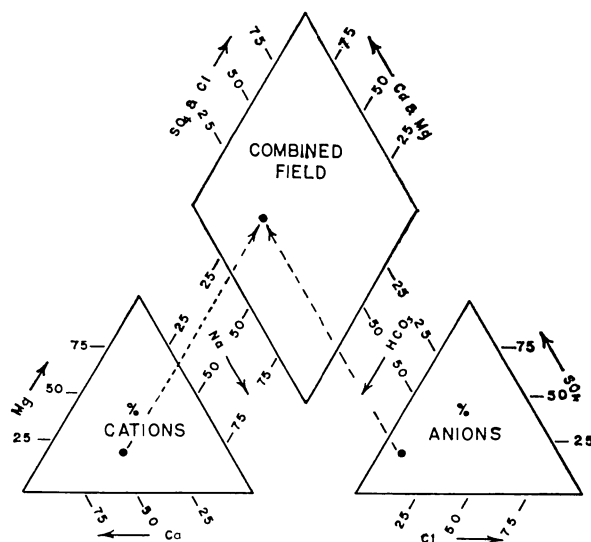


Fig. 3. Trilinear diagram used to represent relative percentage of milligram equivalents of major ionic constituents in water. Each analysis is represented by one point on each field, or three points in the entire diagram.



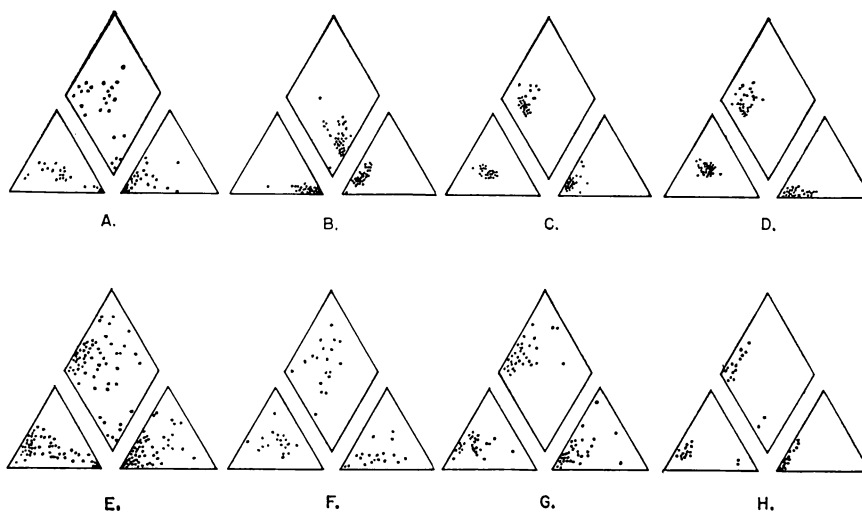


Fig. 4. Relative percentage of ions in water from various localities. A through D are analyses of water with 40 ppm or more  $\text{SiO}_2$ , and E through H are analyses of water having 15 ppm or less  $\text{SiO}_2$ . Regions represented are: A. United States; B. Owyhee County, Idaho; C. Western Kansas; D. Sacramento Valley, California; E. United States; F. Maryland; G. Eastern Kansas; H. Matanuska Valley, Alaska.

Further work is needed to test the hypothesis adequately. Specifically, a larger sample of analyses is needed so adequate statistical tools can be used. The absolute concentration of ions along with their relative proportions should also be considered. A study of field data alone, nevertheless, may not be sufficient, because, as Hem (1959) has pointed out, a deficiency of silica associated with large amounts of calcium may be due to the very small amounts of soluble silica in many calcium-rich sedimentary rocks rather than a reduction in silica solubility by the calcium ion in the water.

Aluminum is the only dissolved constituent in water that is known to reduce significantly the amount of silica that can be held in solution (Okamoto, Okura, and Goto, 1957). Many older water analyses report 1 to 2 ppm aluminum. Recent spectrographic analyses of samples from California, on the other hand, suggest that almost all natural water has less than 0.1 ppm aluminum (W. D. Silvey, personal communication, 1962). These concentrations of aluminum are much lower than those used by Okamoto, Okura, and Goto (1957) in their laboratory studies of silica in sea water. It is doubtful if the low concentrations of aluminum found in most river and ground water will have any measurable effect on natural silica concentrations. Acid water, such as might be found near oxidizing sulfide deposits or accumulations of decaying organic material, could contain several ppm of dissolved aluminum (Hem, 1959) which would have a marked effect on silica solubility.

**Total Dissolved Solids.**—Laboratory experiments have shown that the rate of dissolution, but not the final equilibrium solubility, is increased by an increase in total dissolved solids (Krauskopf, 1959; Siever, 1962). No indication of short-term rates of dissolution in saline water are given by the data studied.

The data do indicate that total dissolved solids do not affect silica concentrations of water which has been in the subsurface for as long as several years. The concentrations in saline water are almost identical with the concentrations in fresh water, provided the rocks in contact with the water are of the same general type (tables 1 and 2). Fresh ground water in Texas has a median of 17 ppm  $\text{SiO}_2$ . Saline water from essentially the same formations but at a greater depth has a median of 16 ppm  $\text{SiO}_2$ . Brine from Pennsylvania has a median of 9 ppm. Fresh ground water from similar rocks in eastern Kansas also has a median of 9 ppm. Brackish water and fresh water in North Dakota, although not from identical formations, have nearly the same silica content.

