

# ORIGIN OF THE MARCASITE SINK-HOLE DEPOSITS OF CENTRAL MISSOURI

W. A. TARR,

*University of Missouri, Columbia, Missouri.*

There are ten known deposits of marcasite (and pyrite in small quantities) in sink-holes in Franklin, Crawford, and Phelps counties in the northeastern part of the Missouri Ozarks, and others probably exist, either still uncovered by erosion or in connection with unmined hematite deposits of filled sinks. Only two mines, the Moselle mine, No. 10, near Rolla, and the Cherry Valley mine, east of Steelville (Fig. 1), were oper-

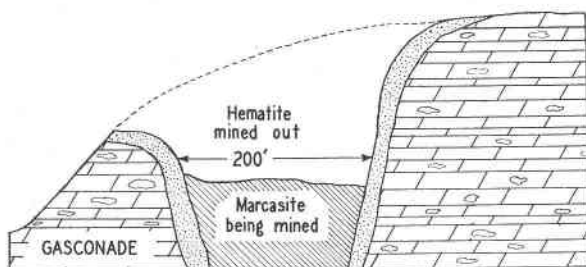


FIG. 1. Marcasite (Sulfur) Mines of Missouri.

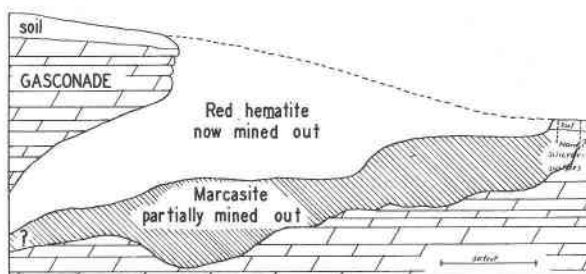
ating in 1936. All the deposits are associated with former hematite mines. The sulfides are mined by underground or open-cut methods, occasionally by both methods at the same deposit. As the sulfides are sold for their sulfur content, the producers try to maintain a minimum of 45 per cent S in their ore, which may average 49 to 50 per cent.

## MODE OF OCCURRENCE OF THE ORES

The sulfides occur in the lower part of sink-holes (Fig. 2), the upper part of which was originally filled with iron ore, now mined out. These sink-holes rarely exceed 500 feet in their greatest dimension and are usually 100 to 300 feet across. They may be rudely circular but more commonly are elliptical or irregular in outline. The sulfides are usually 10 to 30 feet thick, but greater thicknesses have been estimated (for example, 100 feet in Scotia mine, No. 1, Crawford County).<sup>1</sup> The overly-



2a - Sketch of sink-hole sulfide-hematite mine.



2b-Sketch of the Leslie, Mo. Sulfide-Hematite Mine as it is today.

FIG. 2. Sulfides in the lower part of sink-hole hematite deposits.

ing hematite ore was commonly less than 100 feet thick, but in the Ruepple mine, near Stanton, an inclined ore body was followed to a depth of 320 feet. The sulfide ore body in this mine was at a higher level than the bottom of the iron ore as it was reached through a shaft 268 feet deep.

The sulfide ore bodies are essentially flat, but have an uneven contact with the country rock on all sides. Locally, the ores grade into the wall rock, but usually the contact is sharp. The contact with the hematite

<sup>1</sup> Crane, G. W., Iron Ores of Missouri: *Mo. Bur. Geol. and Mines*, vol. 10, p. 219, 1912.

above was also uneven; at any rate, as far as can now be determined.

The deposits occur in the Gasconade (dolomite) and Roubidoux formations (both Ordovician). In the Ruepple mine, the sulfides may occur in the Van Buren (base of the Ordovician) for they apparently occur below the basal member (the Gunter sandstone) of the Gasconade. The stratigraphic range may be 500 feet, but is usually less. Where the ores occur in the upper part of the Gasconade, blocks of Roubidoux sandstone may be found along the sides of the deposit (Fig. 2a) or even within the ore. These represent blocks that were let down into the Gasconade during the formation of the sinks and galleries.

