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Combustibles Minéraux

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Managing Editor: James E. Gill

Associate Editors:

French: Jacques Béland

Assisted by: Bernard Mamet
Jacques Martignole

English: Eric W. Mountjoy

Preliminary editing of this volume: D. W. Axford, R. G. McCrossan,
E. W. Mountjoy, J. Walla, Jr.

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Rédacteur-en-chef: James E. Gill

Co-rédacteurs:

Français: Jacques Béland

collaborateurs: Bernard Mamet
Jacques Martignole

Anglais: Eric W. Mountjoy

Travail préliminaire de rédaction: D. W. Axford, R. G. McCrossan,
E. W. Mountjoy, J. Walla, Jr.

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PREFACE

The 27 contributions that comprise the proceedings of Section 5, Mineral Fuels, were selected to provide scientific interest and a representative international cross-section of current thinking in petroleum geology. The accepted contributions conform to one of the following three major topics:

- The geochemistry of petroleum
- The subsurface environments of petroleum
- The world-wide distribution of petroleum and potential petroleum occurrences

In reviewing, editing and final preparation of the papers, we have been ably assisted by Dr. E. W. Mountjoy, McGill University, and Joseph Walla, Junior, Mobil Oil Canada, Ltd.

Conveners

D. W. AXFORD,
Vice-President, Exploration,
Mobil Oil Canada, Ltd.,
P. O. Box 800,
Calgary 1, Alberta.

R. G. McCROSSAN,
Head, Energy Subdivision,
Institute of Sedimentary and
Petroleum Geology,
Geological Survey of Canada,
3303 - 33 Street N.W.,
Calgary 44, Alberta

PRÉFACE

Les 27 communications qui constituent le programme de la Section 5 intitulée "Combustibles minéraux" ont été choisies selon leur intérêt scientifique et pour donner un aperçu international des idées récentes sur la géologie du pétrole. Les communications acceptées se rapportent à l'un des trois grands sujets suivants:

- La géochimie du pétrole
- Le milieu souterrain du pétrole
- La distribution du pétrole à travers le monde et les découvertes potentielles de pétrole

Nous désirons remercier le Dr E. W. Mountjoy, de l'Université McGill, et Joseph Walla, Junior, de Mobil Oil Canada, Ltée pour l'aide qu'ils nous ont apportée dans la révision, l'édition et la préparation des manuscrits.

Organisateurs:

D. W. AXFORD,
Vice-président à l'exploration,
Mobil Oil Canada, Ltd.,
P.O. Box 700,
Calgary 1, Alberta

R. G. McCROSSAN,
Chef, sous-division de l'énergie,
Institut de géologie sédimentaire
et pétrolière,
Commission géologique du Canada,
3303 - 33 Street N.W.,
Calgary 44, Alberta

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The Geochemistry of Petroleum

La Géochimie du Pétrole

Migration of Interstitial Water in Sediments and the Concentration of Petroleum and Useful Minerals

PARKE A. DICKEY,
U.S.A.

ABSTRACT

As sediments compact and recrystallize, large volumes of interstitial water must find their way to the surface. This migration results in the segregation and concentration of useful substances, including oil, gas and minerals. It is therefore a very important process, but little is known about the physical, chemical and geological mechanisms that control it.

The expulsion of water is often temporarily stopped, because relatively impermeable strata are interposed along the paths of migration. Where the sediments are comparatively unconsolidated this situation results in shale diapirs and mud volcanoes. These are common in Tertiary basins where sediments were deposited rapidly. At greater depths and in rocks more greatly altered, the water which is prevented from escaping sustains much of the weight of the overburden, and therefore is found at pressures approximating that weight. It appears that at depths over 10,000 feet these high pressures are common. The suggestion is made that as metamorphism proceeds, the high-pressure interstitial waters rupture the rocks, depositing ore and gangue minerals in cavities which they themselves create. The origin of some veins thus may be the abnormally pressured water escaping from sediments which are undergoing metamorphism.

