Boron nitride, as I have said, behaves very much like graphite. However, at a pressure just over 100 kilobars it transforms to the wurtzite structure (*16*) shown in Fig. 18. One can see that it is very like an array of buckled hexagonal plates. It is of interest to note that the number and geometry of nearest neighbors are the same in diamond as in wurtzite.

Some time ago a first-order phase change was observed (*12*) in single-crystal (or to some extent in pyrolytic) graphite, with a very large increase in resistance, especially in the plane of the hexagons (see Fig. 19). At that time the high pressure phase was not isolated or identified satisfactorily. At 78°K the transition does not occur at pressures up to 500 kilobars. Upon heating at high pressure it is initiated at 180° to 200°K, which is the crucial temperature range for all the organic systems.

Recently "hexagonal diamond" has been identified in the results of shock measurements on graphite (*17*). Bundy and Kasper (*18*) have made a very thorough study of the static conditions for the formation of this analog of wurtzite. It apparently requires a large volume of very precisely oriented carbon atoms, so that it does not occur in powdered graphite. Although the transition runs at room temperature, it is best stabilized by heating to 1000°C after transformation.

I have cited observations of a wide variety of π electron systems in which the molecules are arranged in a layered structure. Rather generally, when the orbitals are brought sufficiently close together, they react and usually destroy the planar symmetry of the molecules. It is interesting, although a little puzzling, that none of these reactions proceed below about 180°K, but that all are initiated at about that temperature. Further investigation along a number of lines is desirable. One should characterize the conditions, mechanisms, and reaction products more thoroughly. A number of these reactions proceed photochemically at 1 atmosphere. It would be useful to relate high-pressure solid-state chemistry to the field of "topochemistry" (*19*)—the investigation of light-induced solid-state reactions in organic crystals. Current Mössbauer studies in our laboratory (*20*) indicate that a wide variety of ferric compounds tend to reduce to the ferrous state at high pressure and room temperature. Many of these reactions occur photochemically at 1 atmosphere also. It would seem that investigation of the relationship between photochemistry and high-pressure chemistry could lead to a less Edisonian approach to the latter field.

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The Ocean as a Chemical System

Lars Gunnar Sillén

Some 8 years ago I was invited to give a plenary lecture on the physical chemistry of sea water at an international conference on oceanography (*1*). I tried to excuse myself because of ignorance, being no oceanographer but a mere chemist, but the organizers pointed out that I had some experience of the equilibria of ionic solutions. Sea water is obviously an ionic solution, so I was asked to study the subject and tell whatever came to my mind.

This was surely a challenge. The average composition of sea water was easy enough to find in the literature. Table 1 gives the concentrations of the major ions in average sea water of 3.5 percent salinity (content of solid salts). Salinity in the open sea may be varied between 3.2 and 3.75 percent by evaporation or by addition of freshwater (*2*, vol. 1, p. 43); the ratios between the major ions are remarkably constant (*2*, vol. 1, p. 121). The *p*H of the ocean seems to be around 8.1 ± 0.2. Not only is the composition practically uniform, but there seems to be no strong reason to think that it has changed very much during the last few hundred million years.

It was natural for a solution chemist to ask how sea water developed exactly this composition. For instance, how is its *p*H controlled? The standard textbook answer by that time was that *p*H in the ocean is regulated by buffering of the system comprising H_2CO_3, HCO_3^-, and CO_3^{2-}. However, when one begins to think of it one finds that the buffer capacity of the carbonates in solution is pitifully small compared with the amounts of acids and bases that have passed through the ocean system in the course of time. So it seemed to me that either the *p*H of the ocean must be precarious or there must be some other controlling factor. In my 1959 lecture (*1*) I pointed out that the fine-grained silicates (especially the clays) have very great buffering capacity and may well determine the *p*H of the ocean.

The author is on the staff of the Royal Institute of Technology (KTH), Stockholm 70, Sweden.

Table 1. Concentrations of major components in sea water of 3.5 percent salinity, calculated from data in (*2*, vol. 1, p. 121). Unit, mole per kilogram of sea water.

Item	Conc.	Item	Conc.
H_2O	53.557	Cl^-	0.5459
Na^+	0.4680	SO_4^{2-}	.0282
Mg^{2+}	.0532	HCO_3^-	.0023
Ca^{2+}	.0103	Br^-	.0008
K^+	.0099	F^-	.0001
Sr^{2+}	.0001	H_3BO_3	.0004

Too little was then known about the equilibria involved, and the general feeling among ocean chemists was that the silicates react too slowly to be of much importance as regulators. Later experimental work (*3–7*) has given some support to the silicate theory, which has been taken up by Garrels (*5–7*) and Holland (*8*). I have tried to develop it further (*9–11*). Some opponents persist.

Let us now consider the problem of how the composition of sea water is regulated. Are the concentrations of major ions (Table 1) and the *p*H merely the results of chance, or are they more or less fixed ("tethered") by chemical equilibrium conditions? The chemical system that we must consider comprises not only the ocean itself but also the other large reservoirs on Earth's surface that interact with the ocean: air, sediments, and igneous rocks.

Fragments of a Million-Year Budget

The ocean covers 361×10^6 square kilometers, which is 71 percent of Earths' surface: 510×10^6 square kilometers or 5.1×10^{18} square centimeters. The total volume of the ocean has been calculated at 1.37×10^9 cubic kilometers, or 1.37×10^{21} liters. Adding the interstitial water of various sediments and assuming its average composition to be that of sea water (the spread is great), Horn (*12*) has estimated a total of 1.69×10^{21} liters of sea water.

Table 2. Dissolved ions carried to the ocean by rivers; calculated from the data of Clarke (*14*) and Livingstone (*7, 15*). Unit, mole per square centimeter times 1 million years; CO_3^{2-} is counted as half the amount of HCO_3^-.

Ion	According to:	
	Clarke	Livingstone
Ca^{2+}	2.73	2.68
Mg^{2+}	0.75	1.22
Na^+	1.35	1.96
K^+	0.29	0.42
CO_3^{2-}	3.14	3.42
SO_4^{2-}	0.68	0.84
Cl^-	.86	1.57
NO_3^-	.08	0.11

In mass balances for the ocean system, various units are being used that may at first seem confusing; care is needed to avoid the making of mistakes by a few powers of ten. The total amounts involved are often expressed in the units ton (10^6 grams) or "geogram" (10^{20} grams). However, it may be easier to grasp the meaning of the figures if one gives the amounts in moles or grams per square centimeter of Earth's total surface (dividing by 5.10×10^{18}) or per liter of sea water (dividing by 1.37×10^{21} or 1.69×10^{21}).

