V. GYPSUM IN THE FAYETTEVILLE SHALE

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The Fayetteville shale, named for Fayetteville, Arkansas, upper Mississippian (Chester) in age, and ranging from 10 to 400 feet in thickness, is widely developed in northwestern Arkansas and northeastern Oklahoma. The Fayetteville formation has long been known, and its surface distribution in a large part of northwestern Arkansas was mapped in detail in the Fayetteville, Eureka Springs, Harrison, and Winslow quadrangles during the preparation of the United States Geological Survey folios describing these quadrangles.[1] The formation also has a wide distribution north of the Boston escarpment in the southern part of the Ozark plateau east of the Winslow quadrangle and south of the Eureka Springs and Harrison quadrangles. Its distribution, however, in this region has not been mapped in detail.

The distribution of the Fayetteville shale in the Tahlequah quadrangle of northeastern Oklahoma was mapped long ago and described in the Tahlequah folio. Since the publication of this folio the formation has been found to extend northward into Mayes, Delaware, and southern Ottawa counties of northeastern Oklahoma, where it forms the upper member of the Chester group in the absence of the Pitkin limestone which normally overlies the Fayetteville shale.[2]

During the past summer Wiedman traced the Fayetteville formation as far north as Narcissa in west-central Ottawa county.[3]

The Fayetteville formation in Arkansas and in the Tahlequah quadrangle consists mainly of black, fissile, highly carbonaceous clay shale which weathers to a plastic clay of yellow or red color. In the lower part of the formation limestone lentils and calcareous shale beds are present. The middle of the formation consists of a continuous and rather monotonous sequence of thin, black, fissile, clay shale, with limestone beds and calcareous shales almost entirely absent. A massive light gray to brown sandstone, the Wedington member, is persistent at or near the top of the formation.

In Oklahoma north of the Tahlelquah quadrangle the character of the formation changes. Ireland describes the formation in central Mayes county as "primarily a thin-bedded, two to five inches, drab, dense limestone with some interbedded shale, and weathering into whitish cubical and angular fragments. Above this is a thin, black shale about 20 to 40 feet thick. In places where erosion has not removed it, there is an upper limestone."[4] In northern Mayes county and southern Ottawa and northern Delaware counties the character of the Fayetteville again changes, the shale becoming gray rather than black, with an earthy, fossiliferous limestone above, and a thin-bedded limestone below the shale.

In Arkansas and northeastern Oklahoma, except in Mayes, Ottawa and Delaware counties, the Fayetteville shale is normally overlain by the Pitkin limestone, the upper member of the Chester group. The formation is underlain in Arkansas by the thin calcareous Batesville sandstone, or, where this is absent, by the Boone limestone. In the Tahlequah quadrangle of Oklahoma the Boone limestone underlies the Fayetteville shale, but farther north the Mayes limestone of Chester age underlies the Fayetteville. The Fayetteville shale is thus a black shale horizon in a stratigraphic sequence chiefly calcareous.

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[1] Simonds, F. W., The geology of Washington county. Ark. Geol. Surv., Ann. Rept. for 1888, Vol. IV, 1891.

Adams, G. I. and Ulrich, E. O., Fayetteville folio. Geol. Atlas of United States, No. 119, p. 4, 1905.

Purdue, A. H., Winslow folio. Geol. Atlas of United States, No. 154, pp. 2-3, 1907.

Purdue, A. H., and Miser, H. D., Eureka Springs-Harrison folio. Geol. Atlas of United States, No. 202, pp. 12-13, 1916.

Giles, Albert W., and Brewster, E. B., Hale mountain section in northwest Arkansas. Bul. Am. Assn. of Petroleum Geologists, Vol. 14, No. 2, pp. 127-130, 1930.

[2] Taff, J. A., Tahlequah folio. Geol. Atlas of United States, No. 122, pp. 3-4, 1905.

Snider, L. C., Geology of a portion of northeastern Oklahoma. Bul. 24, Okla. Geol. Survey, pp. 35-39, 1915.

Ireland, H. A., Oil and gas in Oklahoma (Mayes, Ottawa, and Delaware counties). Bul. 40, Okla. Geol. Survey, pp. 488-491, 1930.

[3] Personal communication, Oct. 10, 1930.

[4] Op. cit., p. 489.