*Temperature.*—An increase in water temperature will increase both the rate of dissolution and the equilibrium solubility of silica (Kennedy, 1950; Morey, Fournier, and Rowe, 1962; Siever, 1962; White, Brannock, and Murata, 1956). If temperature were the only control of silica solubility, an increase of roughly 50 percent in silica content would be expected between arctic water with temperatures of from 0° to 5°C and tropical water with temperatures of from 25° to 30°C. An even greater difference should be expected between shallow ground water and water from deep oil wells because of the increase in temperature with depth. These large differences simply do not exist. Oil-field waters (table 2) have about the same silica concentrations as shallow ground water (table 1). Furthermore, ground water from subarctic, temperate, and tropical regions shows no difference that could be ascribed to variations of water temperature (table 1). Hot springs contain the only phreatic water that has an anomalously high silica content attributable solely to elevated temperatures (White, Brannock, and Murata, 1956).

Rivers in tropical and temperate regions may have significantly higher silica concentrations than arctic rivers (table 3 and Davis, 1961). Differences, however, are probably not entirely related to water temperature. Removal of silica by diatoms and sponges in abundant arctic lakes within the stream systems as well as contribution of water directly from melting snow with limited opportunity for silica dissolution may account for lower silica in many arctic streams. The fact that some tropical waters are also low in silica (table 4) suggests that silica concentrations in streams are not primarily controlled by temperature. Some of the unusually high values reported for Africa (table 3), moreover, may be due to the dissolution of silica from glass sample containers (Livingstone, 1963).

*Rate of Dissolution.*—The rates of dissolution of all forms of silica are relatively slow provided the water has a temperature of less than 30°C and pH is in the range of 6 to 9. With silica gel, at least 10 days are needed for water at 25°C to reach 50 percent of saturation (Krauskopf, 1956). Kaolinite may take several years to reach equilibrium with respect to dissolved silica (W. L. Polzer, 1962, personal communication). Quartz will certainly take several years, if not centuries, to approach equilibrium at room temperatures (Morey, Fournier, and Rowe, 1962; Siever, 1962). Leaching artificially crushed latite and andesite produced water with 8 to 24 ppm  $\text{SiO}_2$  at 0°C and 32 to 80 ppm  $\text{SiO}_2$  at 35°C after only 3 weeks (Pickering, 1962). The rate of silica leaching from these rocks was found by Pickering to be accelerated by decreasing the

TABLE 4

## Silica in water from Gabon (Africa)

(Unpublished analyses by C. F. Park, Jr., 1958)

Location	Source of Water	pH	Silica, ppm
Bengoue	Artificial pool	4.8	0
"	Ground water in mine	5.1	1
"	"	5.1	0
"	"	4.4	3
"	"	4.5	4
"	"	5.1	0
"	"	6.1	2
"	"	5.2	3
Belinga	Surface stream	5.6	5
"	"	6.4	14
"	Ivindo River	5.4	9
"	Ground water in mine	5.2	0
"	Tap water	7.7	10
"	Small jungle stream	6.8	8
"	"	6.6	8
"	"	6.8	6.5
"	"	6.4	3
"	"	6.7	5
"	"	7.0	4
"	"	6.5	3
"	"	6.8	3.5
"	"	6.8	9
"	"	6.7	8
"	"	6.2	5
"	"	6.5	7
"	"	6.5	4
"	"	6.9	6

pH. In contrast to this relatively rapid solution of silica from artificially crushed rock, Keller and Reesman (1963) found that glacial meltwater having a fine suspension of flour of various rock types did not have more than 17 ppm  $\text{SiO}_2$  with a median of only 1.5 ppm in a total of 17 samples, even though the samples were in their containers prior to analysis for roughly 3 months and were probably at room temperature for a considerable part of this time. Various rocks artificially ground to a fine powder and mixed with distilled water contained a maximum of 21 ppm  $\text{SiO}_2$  after an unspecified length of time (Keller and Reesman, 1963).

If one considers only the equilibrium between quartz and water, silica concentrations in natural water would be expected to increase very slowly over many decades or centuries. Experimental work with amorphous silica and with crushed rock, on the other hand, suggests that some natural water could acquire most of its dissolved silica within a few months or years. Field evidence favors a rapid acquisition of silica. As shown in the previous section, deeply buried, relatively static saline water contains about the same amount of silica as fresh water that is actively circulating in shallow aquifers. In addition, one of the regions with the most silica in ground water is the heavily irrigated eastern side of the Central Valley (Sacramento-San Joaquin) of California (table 1; Davis and Hall, 1959). The imported water used for irrigation has

from 8 to 15 ppm  $\text{SiO}_2$ . This is increased to between 30 and 70 ppm  $\text{SiO}_2$  after only a short distance of subsurface travel which probably takes less than 20 years. An area of high silica water in Hawaii has also been explained by assuming a rapid leaching by irrigation water (Mink, 1962).

The most spectacular evidence for a rapid natural dissolution of silica comes from analyses of stream water. At low discharge, most perennial streams are sustained by ground-water flow, but during periods of high discharge the stream is fed almost entirely by storm runoff. Owing to the dilution of the small amount of ground water by rainwater or snowmelt, the total dissolved solids at periods of high discharge are much less than at low discharge (figs. 5, 6, and 7). Chloride and most other dissolved constituents show a relation to discharge similar to that of total dissolved solids. Silica, on the other hand, maintains about the same concentration despite variations of discharge. This indicates that storm runoff acquires its silica in a few days or less. Several hypotheses for this apparent rapid dissolution of silica are given below.