If we could convert all metal ions in the ocean water to oxides, these oxides would correspond to about 5 kilograms per square centimeter and could thus cover the whole surface of Earth with a layer about 20 meters thick. In contrast, the thickness of sediments and crust is measured in thousands of meters.

Contribution from Rivers

The annual inflow of water from rivers has been estimated at 3.64×10^{16} liters (*13*, p. 28) or 3.3×10^{16} liters (*7, 15*) for 1 square centimeter of Earth's surface and 1 million years (My), inflow amounts to about 7140 liter/(cm^2 · My), if one accepts the former figure.

The rivers carry to the ocean suspended matter and dissolved ions that derive largely from weathering—from the attack of wind and water on rocks. The amounts of ions carried by rivers to the sea are calculated (Table 2) from Clarke's (*14*) and Livingstone's (*15*) estimates of the average ionic concentrations in river water. More accurate data are desirable, notably from some of the world's largest rivers.

The Cl^- in Table 2 is likely to stem largely from salt spray that is continually blown inland from the ocean and washed back; it seems natural to subtract it together with corresponding amounts of Na^+ and Mg^{2+}. Having made this correction, Barth (*16*) defined the period of passage, or residence time, for an ion as the ratio between the total amount of that ion dissolved in the ocean and the (corrected) amount added each year in solution in river water; this period is the average time such an ion spends in the ocean before it is removed into sediments. For instance, Barth has calculated residence times of (millions of years): 120 for Na^+, 23 for Mg^{2+}, 10 for K^+, and 1.3 for Ca^{2+}. For other elements, much shorter residence times have been calculated (years): Ba, 50,000; Al, 3100; Pb, 560 (*2*, vol. 1, p. 163). However, a considerable part of the ion flux in Table 2 may be balanced by the reactions of sea water with clay from the rivers.

For the amount of suspended matter (mostly clays) carried by the rivers to the ocean, Mackenzie and Garrels (*7*) estimated a minimum of 8.3×10^9 tons per year or 1600 g/(cm^2·My), assuming that in ratio of suspended:dissolved matters all rivers equaled the Mississippi. The maximum estimate was 32.5×10^9 tons per year or 6400 g/(cm^2·My) [from Kuenen's estimate of 12 cubic kilometers per year (*17*)]; Strakhov (*13*, p. 5) gives 12.7×10^9 tons per year or 2500 g/(cm^2·My).

Freshwater clays may react with sea water either by ion-exchange reactions or to form new phases; the evidence up to 1965 is summarized by Holland (*8*). One might expect the net result to be release of Ca^{2+} and H^+ and binding of K^+ and Mg^{2+}—perhaps of Na^+ also. An example of the reaction capacity is that about 400 grams of kaolinite or mica (illite) is equivalent to 1 mole of H^+ or K^+ by reaction 2 (to be defined). Even if the inner parts of large clay particles are detrital and not accessible to reaction with sea water in reasonable time, enough reaction capacity is surely available to alter drastically some of the values given in Table 2.

Table 2 is based on analyses performed in the customary way by filtering off the clay and analyzing the clear river water. One would like the analyst sometimes to put a known amount of that moist fresh water clay into a column and let sea water trickle through it very slowly until the water comes out with its composition unchanged; then to determine how much of each ion has been added to the sea water or taken from it by the clay. These amounts (recalculated to the unit of flux) should then be added to or taken from the amounts carried in the solution, if one wishes to determine what ions the river has really added to the ocean water. By summing such data for all the world's rivers, one could produce a table corresponding to Table 2 but probably with considerably smaller net additions to the sea for some ions—perhaps even negative numbers. From such a table one might try to calculate new values for residence times, but what they really mean may remain an open question since there are terms to be considered other than contributions from rivers.

Other Entries in the Budget of the Ocean System

Wind and rain bring a considerable amount of material to the ocean: ions from biologic and photochemical reactions and from sea spray, and dust from the continents. Crude estimates (*18*) suggest that about 0.8 mole of nitrogen, bound in NO_3^- and NH_4^+ would be added per square centimeter per million years. Recent data (*19*) indicate that airborne dust may constitute a major fraction of the sediments in the deep Atlantic; the contribution to the whole ocean may be of the order of 100 g/(cm²·My).

In addition, matter enters the sea from below the sea floor by underwater volcanism and in more discreet ways; a large portion of the South Pacific sediments seems to be products of reactions of sea water with basaltic lava and solutions from underground (*20*).

Uplift and submergence of land are other factors to consider. Some of the world's highest mountains are old marine sediments. Submergence of 200×10^{20} grams of calcium (in the form of $CaCO_3$) to be uplifted every 100 million years (which may be a reasonable order of magnitude), this figure would correspond to removal of $CaCO_3$ at 1 mole/(cm²·My) from marine sediments. Submergence of freshwater clay, or uplift of sea-water clay to be washed out by rainfall, may lead to ion exchange with the sea that escapes bookkeepers at the mouths of rivers.

Sediments, primarily stemming from weathering of rock, accumulate outside the fringes of the continents. Old sediments are buried under new sediments, together with interstitial sea water, and eventually may be brought to temperatures and pressures at which volatiles are driven off toward the surface and new rocks are formed; this process is called *metamorphism*. By movements in Earth's crust metamorphic rocks eventually find their way back to the surface to a new cycle of weathering, sedimentation, and perhaps metamorphism.

Table 3. Balance of materials for the formation of 1 liter of sea water (*27*); calculated from the estimates of Goldschmidt and Horn. Unit, mole per liter of sea water.