Like many black shales, the Fayetteville shale contains much pyrite as crystals, grains, and stringers within the individual beds of shale, and nodules, and thin seams of pyrite as well as small carbonaceous lenses with pyrite between the shale beds.

From time to time reports of gypsum found in the Fayetteville shale have come to the geological laboratory of the Unitversity of Arkansas, and occasionally samples have been submitted. The presence of gypsum in this formation, however, has long been known. In 1905 Adams and Ulrich stated that "in some localities the shale contains gypsum, which occurs as individual crystals or as a coating of calcareous concretions."[5] Since the presence of gypsum might throw light upon the environmental conditions obtained when this typically black shale formation accumulated, the extent and manner of occurrence of the gypsum were thought worthy of investigation.

A study of the Fayetteville shale with particular reference to the problem of its gypsum content was carried on by the junior author at intervals during the college year 1929-30. The gypsum was found to be limited almost entirely to the lower part of the formation, where it is present as concentric layers, and penetrations in associations with limonitic and clay ironstone concretions, as individual grains, stringers, and irregular aggregates in shale beds; as isolated crystals, thin seams, and lenses of crystals and grains between the layers of shale; and as a whitish efflorenscence on the surfaces of outcrops of the formation. Although the manner of occurrence of the gypsum is varied, nothing was found that could be interpreted as indicative of a primary origin of any of the gypsum.

Concretions in the Shale

Concretions are very abundant in the Fayetteville shale, ranging from an inch or less to several feet in diameter. In fresh exposures of the shale the concretions are found as globular, spindle-shaped, and lenticular bodies, which are reddish brown, brown, dark gray, or black in color. The dark color is due chiefly to organic matter, and when broken a fetid or petroliferous odor, it is often distinctly perceptible.

The concretions are of various kinds; some are argillaceous, others limonitic ,or calcareous. They are sporadic in distribution through the shale, and have come into existence in ways analgous to the origin of concretions normal to most shales. But the dominant kind of concretions is clay ironstone;[6] many of the smaller; less than two or three inches in diameter, and all of the larger concretions have this composition. They are localized chiefly to the lower part of the formation.

Nearly every concretion of more than two or three inches in diameter is a septarian with veins of gray or white calcite, which may be darkened locally by organic matter, oxides of iron, or iron carbonate. After exposure to the weather the calcite veins normally become wholly altered to limonite. The septaria are generally lens-shaped; in size they range from two to three inches to more than one foot in thickness, and from a few inches to several feet in breadth. They form continuous horizons in the lower part of the formation, and in many places project as ledges from the weathered surfaces of the shale.

Analyses of unaltered fragments and chips from unweathered and freshly fractured surfaces of the concretions yield an abundance of iron, calcium, aluminum, and the sulphate radical. Some fragments effervesce slowly, others briskly in cold, dilute acid. The composition of the concretions is interpreted, therefore, as a mixture of calcite and siderite with

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[5] Op. cit., p. 5.

[6] Purdue, A. H., and Miser, H. D., Op. cit., p. 13.

clay and calcium sulphate; hence their name, clay ironstone concretions. Organic matter is invariably present. Seams and stringers of pyrite ramify through the interior of many of the specimens. Many of the concretions when broken reveal interiors uniform in color, texture and composition; others possess a core consisting of a mixture of iron and calcium carbonates and calcium sulphate, surrounded by a darker layer of almost pure siderite. After exposure to the weather for some time, the concretions exhibit an outer crust of limonite.

The clay ironstone concretions and septaria are largely localized in the formation to certain layers of calcareous composition which were originally limestone beds, more rarely beds of calcareous shales. This is demonstrated by their occurrence at certain and definite horizons, the juxtaposition of the concretions laterally, their orientation with longer axes parallel to the bedding, the general absence of nuclei in the center of the concretions, the continuation of the layers of concretions into unaltered limestone beds, and their restriction chiefly to the lower part of the formation. Therefore, the concretions are regarded as having originated almost entirely from the alteration of calcareous lenses and beds in the shale.

