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A MICROSCOPIC STUDY OF GOETHITE AND HEMATITE IN THE BROWN IRON ORES OF EAST TEXAS*

F. W. GALBRAITH,

University of Arizona, Tucson, Arizona.

INTRODUCTION

During 1934 Eckel studied the brown iron ores of east Texas for the U. S. Geological Survey.¹ Field relations showed that the ores were formed by the weathering of a greensand. At Mr. Eckel's suggestion, the writer made a study of fifteen polished sections of typical brown ore. The results indicate the value of a line of investigation which has not been extensively applied to the brown iron ores.

The writer is deeply grateful to M. N. Short of the University of Arizona, C. F. Park, Jr., W. T. Schaller, E. F. Burchard and R. C. Wells of the U. S. Geological Survey, and George Tunell of the Geophysical Laboratory for valuable criticism, and especially to E. B. Eckel of the U. S. Geological Survey, who not only furnished the material for this study and helped to direct the progress of the investigation, but also generously contributed the section on geologic relations.

GEOLOGIC RELATIONS²

The brown iron ore deposits of east Texas occupy part of the Coastal Plain Province in the eastern and northeastern parts of the State. All the ores considered here came from the northern part of the field, in Cass, Marion and Morris Counties. The iron ores occur near the tops of the flat-topped, sand-covered hills that are a prominent feature of the landscape in a large part of eastern Texas.

Nearly all the rocks exposed at the surface in this part of the State were laid down during the Eocene division of Tertiary time. Iron ore of commercial grade is confined almost entirely to the Weches greensand member of the Mount Selman formation, which comprises the lower part

* Published by permission of the Director, U. S. Geological Survey.

¹ Eckel, E. B., and Purcell, P. E. M., Iron ores of east Texas: *Univ. of Texas, Bull.* 3401, pp. 485-503, 1935.

² Eckel, E. B., personal communication.

of the Claiborne group. The Weches greensand is a mixture of a granular iron silicate mineral of the glauconite group with varying proportions of quartz, sand, and clay.

The most abundant type of ore is "limonite," or brown ore. In the northern part of the field the ore occurs chiefly in concretionary forms, or as thin lenticular bodies that are distributed irregularly through the weathered zone in the upper part of the Weches greensand. The best ores occur near the outcrop of the Weches and seldom extend beneath heavy cover. Iron carbonate, or siderite, is plentiful in many places. It occurs as white or gray dense nodules or thin lenses, at or near the ground-water level.

Chemical considerations, based on analyses of the greensand, siderite, brown ore, and spring waters, and the observed relation of the ore deposits to the present water table and topography, indicate that the ores have been derived from the greensand by ordinary weathering processes. It is believed that ground waters leach iron from the greensand and deposit it as iron carbonate. This is later altered to "limonite," or brown ore.

THE HYDROUS IRON OXIDES—GOETHITE AND LEPIDOCROCITE

Considerable confusion still exists with regard to the hydrous iron oxides, particularly in the use of the term "limonite." Published results of investigations^{3,4,5,6} carried out during the past few years show that there are two polymorphic forms of ferric oxide monohydrate ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), goethite and lepidocrocite, and that the use of the term "limonite" should be confined to mixtures of ferric iron minerals whose constituents have not been identified, including principally hematite, goethite, lepidocrocite, and jarosite.

IDENTIFICATION AND DESCRIPTION OF THE ORE MINERALS

Hematite, goethite, and lepidocrocite may be identified either by the x-ray powder diffraction method or by measurement of their refractive indices by the immersion method.⁷ The measurement of refractive indices requires the use of high-index melts of sulphur, iodine, selenium, and tellurium which were not available. Identification was therefore made by

³ Posnjak, E., and Merwin, H. E., The hydrated ferric oxides: *Am. Jour. Sci.*, vol. 47, p. 311, 1919.

