Squalus. It can safely be said then that agnathans and elasmobranchs are also alike in sharing a larger extracellular fluid volume than that of Osteichthyes. Other fluid compartment data are not available for the bony fishes.

Whatever may be the physiological significance of the reduction in circulating fluid volume in bony fishes, it would appear that such a reduction is found only in this more advanced group, while the greater plasma and interstitial fluid volumes are associated with the two most primitive of the aquatic vertebrate classes.

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27 February 1959

Clay Minerals in Playas of the Mojave Desert, California

Abstract. Montmorillonite, illite, chlorite, and kaolinite in the playas of southern California are traceable directly to the source areas surrounding the basins. No evidence found in this investigation suggests that these clay minerals are unstable in the sodic or calcic saline lake environment, but this conclusion may not be directly applied to marine evaporite facies where the minerals are rich in potassium and magnesium.

In the last decade several papers have treated clay minerals in sedimentary rocks and the effect of diagenesis on clay minerals in various sedimentary environments. Several investigators (*1, 2*) have suggested that some clay minerals are changed by diagenetic processes in the marine environment, while others (*3*) have reported that clay minerals in most sedimentary rocks are primarily the product of their source and have undergone little diagenetic change even in the marine environment. Millot (*1*) suggested that the fibrous clay minerals such as attapulgite and sepiolite are formed in the supersaline environment, but Millot, Radier, and Bonifas (*4*) recently suggested that attapulgite is formed in the marine environment.

I have undertaken a study of the clay-mineral composition of playa sediments in the western United States and of the effect of the saline environment on diagenetic changes in clay minerals. The Mojave Desert and the surrounding area in southern California contain over a hundred playas ranging in size from a few acres to over 200 square miles. These lakes have a wide range in chemical character, from almost fresh water to very saline, in which deposits of calcium and sodium salts (carbonates, sulfates, halites, borates, and others) are found. Many types of source rocks surround the playa basins and furnish sediments to playas with different chemical environments. By comparing the clay mineral composition of the source rocks and the playa sediments, important data concerning the diagenesis of clay minerals in the saline environment can be obtained. Over 300 samples of sediment were taken from 45 playas and from the source material being transported into the playa basins. This report is concerned with the general conclusions of this study.

Several groups of clay minerals are present in the playas, and their identification is based on standard x-ray analytical techniques. Montmorillonite is present in all samples and ranges in abundance from one to seven parts in ten. A 10-A clay mineral described as illite (*5*) is present in every sample and ranges in abundance from two to six parts in ten. Chlorite is present in about 75 percent of the sediments of the playas and ranges in abundance from one to six parts in ten. In only one lake, Mirage (San Bernardino County), is it the dominant clay mineral, and here it makes up six parts of the total clay mineral composition in ten. Kaolinite is recognized in the sediments in twelve playas, and its abundance ranges from one to two parts in ten. All four of these clay minerals are present in some lakes. For example, in Bristol Lake (San Bernardino County), illite, montmorillonite, chlorite, and kaolinite are found in the playa muds from which halite (NaCl) is being mined. The mother liquor of Bristol Lake is rich in calcium chloride. In every playa studied, no change was seen between the clay mineral composition of the detritus being carried into the basin and the clay mineral composition of the saline muds.

The chemistry of the saline and supersaline evaporite salts in the playas of southern California is complex, but in every case the dominant cations are sodium and calcium. Magnesium and potassium are very abundant in the minerals that are precipitated as the last phases of marine evaporite deposition; however, magnesium and potassium are not in very strong concentration in any of the saline lake deposits in southern California. Therefore the conclusions of this study cannot be applied directly to diagenesis in late-phase marine evaporite deposits. Little work has been done with the clay mineral composition and variation in marine evaporite facies, but it is in marine facies that the regular interstratification of two different clay mineral structures has been found (*6*). These rare, regular, mixed-layered clay minerals are usually high in magnesium and very probably are diagenetic products (*7, 8*).

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8. Many of the lakes sampled are on private land, military reservations and national reserves of various kinds. Permission to enter these areas is gratefully acknowledged. The field work could not have been done without the support of grant G-5659 from the National Science Foundation.

16 February 1959

Gas Diffusion in Porous Media

Abstract. A method has been proposed for deriving a characteristic determining flow in porous systems. This characteristic combines both area and path-length factors used by earlier authors. For a gas, diffusive flow is proportional to the 4/3 power of the gas-filled porosity, and this function has been derived from consideration of the planar distribution of spherical pores and the interaction of two adjacent planes.

The flow of liquid and gas in porous solids has long received attention. In agriculture, irrigation practice and estimation of the possible significance of soil aeration in plant growth depend on accurate definition of the parameters limiting mass and diffusive flow. In the oil industry, the permeability of porous solids is of great significance.