Formation of Clay Ironstone Concretions

The replacement of calcareous beds by ferruginous carbonate has long been known and many examples have been described.[7] Hence the transformation of calcareous beds in the Fayetteville shale into siderite, calcite, and calcium sulphate represents a process already familiar. The alteration is attributed mainly to the action of percolating underground water carrying ferrous sulphate and sulphuric acid in solution derived from the oxidation of pyrite present in the shale.[8] A well known reaction is indicated in equation (1).[8]

$$(1)\ 2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$$

The oxidation takes place in the zone of weathering, and the iron-bearing solutions are carried downward by descending underground water and brought into contact with the calcareous beds replacing the calcium carbonate with ferrous carbonate and hydrous calcium sulphate (gypsum) according to equation (2). The sulphuric acid present reacts with the calcium carbonate to form additional gypsum as indicated in equation (3). The replacement results in an increase in volume which appears in the displacement and flexing of the shales above and below the concretionary masses.

$$(2)\ FeSO_4 + CaCO_3 + 2H_2O = FeCO_3 + CaSO_4{\cdot}2H_2O$$

$$(3)\ H_2SO_4 + CaCO_3 + H_2O = CaSO_4{\cdot}2H_2O + CO_2$$

The gypsum formed in reactions (2) and (3) represents the replacement of limestone beds under considerable pressure. The pressure together with the solubility of the gypsum may result in the removal in solution of considerable quantities of gypsum as rapidly as it is formed. Since the clay ironstone concretions in general react vigorously with cold, dilute acid, it follows that a considerable part of the final product consists of calcium carbonate, indicative of either incomplete replacement or reprecipitation of calcium carbonate taken into solution as the bicarbonate.

Although the replacement of calcareous strata by ferrous carbonate, calcium sulphate, and calcium carbonate appears sufficiently explained by

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[7] Clarke, F. W., The data of geochemistry. Bul. 770, U. S. Geol. Survey, pp. 581-584, 1924.

[8] Gottschalk, V. H., and Buehler, H. A., Oxidation of sulphides. Econ. Geol., Vol. 7, pp. 15-34, 1912.

the process just described, other reactions are possible and it is by no means certain that they have been absent in the alternation of the Fayetteville beds.

Under normal environmental conditions ferrous sulphate slowly oxidizes in acid solutions to ferric sulphate, or to a mixture of ferric sulphate and ferric hydroxide, according to equations (4) and (5). In dilute solutions ferric sulphate hydrolyzes to a basic ferric sulphate which is rather unstable, breaking down to form ferric hydroxide and sulphuric acid. The reactions are as follows:

$$(4)\quad 4FeSO_4+O_2+2H_2SO_4=2Fe_2(SO_4)_3+2H_2O$$

$$(5)\quad 12FeSO_4 + 3O_2 + 6H_2O = 4Fe_2(SO_4)_3 + 4Fe(OH)_3$$

$$(6)\quad Fe_2(SO_4)_3 + H_2O = Fe_2(SO_4)_2O + H_2SO_4$$

$$(7)\quad Fe_2(SO_4)_2O + 5H_2O = 2H_2SO_4 + 2Fe(OH)_3$$

But since the environment is deficient in normal amounts of air and water, and is reducing due to the high carbonaceous content of the shales, it is probable that only very minor amounts of the ferric sulphate can form. Brought into contact with limestone ferric sulphate forms ferric hydroxide and hydrous calcium sulphate according to the following reaction:

$$(8)\quad Fe_2(SO_4)_3 + 3CaCO_3 + 9H_2O = 3(CaSO_4 2H_2O) + 2Fe(OH)_3 + 3CO_2$$

Limonite is essentially absent from the unweathered concretionary masses; hence the preceding reactions are of very subordinate significance in the alteration of the calcareous beds.

It is possible that still another set of reactions may occur, depending on the higher position of calcium relative to iron in the electromotive series. The calcareous beds go into solution in carbonated waters as the bicarbonate equation (9). The calcium replaces the iron of the ferrous sulphate when carried into contact with calcium bicarbonate, forming the soluble ferrous bicarbonate equation (10), which reacts with the calcareous beds to form siderite equation (11).

$$(9)\quad CaCo_3 + H_2CO_3 = Ca(HCO_3)_2$$

$$(10)\quad FeSO_4 + Ca(HCO_3)_2 = Fe(HCO_3)_2 + CaSO_4$$

$$(11)\quad Fe(HCO_3)_2 + CaCO_3 = Ca(HCO_3)_2 + FeCO_3$$

A fourth sequence of reactions is also possible in which the ferrous sulphate is hydrolyzed to ferrous hydroxide, according to equation (12), and when carried into contact with calcium bicarbonate, forming by the action of carbonated underground water on the calcareous beds produces a mixture of iron and calcium carbonates with calcium sulphate, as indicated in equations (13) and (14). The products of the reactions replace the limestone to form the concretionary masses.

