

Reports

Brines and Interstitial Brackish Water in Drill Cores from the Deep Gulf of Mexico

Abstract. *Marked increases in interstitial salinity occur in two drill holes located in the Gulf of Mexico at a water depth of more than 3500 meters. The increases probably arose through diffusion of salt from buried evaporites. In one hole, however, brackish water was encountered on penetrating the oil-permeated cap rock of a salt dome. The phenomenon is attributed to production of fresh water during oxidation of petroleum hydrocarbons and decomposition of gypsum to form native sulfur.*

One of the major discoveries of the Deep Sea Drilling Project is the finding of oil-permeated cap rock on the Challenger Knoll, an intrusive salt plug at a depth of about 3700 m in the central Gulf of Mexico (1) (Fig. 1). Studies of pore waters in sediment cores recovered from this drill hole (hole 2, leg 1) (2) reveal a marked increase in chlorinity from an estimated 20 g of Cl per kilogram (20 per mil) in surficial sediments to 45 per mil at a depth of less than 110 m. Then follows an abrupt drop in chlorinity to 4.8 per mil in the cap-rock zone itself. A source of fresh water is thus indicated in the cap-rock zone. The only available sources for fresh water appear to be oxidation of hydrocarbons and dissolution of gypsum. Outside the zone of diapirs, interstitial chlorinity also increases with depth, leading to the conclusion that salt has diffused from underlying layers through great thicknesses of sediments.

Although the existence of salt had been predicted for the Sigsbee Knolls (3), seismic data revealed no indication of salt at the site of hole 3 in the abyssal plain to the southeast of hole 2. Yet, the existence of increases in salinity and chlorinity in pore water from this hole also suggests the presence of salt at depth.

The methods of sampling, handling, squeezing, and pore water analysis for major inorganic constituents on small core samples are discussed briefly by Manheim *et al.* (2). Sediment samples were taken from interior portions of cores immediately after their recovery

on the deck of the drilling vessel; one portion was usually squeezed immediately and its gross salinity determined by the measurement of the refractive index. Other portions were analyzed in shore laboratories by participating groups (4). Most of the data reported here were obtained from fluid samples ranging from 1 to 3 ml in volume; the quality of the data does not meet accuracy requirements for open ocean waters but is believed to be adequate to reflect larger pore fluid variations. The analyses are believed to be free of systematic errors substantially in excess of standard error of repeatability,

which is usually less than those due to effects attributable to manipulation and transfer of sediments on board ship and in the laboratory. The last decimal shown may be uncertain to greater or lesser extent. Studies in the earlier JOIDES (Joint Oceanographic Institutions Deep Earth Sampling) drilling program off Florida (5) showed that valid (uncontaminated) pore waters could be obtained from drill cores of the present type if proper precautions were maintained; in particular, it was necessary to exclude contaminated exterior portions of cores.

Pore water studies (6) on cores from the northern Gulf of Mexico slope, recovered by the Shell Oil Co. drilling vessel *Eureka* (7), showed that diffusion of salt proceeded from salt diapirs through fine-grained, clayey sediments and that the rate of salt diffusion agreed reasonably well with laboratory determinations of diffusion constants in clayey sediments of comparable porosity. No evidence of appreciable chromatographic or salt-sieving effects was observed. In the absence of salt diapirs, little change in water composition (other than diagenetic loss of Mg and K, and sulfate reduction with corresponding increase in bicarbonate alkalinity) was noted with depth. Positions of the earlier holes are indicated by the small solid circles in Fig. 1, and a plot of chlorinity and water content against depth is shown for one of the holes which actually penetrated cap rock and salt (Fig. 2).

