

OKLAHOMA GEOLOGICAL SURVEY

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BARITE IN OKLAHOMA

by

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Norman

1944

## CONTENTS

	Page
Abstract .....	5
Introduction .....	6
General Survey of Barite.....	8
Properties .....	8
Occurrence .....	8
Non-commercial Occurrences .....	9
Economic Deposits .....	10
Origin .....	11
Uses .....	12
Production .....	13
Specifications .....	14
Prices .....	14
Markets .....	15
Barite in Oklahoma .....	16
Ouachita Mountains .....	16
Arbuckle Mountains .....	17
Residual Deposits from Arbuckle Dolomite.....	17
Other Occurrences .....	21
Central and Southwestern Oklahoma.....	22
Barite in Shale .....	22
Barite in clay-carbonate concretions.....	22
Veins .....	23
Nodules .....	25
Economic considerations .....	27
Barite in Sandstone .....	29
Barite cement .....	29
Sand-Barite rosettes .....	30
Economic considerations .....	36
Origin of Barite in Lower Permian Sediments of Oklahoma.....	37
Hydrothermal solutions .....	37
Leaching of barium from enclosing sediments.....	37
Derivation of barium from marine waters—preferred theory.....	39
Other Occurrences .....	42

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### ILLUSTRATIONS

	Page
Figures	
1. Map of Oklahoma, showing distribution of barite.....	4
2. Internal structure of sand-barite concretions .....	33
Plates .....	Following page 22
I. a. Barite-clay-carbonate concretion.	
b. Coarsely crystalline barite.	
II. Barite nodules and vein barite from lower Permian shales.	
III. Sand-barite concretions from lower Permian sandstones.	
IV. Sand-barite rosettes from Garber sandstone.	

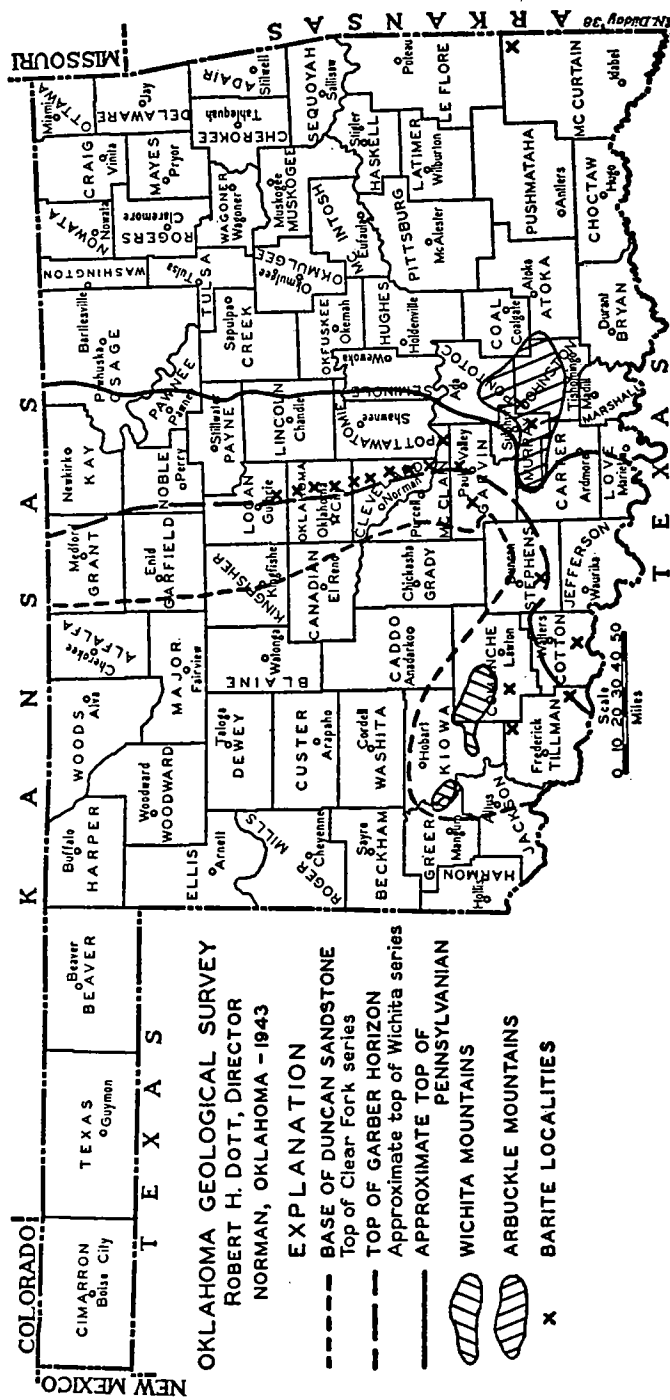


FIG. 1. Map of Oklahoma, showing distribution of barite.

# BARITE IN OKLAHOMA

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W. E. HAM and C. A. MERRITT

## ABSTRACT

Barite deposits in Oklahoma are of three general types, each quite diverse in character and mode of origin. Although of considerable geological interest, the deposits are either so small or of such low concentration that there has been little production for industrial use to date.

The three general types of barite deposits in Oklahoma are: (1) in veins of hydrothermal origin, (2) secondary deposits derived by weathering from Cambro-Ordovician dolomite, and (3) sedimentary deposits in lower Permian sandstone and shale.

Veins of hydrothermal origin containing a small amount of metallic sulfides and barite are found in two localities in McCurtain County, southeastern Oklahoma. The veins cut highly folded shales and quartzitic sandstones (Stanley) of Pennsylvanian age in the Ouachita Mountains.

Secondary deposits derived from Cambro-Ordovician dolomite are present in the Arbuckle Mountains in south-central Oklahoma. The barite occurs as coarsely crystalline masses associated with limonite, ocher, clay, and sand. The deposits appear to occupy small depressions that were filled with detritus that was derived from several sources.

The lower Permian red beds of central and southwestern Oklahoma contain a large volume of barite in the form of concretions, veins, cement, and disseminated grains. In most places the barite is far too scattered or too impure to be of value, but in a few localities there are surface concentrations of high grade concretionary nodules which have possibilities for limited production. Most interesting of the concretionary forms are the sand-barite rosettes, which consist of rosette-shaped aggregates of barite that grew in sandstone. All the barite in the lower Permian is related in origin and time of deposition, and it is believed that barite was introduced into the sediments as secondary concentrations from marine water.

Other occurrences of barite in Oklahoma include small amounts from insoluble residues of various Paleozoic limestones, barite "dollars" from the Arbuckle Mountains, and barite gangue in the zinc-lead ores of Ottawa County.

A general discussion of the properties, occurrence, origin, uses, production, specifications, prices, and markets of barite is included in the opening chapters of the report.

## INTRODUCTION

The market for barite has expanded considerably in the last decade owing to increased use of this mineral as a weighting agent in heavy drilling muds, and, more recently, to its greater consumption in defense industries. The resulting increased demand has given impetus to the search for barite; and this, together with the lack of detailed information on occurrences of barite in Oklahoma, warranted an investigation of the deposits.

The occurrence and origin of barite in Oklahoma have received some attention in the past, but a comprehensive study had never been made. Nichols<sup>1</sup> made chemical and mineralogical studies on specimens of sand-barite "roses" supplied to him by C. N. Gould. Meland<sup>2</sup> described the barite "roses" near Norman and discussed their origin. Mention is made by Honess<sup>3</sup> of the barite occurring in certain metalliferous veins in the Ouachita Mountains. The information on Oklahoma barite available to 1923 was summarized in an excellent short article by Shead<sup>4</sup>. He gave an analysis of the sand-barite "roses", listed the known occurrences, and discussed briefly the origin of Oklahoma barite, including the barite veins and radiating nodules. Gould<sup>5</sup> calls attention to an exceptionally large sand-barite "rose" found in the central Oklahoma region. Dott<sup>6</sup> mentions barite "roses" in Garvin County, and Anderson<sup>7</sup> calls attention to similar occurrences in Cleveland County. Tarr<sup>8</sup> made a brief field study of barite rosettes near Norman and discussed their origin, but he did not visit the area containing barite veins and

<sup>1</sup> Nichols, H. W., "New Forms of Concretions: Sand Barite Crystals from Oklahoma": *Field Columbian Museum*, Geol. Ser. Vol. III, No. 3, pp. 31-35, 1906.

<sup>2</sup> Meland, Norman, "A Contribution to the Study of the Red Beds of Oklahoma: Part One, Sand-Barites", Master's Thesis, Univ. of Oklahoma, pp. 1-15, 1922.

<sup>3</sup> Honess, C. W., "Geology of the Southern Ouachita Mountains of Oklahoma": *Okla. Geol. Surv. Bull.* 32, Part II, Geography and Economic Geology, 1923.

<sup>4</sup> Shead, A. C., "Notes on Barite in Oklahoma with Chemical Analyses of Sand Barite Rosettes": *Okla. Acad. Sci. Proc.*, Vol. III, pp. 102-106, 1923.

<sup>5</sup> Gould, C. N. "Radiate Structure of Sand Barite Crystal Masses": *Okla. Acad. Sci. Proc.* Vol. VI, pp. 239-242, 1926.

<sup>6</sup> Dott, R. H., "Geology of Garvin County" in *Oil and Gas in Oklahoma: Okla. Geol. Surv. Bull.* 40, Vol. II, pp. 119-143, 1930.

<sup>7</sup> Anderson, G. E. "Geology of Cleveland and McClain Counties" in *Oil and Gas in Oklahoma: Okla. Geol. Surv. Bull.* 40, Vol. II, pp. 179-192, 1930.

<sup>8</sup> Tarr, W. A., "The Origin of the Sand Barites of the Lower Permian of Oklahoma": *Amer. Mineralogist*, Vol. 18, No. 6, pp. 260-272, June 1933.

radiating nodules. Several new localities containing barite in small quantities were discovered in 1936 and 1937 by the State Mineral Survey<sup>9</sup>, and new occurrences were reported in the Arbuckle Mountains in 1940.

Many known localities of barite in Oklahoma were studied in the field by the writers during parts of the summers of 1941 and 1942, and several additional deposits were found by field prospecting. Samples were collected and later studied mineralogically and chemically in the laboratory.

*Acknowledgments:* The staff members of the Oklahoma Geological Survey have assisted considerably in the preparation of this report, and their cooperation is gratefully acknowledged. Thanks are due particularly to Robert H. Dott, who examined many of the field occurrences and gave much help in the problems of stratigraphy and to M. C. Oakes, who made most of the photographs.

<sup>9</sup> WPA Project 65-65-538, sponsored and directed by the Oklahoma Geological Survey, 1936-1937.

## GENERAL SURVEY OF BARITE

### PROPERTIES

Barite is known commercially as barite, baryta, barytes, heavy spar, cawk, and locally in Missouri as tiff. It is composed of barium sulfate,  $\text{BaSO}_4$ , and contains, when pure, 65.7 per cent barium oxide ( $\text{BaO}$ ) and 34.3 per cent sulfur trioxide ( $\text{SO}_3$ ). Strontium and calcium commonly are present in small amounts; and silica, clay, and bituminous or carbonaceous matter may be additional impurities. It is rather heavy for a non-metallic mineral, the specific gravity ranging from 4.3 to 4.6. It can be scratched easily by a knife blade, the hardness ranging from 2.5 to 3.5. The color is white or gray when pure; it may be blue, red, pink, or yellow, owing to impurities of iron oxide or other material.

