well in excess of 100 barrels per day.

These estimates, which reflect the bounding assumptions for surface slick conditions, are consistent with the results obtained from oil collection techniques on the ocean floor. For example, a flow of 5 to 8 barrels per day from seep region "a" alone was determined by capturing oil from several major portions of that region. This level of activity was typical of a majority of our observations.

After considering all the factors pertaining to our collected data, we arrive at a total estimated flow rate of the order of 50 to 70 barrels (approximately 8,000 to 11,000 liters) per day. We point out, however, that this estimate is an average and it applies only to the period of our study. The natural seeps off Coal Oil Point have been observed to vary considerably in activity over a period of a few days (possibly by as much as 100 barrels per day).

In assessing the resultant level of shoreline oil pollution, several factors must be considered. From a scientific point of view, very little is known about the mechanism by which an oil globule released from the ocean floor is transformed into a tarry beach deposit. The degree of beach contamination is undoubtedly related to the submarine oil flow rate, but our study indicates that this relationship is far from simple or direct. In addition, the location of Coal Oil Point and the predominant offshore currents in that area generally prevent oil from fouling waters and beaches that are frequently used. The extent of natural seepage therefore goes unnoticed by a majority of people along the coast of Santa Barbara County.

ALAN A. ALLEN
ROGER S. SCHLUETER
General Research Corporation,
Santa Barbara, California 93105
PAUL G. MIKOLAJ
Department of Chemical Engineering,
University of California,
Santa Barbara 93106

References and Notes

1. Summary accounts of the history of natural seepage are contained in the following: "Geology, Petroleum Development, and Seismicity of the Santa Barbara Channel Region, California," *U.S. Geol. Surv. Prof. Pap. 679* (1969); D. W. Weaver, "Geology of the Northern Channel Islands" (American Association of Petroleum Geologists, Tulsa, Oklahoma, 1969); C. P. L. Nicholls, *Shore Beach* **4**, 128 (1936).
2. R. C. Merz, "Determination of the Quantity of Oily Substances on Beaches and Nearshore Waters," *Calif. State Water Pollut. Contr. Board Publ. 21* (1959); A. A. Rosen, L. R. Musgrave, J. J. Lichtenberg, "Characterization of Coastal Oil Pollution by Submarine Seeps," *ibid.*; H. F. Ludwig and R. Carter, "Analytical Characteristics of Oily Substances Found on Southern California Beaches" (Report to Western Oil and Gas Association by Engineering-Science, Inc., Arcadia, California, 1960); *Water Pollut. Contr. Fed. J.* **33**, 1125 (1961).
3. This work is part of a larger study, "Estimates of Surface Pollution Resulting from Submarine Oil Seeps at Platform A and Coal Oil Point" [*Gen. Res. Corp. Tech. Mem. 1230* (November 1969)], undertaken for the County of Santa Barbara, California.
4. Our observations indicate that oil film thicknesses of the order of 10^{-5} cm can significantly retard the spread of a surfacing oil globule.
5. Although a number of solvents could be used, commercial paint thinner was found to be adequate. The instrument used in these tests was a Bausch & Lomb "Spectronic 20" colorimeter, and the wavelength was set at 625 nm.

27 August 1970

Alkalinity and Formation of Zeolites in Saline Alkaline Lakes

Abstract. *The solubility of rhyolitic glass increases with increasing alkalinity, whereas the ratio of silicon to aluminum decreases with increasing alkalinity. The strong correlation observed between alkalinity and zeolite mineralogy in saline, alkaline lakes is thought to be a function of this relationship between pH and the Si/Al ratio. It is suggested that this function is a result of the reaction between silicic glass and alkaline solution whereby (i) a gel forms, whose Si/Al ratio is controlled by the Si/Al ratio of the solution, and (ii) a zeolite forms from the gel, whose Si/Al ratio is, in turn, controlled by the composition of the gel.*

In modern environments, where authigenic silicates are forming, a relationship has been noted between the Si/Al ratio of the low-temperature zeolitic alteration products of silicic glass and the alkalinity of the lake waters responsible for that alteration (*1, 2*). Specifically, more siliceous zeolites such as clinoptilolite and mordenite are the most common alteration products of silicic glass in marine and freshwater environments, whereas less siliceous phillipsite and erionite are the dominant alteration products in saline, alkaline lakes (Table 1) (*3*).

