at a comparable level in open water, because of decreased circulation in and just above the sediment. The "bottom" sample of this profile may not have been lying exactly on the bottom; it was on a tether to allow it to hang past the anchor and the weak-link assemblies.

The relation of rate of dissolution to degrees of undersaturation is not clear. One intuitively feels that the greater the departure of the ion activity product, in the undersaturated sense, from the equilibrium solubility product, the greater will be the rate of the dissolving. This is surely true, in a gross sense, but there seems no assurance that the rate of solution will be related in a simple way to the degree of undersaturation, as this departure becomes small. Masking and coating and exchanging by molecules and ions may be important rate-determining effects under these conditions.

However, the main mass of sea water is undersaturated, with the exception of the upper several hundred meters, and there is an abrupt increase in rate of dissolution at a level reasonably related to the level of principal change of calcium carbonate content in the sediments.

Interpretations of the presence and absence of calcium carbonate in sediments that consider only possible variations in surface productivity and do not entertain the possibility that some predetermining level, such as that described in this report, might be subject to vertical migration, are surely now suspect and must be reviewed.

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30 September 1966

Isotopic Composition and Origin of the Red Sea and Salton Sea Geothermal Brines

Abstract. *Deuterium and oxygen-18 measurements show that the Red Sea and Salton Sea brines are the results of a single process, the leaching of sediments by surface water circulating downward to a geothermal reservoir. The Salton Sea brine is derived from local precipitation but the Red Sea brine originates 1000 kilometers south of its basin, on the shallow sill which controls the circulation of the Red Sea. On this sill sea water penetrates a thick evaporite sequence to a depth of 2000 meters, and, driven by its increased density relative to sea water, flows northward to emerge in the brine-filled deeps.*

Two remarkable occurrences of hot saline waters with salinities almost ten times that of sea water have recently been discovered in extensively faulted tectonic troughs containing thick stratigraphic sequences and igneous intrusions. The Salton Sea geothermal brine (*1*, *2*) was found 1400 m down in the sediment fill of the Salton trough, the landward extension of the Gulf of California; the extrapolated bottom hole temperature of the discovery well is 340°C (*2*). The Red Sea brine (*3*), found at a depth of 2000 m of water in the median rift at the bottom of the Red 56°C, but it is a true geothermal brine Sea, has temperatures of only 44° to considerably hotter than the surrounding bottom water of 22°C. Speculation concerning the origin of the Red Sea brine has been widespread; among the proposed processes are: local solution of exposed salt on the sea floor (*3*), evaporation in coastal lagoons with density flow of brine to the depths (*4*), release of ancient interstitial sea water (connate water) from sediments by heat and tectonic activity (*5–7*), leaching of evaporites in underlying strata (*7*), and extensive evaporation over the entire Red Sea basin in some early stage (*8*). The much hotter Salton Sea brine, which is also much more enriched in heavy metals and trace elements, is a more difficult problem; it was originally suggested that this brine is a pure magmatic water rising from a magma chamber at depth (*9*).

It is clearly fundamental for the development of our knowledge of geothermal systems to know whether these two brines, which occur in such similar geological settings, originate by quite different discrete events such as most of the processes which have been suggested, or whether they represent minor variations of basically similar dynamic circulation and concentration pattern. The multiplicity of working hypotheses cited above reflects the fact that the chemical composition of the brines does not uniquely specify their origin (*10*). They have some similarities to certain oil field brines (*11*) generally considered to be connate or to have dissolved salts from evaporites, but these in turn have compositions somewhat similar to that postulated for magmatic water (*1*); unfortunately, no known examples of actual connate or magmatic water exist for comparison. In this report I compare the concentrations of the isotopic water molecules HDO and H_2O^{18} in the brines and in other waters in the same area, and show that both brines formed by the same process—extraction of salts from sediments by downward circulating surface waters—and that the specific source waters are uniquely identified by natural isotopic labeling resulting from isotopic fractionation in the atmosphere and the sea.