⁴ The system $\text{Fe}_2\text{O}_3 - \text{SO}_2 - \text{H}_2\text{O}$, *Jour. Am. Chem. Soc.*, vol. 44, p. 1971, 1922.

⁵ Tunell, G., and Posnjak, E., The stability relationships of goethite and hematite: *Econ. Geol.*, vol. 26, p. 337, 1931.

⁶ Schneiderhöhn, H., and Ramdohr, P., *Lehrbuch der Erzmikroskopie*, Berlin, vol. 2, pp. 560-566, 1931.

⁷ Tunell, G., and Posnjak, E., *op. cit.*, pp. 342-343.

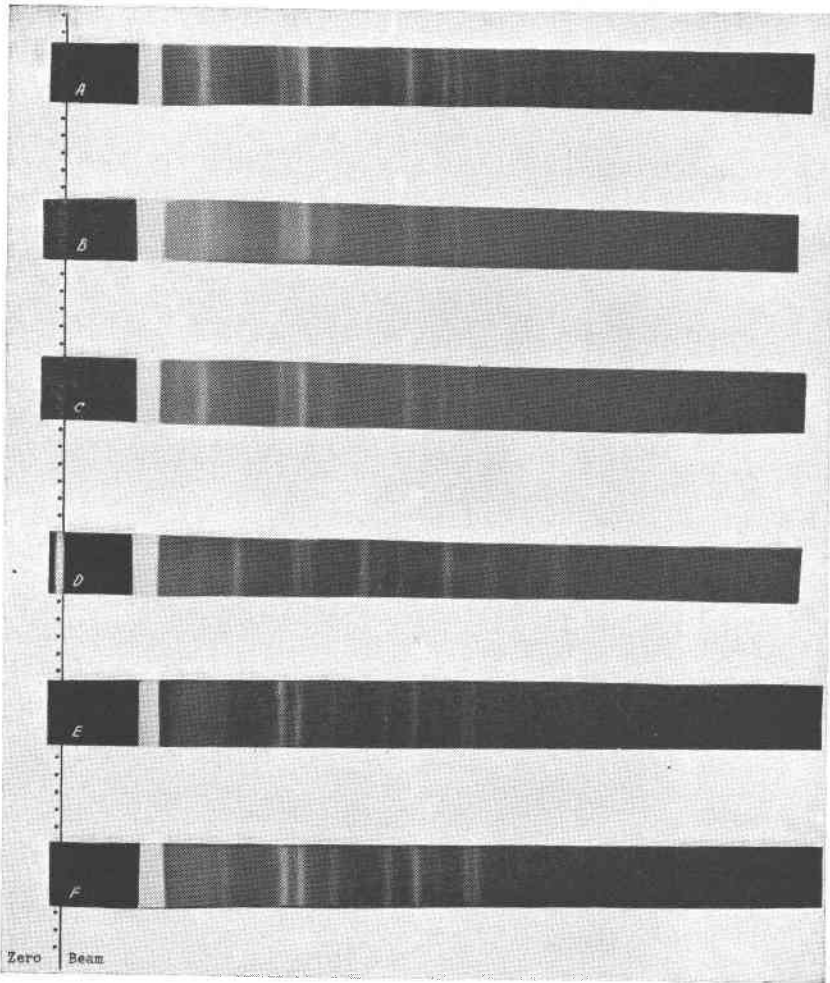


FIG. 1

X-RAY DIFFRACTION PATTERNS

- A. Goethite. Las Vegas, Nevada. U. S. National Museum.
- B. Goethite. Crystalline material from zone 1.
- C. Goethite. Cryptocrystalline material from zones 2 and 3.
- D. Lepidocrocite. Nassau, Germany. U. S. National Museum.
- E. Hematite. Frizzington, England. U. S. National Museum.
- F. Hematite. Material filling vugs in goethite.