In addition, Senderov (*4*) pointed out that an increase in the concentration of hydroxide in the initial synthesis mixture results in the production of a zeolite phase with a lower Si/Al ratio. For example, mordenite is replaced by analcime in experiments characterized by high *p*H. Thus, experimental work on the low-temperature synthesis of zeolites also has shown that a relationship exists between the Si/Al ratio of the zeolite and the alkalinity of the mixture from which it formed (*5*).

In recent years it has been realized that zeolites are among the most common authigenic silicate minerals in sedimentary rocks (*3*). Thus it is important to understand the relationship between the Si/Al ratio of a zeolite and the alkalinity of its environment of formation; this knowledge will result in a significant insight into the chemical mechanisms characterizing sedimentary environments. The purpose of this report is to suggest the following model to explain this relationship: as a consequence of the reaction between silicic glass and alkaline solutions (i) a gel forms, whose Si/Al ratio is controlled by the Si/Al ratio of the solution, and (ii) a zeolite forms from the gel, whose Si/Al ratio is, in turn, controlled by the composition of the gel.

Much of the discussion of authigenic silicate formation has been predicated on the familiar curves of Correns and others, in which the solubility of amorphous silica is plotted as a function of *p*H (*6*). These curves suggest a precipitous rise in the solubility of silica at high alkalinities ($p\text{H} > 9$). More recently, Lagerstrom has shown that with an increase in alkalinity there is a more gradual rise in silica solubility (*7*). This fact has been documented in recent studies of natural environments (*8*). Jones *et al.* have shown that in the alkaline environments they have investigated, such as Lake Magadi, Kenya, the concentration of silica in solution is over 1000 parts per million (ppm). In saline, alkaline lakes of central Wyoming silica also has been found in excess of 1000 ppm (*9*). The fact that these natural alkaline environments are saturated with respect to silica suggests that saturation with respect to amorphous SiO_2 can be achieved. However, the source for the silica in these environments is not volcanic glass, but instead probably the weathering of feldspar [that is, $NaAlSi_3O_8 + 6\tfrac{1}{2}\ H_2O + CO_2 = Na^+ + HCO_3^- + 3\ Si(OH)_4 + \tfrac{1}{2}\ Al_2O_3$ (in clay)] (*8*).

On the basis of a consideration of the solution chemistry of silica alone, the erroneous conclusion can be drawn that in alkaline environments the activity of silica would be high and the more siliceous zeolites would form. An explanation for the lack of correlation

Table 1. Formulas of common sedimentary zeolites. Formulas, taken from Sheppard and Gude (*21*), are standardized in terms of a sodium end-member that has one aluminum atom.

Name	Dominant cations	Formula
Mordenite	Na,K,Ca	$NaAlSi_{4.5-5.0}O_{11.0-12.0} \cdot 3.2–3.5\ H_2O$
Clinoptilolite	Na,K,Ca	$NaAlSi_{4.2-5.0}O_{10.4-12.0} \cdot 3.5–4.0\ H_2O$
Erionite	Na,K,Ca	$NaAlSi_{3.0-3.7}O_{8.0-9.4} \cdot 3.0–3.4\ H_2O$
Phillipsite	Na,K	$NaAlSi_{1.3-3.4}O_{4.6-8.8} \cdot 1.7–3.3\ H_2O$
Analcime	Na	$NaAlSi_{2.0-2.8}O_{6.0-7.6} \cdot 1.0–1.3\ H_2O$

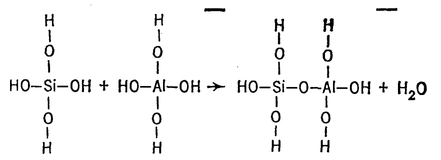
between highly alkaline environments and siliceous zeolites has been offered by Hay (*2*), who suggested that the silica activity is decreased in highly alkaline environments because the hydroxyl ion catalyzes the polymerization of amorphous silica to an inferred semicrystalline silica phase. Relatively low activities of silica would presumably be expected with the semicrystalline phase, as its solubility would be lower than that of amorphous silica. The direct argument against this interpretation is precisely the SiO_2 content of alkaline brines, which are often saturated with respect to amorphous SiO_2.