Component		Source		Now:		
		Primary rock	Volatile	Air	Sea water, 1 liter	Sediments
H_2O			54.90		54.90	
Si	(SiO_2)	6.06/12.25				6.06/12.25
Al	($AlO_{1.5}$, $Al(OH)_3$)	1.85/ 3.55				1.85/ 3.55
Cl	(HCl)	0.01/ 0.02	0.54 /0.94		0.55	–/ 0.40
Na	($NaO_{0.5}$, NaOH)	.76/ 1.47			.47	0.29/ 1.00
Ca	(CaO, $Ca(OH)_2$)	.56/ 1.09			.01	.55/ 1.08
Mg	(MgO, $Mg(OH)_2$)	.53/ 0.87			.05	.48/ 0.82
K	($KO_{0.5}$, KOH)	.41/ .79			.01	.40/ .78
C*		.02/ .03	.60 /2.06		.002	.62/ 2.09
	CO_2)	.02/ .03	.53 /1.05		.002	.55/ 1.08
	(C(s))		.07 /1.01			.07/ 1.01
O_2*			.027/0.022	0.027/0.022		
Fe*		0.55/ 0.91				.55/ 0.91
	(FeO, $Fe(OH)_2$)	.32/ .53				.18/ .32
	($FeO_{1.5}$, FeOOH)	.23/ .38				.37/ .59
Ti	(TiO_2)	.06/ .12				.06/ .12
S*		.01/ .02	.06 / .06		.03	.04/ .05
F	(HF)	.03/ .05				.03/ .05
P	($PO_{2.5}$, H_3PO_4)	.02/ .04				.02/ .04
Mn*	($MnO_{1 \text{ to } 2}$)	.01/ .05				.01/ .05
N_2*			.101/ .082	.101/ .082		

* Affected by changes in *pE*.

There are reasons to think that the present ocean floor is not many hundreds of million years old. For instance, new ocean floor may be welling up at the Mid-Pacific Ridge while old ocean floor may be continuously slipping below the continent of Asia, under the Japanese islands (Fig. 1) (*21*). Again, such changes must represent large entries in the chemical budget of the system (sea water plus sediments).

Carbonates and other minerals dissolve in sea water or precipitate from it. The annual amounts seem hard to estimate and will perhaps have to be the residual terms in the budget when everything else has been estimated.

Even if we stick to the nonvolatile

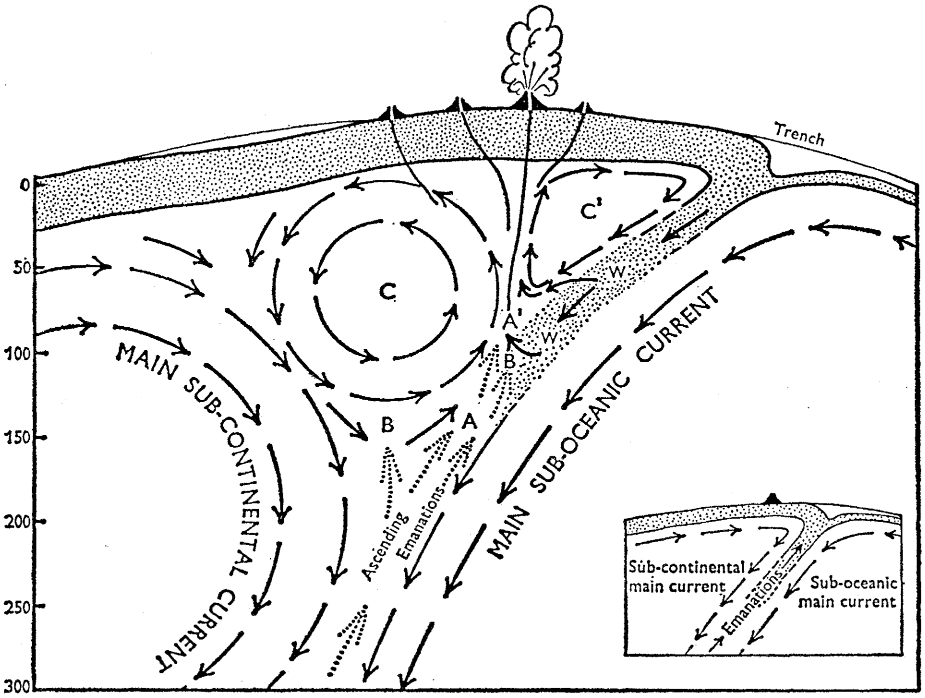

Fig. 1. Diagrammatic section across a typical island arc such as Japan or Kamchatka (from *21*, p. 1022). Ordinate: kilometers.

constituents and leave out H_2O and dissolved gases, it does not seem possible at present to make an accurate hundred-million year budget for the ocean. At any rate, we may compare the amounts of ions dissolved in sea water; multiplying the concentrations in Table 1 by 339 (kilograms of sea water per square centimeter, if we include the interstitial water), we find (moles): 158.7 Na^+, 18.0 Mg^{2+}, 3.5 Ca^{2+}, 3.4 K^+, 185.1 Cl^-, 9.6 $SO_4{}^{2-}$, and 0.8 $HCO_3{}^-$ per square centimeter of Earth's surface. On the other hand we may multiply by 100 the fragmentary estimates for ions in Table 2 and for solids (above) to get the input per 100 million years. The total amount of ions dissolved in sea water is obviously small compared with the amount of matter—dissolved ions and, especially, clay minerals—that have been carried through the ocean system even during the last 100 million years.

So we may ask: Can the ocean maintain a roughly constant composition and, if so, how? Before we try to answer that question let us look at the so-called geochemical balance.

The Geochemical Balance

In 1933 Goldschmidt (*22*) attempted to establish a balance showing how the ocean was formed by a one-way reaction of primary igneous rock with volatiles. For each liter of sea water, about 600 grams of igneous rock had been consumed, according to his calculations; the reaction may be written:

$$\underset{0.6\text{ kg}}{\text{igneous rock}} + \underset{\approx 1\text{ kg}}{\text{volatiles}} \rightarrow \underset{1\text{ liter}}{\text{sea water}} + \underset{\approx 0.6\text{ kg}}{\text{sediments}} + \underset{3\text{ liters}}{\text{air}} \quad (1)$$

Using reasonable values for the average compositions of igneous rock and sediments, Goldschmidt could make ends meet on balance for a number of nonvolatile elements. (The volatiles, of course, come in as a difference.) Several attempts have since been made to improve the geochemical balance; the most sophisticated example is perhaps Horn's (*12*), which gave agreement for about 60 nonvolatile elements. Table 3 gives Goldschmidt's and Horn's figures for the major components, expressed in units of mole per liter of sea water.

According to the now-prevalent "cold theory" of planet formation, Earth was formed by agglomeration of cold particles and heated partly by released gravitational energy, partly by radioactive processes. The present crust (igneous rock) would result from chemical reactions and separation by gravity; the volatiles (such as H_2O, CO_2, and HCl) would have been carried, by distillation, toward Earth's surface from the interior.