Barite crystallizes in the orthorhombic system as tabular or rectangular crystals, the tablets being flattened parallel to the basal pinacoid or elongated parallel to the  $a$  or  $b$  axis. Coarse-bladed or crested crystals with straight or slightly curved faces are commonly arranged in aggregates, and some of these have a rosette appearance. Barite is also found as nodules with a radiating fibrous structure, as parallel needles in veins, in coarsely crystalline, cleavable masses, and finely granular types which resemble marble. Sand-barite "roses" are barite aggregates enclosing sand grains.

Barite has perfect cleavage in three directions, one parallel to the basal pinacoid, and the other two parallel to the unit prism (110). The prismatic cleavage angle is  $78^\circ 22\frac{1}{2}'$ . The mineral is brittle and has an uneven fracture. The luster is vitreous, inclining to resinous, and is commonly pearly on the basal cleavage face. It is transparent to translucent.

Barite is virtually insoluble in mineral acids and water. One part barite dissolves in 400,000 parts of pure water, but the solubility is increased in solutions containing  $\text{CO}_2$ , alkaline carbonates, or chloride ions.

### OCCURRENCE

The element barium is widespread in the earth's crust, being a minor constituent of many rocks. Clarke<sup>10</sup> reports 0.055 per cent

<sup>10</sup> Clarke, F. W., "The Data of Geochemistry": *U. S. Geol. Surv. Bull.* 770, pp. 29, 547, 552, 1924.

barium oxide in the average igneous rock, 0.05 per cent in shales, and 0.05 per cent in sandstones. In igneous rocks barium is generally present in barium-containing silicates, mainly feldspars and micas. In shales and sandstones barium is probably present in detrital feldspar and mica, and in the form of barite. Soils are also known to contain barium<sup>11</sup>. The waters from many springs, oil fields, and mines contain barium in small amounts, and it also is present in sea water.

Barium is deposited from water solutions, either hot or cold, in many different environments and under a wide variety of conditions. It invariably occurs as barium compounds of which barite ( $\text{BaSO}_4$ ) and witherite ( $\text{BaCO}_3$ ) are economically important, the barite being far more abundant.

### NON-COMMERCIAL OCCURRENCES

Many occurrences of barite are only of scientific interest, because of their small size or unusual nature. They include:

- (1) granules in the shells of marine animals, notably certain rhizopod protozoa;
- (2) nodules on the ocean floor. In the Indian Ocean, off the coast of Ceylon, nodules dredged from 675 fathoms contain 75 per cent barium sulfate;
- (3) spring deposits, as in Delta County, Colorado;
- (4) cement in sandstone, as from the Chester (Mississippian) of Indiana, Triassic of England, Nubian (Cretaceous) of Egypt, and Permian of Oklahoma;
- (5) crystals lining geodes in shale, known from the Permian of Oklahoma and elsewhere;
- (6) concretionary forms in shale and sandstone: oolitic, pisolitic, spherical, rosettes, and dollar-shaped;
- (7) disseminated crystals in sedimentary rocks, such as have been observed in the Garber, Hennessey, and Duncan formations of central Oklahoma, and which are probably present in minute quantities in many clastic sediments throughout the world; and

<sup>11</sup> Failyer, G. H., "Barium in Soils"; *Bur. of Soils Bull.* 72, 1910.

(8) gangue in metalliferous deposits. Although present in many ore deposits, barite generally is too difficult to separate and the product is not sufficiently uniform to justify its recovery. The great deposits at Meggen, Germany, are a notable exception, producing pyrite and barite from the same ore body.

#### ECONOMIC DEPOSITS

Economic deposits of barite are of two types: one type includes veins, replacements, or breccia filling in various types of rocks; and a second which consists of residual deposits of barite in clays, many having been derived from the weathering of Cambrian and Ordovician dolomites. Residual deposits supply most of the barite mined in the United States at the present time.

*Veins* consisting essentially of barite, or of barite accompanied by calcite, fluorite, quartz, and metallic sulfides, are found in many localities under various geologic conditions. Some of the veins, for example, traverse crystalline rocks of Pre-Cambrian age, as in the Piedmont Province of the Appalachians and in Nova Scotia; others cut Paleozoic sediments, generally limestone or dolomite, as in Illinois, Kentucky, Missouri, Colorado, California, and Virginia. In many of these deposits the country rock is brecciated and the interstices filled with barite.

*Replacement* deposits are known in various localities, including Arkansas, Belgium, and Westphalia. The Westphalian deposits, near Meggen, Germany, are the largest known in the world and consist of a limestone which has been replaced by barite. Near Hot Springs, Arkansas, barite has replaced shale, and this deposit has a reserve of at least 1,000,000 tons.

*Secondary ore (principally residual)* is formed by the weathering of rock containing barite. The weathering removes soluble constituents and leaves as a residue a more or less concentrated deposit of the comparatively insoluble barite, commonly associated with clay. In many of these deposits the residual materials have been moved a short distance by gravity slumping. The barite in residual deposits is found as boulders, nodules, and small fragments in deeply weathered clay. Other residual products, such as limonite (brown iron ore), manganese oxides, chert, and undecomposed country

rock, may also be present. The thickness of these residual deposits depends upon the amount of weathering and varies from place to place, commonly ranging from 10 to 20 feet but locally reaching 60 feet. The areal extent of these deposits ranges from a few hundred square feet to 100 acres or more.

The barite in residual deposits is derived, by weathering, from veins or replacement masses of this mineral in the country rock of the region. In Missouri and Tennessee the country rock is Cambrian and Ordovician dolomite; in the Georgia deposits the country rock is Cambrian quartzite and shaly limestone; in the Piedmont region of Virginia the country rock consists of Cambrian and pre-Cambrian schists and limestones; and in the Appalachian Valley of the same state the barite-bearing clays have been derived from Cambro-Ordovician dolomite.

#### ORIGIN

Barite deposits are found in various parts of the world and exhibit many different features of occurrence and mineral association. Some of them are clearly related to igneous activity, and some are definitely sedimentary, but many lack criteria sufficiently definite to prove their mode of origin.

Barite present in sandstones and shales in the form of concretions, cement, veins, etc., is in many places genetically related to sedimentary processes. The barium may have been leached from the surrounding rocks by meteoric waters, or derived from marine water. The introduction of barium by sea water was either contemporaneous with the deposition of the sediment or was introduced by a later incursion of the sea.

In replacement deposits which are closely related to igneous intrusions, it seems clear that hot solutions from the intrusion were the source of the barium. The Hot Springs, Arkansas, deposit is of this type. Barite in metalliferous veins containing galena, sphalerite, chalcopyrite, fluorite, siderite, etc., also is considered to have been derived from hydrothermal solutions of igneous origin because of the mineral association: the fluorite-barite-sphalerite veins of the Illinois-Kentucky field is an example. Other igneous occurrences which may be cited are the cinnabar deposits of Orange

County, California, and the silver mines near Barstow, San Bernardino County, California, where barite is a gangue mineral.

In many deposits where barite occurs as veins in limestone or dolomite, evidences pertaining to genesis are not clear and controversies of long standing have resulted. Some geologists contend that such veins were formed from solutions of igneous origin, whereas others believe the barite was precipitated from meteoric waters which leached the barium from the surrounding sediments. Tarr<sup>12</sup> states several objections to the meteoric theory as applied to the barite district of Missouri, the chief one being the lack of barium in the dolomites. But, on the other hand, the existence of igneous rocks intrusive into the barium-containing sediments has not been proved in localities where the origin is in debate.

A comment by Spence<sup>13</sup> on the origin of barite deposits in limestone or dolomite is of interest in this connection:

It does not, however, appear necessary to seek a hydrothermal origin for the barium; that is, to regard it as derived from a deep seated magma, or as having been brought in by solutions from a nearby intrusive. In the case of many deposits in limestones, etc., the barium may equally well have been derived by leaching from underlying crystalline rocks by vadose waters, with subsequent deposition of barium sulphate upon circulation channels in the overlying sediments. In such case, the barium has possibly gone into solution as the chloride or carbonate, and has been deposited as the sulphate when the waters commingled with others carrying gypsum or other sulphates derived from sediments.

It is to be noted further that leaching of barium would be considerably enhanced if the water were warm, as in deep, artesian circulation.

#### USES

The commercial uses of barite depend largely upon its cheapness, high specific gravity, chemical inertness, and white color. It is also the principal source of barium for the chemical trade.

<sup>12</sup>Tarr, W. A., "The Barite Deposits of Missouri"; *Univ. Missouri Studies*, Science Series, Vol. III, no. 1, 1918.

<sup>13</sup>Spence, H. S., "Barium and Strontium in Canada": *Pub. Mines Branch, Canada Dept. of Mines* No. 570, p. 10, 1922.

Barite<sup>14</sup> is used as a crushed and ground mineral, or it is chemically processed to produce various barium compounds. Crushed and ground barite is utilized in large quantities as a weighting agent in oil well drilling muds, and to less extent in the manufacture of glass and as a filler in paper, paint, and rubber. These industries consume most of the ground barite produced in the United States. Other uses include: filler in linoleum, cloth, plastic, resins, leather, printer's ink, face powder, window shades, special kinds of paper such as playing cards; artificial ivory for buttons and poker chips; manufacture of ceramic enamels; indicator in X-ray photography; flux in brass smelting; and a base for the precipitation of lake colors.

The two most important products derived from barite are blanc fixe and lithopone. Blanc fixe, precipitated barium sulfate, is whiter, of higher purity, and finer grained than ground natural barite, and is used as a filler for many of the purposes mentioned above.

Lithopone is a co-precipitated mixture of approximately 70 per cent barium sulfate and 30 per cent zinc sulfide. Before 1938 most of the barite consumed in the United States was utilized in this material. Lithopone is widely used, principally as a white pigment in paints but also as a filler in rubber goods, paper, linoleum, oil-cloth, and window shade cloth. Other chemicals prepared from barite include barium carbonate, barium chloride, barium nitrate, and barium oxide. Barium nitrate has important war-time uses as an igniter in incendiary bombs and as the chief constituent in green signal flares. Precipitated barium carbonate is used in the ceramic industry and in the manufacture of optical glass. Certain barium compounds are used in medicines and in the refining of beet sugar.

#### PRODUCTION

According to the Minerals Yearbook, the amount of barite sold or used by producers in the United States in 1940 was 409,353 short tons; in 1941 this figure had reached an all-time high of 503,156 short tons. Consumption of barite in the United States, in 1940, in short tons, was distributed as follows: ground barite,

<sup>14</sup>Santmyers, R. M., "Barite and Barium Products: Part I, General Information": *U. S. Bur. Mines Information Circ.* 6221, 1930.

Santmyers, R. M., "Barite and Barium Products: Part II, Barium Products" *U. S. Bur. Mines Information Circ.* 6223, 1930.

chiefly for drilling muds, 300,899; lithopone, 136,885; and barium chemicals, 66,604. Crude barite sold or used by producers, by states, in short tons, was: Missouri, 179,455; Georgia, 92,302; Tennessee, 70,767; others, 66,829. Other producing states were Arkansas, California, Colorado, Nevada, South Carolina, Texas, and Virginia. The value of barite produced in 1940 was \$2,596,743. Imports have declined, owing to World War II, from 33,843 tons in 1936 to 7,391 in 1940, and in 1941 they were much smaller.

