THE ORIGIN OF THE SAND BARITES OF THE LOWER PERMIAN OF OKLAHOMA

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The presence of barite as a cementing material that forms concretions and crystal aggregates (known as "sand barites" or "barite rosettes") in the lower part of the Permian (especially the Garber formation and less commonly the Wellington formation), has been known for many years although little has been published about it. Nichols described a small collection of 12 specimens in 1906. Meland described those found near Norman, Cleveland County, Oklahoma, and discussed their origin. Shead notes the distribution of the barite, and gives some analyses of the sand barites. Dotta mentions the sand barites and shows their vertical distribution within the Permian formations in his Garvin County reports. Anderson also mentions their occurrence. Similar sand barites and barite concretions have been found in other countries: Bohemia, Germany, Italy, England, northeastern Africa, and Egypt. The Egyptian occurrence is described by Pogue who includes brief notes of the other occurrences.

The barite discussed in this paper occurs dominantly in the Garber formation of the Enid group of the Permian, but barite occurs also in the upper part of the Wellington formation, in northeastern Cleveland County. Barite is found in the southcentral part of the state from Garvin County northeast through McClain, Cleveland, Oklahoma, and Lincoln counties. Shead reports that barite as veins and radial concretionary masses occurs also in Stephens and Comanche Counties, in the southwestern part of the state. The Garber formation consists of red sandstone and shales with occasional beds of limestone, and the Wellington formation is largely shale with occasional massive sandstone layers.


260
The stratigraphic position of the sand barites is given by Dott in his section of Garvin County. He locates barite rosettes at the base of the Garber formation and at various horizons within the next 100 feet above the base. Toward the top, another zone rich in barite rosettes occurs. The barite rosettes in the Wellington formation are in a sandstone near the top of the formation.

The Garber and Wellington formations of the central barite area are not reported as containing noticeable quantities of either gypsum or salt, although elsewhere the Wellington is salt bearing. A microscopic examination of the Garber sandstone near the barite revealed the presence of gypsum, and qualitative tests of a water solution of the sand showed calcium sulfate but no chlorides. The entire series of Permian Red Beds was once bathed in a saline solution and many parts are still sufficiently salty to make the water from them unpotable. The grains of the sand containing the barite are angular to subangular and subrounded. Angular and subangular shapes predominate. The sand grains were not very well sorted as the following mechanical analysis shows:

<table>
<thead>
<tr>
<th>Mesh</th>
<th>Size of Mesh in mm.</th>
<th>Percentage of Sand Grains</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>0.295</td>
<td>2.67</td>
</tr>
<tr>
<td>100</td>
<td>0.147</td>
<td>65.44</td>
</tr>
<tr>
<td>200</td>
<td>0.074</td>
<td>23.64</td>
</tr>
<tr>
<td>less than 200</td>
<td>0.074</td>
<td>8.25</td>
</tr>
</tbody>
</table>

Hematite-coated quartz grains constitute the major part of the sand, but small grains of deep red shale are scattered all through it. Occasional grains of selenite occur, as well as some calcite. Nichols (ibid., p. 33) reports orthoclase.

The barite occurs as sand barites or barite rosettes (locally called "rock roses") and barite concretions. Both types are crystalline, but the resultant forms are extremely variable. All the sand barites and most of the barite concretions are some shade of red (at least, externally) like the enclosing sandstone. The interior of a few of the sand barites is a medium pinkish-gray. This shows that there has been some transference of the iron oxides, or that the iron oxide was leached as the barite was deposited. This point will be referred to again.
The composition of the sand barites has been determined by Nichols and Shead. Their analyses are given in the following table:

<table>
<thead>
<tr>
<th></th>
<th>Nichols</th>
<th>Shead*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>36.99</td>
<td>45.13</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.36</td>
<td>0.88</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.82</td>
<td>0.96</td>
</tr>
<tr>
<td>MgO</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>CaO</td>
<td>0.51</td>
<td>0.00</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.27</td>
<td>0.31</td>
</tr>
<tr>
<td>SO₃</td>
<td>19.20</td>
<td>17.87</td>
</tr>
<tr>
<td>MnO</td>
<td>n.d.</td>
<td>0.02</td>
</tr>
<tr>
<td>BaO</td>
<td>35.76</td>
<td>34.25</td>
</tr>
<tr>
<td>Organic</td>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>99.26</td>
<td>99.42</td>
</tr>
</tbody>
</table>

* Specimen from S.W. ¼ of S.E. ¾ of Sec. 18, T. 9 N., R. 1 W., near Norman, Okla.