So far, the scene is well set for formation of the ocean by reaction 1. However, it is hard to believe that a one-way process (reaction 1) is a good description of the real system. Indeed, metamorphism may be described as the reversal of reaction 1: the formation of new (igneous) rocks from sediments, often in the presence of interstitial sea water or of salts remaining after evaporation of sea water.

If we accept Barth's (*16*) estimate of the rate of weathering (2.4 kg/$cm^2 \cdot$My), even Horn's estimate (*12*) of the total weathered amount (2.04×10^{18} tons, or about 400 kilograms per square centimeter) was produced within less than 170 million years, whereas the ocean is thought to have existed for more than 2000 million years—perhaps more than 3000. We may conclude, as did Barth, that the sediments have on the average had time to run through many cycles of weathering and metamorphism rather than just a single weathering step (reaction 1). On the other hand, it is a striking fact that Horn could make ends meet for practically all nonvolatile elements, using average analytical data for the compositions of igneous rock and sediments. One cannot escape the feeling that this agreement must have some meaning, and in fact, if one deduces the conditions for a recycling system to have reached a steady state, one gets equations of exactly the same form as those for the balance for the one-way process. The proof will be reported elsewhere (*23*); here I shall only indicate the simple model used.

A Recycling Model

The model (Fig. 2) has five reservoirs, each of uniform average composition: continental rock *C*, basaltic rock *B*, "continental" sediments S_C, "basaltic" sediments S_B, and ocean *O*. In Fig. 2b, S_C and S_B are the shaded areas. By weathering and other processes, matter is continually being transferred from *C* to S_C and *O*, and from *B* to S_B and *O*. On the other hand, parts of S_B, S_C, and *O* are continually moving down to depths where metamorphism occurs; the products will eventually add to *B* or *C* by separation processes that need not concern us here. There may also be some transport of material from below to *B* and between *B* and *C*.

The model as drawn in Fig. 2 reminds one of the illustration that has been suggested for the movement of ocean floor plus sediments below the continents (Fig. 1). However, this geometric arrangement is not important for calculations from the model. Metamorphism can just as well be achieved by moving a trough filled with sediments straight downward to a sufficient depth. In real life it may be hard to draw sharp limits between *C* and *B* and between S_C and S_B for *C* and *B* are mixed, the sediments are spread all over and there are intermediate stages of metamorphism.

The Equilibrium Model

Whichever way we interpret the geochemical balance, the last two columns in Table 3 give us the amounts of the main components in 1 liter of sea water and the corresponding amounts of various sediments. The difference between Goldschmidt's and Horn's values, large as it may seem, is of little importance; we may use either in the following discussion.

In 1959 I suggested (*1*) that it may help us to understand the real system if we try to compare it with an equilibrium model containing the same amounts of all these components, with the difference that in the model they are allowed to reach true equilibrium.

This does not mean that I suggest that there would be true equilibrium in the real system. In fact practically everything that interests us in and around the sea is a symptom of nonequilibrium: the various forms of life, the currents, the shifting weather and so on. What one can hope is that an equilibrium model may give a useful first approximation to the real system, and that the deviations of the real system may be treated as disturbances.

As one example of equilibrium plus disturbances, let us consider a column of sea water, at uniform temperature, having an excess of a solid substance whose solubility increases with pressure —such as $CaCO_3$. The curve of solubility versus depth would then be something like the solid curves in Fig. 3. (Since $[Ca^{2+}]$ varies very little in the ocean, we might let the "solubility" of $CaCO_3$ be represented by the concentration $[CO_3{}^{2-}]$ at equilibrium.) If true equilibrium were reached, the solid would sit on the bottom. The solution would be saturated at the bottom, but increasingly undersaturated with decreasing depth, and the concentration would follow a curve like the broken line in Fig. 3a. Attainment of such a true state of equilibrium would require that diffusion be fast relative to stirring.

In the ocean, however, the stirring is fast (of the order of one turn per millennium), thus disturbing the equilibrium and tending to level the concentration. If stirring were the only disturbance, one would expect a state as in Fig. 3b, where the solution is undersaturated at the bottom and supersaturated in the upper part; the solid would then collect in the upper part. (The ocean, of course, offers convenient places for a solid to be deposited at any of various depths.) In fact, this is roughly what one observes: there is a "snowline" at a depth of about 4000 meters, below which $CaCO_3$ becomes very scarce (*2*, vol. 2, p. 127).

To explain further details in the real picture, one would have to consider further disturbances, especially temperature gradients and the action of various forms of life. For instance, the equilibrium form of $CaCO_3$ would be calcite containing a small amount of $MgCO_3$ in solid solution. In fact some creatures prefer to build shells of Mg-rich calcite, or of aragonite (another form of $CaCO_3$), which may remain unchanged for very long periods; with increasing age and depth, however, the equilibrium form is favored (*2*, vol. 2, p. 127).

[The pessimistic view is sometimes held that an equilibrium model cannot be used even as a first aproximation; in order to understand the stability of the natural system one must determine the rate laws for all important processes and solve the rate equations. This procedure would of course be flawless (could it be carried through correctly), but in practice the task may easily become very complicated. We may remember that even in an instance in which the equilibrium laws give a very clear and simple description—as in calculation of the solubility of AgCl in an aqueous solution or of the *p*H of an acetic acid–acetate buffer—it would be possible to describe the situation without mentioning the word "equilibrium"; one would only have to determine the rate laws for the back-and-forth reactions and to set up the kinetic equations. Whether this would be the most practical approach is another question.]

Here we shall consider briefly two stages of the model: stages I and III; it has been discussed in more detail (*1, 9–11*).

Stage I: A Simplified Ocean Model

Let us first mix the five components HCl, H_2O, KOH, $Al(OH)_3$, and SiO_2 and let them reach equilibrium. This is an "ocean model": the two first components correspond to the volatiles; the other three, to the components of igneous rock. It is "simplified," since some even major components are missing, notably Na, Mg, Ca, CO_2, and Fe. However, it shows some characteristics that may help one understand the complete model.