In both diffusive and mass flow in porous solids, the cross-sectional area available for flow and a path-length increase, or tortuosity factor, are regarded as common determinants.

Concerning diffusive flow, Buckingham (*1*), from his investigations on moist soils and some dry soils, suggested the relationship

$$D/D_0 \propto \varepsilon^x \; (x = 2) \qquad (1)$$

where D is the diffusion coefficient of the gas through the porous solid (see Penman, *2*), D_0 is the diffusion coefficient of the gas in free air, and ε is the gas-filled porosity in cubic centimeters per cubic centimeter of bed volume. Subsequently, Penman (*2*) proposed a general relationship for both dry and moist porous solids

$$D/D_0 = (1/k)\varepsilon (0 < \varepsilon < 0.6) \qquad (2)$$

where D, D_0, and ε are the same as they are in Eq. 1, and k is the tortuosity factor and equal approximately to $2^{1/2}$. Over the range stated, Penman's data fitted the linear relationship

$$D/D_0 = 0.66\varepsilon \qquad (2a)$$

that is, k remained constant for a number of porous materials both wet and dry, but evaporative loss of water during experiments on wet soils could lead to overestimates of D/D_0 values at low gas-filled porosities.

The area "available" for flow in porous systems may be related to the pore volume distribution thus

$$A/V = (n^2\pi r^2/n^3\pi r^3)\,(k_1/k_2) \qquad (3)$$

where A is the area of pores, V is the volume of pores, n^3 is the number of pores per unit volume, r is the pore radius and k_1, and k_2 are characteristics of the pore shape.

If the number of pores per unit volume is n^3, then the number encountered in section is n^2 and in length, n. In general, flow theory for porous media has neglected this concept of spatial distribution of pores in length, area, and volume.

From Eq. 3 it can be shown that area A of pores "available" for flow per unit area is

$$A \propto \varepsilon^{2/3} \qquad (4)$$

The probability of continuity of pores in adjacent planes (Childs and Collis-George, *3*) further determines the operative flow area per unit area and thus

$$D \propto (\varepsilon^{2/3})^2 \propto \varepsilon^{4/3} \qquad (5)$$

For a porous solid with pores of radius $r_1 > r_2 > r_3 > \ldots r_m$ comprising m equal-volume porosity components (see Marshall, *4*), summation gives

$$D/D_0 \propto m^2(\varepsilon^{4/3}/m^2) \qquad (6)$$

This expression will apply to all dry isotropic porous solids.

When liquid is included in the porous solid, the effective area for diffusive flow of a sparingly soluble gas is determined by the number of pore classes drained—that is, gas-filled pore space such that

$$D/D_0 \propto n^2(\varepsilon_1^{4/3}/m^2) \qquad (7)$$

where ε, the total porosity, is made up of m equal-volume components of which n are drained and

$$\varepsilon_1 = n\varepsilon/m$$

Assuming the pores approximate spheres,

$$D/D_0 = n^2(\varepsilon_1^{4/3}/m^2) \qquad (7a)$$

and k_1 and k_2 of Eq. 3 do not greatly affect the result.

There is therefore a characteristic relationship between D/D_0 and gas-filled porosity for each value of total porosity in porous solid-liquid-gas systems.

In the problem of vapor transfer in a porous solid-(liquid-vapor)-gas system, the vapor flow is largely determined by the area of the liquid-gas interfaces, which is a function of

$$[2n(m-n)/m^2]\varepsilon^{4/3} \qquad (8)$$

Returning to the tortuosity factor of Eq. 2 for dry, porous solids and steady diffusive flow,

$$D/D_0 = 1/k_2\varepsilon = \varepsilon^{4/3}$$

and

$$k = 1/\varepsilon^{1/3} \qquad (9)$$

This treatment endows k with characteristics of length and is an index of the number of pores per unit length.

In Figs. 1 and 2 comparisons are given between experimental results and the theory proposed here. The data of Taylor (*5*) are mean values based on materials with similar total porosity (varying between 0.47 and 0.53 cm^3/cm^3). In computed curve *a* (Fig. 2), which approximates the data of Taylor, no change in ε was made as the water content changed.

In curve *b* (Fig. 2), the computation was made with appropriate variation in ε with water content. It is considered that curve *b* represents the true theoretical relationship between D/D_0 and gas-filled porosity and that the apparently reasonable agreement between Taylor's data and curve *a* is fortuitous. Taylor's data are suspect, for appreciable flow occurred through some of his materials where the water content, expressed as cubic centimeters per cubic centimeter, exceeded the total pore space of the material—for example, with quartz sand of apparent density of 1.60 g/cm^3, the total porosity is 0.394 cm^3/cm^3 and gas flow occurred when the water content was given as 0.480 cm^3/cm^3. Curve *a* was inserted at first because there was some doubt about the value of ε adopted for gas flow in wet porous solids, and because the agreement of curve *a* with Taylor's data appeared good.