(1) Suspended silt and clay-size particles present in storm runoff will expose a much larger surface area to solution than is normally present during periods of lower discharge. This should favor a rapid dissolution of silica.

(2) Turbulent streams with a coarse bed load will fracture minerals, particularly quartz, which could produce strained surfaces subject to rates of dissolution much greater than on the unstrained surfaces. This effect in quartz has been measured in the laboratory by Lier (1959) and Morey, Fournier, and Rowe (1962).

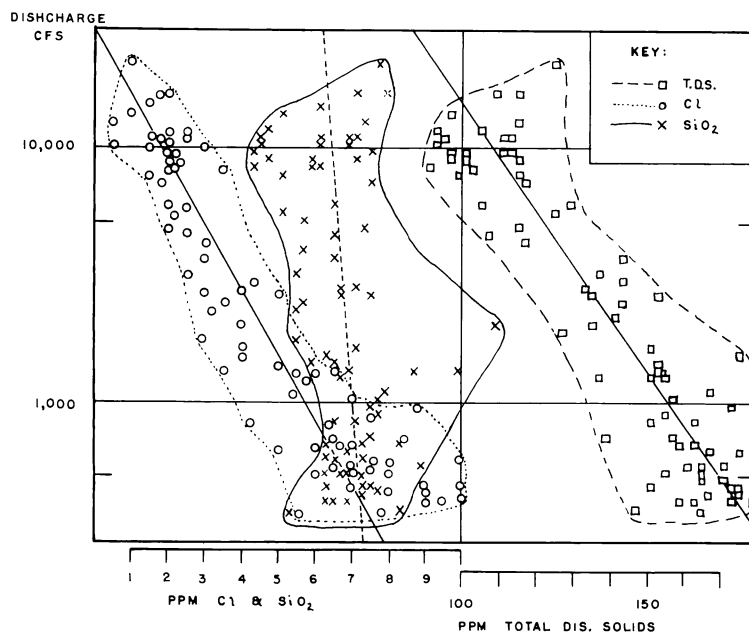


Fig. 5. Variation of chloride, silica, and total dissolved solids with discharge in the Matanuska River, Alaska.

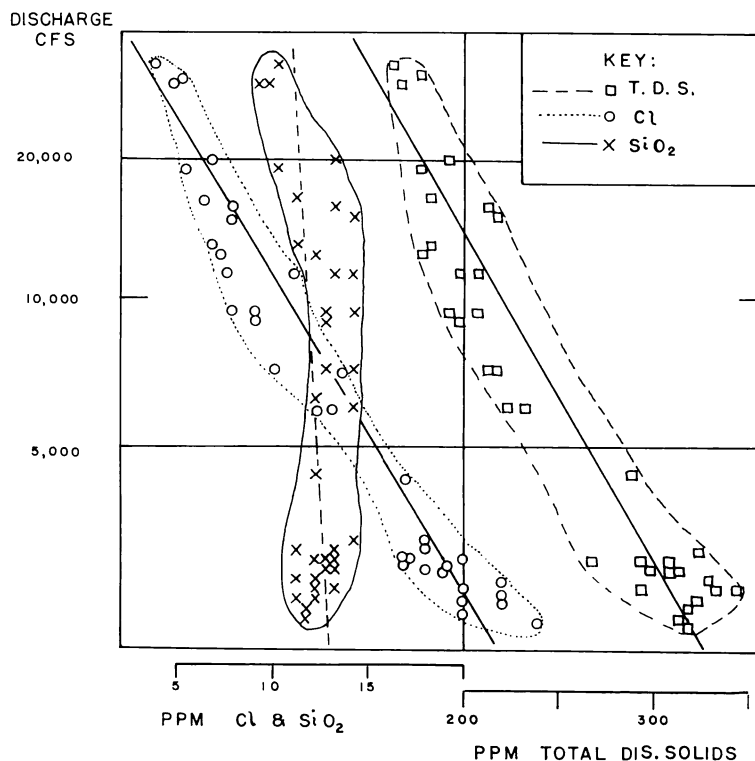


Fig. 6. Variation of chloride, silica, and total dissolved solids with discharge in the Snake River, Idaho.

(3) Much runoff during and shortly after storms will actually travel through the upper part of the soil profile; this is the “interflow” of hydrologists (Linsley, Kohler, and Paulhus, 1958, p. 150). Thus, storm water arriving at a stream may contain considerable silica leached from the soil. Jones and Hendreck (1963) report 6 to 67 ppm  $\text{SiO}_2$  in normal soil water. Some of this could be displaced by infiltrating rain water.

(4) During low discharge the travel time of the water in the stream channel will be much longer than during high discharge. Biological activity, particularly that of diatoms, will, therefore, be more efficient at low discharge in the removal of silica which is introduced into the stream by ground water.