In order to understand the behavior of Si and Al in authigenic environments, we have determined the solubility of rhyolitic glass with respect to silica and alumina at various alkalinities. Figure 1 shows the rate of solution of silicic glass and demonstrates that the solubility data obtained in this experiment are not saturation values. The glass used in these experiments was synthetic (*10*) with a composition in percentage (by weight) as follows: SiO_2, 78; Al_2O_3, 12; and Na_2O, 10. The different alkalinities were adjusted with NaOH and each experiment lasted 70 days at a temperature of 80°C (*11*). Figure 2 demonstrates the decrease in the Si/Al ratio of the solution with an increase in alkalinity (*12*). In these alkaline solutions the activity of silica is high, but the activity of alumina increases more rapidly with increases in alkalinity. As a consequence of increasing *p*H, zeolites like phillipsite (relatively low Si/Al ratio) would be favored over zeolites like clinoptilolite (relatively high Si/Al ratio).

In order to test this hypothesis the solutions from these experiments, after 70 days, were allowed to cool for 24 hours; the result was the formation of sodium aluminosilicate gels. The gels not only formed in the solutions, but were found adhering to some glass fragments as gelatinous precipitates. In many cases the spatial relationships between gel and glass fragments were very similar to the textural patterns observed in altered rhyolitic tuffs where zeolites have partially replaced glass shards. The gels and solutions were reheated to 80°C and were kept at that temperature for 2 weeks; as a result phillipsite crystallized. The phillipsite that crystallized from the gels formed in the solutions at *p*H 9.1, 10.5, and 11.5 had Si/Al ratios of 3.4/1, 2.4/1, and 2.2/1, respectively (*13*). Thus, it appears that the Si/Al ratios of the solutions, gels, and zeolites were controlled by the alkalinity.

Figure 3 shows the relation between these synthetic phillipsites and phillipsites found in saline, alkaline lake deposits. The Si/Al ratios of the zeolites synthesized from the solutions with a *p*H of 9.1 and 10.5 are very similar to the Si/Al ratio of natural phillipsite from saline, alkaline lake deposits, whereas the phillipsite synthesized from the solution with a *p*H of 11.5 had a Si/Al ratio too low to be considered typical of such deposits. Moreover, in the few modern saline, alkaline lakes where phillipsite has been described, the *p*H of the brines ranges from 9.0 to 10.0. For example, Hay (*2, 3*) describes phillipsite at Teels Marsh in Nevada with an average Si/Al ratio of 3.3/1 forming in association with brines ranging in *p*H from 9.1 to 9.4.

It has been demonstrated that the solubility of rhyolitic glass (*14*) increases with increasing alkalinity. Presumably the prominent Si and Al species in solution, in addition to hydrated cations, would include $Si(OH)_4$, $SiO(OH)_3^-$, $SiO_2(OH)_2^{2-}$, and $Al(OH)_4^-$ (*7, 15*). The gels may result from the reaction between the uncharged silica species $Si(OH)_4$ and the charged alumina species $Al(OH)_4^-$ to form aluminosilicate chains as follows:



$$\begin{array}{ccc} & \mathrm{H} & \\ & | & \\ & \mathrm{O} & \\ & | & \\ \mathrm{HO{-}} & \mathrm{Si} & \mathrm{{-}OH} \\ & | & \\ & \mathrm{O} & \\ & | & \\ & \mathrm{H} & \end{array} + \begin{array}{ccc} & \mathrm{H} & \\ & | & \\ & \mathrm{O} & \\ & | & \\ \mathrm{HO{-}} & \mathrm{Al} & \mathrm{{-}OH} \\ & | & \\ & \mathrm{O} & \\ & | & \\ & \mathrm{H} & \end{array}^{-} \rightarrow \begin{array}{ccccc} & \mathrm{H} & & \mathrm{H} & \\ & | & & | & \\ & \mathrm{O} & & \mathrm{O} & \\ & | & & | & \\ \mathrm{HO{-}} & \mathrm{Si} & \mathrm{{-}O{-}} & \mathrm{Al} & \mathrm{{-}OH} \\ & | & & | & \\ & \mathrm{O} & & \mathrm{O} & \\ & | & & | & \\ & \mathrm{H} & & \mathrm{H} & \end{array}^{-} + H_2O$$

To maintain electrical neutrality these chains would tend to group around hydrated cations; their close proximity would then lead to additional dehydration reactions between adjacent chains, resulting in the production of the cage-