Pore water analyses for holes 1, 2,

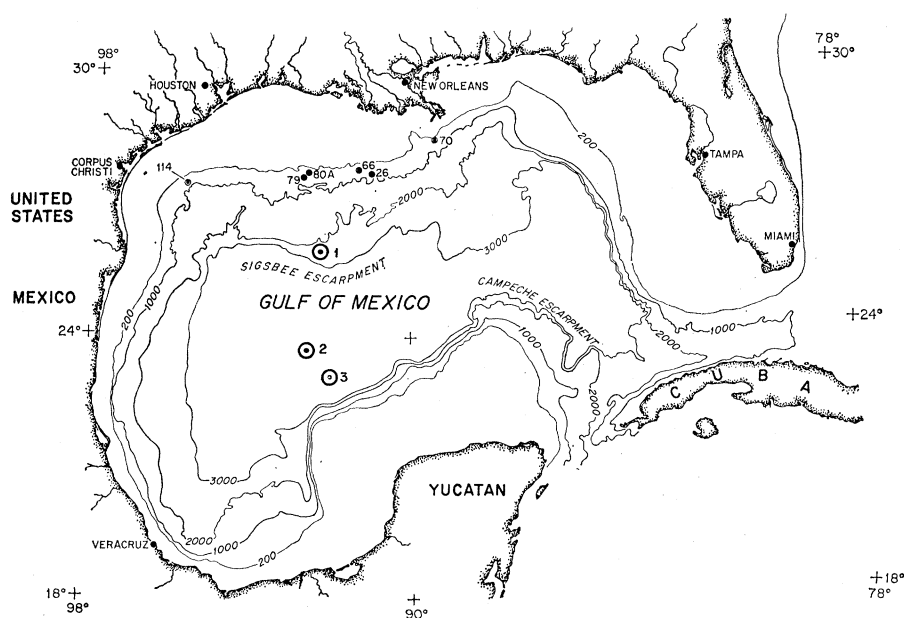


Fig. 1 Location of drill core stations in Gulf of Mexico. Depth contours in meters. Large circles indicate Deep Sea Drilling Program stations; small circles, *Eureka* stations (5).

and 3 are shown in Table 1, and the data for holes 2 and 3 are plotted in Fig. 3. The main features to be explained in hole 2 are the presence of brackish water in the cap rock and the relatively moderate salinity concentration gradient with depth. The chlorinities near the cap rock are lower than in the analogous situation shown in Fig. 2, although the age of the salt intrusion must be greater than the Pliocene age inferred for hole 114 (7). The sediments in Challenger Knoll also have a much lower clay content (8) and hence are presumed to be more permeable to diffusion.

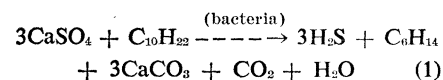
Several alternative sources of fresh water have been considered. Contamination from drilling fluid has been excluded, since no fresh drilling mud was used until after all coring operations were completed (9). Waters freshened by membrane filtration or osmosis (10) are unlikely to have played a role, for no such influence of fresh water was found in hole 1 or in previous studies of holes (for example, Fig. 2) on the continental slope of the northern Gulf of Mexico, where sediments have much better membrane characteristics (higher clay content) than do the calcareous pelagic oozes which characterize hole 2 strata. [See also factors cited by Manheim and Horn (11).] Moreover, the proximity of salt to the pervious cap rock should promote higher, rather than lower, salt concentrations in pore fluid. Current communication with land aquifers is highly unlikely, since the

Challenger Knoll is surrounded by thick deposits of fine-grained sediments which, to judge from hole 3, contain water whose salt content is equal to or greater than that of seawater. The possibility that the Challenger Knoll contains fossil groundwaters, because it might have been exposed to groundwater in a former shallow-water regime, has been suggested by some workers (12). This concept would require down-dropping of a major part of the floor of the Gulf of Mexico since the supposed shallow conditions. Although we do not take a position on the question of subsidence in the Gulf, we believe that the evidence does not support a fossil groundwater origin for the brackish water, as the following arguments will show.

Dominance of pelagic sediments and organisms in hole 2, and the absence of "turbidites" or coarser sediments that would indicate bottom transport from shallower zones, indicates that the area has been an isolated positive feature on the sea floor at least since Miocene time. Thus any episode in which groundwater could have formed or invaded the cap rock must have occurred more than 10 million years ago. If groundwater did invade in Miocene or pre-Miocene time, however, diffusion of salt from both the salt plug and surrounding sediments should have brought any trapped fresh waters close to or beyond seawater salinity within a million years after fresh water supply was cut off. This conclusion is con-

firmed by studies of interstitial salts in sediments overlying salt domes on the slope of the Gulf of Mexico (6), where diffusion rates were found to agree semiquantitatively with those determined in the laboratory on similar types of sediments. Moreover, the pattern of salt enrichment in the sediments above the cap rock in Challenger Knoll indicates that a concentration gradient was formed first above the salt, and the influx of fresh water came afterward. In fact, the low chloride levels in the cap rock and the high permeability of the cap rock zone suggest that production of fresh water must be active currently or must have been active very recently for such anomalous chlorinities to be maintained in the face of tendencies for diffusion of salt toward the cap-rock zone from above as well as from below.