The Gasconade and Roubidoux formations normally dip gently to the northwest. Minor departures from this occur throughout the region, but the most noticeable variations are in local areas that show the results of settling associated with the sink or cavern structure. The Gasconade ( $300 \pm$  feet thick) was the seat of most of the solution work, which developed galleries and shafts throughout the formation. Where these features reached the comparatively insoluble Roubidoux ( $125 \pm$  feet thick) above, they were necessarily extended laterally beneath it, finally causing its collapse into the Gasconade. These collapsed portions of the Roubidoux lie at all angles within the sinks and dip steeply inward along their margins. No sandstone is found within or around some sink-holes, either having been entirely replaced or the sink-holes having developed wholly within Gasconade beds.

#### DESCRIPTION OF THE MINERALS

The sulfide ores consist overwhelmingly of marcasite,<sup>2</sup> with only subordinate amounts of pyrite. No other sulfides have been identified by the writer, but the presence of metallic copper in the mine waters of the Ruepple mine indicates that the ores probably contain traces of some copper mineral, possibly chalcopyrite. Quartz, containing limonite as a coloring material, occurs sparingly as the only other mineral in the ores.

The marcasite is a typical metacolloid having reniform, botryoidal (fig. 3), mammillary, and rod-like structures, aggregates of which commonly assume beautiful plumose and feathery radiating forms (Fig. 4). Stalactitic structures (Fig. 5) are common in some mines. The marcasite also occurs massive, as a fine granular powder, and in druses and large (maximum, 2 cm. across) crystals. Some of the crystals show twinning. Coxcomb structures, such as those so well developed in the Tri-State district, are extremely rare. The metacolloidal structures are normally fibrous. These fibers are so small in some solid mammillary ores that

<sup>2</sup> It is not improbable that some of the marcasite has inverted to pyrite, but the material examined by the writer was marcasite.

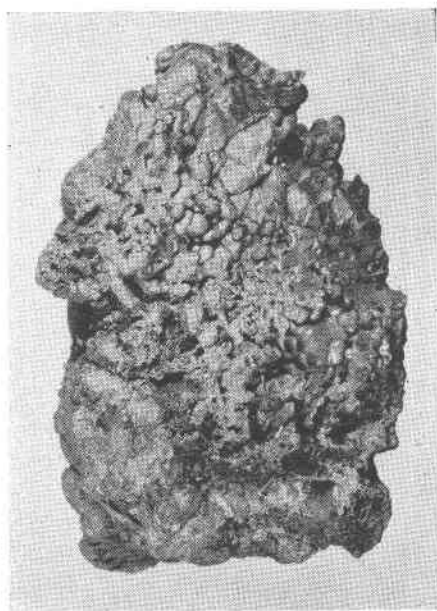


FIG. 3. Metacolloidal marcasite (botryoidal) from the Hobo mine. Slightly reduced.

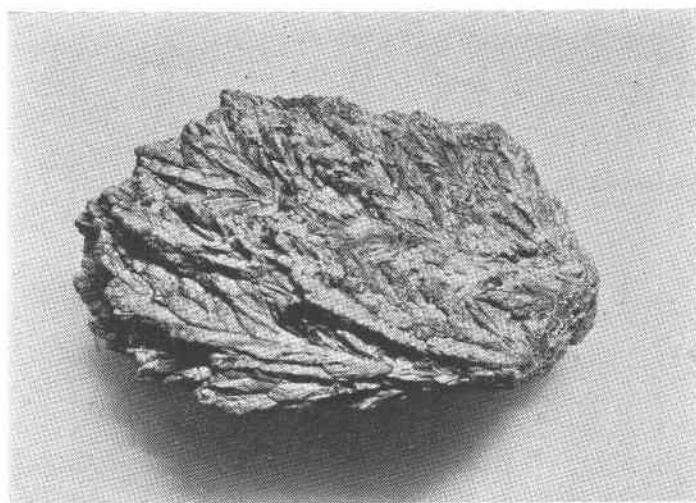


FIG. 4. Plumose marcasite from the Leslie mine. Slightly reduced.

their presence can be detected only by the sheen exhibited by reflected light. Not uncommonly, the fibrous metacolloid structures give way to dominantly finely granular marcasite containing barely sufficient fibers to support the aggregate. The plumose forms developed in the closing stages of deposition and contain many open spaces. Marcasite was not usually the last mineral to be deposited, but it may have been last.