Figure 1 is a deuterium versus oxygen-18 diagram showing the isotopic data measured on surface and subsurface waters of the Salton Sea geothermal region (*12*). The solid line with slope 8 and intercept 10 is the isotopic relationship established for worldwide precipitation (*13*); this relationship, the result of the several isotopic fractionation effects in the ocean-atmosphere water cycle, labels fresh waters on the earth's surface unaffected by excessive evaporation. Evaporation of fresh waters produces an isotopic enrichment with a slope of about 5 because of kinetic effects in liquid-vapor molecular exchange (*14*, *15*); the Salton Sea water is related to the water of Lake Mead in this way but is unrelated to the subsurface geothermal waters which are derived from local precipitation.

The relationship of the geothermal waters in Fig. 1 is a striking example of the "oxygen isotope shift," the increase in oxygen-18 content of local surface water with constant deuterium content, observed in seven of the world's major geothermal systems (*16*). Isotope exchange with carbonates and silicates increases the oxygen-18 content of the local meteoric water, but the deuterium content is unaffected because of the small amount of hydrogen in rocks. In the seven systems studied, the deuterium values for the local surface waters are spread along the precipitation locus over a range of more than 100 per mil; the parallel oxygen isotope shift lines show no tendency for convergence at high enrichments, showing that there is no significant admixture of a juvenile water of fixed deuterium content (*16*).

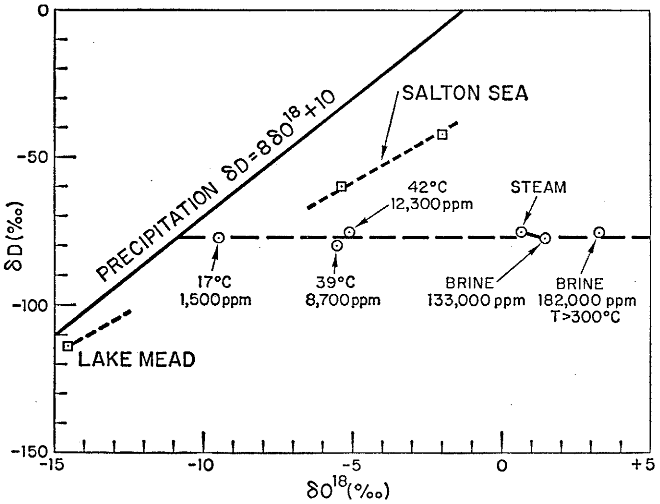
Figure 1 identifies the source of the Salton Sea brine as local precipitation entering the subsurface system along faults at the base of the Chocolate Mountains, east of Salton Sea. Two models can be made for the progressive increase in temperature, salinity, and oxygen-18 content of the waters in this system. The sequence could represent a progressive enrichment in oxygen-18 and salinity by continuous interaction with the sediments, or simply an increasing admixture of water from a deep reservoir where isotope exchange and solution begin suddenly to affect inflowing surface water. The choice between these models is given unequivocally by the relationship between chloride and oxygen-18 enrichment shown in Fig. 2, which includes data on additional waters in the system, and shows that the relationship is doubly logarithmic rather than linear. Chloride and oxygen-18 are added to the descending surface water by continuous interaction with the sediments. The chemical processes involved are such that the ratio of the fractional increase in chloride atoms to the fractional increase in oxygen-18 atoms at any time is almost constant, varying from 400 for the dilute waters to about 680 for the brine. In absolute terms, the ratio of atoms of chloride to atoms of oxygen-18 added to the water at any point varies from 100 at the start, to 1000 at an isotope shift of 6 per mil and chloride content of 10^4 parts per million, to 55,000 at the brine stage. Other elements show similar relationships which cannot be explained by mixing, with slope variations related to chemical reactions with minerals (*17*).

Table 1. Isotopic data (relative to SMOW) and chloride concentrations (by Mohr titration) in Red Sea brine samples (duplicate analyses).