Over a wide range of mixing ratios there may be five phases at equilibrium: a gas phase (mainly H_2O), an aqueous solution, quartz (SiO_2), kaolinite [$Al_2Si_2O_5(OH)_4$], and potassium mica [$KAl_3Si_3O_{10}(OH)_2$]. The system at equi-

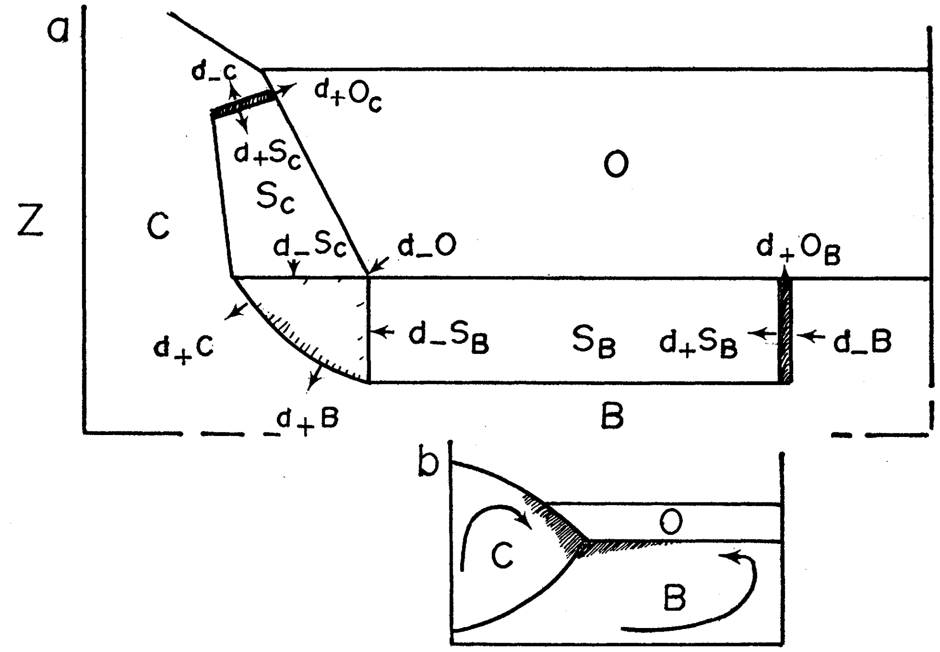

Fig. 2. A recycling model (*23*). (a) Reservoirs *B, C, O,* S_C, and S_B are indicated; arrows indicate transport of matter into or out of a reservoir. The weathering of *B* and *C* is indicated by the two thin fields at the ends of S_B and S_C; metamorphism, by the triangular field. (b) Directions of movement in the model; sediments S_C and S_B are indicated by shading.

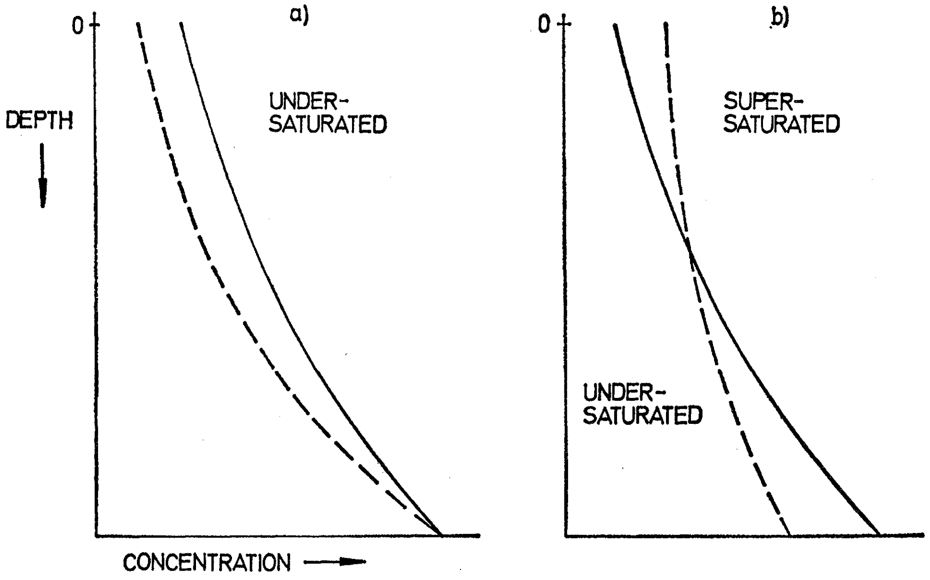

Fig. 3. Schematic curves of concentration versus depth (broken lines) for a solid whose solubility (solid curves) increases with pressure: (a) at complete equilibrium with solid at bottom; (b) when equilibrium is disturbed by stirring.

librium is characterized by the variables p [total pressure, mainly $p(H_2O)$], T (temperature), and the ionic concentrations $[H^+]$, $[K^+]$, and $[Cl^-]$. From Gibbs's phase rule it follows that only $(5 + 2 - 5 = 2)$ of these variables can be varied independently. The practical choice is T and $[Cl^-]$, since Cl^- cannot escape from the solution under the conditions of interest. Once one has chosen the values for T and $[Cl^-]$, it follows from the phase rule that $[K^+]$ and $[H^+]$ are fixed.

This result can also be understood by applying the law of mass action, omitting the activity factors for simplicity. For the reaction

$$1.5\ Al_2Si_2O_5(OH)_4(s) + K^+ \rightleftarrows KAl_3Si_3O_{10}(OH)_2(s) + H^+ + 1.5\ H_2O \quad (2)$$

the equilibrium condition is

$$[H^+]/[K^+] = K \text{ (a constant)} \quad (3)$$

On the other hand, the charge condition for positive and negative ions gives

$$[K^+] + [H^+] = [Cl^-] + K_w/[H^+] \quad (4)$$

The last term stands for $[OH^-]$. For a given temperature both K and K_w are fixed. If $[Cl^-]$ also is given, we have the two Eqs. 3 and 4 for the two unknowns $[H^+]$ and $[K^+]$, which are then uniquely determined. To a mixture of these phases one could add large amounts of KOH or HCl; at equilibrium the system would return to the same pH and $[K^+]$ as long as no phase disappeared completely and $[Cl^-]$ was kept constant. Hence we have a pH-stat rather than a buffer.

Stage III: Nine Components

Next we add four more components to get the nine: HCl, H_2O, CO_2, NaOH, KOH, CaO, MgO, SiO_2, and $Al(OH)_3$. If we had an equilibrium assemblage of nine phases, the system would have only $(9 + 2 - 9 = 2)$ independent variables. Hence, after we had chosen T and $[Cl^-]$, the compositions of the aqueous phase and the gas phase would again be completely fixed.