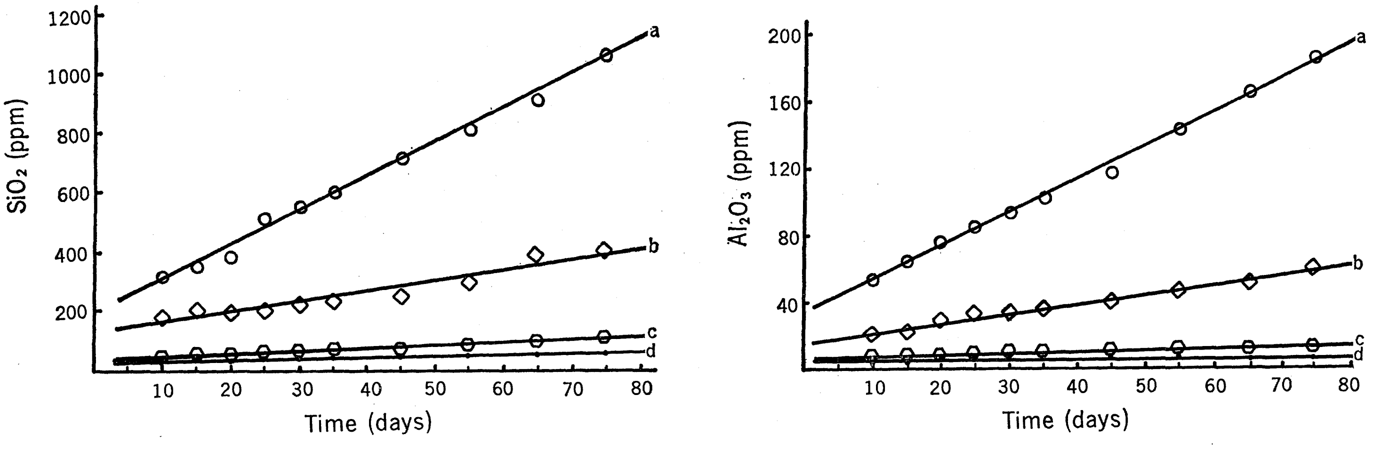
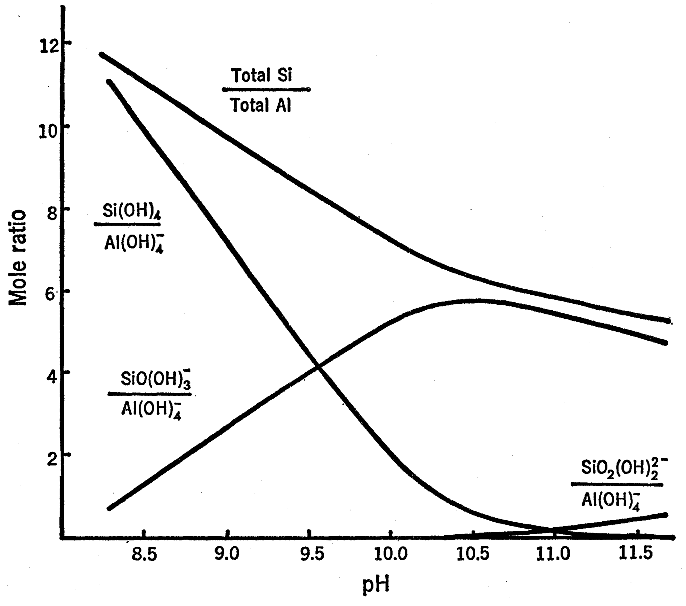


Fig. 1. Solubility of SiO_2 and Al_2O_3 as a function of time. Curve a, $pH = 11.5$; curve b, $pH = 10.5$; curve c, $pH = 9.1$; and curve d, $pH = 8.5$.



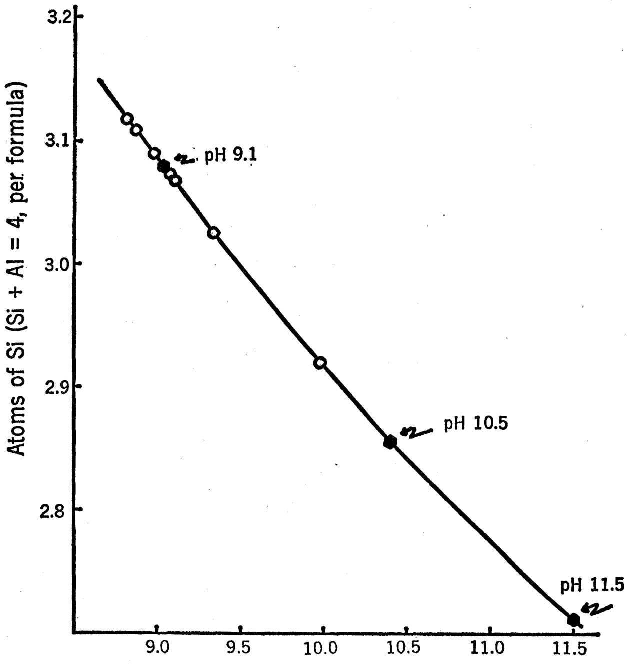


Fig. 2 (above). Mole ratio of total silica to total alumina, and of various silica species in solution to the alumina species in solution, as a function of *p*H.