An important source of fresh water is inherent in the reactions producing native sulfur in the cap rock of Challenger Knoll. We believe these reactions may help account for the phenomena. Feely and Kulp (13) suggested that the following schematic reactions produce sulfur by reduction of sulfate by bacteria, while simultaneously oxidizing petroleum and forming authigenic calcite.



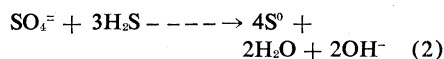
The hydrogen sulfide formed by bacteria from the sulfate reacts inorgan-

Table 1. (A and B). Composition of pore fluids, JOIDES stations 1 to 3. Refractometry and salinity from an additional core sample from 02D-05-06 showed values similar to those reported here. In addition, qualitative observations by oil company laboratory personnel, who examined the oil-permeated materials, also confirmed the brackish character of fluid from this horizon. (A) Pore water analyses, JOIDES leg 1. Major elements are reported in grams per kilogram (per mil). Total water content in percentage of original bulk weight.

Sample designation	Depth (m)	Age	Description	Total water	Na	K	Ca	Mg	Cl	SO ₄	HCO ₃ *	Sum
<i>Hole 1; 25°51.5'N, 92°11.0'W; water depth, 2827 m; Sigsbee Scarp, Gulf of Mexico; Cl bottom water = 19.3</i>												
01D-02-03 (117-122)	308	Pleistocene	Silty mudstone	40.4	10.3	0.23	0.42	1.08	18.7	0.66	(1.3)	32.7
01D-07-04 (143-150)	704	Pleistocene	Calcareous mudstone	32.7	11.7	.30	.38	1.23	20.6	2.48	(0.1)	36.8
01D-09-05 (145-150)	761	Pleistocene	Calcareous mudstone	39.5	11.3	.24	.38	1.23	20.4	†		
<i>Hole 2; 23°37.3'N, 92°35.2'W; water depth, 3579 m; Challenger Knoll, Gulf of Mexico; Cl bottom water = 19.2</i>												
02D-05-02 (top and bottom)	140	Miocene-Jurassic	Cap rock	29.5	2.5	0.10	1.7	0.19	4.8	2.52	(1.4)	13.3
<i>Hole 3; 23°01.8'N, 92°02.6'W; water depth, 3747 m; abyssal plain, Gulf of Mexico; Cl bottom water = 19.2</i>												
03D-01-02 (45-50)	34	Pleistocene	Calcareous silt, clayey	56.1	11.0	0.26	0.48	1.05	20.0	0.58	(1.2)	34.6
03D-04-01 (29-33)	209	Pleistocene	Coccolith ooze, clayey	12.0	.46	.50	.90	21.2	.93	(1.0)		37.0
03D-05-02 (04-07)	323	Pliocene	Coccolith ooze, clayey	47.3	13.6	.58	.48	1.08	24.2	.61	(1.5)	42.0
03D-07-01 (13-21)	382	Pliocene	Coccolith ooze, clayey	54.1	14.2	.60	.55	1.08	25.8	†		
03D-08-03 (10-18)	435	Pliocene	Coccolith ooze, clayey	48.3	15.5	.54	.53	1.06	27.5	.70	(0.7)	46.6
03D-09-02 (8-16) (4-12)	535	Miocene	Calcareous mudstone, ash layers	45.3	15.7	.53	1.0	1.28	29.5	.57	(.6)	49.2
03D-0-02 (44-50)	619	Miocene	Calcareous mudstone	48.7	17.0	.61	1.6	1.37	33.3	.38	(.3)	54.6
Standard ocean water					10.8	.39	0.41	1.29	19.4	2.71	(.14)	35.0

*Excess of cations over anions calculated as HCO₃⁻ alkalinity which was not directly determined. Values from -0.2 to 0.3 represent mainly analytical scatter, small HCO₃⁻ content (similar to oceanic values of about 0.1), and properly balanced ions. These values give a rough guide to bicarbonate concentration in samples in their state after squeezing in the laboratory, if one assumes that bicarbonate is the main undetermined anion species. †Insufficient sample for SO₄ determination.