Brine sample	Cl (g/kg)	δD (per mil)	δO^{18} (per mil)
No. 1. Discovery Deep (Ref. *3*, Station 5580)	155.4 155.6	7.6 7.3	1.22 1.22
No. 2. Atlantis II Deep (Ref. *7*, Station 544)	155.3 155.5	7.4 7.6	1.18
Average values	155.5	7.5	1.21

An isotopic diagram for waters of the Red Sea, covering the salinity range from inflowing Gulf of Aden water (36.2 per mil) to Red Sea Deep Water (40.6 per mil), is shown in Fig. 3. The isotopic relationship in these waters is observed to be linear with slope 6.0 and zero intercept (*18*). Isotopic and chlorinity measurements on Red Sea brine samples from the two known locations (*19*) are given in Table 1 and the isotopic data are plotted in Fig. 3. The data show that the two depressions contain brine of identical isotopic composition and chloride content. The isotopic composition plots exactly on the locus of normal Red Sea waters, showing that the brine has developed from sea water in the Red Sea basin. Outside the sill which terminates the Red Sea at the south, the Gulf of Aden and Indian Ocean waters are all less saline than the entering Gulf of Aden water shown in Fig. 3, and plot at lower isotopic delta values than the 36.2 per mil salinity water shown.

A fresh water origin for the water of this brine would require either an



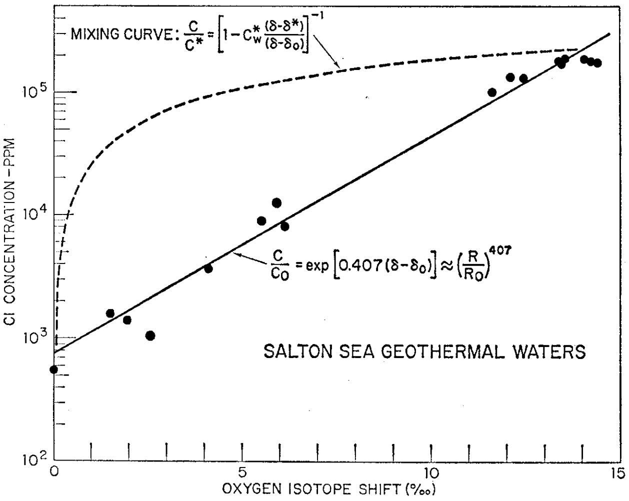
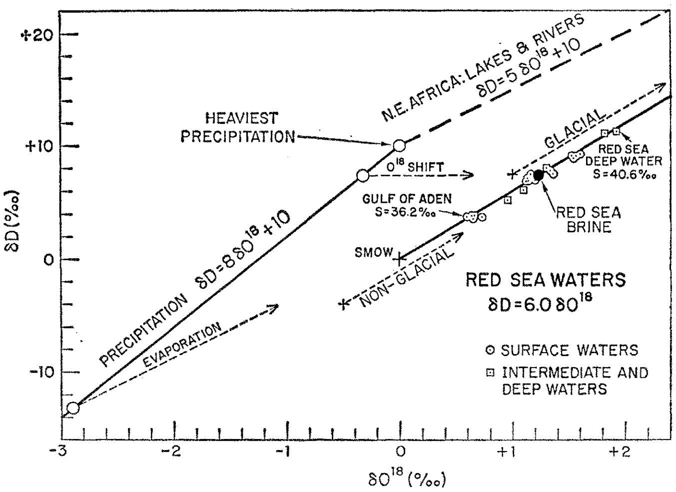


Fig. 1 (left). Isotopic composition of waters in the Salton Sea geothermal area; temperatures and chloride concentrations (parts per million) shown for subsurface waters (open circles). The water of the Salton Sea itself (upper two squares—composition varies with distance from inlet) comes from the Colorado River at Lake Mead via irrigation ditches; the short dashed line for this system has a slope of 5 because of kinetic effects in evaporation and molecular exchange. The geothermal waters are derived from local precipitation with δO^{18} of -11 per mil; in order of increasing oxygen-18 enrichment they are: a spring at the base of the Chocolate Mountains east of Salton Sea, water issuing from the "mud volcanoes" on the east shore, water from the old CO_2 production wells about 300 m deep, and two geothermal wells (WGS-3, IID-1). Fig. 2 (right). Chloride concentration (C) versus oxygen isotope shift $(\delta - \delta_0)$ relative to initial surface water ($\delta_0 = -11$ per mil) in the Salton Sea geothermal system. The observed relationship is actually doubly logarithmic because ($\delta - \delta_0$ is approximately $10^3 \ln (R/R_0)$ where R is the O^{18}/O^{16} ratio. (A better fit is obtained with chloride/water ratios.) A two-component mixture of brine and surface water would follow the almost linear relation shown by the dashed curve, where C^*, C^*_w, and δ^* refer to chloride, water, and oxygen-18 concentrations in the brine. The actual process is a continuous leaching and isotope exchange characterized by $d \ln C / d \ln R \approx 407$.