#### SPECIFICATIONS

The specifications on crude barite vary in accordance with the desired usage, although barite of high purity with a white color commands highest prices. In the trade two general types of crude ore are recognized—"soft" and "hard crystalline". The soft ore grinds easier and roasts better and is consequently preferred for the production of ground barite. The hard crystalline variety is used principally in the lithopone and barium chemical industries.

Practically all consumers demand 90 per cent barium sulfate and specify the maximum allowable content of iron and other impurities, but barite used for drilling muds may have a minimum of 89 per cent provided the specific gravity is 4.2 or higher. Most commercial crude barites contain at least 93 per cent barium sulfate, and the better grades contain 95 per cent with 1 to 3 per cent silica. Some off-color ores must be bleached with sulfuric acid, after grinding, to reduce the iron content to the allowable limit. For the manufacture of glass only the highest quality barite is used—the iron content, in particular, must be low.

#### PRICES

The price on barite fluctuates with the demand, and on the Atlantic seaboard in normal times it has been influenced largely by the importation of foreign stocks, chiefly from Germany. Prices during 1940 on domestic crude barite, per long ton, f. o. b. mine shipping points, were: Georgia, \$7.00; Missouri (minimum 95 per cent BaSO<sub>4</sub>; maximum 1 per cent iron) \$6.25 to \$7.00. The average value of crude barite f. o. b. mine shipping point for the United States was \$6.23 in 1941. Ground barite was quoted

at \$25.15 to \$27.65 per short ton in 1941. On all grades, off-color barite is quoted at a lower price.

#### MARKETS

Barite deposits occur in many parts of the world. This wide distribution keeps prices low, and therefore deposits are developed only where the mineral occurs in rather large concentrations, where a market is readily available, and where mining costs can be kept low.

Most of the principal world powers have sufficient supplies of barite. There is, however, some international trade in barite in peace times, limited largely by cost at the point of consumption rather than by reserves or point of origin. Thus in normal times the Atlantic seaboard states import cheaper German barite rather than using domestic barite from Georgia and Tennessee, in spite of the large reserves in those states. Low labor costs and cheap ocean transportation are largely responsible.

Markets for barite in the United States are located in three general areas: Atlantic seaboard; Central States, chiefly Missouri and Illinois; and California<sup>15</sup>. The Atlantic states are normally supplied by German imports, southern United States producers, and Missouri, whereas California consumers utilize barite from that state. The Central States market is supplied chiefly with Missouri barite, and barite for heavy drilling muds used in Mid-Continent and Gulf Coast oil fields is obtained principally from Missouri and Arkansas. The limited market in Colorado (beet-sugar industry) draws on Colorado deposits and imported witherite, whereas the Kansas lithopone industry obtains barite from Missouri and Colorado.

According to recent information<sup>16</sup> there has been a great expansion of the barite industry in the United States, caused largely by activity in new, deep oil fields and increased consumption of rubber and paint for defense industries. Missouri obtained 11 new barite washing plants during 1941 and the early part of 1942, and a new plant near Malvern, Arkansas, began operations in

<sup>15</sup> Johnson, B. L., "Marketing of Barite": *U. S. Bur. Mines, Information Circ.* 7149, 1941.

<sup>16</sup> "12 New Barite Plants": *Rock Products*: Vol. 45, no. 6, p. 86, June 1942.



1940. The Arkansas plant uses an all-slime flotation process which enables it to utilize ore containing only 60 to 70 per cent  $\text{BaSO}_4$  and produce a flotation product containing 97 per cent  $\text{BaSO}_4$ . This plant has had to increase its capacity several fold recently, and markets its product chiefly to Gulf Coast oil field operators. A second company has recently started production in the same area.

### BARITE IN OKLAHOMA

Barite has been found in small amounts in many places in Oklahoma, and in one or two localities it has been found in sufficient abundance to indicate economic possibilities. The regions of Oklahoma in which barite is found include the following: (1) Ouachita Mountains, (2) Arbuckle Mountains, (3) Lower Permian sediments of central and southwestern Oklahoma, and (4) other areas.

### OUACHITA MOUNTAINS

Barite is known to be present in small amounts as a gangue mineral in two abandoned zinc prospects in McCurtain County. One of these prospect pits, known as the Eades Mine, is located about 2 miles southwest of Watson in the SE $\frac{1}{4}$  NW $\frac{1}{4}$  sec. 33, T. 1 S., R. 26 E. At the present time there is little evidence of a working, for nothing remains except a shallow pit which has been partly filled with material from the shaft diggings. Honess<sup>17</sup> examined the prospect in 1917, and stated that a 40-foot shaft had been sunk in slates, shales, and quartzites of the Stanley formation. He observed sphalerite, barite, dolomite, quartz, and a little pyrite as vein material in the shattered country rock. At that time approximately 3 tons of sphalerite and half a ton of barite had been taken from the shaft and sorted into ore piles, but there is no information indicating that any ore was sold from this prospect. The writers visited the area in 1941 and found a few pieces of barite scattered around the working. The barite is coarsely crystalline, white, and has a porcelain-like appearance.

Another prospect pit, located about 3 $\frac{1}{2}$  miles south of Watson, near the center of sec. 10, T. 2 S., R. 26 E., McCurtain County,

<sup>17</sup> Honess, C. W., "Geology of the Southern Ouachita Mountains of Oklahoma": *Okla. Geol. Surv. Bull.* 32, Part II, *Geography and Economic Geology*, p. 39, 1923.

was visited by the writers and found to contain barite, sphalerite, and galena in a vein cutting quartzites of the Stanley formation. Only a few pieces of barite and sulfides could be found in the dump. The barite and the sulfide minerals in both prospects undoubtedly were formed by precipitation from hydrothermal solutions of igneous origin. There is nothing in either of these prospects to indicate large quantities of barite.

### ARBUCKLE MOUNTAINS

Barite is known to occur in small amounts in several locations in the Arbuckle Mountains, and in the eastern part of the region a limited amount of prospecting has been done.

#### DEPOSITS DERIVED FROM ARBUCKLE DOLOMITE

The largest amount of barite found to date in this area is on the Thompson Ranch, about 6 miles northeast of Mill Creek, Johnston County, near the west line of the NW $\frac{1}{4}$  sec. 15, T. 1 S., R. 5 E. Barite and iron oxides cover a surface area of about an acre on the west side of a low hill of Arbuckle dolomite. At this deposit several hundred tons of iron ore have been recovered from the surface and a shallow open cut by the Concho Sand and Gravel Company. Barite was discovered in the open cut during the iron-mining activity. No special prospecting was done for barite, however, until after the iron-mining ceased. The later explorations for barite consisted of enlarging the open cut to a depth of about 7 feet, sinking a shaft to a depth of about 20 feet, and digging several small pits. About 20 tons of barite was recovered and stacked in ore piles around the workings, and another 10 tons could be seen in the workings. At the present time all exploration has ceased and the shaft has been filled.

The barite occurs mainly in irregular masses and coarse crystals embedded in a plastic, dark brown clay and ochreous limonite. The masses, some of which weigh half a ton, consist of coarsely crystalline barite with many coarse bladed or crested crystals which measure a fraction of an inch up to 3 inches in length. (Pl. I, b). The color varies from porcelain-white to translucent pale blue, with some crystals showing zonal growths of these colors. Phantom crystals of white barite with bluish interiors are common.

In addition to the clay, barite is associated with iron ore, principally limonite and goethite, and a small amount of pyrite. Some of the limonite shows coarse cube faces or consists of crystal aggregates arranged in branching, fern-like form, indicating it is pseudomorphic after pyrite. Other limonite masses are cellular and porous or ocherous, and do not appear to be pseudomorphic. Many of the barite masses are coated with limonite or limonitic sand whereas other masses consist of an intimate mixture of small barite crystals and cellular limonite in variable proportions. Some euhedral barite is present in fragments of ferruginous sandstone. In the deposit are some boulders of undecomposed dolomite, sandstone blocks, and fragments of chert.

That barite was formed in at least two generations is indicated by the presence of thin blue-gray barite crystals coating older crystals of white, coarse barite. The age relationship of barite to pyrite is unknown, for they do not occur in contact. The cellular limonite appears to be younger than the white barite because it occurs as surface stains and coatings on the latter mineral. The intimate mixtures of the younger, small barite crystals and cellular limonite, some of which show a banding of white barite with dark brown limonite, indicates contemporaneous or intermittent deposition.

It seems probable that the older barite is detrital and that the younger barite and cellular limonite were precipitated in place.

The large size of some of the barite masses seems to preclude transportation for any appreciable distance, for the mineral has good cleavage and is so brittle that it is easily fragmented. Some of the materials in the deposit, however, particularly the sandstone blocks, must have been transported as detrital fragments, at least for a short distance. The association of sandstone blocks, sand, clay, barite, and iron ore indicates that the deposit was supplied from different sources. They probably are erosional products deposited together in a central depression or on a hillside. A reworking of the detrital fragments by ground water would precipitate the secondary cellular limonite and euhedral barite, or sec-

ondary precipitation would take place if the depression were water-filled.

The barite is of the hard, coarsely-crystalline variety. The iron content is high, and it is probably best suited for drilling muds wherein the excessive iron content is not objectionable. The quantity mined to the present time is some thirty tons and is important only as suggestive of the possibility of other barite deposits in the region.

There is a small residual deposit of barite south of Sulphur on the Lowrance Ranch, in sec. 24, T. 1 S., R. 3 E., Murray County. The barite is very similar to that found on the Thompson Ranch, being coarsely crystalline, coated with cellular limonite, and occurring in a residual red clay containing some fragments of chert. Several small patches were found at the surface on Arbuckle dolomite (Lower Ordovician) near a fault separating this rock from the younger Oil Creek sandstone (Simpson group, Lower Ordovician), which stratigraphically overlies the dolomite. Shallow prospect pits and trenches placed at irregular intervals for a distance of approximately 600 yards near the fault revealed that the barite occurs in residual clay to a depth of 1 or 2 feet, and in some of the pits no barite was found. Not more than 5 tons of poor quality barite, which apparently represents all the material recovered, has been piled around the various workings.

The two barite occurrences in the Arbuckle Mountains mentioned above offer meager evidence concerning their origin. Barite was not observed in the adjacent bedrock, and consequently barite-dolomite relationships can not be proved. By analogy with deposits in other states, however, it is probable that the barite occurred originally as veins, cavity fillings, or replacement masses in the dolomite. On the Lowrance Ranch the replacements were probably along or near the fault and weathered from the rock essentially in situ. No fault was observed at the deposit on the Thompson Ranch, but as previously pointed out the materials there were transported and do not occur in place. Inasmuch as no barite could be found in place in the bedrock, it is presumed that the replacement bodies were small and have been completely weathered from the exposed rock. It is possible that other re-

placements of barite are present at depth, and as yet are not uncovered by erosion.

The origin of the barite is probably similar to that of the brown iron ores of the Arbuckle Mountains. Some of the iron ore deposits are known to be oxidized pyrite replacement bodies in dolomite, and others are in shallow sedimentary basins associated with clay and sand. The sedimentary iron ores were in all likelihood derived from older, primary replacements. In some places barite occurred in nearby rocks, and in a similar manner contributed to secondary deposits.