FLUID PRESSURES IN SEDIMENTS

THE PRESSURE OF interstitial fluid in sediments, usually water but occasionally gas or oil, is measured as pounds per square inch (psi) or kilograms per square centimeter (kg/cm^2). In a continuously permeable stratum containing water, the pressure increases linearly with depth according to the density of the water. It is a general rule that the pressure of the interstitial fluid at any depth is approximately that required to sustain a column of water to the surface of the ground; that is, 0.45 psi per foot of depth.

Where the bed has continuity of permeability to the outcrop it may be supposed that the elevation of the outcrop determines the height to which the water will rise in the well bore, (Fig. 1, A). In this simple case the value of the subsurface pressure is determined by the density of the water. However, stagnant subsurface waters are usually salty and their density is greater than 1.00. Furthermore, their concentration usually increases with depth. In this situation the exact value of the hydrostatic pressure potential at any depth is difficult to estimate (Bond and Cartwright, 1970).

In the case of permeable beds which do not outcrop (Fig. 1, B) it is normal for the fluid pressure at any depth to be that required to sustain a column of water to the surface. The reason for this is not clear. It could be supposed that

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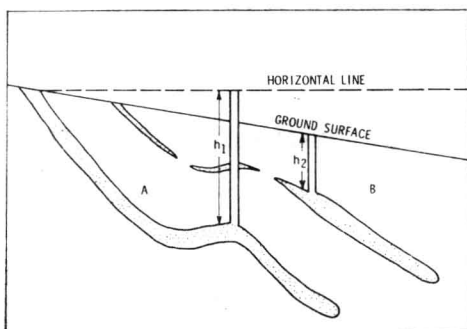


FIGURE 1 — Diagram to show origin of fluid pressure in sediments. In the case of A, the normal pressure in the reservoir is determined by the height of the outcrop above the point of measurement. In the case of B, it is not clear what determines the pressure.

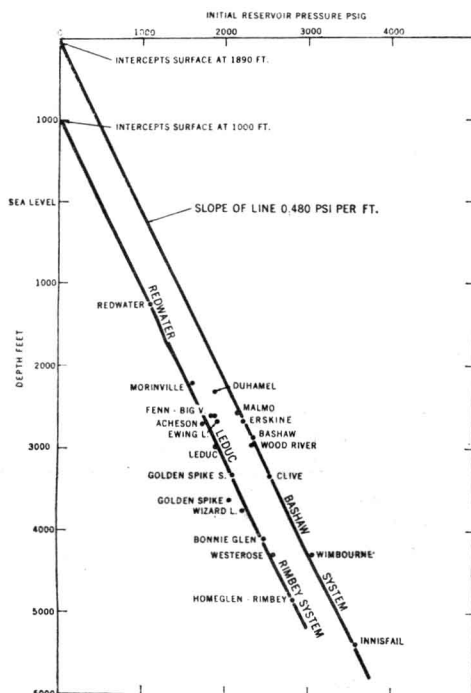


FIGURE 2 — (right) — Pressures of oil reservoirs in Devonian reefs of Alberta plotted against depth. The reefs in the Redwater-Leduc-Rimbey system plot on one line, and those of the Bashaw system on another. The reefs in each system are hydraulically connected, but the two systems are not connected with each other.

the enclosing shales have small but finite permeability to water, or that thin sandy beds provide continuity of permeability to the outcrop. Then over geologic time the water in the formation would accept more water from above if its pressure were too low, or bleed water upward if it were too high. However, there are so many exceptions to this rule, and so many oil fields with pressures either higher or lower than "normal", that it may be doubted whether compacted shales have any permeability at all to water, at least at right angles to the bedding.

This situation is well illustrated by the actual pressure pattern in the Devonian reef oil pools of Alberta. There are two parallel lines of reefs, 50 miles apart. Figure 2 shows the pressures of the various pools plotted against depth. All the pools on the Leduc-Rimbey trend lie on one line and those on the Bashaw trend lie on another. The slope of both lines is 0.480 psi per foot, which corresponds to a density of water of 1.110. For any given depth the Bashaw system has a pressure about 500 psi higher than the Leduc-Rimbey trend. It may be deduced from this that all the pools in one trend are hydraulically connected with each other, but that the two trends are separated from each other by a hydraulic barrier.

