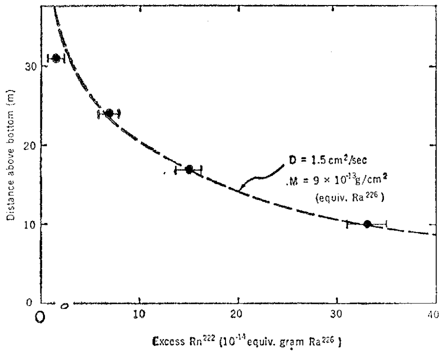

Fig. 3. Excess Rn^{222} as a function of distance above the sea bottom in the South Atlantic at 22°47′S, 32°37′W.

In our previous report it was shown that the following relation existed between the radon excess, C_x^*, and the distance from the bottom.

$$C_x^* = M\sqrt{\frac{\lambda}{D_E}}\ \exp\left(-x\sqrt{\lambda/D_E}\right)$$

where M is the standing crop of radon lost by the sediments, and λ and D_E are as defined above. Data for the profile 23°S, 33°W in the South Atlantic are plotted in Fig. 3. The points can be fit by the theoretical equation if D_E is 1.5 cm^2/sec and M is 9×10^{-13} gram equivalent of Ra^{226} per liter. As previously published (*1*) measurements of radon leakage from the tops of trigger-weight cores yield standing crops of from 1.5 to 35×10^{-13} gram equivalent of Ra^{226} per square centimeter. This amount of radon is also what would be expected from molecular diffusion from the radon-rich pore water [see (*1*)].

For the other two profiles roughly the same standing crop of excess radon is required, but the eddy diffusion rate must be about 30 times higher (that is, ~50 cm^2/sec). Hence the study of the distribution of excess radon near the ocean bottom will prove to be a powerful tool in determining rates of vertical mixing.

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Silica in Alkaline Brines

Abstract. *Analysis of sodium carbonate-bicarbonate brines from closed basins in volcanic terranes of Oregon and Kenya reveals silica contents of up to 2700 parts per million at* pH*'s higher than 10. These high concentrations of* SiO_2 *can be attributed to reaction of waters with silicates, and subsequent evaporative concentration accompanied by a rise in* pH. *Supersaturation with respect to amorphous silica may occur and persist for brines that are out of contact with silicate muds and undersaturated with respect to trona; correlation of* SiO_2 *with concentration of Na and total* CO_2 *support this interpretation. Addition of more-dilute waters to alkaline brines may lower the* pH *and cause inorganic precipitation of substantial amounts of silica.*

The SiO_2 content of natural waters that are not associated with areas of geothermal activity very rarely exceeds 100 parts per million (ppm) (*1*). Commonly accepted saturation values with respect to amorphous silica at 25°C and a *p*H lower than 9.2 are 110 to 140 ppm (*2*). Some chert deposits are thought to have formed by inorganic precipitation of silica (*3*). In recent studies of alkali carbonate brines of a number of closed basins we have encountered waters having exceptionally high silica contents—up to 2700 ppm. These data suggest a simple mechanism for the inorganic precipitation of chert.

Silica contents of brines from four closed basins, three of which belong to the Great Basin province of the western United States, have been plotted against *p*H (Fig. 1), Na (Fig. 2), and total CO_2 when sufficient sample was available (Fig. 3). Silica was determined colorimetrically as the β-silicomolybdate complex (*4*). We have paid special attention to *p*H control and elimination of reductants, and have used tartaric acid to eliminate phosphate interference (*5*). All analyses were repeated several times and checked against synthetic brines of similar composition. Interference by boron or fluoride was negligible. Exceptionally high values of SiO_2 were checked by gravimetric and fusion procedures.

Brines were stored in polyethylene bottles and filtered under pressure through 0.45-μ membranes prior to analysis, although filtration through pore sizes down to less than 0.1 μ showed no effect on silica content. Precipitation of silica during storage was checked by digestion of the complete bottles of duplicate samples. Differences were usually less than 5 percent of the silica content at high concentrations of SiO_2, and much less at low concentrations.