The sand varied from 37 to 45 per cent in these Oklahoma sand barites. Pogue reports from 44 to 53 per cent of sand from the Egyptian occurrences.

The Sand Barites. The sand barites are the more striking of the two modes of occurrence, primarily because of the rosette form they develop (Figs. 1, 4, 5). They consist of a series of tabular crystals of barite intergrown in a most intricate manner but assuming dominantly the form of a rounded cluster of crystals with a central depression. The rounded edges of the tabular barite crystals encircling this depression strikingly resemble a rose, hence the name "rosettes" or "roses" (Fig. 1). All the sand barites are aggregates of these tabular barite crystals, but the method of aggregation varies widely. Probably the most common type or aggregate consists of a large tabular crystal of barite with clusters of smaller crystals on both sides. Generally, the cluster on one side is larger (Fig. 6). The crystals rarely continue through the central plate; those on each side being independent in position and shape of those on the opposite side. The central crystal may be thin, or it may have a thickness of three-quarters inch. It usually exceeds all others in size. The typical habit of barite of developing a tabular crystal parallel to c(001) is seen in these crystals. As long as the

⁷ Nichols, H. W., *ibid.*, p. 34.  
⁸ Shead, A. C., *ibid.*, p. 104.
development along $a$ and $b$ axes is about equal, the crystal is equi-dimensional and the rosette is rounded. Development parallel to the $b$ axis gives an elongated form, but this is not common and neither is it possible from the crystal shape to prove that such elongation is always parallel to the $b$ axis. There is no apparent relationship in the development of the crystals in the side clusters.

Fig. 1–6. Barite rosettes (Figs. 1, 3, 4, 5, 6) and barite concretion (Fig. 2) from Garber Formation (Permian), near Norman, Oklahoma. Fig. 1 is a typical rosette (maximum length is $2\frac{3}{8}$ inches.) Fig. 2 is a concretion. Fig. 3 shows three rosettes united irregularly. Fig. 4 shows bedding planes on the side of a vertical rosette. Fig. 5 is the top view of a horizontal rosette. Fig. 6 shows a large vertical rosette from above.

They lie in all positions (from nearly parallel to right angles) to the central crystal plate (Fig. 5), and are arranged through every possible angle in azimuth if the central plate is considered as horizontal (Fig. 1). Pogue expressed the opinion regarding the sand barites from Egypt that some of these crystals on the sides possessed the $b$ axis in common with the central plate. An illustration accompanying his paper would seem to favor such an interpretation. In the Oklahoma sand barites, there does not appear to be
any crystallographic relationship, although Meland so interprets the position of some crystals. Nichols recognized that many of the side crystals were inclined about 30° to the central plate, but had he been able to study a larger suite he would have seen that their position shows all sorts of angles. The writer does not believe that one or two side crystals would develop with a definite crystallographic relationship (although this might occur) without giving rise to a more definite form than exists among these crystal clusters. These side clusters are aggregates of crystals growing irregularly just as one finds in barite vein deposits. Their rudely circular arrangement on the side of the larger crystal is a result of the physical character of the medium in which they formed.

The sand barites evidently developed in all positions in the sandstone. Using the central tabular crystal as the means of orientation, this crystal varies in position from horizontal to vertical. Where horizontal (Figs. 1 and 5), the side clusters are above and below (which position predominates is unknown, as an insufficient number were seen in place); where vertical (Figs. 4 and 6), they are on the sides. Some central crystals doubtless developed along a horizontal bedding plane, but obviously the vertical or steeply inclined rosettes did not. Their development probably followed joints. Evidence that the original bedding planes pass through the rosettes and concretions is usually seen on their surfaces (Figs. 2 and 4), and this fact was confirmed by examination of the barite in place. Where the sands were crossbedded, the central crystal might or might not follow the plane of the crossbedding but, as a rule, it did so. It is evident from these statements that the sand barites are directly related to the divisional openings (bedding planes or joints) of the sandstone, and that they were formed subsequent to its deposition. Vertical and inclined forms have different sized clusters on the two sides, as do the horizontal forms. This difference in size is probably due to variations in the source of supply of the barium salts.