Objections can be found for each of the hypotheses. The low silica concentrations found in glacial milk by Keller and Reesman (1963) suggest that the increased surface area of abundant suspended rock and mineral fragments during a storm runoff may not cause a rapid dissolution of silica. Fracturing minerals plus minor abrasion, nevertheless, may be important. Water in contact with quartz in a rapidly rotating polyethylene bottle required 15 days or more to reach a concentration of 10 ppm (Morey, Fournier, and Rowe 1962). Keller, Balgard, and Reesman (1963) achieved a much faster release of silica

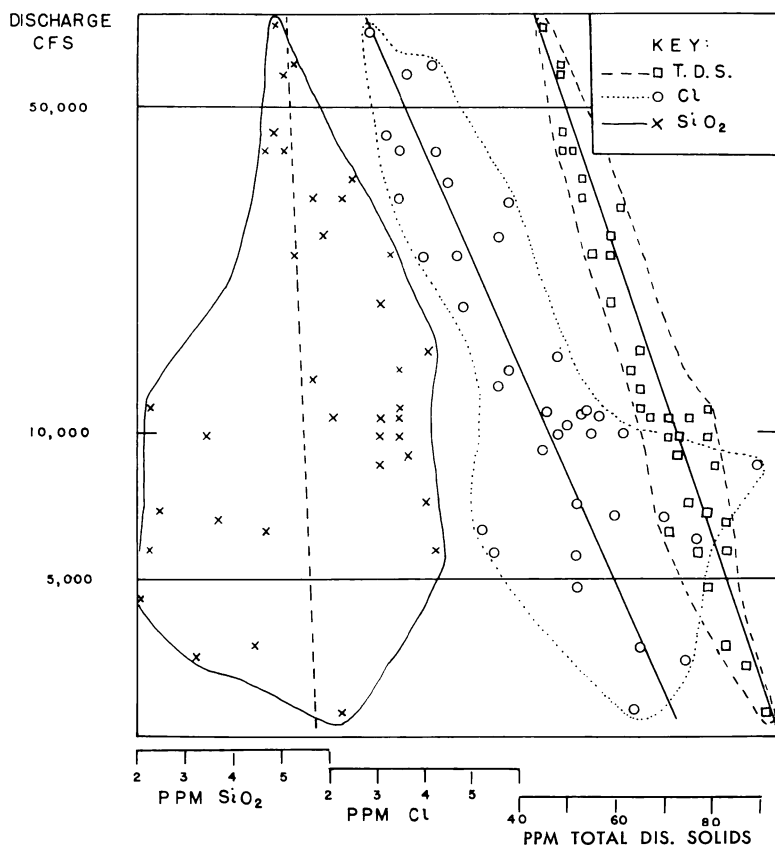


Fig. 7. Variation of chloride, silica, and total dissolved solids with discharge in the Connecticut River, Connecticut.

by fine-grinding of various minerals in distilled water. A difficulty with postulating a silica source from most rockforming minerals is that other material in addition to silica should also go into solution which is contrary to the observed decrease in total dissolved solids in storm runoff. This argument could also be applied to the theory of obtaining silica from the soil horizon. If weathering processes in the soil prepare material for leaching by interflow, other dissolved constituents should also be removed. The biological activity theory is also weak. Streams that head in mountains and receive little inflow in lower reaches generally fail to show a progressive decrease in silica which would be expected if diatoms were important in removing silica from stream water.

*Amount of Water Available.*—The amount of silica removed in solution from various drainage basins in the United States has been computed using weighted mean values of dissolved silica of the United States Geological Survey (table 5). A plot of the silica removed in relation to total annual runoff in the basins indicates that rates of removal are directly related to runoff (fig. 8).

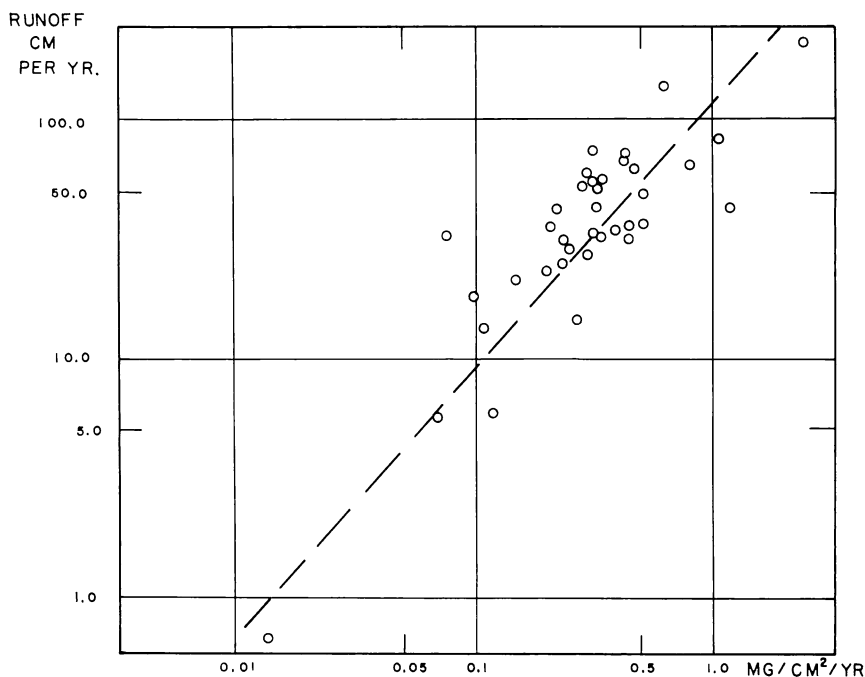


Fig. 8. Relation of runoff to removal of silica from various drainage basins in the United States. Data are also given in table 5.

This is consistent with Loughnan's (1962) conclusion that rates of silica removal were closely related to the leaching potential. Durum, Heidel, and Tison (1961) present a diagram similar to figure 8 which shows that the amount of total dissolved solids removed from basins is also directly related to the runoff from the basin.