Fig. 3 (right). A plot of the number of atoms of Si (on the assumption that Si + Al = 4) in synthetic phillipsites (solid circles) as a function of *p*H. Numbers of atoms of Si in natural phillipsites from saline, alkaline lake deposits are plotted for comparison (open circles). All phillipsite analyses were standardized to the following formula: $Na_x(Al_xSi_y)_4O_8 \cdot 3H_2O$, with $x + y = 4$ per formula.

like polyhedral units characteristic of zeolites. In the subsequent ordering process these basic polyhedral units would be joined by shared oxygen atoms, and the formation of small zeolite crystallites would follow.

The silica species $Si(OH)_4$ was considered to be the important species for two reasons:

1) It is difficult to imagine two negatively charged species being brought together, that is, either $SiO(OH)_3^-$ or $SiO_2(OH)_2^{2-}$ and $Al(OH)_4^-$.

2) By use of Lagerstrom's (*7*) data, the curves for $Si(OH)_4/Al(OH)_4^-$, $SiO(OH)_3^-/Al(OH)_4^-$, or $SiO_2(OH)_2^{2-}/Al(OH)_4^-$ as a function of *p*H for these experiments can be plotted (Fig. 3); the curve of $Si(OH)_4/Al(OH)_4^-$ as a function of *p*H is the only one that fits the observed relationship.

Most important to this hypothesis is the proposal that the charged alumina species catalyzes the formation of a hydrous sodium aluminosilicate gel. If the charged alumina species were not present, as the alkalinity increases, the silica would continue to go into solution and no gel would form (*16*). An excellent example of this latter case is the present-day brines of Lake Magadi where SiO_2 values range up to 1900 ppm and Al_2O_3 values are less than 1 ppm (*17*). Jones *et al.* (*8*) documented that the high silica content of the brines is due primarily to evaporative concentration rather than to unusual silica sources, such as the solution of silicic glass. Eugster (*17*) has suggested that magadiite precipitates directly from these brines without the formation of silica gel [that is, $7H_4SiO_4\ (aq) + Na^+\ (aq) = NaSi_7O_{13}(OH)_3 \cdot 3H_2O\ (s) + 9H_2O\ (aq) + H^+\ (aq)$]. Rooney *et al.* (*18*) have documented the formation of magadiite by surface precipitation from alkali brines at Alkali Lake, Oregon.

On the other hand, Eugster and Jones (*19*) have described modern sodium aluminosilicate gels forming by the interaction of alkaline spring waters (67° to 87°C; *p*H, about 9) with alkali trachyte rocks. When purified and recrystallized hydrothermally at 350°C and 2 kb, these gels yielded 100 percent analcime. The gels Eugster and Jones describe are forming by a process similar to the one proposed in this report for the formation of gels in saline, alkaline lakes. The natural gels described by Eugster and Jones (*19*) are very delicate, are easily eroded, and are preserved only in almost stagnant pools of water. In contrast, according to the gel-formation mechanism we propose, gels would be forming in a protected environment in the interstitial brines associated with the ash bed, or at the interface between the glass shard and the solution. The reaction of feldspars or clays with alkaline solutions probably would also result in the formation of gels.

In these experiments no gels were observed in the *p*H range 7 to 9, where the more siliceous zeolites like mordenite and clinoptilolite should form (*20*). This lack of gels can be explained as a result of the relatively low solubility of Al in the *p*H range 7 to 9 (Fig. 1). In longer experiments, or in a natural environment, the kinetic effect should be reduced. However, if the proposed model is correct, and if formation of the gel is dependent on the charged aluminum species in solution, the formation of the more siliceous zeolites would be more sluggish.

In conclusion, the observation that there is a correlation between alkalinity and zeolite composition in sedimentary environments can be explained experimentally. This observation is the result of the relationship between *p*H and the Si/Al ratio of the solution in contact with the siliceous tuff.