ically with more sulfate to form native sulfur according to the reaction



Reduction of sulfate and simultaneous breakdown of petroleum hydrocarbons by mixed cultures of bacteria including sulfate-reducing bacteria (not, however, by pure cultures of sulfate-reducers) is well documented (14). The second, sulfur-forming step (Eq. 2) is much less certain. The direct reaction would probably require very high H_2S concentrations (15). Berner (16) has drawn our attention to the fact that the experiments of Feely and Kulp which purported to show the feasibility of inorganic (anoxic) reaction

of SO_4 and H_2S to produce native sulfur did not specify that oxygen had been excluded from the system. Presence of oxygen would nullify the value of the experiment, since H_2S is readily oxidized to S^0 in the presence of limited oxygen, especially where bacteria are present. Recent experience indicates experimental failure to produce native sulfur in the presence of sulfate and hydrogen sulfide but in the absence of molecular oxygen or other oxidizing agents (17). Several empirical evidences that native sulfur in salt domes forms solely by reaction of H_2S with oxygen through the agency of aerobic bacteria such as *Thiobacillus* are cited by Ivanov (18).

Davis and Bray (19) have also regarded molecular oxygen as the immediate agent permitting the oxidation of H_2S to native sulfur at Challenger Knoll, but the downward migration of molecular oxygen through more than 100 m of sediment above Challenger Knoll in sufficient amount and with enough speed to supply reactions proceeding in the cap rock poses problems. Thus, the formation of the native sulfur by other than the $\text{H}_2\text{S}-\text{O}_2$ reaction still is in an uncertain state at the present time; the latter reaction, possibly mediated by sulfur bacteria (*Thiobacillus*), seems to have dominant applicability to the formation of native sulfur deposits.

Whatever the step governing formation of native sulfur, petroleum hydro-

carbons or other organic matter must be oxidized to reduce the sulfate and produce the isotopically light carbon in the cap-rock calcite (20). The oxidation of petroleum hydrocarbons of the type found in the cap rock and H_2S will produce on the order of one molecule of water or more per molecule of CaSO_4 reduced. One would expect this water or any admixture of it and preexisting seawater or brine to be "lighter" than mean seawater in terms of D : H ratios, because petroleum is typically depleted in D with respect to seawater. The fact that deuterium concentrations of +1.88 percent [SMOW, (standard mean ocean water)] were observed in two samples of cap-rock water (2) is unexpected and cannot be explained by us. At first, we hypothesized that primary gypsum with "heavier" hydrated water might have been involved as a primary source of water. After publication of these data (2), however, Irving Friedman communicated to us a value of -2.0 percent D (SMOW) for water of hydration in gypsum crystals from barrel 6 (below the water sample in the Challenger cap rock). This value offers no support for a source of heavy hydrated water and is in agreement with the expectation that gypsum probably formed secondarily by hydration of anhydrite in the leached residue of the salt dome.

With due regard for the above uncertainties, some events in the development of the salt-sediment interactions

Table 1 (continued). (B) Deuterium and minor constituents [from (2)]. Values in parts per million except where indicated.

Sample designation	D (%)	Sr	Ba	B
01D-02-03	+0.12	15	1.8	5
01D-07-04		12	.4	9
01D-09-05		16	3.0	6
02D-05-02	+1.88	4.0	.2	8
03D-01-02	+0.84	13	0.2	12
03D-04-02		10	1.1	8
03D-05-02	+ .22	11	1.5	2
03D-07-01		14	2.3	5
03D-08-03		101	1.6	5
03D-09-02		125	2.2	3
03D-10-02	-.67	139	7.0	2
Standard ocean water	.0	8.0	<.1	4.3