The pyrite occurs primarily as drusy surfaces on the marcasite, as fibrous concentric bands or layers *alternating* with the marcasite, or as well developed crystals (normally 1–2 mm. across but, rarely, 2 cm.).

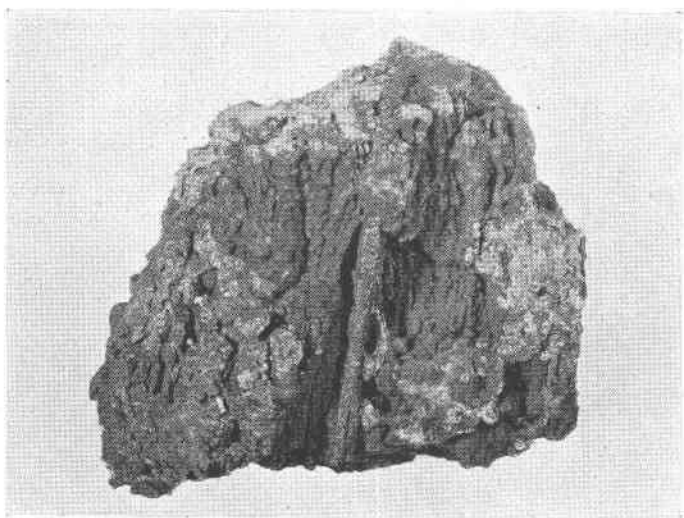


FIG. 5. Stalactitic marcasite. Moselle mine. Slightly reduced.

Some of the alternating bands are .05 millimeter or less in thickness, others may be one or two millimeters. Usually, the drusy layer is last and is a millimeter or less in thickness, but very rarely there may be a concentric layer of fibrous pyrite, two or three inches thick, terminating in crystals one inch across. Short (a few millimeters in length), lenticular (but concentric) layers of pyrite may occur within a fibrous radiating mass of marcasite.

The crystals of pyrite are usually cubes modified by octahedrons (less commonly by pyritohedrons) or octahedrons modified by cubes. A particular form or combination of forms usually dominates at each mine; thus pyritohedral forms on cubes are more common at the Ruepple and Moselle mines than elsewhere. Layers of cubes (modified by octohedrons)

of pyrite occur in the Ruepple mine. Rarely, marcasite was deposited on pyrite as the last mineral, but the usual occurrence was pyrite last.

The quartz occurs as a clear transparent material filling interstices within the sulfides, or as crystals within the cavities. Rarely, it is amethystine or yellow, the latter, due to included limonite. The limonite was deposited with the first quartz on the walls of the cavities, and usually forms a colored layer about a millimeter thick. Transparent quartz followed if space was available. The quartz was deposited later than the sulfides and not uncommonly replaced them. This replacement usually occurred in the fibrous portions rich in granular marcasite, which was the first part to be replaced. The fibrous part was then replaced by quartz which was pseudomorphic after the marcasite, or, more rarely, enclosed it. If both marcasite and pyrite were present in alternating bands, the marcasite was replaced and the pyrite left to form alternate layers with the quartz. Later, the pyrite was leached out leaving the thin shells of quartz.

The sulfides were deposited in the open spaces (shafts or sink-holes) developed within the Gasconade or other formations, or they replaced any dolomite, chert, or sandstone therein. Both sulfides are found replacing the chert and sandstone, and it can scarcely be doubted that any dolomite present would have been replaced early in the mineralization. Residual masses of chert, sandstone, and clay occur within the ore, but no masses of dolomite. Possibly, all the dolomite had been removed during the development of the solution cavities.

The sulfide ore is soft and brecciated, and thus slumps and caves easily. This makes mining by underground methods very difficult and dangerous. Where possible, stripping is resorted to and the mining accomplished by open cut methods.