The western Great Basin has several intermontane areas of interior drainage in igneous rock terranes. Most of these basins contain saline lakes or playas with brines high in carbonate; the brines have been derived principally by evaporative concentration. Sodium and carbonate are the dominant ions in solution because alkaline-earth carbonates precipitate, and sources of sulfate or chloride are lacking.

Abert Lake of south-central Oregon, with an area of about 130 km^2, is one of several highly saline remnants of the large pluvial lakes that once occupied the western Great Basin (*6*). The present lake has no outlet, and its level and total surface area reflect the long-term balance between inflow, principally the Chewaucan River, and loss of water by evaporation. Sodium, carbonate species, and chloride ions comprise over 90 percent of the dissolved constituents in Abert Lake and associated springs. In addition to waters from Abert Lake itself, and interstitial solutions from associated lacustrine sediments, we have included a sample from a brine pond on the salt flats at the north end of the lake; here a small seep similar to the lake in solute composition, but of 1/100th the concentration, feeds a pool of highly concentrated chlorocarbonate brine.

Alkali Lake, in Alkali Valley, is a playa of approximately 13 km^2 immediately north of the Abert basin (*7*). More than half the playa area contains numerous circular depressions or potholes, some as much as 9 m across and 1 m or more in depth; the largest contain masses of crystalline sodium salts, chiefly carbonate. Many of them also contain extremely variable and highly concentrated carbonate brines, which apparently result from long-term evaporation of artesian waters at a rate roughly equivalent to discharge (*8*). Samples came from several potholes and the main playa pond.

Deep Springs Lake, in Deep Springs Valley, California, is an intermittent saline water body in a small basin (*9*); about a third of its 13-km^2 area is covered by saline crusts. Inflow is chiefly from groups of springs discharging from a prominent zone of recent faulting. Also within the fault zone are two sag ponds, one of which has no outlet at low stage. Carbonate species predominate in the ponds and springs but are subordinate to sulfate in the lake area.

In addition to the alkaline waters from Oregon and California, several samples from Lake Magadi in Kenya were studied. Baker (*10*) has summarized the geology, mineralogy, and geochemistry of the area; the lake lies in the Gregory Rift Valley and contains a vast deposit of trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$). It is intermittently dry, but has a number of perennial brine pools (lagoons) near the margins; it has no visible outlet and is fed primarily by a number of perennial hot springs and by runoff during rainy seasons. Samples were collected from hot springs, open brine pools, and brines interstitial to trona crusts.

Figure 1 shows that the silica content increases drastically for brines having a *p*H greater than 9.2; this finding agrees with the reported increase in solubility of amorphous silica with *p*H (*2*). With the exception of those for the interstitial solutions, most *p*H values plotted in Fig. 1 are based on field measurements at ambient temperature; for samples not in immediate contact with muds, *p*H may change by as much as 1 unit during subsequent storage.