*Activity of Organisms.*—The efficiency of microorganisms to remove silica from lake and ocean water is well documented (Hutchinson, 1957, p. 791-800). Lovering (1959) has also shown that trees, particularly those of the tropics, will concentrate silica in leaves and wood and has suggested that a tropical rainforest might be an environment of maximum rates of silica removal due to mobilization of the silica by plants. Lovering's hypothesis is difficult to test with the data reviewed for the present paper. Rates of silica removal given in table 5 do not show any increase related to semi-tropical vegetation. Some of the highest values are from Alaska, and some of the lowest are from Florida. Modern information on rivers draining tropical rainforests is particularly difficult to locate in the published literature. Incomplete information for the Congo and Mekong rivers (Durum, Heidel, and Tison, 1960 and 1961) suggest rates of silica removal similar to those of the San Joaquin River, California: Columbia River, Washington; and Matanuska River, Alaska. Leneuf and Aubert (1961) have estimated rates of silica removal of from 0.7 to 2.5 mg/cm<sup>2</sup>/yr in the Ivory Coast where the rainfall varies from 1800 to 2500 mm/yr.

Runoff is probably between 800 and 1500 mm/yr. A watershed on Oahu Island, Hawaii, has been reported a rate of silica removal of 3.6 mg/cm<sup>2</sup>/yr with a rainfall of 1400 mm/yr (Moberly, 1963). These runoff and silica removal rates are within the probable range of values for streams of temperate and subarctic regions (table 5, fig. 8). Rates calculated for Uganda (Trendall, 1962) are roughly 0.63 mg/cm<sup>2</sup>/yr, the exact amount depending on certain assumptions as to rates of surface erosion.

*Mineral and Rock Types.*—Laboratory studies of silica solubility suggest that the most important control of silica in ground water should be the mineralogy of material in contact with the water. Water in equilibrium with quartz at room temperature will have from 6 to 12 ppm SiO<sub>2</sub> in solution (Morey, Fournier, and Rowe, 1962; Lier, 1959). Water in equilibrium with silica gel and other forms of amorphous silica will have from 100 to 140 ppm SiO<sub>2</sub> (Krauskopf, 1956); the presence of oxides of iron and aluminum, however, will materially reduce the silica in solution (Jones and Handreck, 1963). Equilibrium concentrations for clay minerals, feldspars, micas, and other siliceous rock-forming minerals are probably intermediate between the extremes for quartz and amorphous silica (Siever, 1962; Keller, Balgord, and Reesman, 1963). From the experimental data, one would expect the most silica in water from partly weathered to unweathered volcanic rocks and the least from limestone or dolomite. Field data support these conclusions. Patterson and Roberson (1961) found only 5 ppm SiO<sub>2</sub> in water from weathered basalt which contained abundant clay minerals and other products of weathering, whereas 50 ppm SiO<sub>2</sub> was in water from unweathered basalt in the same area. Water from volcanic rocks in Pagan Island, Marianas, has about seven times the amount of silica that is found in water from limestone aquifers in Saipan Island, Marianas (table 1).

Records of the lowest silica concentrations are from analyses of water from limestone aquifers in eastern Kansas, Saipan, and Maryland (table 1). Next are those from sandstones (Dakota Sandstone and Fort Union Formation, table 2). Waters of considerably higher silica concentrations are from sands containing feldspar with some interstratified volcanic detritus (Sacramento Valley, California, and Western Kansas, table 1) and from basaltic and andesitic rocks (Pagan, Marianas, and Oahu, Hawaii, table 1). The greatest amount of dissolved silica is found in sediments rich in pyroclastics (Owyhee County, Idaho, table 1).

The uniformity of silica concentrations in water from aquifers of the same composition is further indication that mineralogy is one of the most important factors controlling silica in ground water. If water temperatures were important, wells of vastly different depths such as are found in the Central Valley, California, should show a much greater difference in silica due to a rapid increase in water temperature with depth (Davis and Hall, 1959). If rates of dissolution were critical, wells located at increasing distances from recharge areas should also show systematic increases in silica. Such trends are not apparent. A highly uniform silica concentration in an alluvial aquifer of uniform composition is shown in the data from Salinas Valley, California (table 1).



TABLE 5  
Silica removed by streams

River	Sampling point Nearest city	State	Number of Analyses	Runoff cm/yr	Silica Weighted Avg ppm	Watershed Area km <sup>2</sup>	Silica Removed mg/cm <sup>2</sup> /yr
Anchor	Anchor Point	Alaska	45	43	24	585	1.26
Matanuska	Palmer	"	77	68	6.7	5,360	0.46
Ship	Anchorage	"	44	54	6.5	236	0.35
Trail	Lawig	"	37	138	4.8	505	0.67
Tosina	Tosina	"	38	76	4.5	1,090	0.34
Yukon	Eagle	"	35	21	7.5	294,000	0.16
Yukon	Rampart	"	44	18	6.0	516,000	0.11
Carmel	Carmel	California	10	5.8	23	505	0.13
San Joaquin	Biola	"	28		11		
(discharge at Friant)				49		4,670	0.54
Smith	Crescent City	"	16	210	12.5	1,590	2.63
Yuba	Smartsville	"	18	82	13.5	2,860	1.12
Housatonic	Falls Village	Connecticut		59	5.5	1,635	0.32
Quinnipiac	Wallingford	"	30	66	13	282	0.85
Willimantic	S. Coventry	"	31	61	8.5	313	0.51
Hillsborough	Zephyrhills	Florida	35	42	8.3	570	0.35
Little Manatee	Wimauma	"	36	42	5.8	376	0.24
Moultrie	St. Augustine	"	37	33	14	60	0.46
St. Johns	Cocoa	"	38	33	2.5	3,220	0.082
Suwannee	Branford	"	35	30	8.4	18,300	0.25
Snake	Heise	Idaho	36	35	10	14,900	0.34
Tennessee	Kentucky Dam	Kentucky	36	55	6.3	104,000	0.35
Mississippi	Francisville	Mississippi	36		8.8		
(discharge at Vicksburg)				13		3,740,000	0.12