#### ALTERATION OF SULFIDES TO IRON OXIDES

The primary sulfides in the upper part of the sinks were converted into the iron ores by oxidation. This was accomplished after erosion (aided by elevation of the region) had brought the top of the sulfide ore bodies to the surface, establishing a variable portion of them above the ground-water level. Oxidizing solutions then penetrated this part of the ore body and converted the sulfides into hematite and limonite. Much of the resulting product was structureless, the alteration having reduced the sulfides to soft iron oxides. In local areas, however, masses of the iron oxides are pseudomorphic after the sulfides, preserving the details of the colloform and crystalline material. From specimens showing the successive stages of alteration, it is seen that the more easily altered marcasite (a condition furthered by greater porosity,

especially of the granular aggregates) was the first to be attacked and converted into the iron oxides. Where the topographic position of the sulfide deposit prevented the rapid ingress of water with its oxygen, the alteration progressed slowly. Furthermore, the texture and composition (the relative amounts of the two sulfides) of the aggregates influenced the rate of oxidation. Slow alteration produced chiefly soft hematite, which, as far as can be determined from published descriptions, predominated in the iron ores.

The rapid alteration of a deposit produced much heat which induced significant changes in the alteration products. As the heat escaped upward through channels, or, more slowly, by conduction through the iron oxides, the oxides were dehydrated, and the temperatures were, locally at least, high enough (probably 250°–300°C.) to convert the red hematite into specularite (the "hard blue ore" of the earlier accounts of the mining of these deposits). At lower temperatures, the hematite became goethite. Locally, iron oxides in solution were deposited as beautiful crystals and rosettes of specularite in cavities in the ores. It is very probable that hot sulfur-bearing springs existed at the surface over these altering sulfide deposits.

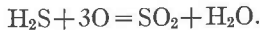
Another important mineralogical change accompanied this heat development. The hot solutions took silica (from sandstone and chert) into solution and redeposited it in the surrounding sandstones (converting them into quartzites), or, carrying it down into the unaltered sulfides, deposited it as quartz (rock crystal, both limonitic and amethystine) in the openings of the sulfides, or as a replacement of them. These were not oxidizing solutions, as the sulfides remaining were unaltered. Near the top of the sulfide ore body, a little limonite from above was occasionally deposited *with* the quartz. The quartz is most abundant in the top of the sulfide ores and decreases rapidly downward, showing that it came from above. Later solutions (probably cool) deposited small amounts of dolomite, calcite, barite, and some rare minerals in the iron ores.

#### ORIGIN OF THE MARCASITE

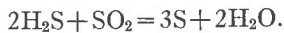
It is believed that these marcasite ore bodies were deposited by magmatic waters within galleries and shafts previously formed by ground water below the ground-water level. The magmatic waters had their source in a telemagmatic batholith underlying the region. These solutions were acid and had a temperature of 100° to 125°C., which represents the optimum conditions for the deposition of marcasite. They probably transported the iron as the chloride. Hydrogen sulfide, also from the magma, entered the galleries and shafts and, where trapped in

these openings, became sufficiently concentrated to react with the  $\text{FeCl}_3$  to precipitate  $\text{FeS}_2$ . This marcasite or pyrite reaction was aided by the absence of much oxygen in these trapped solutions as the galleries and shafts were unconnected with the surface. The tops of the solution chambers were all below ground-water level at the time of the ore formation.

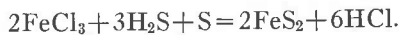
Possible reactions involved in the precipitation under the above conditions are as follows:



Because there was insufficient oxygen to convert all the  $\text{H}_2\text{S}$  into  $\text{SO}_2$ , the  $\text{SO}_2$  reacted with the  $\text{H}_2\text{S}$  to form free S:



In the presence of  $\text{FeCl}_3$ , conditions were then satisfactory to precipitate  $\text{FeS}_2$ , thus:



The HCl formed was used in dissolving the dolomite and some other substances, in this way facilitating replacement.

The following sequence presents briefly the writer's interpretation of the events involved in the origin of the sulfides, and in the alteration to iron oxides of that portion of the ore body occupying the upper part of the sinks.

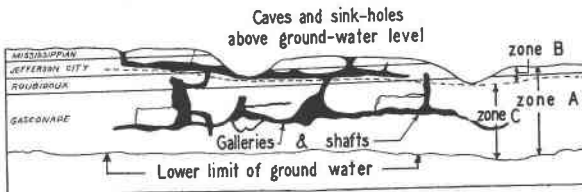


FIG. 6. Sketch to show the relationship of the various cavities to water level (dotted line).