If the lines are extrapolated to zero pressure, the Leduc-Rimbey line indicates a surface outcrop at 1000 feet above sea level, and the Bashaw intercept is 1900 feet above sea level. It may be that the Leduc-Rimbey trend subcrops under permeable Cretaceous beds far to the north. The Bashaw trend, however, loses permeability up-dip before it outcrops. It is not known what determines its pressure.

Many fields have abnormally low pressures. They include Gilby in Alberta, Bisti in New Mexico and Wilburton in Oklahoma. All are lenticular sand bodies completely surrounded by shale, and all have only limited amounts of water down-dip from the oil. Obviously, if they had a permeable connection to the outcrop, the pressure would have become normal. The fact that the low pressures exist indicates that some shales, at least, have no permeability to water, even over geologic time.

The reason for the low pressures is unknown, but it may have been caused by the removal of large thicknesses of overburden. Studies of pressure behavior in petroleum reservoirs as fluids are withdrawn show that the pores expand about one part in 7×10^{-6} for each psi drop in pressure. Water has a bulk compressibility of 3×10^{-6} per psi. Thus, removal of the overburden causes the pores to expand more rapidly than the water can expand to fill them, which gives rise to a drop in pressure.

Where a continuously permeable bed outcrops in one place at a high elevation and in another place at a low elevation, meteoric water will enter at the higher outcrop and flow through the bed to come out at the lower. Such flow is usually peripheral, from higher to adjacent lower outcrops. The meteoric water is not usually able to displace the heavier salt water in the deeper parts of sedimentary basins. However, in the Rocky Mountains and other basins in the Cordilleran and Himalayan-Alpine chains it is not uncommon for a stratum to be flushed by meteoric water.

It is a mistake to assume, as has often been done, that differences in fluid potential between separate aquifers or reservoirs indicate flow between them. On the contrary, differences in potential between aquifers can be more logically interpreted as indicating lack of hydraulic connection.

THE MECHANISM OF COMPACTION OF SEDIMENTS

The expulsion of pore water from unconsolidated clays as they compact has been studied by soil mechanics engineers, notably Karl Terzaghi (Terzaghi and Peck, 1968). The process is visualized by means of an imaginary model (Fig. 3). It consists of a cylinder full of water, in which are several plates. The plates are perforated with small holes, and are separated by springs. The holes represent the fact that clays have low permeability to water; the springs represent the fact that the clay minerals have strength and can themselves sustain the weight of the overburden. Between the plates, at various levels, manometers measure the pressure of the water. At equilibrium, before loading, the water in the manometers stands at the level of the top plate.

If, now, a load is suddenly placed on the model, it will cause the springs to compress, and the water to be expelled from between the plates. However, the holes are small, and the water can escape only slowly. This prevents the springs from compressing, and the full weight of the load is carried by the water. There is thus an excess of hydrostatic pressure in the water, which is indicated by the manometers. After a while the water will have bled out of the upper part of the model, and the pressure falls in the upper part but remains high in the lower part. The pressure gradually bleeds off the lower part also, and finally the excess hydrostatic pressure becomes very small. The full weight of the load is now carried by the springs.

The rate at which compaction of clay occurs depends on the permeability of the clay and its volume compressibility. It also depends on the square of the thickness of the bed which is being compacted.

As sediments are deposited under water they pile up, increasing the load on those deposited previously, which then compact by the mechanism just described. Sand particles bridge against each other and they compact very little. Shales compact a great deal, losing porosity from near 80 per cent when first deposited to very low values at great depths. This loss in porosity involves the expulsion of large volumes of water and takes a very long time. Thus excess hydrostatic pressures are common in recently deposited sediments.