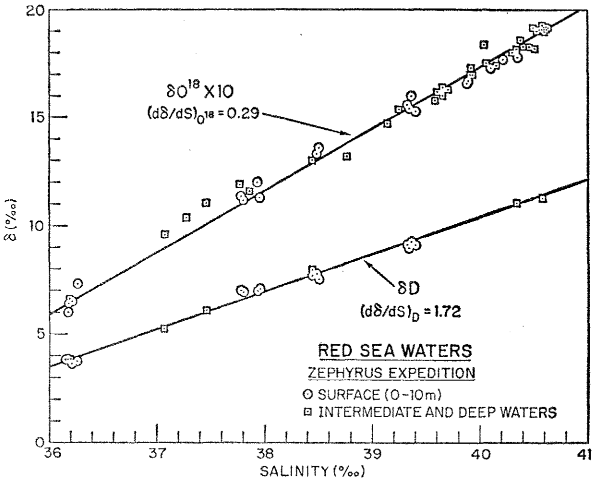


Fig. 3 (left). Isotopic diagram for the waters of the Red Sea region. The point marked "heaviest precipitation" is the end point for normal precipitation, the most highly enriched unevaporated rains I have observed. It is also the starting point for the locus of rivers and lakes of Northeast Africa (*13*) which lie along an evaporation trajectory with slope 5. The measured points for Red Sea waters lie on an offset trajectory of slope 6 and intercept zero; salinities are noted for the homogeneous deep water and inflowing water of the Gulf of Aden. SMOW is the mean ocean water standard (*12*). The dashed lines above and below the Red Sea points begin at crosses marking the isotopic composition to which SMOW would shift in glacial and nonglacial times, with maximum amounts and complete melting of continental ice. Red Sea waters would plot somewhere along these lines at such times, unless conditions in the Red Sea changed drastically. The "O^{18} shift" and "evaporation" dashed lines refer to hypothetical fresh water origins for the brine (see text). Fig. 4 (right). Isotopic-salinity relationships for Red Sea waters. The slopes are about half those observed at high latitudes in the open oceans (*15*). The deuterium and oxygen-18 isotopic delta values for the Red Sea brine (+7.5 and +1.2) correspond to an initial salinity of 38.2 ± 0.2 per mil for the water which formed the brine.

oxygen "isotope shift" from the open circle so labeled on the precipitation locus in Fig. 3 ($\delta O^{18} = -0.3$, $\delta D = +7.5$), or a previous isotopic enrichment by evaporation along the kinetic slope from a water much lower in deuterium and oxygen-18 (lower open circle on the precipitation locus, $\delta O^{18} = -2.9$, $\delta D = -13.2$). Either hypothesis requires two coincidences: an exactly specified initial isotopic composition, coupled with a process intensity (isotope exchange, evaporation) producing the exact displacement along the isotopic trajectory to terminate it at the intersection with the sea water locus. The probability of two such coincidences occurring simultaneously is sufficiently remote to eliminate both possibilities and leave no doubt of the origin of the brine from Red Sea water.

In order to determine how much mixing may have occurred between brine and deep water overlying the reservoirs, NaCl was added to the brine to saturate it. The saturation chloride content was found to be 160.8 g/kg (25°C), about 3 percent greater than the actual concentration of 155.5 g/kg (Table 1). A saturated NaCl solution at room temperature contains 265 g/kg of salt, about 4 percent more than the observed salinity of 255 g/kg (*5*). Thus not more than about 5 percent of the water of the brine could be derived from Red Sea Deep Water diluting an originally saturated brine. Such dilution would have shifted the original brine composition along the Red Sea locus in Fig. 3 by only 0.2 and 0.04 per mil for deuterium and oxygen, respectively.