TABLE 5 (Continued)

River	Sampling point Nearest city	State	Number of Analyses	Runoff cm/yr	Silica Weighted Avg ppm	Watershed Area km <sup>2</sup>	Silica Removed mg/cm <sup>2</sup> /yr
Embarrass	Embarrass	Minnesota	15	26	10	242	0.26
Partridge	Aurora	"	17	29	9.2	404	0.27
West Two	Iron Junction	"	17	23	9.2	177	0.21
Pecos	Artesia	New Mexico	46	0.73	20	39,600	0.0014
Chenango	Greene	New York	31	53	5.8	1,550	0.31
Mohawk	Little Falls	"	27	71	6.4	3,490	0.45
Unadilla	Rockdale	"	31	55	6.5	1,340	0.36
Neuse	Selma	North Carolina	14	37	15	3,050	0.55
(discharge at Clayton)							
Tar	Grimesland	"	37	35	13	7,100	0.46
(discharge at Tarboro)							
Trent	Trenton	"	38	35	6.4	435	0.22
Columbia	The Dalles	Oregon	37	34	13	614,000	0.42
Brazos	Richmond	Texas	37	5.8	13	114,000	0.075
Neches	Evadale	"	37	27	12	20,500	0.33
Sabine	Ruliff	"	38	52	11	24,500	0.36
Trinity	Romayor	"	41	15	19	44,500	0.28

Data for this table are taken from various Water Supply Papers of the U. S. Geological Survey; the following were most useful: 1450, 1451, 1452, 1453, 1466, 1486, 1500, 1520, 1524, 1570, and 1640.

Comparisons similar to those made with silica in ground water are difficult to make for surface water because most of the watersheds for which data are given in tables 3, 4, and 5 are of composite lithology. There is a suggestion, however, that silica in California streams which drain mostly igneous and metamorphic rocks is somewhat higher than silica in Florida streams which drain marine sedimentary rocks (table 5).

#### ORIGIN OF LATERITES

Geologists and geochemists commonly assume that silica is much more mobile in tropical regions than in temperate or subarctic regions (Dapples, 1959, p. 167; Goldschmidt, 1954, p. 371; Rankama and Sahama, 1950, p. 272). The present study, though somewhat lacking in data from tropical areas, strongly suggests that air temperature and type of vegetation have little overall effect on silica mobility in the hydrosphere. If removal of silica were the sole factor to consider, then one might conclude that, given enough time, laterites could form in any climate having sufficient precipitation to leach material from the soil profile. Rates of evapo-transpiration, microbiological activity, chemical character of forest litter, and other factors related indirectly to climate, however, could be important in the process of laterization. For example, intense biological activity in tropical soils may promote silica leaching primarily near the surface. Water percolating downward from the zone of intense leaching would be almost saturated with respect to silica. In regions of less intense biological activity, the dissolution of silica may not be localized near the surface but may also take place within deeply buried aquifers. Tropical and temperate regions could thus contribute the same amount of silica per unit area to streams, but the silica would originate in different parts of the drainage basins. Nevertheless, until better comparative data are available, reasonable doubts can be raised concerning the traditional assignment of all laterization to tropical environments. A similar conclusion has been reached by Pickering (1962) who reviewed chemical and mineralogical data of various soils and failed to find evidence that would restrict laterization or podzolization to unique climatic regions.

Products of lateritic weathering will not accumulate if rates of mechanical erosion exceed rates of chemical weathering. In areas of rapid erosion, the top of the soil will be removed after the initial silica content has been reduced by only a few percent through chemical leaching. Figure 9 shows the relation between rates of chemical leaching of silica, mechanical erosion, and accumulation of silica-free residuum for a rock with an original  $\text{SiO}_2$  content of 50 percent. Present-day mechanical erosion in most large drainage basins probably averages between 5 and 10 mg/yr/cm<sup>2</sup>. From a study of small watersheds, Brune (1948) found that sediment production rates in midwestern United States varied between about 3 and 400 mg/yr/cm<sup>2</sup>. Highest rates were associated with cultivated land and were as much as 75 times greater than rates that probably existed prior to cultivation. Thus, under original conditions, rates of from 1 to 5 mg/yr/cm<sup>2</sup> probably prevailed. Inasmuch as most present rates of silica leaching are less than 1.0 mg/yr/cm<sup>2</sup>, it is doubtful that a silica-