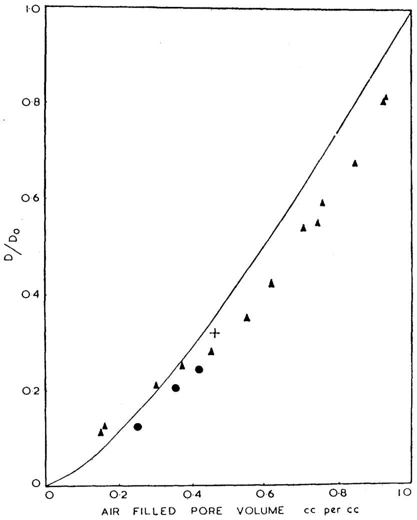

Fig. 1. Gas diffusion in dry, porous solids—a comparison of experimental results [Penman (*2*), triangles; Taylor (*5*), cross; and Van Bavel (*8*), circles] with $D/D_0 = \varepsilon^{4/3}$.

In computing gas and liquid Poiseuille permeability, variation in ε with water content has been made in calculation of unsaturated permeabilities (*6*).

The curvilinear relationship between D/D_0 and gas-filled porosity is due to the nature of the change in probability of continuity of pores both when total porosity varies in dry solids and when gas-filled porosity is varied by water content in single porous systems. I published experimental data to support this in 1957 (*7*) and drew an analogy between this approach to diffusive flow

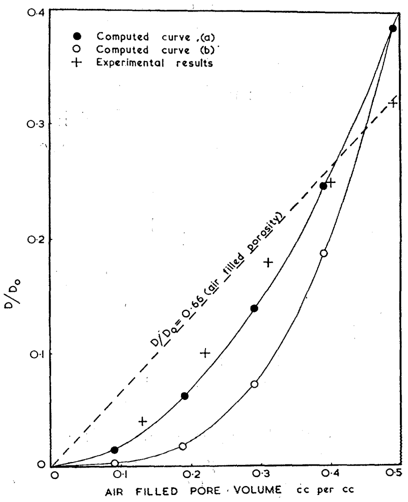

Fig. 2. Gas diffusion in a porous solid-liquid-gas system—a comparison of experimental results (Taylor, *4*) and (*a*) $D/D_0 = n^2\;(\varepsilon^{4/3}/m^2)$ and (*b*) $D/D_0 = n^2\;(\varepsilon_1^{4/3}/m^2)$.

and that of Childs and Collis-George (*3*) for Poiseuille permeability. Recently Marshall (*4*) has used this concept of two-plane interaction in determining diffusive flow; however, he has not recognized basic differences between gas diffusion in wet and dry porous systems.

The nature of the coefficients k_1 and k_2 is being considered and will probably introduce a factor varying between 0.8 and 1.2 in the end result. A value of about 0.85, when applied to the data of Fig. 1, results in very close agreement between the experimental data and the computed values.

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18 May 1959

Clay Mineral Composition of Borate Deposits and Associated Strata at Boron, California

Abstract. X-ray analyses of samples from lacustrine deposits in the Kramer borate district of California show that montmorillonite is the dominant clay mineral, and that illite is abundant in red siltstones, common in green and gray borate-barren claystones, and sparse in borate-bearing rocks. Kaolinite is present only in red siltstones. The distribution of clay minerals is related to the geologic history of borate deposition.

Throughout much of the Cenozoic era, a "boron-rich province" existed in California, southern Oregon, and western Nevada (*1*). Boron-rich waters resulting from volcanism collected in playa basins and formed segregated calcium and sodium borate beds in many places in the boron province. Such deposits are geochemically distinct from magnesium-rich borate deposits of marine origin.

As a part of a more encompassing project (*2*), samples of borates and associated lake clays were collected in the Kramer district at the open-pit mine of the Pacific Coast Borax Company, Boron, Calif. The objectives were to determine the relationships between clay minerals and borate minerals and to relate effects of environmental factors on clay mineral formation, stability, and diagenesis.

In the Kramer district (*3*) Quaternary alluvium and fanglomerates are underlain by Upper Miocene and Pliocene red playa sediments and green and gray lacustrine claystones and siltstones. Various sodium and calcium borates characterize the various layers in the lacustrine sequence, and thick beds of sodium borates are interbedded with claystone (*4*). An olivine basalt (Upper Miocene?) occurs beneath the lacustrine sediments.