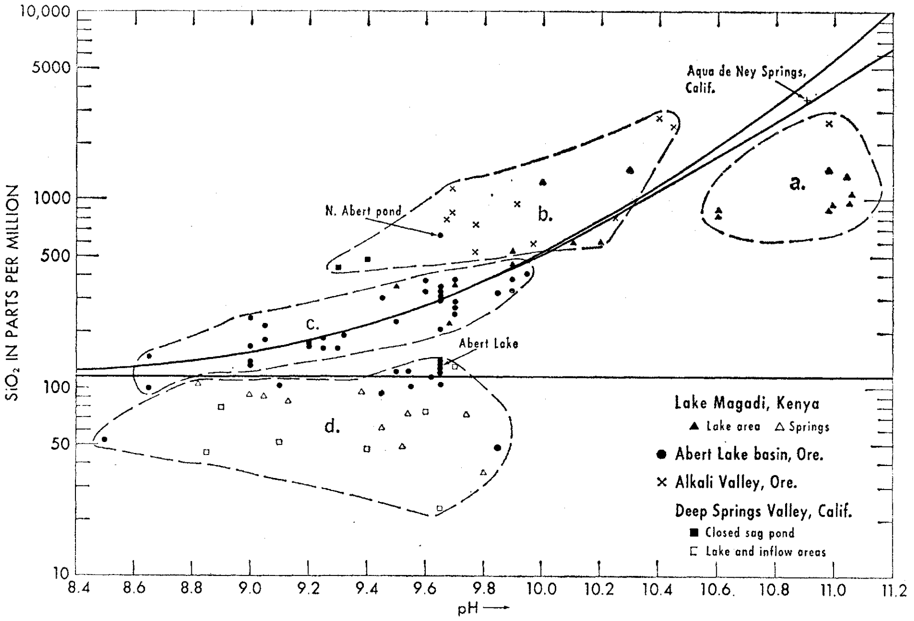

Fig. 1. Silica in solution versus *p*H. The three solid curves are (from low to high SiO_2) for $Si(OH)_4$, $SiO(OH)_3^-$, and $SiO_2(OH)_2^{--}$ Areas *a–d* are discussed in text.