The barium and iron probably were introduced during or shortly after the folding and faulting of the surrounding rocks, which in the Hunton-Tishomingo arch portion of the Arbuckle Mountains is considered by Dott<sup>18</sup> to be post-Wapanucka, pre-McAlester (early Middle Pennsylvanian). The area is in many places structurally complex, and the openings provided by the folds, faults, joints, and bedding planes would be adequate for the movement of mineralizing solutions.

The barium and iron must have been derived either from hydrothermal solutions or by leaching of surrounding sediments by ground waters. No outcrop or other evidences of igneous rocks intruding the sediments have been found, despite favorable exposures resulting from the erosion of approximately 10,000 feet of folded sediments. The present writers believe the barium and iron were leached from surrounding rocks by ground waters. The most probable source of these elements appears to be the underlying pre-Cambrian igneous rocks and Reagan (Cambrian) arkosic sandstone, for Clarke has shown more barium in sandstone, shale, and igneous rocks than in limestone and dolomite. The ground waters, if circulating in deeply buried rocks, would be warmer and more effective solvents than surface waters. This circulation was probably artesian in character, as some artesian wells and many artesian springs are present in this region today. The rising warm meteoric waters would seek out and follow the loci of structural weakness, and the dissolved salts would replace the

<sup>18</sup> Dott, R. H., "Overthrusting in Arbuckle Mountains, Oklahoma": *Bull. Amer. Assoc. Petro. Geol.* Vol. 18, No. 5, pp. 567-602. 1934.

country rock in the cooler zones near the surface. Deposition from warm artesian waters has been postulated for the manganese carbonates and primary oxides near Bromide by Hewett<sup>19</sup>, and it is possible that the sphalerite deposits near Davis were formed in a similar manner. The barite, iron, manganese, and zinc deposits in the Arbuckle Mountains thus may be genetically related.

#### OTHER OCCURRENCES

Thin, flat, circular crystal aggregates of barite, known as barite "dollars", are found sparingly in the Sylvan shale in sec. 20, T. 2 S., R. 3 E., Murray County, near White Mound. They are thin and disc-like, resembling a coin in shape, and are made up of fine needles radiating from a central point. Similar barite "dollars" are reported in Nebraska and Egypt; and in England they are irregularly distributed along bedding planes in Lias sediments. It is probable that the "dollars" in the Arbuckle Mountains are secondary precipitates along bedding planes.

Residues insoluble in hydrochloric acid obtained from the Haragan (Devonian) marl show a few barite "dollars" and broken fragments of them. They have been noted in Murray County in sec. 5, T. 2 S., R. 1 W.; sec. 34, T. 1 S., R. 2 E.; and at White Mound, sec. 20, T. 2 S., R. 3 E.

A small amount of barite occurs in the Woodford siliceous shale (Mississippian) in a prospect pit in sec. 3, T. 2 S., R. 3 E., Murray County, south of Sulphur. The barite consists of thin radiating crystals contained within hard calcareous nodules and boulders. The relationship of the boulders to the enclosing rock could not be determined in the open cut, and no barite was found in the surrounding rocks.

Insoluble residues of the Bois d'Arc limestone (Devonian) from sec. 8, T. 1 S., R. 8 E., Coal County, near Hunton School, yield a few glassy barite fragments associated with altered pyrite cubes and glauconite.

Insoluble residues of the Wapanucka (Pennsylvanian) limestone from secs. 4 and 5, T. 2 S., R. 8 E., Johnston County, likewise show a little glassy barite associated with glauconite and chalcedony.

<sup>19</sup> Hewett, D. F., "Manganese Deposits near Bromide, Oklahoma": *U. S. Geol. Surv. Bull.* 725-E, 1921.

## CENTRAL AND SOUTHWESTERN OKLAHOMA

Barite has been found at many localities in Oklahoma in sediments of Lower Permian age. The greatest concentrations are found in southwestern Oklahoma, south and east of the Wichita Mountains, and in central Oklahoma. In these areas barite occurs in the following forms: veins, nodules, and barite-clay-carbonate concretions in shale; and in sandstone as a cement and as sand-barite concretions. At a number of places the barite is associated with disseminated copper carbonates and chalcocite, an association noted long ago in sedimentary copper ores of New Mexico and Colorado.<sup>20</sup>

Surface exposures of lower Permian sediments in central and southwestern Oklahoma consist of red or gray sandstone interbedded with red shales. Limestones are conspicuously absent, and carbonate material, except for small, local lenses of dolomitic clay conglomerate, is present only in concretions and as irregular patches of cement in sandstone.

## GENERALIZED STRATIGRAPHY OF CENTRAL AND SOUTHWESTERN AREAS

	CENTRAL OKLAHOMA	SOUTHWESTERN OKLA. & NO. TEXAS
LOWER PERMIAN	Duncan ss.	Duncan ss.—San Angelo ss.
	Hennessey sh.	Clear Fork sh.
	Garber ss.	Wichita group
	Wellington ss. and sh.	
	Stratford sh. and Stillwater fm.	
PENNSYLVANIAN	Vanoss fm. and Vamoosa ss.	Cisco series

## BARITE IN SHALE

*Barite in clay-carbonate concretions.* Concretions composed essentially of clay and calcite are abundant at many localities in shales of lower Permian age in Oklahoma, and some of them contain barite. Generally the concretions are rounded to irregular with

<sup>20</sup> Lindgren, W., Graton, L. C. and Gordon, C. H., "The Ore Deposits of New Mexico": *U. S. Geol. Surv. Prof. Paper* 68, p. 77, 1910.

Lindgren, W., "Notes on Copper Deposits in Chaffee, Fremont, and Jefferson Counties, Colorado": *U. S. Geol. Surv. Bull.* 340, pp. 170-174. 1908.



a



b

PLATE I. a. Barite-clay-carbonate concretion, Stephens County, Oklahoma. Coarsely crystalline barite, showing rectangular cleavage, has completely filled the interior of the clay-carbonate concretion. Note dark colored veins of barite at top. Other, similar concretions in southwestern and central Oklahoma have hollow interiors that are lined with well developed barite crystals. Natural size.  
b. Coarsely crystalline barite from Arbuckle Mountains, south-central Oklahoma. Limonite (dark color) lines cavities and coats the outside of specimen. 2/5 natural size.

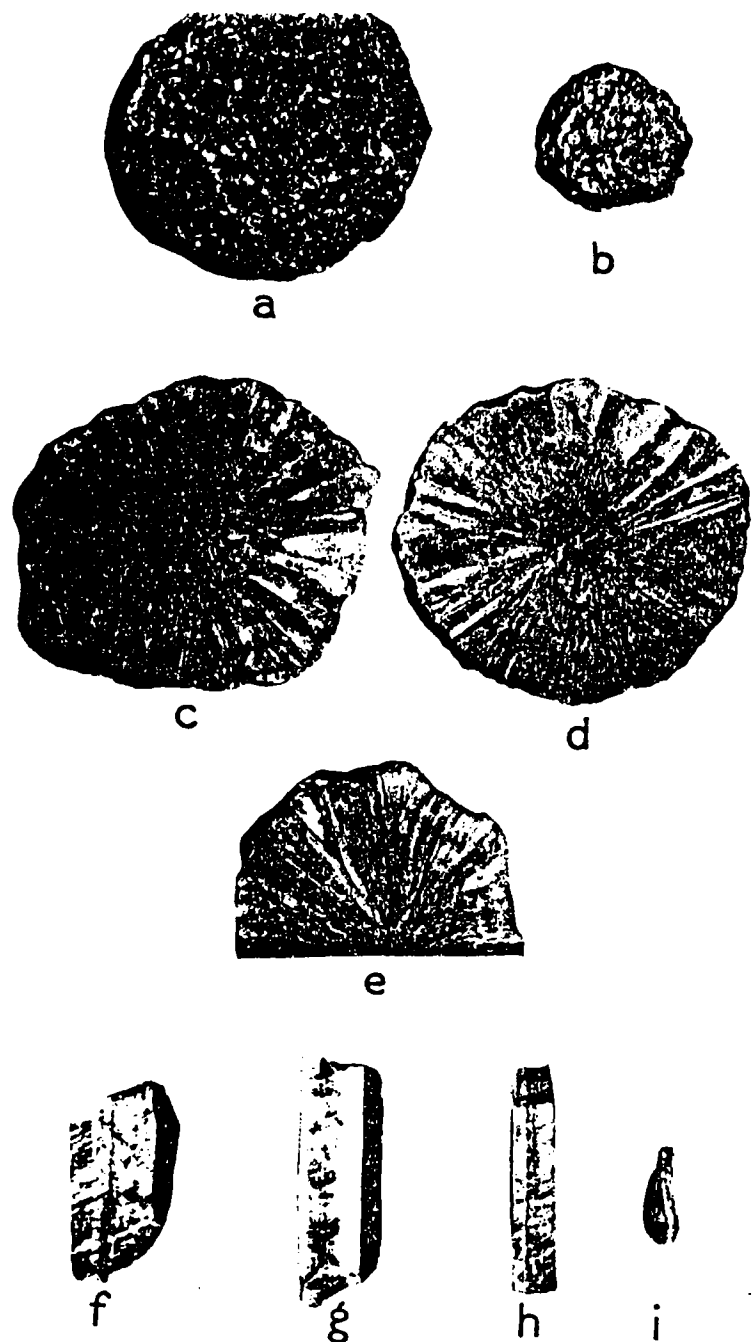


PLATE II. Barite nodules and vein barite from lower Permian shales, southwestern Oklahoma.

a-b. Specimens showing pitted surface and spherical shape.  $\frac{1}{2}$  natural size.

c-e. Sections of similar nodules, showing internal structure of radiating crystals; many of the crystals are fibre-like and curved.  $\frac{3}{4}$  natural size.

f-i. Fragments of vein barite, showing parallel needles and color zones.  $\frac{3}{4}$  natural size.