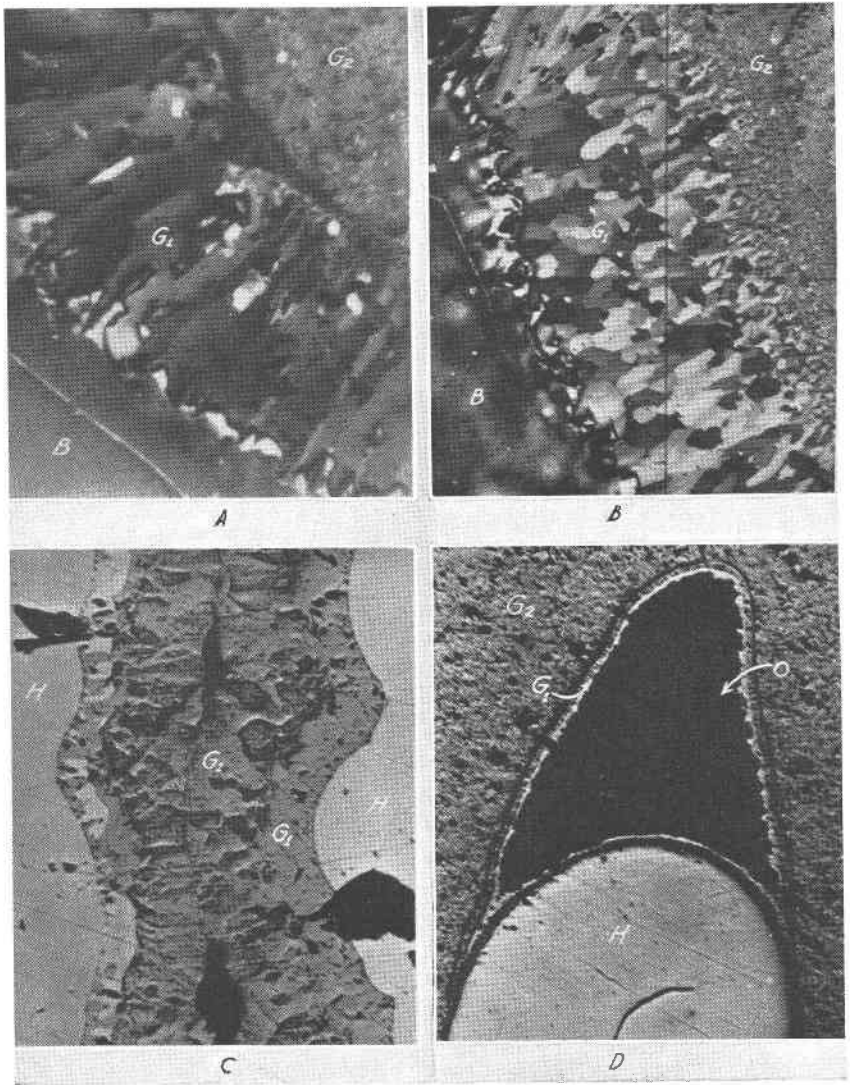


FIG. 2

A. Flamboyant internal structure of a colloform shell of crystalline goethite lining a balsam filled vug in cryptocrystalline goethite. Crossed nicols. Enlarged 68 diameters.

B. Granular internal structure of a part of the same colloform shell of goethite as in A. Crossed nicols. Enlarged 68 diameters.

C. Lobate boundary separating a colloform shell of crystalline hematite from goethite. Plain reflected light. Enlarged 52 diameters.

D. A vug in cryptocrystalline goethite partly filled with crystalline hematite. The unfilled part of the vug is lined with a thin layer of crystalline goethite. Plain reflected light. The narrow black band separating the goethite G_1 from G_2 and hematite from goethite is open space. Enlarged 53 diameters.