ROBERT H. MARINER
RONALD C. SURDAM
Department of Geology, University of Wyoming, Laramie 82070

References and Notes

1. K. S. Deffeyes, *J. Sediment. Petrol.* **29**, 602 (1959).
2. R. L. Hay, *Amer. Mineral.* **49**, 1366 (1964).
3. ———, *Geol. Soc. Amer. Spec. Pap. 85* (1966), p. 130.
4. E. E. Senderov, *Geochem. Int. No. 9* (1963), p. 848.

5. D. S. Coombs, A. J. Ellis, W. S. Fyfe, A. M. Taylor, *Geochim. Cosmochim. Acta* **17**, 53 (1959); E. E. Senderov, *Geokhim. Issled. Obl. Povysh. Davlenii Temp.* **1965**, 173 (1965).
6. C. W. Correns, *Einführung in die Mineralogie* (Springer-Verlag, Berlin, 1949); G. B. Alexander, W. M. Heston, R. K. Iler, *J. Phys. Chem.* **58**, 453 (1954); G. Okanmoto, T. Okura, K. Goto, *Geochim. Cosmochim. Acta* **12**, 1923 (1957).
7. G. Lagerstrom, *Acta. Chem. Scand.* **13**, 722 (1959).
8. B. F. Jones, S. L. Rettig, H. P. Eugster, *Science* **158**, 1310 (1967).
9. C. Waldon, personal communication.
10. Glass was prepared according to the method outlined by J. F. Schairer and N. L. Bowen [*Amer. J. Sci.* **245**, 193 (1947)].
11. Silica concentrations were determined by use of the molybdate blue method [*U.S. Geol. Surv. Water Supply Pap. 1454* (1960), p. 260], and aluminum concentrations were determined by use of the aluminum colorimetric method [*Standard Methods of the Examination of Water and Waste Water* (American Public Health Association, New York, ed. 12, 1965), p. 53].
12. A similar relationship can be demonstrated for natural rhyolitic glass [E. A. Gloor, thesis, University of Wyoming (1969)].
13. Ratios of Si to Al in the phillipsite crystals were determined with an electron-probe microanalyzer (Hitachi model XM-AS). Natural phillipsite samples were used as standards.
14. The rims of the glass fragments also are depleted with respect to sodium.
15. J. D. Hem and C. E. Roberson, *U.S. Geol. Surv. Water Supply Pap. 1827-A* (1967), p. 55; A. L. Reesman, E. E. Pickett, W. D. Keller, *Amer. J. Sci.* **267**, 99 (1969).
16. The only inorganic precipitation of silica gel in a modern sedimentary environment known to us was reported by M. N. A. Peterson and C. C. von der Borch [*Science* **149**, 1501 (1965)]. This gel precipitated when the *p*H of an alkaline lake (*p*H 9.5 to 10.2) drastically decreased (*p*H 7.0 to 6.5).
17. H. P. Eugster, *Contrib. Mineral. Petrol.* **22**, 1 (1969).
18. T. P. Rooney, B. F. Jones, J. T. Neal, *Amer. Mineral.* **54**, 1034 (1969).
19. H. P. Eugster and B. F. Jones, *Science* **161**, 160 (1968).
20. L. L. Ames [*Amer. Mineral.* **48**, 1374 (1963)] has shown experimentally that mordenite and a clinoptilolite-like phase are stable over a *p*H range from 7.1 to 8.7.
21. R. A. Sheppard and A. J. Gude, III, *U.S. Geol. Surv. Prof. Pap. 597* (1968).
22. We thank R. A. Sheppard for supplying samples of natural phillipsite. Laboratory work supported by grant 3809-A2 from the Petroleum Research Fund of the American Chemical Society. We thank H. P. Eugster for his instructive discussion during the progress of this work and for his comments on the manuscript.

22 June 1970; revised 19 August 1970 ■

Carbon Isotope Fractionation in the Fischer-Tropsch Synthesis and in Meteorites

Abstract. *Carbon dioxide and organic compounds made by a Fischer-Tropsch reaction at 400°K show a kinetic isotope fractionation of 50 to 100 per mil, similar to that observed in carbonaceous chondrites. This result supports the view that organic compounds in meteorites were produced by catalytic reactions between carbon monoxide and hydrogen in the solar nebula.*

Most of the carbon in carbonaceous chondrites exists in reduced form, largely as an aromatic polymer and, to a lesser extent, as extractable organic compounds (*1*). A minor part (~ 3 to 5 percent) exists in oxidized form, as the carbonates breunnerite [$(Mg,Fe)CO_3$] and dolomite [$MgCa(CO_3)_2$] (*2*).