The rosettes range in size from 1/8 inch to several inches across the central crystal or plate. The largest seen by the writer was nearly seven inches across. The rosettes occur singly or in united forms (Fig. 3). These rosettes are regarded by geologists as horizon markers, but this criterion must be used with care, as their distribution, both vertical and horizontal, through the sandstone is very irregular, as is likewise their position within a bed.
In a massive portion of the sandstone, one group with the central plate vertical or nearly so occurred within four feet of another group in which the central plate was essentially horizontal. A few barite sand clusters occurred in the area between, otherwise it was barren. These occurrences in massive sandstone show that the shape and position of the aggregate depends upon the character of the enclosing material. In another exposure, sand barites occurred dominantly along the cross-bedding planes, the central plate rudely paralleling the cross-bedding. Sand barites were irregularly distributed through other portions of the sandstone. Undoubtedly, irregularity is the rule in the distribution of the sand barites, but where there is a control it is primarily some physical factor, such as bedding planes, cross-bedding, or variations in texture.

The internal structure of the sand barites or rosettes is simple. The crystalline barite fills the interstices of the sandstone, and some believe that the sand grains have been moved apart by the introduction of this barite cement. This is doubtful, however, as it is not in keeping with our usual concept of cementation. The barite cement was in optical continuity throughout any crystal. Adjacent crystals could be easily distinguished.

**Barite Concretions.** Barite concretions differ from barite rosettes in having little or no external evidence of crystals and in generally having a rounded, elliptical (Fig. 2), or irregular form. The specimens seen by the writer range from $\frac{1}{8}$ inch to 3 inches in diameter, the smaller sizes predominating. The exterior of the concretions may be rough and sandy, or pitted. Internally, these two types of concretions differ markedly. Those of the rough, sandy group are massive and are due to the cementation of the sandstone. The pitted concretions are pure barite and have a fibrous structure. The internal arrangement of the fibers is complicated. Their position is dominantly radial, but in the outer part some fibers lie nearly at right angles to each other. Instead of each fiber increasing in size outward, new ones appear that may or may not lie parallel to the longer fiber. These interesting concretions were not seen in place and their origin is not discussed in this paper. They occur in the southwestern part of the state. Their purity suggests that they were either syngenetic in origin or were replacements.

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8 The writer wishes to thank Dr. V. E. Monnett and Mr. Don Vieaux for making it possible for him to see sand barites in place in the vicinity of Norman, Oklahoma.
Origin of the Barite Rosettes

The barite rosettes are crystals or aggregates of crystals that were deposited epigenetically in sandstone. They may or may not be related to the major structural features, such as bedding planes and joints, of the beds. The crystals incorporate the sand of the sandstone. Single crystals and aggregates may occupy any position between horizontal and vertical. These facts show that the sand barites were deposited in the sandstone by solutions capable of transporting barium. The problem of their origin involves explaining (1) the source of the barium, (2) its transportation, and (3) the cause and method of its deposition as the sulfate.

Source of the Barium. Small quantities of barium are common in igneous rocks, especially those rich in feldspars, of which there are two barium varieties, celsian and hylolaphane. Clarke and Washington give 0.055 per cent barium as the average for igneous rocks. Barium is found in other rocks as well, but not in such large quantities as in the igneous rocks. The writer collected the available evidence as to the barium in sediments some years ago and was surprised to find that shales averaged about 0.05 per cent and sandstones 0.05 per cent, but that limestones contained none. Locally, barium has been reported in limestones, but these occurrences have been in mineralized regions where the barium salts were undoubtedly introduced into the limestone by mineralizing solutions.

In connection with the geological distribution of barium, the results of Failyer's studies of the soils of the Great Plains are of interest. He found that the average barium content of those soils was 0.06 per cent, and that all the soils contained barium, the maximum amount being 0.11 per cent. Failyer ascribed the source of the barium to the feldspar in the clastic materials that are carried eastward from the Rocky Mountains.