1) Following the deposition of the Mississippian beds in the central Missouri area, the sea retreated, and post-Mississippian erosion subjected the region to peneplanation. The bottom of the ground-water zone was then (as at present) at variable depths below the surface. Within this zone (Fig. 6-A), the development of solution cavities was possible (and probable) both above (zone B) and below ground-water level.<sup>3</sup> As the formations involved were dolomites and sandstones, the

<sup>3</sup> Davis, W. M., Origin of limestone caverns: *Bull. Geol. Soc. Am.*, vol. 41, pp. 477-628, 1930.



lower ones of which (the Gasconade and Roubidoux) had been previously subjected to the attack of ground water and thus doubtless already contained solution cavities, it seems reasonable to assume that various types of solution cavities, galleries, and shafts were more or less fully developed below the water level (Fig. 6-C), as were caves and sink-holes also above it (Fig. 6-B). These openings were formed in the Mississippian (now removed from this area), Jefferson City (200 feet thick), Roubidoux, and Gasconade formations. It should be noted that the network of galleries and shafts of zone C were connected with the branch work of caves and sink-holes of zone B. At a late stage in the development of the peneplain, the water level was near the surface, hence the major solution work took place below this level, which favored the formation of many galleries and shafts.

2) In the area of the sulfide deposits, the Roubidoux and Gasconade formations were near or at the surface and were the seat of active solution work. Parts of these formations were evidently readily soluble as they contain numerous caverns today, many of which are believed to date to the pre-Pennsylvanian period of solution.<sup>4</sup>

3) Galleries formed wherever the top strata were strong enough to form a roof. Shafts developed where joints in the roof occurred, permitting vertical movements of the ground water (Fig. 7-A). The Gasconade is very cherty and the removal of the dolomite left the galleries partially filled with a brecciated mass of chert and clay but with ample space for circulation of the water.

4) The Pennsylvanian sea submerged the area, and sands and shales were spread over it, filling the sinks and sealing up the water in zone A (Fig. 6-A).

5) Following elevation at the close of the Paleozoic era, erosion was probably in progress throughout much if not all of the Mesozoic. Total erosion appears to have been small, as a thin sheet of Pennsylvanian beds is still present in nearby areas. This was probably due to the nearness of the land surface to sea level, and not improbably to submergence beneath Cretaceous seas although there is no proof of this. It is not believed that the Pennsylvanian formation was entirely removed from the area during Mesozoic time. The solution work of post-Mississippian times continued throughout the Mesozoic.

6) The sulfides were deposited by magmatic waters (in the manner shown above) during late Cretaceous time (Fig. 7-B), probably at much

<sup>4</sup> Lee, Wallace, Geology of the Rolla Quadrangle: *Mo. Bur. Geol. and Mines*, vol. 12, p. 70, 1913.

the same time as the occurrence of the mineralization in the Southeastern Missouri Lead district<sup>5</sup> and in the Arkansas and Tri-State areas.

7) The H<sub>2</sub>S and the magmatic waters rose from below and entered the galleries and shafts, the H<sub>2</sub>S collecting in the highest parts of the gallery-shaft system (the present "filled sinks"), and thus being trapped under the Roubidoux, Jefferson City, or Pennsylvanian formations.