$$(12)\quad FeSO_4 + 2H_2O = Fe(OH)_2 + H_2SO_4$$

$$(13)\quad Ca(HCO_3)_2 + Fe(OH)_2 = FeCO_3 + CaCO_3 + CaCO_3 + 2H_2O$$

It is obvious that if reactions (12) and (13) are significant in the alteration of limestone, the sulphuric acid formed must be neutralized immediately if the reactions are to be completed. The acid may be utilized by reacting with the limestone directly, equation (3), or by reacting with any of the bicarbonate that may be forming equation (14).

$$(14)\quad Ca(HCO_3)_2 + H_2SO_4 = CaSO_4 + 2H_2O + 2CO_2$$

All four sets of reactions may be operative in replacing the calcareous beds of the formation, but the first set is regarded as of major importance. There is ample experimental evidence that siderite may be formed by replacement where iron solutions, particularly ferrous solutions, act upon limestone.[9]

Owing to the nature of the reactions demanding both air and water in some quantity, and the compact character of the shale, it seems doubtful whether clay ironstone concretions can form in the shale far from the outcrop, but the transformation takes place largely if not entirely below the zone of weathering.

Formation of Limonite Concretions

Limonite concretions formed by gradual alteration of clay ironstone concertions are numerous in most weathered outcrops of the shale. The concretions are very porous, easily disintegrated, and consist of concentric shells of limonite loosely held together. Their condition results from the normal shrinkage, estimated at about twenty-five percent, when siderite alters to limonite, and from loss of calcium carbonate and calcium sulphate in solution. In larger concretions the outer part only has been altered to limonite, but many samples when broken reveal penetrations of limonite throughout their interiors. Careful search of recent and unweathered exposures of the shale has revealed very few limonite concretions; therefore, it follows that their formation takes place close to the surface, in the zone of weathering, with air and water abundant, and continues after exposure when incomplete.

In the formation of the limonite concretions the calcium carbonate and the calcium sulphate of the clay ironstone are removed in solution, and the iron carbonate may be slowly hydrolyzed and oxidized to ferric hydrate, and the latter partially dehydrated to limonite, according to equations (15) and (16).

$$(15)\ 4FeCo_3 + 6H_2O + O_2 = 4Fe(OH)_3 + 4CO_2$$

$$(16)\ 4Fe(OH)_3 + nH_2O = 2Fe_2O_3 \cdot nH_2O + 3H_2O$$

Equation (15) is based on the fact that ferrous carbonate will slowly hydrolyze when bathed in water free from acids, but since underground water normally contains carbonic acid, it is more likely that the iron carbonate, at least in greater parts, goes into solution as the bicarbonate, and and this oxidizes to the ferric hydroxide. The reactions are given in equations (17) and (18).

$$(17)\ FeCO_3 + H_2O + CO_2 = Fe(HCO_3)_2$$

$$(18)\ 4Fe(HCO_3)_2 + 2H_2O + O_2 = 4Fe(OH)_3 + 8CO_2$$

The easy alternation of ferrous carbonate to limonite is well known, and slowly takes place in air alone.

Formation of Gypsum

Concretions with gypsum are relatively rare. They are never found in old outcrops, because of the rapid disintegration of the concretions following exposure and the easy solubility of the gypsum. Search in the banks of shallow cuts in the shale recently made in building improved roads will usually reveal one or more layers of gypsum-bearing concretions. Most satisfactory results are obtained where the road leads through the lower

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[9] Clarke, F. W., The data of geochemistry. Bul. 770, U. S. Geol. Survey, pp. 581-584, 1924.

part of the formation, since the original calcareous layers are chiefly below the middle of the formation.

The gypsum occurs as the outermost layer of the concretion, or it may be enclosed by outer layers of limonite or yellow or brown ferruginous clay. Concentric layers of gypsum may alternate with layers of limonite. The center of the concretion may be unaltered, or it may be penetrated by stringers, seams, and irregular aggregations of gypsum crystals. A few of the concretions are merely "balls" composed of an alternation of black shale and gypsum.