It should be noted that barium is adsorbed by certain colloids, notably manganese oxide (as in psilomelane which usually shows some barium). It is not improbable that the barium of soils is also adsorbed and held by the soil colloids.

There is another possible source of the barium which should be mentioned, at least. In studies of the heavy mineral suites of the

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8 Clarke, F. W., and Washington, H. S., Prof. Paper 127, p. 16.
clastics, some have shown the presence of detrital barite. Although not a hard mineral (H = 2.5 to 3.5), barite is heavy and extremely insoluble, and so if it had not traveled too great a distance, it might well occur as a detrital mineral in sands and clays. It was shown by Lewis\textsuperscript{12} that detrital barite occurs in the Permian sands of Central England. However, barite occurs as a cement in sandstones and less commonly as nodules in shales, and so some of the detrital grains found in well cuttings may be the result of the crushing of such a cement by the drill.

It is the writer's view that the barium found as the sulfate in the sand barites had its source (at least, dominantly) in the silicates within the associated sands and shales. Other sources may have been detrital grains and the barium adsorbed in any colloidal materials. The occurrence of veins of barite in the rocks about 75 miles to the southwest of the barite area under discussion suggests that there were solutions rising from below, but such a source does not seem probable for the concretions and sand barites.

**Transportation of the Barium.** Some barium salts are readily soluble in water, others are very insoluble in water. There can be no doubt that the barium in these concretions and rosettes was transported, because the barite cements the sand grains together. The barium might be easily transported as the chloride; less likely, as the carbonate; and only with extreme difficulty as the sulfate. The solubility in water of these salts is as follows:

<table>
<thead>
<tr>
<th>Salt</th>
<th>Grams Soluble in 100 Grams of Water at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCl\textsubscript{2}·2H\textsubscript{2}O</td>
<td>26.3</td>
</tr>
<tr>
<td>BaCO\textsubscript{3}</td>
<td>0.0023</td>
</tr>
<tr>
<td>BaSO\textsubscript{4}</td>
<td>0.00024</td>
</tr>
</tbody>
</table>

It is evident at a glance that BaSO\textsubscript{4} is an extremely insoluble salt; a common statement\textsuperscript{13} is that one part of BaSO\textsubscript{4} is soluble in 400,000 parts of water. A careful search through the literature reveals the fact that a few spring waters and an occasional well water contain barium, but these are always chloride waters. It is extremely rare that any sulfate radical is present in the solution.

A few examples of chloride waters that contain barium will be given, as they show something of the quantity present. Bischof\textsuperscript{14}


gave analyses of brines from three bore holes along the Alleghany River near Tarentum, Pennsylvania, that contained 0.91 per cent, 0.93 per cent, and 1.25 per cent of BaCl₂ but no sulfates. Clarke\(^{15}\) gives analyses of 8 chloride waters that contain barium (Ba) in amounts ranging from 0.01 per cent to 0.82 per cent. Some of these waters contain small quantities of the radical SO₃, and some contain a large amount of CO₂. Schweitzer\(^{16}\) gives an analysis of a sulfate water from central Missouri (Randolph County) that contained 2.21 grams of BaSO₄ in a total of 227.27 grams. This is the only sulfate water the writer knows of that contains barium. A strong chloride water from Saline County, Missouri, contained 8.15 grams of BaSO₄. Barium occurs in some of the brines found in oil fields. The analysis of a brine from a depth of 2,297 feet in the Bartlesville sand was furnished the writer by Mr. W. B. Wilson of the Gypsy Oil Company. It had been noted that when a sulfate water from the Ordovician formation below mingled with this brine a precipitate formed that clogged up the pipes. Mr. L. C. Case, also of the Gypsy Company, determined the precipitate to be BaSO₄, and upon analyzing the brine from the Bartlesville sand found 224 parts of barium per million. Barite was precipitated around the pipes in some of the wells in the Batson and Saratoga Oil Fields in Hardin County, Texas. Its source was undoubtedly the brines of the well, and the mingling of the chloride waters with sulfate waters in the casing brought about the precipitation of the barite. Very probably many natural brines would show barium if they were completely analyzed.