In 1959 I dared to suggest (*1*) that in the equilibrium model we have the right number of phases to fix the composition of the aqueous solution; and, moreover, that the composition (including the pH) of sea water is not far from that of the aqueous solution in the equilibrium model at this stage.

The general objection was that silicates react too slowly to come anywhere near equilibrium with ocean water. It is true that the sediments consist largely of detrital grains—fragments of continental rock transported by wind and river—and that the inner parts of such grains have not had much chance to react and may not be in equilibrium with sea water. On the other hand, the fine-grained material, especially the clay fraction (finer than 2 microns), reacts at an appreciable speed. For instance, Whitehouse and McCarter (*24*), studying the reaction of freshwater clays with sea water, found (i) ion-exchange reactions practically completed within the first 24 hours, and (ii) phase transformations of montmorillonite to chlorite and illite in the course of a few years. As I have mentioned, such reactions are likely to occur at the mouths of rivers. Mackenzie and Garrels (*6*) found that sea water dissolves silica from various clay minerals and reaches a sort of saturation in the course of a few months; these are short times in geology.

Hence, when we are looking for candidates for the solid phases in our equilibrium assemblage, we may reasonably pay special attention to the phases in the clay fraction both on the continental shelf and in the deep ocean.

A Working Hypothesis

Some time ago I suggested (*11*) as a working hypothesis that the equilibrium assemblage for the nine-component equilibrium model would contain the following phases: (i) gas phase; (ii) aqueous solution; (iii) quartz; (iv) kaolinite; (v) illite (hydromica) closely related to the mica phase in the simplified model; (vi) chlorite, a Mg-rich layer mineral; (vii) montmorillonite, another layer mineral, especially rich in Na; (viii) calcite, $CaCO_3$; and (ix), tentatively, phillipsite, a zeolite mineral found to grow in many parts of the Pacific.

To compare the equilibrium model with the real system, one would need to know more about both. At present, Hemley *et al.* (*3, 4*) seem to be the only scientists to have made experiments in which two well-defined aluminosilicate phases have come reasonably close to equilibrium with each other and with an aqueous solution of known composition. Extrapolation to sea-water temperature from his data (*3*) for the K-mica equilibrium (reaction 2) gives a value for K, defined by Eq. 3, between $10^{-6.0}$ and $10^{-6.5}$, which is interesting close to the ratio $[H^+]:[K^+]$ in sea water—about $10^{-6.2}$. Exact agreement could not be expected, even with complete equilibrium, since the oceanic hydromica is not pure K mica but also contains other components. For the equilibria with Na montmorillonite (*4*), the extrapolation is more uncertain but again agrees reasonably (*8*). For systems with Mg and Ca, laboratory data are missing.

Turning to the real system, one would like someone to separate the phases in various types of ocean sediments and study each phase separately by chemical and x-ray methods. Such a separation, without chemical alteration of the phases, is a difficult experimental task which could perhaps best be achieved by continuous electrophoresis in sea-water medium. If the ocean is to resemble the equilibrium model, one would expect montmorillonites, from various parts of the ocean, to have generally similar chemical composition; chlorites and hydromicas, likewise.

For six of the seven solid phases (phases 3–8) in our working hypothesis, there is good evidence that they exist in large amounts in oceanic sediments, seemingly at equilibrium with sea water. For phillipsite the evidence is much weaker; there are even observations indicating that it will dissolve in sea water. One might make several other guesses for the last solid: a Ca-rich montmorillonite (with a miscibility gap to Na-montmorillonite), a feldspar, another zeolite, some very badly crystallized layer silicate that does not show up much in the x-ray diagrams, and so on.

Holland (*8*) has recently suggested a model in which the main cations are regulated by the seven solid phases that I have just mentioned, except that the dubious phillipsite is replaced by dolomite, $CaMg(CO_3)_2$. In essence, his starting point is an equilibrium model with all cation concentrations locked. However, because of the notoriously slow equilibration of dolomite, somewhat larger excursions from equilibrium —especially for $[Ca^{2+}]$ and $p(CO_2)$— may be possible than if the last phase had been a fine-grained silicate. Again, there is a little flaw in this model: dolomite has been found to grow in solutions higher in $Mg^{2+}:Ca^{2+}$ ratio than sea water, but not yet in sea water itself.

We may hope that, in the not-too-distant future, equilibrium studies and phase separation of many sediment samples will give us a better basis for discussion of the "missing link." I have let phillipsite remain in the equilibrium assemblage just like the old house in

Hans Christian Andersen's tale of the ugly duckling: the house was so miserable that it could not even make up its mind on which side to fall, and so it remained standing.

It may be noted in passing that, if the ninth phase is a silicate, one may take away $CaCO_3$ and the small amounts of carbonate ions and CO_2 and get an eight-component system having practically the same $[Ca^{2+}]$ and pH; thus the carbonate system, rather than determining the pH of sea water, may serve as an indicator for the pH and $[Ca^{2+}]$ already established by the aluminosilicate equilibria.

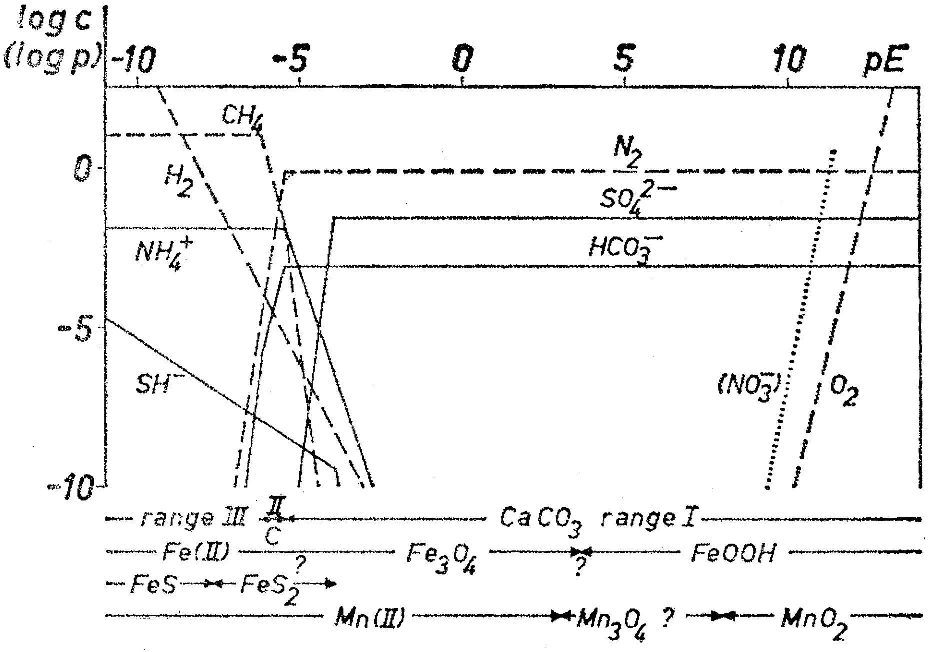

Fig. 4. Logarithmic redox diagram (*28*) showing log c (solid line) or log p (broken line) for the main variable species as a function of pE in the model system. At the lower end are shown the ranges in which various solids would be stable.