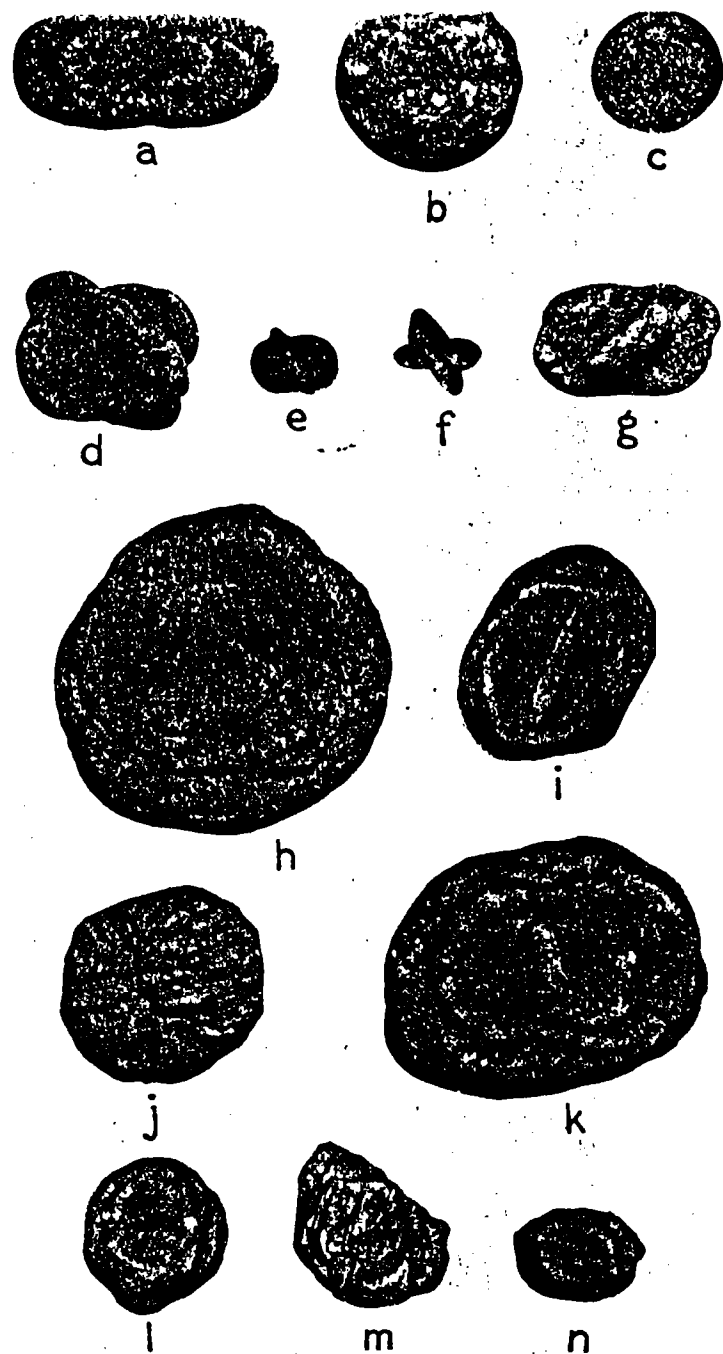


PLATE III. Sand-barite concretions from lower Permian sandstones of central and southwestern Oklahoma.

a-g. Concretions of simple forms, composed of circular and rectangular tablets. With the growth of additional tablets, these concretions would have developed into typical rosettes.

h-n. Rosettes of complex form.

m. Nearly pure barite, the others are typical sand-barite rosettes composed of approximately 50 percent barite and 50 percent quartz sand. Note similarity of form of l, m, and n. All specimens  $\frac{3}{4}$

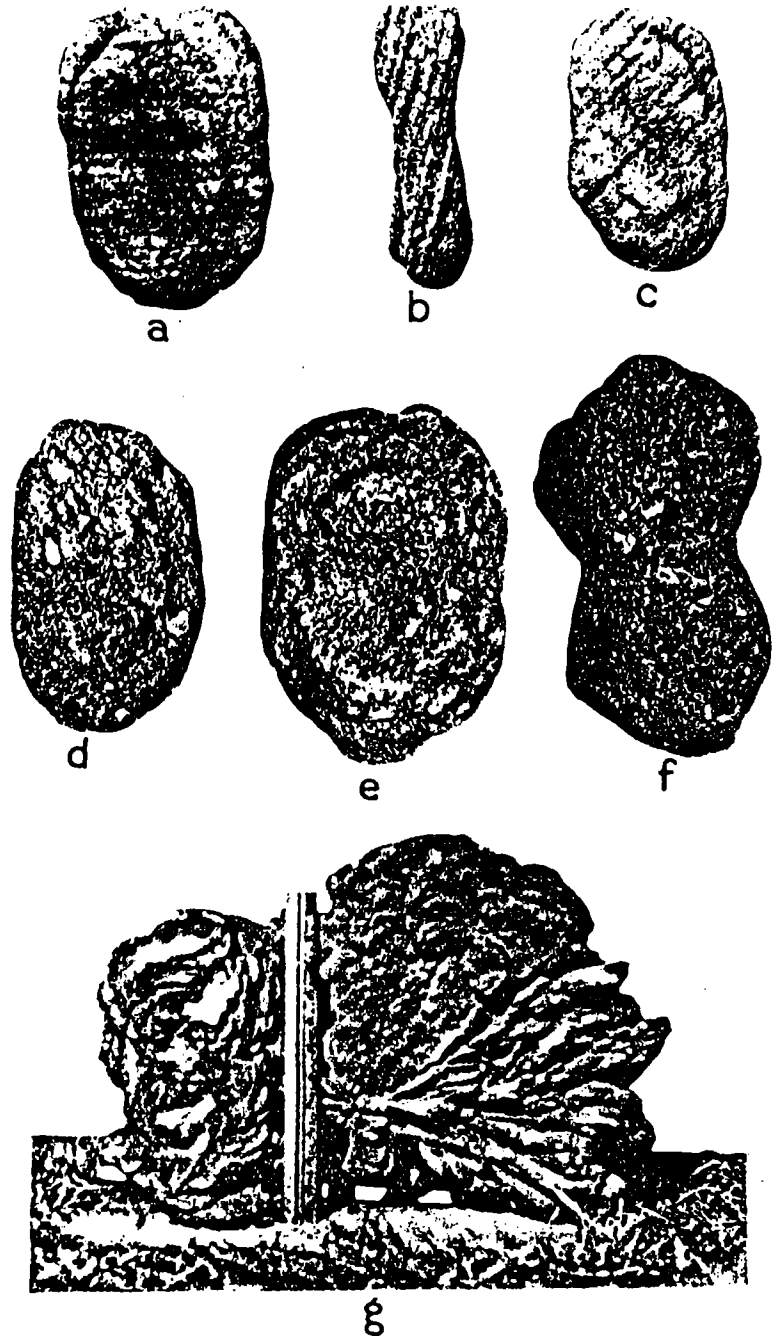


PLATE IV. Sand-barite rosettes from Garber sandstone, Cleveland County, Oklahoma.  
 a-c. Specimens showing bedding laminae of the sandstone in which the crystals grew. 3/5 natural size.  
 d-f. Specimens showing coarse size of sand grains, and presence of weathered chert pebbles. 1/4 natural size.  
 g. Largest known aggregate of sand-barite rosettes. Size indicated by the 1-foot rule.

a botryoidal surface, brick-red or maroon in color, and not uncommonly they are stained black on the exterior by manganese oxide. Some of them are crudely mottled with white spots and a few show surface stains and veinlets of malachite. In size they range from an inch up to masses having a diameter of 1 foot. They are distributed throughout the shale in lens-like zones or beds and as isolated individuals.

The barite inside such concretions is ordinarily in coarsely crystalline masses, showing a good cleavage (Pl. I, a.), but less commonly as euhedral crystals or fibrous blades in a hollow cavity. It is either colorless, pale green, yellowish green, or porcelain-white. The crystals and blades are generally associated with secondary calcite crystals showing rhombohedral or scalenohedral faces.

Clay-carbonate concretions containing barite generally are associated with barite nodules or veins. They have been found in Garvin, Cleveland, Noble, Lincoln, Comanche, Tillman, and Stephens Counties. Selected localities include the following: Tillman County: sec. 31, T. 1 N., R. 16 W.; Stephens County: secs. 25 and 31, T. 2 S., R. 7 W.; Garvin County: sec. 7, T. 4 N., R. 1 E.; and Noble County: sec. 5, T. 20 N., R. 1 W. There is little question that they are far more widespread than here indicated. It is thought that the clay-carbonate concretions are syngenetic in the sense of being deposited contemporaneously with the enclosing shale, and that the barite has been introduced into the concretions at a later date.

Where studied in detail the barite-bearing concretions were found associated with a large number of concretions which contained no barite. The specific gravity of those containing barite is higher, but unless a considerable amount of barite is present this will not be noticed, and it is necessary to break a concretion open to determine whether it contains barite. Because of the factors mentioned above, the barite-bearing concretions offer no commercial possibilities.

*Veins.* Veins of nearly pure barite occur in maroon or brick-red shale of lower Permian age in McClain, Garvin, Comanche, Tillman, Stephens, and Cotton Counties. Well developed veins

may be found at the following places: Comanche County: secs. 7 and 18, T. 1 N., R. 13 W., sec. 26, T. 1 N., R. 14 W., and sec. 32, T. 2 N., R. 13, W.; Tillman County: sec. 35, T. 1 N., R. 16 W.; Cotton County: sec. 26, T. 4 S., R. 11 W.; and Stephens County: sec. 6, T. 3 S., R. 6 W., and secs. 23, 25, and 31, T. 2 S., R. 7 W. It is probable that additional occurrences are present in contemporaneous sediments of nearby counties. The barite is reddish-brown and translucent, and occurs as fibrous needles which grew perpendicular or nearly so to the vein wall. (Pl. II, f-i) Faint color banding parallel to the length of the vein is common, indicating either a temporary cessation of deposition or a slight change in the character of the depositing solution. The veins are generally thin, 1/16 to 1 inch wide, the width varying from place to place, and their length varies from a few inches up to one traceable for 35 feet along the outcrop. Many are rather straight and have vertical dip, but some are inclined at high angles. The vein walls are commonly smooth, striated to slightly irregular surfaces resembling slickensides.

It is not known to what depth the barite extends. Direct observations can be made in stream gullies and badland amphitheatres where the veins are best exposed. In such areas veins can generally be seen in place, and material weathered from the veins may be scattered over the surface. On the uneven gully floor in the SE $\frac{1}{4}$  sec. 7, T. 1 N., R. 13 W., Comanche County, some individual veins of barite about 3/4 inch thick can be traced for a vertical distance of about 10 feet. In this same locality vein barite occurs along the sides of the gully, which exposes about 30 feet of maroon shale. This indicates that a given system of barite veins may reach a depth of at least 30 feet although individual veins may have a vertical range of less magnitude. Many veins extend only to a very shallow depth, for some of them were observed to play out a few feet from the surface.

As a general rule, very few minerals are associated with the vein barite. Nodules of barite, clay-carbonate concretions, and fragments of purplish-black hematite are rather common, and in the NW $\frac{1}{4}$  NE $\frac{1}{4}$  sec. 35, T. 1 N., R. 16 W., Tillman County, one barite vein was observed to grade along the strike into fibrous calcite (paramorphous after aragonite). One or two thin selenite

veins were found in the deposit in SE $\frac{1}{4}$  sec. 7, T. 1 N., R. 13 W.

Not uncommonly reworked pebbles of residual terrace gravels are found on the gully floor. A red or white cross-bedded sandstone, locally containing chalcocite and malachite, caps the ridges above the gullies, but this sandstone is not necessarily the same bed at all localities, and in some places such sandstone cap rock is absent.

The ratio of vein barite to shale differs from place to place. In most localities the barite amounts to a fraction of one per cent and only in a few places is there 1 per cent or more barite. On the gully floors, however, residual barite has been concentrated by erosional weathering processes. The amount of barite present depends, in general, upon the original barite content of the shale and the size of the gully. The greatest concentrations are found in the larger gullies, although many large gullies contain practically no barite.

The barite veins obviously were introduced secondarily into the enclosing shale, the barite being deposited in tabular openings such as joints as a precipitate from water solution.