They were actually measured in the Recent sediments of the Orinoco delta at Pedernales, Venezuela by Kidwell and Hunt (1958). They found (Fig. 4) that the excess pressures increased to 8 psi and more at depths of 120 feet below the surface. They decreased upward to zero at a permeable sandy bed, and also downward to about 4 psi at the pre-Paria unconformity, which is obviously acting as a channel to bleed off the water.

Hedberg (1936) and Athy (1930) measured the changes in shale density with depth. They recognized the importance of the migration of the water in the removal of oil from source rocks. More recently other measurements of shale density have been made, and the values cover a surprisingly large range. At a depth of 6,000 feet on the Louisiana Gulf Coast the average density is 2.3, in Venezuela 2.5, and in Oklahoma 2.6. These densities correspond to porosities of 0.13, 0.06 and 0.02 respectively. Information from several authors is compiled in Figure 5. Presumably depositional environment, mineralogy and time all affect the density-depth relationship.

Obviously the shales must have permeability to water in order for the water to escape. Few data on the permeability of natural shales are available. Gondouin and Scala (1958) give values between 4×10^{-4} and 2×10^{-6} md. Young *et al.* (1964) measured values from 8×10^{-4} and 2×10^{-6} md. Undoubtedly the permeability of shales varies widely, depending on differences in mineralogy and on degree of compaction. Miller and Low (1963) believe that water in fine pores behaves as a solid and does not obey Darcy's law. They found that there is a threshold pressure gradient below which no flow occurs in compacted montmorillonite. This may explain the apparent lack of permeability of compacted shales to water.

Bredehoeft and Hanshaw (1968) calculated the rate of expulsion of water from a thick sedimentary section receiving sediments at a constant rate. They

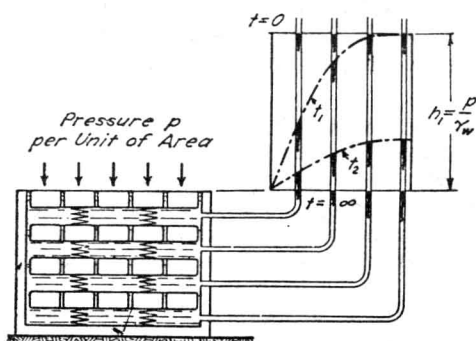


FIGURE 3 — Terzaghi's model of the compaction process. When a load is dropped on the cylinder, the water first carries the full load. As it escapes, the springs sustain the load and the water pressure drops to normal hydrostatic.

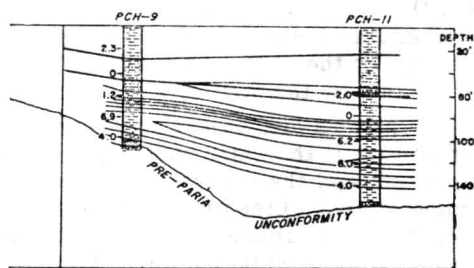


FIGURE 4 — Excess hydrostatic pressures in the recent sediments of the Orinoco river, Pedernales, Venezuela. As the muds compact, pure water is bleeding upward to a permeable bed at depth of about 30 feet, and also downward to the pre-Paria unconformity, which is also permeable laterally (from Kidwell and Hunt).

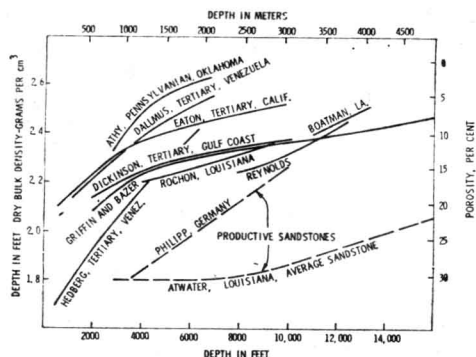


FIGURE 5 — Sediment density and porosity plotted against depth of burial. There is a surprising range of values, resulting from depositional environment and age of the rocks.