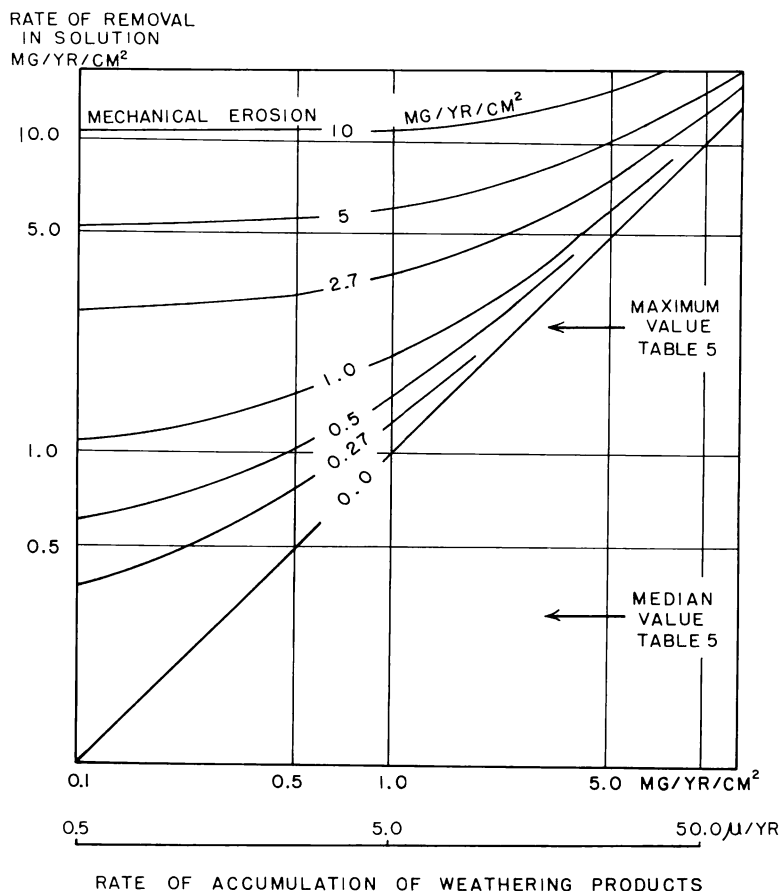


Fig. 9. Theoretical relation between the rate of silica removal in solution, rate of mechanical erosion of silica-free residue, and the rate of accumulation of silica-free residue. Parent rock is assumed to be 50 percent  $\text{SiO}_2$  by weight, and the products of weathering are assumed to have a density of 2.0 g/cm<sup>3</sup>.

free residuum could eventually accumulate in most areas of the United States even if sufficient time were available and erosion rates were reduced to those of the virgin land. Soils with a marked reduction of silica have formed in parts of the United States. Whether or not it would be possible for these soils eventually to approach the characteristics of laterites most certainly depends on the relative intensity of leaching as compared with mechanical erosion.

Lovering (1959) has suggested that removal of plant remains by wind, animals, and running water could account for much of the loss of silica during laterization. Running water is probably more important than either wind or animals. Water, however, might erode much of the upper part of the soil profile and greatly reduce the rate of laterite accumulation.

## CONCLUSIONS

1. The silica content is less variable than any of the other major dissolved constituents of natural water.
2. The amount of silica in ground water is primarily dependent on the rock and mineral types in contact with the water. Largest amounts are in association with volcanic rocks; intermediate amounts in association with plutonic rocks and sediments containing feldspar and volcanic rock fragments; small amounts of silica are found in water from marine sandstones; the least is from water in carbonate rocks.
3. Data studied failed to show any marked influence on silica concentrations of pH, salinity, climatic regions, surface vegetation, or temperature variations unless above 35°C.
4. Stream water appears to acquire most of its silica within a relatively short period of time, perhaps less than 3 days.
5. Total silica removed in solution from drainage basins by stream water is related directly to the total runoff from the basins.
6. Modern published analyses fail to show a greater mobility of silica in tropical streams and ground water than in waters of other climatic zones, with the possible exception of the arctic.
7. Although other factors may be more significant, rates of silica removal from drainage basins suggest that laterization is not confined to tropical regions.

## ACKNOWLEDGMENTS

Valuable information has been supplied by J. H. Feth, W. D. Silvey, W. L. Polzer, and others of the U. S. Geological Survey. Silica analyses of water from Gabon were generously supplied by C. F. Park, Jr. I am particularly indebted to K. B. Krauskopf for helpful discussions and for critical reading of the manuscript.

## REFERENCES

- Brune, G. M., 1948, Rates of sediment production in midwestern United States: U. S. Dept. Agriculture Soil Conserv. Tech. Pub. 65, 40 p.
- Cameron, C. C., Flint, D. E., and Saplis, R. A., 1958, Military geology of Okinawa-Jima, Ryūkyū-Rettō, v. 2, water resources: Washington, D. C., U. S. Army Engineers, Intelligence Div., Strategic Study, Subfile 7, 82 p.
- Corwin, G., Bonham, L. D., Terman, M. J., and Viele, G. W., 1957, Military geology of Pagan, Mariana Islands: Washington, D. C., U. S. Army Engineers Intelligence Div., Strategic Study, Subfile 19, 259 p.
- Dapples, E. C., 1959, Basic geology for science and engineering: New York, John Wiley and Sons, 609 p.
- Davis, D. A., 1959, Military geology of Saipan, Mariana Islands, v. 2, water resources: U. S. Army, Intelligence Div., Strategic Study, Subfile 19, 96 p.
- Davis, S. N., 1961, Reconnaissance of emergency water supplies in East Greenland, in Hartshorn, J. H., and others, Investigations of ice-free sites for aircraft landings in East Greenland, 1959: Bedford, Mass., L. G. Hanscom Field, U. S. Air Force Surveys in Geophysics, no. 127, p. 119-139.
- Davis, S. N., and Hall, F. R., 1959, Water quality of eastern Stanislaus and northern Merced counties, California: Stanford Univ. Pubs. Geol. Sci., v. 6, no. 1, 112 p.
- Durum, W. H., Heidel, S. G., and Tison, L. J., 1960, World-wide runoff of dissolved solids: Internat. Assoc. Hydrol. Surface Waters Comm., Gen. Assembly Helsinki, Pub. 51, p. 618-628.
- 1961, Worldwide runoff of dissolved solids: U. S. Geol. Survey Prof. Paper 424-C, p. 326-329.