*Nodules.* Barite nodules whose interior structure consists of radiating needles are found in many places in maroon shale of lower Permian age. The principal occurrences are in the district south and east of the Wichita Mountains, in Comanche, Kiowa, Stephens, and Tillman Counties; but they are also locally abundant in McClain and Garvin Counties of south-central Oklahoma. Selected localities where barite nodules occur include the following: Comanche County: secs. 7 and 18, T. 1 N., R. 13 W.; Stephens County: secs. 23, 25, and 31, T. 2 S., R. 7 W., and sec. 6, T. 3 S., R. 6 W.; Garvin County: sec. 18, T. 4 N., R. 1 E.; McClain County: sec. 33, T. 5 N., R. 2 E.

It is probable that other occurrences will be found in sediments of the same age in these and neighboring counties. Similar nodules have been reported from near Electra, Wichita County, Texas, where they have weathered out of maroon shale which lies near the top of the Wichita series.<sup>21</sup>

<sup>21</sup> Fath, A. E., "Copper Deposits in the 'Red Beds' of Southwestern Oklahoma": *Econ. Geol.*, Vol. 10, p. 149, 1915.

The nodules are nearly pure BaSO<sub>4</sub>, as indicated by the following analysis of washed specimens.

SAMPLE FROM SE $\frac{1}{4}$  SEC. 18, T. 1 N., R. 13 W., COMANCHE COUNTY

Lab. No. 8309-a.†

SiO .....	0.73	SrO .....	trace
R <sub>2</sub> O <sub>3</sub> .....	0.57	BaO .....	64.85
*Fe <sub>2</sub> O <sub>3</sub> .....	0.27	L.O.I. ....	0.25
Mn <sub>2</sub> O <sub>4</sub> .....	trace	*CO <sub>2</sub> .....	0.16
CaO .....	none	SO <sub>3</sub> .....	33.15
MgO .....	none	P <sub>2</sub> O <sub>5</sub> .....	none
		Total .....	99.55
		Specific gravity..	4.44

† Analysis by W. L. Howard, under the direction of A. L. Burwell, Chemist, Oklahoma Geological Survey.

\* Not included in total.

ANALYSIS CALCULATED TO MINERAL COMPOSITION

BaSO <sub>4</sub> .....	97.93
BaCO <sub>3</sub> .....	0.67
Clay minerals and quartz .....	1.12
Hematite .....	0.27

The nodules are translucent, have a dark reddish-brown, tan, or gray color, and the outer surface is characteristically pitted with numerous rough indentations and cusps. (Pl. II, a-b) The smaller ones are spherical in shape, and the larger ones ovoid or somewhat irregular. The nodules range from  $\frac{1}{4}$  to 3 inches in diameter, most of them 1 inch or less, except in sec. 7 and 18, T. 1 N., R. 13 W., Comanche County, where many have a diameter of 2 to 3 inches.

The internal structure is characterized by needle-like barite crystals of variable length (Pl. II, c-e). The longer crystals radiate from a central point to the outer margin of the nodule. The shorter ones, ordinarily in the outer portion of the concretion, are either parallel or sub-parallel and slightly divergent, and form wedge-shaped aggregates which abut against bundles of longer needles. Some of the nodules have concentric color bands caused by zonal growth, and a few have a core of earlier dark gray barite with poorly defined radiating structure. As a general rule the barite needles in the interior of the nodules have a marked pearly luster. Although most of the nodules consist of many individual needles, some have become single crystals through recrystallization; these, however, still preserve a phantom needle structure.

In places the nodules have been concentrated on gully floors by weathering from shale. Where observed in shale, they appear to be aligned along joints or cracks; a few are attached to veins of barite, and apparently grew from the veins. In rare specimens, clay-carbonate concretions are coated with parallel needles of barite, and some of these concretions contain coarsely crystalline barite in the interior.

Thin, cross-bedded, red or white sandstones are commonly interstratified with the maroon shales containing the barite, and locally, a clay-carbonate intraformational conglomerate is found. The sandstone in a few places contains dolomite as a cement or in black nodular masses, and in many places minute amounts of chalcocite and malachite are present. In the Paoli district a sandstone is locally cemented with barite and also contains abundant hematite, and the associated sandstones contain a few barite rosettes.

The barite nodules apparently began their growth from a central point, and the first deposition occurred in an open space. But the concentric growth rings and the complex structure in the outer part of the nodules indicate that deposition was not continuous. As a nodule grew larger, it was necessary for the growing fibers to push the shale aside, and thus they are displacive concretions. Because the nodules are in some places attached to vein barite, it is probable that both had a similar origin and were closely related in time of deposition. The source of the barium and other details of genesis are considered later in the section on origin.

*Economic considerations.* At most places examined by the writers the amount of barite visible at the surface would not exceed a few tons, and no commercial possibilities are indicated. In several localities, however, surface weathering of the shale has concentrated rather large quantities of vein and nodular barite on gully floors, and these justify commercial consideration.

Barite is scattered over the nearly flat floor of an erosional amphitheater covering about 4 acres in the NW $\frac{1}{4}$  NE $\frac{1}{4}$  sec. 35, T. 1 N., R. 16 W., Tillman County, about 9 miles east of Manitou. The country rock, maroon clay shale of which about 10 feet is exposed, contains abundant barite veins. Most of the veins measure



$\frac{1}{8}$  to  $\frac{3}{4}$  inch in width, their length ranging from a few inches up to 35 feet. A few radiating barite nodules and some coarse barite in clay-carbonate concretions were also observed, together with one piece of sandstone "float" which contained poorly developed barite rosettes. Possibly a few hundred tons of barite have been concentrated by weathering, but this is not enough to supply more than a small need for some local industry.

Barite nodules and vein material partly cover the floors of two large erosional gullies on the east side of West Cache Creek in the SE $\frac{1}{4}$  sec. 7 and SE $\frac{1}{4}$  sec. 18, T. 1 N., R. 13 W., Comanche County, about 5 miles south of Cache. Both gullies have been carved from maroon clay shale of lower Permian age; each covers an area of approximately 40 acres and is about 30 feet deep. The rim of the north gully is capped with a thin layer of loose arkosic gravel, and many of the pebbles from this source are present on the valley floor along with barite nodules. This gravel is absent from the south gully, the rim of which is capped with a sandstone containing a few pieces of malachite and chalcocite and a small number of barite rosettes.

Barite nodules and vein barite have been weathered from the maroon shale and are now lying loose along the slopes and on the surface of the gully floors. Calcareous concretions, some of which contain coarsely crystalline barite, have in like manner been weathered from the shale and are associated with the barite nodules and vein material.

Many veins of barite and a few nodules can be found in the shale. There is nothing to indicate that the barite is concentrated in a thin layer, and it appears likely that both veins and nodules have a sparing, haphazard distribution. No detailed sampling was made to determine the amount of barite in the shale, but it probably is less than 1 per cent. The barite now visible has been concentrated by the weathering of thousands of cubic yards of shale, and this residual material would constitute the only mineable ore. The residual barite exposed in these two deposits is estimated to be of the order of several thousand tons. Further detailed field examination may reveal other gullies in the area which contain comparable amounts.

The barite nodules and veins are of rather high purity. One analysis of selected, washed nodules gave 97.93 per cent BaSO<sub>4</sub> and 0.27 per cent Fe<sub>2</sub>O<sub>3</sub>, and it is probable that the veins are equally pure. This material is, therefore, nearly of chemical grade in the crude state, and as it is very brittle, it should be easy to grind. The nodules can be easily extracted from the shale by screening and washing. The known deposits are located on improved dirt roads and could be trucked to the Frisco railroad at Cache, a distance of about 6 miles. Some of these deposits are located on restricted Indian land, and all mineral leases on such properties must be obtained through Federal Indian agencies.

Barite for making chemicals, lithopone, or blanc fixe must first be reduced to barium sulfide, necessitating considerable expenditure for plant and equipment. Unless larger deposits are found there seems to be no justification for considering the erection of a local plant, but the ore might be shipped to barium plants in surrounding states.

The barite of the Cache area would be an excellent weighting agent for oil-well drilling muds. The demand for this purpose has increased greatly in recent years, owing to deeper drilling in the Gulf Coast and other areas, and the deposits are well located with respect to these markets. The barite could be crushed for use as a filler for various purposes or in glass manufacture, and the possibility of developing a regional market of this type should be investigated.

#### BARITE IN SANDSTONE

*Barite cement.* Barite cement in sandstone has been observed in the Garber formation in Garvin County, near Paoli and Pauls Valley, and in NW $\frac{1}{4}$  NE $\frac{1}{4}$  sec. 13, T. 9 N., R. 2 W., Cleveland County. East of Paoli, in the SW $\frac{1}{4}$  sec. 18, T. 4 N., R. 1 E., barite cement occurs in a 30-inch bed of sandstone which also contains hematite, chalcocite, and malachite. On a freshly-broken surface the barite appears as an interlocking mosaic of small barite plates with a satiny luster, and the abundant sand grains give it a sugary texture. A specific gravity of 3.1 was determined on a piece of barite sandstone which was relatively free from other constituents. Thus the specimen is composed, by weight, of 34 per

cent barite and 66 per cent quartz sand; or, by volume, 76 per cent quartz sand and 24 per cent barite. This material has no economic possibilities because of the small amount of barite present in the sandstone, its limited extent, and difficulty of extraction.

Barite in small grains has been found by heavy mineral investigations from many places in the Garber, Hennessey, and Duncan formations. Many of the grains are anhedral and probably acted as a cement, but the amount present is so small that the barite would not be detected without special examination. In a few places small euhedral crystals of barite have been found.

It is probable that the barite was introduced after deposition of the sandstone and that it is related in origin to the barite rosettes, veins, and nodules.

*Sand-barite rosettes.* The peculiar rose-shaped crystal aggregates of barite in sandstone from central Oklahoma have been called "barite roses", "barite rosettes", "petrified roses", "rose rocks", "petrified walnuts", "sand barites", "sand crystals", "sand barite rosettes", and "sand barite crystals". The rose-like appearance of these aggregates has made them prized by collectors, for rock gardens, and other decorative purposes, and thus they become widely known. Because barite rosettes are found only in a few places in the world, they also have created scientific interest, and several attempts to explain their origin have been made. The concept that barite rosettes occur only in Oklahoma is erroneous, for similar specimens have been reported from Salina County, Kansas; Caeyama Valley, California; and Egypt. They are rather abundant in certain portions of Oklahoma, and have been reported from Cleveland, Logan, Lincoln, Okfuskee, Oklahoma, Pottawatomie, McClain, Garvin, Comanche, and Tillman Counties. Selected localities where barite rosettes occur include the following: Garvin County: sec. 7, T. 4 N., R. 1 E.; Tillman County: secs. 27 and 28, T. 3 S., R. 14 W.; Cleveland County: sec. 18, T. 9 N., R. 2 E.; secs. 18, 22, 30, and 31, T. 9 N., R. 1 E., secs. 18, 19, 30, and 31, T. 9 N., R. 1 W., secs. 22, 30, and 31, T. 9 N., R. 2 W., and secs. 5, 8, and 25, T. 8 N., R. 1 W.; Oklahoma County: sec. 22, T. 14 N., R. 2 W., secs. 7 and 35, T. 12 N., R. 2 W.; and secs. 12 and 24, T. 11 N., R. 3 W.