Spring waters, both cold and warm, deposit barite at the surface. Lindgren\(^{17}\) has brought together the data relative to barium in spring deposits, and emphasizes the fact that chloride waters are the most common carriers of barium. Lindgren notes that strong carbonate waters may also hold barium in solution, even if sulfates are present. It is undoubtedly the strong brine that retains the barium even though there is a small amount of the sulfate present.

The evidence cited shows that barium is commonly transported as the chloride, and that carbonate waters may assist in keeping the barium in solution though probably not in the form of the

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\(^{15}\) Clarke, F. W., Data of Geochemistry, Bull. 770, U.S.G.S., pp. 186, 188.


\(^{17}\) Lindgren, W., Mineral Deposits, 3rd Edit., pp. 80–88, 1928.
carbonate. Sulfate waters, as one would expect, almost never transport barium.

It is generally known that the Permian formations of Oklahoma have been saturated with chloride and sulfate waters in the past and still contain brines in many localities. Potable waters are difficult to secure from deep or even shallow wells in many parts of the region underlain by Permian beds. The numerous salt plains of the northwestern part of the state show the presence of salt in the rocks of those regions. However, as far as the writer knows, there is no salt in the Garber formation in the area where the sand barites occur. 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, the adsorbed barium from colloids, or detrital barite from sands or clays. The more or less localized distribution of the barite suggests that certain portions of the Permian Seas were receiving sands and silts from areas locally rich in barium salts, or that the chloride waters were more efficient solvents for barium in these local areas.

Meland suggests in his hypothesis (M. A. Thesis, 1922, p. 15) that the barium was brought into a lake by the ordinary inflow (rivers) to such bodies (an assumption unsupported by stream analyses), and that as this lake evaporated the barite was precipitated in localized areas, the precipitation occurring "in the order of insolubility of the dissolved salts." Apparently, he assumes that the sand barites were formed as the BaSO₄ was precipitated, an assumption that is opposed by the occurrence of the barite in the sandstone. However, that such a concentration of barium would occur in a saline body of water (however strongly chloride) is not supported by a study of the composition of any body of salt water in existence today, for none show barium nor do any of the saline deposits which were formed by evaporation in the manner outlined by Meland show barite. (See Clarke, Bull. U. S. G. S. 770, Chapter 5, pp. 156-180, and chapter 7, pp. 218-260.)

It is not believed that the barium was carried far through the formation. The mode of occurrence and distribution of the barite in the sandstone indicate a comparatively nearby source for the barium. The fine-grained materials constituting the sand (or any siltstone) would favor the solution of the barium from any of the
materials in which it occurred. The solutions that carried the barium as BaCl$_2$ moved through the uniform sands in all directions, but also followed any type of divisional opening that occurred in the rocks.

Precipitation of the Barite. If the mode of transportation of the barium as the chloride (which appears to be the only feasible method) is accepted, the precipitation is a relatively simple matter as the marked insolubility of barium sulfate would favor its being deposited whenever and wherever sufficient sulfate was present. The utilization of BaCl$_2$ as the precipitating agent in testing for sulfates, even in traces, is sufficient authority for the certainty of this reaction. As small a quantity of the SO$_4$ radical as 0.001 per cent can be detected by this method. The addition of H$_2$SO$_4$ to a solution containing barium will detect 0.0001 per cent of barium. The delicacy of this reaction and the insolubility of BaSO$_4$ would cause the precipitation of any barium in solution. When a little sulfate is present in chloride waters along with barium, it is probable that the barium is actually combined as the sulfate but in so finely divided a state as to be essentially colloidal in size and hence is carried with the solution.

The occurrence of the barite as a cement in the sandstone favors the view that the barite resulted from the mingling of solutions. Water follows the more open spaces through a sand. These spaces may be within a massive or a more porous bed, along bedding planes, or along joints; hence mingling of solutions and deposition might occur any where.