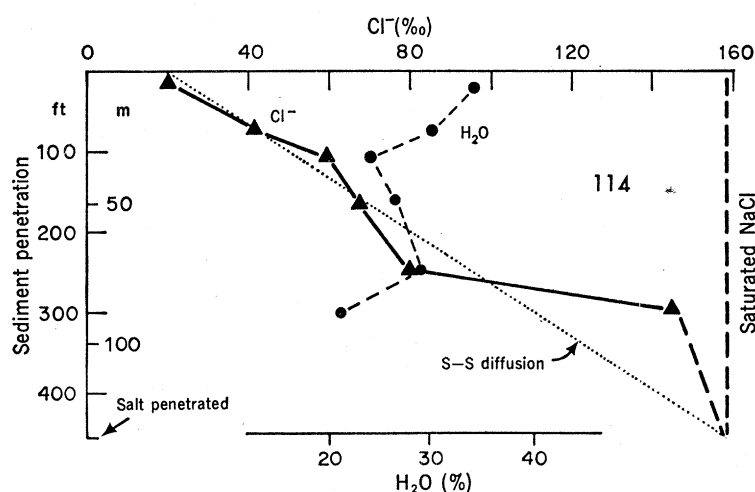
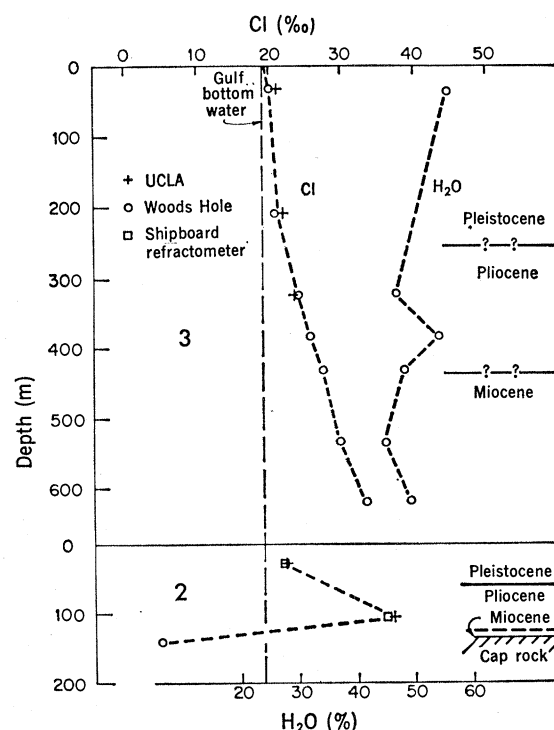


Fig. 2 (above). Distribution of Cl^- and H_2O with depth on station 114, northern Gulf of Mexico (6). Water depth, 292 meters. S-S, steady-state. Fig. 3 (right). Distribution of Cl^- and H_2O with depth for JOIDES stations 2 and 3. Woods Hole refers to data from this report; UCLA refers to data from Kaplan and Presley (4). Figure is modified from preliminary version in Manheim *et al.* (2), where UCLA units were uncorrected to grams per kilogram units. Refractive index is corrected to chlorinity by using relationships of $\Delta n/\text{Cl}$ which apply to pore waters in hole 3.



can nevertheless be outlined. The first step is intrusion of a salt plug from thick, deep, and warmer salt layers into Tertiary sediments, in a manner analogous to widespread phenomena noted on the margins of the Gulf Coast (21). Rock salt diffused into surrounding and overlying sediments gradually, leaving behind a granular crust of anhydrite and other less-soluble inclusions in the original salt mass. At the same time, a concentration gradient of (mainly) NaCl extended from the near-saturation conditions prevailing at the margin of the solid salt upward and outward, with decreasing concentrations in pore fluids of surrounding sediments. On a much smaller scale, a concentration gradient of less-soluble calcium sulfate also probably extended into pore fluids of surrounding sediments; sulfate reduction within the sediments reduced some of the added sulfate, and additional authigenic calcium carbonate (including metastable aragonite ?) may have formed at the periphery of the salt body during this initial phase. As the salt body rose to cooler, lower-pressure layers and anhydrite residues were exposed to pore waters, hydration to gypsum may have taken place to produce hydration water having D:H ratios somewhat less than those of seawater (pore water) as observed in the analyzed gypsum specimen.

As porosity was created in the thickening cap-rock zone, petroleum migrated into the structural trap created by the enclosing finer-grained sediments. The advent of large amounts of hydrocarbons permitted large-scale reduction of cap-rock sulfate, with ensuing formation of H₂S, native sulfur, calcite, and water. The H₂S diffused into sediments surrounding the cap rock, causing extensive pyritization above as well as within the cap rock. Hydrocarbons soluble in water would also have tended to diffuse into and through overlying sediments via the same pathways by which chloride diffused, but the diffusion of dissolved constituents does not necessarily imply any appreciable migration of bulk fluids in an outward direction. Faulting may, however, have created some preferential fluid channels.

The water produced in the petroleum-sulfate-native sulfur reaction soon diluted the salt solutions within the cap rock and began to reverse the salinity gradient established earlier. It did this in spite of the fact that production of fresh water, and hence sharper concentration gradients, would tend to

speed up the leaching of the salt. Possible osmotic circulation of fluid should also be considered in this connection (22).

The salinity gradient in hole 3 carries quantitatively different implications from that in hole 2, for hole 3 is in the abyssal plain region outside the zone of diapiric salt intrusions (23) and no intervening salt bodies or evaporitic sequences can be interpreted from previous geophysical data or the site surveys. The salt source, which we presume must exist at depth, lies below at least 4 km of sediments, depending on the seismic velocity chosen for the sediment prism (24).