G_1 —Goethite (crystalline)

B—Balsam

G_2 —Goethite (cryptocrystalline)

O—Open Space

H—Hematite

comparing x -ray diffraction patterns of the unknown materials with patterns of tested minerals supplied by the U. S. National Museum. The comparison shows that goethite and hematite are present in the east Texas ores and that lepidocrocite is absent. In Fig. 1, the diffraction patterns of B and C, representing crystalline and cryptocrystalline material from the East Texas ores, are identical with that of known goethite from Las Vegas, Nevada (A), and quite different from the pattern obtained from known lepidocrocite from Nassau, Germany (D). The x -ray diffraction patterns were made by R. G. Picard of the Department of Physics, University of Arizona.

The polished sections examined consist of approximately 80 per cent goethite and 20 per cent hematite. The characteristics of the goethite are identical with those described by Schneiderhöhn and Ramdohr.⁸ In vertically reflected light the color varies from dull gray to bright gray. The variation depends largely upon texture, but somewhat upon the orientation of individual grains, as the mineral is faintly pleochroic, and many pure masses of goethite appear to be made up of more than one mineral. Crystalline goethite has a high degree of reflectivity and is brighter than cryptocrystalline material.

The crystalline goethite is strongly anisotropic under crossed nicols, in vertically reflected light, and a delicately flamboyant to coarsely granular structure is brought out (Fig. 2, A and B). The polarization colors range from blue-gray to salmon-brown when the specimen is illuminated by the carbon arc. Owing to the fact that the crystallographic axes could not be identified in polished section it is not possible to designate the corresponding polarization colors. Anisotropism of cryptocrystalline goethite is masked by the yellowish internal reflection. The color of the powdered mineral under crossed nicols in reflected light is brilliant orange-yellow to golden-yellow.

The goethite is stained by a saturated solution of stannous chloride in 1:5 HCl. The stain, which is dark brown on crystalline goethite and yellowish brown on cryptocrystalline material, usually becomes visible in less than one-half minute, but some specimens require treatment for two minutes before even a faint stain appears.

⁸ Schneiderhöhn, H., and Ramdohr, P., *op. cit.*, pp. 561-564.

The hematite in the polished sections of the east Texas ores is easily recognized by its brighter white color and greater hardness than goethite (Fig. 2, C and D). It is strongly anisotropic under crossed nicols in vertically reflected light, with blue-gray to salmon-brown polarization colors and a prominent flamboyant internal structure. The powdered mineral is bright red under crossed nicols in vertically reflected light.

Although *x*-ray diffraction patterns showed lepidocrocite to be absent in the east Texas ores, a polished section of lepidocrocite was studied and the characteristics of the mineral were carefully compared with those of goethite. The differences consist of a somewhat brighter color in plain reflected light and a reddish color of most of the powdered mineral under crossed nicols. The writer believes that these slight differences are insufficient to establish the presence or absence of lepidocrocite without the confirmatory evidence of *x*-ray diffraction patterns or refractive indices.

STRUCTURE OF THE ORES

Roughly ellipsoidal structures characteristic of the iron carbonate concretions from which the brown iron ores have been derived⁹ appear in most of the polished sections. Three zones can be distinguished in most specimens, each of which contains goethite of a different character. Hematite occurs in variable amounts in all three zones.

Zone 1, a central or inner zone, consists mainly of crystalline goethite as a band of varying thickness around a vug, or as a solid core. It takes a relatively high polish and usually is bright gray, although variation in reflectivity is common. In places the grain boundaries are visible in plain vertically reflected light (Fig. 3, C), but under crossed nicols the structure of the goethite is predominantly flamboyant (Fig. 2, A), although some areas are granular (Fig. 2, B). Crushed fragments of the mineral appear flamboyant when immersed in oil in plain transmitted light; under crossed nicols the individual fibers are distinctly anisotropic and have parallel extinctions.

Zone 2 is a concentric envelope of goethite with lower reflectivity and a darker gray color than that of zone 1, and is separated from it by a lobate boundary in most of the sections examined. Under crossed nicols the material is cryptocrystalline and distinctly brown, apparently due to internal reflection. Aggregate anisotropism is weak. Powdered goethite from this zone immersed in oil under crossed nicols does not appear flamboyant, but individual grains are moderately anisotropic.