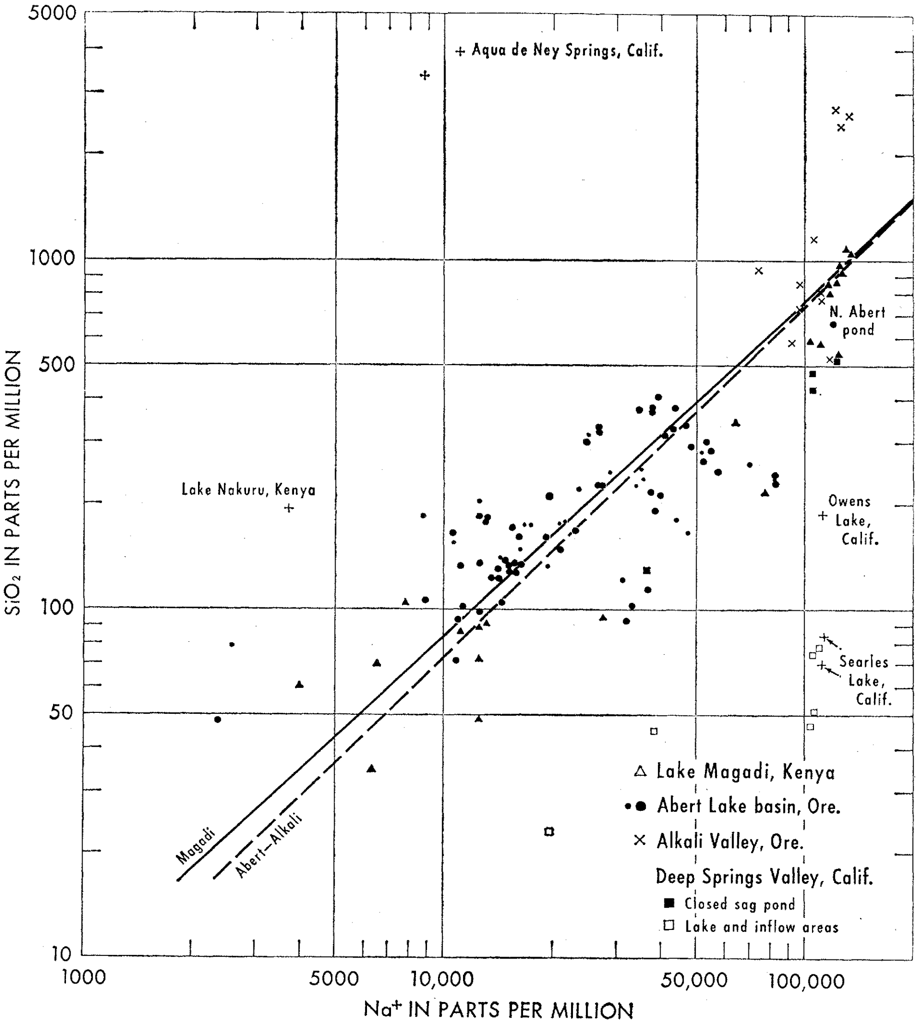

Fig. 2. Sodium versus SiO_2 for alkaline brines from Kenya, Oregon, and California. Regression lines have been derived independently for the Oregon and Magadi points. Small dots represent samples for which *p*H and total CO_2 data were not obtained.

In contrast, changes in total CO_2 during storage fell within the analytical error of 2.5 percent. The curves (Fig. 1) were calculated for 25°C from the data of Lagerstrom (*11*), as verified by Ingri (*12*), for equilibrium constants of silica species in solution.

According to Fig. 1, our data can be divided into four groups: (*a*) concentrated, intracrustral high-*p*H brines from Lake Magadi and Alkali Valley; (*b*) concentrated brines from open pools in Alkali Valley and Lake Magadi, from the brine pool north of Abert Lake, and from the closed sag pond of Deep Springs Valley; (*c*) brines of intermediate concentration, interstitial to saline muds from Albert and Magadi lakes; and (*d*) Abert Lake, plus saline springs and interstitial fluids from adjacent mud flats, inflow brines from springs of the Lake Magadi area, and brines from the area of Deep Springs Lake, No systematic correlation exists between silica content and temperature at the time of collection of each brine, although some of the scatter (Fig. 1) may be due to temperature differences.

Groups (*a*) and (*d*) are undersaturated with respect to amorphous silica, group (*c*) is of intermediate *p*H and near saturation, while group (*b*) is close to supersaturation or substantially supersaturated. The only other nongeothermal water reliably reported to have a very high *p*H and silica content, from Aqua de Ney Springs, California (*13*), plots very near the saturation curve for amorphous silica. The correlation between *p*H and SiO_2 for each group can be explained by their special history. We believe that the enrichment in silica in the brines is primarily due to evaporative concentration.

Points of group (*a*) show a high *p*H because of the depletion in HCO_3^-, caused by trona precipitation; the *p*H has increased more rapidly than evaporative concentration of SiO_2; exchange with the atmosphere is apparently too slow to check this trend.

The open pools of group (*b*) are either undersaturated with respect to sodium carbonate minerals or saturated with natron ($NA_2CO_3 \cdot 10H_2O$). Evaporative concentration of SiO_2 is apparently more rapid than nucleation and precipitation of silica.

The brines in contact with saline muds, containing abundant silicates [group (*c*)], plot near saturation with respect to amorphous silica. Higher SiO_2 values are from samples of bottom sediment near the water-mud interface; lower values, from interstitial waters deeper in the sediment. This fact suggests that initial equilibrium is established with respect to an amorphous surface layer on silicates (*14*); subsequent recrystallization lowers SiO_2 content.

The compositions of the springs of Lake Magadi [group (*d*)] are governed by their underground history. A reverse trend appears to exist between *p*H and SiO_2 and probably reflects adsorption of silica on freshly precipitated sesquioxides (*15*). The other points of group (*d*) are for waters of Abert or Deep Springs Lake; they are either dilute or have been concentrated from waters having distinctly lower SiO_2 content.

If silica is indeed concentrated by evaporation, this concentration should be reflected in a correlation between SiO_2 and sodium, the predominant cation of these brines (Table 1). As Fig.

Table 1. Representative alkaline brines from Alkali Valley (Alkali Lake, AIL) and Abert Lake (AL) basin, Oregon, Deep Springs Lake (DSL) and sag pond, Calif. (Deep Springs Valley, DSV), and the Lake Magadi (LM) area, Kenya. Included are brines with relatively high contents of CO_2, even though chloride or sulfate may in fact dominate the anions. Little Magadi Lake, Kenya, LML.