- Feth, J. H., Rogers, S. M., and Roberson, C. E., 1961, Aqua de Ney, California, a spring of unique chemical character: *Geochim. et Cosmochim. Acta*, v. 22, p. 75-86.
- Goldschmidt, V. M., 1954, *Geochemistry*: Oxford, Clarendon Press, 730 p.
- Hem, J. D., 1959, Study and interpretation of the chemical characteristics of natural water: U. S. Geol. Survey Water-Supply Paper 1473, 269 p.
- Hutchinson, G. E., 1957, *A Treatise on Limnology. V. 1: Geography, Physics, and Chemistry*: New York, John Wiley and Sons, 1015 p.
- Jones, L. H. P., and Handreck, K. A., 1963, Effects of iron and aluminum oxides on silica in solution in soils: *Nature*, v. 198, no. 4883, p. 852-853.
- Kegel, Wilhelm, 1955, Aqua subterânea no Piauí (Brazil): *Brazil Div. Geologia e Mineralogia Bull.* 156, 60 p.
- Keller, W. D., Balgord, W. D., and Reesman, A. L., 1963, Dissolved products of artificially pulverized silicate minerals and rocks: Pt. 1: *Jour. Sed. Petrology*, v. 33, p. 191-204.
- Keller, W. D., and Reesman, A. L., 1963, Glacial milks and their laboratory simulated counterparts: *Geol. Soc. America Bull.*, v. 74, p. 61-76.
- Kennedy, G. C., 1950, A portion of the system silica-water: *Econ. Geology*, v. 45, p. 629-653.
- Krauskopf, K. B., 1956, Dissolution and precipitation of silica at low temperatures: *Geochim. et Cosmochim. Acta*, v. 10, p. 1-26.
- , 1959, The geochemistry of silica in sedimentary environments, in Ireland, H. A., *Silica in Sediments—a symposium*: Soc. Econ. Paleontologists and Mineralogists, Spec. Pub. 7, p. 4-19.
- Lenef, N., and Aubert, G., 1961, Calculation of the rate of ferralitization (in French): *Internat. Cong. Soil Sci.*, 7th, 1960, Trans., v. 4, p. 225-228.
- Lewin, J. C., 1961, The dissolution of silica from diatom walls: *Geochim. et Cosmochim. Acta*, v. 21, p. 182-198.
- Lier, J. A. van, 1959, The solubility of quartz: *Utrecht, Kemink en Zoon*, 54 p.
- Linsley, R. K., Kohler, M. A., and Paulhus, J. L. H., 1958, *Hydrology for engineers*: New York, McGraw-Hill, 340 p.
- Livingstone, D. A., 1963, Chemical composition of rivers and lakes, in *Data of geochemistry*, 6th ed.: U. S. Geol. Survey Prof. Paper 440 G, 64 p.
- Loughnan, F. C., 1962, Some considerations in the weathering of the silicate minerals: *Jour. Sed. Petrology*, v. 32, p. 284-290.
- Lovering, T. S., 1959, Significance of accumulator plants in rock weathering: *Geol. Soc. America Bull.*, v. 70, p. 781-800.
- , 1962, The origin of jasperoid in limestone: *Econ. Geology*, v. 57, p. 861-889.
- Mink, J. F., 1962, Excessive irrigation and the soils and ground water of Oahu, Hawaii: *Science*, v. 135, p. 672-673.
- Moberly, Ralph, Jr., 1963, Rate of denudation in Hawaii: *Jour. Geology*, v. 71, p. 371-375.
- Morey, G. W., Fournier, R. O., and Rowe, J. J., 1962, The solubility of quartz in water in the temperature interval from 25° to 300°C: *Geochim. et Cosmochim. Acta*, v. 26, p. 1029-1043.
- Okamoto, G., Okura, T., and Goto, K., 1957, Properties of silica in water: *Geochim. et Cosmochim. Acta*, v. 12, p. 123-132.
- Patterson, S. H., and Roberson, C. E., 1961, Weathered basalt in the eastern part of Kauai, Hawaii: U. S. Geol. Survey Prof. Paper 424-C, p. 195-198.
- Pickering, R. J., 1962, Some leaching experiments on three quartz-free silicate rocks and their contribution to an understanding of laterization: *Econ. Geology*, v. 57, p. 1185-1206.
- Piper, A. M., 1944, A graphic procedure in the geochemical interpretation of water analyses: *Am. Geophys. Union Trans.*, 25th Ann. Mtg., pt. 6, p. 914-923.
- Rankama, Kalervo, and Sahama, Th. G., 1950, *Geochemistry*: Chicago, Illinois, Univ. Chicago Press, 911 p.
- Siever, Raymond, 1962, Silica solubility, 0°-200°C, and the diagenesis of siliceous sediments: *Jour. Geology*, v. 70, p. 127-150.
- Trendall, A. F., 1962, The formation of "apparent peneplains" by a process of combined lateritization and surface wash: *Zeitschr. Geomorphologie*, v. 6, no. 2, p. 183-197.
- White, D. E., Brannock, W. W., and Murata, K. J., 1956, Silica in hot-spring waters: *Geochim. et Cosmochim. Acta*, v. 10, p. 27-59.
- White, D. E., and Sigvaldson, G. E., 1963, Epidote in hot-spring systems, and depth of formation of prophylic epidote in epithermal ore deposits: U. S. Geol. Survey Prof. Paper, 450-E, p. 80-84.