It is possible that replacement of a sulfate, such as CaSO$_4$, might occur. However, CaSO$_4$ as it occurs in sandstones or siltstones is dominantly in the form of nodules or veins and not as a cement. It may be that the pure nodules (radial concretions) of barite and the veins of barite occurring to the southwest of the area under discussion originated by replacement of CaSO$_4$. This should be investigated. In the Garber formations, the barite was undoubtedly an original deposit as the crystal form of the rosette aggregates shows. The crystal form is the normal habit of the barite, which is, therefore, not a pseudomorph after any previously existing sulfate. Furthermore, no evidences of other sulfates were found within the barite, nor did any of the concretions show evidence of having replaced any previously existing mineral. The same reason applies to the sand calcites. They developed their
scalenohedral form by initial deposition and not by replacement. It has been suggested that the barite replaced dolomite. Such a reaction is possible, but, in view of the fact that the barium is transported as the chloride and must react with a sulfate radical to form barite, introducing a replacement of dolomite or any carbonate is merely introducing a wholly unnecessary factor since the carbonate played no part in the reaction. The reaction of the chloride with the sulfate formed the BaSO₄ which was precipitated at once. Any open space was sufficient and no nucleus was necessary. Subsequent replacement might occur, but it in no way influenced the reaction. There is no more need of introducing replacement than there is of holding that all cementation of sandstones must be replacement. The barite, whether as concretions or rosettes, was a primary deposit within the interstices of the sand grains and was due to the reaction of the readily soluble BaCl₂ with a sulfate radical. The lighter gray color of the interior of some barite rosettes may be due to a leaching of the iron oxides on the sand grains by the chloride released in the reaction, especially if some HCl were liberated.

The rounded sandy barite concretions represent the addition of barium sulfate to all sides of an originally small barite grain. Variations in texture or in the direction from which the solutions approached would cause variations in the shape of the concretions. Probably, their rate of growth was faster than that of the crystals of the rosettes.

The crystal aggregates are typical of barite. Nodules and radiating aggregates are common features of the barite in any barite deposit. Barium sulfate crystallizes readily, and the haphazard orientation of any small crystal permits growth in any direction. A number of such crystals irregularly arranged would result in the sand barite aggregates. The dominance of a single central crystal indicates that the earlier growth was slow and chiefly along one plane. Doubtless at the initiation of such growth, other, but differently oriented grains, were deposited. That grain in which the crystallographic orientation was such as to parallel the bedding or joint plane was in a favored position to grow fastest and so outstripped its fellows. Some of the solution found its way past the edges of this fast-growing crystal so that the other grains continued to grow, but more slowly. Thus, the central crystal became large, but those on the sides also developed. Later variations in the flow
of the feeding solutions might favor the growth of the crystals on the sides. Once a crystal was well started, its orientation rather than the movements of the solutions dominated the direction of growth.

The character of the sulfate that caused deposition has not been indicated. It probably was CaSO₄, although not necessarily so, as magnesium sulfate, for example, might act similarly. Calcium sulfate is soluble in 536 parts of water at about 15° C., and is known to be transported by ground waters. The base exchange with BaCl₂ would result in a very insoluble salt and the readily soluble CaCl₂. Other sulfates may have played a part (the local production of H₂SO₄ from the alteration of a sulfide or the oxidation of H₂S might have been a source of the sulfate), but it seems more probable that it was the calcium salt.

The time of deposition was probably not long after the burial of the formations and before the brines they once contained had been fully removed through evaporation or displacement by fresh waters.

Summary

Barite concretions and barite crystal aggregates, known as "sand barites" or "barite rosettes," occur in sandstones in the Garber formation (and to a less extent in the underlying Wellington formation) in central Oklahoma. They are rather local in horizontal and vertical distribution. The barite in both types cements the sand grains together. The crystals of barite in the rosettes have various orientations. It is believed that the barium was derived (chiefly) from barium silicates (such as barium feldspars), barium adsorbed in colloids, or from detrital grains of barite. It was leached out by chloride waters (original brines), forming BaCl₂; carried a variable distance (probably short); and deposited as a cementing material in the sandstone through reaction with some soluble sulfate to form the extremely insoluble BaSO₄, which assumed the form of the rounded concretions or the crystal aggregates. The time of deposition was probably not long after the formation of the sandstone.