Sample				*p*H		Contents (ppm)							
Description	Source coordinates	Collection time	Water temp. (°C)	Field	Laboratory	Silica (SiO_2)	Sodium	Potassium	Bicarbonate (HCO_3)	Carbonate (CO_3)	Sulfate (SO_4)	Chloride (Cl)	Dissolved solids (calc.)
Brine from pit next to pothole near log road on SW side, AIL playa	120°03′W,42°57′N	8–6–63	25	9.97	10.0	590	91,400	5090	trace	99,500	20,200	19,800	237,000
Surface brine from pothole near log road on SW side, AIL playa	120°03′W,42°57′N	8–6–63	40		10.4	1270	121,000	8080	trace	133,000	25,000	27,900	318,000
At gage, AL	120°11′W,42°36′N	7–22–64	23	9.75	9.65	128	15,200	604	3840	6920	792	12,700	39,300
At mouth of Chewaucan River, surface, AL	120°15′W,42°31′N	7–25–64	30	9.82	9.85	48	2360	112	758	972	135	2190	6220
Brine from within very porous salt crust, central DSL	118°02′W,37°17′N	8–18–63	41		8.9	78	108,000	22,000	4990	20,700	56,200	120,000	332,000
Closed sag pond, DSV	118°1.5′W,37°17′N	8–15–61	33	9.90	10.0	524	119,000	10,900	3630	66,100	90,900	41,000	330,000
Interst, brine from bottom mud, S end, near W shore, AL	120°15′W,42°32′N	8–6–63	22		9.05	211	19,500	1360	10,200	6370	949	16,900	50,300
Interst, brine from bottom mud, SW end, AL	120°15′W,42°33′N	8–6–63	22		8.65	148	20,800	1350	14,600	4780	1270	16,800	52,300
Interest, brine from bottom mud, near mouth of Chewaucan River, AL	120°15′W,42°31′N	8–8–63	22		9.25	162	16,100	1200	4280	5180	1860	13,800	42,700
Hot spring, LML	36°16′E,01°44′S	6–66	81	9.05	9.05	90	12,600	239	15,600	3540	147	5950	30,200
Saturated brine, LM	36°15′E,01°54′S	6–66	34	11.06	10.25	1055	132,000	2280	trace	106,000	219	84,400	324,000
Saturated brine, LM	36°17′E,01°50′S	6–66	36	10.11	9.5	583	110,000	1530	trace	95,600	97	50,700	247,000

2 shows, most of the points for the Lake Magadi, Alkali Valley, and Abert Lake areas fall near a straight line having a slope of approximately 45° over the entire range of sodium concentration from 2400 to 132,000 ppm. The greatest scatter is in the points for the most dilute brines; they represent inflow waters not yet subjected to much evaporation. A number of the interstitial solutions, having SiO_2 contents below the general evaporative trend, may result from silica sorption during long-term contact with silicate solids. The highest sodium values reached are between 100,000 and 132,000 ppm and are for brines saturated with respect to sodium carbonate minerals. In these saturated brines, silica may be further enriched through fractional crystallization of trona or of natron and halite, or of all three.

The data for the Oregon and Kenya brines, in which carbonate and bicarbonate are the dominant anionic species, were examined by simple-regression analysis. The equations for the lines of best fit were (ppm):

$$Na^+ = 8180 + 127\ SiO_2$$

for the Lake Magadi area

$(\sigma = 53{,}400 \text{ ppm } Na^+, r = .94)$

$Na^+ = 6316 + 113\ SiO_2$ for the combined Abert Lake and Alkali Valley systems

$(\sigma = 29{,}000 \text{ ppm } Na^+, r = .80)$

Brines that contain much sulfate, chloride, and other anions in addition to HCO_3^- and CO_3^{--}, such as those from Deep Springs and Owens and Searles lakes (*16*), plot well below these lines; they do not reach the high *p*H values necessary to keep large amounts of SiO_2 in solution. Conversely, waters from Lake Nakuru, another closed basin in the rift valley 270 miles north of Lake Magadi, and Aqua de Ney Springs are high in silica relative to sodium, presumably because of initially higher *p*H values.