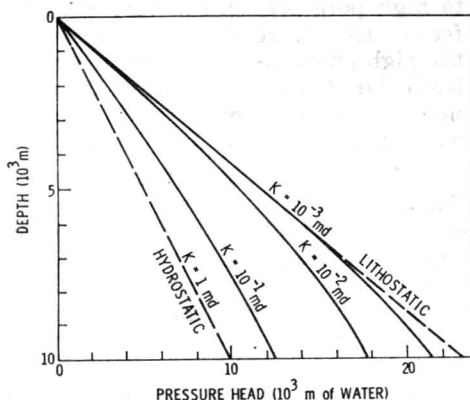


FIGURE 6 — Graphs showing calculated pore pressure versus depth for a situation similar to that of the Gulf Coast. It is assumed that sediments are deposited continually and compact as a result of vertical expulsion of water. If shale permeability is between 10^{-4} and 10^{-7} md, it is obvious that little water escapes vertically. (Modified from Bredehoeft and Hanshaw.)

assumed values comparable to those of the Gulf Coast. Their calculations showed that if the shales had a vertical permeability of 10^{-3} md the water would be expelled extremely slowly so that the pore pressures would remain close to those imposed by the weight of the overburden (lithostatic). For the interstitial pressure to be that of a column of water to the surface (hydrostatic) the sediments would have to have a permeability of 1 md. This is in the range of permeability of sands, and it is doubtful that even in thick sands the gross vertical permeability is as great as 1 md. As a matter of fact, normal pressures in the Gulf Coast down to a depth of about 10,000 feet are all very close to 0.465 psi per foot of depth (1.07 kg/cm^2). This is in the part of the section containing abundant sands. Probably the sands connect through thin and silty but relatively permeable stringers to the contemporaneously deposited "massive sand" facies which is found landward of the oil and gas producing zones.

ABNORMALLY HIGH PORE PRESSURES

In the more shaly facies to the seaward, abnormally high pore pressures are very common. Dickinson (1953) showed that extremely high pressures, sometimes almost equal to the weight of the overburden, are found in lenticular sands which are completely surrounded by shale. Obviously the shales must lack permeability to water almost totally. The water in them was unable to escape as sedimentation proceeded. It remained locked in the pores and was forced to carry much of the weight of the overburden.

Hottman and Johnson (1965) showed that the shales containing the sands with abnormal pressures have abnormally high porosity for their depth of burial. This high porosity is reflected in abnormally low electrical resistivity and seismic velocity.

The depth to the first high pressure on the Gulf Coast is quite variable, ranging from less than 4,000 to over 20,000 feet. Often the transition from normal

to high pore pressure is very abrupt, taking place in a vertical interval of 100 feet or less. More often it covers an interval of several hundred feet. In general the high pressures occur only where the section is mostly shale and the sands are lenticular. Contemporaneous faulting often controls the boundaries of the high-pressure zones. Apparently the faulting cut off the routes of escape of the water, which must have been mostly parallel to the bedding planes, (Dickey *et al.*, 1969).

High pressures are found in many other areas. The unfortunate blow-out at Santa Barbara, California gave them much notoriety. In the Green River Basin of Wyoming high pressures are found at depths of 10,000 feet both on the west side of the basin in front of the "overthrust belt" and on the east side at the foot of the Wind River mountains. The suggestion has been made that the high pressures originate from laterally directed stresses of tectonic origin (Dickey and Rathbun, 1969). However, it seems improbable that the comparatively unconsolidated shales could transmit horizontal stress. It is more likely that rapid sedimentation trapped the water in shales that had effectively zero permeability to water. Similar situations of high pressures in shaly sections at the foot of mountains occur in the Magdalena Valley of Colombia, in the pre-Caucasus region of Russia, and many other places. Perhaps the most astonishing of these is the Anadarko Basin of Oklahoma, where Pennsylvanian shales contain sand lenses with gas at abnormally high pressures. The water here must have remained locked in the pores since Pennsylvanian time.

