Illinois Academy of Science Transactions, Vol. 45, 1952

ENVIRONMENTAL CONTROL OF IRON MINERAL DEPOSITION

N. KING HUBER
Northwestern University, Evanston

Many iron formations, including those of pre-Cambrian and of later ages, are generally believed to be of sedimentary origin. Many differences of opinion have arisen, however, as to the source of the iron for these deposits, the nature of the transporting medium, the nature of the depositional environment, and the primary minerals in the deposits.

Assuming that the high iron content of these formations is primary, it is possible that the present iron mineralogy represents to a large degree that of the original deposit—at least in the unmetamorphosed or only slightly metamorphosed areas. Many of these deposits can be divided into distinctive facies on the basis of their iron mineralogy. For example, Harold L. James has divided the pre-Cambrian iron formations in the Iron River district of Michigan into an iron sulfide, an iron carbonate, and an iron silicate facies, each of which he believes represents the primary iron mineralogy of that part of the deposit (James, 1951). If this is so, the present iron minerals should reflect the chemical environment of their original deposition.

One line of approach that might help in answering some of the problems concerning these environments is a study of the relations between equilibrium mineral associations that would be expected under postulated conditions of primary sedimentation, and the mineral associations actually observed in the field. Besides indicating the degree of equilibrium of the field relationships, such a study might shed some light upon the problems of the transportation of iron, the nature of the terrain from which the iron was obtained, and other problems concerning the genesis of iron formations.

EH-PH STABILITY FIELDS

The depositional environment of minerals precipitated from surface waters can be considered to have essentially constant temperature and pressure. In many such natural systems the chemical reactions involved may be characterized almost entirely by the hydrogen ion concentration and the oxidation-reduction potential, Eh, of the environment (Krumbein and Garrels, 1952). By considering the Eh and pH relationships of a postulated environment, the various mineral associations can be predicted and their fields of stability plotted on an Eh-pH diagram comparable to a temperature-pressure diagram. The assumption must always be made that the various minerals present in a given environment are in equilibrium with that environment. With some exceptions, the close agreement between expected mineral associations and observed field relationships indicates that natural systems are essentially equilibrium systems.

The Eh-pH stability fields have been calculated for hematite, siderite and pyrite in normal sea water and are shown in figure 1. They indicate that hematite is stable and will precipitate in oxidizing environments, siderite in intermediate or slightly reducing environments, and pyrite in strongly reducing environments. A position within any of the stability fields indicates that the activity product of only that mineral is exceeded and it will precipitate to the exclusion of the other minerals on the diagram. Furthermore, a mineral if moved from its stability field, by a change in Eh-pH conditions, to a field in which it is unstable, will tend to go back into solution or change in composition until equilibrium is again reached. The field boundaries for these iron compounds are essentially independent of the concentration of the components. For example, since the ferric-ferrous ratio is constant at a given Eh, increase in total iron would increase the amount of siderite or hematite precipitated but would not cause a change from siderite to hematite. A change in precipitation from one mineral to another will not take place unless there is a change in the Eh or the pH of the environment.

A series of experiments were conducted in which iron in the ferrous state was introduced into various Eh-pH environments (Huber, 1952). The experimental work indicated that hematite and siderite actually will precipitate under the predicted environmental conditions. The experiments also contributed to the evidence that sulfate cannot be reduced to sulfide in a strictly inorganic system, and therefore indicate the necessity of sulfate-reducing bacteria or other organic agents for the formation of pyrite. Regardless of organic activity, however, pyrite is not stable and cannot be formed unless the Eh-pH conditions lie within the pyrite stability field. The experimental work, therefore, supports the validity of predicting mineral occurrences on the basis of Eh-pH stability diagrams.

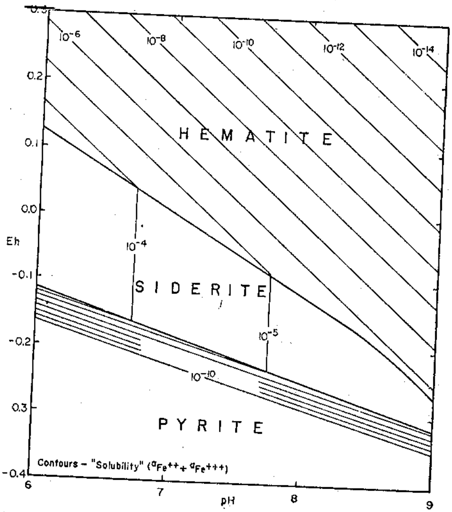

Fig. 1.—Eh-pH stability fields for hematite, siderite, and pyrite in sea water.