Carbon Dioxide

Several articles apply (*26*). In the equilibrium model, $p(CO_2)$ would be fixed by the T and $[Cl^-]$ chosen. In the real system, the CO_2 content of the air may be important for Earth's climate since it helps to diminish the loss of heat by radiation from Earth's surface. It has been suggested that a certain increase in the average temperature during the last few decades is connected with a general increase in $p(CO_2)$, of the order of 10 percent, that has been ascribed to industrial combustion. Perhaps I should make two comments:

1) In the equilibrium model, increased temperature would again give an increase in $p(CO_2)$; the crudest of equilibrium calculations (*27*) suggests an increase of about 10 percent in $p(CO_2)$ for increase by 1°C. Thus even a slight increase in $p(CO_2)$ might lead to an explosive development if there were no process acting in the other direction. Let us, however, remember that increased temperature is likely to cause increased cloudiness, so that a smaller fraction of the energy from solar radiation reaches Earth's surface (*10*).

2) Great variations in climate were known even before industrial combustion commenced. In determining climate, industry may be less important than changes in solar radiation or in systems of currents in ocean and atmosphere.

The Complete Model and the Real System

One may complete the equilibrium model by adding more and more components. Before Fe and Mn are introduced, it is convenient to characterize the oxidation state of the system by means of the quantity pE, which is analogous to

$$pH = -\log \{H^+\}$$

and defined as

$$pE = -\log \{e^-\} \qquad (5)$$

The scale for the electron activity $\{e^-\}$ is defined so that

$$pE = e/0.05916 \ (25\,^\circ C),$$

where $e(=E_h)$ is the reversible redox electrode potential measured against a standard H_2 electrode. Under the present conditions

$$[p(O_2) = 0.21 \text{ atm}, pH = 8.1]$$

we would have $pE = 12.5$, and $FeOOH(s)$ and $MnO_2(s)$ would be the solid forms of Fe and Mn at equilibrium (*1*). These are also found abundantly in the ocean sediments.

When the other, minor, components are added, some will add a new phase to the model: $TiO_2(s)$ for Ti, $BaSO_4(s)$ for Ba. Others will enter some existing phase and add a new concentration variable: $p(N_2)$ for N_2, $[SO_4^{2-}]$ for S, and the mole fraction x_{Sr} in $(Ca,Sr)CO_3(s)$ for Sr.

Except in regions influenced by biologic reduction, the solid phases found in ocean sediments roughly correspond to what one would expect for equilibrium, as far as one can judge from the present studies of incompletely separated mixtures. On the other hand, some metals exist in sea water at much higher concentrations than one would expect at equilibrium with the solid phases. For instance the total concentration of Mn is around $10^{-7}M$, whereas the highest equilibrium concentrations calculated for known species are $[Mn^{2+}] \approx [MnO_4^-] \approx 10^{-16}M$. The situation is similar for Fe, and one may suggest that Mn and Fe exist as dissolved species with formulas that cannot yet be found in the standard textbooks. Perhaps the important species are OH-complexes such as $Fe(OH)_3$, but it is equally possible that they are complexes with phosphate or with some organic substance in sea water.

Some Disturbing Factors

As I indicated during discussion of Fig. 3, differences in temperature and pressure may cause large-scale transport of material such as $CaCO_3$, but one may reasonably hope that the composition of sea water will correspond to the equilibrium values at some intermediate temperature and pressure. More complicated are the nonequilibrium processes such as photochemical and life processes. They are not so likely to affect the concentrations of the major ions, or the compositions of phases that do not form part of an organism. On the other hand, minor components of sea water, such as Si and P, may be depleted, in some regions, far below the values for saturation with solid phases (quartz or hydroxyapatite).

An especially blatant example of nonequilibrium is nitrogen. At the present *p*H and *pE* of sea water, practically all N should be present as nitrate ions (NO_3^-) in sea water rather than as N_2 in the atmosphere. Attempts (*18*) to make a nitrogen balance for the whole ocean, or for a certain area, indicate that a term is missing: N_2 is transformed to nitrate and other N compounds by processes in the air and by the work of bacteria in the soil and in the ocean. Rain and rivers carry a steady flow of nitrate and other N compounds to the ocean, and the only known process working the other way seems clearly insufficient: it is the reduction of nitrate to N_2 in certain reducing pockets in the ocean. To explain the data one would like to have a source of N_2 close to the ocean surface: a process, probably biochemical, that transforms nitrate (or other bound N) to elementary nitrogen even in the presence of excess O_2. However, such a process has not yet been discovered (*28*).

Models for Earlier States

Other phase assemblages? Let us assume that our real system resembles the recycling model in Fig. 2, and that ocean plus sediments are approximately described by an equilibrium model. If the ratio $HCl:H_2O$ is given from the original composition of Earth and if the compositions of the basaltic and continental layers are given by high-temperature equilibria, was then the composition of the sea already determined before it formed, and has it always been practically the same?

As we have seen, the composition of sea water may be tethered to the equilibrium composition corresponding to a certain phase assemblage, and to the average temperature. If so, we may expect that small variations in the temperature or in the ratios of various components would not change the assemblage. However, very large changes might do it: for instance, earlier the sea may have had access to more basalt and less granite with which to react than now, and thus there may have been less K and Na and more Mg and Ca in the sea-sediment system. These differences may have sufficed to overthrow the present equilibrium and to replace one or two phases by others that may tether the sea-water composition to some other fixed point. Phase studies of very old sediments might give some indication.