The goethite in the outer zone 3 is soft and porous, with a much lower reflectivity and duller color than that of zone 2. Under crossed nicols

⁹ Eckel, E. B., and Purcell, P. E. M., *op. cit.*, p. 494.

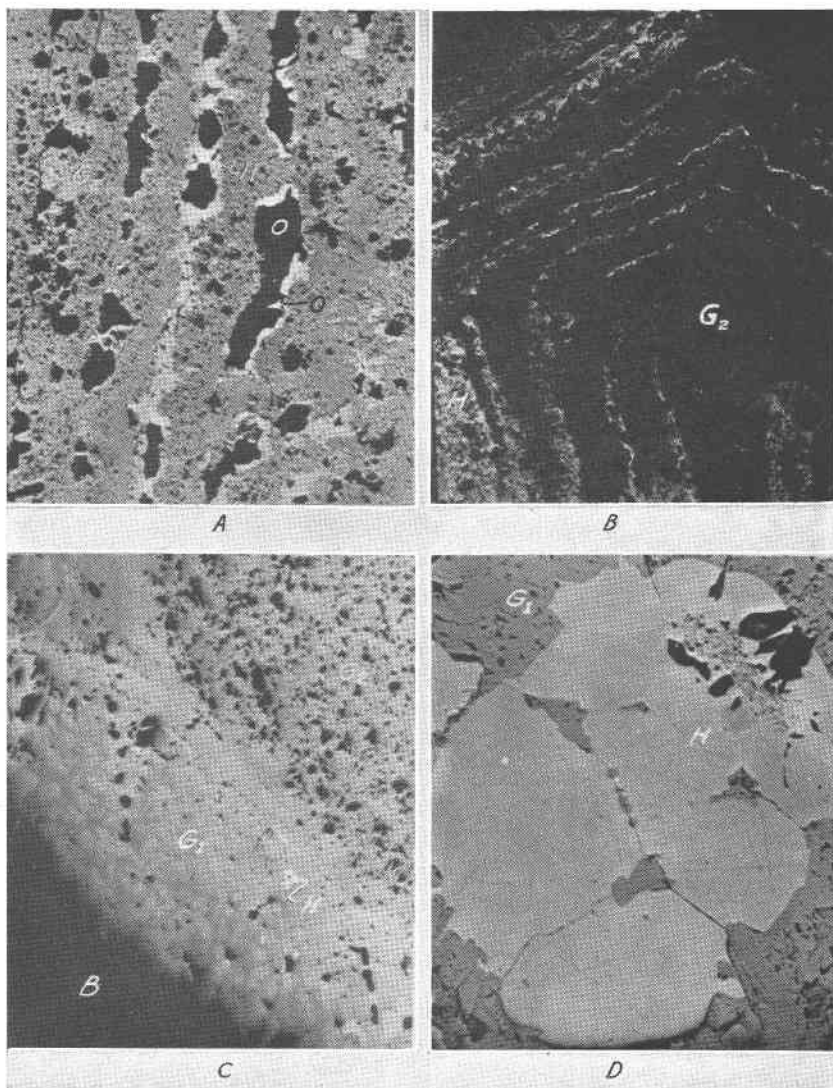


FIG. 3

A. Crystalline hematite (white) partly filling vugs in cryptocrystalline goethite. Plain reflected light. Enlarged 48 diameters.

B. Alternate bands of cryptocrystalline goethite (black) and hematite (white). The goethite is so porous that it has little reflectivity and appears black in the photograph. Plain reflected light. Enlarged 45 diameters.

C. Colloform shell of crystalline goethite lining balsam-filled vug in cryptocrystalline goethite. Same area as in Fig. 2, A. Plain reflected light. Enlarged 54 diameters.