The thought of salts diffusing through several kilometers of sediments on the floor of the Gulf of Mexico may seem startling, but we see no alternative explanation for the systematic increase in interstitial salinity with depth. Given the diffusion assumption, the change of the chlorinity-depth gradient from a marked linear relationship below the Pleistocene boundary to a flatter curve above it agrees with the more rapid sedimentation in post-Pliocene time, interpreted from the faunal data (25). Earlier studies on a number of Gulf of Mexico slope drill holes (6) also confirmed the effective diffusive flux of salt through highly clayey sediments, without evidence of appreciable bulk fluid flow.

A crude estimate of the minimum time required for chloride diffusion from a layer of solid salt at a depth of 4000 m to achieve a chlorinity of 32 g of Cl per kilogram at a depth of 600 m can be made, if several assumptions are permitted. Let Cl be fixed in pore water at the salt-sediment interface at 160 g/kg (per mil), or approximately saturation with NaCl, and let Cl at the sediment-seawater interface be 19 per mil. Let the diffusion constant of $k = 4 \times 10^{-6}$ cm²/sec apply and be constant with depth. We wish to know how much time would be required for diffusion of Cl to create a chlorinity of 32 per mil at a depth of 600 m, approximately equal to that observed in hole 3. The diffusion problem is described by Fick's 2nd Law

$$\frac{\partial c}{\partial t} = -k \frac{\partial^2 c}{\partial x^2} \quad (3)$$

where c is concentration; x , distance from the salt; t , time; and k , the diffusion constant. This is analogous to the heat flow problem involving a solid bounded by two parallel planes, each of which is maintained at a constant

temperature. If we set the upper chlorinity boundary to 0 and the lower to 140 per mil, a nomogram is available for the transient heat flow case (26), which enables us to quickly evaluate the time necessary to reach the observed salinity gradient—150 million years, assuming salt was introduced instantaneously at the given depth.

This estimate is unreliable for several reasons—principally because continuing sedimentation during the diffusion period has been ignored; the sediment character at greater depth, and hence its diffusion constants, are unknown; and other complicating factors, such as possible bulk fluid movements, have likewise been ignored. The salt layer is presumed to be approximately Jurassic in age (1), similar to and possibly coherent with the Louann salt layer of the northern Gulf of Mexico, or with the Louann equivalent extending from Yucatan (27). An analysis of the diffusion problem (28), incorporating continuous sedimentation among the boundary conditions, arrived at a chlorinity of about 24 per mil at a depth of 600 m in the course of 150 million years. Lacking information on sedimentary properties for most of the depth to the highly reflective (basement) layers, we perhaps cannot expect better agreement between calculated and observed salt distribution in the pore waters. However, the estimates of diffusion do suggest that over geologic time diffusional migration of salt can proceed through several kilometers of sediments of the type found in the Gulf of Mexico and influence the composition of their pore fluids.

The foregoing data and discussion confirm, in our opinion, the existence of deep salt outside the known diapiric zone in the Gulf of Mexico. They provide some practical illustrations of the magnitude of salt diffusion in sediments and confirm the earlier suggestion that chlorinity distribution in interstitial waters of sediment cores can help predict the presence of and provide some information on distance to salt bodies at a distance from the penetrated strata (2). The data also indicate that production of fresh water during the reactions giving rise to native sulfur is significant, although these reactions are as yet not fully understood.