The sand-barite rosettes of Oklahoma are found only in sandstone of lower Permian age or in Quaternary gravels derived from the weathering of these sandstones. They are especially abundant in central Oklahoma, the upper 100 feet of the Garber sandstone being the most prolific zone. This rosette-bearing zone follows the regional strike of the formation which has a general north-south trend and extends from Pauls Valley northward to Guthrie, a distance of approximately 80 miles. In the central area the rosettes also are present near the base of the Garber, in the Wellington formation, and in sandstone that may be of lower Hennessey age. In southwestern Oklahoma the rosettes occur in Clear Fork-Wichita strata, which are probably time equivalents, at least in part, of the above units in central Oklahoma.

The sandstones containing the rosettes are generally cross-bedded and are composed of sub-rounded to sub-angular grains whose grade size lies principally between 1/16 and 1/4 mm. They have a pink, gray, red, or purplish color. In sec. 9, T. 9 N., R. 1 W., Cleveland County, however, rosettes occur in a coarse-grained conglomeratic sandstone containing decomposed chert pebbles up to 1 inch in diameter, (Pl. IV, d-f). Near Paoli, Garvin County, sand-barite concretions are present in a dolomitic sandstone.

Thin sections show that the rosettes are composed of barite, sand grains, and a little hematite. The sand is detrital and consists mainly of quartz, with a small number of chert and feldspar grains. The barite occurs as crystals which occupy the space between sand grains, but does not replace them. Chemical analyses, cited below, indicate that the sand-barite rosettes contain, by weight, an average of 52.38 per cent BaSO<sub>4</sub> (barite), 45.17 per cent SiO<sub>2</sub> (mainly as quartz), 0.95 per cent Fe<sub>2</sub>O<sub>3</sub> (hematite), and 0.87 per cent Al<sub>2</sub>O<sub>3</sub> (combined in clay minerals and feldspar).

## ANALYSIS OF SAND-BARITE ROSETTES

	A <sup>22</sup>	B <sup>23</sup>
SiO <sub>2</sub>	45.13	45.20
Al <sub>2</sub> O <sub>3</sub>	0.88	0.86
Fe <sub>2</sub> O <sub>3</sub>	0.96	0.93
MgO	0.00	0.00
CaO	0.00	0.00
H <sub>2</sub> O	0.31	0.36
P <sub>2</sub> O <sub>5</sub>	faint trace	trace
SO <sub>3</sub>	17.87	18.14
MnO	0.02	0.02
BaO	34.25	34.50
SrO	n. d.	0.00
CO <sub>2</sub>	0.00	0.07
Total	99.42	100.08
Specific gravity	3.36	3.36

The surfaces of the rosettes are generally colored pink or brick red by a coating of soft iron oxide, whereas the freshly-broken interior is typically light pink or gray. In size they range from a fraction of an inch to 17 inches. The largest rosette for which a record is available is 17 inches in diameter, 10 inches high, weighs 125 pounds, and consists of 20 radiating arms, as reported by Gould<sup>24</sup> from sec. 29 T. 9 N., R. 1 W., Cleveland County, about 6 miles east of Norman. (Pl. IV, g) The majority of the rosettes, however, range from ¼ to 4 inches in diameter.

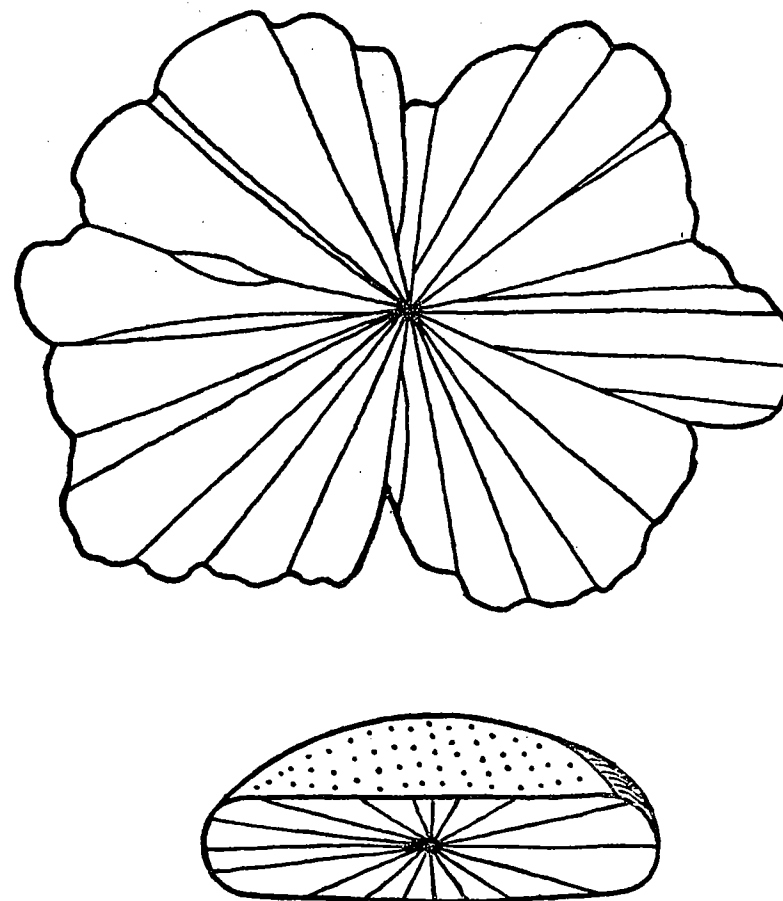
The shape invariably is determined by a particular arrangement of flat plates or tablets, which are the structural units of the rosettes. These tables, composed of barite and sand grains, vary in outline from crudely rectangular to rounded. In rosettes of simple structure, the plates are about equal in size and diverge outward, retaining a common crystallographic axis. (Pl. III, d,f) In more complex types the plates are of unequal size and diverge in a complex manner so that only a few have common crystallographic axes (Pl. III, h, i, j). Most rosettes contain 10 or more plates, and a few have as many as 25. Some have a large central plate to which several smaller ones are attached; the larger plate grew in a more porous zone or was otherwise favored and

<sup>22</sup> Shead, A. C., "Notes on Barite in Oklahoma with Chemical Analyses of Sand Barite Rosettes": *Okla. Acad. Sci. Proc.*, Vol. III, p. 104, 1923.

<sup>23</sup> Analysis by J. C. Fairchild, U. S. Geol. Surv.: cited by Shead, *op. cit.* p. 104.

<sup>24</sup> Gould, C. N., "Radiate Structure of Sand Barite Crystal Masses"; *Okla. Acad. Sci. Proc.*, Vol. VI, p. 241-242, 1926.

probably is the earliest one formed in a particular aggregate. The variability of the angles and the evidence from thin sections prove that the rosettes are not crystallographic twins. Some of the concretions are dumb-bell shaped.



Scale 0 1 2 3 inches

FIG. 2. Internal structure of sand-barite concretions.

- Section through a large sand-barite rosette. Note the radiating structure of barite segments, and compare this with the structure of barite nodules, Pl. II, c, d, e.
- Section through a tabular, biscuit-like concretion. The radiating structure is present although the rosette shape has not developed.

A broken surface through the center of a "rose" commonly shows a structure consisting of wedge-shaped barite segments radiating outward from a central point (fig. 2, a). Near the center they are very thin, but each widens out, like a fan, to the outer edge of the aggregate. The maximum size of an individual segment is about 3 inches long and  $\frac{3}{4}$  inch thick at the outer edge. The radiating structure is generally imperfect, for there apparently were secondary growths of wedge-shaped segments which filled the space between adjacent arms of many rosettes. It can also be observed that the tablets which form the exterior of the rosette are themselves composed of these radiating segments. Such segments are subparallel and radiating in the central portion of the rosette and become nearly parallel where the tablet emerges as an arm of the rosette. The flat sides of the tablets are the basal pinacoid (001) faces of the barite segments and, although a few plates show crudely developed prism faces (Pl. III, l-n), in general the edges are rounded.

The shape of the barite rosette is dependent upon two factors: (1) the unequal development of the barite plates, and (2) their arrangement in a radial fashion. The inclusion of sand grains is merely incidental and apparently has little effect other than retarding the growth of the prism and dome faces. One barite concretion found loose on the surface in the barite zone east of Norman contains no sand and is nearly pure barite. It consists of barite plates, each showing basal pinacoid and prism faces, arranged in a radiating manner (Pl. III, m). It has the typical rosette shape, and it is believed that this concretion would have been a sand-barite rosette had it grown in sandstone instead of an open space.

Flat tablets of sand-barite up to  $\frac{1}{2}$  inch thick and 3 inches wide, composed of barite and quartz sand in the same ratio as in the "roses", are in many places associated with typical "roses" (Pl. III, c). Many of these show on the interior a radiating structure of individual barite plates (fig. 2, b) and, except for the presence of sand inclusions and coarser radial plates, are very similar to barite "dollars" found in the Sylvan shale in Oklahoma, in England, and elsewhere. The flattened surfaces of the tablets rep-

resent the emergence of many radiating crystals and therefore do not correspond to the basal pinacoid. The barite probably was precipitated along a thin, porous zone in the sandstone, such as a cross-bedding lamina. Similar flattened surfaces found on some specimens of barite "roses" were probably formed in the same way. Indeed, the flat tablets themselves would probably have developed into barite "roses" if their outlines had not been confined to rather narrow limits by some factor such as differential porosity.

Some of the barite "roses" show, on the outside surface, a set of parallel ridges and grooves spaced 1 to 2 mm. apart (Pl. IV, a-c). In all probability they represent cross-bedding laminae present in the sandstone. Different specimens show that these grooves are oriented in all directions with respect to the longest dimension and plates of the rosette.

The barite rosettes generally occur as isolated individuals scattered through sandstone. The concentration of the rosettes in surface outcrops ranges from less than one per cubic yard up to scores, and there are a few outcrops that consist dominantly of sand-barite aggregates. Because barite is less soluble than other cementing material in the sandstone the rosettes weather into positive relief on an exposed rock face.

The writers made a careful field examination to determine the relationship of the rosettes to joints and conclude that regular systems of joints in the massive sandstones are lacking and that the barite rosettes have no constant relationship to the poorly developed joints which are commonly present. Neither are the rosettes localized at the intersection of joints. As a general rule they are present in the unjointed, massive portion of the sandstone, and various orientations of the long axes of the barite plates can be found in a single small outcrop.

The barite, however, is undoubtedly a secondary introduction into the sandstone. The principal evidences are as follows:

(1) Cross-bedding laminae of the sandstone are preserved in the sand-barite rosettes. This means that the barite, which is a chemical precipitate, was introduced after the cross-bedded struc-

ture of the sandstone had developed. These structures have aided the localization of the barite by providing zones of greater porosity along which solutions have migrated, but they do not have complete control, for the barite tablets may be elongated in any direction with respect to the cross-bedding laminae. The typical rose shape remains constant regardless of the orientation of these laminae.

(2) The presence of "veins" of sand-barite cutting sandstone indicates barite is later than the host rock. Four such occurrences were found at the NW cor. sec. 1, T. 9 N., R. 2 W., Cleveland County, about 6 miles northeast of Norman. The vein material has a specific gravity of 3.4, which indicates 47 per cent quartz and 53 per cent barite by weight, or 59 per cent quartz and 41 per cent barite by volume; this ratio of barite to quartz is essentially the same as in a sand-barite rosette. The "veins" are about  $\frac{3}{4}$  inch wide and several feet long. They dip at variable angles and their strikes are notably different. In some of the "veins" barite rosettes were present as well as masses of coarsely crystalline barite where the "vein" swelled. These "veins" may correspond to joints and thus it is possible that such structures have aided the localization of the rosettes.