D. Crystalline goethite is apparently replacing the irregular area of hematite along fractures. This is the only suggestion of replacement encountered in the polished sections of the east Texas ores. Plain reflected light. Enlarged 51 diameters.

the material is cryptocrystalline and has a strong purplish-brown to light brown internal reflection which completely masks anisotropism.

Oil immersion of crushed fragments shows that the goethite in the two inner zones is very pure, whereas that of the outer zone contains a large amount of impurity. Material from zone 1 contains less than one per cent of quartz; that from zone 2 not over one per cent of quartz and a trace of the glauconitic mineral; whereas zone 3 contains about 50 per cent iron stained quartz and a small amount of brown clay mineral.

Hematite is present in nearly every section examined. It occurs in all three zones, either as a filling in the vugs (Fig. 3, A) or as narrow bands alternating with goethite (Fig. 3, B).

PARAGENESIS

The paragenetic relationships between goethite and hematite in the brown iron ores of east Texas are not clear. In only one section is any evidence of replacement observed and this is not regarded as conclusive. (Fig. 3, D). This lack of definite evidence of replacement of goethite by hematite or vice versa seems to call for some process which would deposit both minerals contemporaneously or almost contemporaneously. Such a process is difficult to explain on physico-chemical grounds.

The lobate boundary that separates goethite areas of different texture, and goethite from hematite (Fig. 2, C) is a striking feature of the ores. Similar colloform structures have been interpreted¹⁰ as indicating original deposition as a colloid. The flamboyant structure of some of the colloform shells (Fig. 2, A) is believed to indicate subsequent recrystallization.¹¹ The banding of goethite and hematite in the outer zones (Fig. 3, B) appears analogous to banding in manganese oxides where it is believed to result from rhythmic precipitation.¹²

Dehydration may cause hematite to form from goethite and hydration may form goethite from hematite. If either process had been effective to an important extent in these ores it is believed that definite evidence of replacement would have been found. The evidence of contemporaneity offered by the polished sections combined with the field evidence that the ores have been formed by ordinary weathering processes under near surface conditions leads to the conclusion that both the hematite and goethite were deposited at ordinary temperature and that the determining factor was probably chemical.

¹⁰ Cooke, S. R. B., Microscopic structure and concentrability of the important iron ores of the United States: *U. S. Bureau of Mines, Bull.* 391, pp. 52-53, 1936.

¹¹ Cooke, S. R. B., *op. cit.*, pp. 53-56.

¹² Thiel, G. A., The textural relationships of the opaque manganese minerals in Fairbanks, E.E. and others: *Laboratory Investigation of Ores*, pp. 169-171, New York, 1928.

SUMMARY

The foregoing discussion shows that the relations of the iron oxide minerals of the brown ores may be effectively studied in polished sections. The first step in the study of the ores from a district should be the positive identification of the minerals present by means of x -ray diffraction patterns, or the measurement of refractive indices. Once it is known what minerals are present it is usually possible to recognize them in polished sections by ordinary methods.

Significant features of the east Texas ores are as follows:

1. The iron oxide minerals consist of about 80 per cent goethite and 20 per cent hematite. Lepidocrocite is absent. Quartz is the predominant impurity, but the total amount is not large.
2. The presence of both crystalline and cryptocrystalline goethite and hematite.
3. Roughly ellipsoidal structure characteristic of the iron carbonate concretions from which the brown ores have been derived.
4. Prominent colloform structure of both goethite and hematite.
5. Flamboyant internal structure of many of the colloform shells.
6. Banding of goethite and hematite, particularly in the outer zones.
7. Absence of definite evidence of replacement.

It appears that both hematite and goethite are essentially contemporaneous; that both were deposited at ordinary temperatures and that there has been little if any alteration of goethite into hematite, or of hematite into goethite.

This paper is presented with the hope of stimulating further interest in the investigation of the brown iron ores in order that their paragenesis may be definitely established.