Reduced states. There seems to be no way by which considerable amounts of free oxygen could have been brought to Earth's primeval atmosphere either with the "hot" or with the "cold" theory for formation of the planet. Free oxygen must have been added later, and two reactions have been suggested: photochemical dissociation of $H_2O(g)$ (with subsequent loss of H_2 to outer space),

$$2H_2O(g) \rightarrow 2H_2(g) + O_2(g) \qquad (6)$$

and photosynthesis, which leads to the formation of free oxygen and organically bound carbon,

$$CO_2(g) \rightarrow C(\text{org}) + O_2(g) \qquad (7)$$

Biologic oxidation is the reversal of reaction 7, and in order to obtain a net excess of oxygen some of the carbon must be buried. On the other hand, there are reactions that consume oxygen, especially the oxidation of iron (II) to iron (III) and of sulfide to sulfate. There are recent discussions of the evolution of the atmosphere (*25, 26*).

To get an idea of what the earlier states of our real system may have looked like, I have tried to calculate (*27, 28*) the effect on the equilibrium model of reduction by, for instance, addition of H_2, letting equilibrium be reached after each addition. I assumed that the *p*H of the model was always kept about 8.1 by aluminosilicate equilibria, that the temperature was kept at 25°C, and that ammonium ions were distributed between solution and aluminosilicates in the same ratio as is K^+ in the ocean system nowadays. The choice of temperature had no other justification than the existence of extensive tables of equilibrium constants at 25°C; calculations were also made for 100°C.

The main results are indicated in the logarithmic diagram (Fig. 4). The horizontal scale gives *pE* (Eq. 5), and the vertical scale gives log *p* for gases (broken lines) and log *c* for substances in solution (solid lines); only the most important species is given for each variable element. At the lower end are indicated the solid phases that might exist at equilibrium; the present state is at $pE \approx 12.5$ [$\log p(O_2) = -0.69$] and the reduced states are to the left. With good luck they may correspond to earlier states of the system sea water plus air plus sediments.

I must refer to the original for detailed discussion, which also includes the oxidation balance of the ocean system, and the concentrations of organic substances. On one point I wish to apologize: I would not have applied the expression "The myth of the probiotic soup," to the idea that the whole primeval ocean was a thick soup of organic substances, had I been aware that the English word "myth" is only derogatory. I had in mind the Greek meaning of μυϑος—saga, oral tradition, told but not (yet) proved—which is the same as the Swedish meaning of *myt* in serious (for example, historical) contents.

Conclusion

This discussion may have given the feeling that the present composition of ocean water does not result just from blind chance. The composition may in the main be given by well-defined equilibria, and the deviations from equilibrium may be explainable by well-defined processes. However, much remains to be discovered by laboratory work and studies of the natural systems.

For any discussion of equilibria between sediments and sea water to become really fruitful and decisive, one must achieve a much better separation of the various sediment phases than has been obtained hitherto. Equilibrium data for various silicate systems are highly desirable. Studies of various elements indicate that there are serious gaps in our knowledge of soluble species and of equilibrium constants for known species; equilibrium measurements in the ionic medium, sea water, are scarce and not too reliable.

Obviously, better understanding of the system ocean plus air plus sediments and of its history will require close cooperation between geologists, biologists, and chemists of various specialties.

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Behavior of Vervet Monkeys and Other Cercopithecines

New data show structural uniformities in the gestures of semiarboreal and terrestrial cercopithecines.

Thomas T. Struhsaker

The number of field studies on the behavior of nonhuman primates has increased greatly during the past decade, the majority being on Old World monkeys (*1*). These studies provide normative information on such diverse topics as social organization, population density, predator-prey relations, communication, home range utilization, and mother-infant relationships. One of the more interesting features of these studies is their potential contribution to our understanding of the evolution of primate communicative behavior. The evolutionary and functional significance of the behavior and social organization of any species is much more clearly understood when the species is observed under natural rather than artificial conditions. Because many of the Old World monkeys are readily observable under free-ranging or field conditions, they offer an outstanding opportunity for study of their behavioral evolution.

In order to develop theories on the evolution of communicative behavior, certain information must be available. First of all, it is imperative to have representative and detailed descriptions of the behavioral repertoires of the species to be compared. Ideally, these descriptions should be not only qualitative but also quantitative, and should specify the range of variation and the central tendency of the behavior within and between populations of the species.

Given adequate descriptions, the second problem is one of classification as it is involved in the establishment of behavioral repertoires. In determining the natural units of social behavior, Altmann (*2*) divided the continuum of behavioral action wherever the monkeys did. However, in itself this approach is not completely satisfactory for the establishment of a behavioral repertoire. It does not permit distinction between the variations of one behavior pattern, all of which have the same communicative function, and a graded system of behavior, in which there are an infinite number of functions. It is suggested that repertoires of communicative behavior be based primarily on the structurally distinct units of behavior, as suggested by Altmann, and secondarily on the communicative function of these signals, as manifested by the responses that they evoke in other animals.

Thus, if a structurally distinct pattern evokes several responses, it is classed as one unit. When several patterns that are structurally very similar evoke the same response, they are classed as variations of one pattern. On the other hand, if the patterns are radically different in form but evoke the same response, they are classed as different signals. The most obvious weakness of this method is the subjective judgment involved in deciding whether patterns are radically different in structure or not. However, as already pointed out, repertoires established on the basis of structure alone also have their deficiencies. It is my opinion that a more realistic approach to the delineation of behavioral repertoires is one based on consideration of both structure and function. For example, in most Old World monkeys the response to a threatening stare depends on whether the displayer is standing or running toward the recipient. The recipient is more likely to run away if the stare is accompanied by running than if it is not. Thus, because staring and running can occur together or alone and evoke different responses accordingly, three patterns must be recognized: staring, running, and attack (the combination of staring and running).

Finally, in any evolutionary consideration, homologues and analogues must, eventually, be distinguished. The extent of homology is indicative of the degree of phylogenetic affinity and, thus, is critical to the problem of evolution. In morphological studies the distinction between homologous and analogous characters is based on embryology, form, and specific function. Until more information is available on the form, ontogeny, and function of various behavior patterns in primates, it will be extremely difficult to distinguish homologues from analogues.

Because of the difficulty of meeting the requirements described in the preceding paragraphs and the fact that field studies of primate behavior are still in relative infancy, I restrict myself here to consideration of the sub-

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Dr. Struhsaker is research zoologist at the New York Zoological Society and assistant professor of zoology at Rockefeller University, New York, New York.