Various borate minerals are associated together in specific units. Ulexite ($NaCaB_5O_9 \cdot 5H_2O$) and colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) nodules in claystone matrices are widely scattered in beds above and below the main borax-tincalconite-kernite unit. Colemanite, probably a secondary mineral after primary ulexite (*5*), is most common near the top of the borate-bearing beds. Borax ($Na_2B_4O_7 \cdot 10H_2O$), tincalconite ($Na_2B_4O_7 \cdot 5H_2O$), and kernite ($Na_2B_4O_7 \cdot 4H_2O$) occur in three main layers interbedded with claystones that collectively form a lentil about 1 mile in diameter in the center of the larger ovate sodium-calcium borate basin. Borax represents the primary precipitate, and tincalconite and kernite are secondary after borax (*5*). Less common are probertite ($NaCaB_5O_9 \cdot 5H_2O$), inderite ($Mg_2B_6O_{11} \cdot 15H_2O$), inyoite ($Ca_2B_6O_{11} \cdot 13H_2O$), howlite [$Ca_2SiB_5O_9(OH)_5$], and sassolite ($H_3BO_3$) (*6*).

Forty-five channel samples were collected from various clayey borate beds and from over- and underlying evaporite-barren beds. Borate and clay mineral compositions were determined by direct-recording x-ray diffractometer analyses by standard powder and oriented-sample techniques.

Montmorillonite and illite are, with few exceptions, the only clay minerals present, and the former is the dominant mineral in all of the samples studied. The ratio of the intensity of the unheated 10-A diffraction peak to the gain in intensity of the 10-A peak after heating to 450°C is used as a measure of the illite-to-montmorillonite ratio. Terms used to describe the amount of illite present are abundant, common, sparse, and trace, depending on whether the illite to montmorillonite ratio is 1:1 to 1:2, 1:2 to 1:4, 1:4 to 1:16, and less than 1:16, respectively. Grouping into these ratios is subject to considerable error, but it is desirable to use semi-quantitative limits of some kind in order to compare relative clay mineral abundances in different rock units. Kaolinite and vermiculite-chlorite are found in trace amounts only and do not complicate the quantitative scheme.

Illite is abundant in the red sandy siltstones and is common in borate-barren green and gray claystones above and below the borate units. However, ratios of montmorillonite to illite in the barren claystones are variable, illite ranging between sparse and abundant. Illite is invariably sparse in the borate beds and associated claystones. Kaolinite is present only in red sandy siltstone and probably represents a weathering product of feldspar. A vermiculite or degraded chlorite was found in minor amounts in the upper ulexite-claystone unit.

Influx of terrigenous illite and illite-like mica apparently remained rather constant during the life of the playa lake. Increased increments of montmorillonite derived during the pulsating episodes of volcanism caused a decrease in the illite-montmorillonite ratio. The more saline volcanic waters caused clay to flocculate and permitted deposition of thick sodium borate beds. Clay entering the basin flocculated immediately and was deposited around the edges of the basin. However, during times of low salinity, clay minerals stayed in suspension longer, permitting deposition in all parts of the basin. In laboratory suspensions, flocculation occurred only in samples with high borate content.

The presence of kaolinite in the red playa sediments, as well as the absence of this mineral in underlying green and gray claystones, is noteworthy. In the latter case, kaolinite was either absent in the detritus from the source rocks (*7*) or has been altered by diagenesis to another mineral in the high *p*H environment. It is hoped that further investigation will explain the distribution of kaolinite (*8*).

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2. This project was made possible by National Science Foundation grant G-5659, and by the recipient of the grant, J. B. Droste. I am indebted to Droste for guidance; to G. S. Gordon of the U.S. Borax Research Corp., D. M. Cooper, W. H. Wamsley, and W. J. Diffley of the Pacific Coast Borax Co. for their cooperation; and to D. J. McGregor, W. N. Melhorn, and J. L. Harrison for their comments on the manuscript.
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4. Pre-Quaternary rocks referred to in this paper have been called Ricardo formation by H. S. Gale (*3*), but have recently been included in the Tropico group by T. W. Dibblee, Jr. [*Bull. Am. Assoc. Petroleum Geologists* 42, 136 (1958)].
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6. G. L. Smith, H. Almond, D. L. Sawyer [*Am. Mineralogist* 43, 1068 (1958)] reported an occurrence of sassolite in the Kramer district; however, I did not find this mineral.
7. Elsewhere in this issue, J. B. Droste studies the clay mineral composition of playa surfaces and concludes that the type of clay mineral present is strictly a function of source rather than a matter of diagenesis.
8. This report is published with the permission of the State Geologist, Indiana Geological Survey.

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