The shape of the rosettes can be adequately explained by the crystallization of barite as bladed crystals which are aggregated together as rosettes. The erratic distribution of the rosettes indicates that the porous zones in which they were deposited were likewise erratic.

*Economic considerations.* The barite present in the "roses" and as a cement in sandstone comprises, in general, less than 50 per cent of the sand-barite mass, the remainder being mostly quartz sand. This low barite content makes its recovery impractical. In addition, the concentration of barite in the barite-bearing rocks is in most places too small to indicate any commercial possibility. Locally the barite rosettes are weathered out of the sandstone or occur in terrace gravels associated with chert and quartzitic pebbles. The writers have seen no place where more than a few tons of barite "roses" could be recovered.

#### ORIGIN OF BARITE IN LOWER PERMIAN SEDIMENTS OF OKLAHOMA

The barite rosettes, veins, and nodules found in the lower Permian sediments of Oklahoma are similar in many respects. For example, all have been introduced secondarily into the sediment. The fibrous crystal habit is common to both veins and radiating nodules, and the rosettes differ from them principally in the coarser size of their radiating crystals. The difference in composition and crystal habit is due to the fact that rosettes grew in sandstone and the growing barite crystals incorporated sand grains, whereas barite growing in shale did not readily incorporate argillaceous material and the resulting mineral aggregate was comparatively pure. All types are found closely related in some localities. For example, in the Paoli district rosettes are found in sandstone, and veins and nodules occur in the associated shale. These close associations and similar structures, together with their limitation to lower Permian strata, indicate all are related in time, source, and manner of deposition. The origin of the barite may thus be considered as a unit.

Possible theories to explain the origin of the barite include the following:

- a. Hydrothermal solutions
- b. Leaching of barium from enclosing sediments
- c. Precipitation from sea water

*Hydrothermal solutions.* Many veins and replacement masses of barite in other parts of the world have been ascribed to a hydrothermal origin. In the barite region under discussion, however, such an origin seems improbable, for igneous rocks intruding Permian sediments are unknown and there is no other evidence to indicate hydrothermal action. The igneous rocks in the Wichita Mountains are considered to be entirely of pre-Cambrian age. Furthermore, the veins of barite in the Permian shales play out at very shallow depths and therefore must have been precipitated from descending waters.

*Leaching of barium from enclosing sediments.* Sandstone and shale contain an average of 0.05 per cent BaO and this source would be adequate for small isolated occurrences of barite, for

barium undoubtedly can be leached by chloride-rich waters from sediments and redeposited therein as barite. Two writers of earlier papers on the barite rosettes of central Oklahoma appealed to the leaching hypothesis. Tarr<sup>25</sup> states: "...the barium found as the sulfate in the sand barites had its source, at least dominantly, in the silicates within the associated sandstones and shales. The Garber and other formations were laid down under arid conditions, and so there is little doubt that they once contained much brine. It was this brine that dissolved the barium from the silicates...." Meland<sup>26</sup> says: "The immediate source (of the barium) would be the sediments in which the lake formed." He assumed, furthermore, that the lakes were saline and that the chloride waters leached the barium from the sediments. Both writers thus used leaching by surface waters as their favored hypothesis, and to this method may be added the possibility of leaching by ground waters.

The leaching theory, whether by brines or by ground waters, fails to account satisfactorily for the localization of the barite in the Permian occurrences of Oklahoma. First, there is a stratigraphic limitation to the deposits. In central Oklahoma barite occurs principally in the Garber sandstone, in sandstones near the base of the Hennessey in Garvin County, and to a lesser extent in the Wellington sandstone — all of lower Permian age. The barite of southwestern Oklahoma occurs in sediments of Clear Fork-Wichita (lower Permian) age, and thus the barite-containing strata are nearly equivalent. Furthermore, in central Oklahoma there are at best only a very few rosettes in the underlying upper Pennsylvanian (Virgil) Vamoosa sandstone and in the overlying Hennessey and Duncan formations of Permian age. The upper Clear Fork shale and the Duncan sandstone in southwestern Oklahoma also are barren.

The barite is further localized in these lower Permian sediments, although it is difficult to evaluate the size, extent, and correlations of the various occurrences in the field owing to irreg-

<sup>25</sup> Tarr, W. A., "The Origin of the Sand Barites of the Lower Permian of Oklahoma": *Amer. Mineralogist*, Vol. 18, No. 6, pp. 267, 269, June, 1933.

<sup>26</sup> Meland, Norman, "A Contribution to the Study of the Red Beds of Oklahoma: Part One, Sand-Barites": Master's Thesis, Univ. of Oklahoma, p. 16, 1922.

ularities of bedding, lack of exposures, and absence of reliable key beds. Little can be said other than the occurrences probably have lens-like form. In the Garber the barite rosettes are disseminated in lenses covering several hundred feet or less up to several miles in lateral extent, the latter indicating at least minor stratigraphic localization. These lenses are separated horizontally and vertically from other lenses by rocks that contain no rosettes. The fewer outcrops in the Clear Fork-Wichita sediments make individual correlations even more difficult, but the few large concentrations appear to be lens-like or otherwise limited in extent.

The objection to the leaching theory is that the limitation of the barite to lower Permian strata, and its distribution within those beds, is unexplained. It assumes the barium in the rosettes of central Oklahoma was obtained from the sediments enclosing the barite. The Garber and Wellington formations are part of a much thicker sequence of deltaic sediments that was derived from reworked sedimentary materials, largely of Pennsylvanian age, which lay to the eastward. The Vamoosa, Stillwater, Wellington, Garber, Hennessey, and perhaps Duncan formations in central Oklahoma all were a part of the same or of a related delta and their sediments were obtained from a common source. Under the leaching hypothesis one would thus expect barite to be more or less uniformly distributed throughout the entire sedimentary section, and this is not the case.

The objection holds regardless of whether the barium was leached by brines or by ground waters. If leaching were accomplished by brines, as supposed by Tarr, it is to be expected that those brines would also precipitate barite in the associated sediments. The barium should be present in the other sediments, to which brines would be available just as they were available to the Garber and Wellington, and yet they contain no barite. In the same way, a limited stratigraphic control cannot be explained by the action of ground waters. The barite should be uniformly distributed in sediments of the same type if its formation were dependent on this agency and source.

*Derivation of barium from marine water — preferred theory.*  
The present writers believe that a marine source for the barium

most satisfactorily explains the stratigraphic control of the Permian barite in Oklahoma. Marine water can provide adequate quantities of barium. Thompson and Robinson<sup>27</sup> report 0.2 mg. barium per liter (2 p.p.m.) of sea water, and furthermore barite is being precipitated at the present time on the sea floor off the coast of Ceylon. Moreover, it is not inconceivable that barium had even higher concentrations in epiceric seas during limited spans of the geologic past. Analogous examples are shown by local concentrations of strontium, in the form of celestite, in the Silurian of Michigan, Permian of Oklahoma and Texas, and Lias of England.

It has been shown previously that the deposition of barite in shale took place in secondary openings and therefore it was not precipitated syngenetically on the sea floor. Furthermore, the disappearance of many barite veins at very shallow depth indicates that the solutions came from above. The writers believe the barium was introduced by marine waters in which the sediment was deposited or which covered previously deposited sediments and migrated downward through various openings. Where the openings were sub-capillary in size the barium ions moved by diffusion. Where marine waters inundated consolidated, compacted sediments, the downward-moving solutions followed most readily such porous zones as bedding planes, joints, and localized areas caused by differential cementation; and these small local differences in porosity favored localization of the barite. If the sand were uniformly permeable, the barite conceivably could take the form of massive cement or occur in disseminated grains, depending upon the concentration of the barium and sulfate ions. In clay, solutions followed joints and other openings and barite was precipitated in the form of veins or radiating nodules.

The lenticular distribution of the barite zones harmonizes with the nature of sea incursions on an oscillating shore line. The sediments now containing the barite were not continuously exposed to the sea water, but at a particular time certain portions of the strata were undoubtedly covered by local and temporary

<sup>27</sup> Thompson, T. G., and Robinson, R. J., "Chemistry of the Sea": in *Oceanography, National Research Council Bull.* 85, pp. 114, 116, 1932.

marine embayments. The barium was introduced into the sediments from the marine waters in the embayments, and the concentration and areal extent of the resulting barite zone depended upon the concentration of barium in the sea water and upon the extent and duration of the embayment. Isolated barite zones occurring along a stratigraphic horizon were deposited more or less simultaneously in separated embayments of the same sea, and any such zones stratigraphically higher were caused by marine transgressions in later times. Because the depositional sites varied with the fluctuations of the shore line and the changing position of the embayments, it follows that the barite deposited therefrom would have a similar variation both horizontally and vertically.

It is probable that the lower Permian seas in Oklahoma had a higher concentration of barium than normal seas and that these high concentrations were terminated by the end of Hennessey-Clear Fork time. This factor apparently was largely responsible for the limitation of the barite to lower Permian sediments.

The lower Permian sandstones and shales which crop out in central Oklahoma probably were deposited on a broad delta<sup>28</sup>, a depositional environment commonly containing both marine and non-marine sediments. Some of the beds locally contain land plants and terrestrial vertebrates, indicating non-marine deposition; most of the beds, however, lack fossils altogether. The marine phases of the deltaic series probably are represented by some of the sandstones and shales, as well as such beds as dolomitic-clay intraformational conglomerates and dolomitic sandstones. Dolomitic rocks are particularly suggestive of marine origin, and such rocks are associated with barite at Paoli and in the barite rosette zone east of Norman. In the region south and east of the Wichita Mountains the predominant sediment is maroon shale which does not clearly show deltaic characters and may be largely of marine origin.

<sup>28</sup> Anderson, G. E., "Origin of Line of Color Change in Red Bed Deposition": *Bull. Geol. Soc. Am.*, Vol. 52, pp. 211-218, 1941.

## OTHER OCCURRENCES OF BARITE IN OKLAHOMA

The few additional occurrences of barite mentioned below merely indicate that small amounts of this mineral may be found at random throughout the state. They are of scientific interest only.

Insoluble residues of the Checkerboard limestone contain a few microscopic pieces of transparent, white barite with a platy structure at the following localities: sec. 14, T. 27 N., R. 15 E., Nowata County; sec. 36, T. 21 N., R. 12 E., Tulsa County; and sec. 8, T. 23 N., R. 14 E., Washington County.

Insoluble residues of the Day Creek dolomite in Harper County show a small amount of barite of a clear or clouded appearance, and similar treatment of a Permian dolomite in sec. 36, T. 12 N., R. 14 W., Washita County, showed a few small fragments of this mineral.

Clear, transparent, coarsely crystalline barite has been reported from sec. 30, T. 8 N., R. 9 E., Hughes County.

Insoluble residues of the Belle City limestone from Seminole County show a few grains of colorless, coarsely crystalline barite.

Bladed crystals of barite occur sparsely as a gangue mineral in the zinc-lead ores in the Tri-State district of Oklahoma, Missouri, and Kansas. Analyses show 0.82 per cent  $\text{BaSO}_4$  in zinc concentrates from 3800 shipments made in 1904 from the Joplin area.