I now show that the isotopic composition of the brine indicates that it must have a very young age. In the first place, it is certainly younger than early Pliocene, when the present Red Sea circulation was established by final uplift of the Suez isthmus and the ripping open of the Straits of Bab-el-Mandeb (*20*); the isotopic locus of Red Sea waters must have been quite different before these events. The water in the brine is not Pliocene ocean water, because melting of present continental ice into the sea would shift the composition of ocean water and the present Red Sea isotopic locus (*21*). In Fig. 3, water with the composition of SMOW (mean ocean water standard) (which is close to the true ocean mean) would move to the lower cross terminating the "nonglacial" locus, and Red Sea waters would lie somewhere along that locus. During Pleistocene periods of maximum glaciation, water with the composition of SMOW would shift to the upper cross terminating the "glacial" locus, which would approximately represent Red Sea waters in such periods. If some circulation into the Red Sea was maintained throughout the Pleistocene, the Red Sea water locus would have oscillated between these two lines with a period of about 40,000 years, moving off the glacial locus toward its present position about 18,000 years ago. At that time Red Sea water corresponding to the present brine composition would have had a composition $\delta D = +14.9$, $\delta O^{18} = +2.2$, if its position relative to SMOW were the same.

The composition of the brine should follow the sea water with a damped oscillation and phase shift characterized by two time constants: an aquifer flow time for water from the source, and a residence time for water in the mixed reservoir of the basin it occupies. After an initial transient phase, water of present brine composition would oscillate around a mean composition $\delta D = +9.2$, $\delta O^{18} = +1.5$ (*22*). Two time constants can be adjusted to any arbitrary time of origin to fit the brine exactly on the Red Sea locus; this requires a coincidence which may have occurred. I think it far more likely that both time constants are very short—a few thousand years. A radiocarbon measurement on the brine, which has about 7 percent as much carbon as sea water (*5*), would provide the necessary data for limits on the values of the time constants.

The brine is certainly not old enough to be a connate water, and must be part of a dynamic system. If the time constant for residence in the brine basin is even as short as 1000 years, the flux of brine into the Red Sea adds only 2.5×10^5 metric tons of salts each year, compared to 3.6×10^{10} tons of salts added by evaporation; the addition of brine is therefore insignificant for the salt balance of the Red Sea unless the time constant is of the order of 10 years or unless several hundred more such brine-filled depressions exist. Either condition is improbable (*23*).

The specific source water for the brine is identified from the isotopic-salinity relationships for Red Sea waters shown in Fig. 4 compared with the isotopic composition of the water in the brine. The source water is Red Sea water of 38.2 per mil mean salinity. It cannot be highly evaporated sea water because such water would be much more enriched in deuterium and oxygen-18 until an evaporation stage was reached at which the activity of water in the brine equaled the mean relative humidity; at this point an isolated body of brine would no longer evaporate but molecular exchange would bring its isotopic composition back toward the precipitation locus on a different trajectory below the Red Sea locus (*24*).

Source water of 38.2 per mil salinity is found only in the southern end of the Red Sea; it is, in fact, almost exactly the mean bottom water on the sill which controls the exchange with the Gulf of Aden. The sill, which is located at 13°41'N in the Hanish Islands, well north of the narrow entrance to the Red Sea, rises to a sill depth of about 100 m and then falls off sharply in the axial trough to the north. The 38.2 per mil isohaline is restricted to latitudes below 20°N and depths of less than 150 m; in summer it intersects the sill at depths of about 150 m on each side, while in winter it rises about 40 m above the sill in response to the change in wind regime. Thompson, who studied the water exchange over the sill in both its winter and summer modes, found that the salinity of the bottom water flowing out over the sill goes through a maximum of about 40.4, and a minimum of about 36.4, per mil at the extremes of the winter and summer circulation patterns; subsequent expeditions have confirmed these values (*25*). The average water lying on the sill will therefore have a salinity very close to the source water of the brine and this is probably the point where the flow to the saline basins begins. A borehole on the island of Dahlak (15°N) penetrated 2000 m of evaporite series without leaving salt; salt domes occur on islands and the shores in this region, and a seismic section at the sill showed 2500 m of 3.7 km/sec velocity material attributed to evaporites, covered by 250 m of unconsolidated sediment and lying on the crystalline basement (*26*). The sill water must penetrate this section along a fault and flow downward until it emerges 2000 m lower and 1000 km farther north, in the center of the Red Sea.