Figure 3 shows the correlation between SiO_2 and total CO_2. The equation for the regression line obtained from the combined Oregon and Magadi data, exclusive of the most supersaturated pools, is (ppm)

$$\text{Total } CO_2 = 1542 + 79SiO_2$$

$(\sigma = 25{,}300 \text{ ppm total } CO_2, r = .92)$

Again, evaporative concentration can account for the trend shown. The good correlation between total CO_2 and SiO_2 content of the brines also suggests that SiO_2 is derived from hydrolysis of silicates in the presence of CO_2, rather than by dissolution of free SiO_2, such as opal, cristobalite, or quartz. A schematic reaction such as

$$\underset{\text{in feldspar}}{NaAlSi_3O_8} + 6\tfrac{1}{2}H_2O + CO_2 =$$

$$Na^+ + HCO_3^- + 3Si(OH)_4^0 + \tfrac{1}{2}\underset{\text{in clay}}{Al_2O_3}$$

illustrates this process (*16*). The atmosphere supplies the CO_2 necessary to maintain ionic balance during silicate breakdown. This simple reaction requires a direct relation between Na^+:H^+ and SiO_2. However, field *p*H's apparently are affected by factors other than the CO_2–SiO_2 equilibria, and a plot of Na^+:H^+ versus SiO_2 shows great scatter.

Saturation of solutions with respect to sodium carbonate minerals limits the CO_2 enrichment; the limits are dependent upon other anions present, such as chloride. The Alkali Valley brines have the highest total CO_2:Cl ratio throughout and reach the greatest concentration in SiO_2 and CO_2 species at saturation. In contrast, the CO_2 values of the Magadi brines do not exceed 70,000 ppm because they contain much Cl (Table 1). The brine pool north of Abert Lake is saturated with trona and halite and has still less CO_2 (43,300 ppm). The most concentrated brines show definite SiO_2 enrichment, compared with CO_2:SiO_2 trend set by evaporative concentration; this enrichment is probably caused by the fractional crystallization of sodium carbonate minerals.

As in Fig. 2, the silica value for Aqua de Ney Springs plots well above the trend for sodium carbonate brines. The sodium and silica contents of these waters probably result from the hydrolysis of silicate in the absence of CO_2.

In summary, evaporative concentration of sodium carbonate waters leads to high-*p*H brines, which can retain all the silica initially in solution. The final values of SiO_2, *p*H, and Na^+ and CO_2 species depend on the initial solution composition, on the extent of equilibration with the atmosphere and silicate muds, or with both, and on the fractional precipitation of sodium carbonate minerals. The amount of silica stored