F. T. MANHEIM

U.S. Geological Survey, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543

F. L. SAYLES

Woods Hole Oceanographic Institution

References and Notes

- C. A. Burk, M. Ewing, J. L. Worzel, A. O. Beall, Jr., W. A. Berggren, D. Bukry, A. G. Fischer, E. A. Pessagno, Jr., *Bull. Amer. Ass. Petrol. Geol.* **53**, 1338 (1969).
- F. T. Manheim, F. L. Sayles, I. Friedman, in *Initial Reports of the Deep Sea Drilling Project*, T. R. Davies, Ed. (National Science Foundation, NSP1, Washington, D.C., 1969), p. 403.
- J. Ewing, T. L. Worzel, M. Ewing, *J. Geophys. Res.* **67**, 2509 (1962).
- I. R. Kaplan and B. J. Presley, in *Initial Reports of the Deep Sea Drilling Project*, T. R. Davies, Ed. (National Science Foundation, NSP1, Washington, D.C., 1969), p. 411.
- F. T. Manheim, *Trans. N.Y. Acad. Sci., Ser. II*, **29**, 839 (1967).
- and J. L. Bischoff, *Chem. Geol.* **4**, 63 (1969).
- P. Lehner, *Bull. Amer. Ass. Petrol. Geol.* **53**, 2431 (1969).
- R. W. Rex, in *Initial Reports of the Deep Sea Drilling Project*, T. R. Davies, Ed. (National Science Foundation, NSP1, Washington, D.C., 1969), pp. 354–367.
- D. Wirth, Scripps Institute of Oceanography, personal communication (1969).
- E. T. Degens and G. V. Chilingar, in *Diagenesis in Sediments*, G. Larsen and G. V. Chilingar, Eds. (Elsevier, New York, 1967), pp. 477–502; F. A. F. Berry, *Chem. Geol.* **4**, 295 (1969).
- F. T. Manheim and M. K. Horn, *Southeast. Geol.* **4**, 215 (1968).
- Related to us by J. L. Worzel, Lamont Geological Observatory, oral communication (1969); see also P. L. Lyons, *Trans. Gulf Coast Ass. Geol. Soc.* **7**, 1 (1957).
- H. W. Feely and J. L. Kulp, *Bull. Amer. Ass. Petrol. Geol.* **41**, 1802 (1957); see also G. E. Jones, R. L. Starkey, H. W. Feely, J. L. Kulp, *Science* **123**, 1124 (1956).
- D. R. Postgate, *Annu. Rev. Microbiol.* **13**, 505 (1959); G. J. Guynes and E. O. Bennett, *Appl. Microbiol.* **7**, 117 (1959); M. V. Ivanov (see 18), and references in these publications.
- For Eq. 2 a net free energy ΔF^0_R calculation gives

$$\Delta F^0_R = 4\Delta F^0_{f_s} + 2\Delta F^0_{f_{H_2O}} + 2\Delta F^0_{f_{OH^-}} -$$

$$\Delta F^0_{f_{SO_4}} = -3\Delta F^0_{f_{H_2S}} = 0 - 113.4 -$$

$$75.18 + 177.34 + 19.62 = 8.38$$
at unit activity and standard temperature and pressure (f is the particular species). Actual pressure and temperature are different but will not change the magnitude of the result. Then at equilibrium $\Delta F^0_R = -RT \ln k$:

$$-RT \ln k = 8.38, \text{ and } k = 10^{-6.16} =$$

$$\frac{(S^0)^4(OH^-)^2(H_2O)^2}{(SO_4)(H_2S)^2_{aq}}$$
where R and T are the gas constant and absolute pressure, and k is the equilibrium constant. For $pH=7$ or $(OH^-)=10^{-7}$, $(S^0)=1$ (solid has unit activity), $(SO_4)=0.01$; ignoring activity coefficients, we obtain $(H_2S)_{aq}=10^{-2}$. Thus, more than 0.01 mole of H_2S per liter (360 mg/liter) would theoretically be required to produce solid S^0 under the assumed conditions. Note, however, that Millet, cited by Postgate (14), demonstrated that sulfite, which can readily react with H_2S to produce sulfur, can be an intermediate in bacterial sulfate reduction.
- R. A. Berner, Yale University, personal communication (1969).
- , *Amer. J. Sci.* **268**, 1 (1970).
- M. V. Ivanov, *Ro' mikrobiologicheskikh protsessov v genezise mestorozh denii samorodnoi sery (Microbiological processes in the formation of sulfur deposits)* (Izdatel'stvo "Nauka," Moscow, 1964); translated by Israel Program of Scientific Translation (1968).
- J. B. Davis and E. E. Bray, in *Initial Reports of the Deep Sea Drilling Project*, T. R. Davies, Ed. (National Science Foundation, NSP1, Washington, D.C., 1969), p. 415.
- J. G. Erdman, R. L. Borst, W. J. Hines, R. S. Scanlan, in *ibid.*, p. 461.
- E. Uchupi and K. O. Emery, *Bull. Amer. Ass. Petrol. Geol.* **52**, 1162 (1968); G. F. Murray, *ibid.* **68**, 1725 (1966).
- R. R. McLeod, *Trans. Gulf Coast Ass. Geol. Soc.* **10**, 151 (1958); see also (11).
- J. L. Worzel, R. Leyden, M. Ewing, *Bull. Amer. Ass. Petrol. Geol.* **52**, 194 (1968).
- J. L. Worzel, Lamont Geological Observatory, personal communication (1969); see also (3).
- W. H. Berggren, G. A. Pessagno, Jr., D. Bukry, in *Initial Reports of the Deep Sea Drilling Project*, T. R. Davies, Ed. (National Science Foundation, NSP1, Washington, D.C., 1969), p. 594.
- H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford Univ. Press, New York, 1959), p. 101.
- J. W. Antoine and W. R. Bryant, *Bull. Amer. Ass. Petrol. Geol.* **53**, 2543 (1969).
- D. J. Ekstrand and F. T. Manheim, in preparation.
- We express thanks for core materials from cap rock in hole 2, obtained from Mobil Oil Co., through J. M. Hunt. Use of data from Irving Friedman on hole 2 is appreciated, as is loan of atomic absorption equipment by D. Spencer. Assistance and discussion by Galen Jones, J. M. Hunt, J. L. Worzel, C. E. Zobell, David Wirth, Anthony G. Pimm, F. E. Deiler, and R. A. Berner are acknowledged. Thanks are extended to all those who assisted with recovery, analysis, and packaging of samples on board *Glomar Challenger*. Publication approved by director, U.S. Geological Survey. Contribution No. 2465 of the Woods Hole Oceanographic Institution.