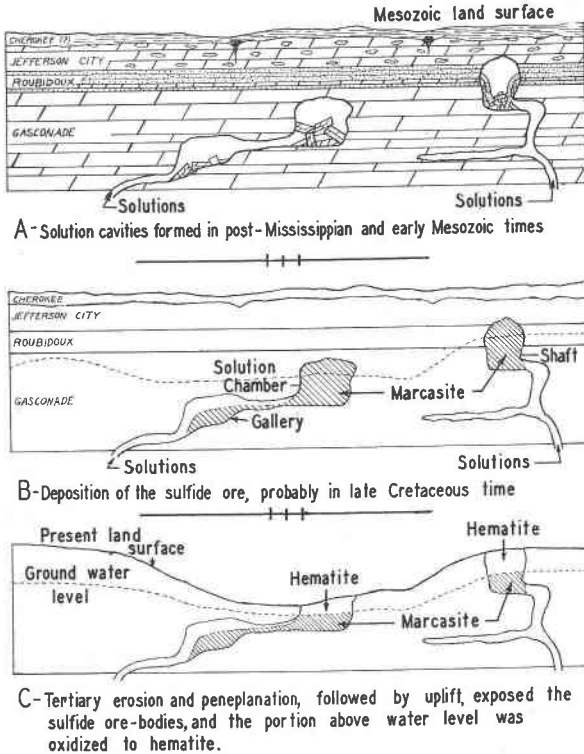


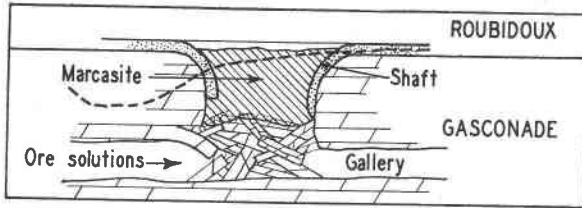
FIG. 7. Sketches to illustrate the sequence of events in the origin of the sulfide deposits.

8) Precipitation of marcasite (and pyrite) occurred in the open spaces in these traps, both sulfides being deposited as colloids (later becoming metacolloids) and crystalloids. Of the two, pyrite was more commonly deposited in crystalline form. The marcasite was deposited first from acid solutions, probably at about 100°C.,<sup>6</sup> and then, as the solution of

<sup>5</sup> Tarr, W. A., Origin of the southeastern Missouri lead deposits: *Econ. Geol.*, vol. 31, pp. 712-754, 832-866, 1936.

<sup>6</sup> Allen, Crenshaw, and Johnston, The mineral sulphides of iron: *Am. Jour. Sci.*, 4th series, vol. 33, p. 169-236, 1912.

the dolomite neutralized the waters, pyrite was deposited. This alternation of deposition of the two sulfides was repeated often as the solutions changed back and forth from acid to neutral or slightly acid, but always the amount of pyrite deposited was very subordinate. A similar alternation has been observed in a marcasite deposit in Madison County, Missouri.<sup>7</sup> The abundance of maracite and its universal colloform structure indicate predominant acid conditions and rapid deposition.



Ideal sketch of original conditions after deposition of the sulfides. Dashed line is the present land level.



The hematite was formed from the sulfides after the water level was lowered by the downward cutting of the valley.

FIG. 8. Sketch to show the origin of a sink-hole deposit of hematite and the sulfides.

9) Uplift at the close of the Mesozoic period reestablished the surface drainage and initiated a new period of peneplanation with its attendant ground-water system.

10) The near-surface water level of the Tertiary peneplanation period prevented oxidation of the sulfides, unless or until erosion exposed one of the shafts or gallery traps containing ore.

11) Late in the Tertiary period occurred the uplift that rejuvenated the Ozark streams which then vigorously entrenched themselves into the peneplain they had developed. The water level was thus lowered, and all the sulfide deposits above the level (the vadose zone) were vigorously attacked by oxidizing solutions (Figs. 7 C and 8). Marcasite is readily altered by oxygen and water, and the abundance of fine, granular (as

<sup>7</sup> Tarr, W. A., Alternating deposition of pyrite, marcasite, and possibly melnikovite: *Am. Mineral.*, vol. 12, pp. 417-421, 1927.

well as fibrous) marcasite in the very porous and brecciated (due to slumping) ore body intensified the oxidation which proceeded rapidly. The large amount of heat thus generated still further stimulated the reactions.

12) Parts of the resulting soft iron oxides above the zone of active alteration were changed by the hot gases and solutions to specularite (blue ore). The hot solutions, likewise, aided in removing silica, and where the circulation was favorable carried some of it down into the upper part of the unoxidized sulfides, depositing it as quartz in cavities or as replacement of marcasite.

13) That the oxidation of the marcasite deposits was related to this entrenchment and lowering of the water level is shown by the fact that the marcasite of the filled sinks is at about the level of nearby streams. In deposits on ridges where the water level is higher, the sulfides are higher than the adjacent streams (Fig. 8).

14) As grade was reached by the larger streams, down-cutting by all of them ceased; the water level became essentially stationary, and oxidation practically stopped, or it became so slow that all heat resulting from it was dissipated. Little change has occurred in either the iron ores or the remaining sulfides in recent geologic times, although the removal of the former within the last 50 or 75 years has exposed the latter to renewed (but slight) oxidation.