Where an impermeable bed A overlies a permeable bed B, as in Figure 7, the stress due to the weight of the overburden, S , is sustained by the stress σ in the skeleton of solid grains, and also by the upward hydrostatic pressure of the pore fluid, p . If the upward pressure p approaches the downward pressure S , then the skeleton pressure σ goes to zero, and the overlying bed A is virtually floating. Hubbert and Rubey (1959) showed that a very small tilt of the contact will cause bed B to slide. Submarine slides can occur on a large scale, resulting in low-angle overthrust faulting. High pore pressures also facilitate small-scale slumping. In the case of a prograding delta, sediments are deposited on a gently sloping bottom. Suppose a bed of fairly rigid and permeable sand a few feet thick is deposited on a mud of low permeability. If the sand is deposited rapidly, the pore pressure in the shale will approach the overburden pressure, and the sand bed may slide down the slope, crumpling and rolling up and producing contorted bedding.

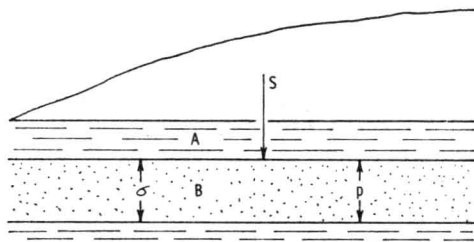


FIGURE 7 — Diagram to illustrate vertical stress in sediments. The weight of the overburden (S) is sustained by the stress in the skeleton of the solid grains (σ) and the pore pressure in the interstitial fluids (p). If the pressure p approaches S , σ drops to near zero, and bed B is practically floating. If the pressure exceeds S , rupture of a bed will occur.

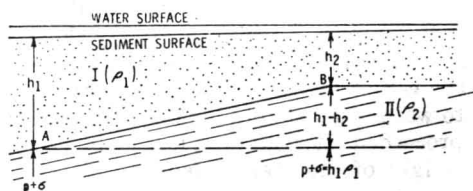


FIGURE 8 — If a heavier, well-compacted sediment overlies a lighter, undercompacted one on a sloping surface, a condition of instability will result. At point B the upward pressure will exceed the downward pressure, and a mud diapir will form.

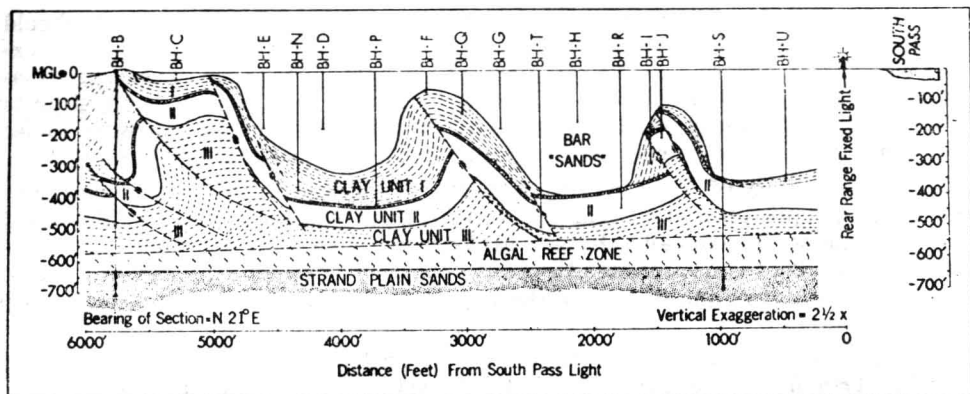


FIGURE 9 — Structure of mud lumps at the mouth of the Mississippi river (from Morgan, *et al.*). Low-density clays (Units I, II and III) have pushed up through the denser bar sands.

Imagine a situation in front of an advancing delta (Fig. 8). Prodelta clays of very low permeability are overlain by fluvial sandy muds of much greater permeability. The sandy muds will compact quickly, reaching a porosity appropriate to their depth of burial. Kidwell and Hunt (1958) found densities of about 1.85 at 140 feet below the bottom, in shales that had not yet compacted completely. Estimates of density at 1000 feet vary from 1.8 to 2.15 (Fig. 5). It is certainly possible that density in the upper bed (I in Fig. 8) could be considerably more than that in the lower bed. The upper bed would have some compressive strength but very little tensile strength. The lower bed, (II) being undercompacted, would have very little strength, and would transmit pressure almost like a fluid.