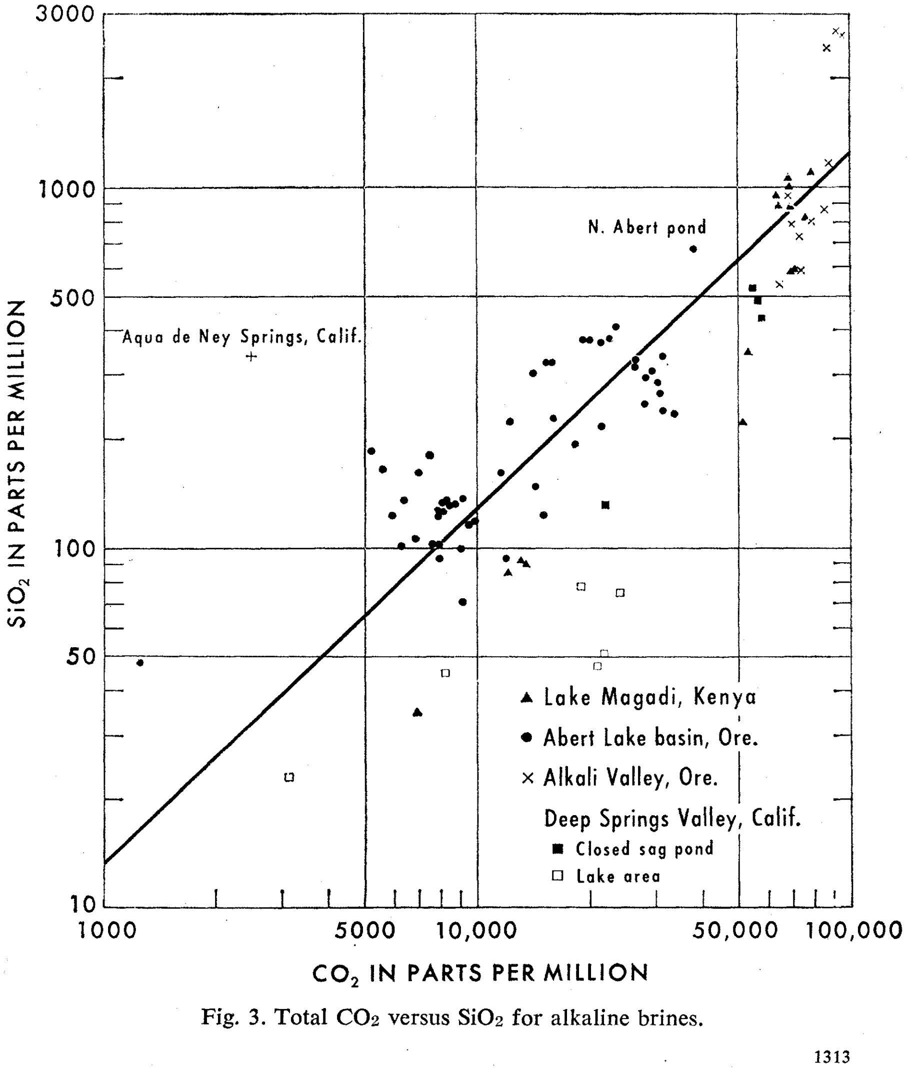

Fig. 3. Total CO_2 versus SiO_2 for alkaline brines.

in solution can be large. Interaction of silica-rich brines with flood runoff may cause relatively sudden supersaturation with respect to amorphous silica, and thereby lead to inorganic precipitation of chert. If there is rapid mixing of runoff with brine, much silica may remain in the diluted waters. If a stratified lake forms, however, biogenic CO_2 may be retained in the hypolimnion and reduce the pH of the bottom brines; in this manner the bulk of the dissolved silica can be precipitated. Figure 1 shows that a drop in pH from 11.0 to 8.5 can cause precipitation of as much as 3000 ppm SiO_2, which corresponds to a 1.5-mm-thick layer of chert for each meter of depth of brine. Silica layers that were probably formed by this mechanism have been found in the High Magadi beds, of Pleistocene age, and within the Alkali Valley playa deposits (*17*).

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22 August 1967

Coccoliths as Paleoclimatic Indicators of Pleistocene Glaciation

Abstract. *Selected species of Coccolithophoridae from recent sediments and mid-Wisconsin glacial sediments of the North Atlantic were examined in an attempt to determine cooling effects. All species showed a definite shift southward during the glacial period. The average shift in this planktonic population was 15 degrees of latitude, with the greatest change in the eastern Atlantic. A paleoisotherm map can be drawn on the basis of the temperature boundaries of coccolithophorids. The species boundaries indicate a possible shift in position of the subtropical gyral to a glacial position roughly parallel to the 33-degree line of latitude.*

The dramatic fluctuations in Pleistocene climate are recorded in sediments in the Atlantic Ocean (*1*), but unfortunately the means of procuring these data are poorly developed. The only direct technique available at the present time is the use of oxygen isotopes (*2*). This report deals with a new approach —plotting the migration of biogeographic boundaries for temperature-restricted species of Coccolithophoridae due to Pleistocene glaciation.