22 May 1970

Surface Films Compacted by Moving Water: Demarcation Lines Reveal Film Edges

Abstract. When water flows under the edge of a surface film the large viscous shear stress at the edge prevents the film from spreading and raises a ridge on the water surface. Near the top of its downstream flank the ridge has an abrupt change in curvature that we see as a line on the water.

On a calm day an observer who finds the right place on a stream or river will see an unobtrusive yet startling phenomenon, a line on the surface of the water. The line may lie still, or it may contort itself, one way and another, in response to eddies. Very likely he will think a spider thread has fallen onto the water and try to cut it with his canoe paddle. As the disturbance caused by the cutting fades, the line reappears, mended and whole.

With luck the observer will see a little animal supported by surface tension drift across the line, hop back to the other side, drift across, hop back, and so on through many repetitions. The line divides good surface from bad, in the little animal's view. If conditions are right, our observer will see that the bad surface looks dirtier than the good, with more specks of debris upon it. And if he uses the water surface as a mirror, he will see that it forms a shallow ridge, a centimeter or so wide, with the line about at its top.

The line is a line of demarcation, D-line for short, between surface regions with different amounts of contamination. What can maintain such a discontinuity against the tendency of surface films to spread into equilibrium? What causes the D-ridge on which the line sits? The line itself must be some sort of kink in the profile of the ridge; but what sort, and how is it produced?

The next clue requires a lake shore and an onshore breeze. Stick a shovel into the lake and heave the water upward to make a local upwelling. If the breeze has compacted a dense enough film of contaminants, a D-line will form

at the outward-flowing edges of the upwelling boil of water. As the boil quiets down, the loop of line will contract and eventually "annihilate" itself, launching a ring of ripples as it does so. If the film is less compacted, the D-line may weaken and become invisible without contracting. Squeeze the film between a boat and the shore: The D-line will run its full course through contraction and annihilation.

Now invert the experiment. Go to where there is an offshore breeze and touch the surface with a pipe cleaner soaked in Mazola corn oil. The oil will spread, sending before it an expanding circle of ripples. Look sharp at the right moment and you will see that a ring of D-line gets left behind by the

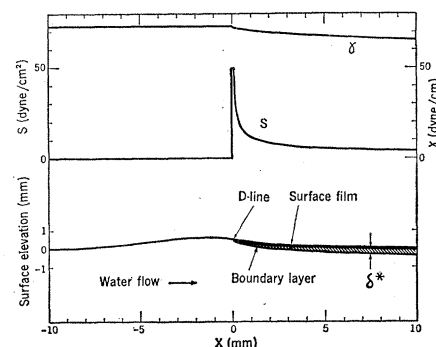


Fig. 1. The D-ridge elevation profile at a water speed below 23.2 cm/sec, showing the surface film downstream of the D-line, and the displacement thickness δ^* of the boundary layer beneath the film. The D-line is perpendicular to the paper, and the surface dam is off scale to the right. Also illustrated are the shear stress S exerted on the film by the flowing water at a speed of 23.2 cm/sec, and the surface tension γ . Note how γ is reduced by the shear stress.