At point A in Figure 8 the downward stress would be $h_1\rho_1$, where h_1 is the thickness and ρ_1 the density of the upper bed. It is matched by the upward stress $p + \sigma$. At point B the downward pressure is $h_2\rho_1$, and the upward pressure is $h_1\rho_1 - (h_1 - h_2)\rho_2$. If h_1 is greater than h_2 , and ρ_1 is greater than ρ_2 , then at point B the upward pressure will exceed the downward pressure by $(\rho_1 - \rho_2)(h_1 - h_2)$. The unconsolidated muds will burst upward through bed I, forming a shale diapir.

Such intrusions of soft, undercompacted shale into overlying strata occur at both shallow and deeply buried strata.

At the mouth of the Mississippi River "mud lumps" have appeared continuously successively farther seaward as the river builds its delta outward (Morgan *et al.*, 1968). They form at the rate of one or two per year off the jetties at South Pass, and also off the mouths of other distributaries that are actively depositing large amounts of sediment. Figure 9 shows the structure of the mud lumps as determined by drilling. The soft mud which flowed came from depths of about 500 feet below the bottom.

Shepard reports (1969) larger lumps that he believed to be shale diapirs off the mouth of the Magdalena River, Colombia (Fig. 10). The intrusive shale appears to have come from 400 meters or more below the bottom. Similar lumps have been noted off the constructional slopes near the mouths of rivers in many other places.

Where shale diapirs of this type are found it must be assumed that there is undercompacted shale at depth, which probably contains fluids at abnormally high

pressures. Bumps on the sonic reflection profiles resembling shale diapirs should be a warning to drillers that both high pressures and heaving shales can be expected at depth. There is no way to guess at the depth where the dangerous situation may occur. Shale in diapirs may have come from as little as a few feet or as deep as several kilometers. The high-pressure zones are not only directly under the diapirs, but may extend many kilometers laterally away from them.

In the vicinity of Buku, USSR, mud, methane gas and salty water issue from the earth and pile up into mounds tens or even hundreds of meters in height, called mud volcanoes. Occasionally the gas explodes violently. Oil sometimes accompanies the gas. This same area was the first important oil-producing area in Europe, and geologists were impressed by the apparent relation between mud volcanoes and petroleum.

Mud volcanoes occur in many areas of geologically recent sedimentation, notably Trinidad, northwest Colombia, northeast Venezuela, Burma, New Zealand, and the Copper River Valley of Alaska.

Most geologists have ascribed mud volcanoes to pockets of gas at depth which burst their way to the surface, or to tectonic forces related to mountain building (Kugler, 1938; Yakubov, 1959). It seems more probable that they result from a low-density bed of shale in the subsurface, from which the pore water has not been expelled. Such shales are characterized by abnormally high fluid pressures. This relationship was first pointed out by Kalinko (1960). Shale diapirs thus have basically the same cause as salt domes, which they resemble in many respects. Strata on their flanks are often steeply inclined, as they are on the flanks of salt domes and salt anticlines. The water and mud which oozes out originally doubtless contained large amounts of gas in solution. As the water approaches the surface the pressure reduces, and the gas comes out of solution, forming pockets of free gas, which expand as they rise. On reaching the surface they may erupt violently.

In Trinidad, Colombia, Venezuela and Alaska, wells drilled near the mud volcanoes encountered abnormal pressures. No abnormal pressures, however, have been reported from the Baku area. Mud volcanoes should be taken as a warning of high pressures and heaving shales at great depths. Blowouts should be expected when drilling in such areas.

CHEMICAL PROCESSES ASSOCIATED WITH COMPACTION

The expulsion of water from shale is accompanied by mineralogical and chemical changes which are extremely important to applied geology, but they have been little investigated.