Among all the microorganisms that leave fossil records in oceanic sediments, the Coccolithophoridae probably have the greatest potential as paleoclimatic indicators. In addition to their wide geographic distribution and stable mineral skeleton (calcite), these marine algae inhabit the upper euphotic zone (*3–5*) and consequently are under direct climatic control. In living species it is possible to correlate biogeographic boundaries with surface water isotherms (*4*), and this is the basis of my report.

The method of attack, being biogeographic, requires the widest possible geographical distribution of core material. This is not easily obtained, for, although the North Atlantic has been the site of intensive sampling, there remain large gaps in the core distribution. A limiting factor is that large areas of the North Atlantic basin are below the carbonate compensation level, with a consequent lack of coccolith flora. Thus the 23 cores sampled (Table 1) are restricted to three linear belts. Two cover the shelf, slope, and rise of both North America and Europe-Africa; the third, the Mid-Atlantic Ridge.

Choice of the particular species to be examined requires that two separate cri-

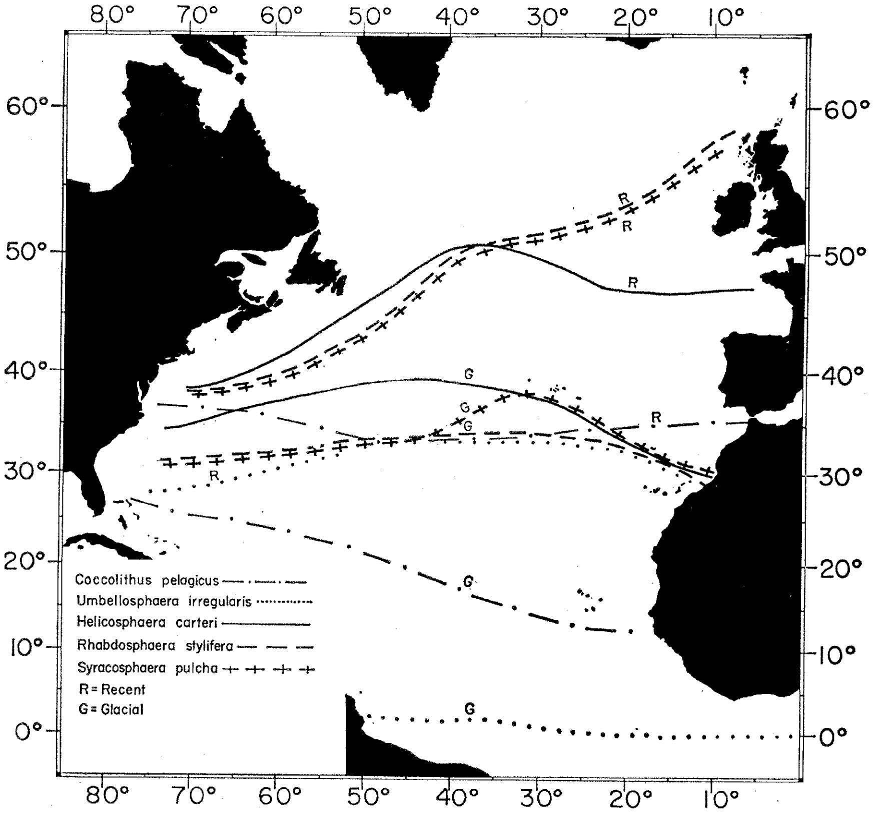

Fig. 1. Species population boundaries for Recent and mid-Wisconsin time.