The brine cannot flow along the bottom of the Red Sea; deeper basins containing normal sea water are found along the way (*7*). The underground circulation to the central basin is driven by the density difference between 2000-m columns of brine and normal sea water. The high temperature of the brine is due to the geothermal gradient in the vertical column of sediments it must pass through; with a geothermal flux of 4×10^{-6} cal/cm^2 sec and conductivities of 5 and 10×10^{-3} cal/cm per second per degree for loose sediment and evaporite, the temperature 2000 m below the sill will be 110°C, which is more than sufficient.

With the composition of the source water established, the composition of the added salts can be calculated from the brine analysis (*27*). The result is that each kilogram of 38.2 per mil sea water has lost 2.5 g of $MgSO_4$ and gained 296.5 g of salt with a composition (percent): NaCl, 92.9; KCl, 1.5; $CaCl_2$, 5.3, and (in parts per million): Mg, 430; Sr, 175; Br, 281; Mn, 231; B, 17; Zn, 4; Fe, 1; Li, 0.5; and Cu, 0.04. In addition, 95 percent of the fluorine and 40 percent of the iodine of the sea water have been lost. The $MgSO_4$ loss corresponds to removal of 26 and 67 percent of the original magnesium and sulfate, respectively, in almost stoichiometric proportions. It is difficult to believe that $MgSO_4$ has been precipitated, but in any event magnesium has not been exchanged for calcium in dolomitization of carbonate, for at these temperatures an oxygen isotope shift would almost certainly occur in the water. The trace element composition of the added salt is quite reasonable for the halite-sylvite zone of a salt deposit (*28*).

These two remarkable brines are found, then, to have related origins in a dynamic circulation of surface water through sediments to a subterranean reservoir. When soluble salts are available a brine can form, as in the Red Sea, at very moderate temperatures. At higher temperatures if conditions are such that water can flow out of the reservoir as both steam and liquid, even very dilute ground waters will in time produce saturated brine reservoirs because the steam cannot carry away the material brought in. I have proposed elsewhere that the so-called "superheated" geothermal steam at Larderello and The Geysers, California, has separated from such geothermal brine reservoirs as saturated steam; it is superheated only by comparison with the boiling point curve of pure water (*24*, p. 204).

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10. The Red Sea brine is an almost pure NaCl brine (*5*); the Salton Sea brine is a Na-Ca-K-Cl brine with 24,000 parts per million K (*1*). Both brines are relatively low in magnesium, sulfate, and bicarbonate. All waters in each of these two geothermal systems, including the brines and sea water, obey the "NaCl sum rule": the sum of the cations divided by chloride (all weight percent) is equal to the ratio in pure NaCl, that is, 0.65.
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18. The Red Sea water samples were collected by me in September 1962 on Scripps Institution Expedition Zephyrus; the hydrographic data (16 stations) are available on computer print-out. North Atlantic and North Pacific waters have very similar isotopic relationships, with slopes of about 6.5 and 7.5 and zero intercept. Ocean waters are offset from the precipitation locus because of the kinetic effects in evaporation and air-sea exchange (*15*).
19. The brine is found in approximately 150-m isothermal, isohaline layers at the bottom of the Discovery Deep (*3*) and the Atlantis II Deep (7), about 5 miles (8 km) apart in the center of the Red Sea. Temperatures of the brine layers are 44.8° and 55.9°C respectively, but the chloride concentrations are identical in both deeps; reported data (*5, 6*) agree within experimental error with the present measurements. The Discovery brine sample was obtained through the courtesy of E. C. Bullard; the Atlantis II sample was provided by A. Jokela.
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22. This value is calculated assuming melting of all present continental ice during interglacial periods. W. Broecker has pointed out that sea level during the last two interglacials was probably close to the present level; if the present amount of continental ice was maintained during interglacials, the calculated mean brine composition is $\delta D = +11.2$, $\delta O^{18} = +1.7$, even more different from the present values. This calculation also assumes that the position of the brine relative to SMOW is maintained as the locus shifts.
23. I assume two brine depressions, each with a diameter of 2 km and depth of 150 m (7) and a salinity of 255 per mil (*5*); together they contain 10^9 tons of brine and 2.5×10^8 tons of salts. The Red Sea contains 2.2×10^{14} tons of sea water and 9×10^{12} tons of salts; the evaporation rate is 2 m a year, over an average depth of 500 m.
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28. An oil field brine, of composition very similar to Red Sea brine, has been found at a depth of 2500 m in Louisiana [(*11*), analysis No. 3 in Table 13), only 66 m from salt near the crest of a salt dome lacking an anhydrite cap, with a temperature of 87°C. These brines have surely dissolved salt from the same type of deposit.
29. I thank L. I. Gordon, D. E. White, and H. C. Helgeson for aid in the field work at Salton Sea, N. Anderson for the hydrographic work in the Red Sea, and W. Broecker for discussion. Supported from NSF grants GP-1885, GP-3347, and G-24479, and by ONR grant NONR-2216(23).