The interstitial water in muds changes very little in chemical composition during the first few hundred meters of burial. Many samples have been analyzed from cores from the Deep Sea Drilling Program, and the water composition is almost exactly the same as that of the overlying sea water. In only a few cases has there been notable depletion of the magnesium (Manheim, 1970; Drever, 1971).

At greater depths and longer times of burial the changes in pore water from sea water are profound. Waters produced from porous and permeable sandstones and limestones have usually lost all or almost all their sulfate and bicarbonate, so that practically the only anion is chloride. The calcium is enriched and the magnesium is reduced, so that there is usually 3 to 5 times as much calcium as magnesium. In sea water there is three times as much magnesium as calcium. These waters have been classified by Russian geochemists as "chloride-calcium" brines,

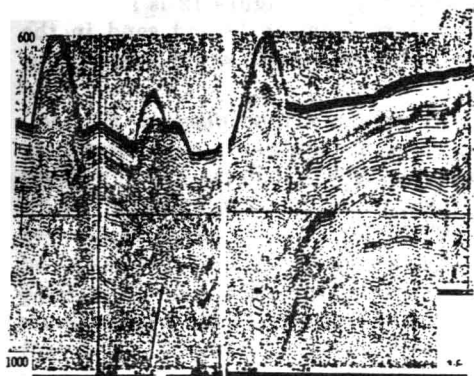


FIGURE 10 — Diapirs, probably shale, coming from depths of 400 m below the sea bottom off the mouth of the Magdalena river, Colombia (from Shepard, 1967).

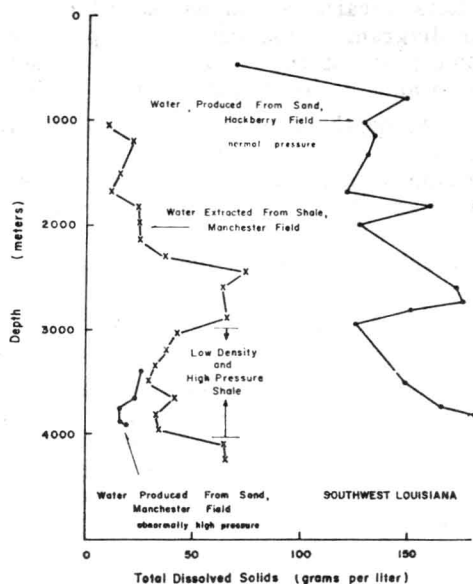


FIGURE 11 — Concentration of interstitial water with depth, southwest Louisiana. The water in the pores of the shale is much less concentrated than that in the adjacent sands. Water in the sands of the high-pressure zone at Manchester is much less concentrated than that in the equivalent normal-pressure sands at Hackberry (from Schmidt, 1971).

(Dickey, 1966). They range in concentration of total solids from less than sea water to almost saturation. Usually there is an increase in concentration with depth, often around 50,000 mg/l per 1000 feet.

The chemistry of the processes by which the sea water is altered and concentrated is very poorly understood. The concentration has been ascribed to reverse osmosis, but this mechanism does not seem to fit the geometry of the actual subsurface situations.

Waters from the abnormally pressured zones conform to the chemical pattern of the chloride-calcium brines, but their concentration is often much less than normal for their depth of burial. This suggests that if the mechanism causing compaction of the shales is inhibited, the process causing the concentration of the water will be inhibited also. At Hackberry, Louisiana, waters produced from normally pressured sand at depth of 3000 to 4000 meters have concentrations ranging from 120,000 to 180,000 mg/l. In the nearby Manchester field, water from equivalent sands at the same depth has abnormally high pressure, and the water concentrations range around 30,000 mg/l, (Schmidt, 1971, Fig. 11).

The water in the pores of shales has seldom been analyzed. It appears to be quite different in composition from the water in the adjacent permeable sands. In Louisiana it has a concentration one-half or one-third that of water in the adjacent sands. Very little calcium or magnesium is present, so that sodium is practically the only cation. It contains sulfate in amounts approximating those of chloride, which is most surprising in view of the absence of sulfate in the sand