These two types of reduced carbon differ greatly in their isotopic composition. The polymeric carbon is light: $\delta C^{13} = -15$ to -17 per mil in both type I and type II carbonaceous chondrites (*3*). The carbonate carbon is much heavier: $\delta C^{13} = +60$ to $+70$ per mil in type I and $+40$ to $+50$ per mil in type II carbonaceous chondrites (*3*, *4*), for a total difference of 83 to 87 and 57 to 67 per mil. For comparison, terrestrial organic matter and carbonates (including that formed cogenetically, for example, by shellfish) generally differ by only about 25 per mil, typical values being -25 to -30 per mil for organic carbon and ~ 0 per mil for carbonates. The meteoritic carbonates fall well outside the range of terrestrial carbon, -80 to $+25$ per mil (*5*).

Clayton (*4*) has considered four possible origins of the meteoritic carbon isotope fractionation. The first of these possibilities, single-stage equilibrium fractionation, can, in principle, give an effect of the right sign and magnitude. Data for organic molecules of appropriate complexity are unavailable, but if calculations for CH_4 and CO_2 (*6*) are used as a first-order approximation, temperatures of 265° to 335°K would seem to be required for the observed fractionations in type I and type II carbonaceous chondrites. However, no mechanisms on earth are known that would establish equilibrium at the lower of these temperatures. Kinetic isotope effects are a second alternative, but in the reactions studied thus far, the fractionation was too small (20 to 40 per mil) and in the wrong direction, the oxidized carbon becoming lighter rather than heavier (*7*). The third possibility, biological activity, produces fractionations of the right sign, but usually of insufficient magnitude [algae, 10 to 12 per mil; vascular plants, 20 to 30 per mil (*8*)]. Finally, it is conceivable that the differences reflect nuclear processes, the two types of carbon having had different histories of nucleosynthesis. This alternative was favored by Urey (*9*). However, all work to date has failed to bring to light any isotopic differences that might be attributed to incomplete mixing in the solar nebula.

The origin of the organic compounds is, of course, pertinent to this problem. Studier *et al.* (*10*) have shown that nearly all compounds identified in meteorites can be produced by a Fischer-Tropsch type of reaction between CO, H_2, and NH_3 in the presence of a nickel-iron or magnetite catalyst. They proposed that the organic compounds in meteorites were made by such reactions, catalyzed by dust grains in the solar nebula.

The Fischer-Tropsch reaction produces both oxidized and reduced carbon. Much of the oxygen from CO usually is converted into H_2O (Eq. 1), but a variable proportion is converted to CO_2 (Eq. 2):

$$n\,CO + (2n + 1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O \qquad (1)$$

$$2n\,CO + (n + 1)\,H_2 \rightarrow C_nH_{2n+2} + n\,CO_2 \qquad (2)$$

Nothing is known about carbon isotope fractionation in this reaction, however. We, therefore, decide to investigate it.

A difficulty encountered in our experiments was the tendency of any CO_2 formed to disappear by secondary reactions. [Hydrogenation of CO_2 to hydrocarbons is thermodynamically feasible (*11*).] We circumvented this problem by collecting CO_2 as fast as it was formed, using a $Ba(OH)_2$ absorbent.

For our syntheses, we heated 0.8 liter of an equimolar mixture of CO and H_2, initially at 1 atm, to 400° ± 10°K in a Vycor flask in the presence of 1.5 g of cobalt catalyst (*12*). (Cobalt was chosen because it is effective at lower temperatures than iron catalysts; otherwise there is little difference between the two.) As the reaction progressed CO_2 was removed continuously by absorption in 5 ml of a saturated $Ba(OH)_2$ solution in a 35-ml sampling tube, connected to the reaction vessel by a side arm. The sampling tube was replaced from time to time. In order to ensure complete recovery of all CO_2 formed during the sampling interval, the tube was cooled to −196°C just before removal. All condensable gases were thus frozen out. After closing the stopcock between the sampling tube and the reaction flask, we warmed the tube to room temperature and shook it to promote absorption of CO_2. The stopcock was opened briefly to equalize pressure,