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Fluorine Content of Microsaur Teeth from the Carboniferous Rocks of Joggins, Nova Scotia

Abstract. *Because the Carboniferous deposits at Joggins, Nova Scotia, contain the earliest fauna of terrestrial vertebrates, the extremely well-preserved teeth of these ancient animals are of special interest. The "mineral" composition of teeth from the Joggins microsaur* Hylerpeton dawsoni *is crystallochemically identical with francolite, a carbonate fluorapatite. The fluorine content of the fossilized dentin is 3.1 percent, which is much higher than any previously recorded for fossil teeth.*

The oldest fossil vertebrates that were land animals have been found in the Carboniferous sedimentary rocks of Joggins, Nova Scotia. These vertebrates include the earliest terrestrial labyrinthodonts, the earliest known reptiles, and the earliest typical microsaurs, and all have teeth that are in an excellent state of preservation. Carroll (*1, 2*) has restudied all known vertebrate specimens from Joggins, and as a follow-up to his work, we have made a mineralogical study of the teeth. We have identified dentin from microsaur teeth as francolite, with a fluorine content much higher than any previously reported from analyses of fossil teeth.

These fossils occur in rocks of the Cumberland group, facies B (*3*), exposed along 40 miles (64 km) of sea cliffs on the south shore of Chignecto Bay at the head of the Bay of Fundy. They were first studied by W. M. Dawson who, with Sir Charles Lyell, visited the site in 1851 and discovered vertebrate fossils in one of the fossil tree stumps that had fallen to the beach from the cliff near Coal Mine Point. A series of papers by Dawson (*4*), Lyell (*5*), and Sir Richard Owen (*6*) were culminated in Dawson's comprehensive work (*7*), published in 1882. Despite the development of geology and paleontology since then, and the extensive field work that has been carried on in Nova Scotia and elsewhere during the intervening years, this fauna continues to be of unique interest since there are no terrestrial deposits earlier than Joggins (*2*) that contain remains of vertebrates. Because the rocks also contained well-preserved plant fossils, Bell (*8*) was able to date the sediments as Westphalian B (similar in age to the Pottsville deposits of Pennsylvania); hence these animals lived approximately 250 million years ago.

Most Carboniferous deposits throughout the world are from coal swamps. Although they present a fairly complete record of aquatic forms, they furnish little information about life on land. However, during Westphalian B, the Joggins area was apparently a restricted basin of rapid deposition. Sediments approximately 3.2 km thick are exposed along the cliff, and all were deposited in a relatively short period of time. At least 40 successive forests were buried so rapidly that the trees remained upright in their original position. Most of the trees were lycopods of the genus *Sigillaria*, and they formed stumps that were particularly favorable for trapping land animals. During the deposition of several layers, conditions were such that the broken ends of the trees remained exposed at the level of a new land surface. Since the interior of the stumps had a rather pulpy composition, it rotted out, leaving large well-like holes. These hollow cylinders served as traps for animals living on the new land surface; they fell in and could not climb out again (Fig. 1). Such a method of entrapment would favor the preservation of terrestrial rather than aquatic animals, as Carroll (*2*) has pointed out. In addition to the vertebrates, the fossil material that has been found at the base of these stumps includes the earliest terrestrial gastropods, many millipeds, some insects, and many eurypterids.

Dawson appears to have been particularly interested in the teeth of the tetrapods. No doubt the excellent preservation of many of the teeth, in contrast to the crushed and intermingled condition of many of the bone fragments, led to a natural emphasis on