The gypsum is beautfully crystallized, colorless and transparent, or white and translucent in layers one-sixteenth to one-half inch thick. In specimens that have been near the surface for some time, insufficiently protected from weathering action, the gypsum has become granular or flaky. Gypsum crystallized in the interiors of the concretions is normally red, or brown, or almost black.

The origin of the gypsum is attributed in large part to the oxidation of pyrite present within the concretions and in the shales adjacent to the concretions, the reaction proceeding according to equation (1). The sulphuric acid reacts with the calcium carbonate of the concretion forming gypsum, and with the iron carbonate forming ferrous sulphate according to equation (19) and (20).

$$(19)\ CaCO_3 + H_2SO_4 + H_2O = CaSO_4{\cdot}2H_2O + CO_2$$

$$(20)\ FeCO_3 + H_2SO_4 = FeSO_4 + H_2O + CO_2$$

The ferrous sulphate oxidizes to ferric sulphate equation (4) which either forms ferric hydroxide and limonite equations (5-7) and (16) or more probably reacts with the calcium carbonate of the concretion to form more gypsum, equation (8). Some of the gypsum may form by hydration of the calcium sulphate present as a part of the concretion. Progressing gradually inward from the exterior, the gypsum replaces the concretion forming concentric layers. During the process the part of the original calcium carbonate of the concretion escaping attack by the sulphuric acid is lost in solution, equation (9), together with some of the calcium sulphate that is being formed. Any of the original ferrous carbonate that is not altered to ferrous sulphate is converted into bicarbonate equation (17) and is in part lost in solution, and in part oxidized and dehydrated to form the concentric layers of limonite equations (18) and (16). Since the layers of limonite and gypsum are distinctly separated, there must be some segregation of both during their formation.

The gypsum present within the concretions is formed as a result of the oxidation of the pyrite within the concretions, and from the hydration of calcium sulphate present. The formation of the gypsum, like the formation of the limonite, takes place close to the surface in the zone of weathering where air and water are present in quantity.

The isolated crystals and aggregates of crystals and grains, seams, and stringers of gypsum found between beds of shale and within the shale beds are interpreted as forming essentially in the same way as the gypsum of the concretions. The oxidation of pyrite in the shale results in the formation of ferrous sulphate and sulphuric acid, which react with the calcareous beds forming gypsum and ferrous carbonote. The latter is largely removed in solution as the bicarbonate. A part of the gypsum present in the shales represents the reprecipitation of gypsum dissolved from the concretions.

Although the distribution of gypsum is very irregular in the shale and largely confined to the lower part of the formation, yet it is sufficient in amount to make an efflorescence in many places where water is issuing from beneath the surface; and the shales below high water level along many streams have a white coating of gypsum.

Summary

For nearly thirty years the occurrence of gypsum in the Fayetteville shale has been known. The gypsum is found chiefly in the lower part of the formation as concentric layers and penetrations of clay ironstone concretions; as grains, stringers, and irregular aggregates in the shale beds; as isolated crystals, thin, seams, and lenses of crystals and grains between the layers of shale; and as a whitish efflorescence on the surfaces of outcrops of the formation.

The Fayetteville shale is upper Mississippian in age and consists chiefly of black, fissile, highly carbonaceous clay shale that contains pyrite as crystals, grains, stringers, seams, and nodules. Limestone lentils and calcareous shale beds are present in the lower part of the formation. Calcareous, limonito, and argillaceous concretions are abundant in the shale, but clay ironstone concretions and septaria dominate and are found chiefly in the lower part of the formation. Their origin is attributed to the alteration of calcareous beds and lenses by percolating water carrying sulphuric acid and ferrous sulphate in solution, derived from the oxidation of pyrite. As a result the limestone layers are replaced with calcite, siderite, and calcium sulphate to form the concretionary masses.

When brought into the zone of weathering by the erosion of overlying shales, the clay ironstone concretions are transformed into limonite and weather out as porous, reddish brown masses. In many of the larger concretions, however, gypsum is developed as a result of the action upon the concretions of solutions carrying ferrous sulphate and sulphuric acid, derived from the oxidation of pyrite. The stringers, seams, and aggregates of crystals and grains of gypsum present within and between the shale beds have a similar secondary origin. The efflorescence of gypsum upon outcrops is due to precipitation of gypsum dissolved by underground water as it penetrates the gypsum-bearing shales on its way to the surface.