Transportation of Iron

One of the major problems in considering the genesis of iron formations is the transportation of iron to the depositional basins. Among the factors to be considered are the amount of iron that can be carried by streams and the state in which the iron is carried.

Iron can be carried in significant quantities in true solution only under rather restricted conditions. Reference to the solubility contours on the Eh-pH stability diagram shows that the conditions under which one part per million or more of iron ($>10^{-5}$ moles/liter) can be carried in true solution to be a pH of 7.5 or less and an Eh ranging from + 0.2 to — 0.15. Natural fresh-water streams are on the average neutral or slightly acid and thus satisfy this part of the environmental requirements. However, only under conditions of oxygen deficiency can the Eh requirements be met. It is possible that slow-moving, partially-stagnated streams draining noncalcareous terrain would have a great enough oxygen deficiency to carry large quantities of iron in true solution.

Iron carried in colloidal form is not subject to the same Eh-pH requirements as iron carried in true solution, and it is believed that most streams carry more iron in this manner than in true solution. However, in order to form extensive clastic-free iron deposits some mechanism must be provided to separate this iron from other colloids including clay minerals.

DEPOSITION OF IRON

Upon reaching a body of water, such as a marine basin, the iron in the streams emptying into that body of water will tend to conform with the new environmental controls imposed upon it. In marine waters the iron will be virtually completely precipitated and the iron minerals formed will depend upon the Eh and the pH of the environment.

Hematite should be precipitated if the environmental conditions are within the hematite field of stability, such as in a well-aerated basin, shallow enough to allow waves and currents to keep the water well-oxygenated. Ripple marks and oolites in some of the hematite beds are evidence of this type of an environment.

Siderite should precipitate if the environmental conditions lie within its stability field. The Eh limits of this environment vary somewhat with pH, but in the range from pH 7 to pH 8, which is likely in marine environments, conditions are moderately reducing, becoming more reducing with increasing pH. Such an environment might occur in a restricted basin deficient in oxygen. An environment slightly more acid than normal sea water would cause formation of siderite rather than calcium carbonate.

The environment under which pyrite is stable is one of moderate to strongly reducing conditions. However, as the reduction of sulfate is negligible in a low-temperature inorganic system, sulfate-reducing bacteria or some other agent producing hydrogen sulfide appear to be necessary for the formation of pyrite. Thus the optimum conditions for the formation of pyrite require a highly restricted anaerobic environment, such as a stagnant lagoon or euxinic basin.

SUMMARY AND CONCLUSIONS

In summary, a study of the theoretical and experimental relations between equilibrium iron mineral associations indicates that the environmental conditions for the primary deposition of these minerals can be delineated by Eh-pH stability fields.

Several general conclusions can be drawn from this study:

1. The experimental work shows that hematite and siderite precipitate under conditions predicted from Eh-pH stability relations.

2. The experiments also contributed to the evidence that sulfate cannot be reduced to sulfide in an inorganic system at low temperatures, and therefore indicate the necessity of sulfate-reducing bacteria or other organic agents for the formation of pyrite.

3. Iron can be carried in true solution in quantities greater than one part per million only under restricted conditions; pH of 7.5 or less and Eh values from + 0.2 to — 0.15.

4. Fresh-water streams, which on the average are neutral or slightly acid, can carry significant quantities of iron in true solution only if they are so deficient in oxygen as to maintain Eh in the range + 0.2 to — 0.15.

5. Present tropical streams carry large quantities of iron. If the streams are well aerated the iron must be carried colloidally. If the streams are partially stagnated iron can be carried in significant quantities in true solution.

6. If iron is carried colloidally, some mechanism is necessary for the separation of this iron from other colloids, such as clays, in order to form clastic-free iron formations.

7. Finally, it is suggested that iron made available by weathering processes and transported by slow-moving, partially stagnated streams, especially under humid-tropical or humid-subtropical conditions, is sufficient to form extensive iron-rich deposits. The iron minerals formed depend upon the immediate depositional environment rather than the form in which the iron is transported. The major factors controlling the minerals formed are the Eh and the pH of the depositional environment.

REFERENCES

Huber, N. K. (1952) A study of environmental controls of iron mineral deposition and their relation to pre-Cambrian iron formations: Unpublished master's thesis, Northwestern University

James, Harold L. (1951) Iron formation and associated rocks in the Iron River district, Michigan: Geol. Soc. Am. Bull., vol. 62, pp. 251-266.

Krumbein, W. C. and Garrels, R. M. (1952) Origin and classification of chemical sediments in terms of pH and oxidation-reduction potentials: Jour. Geol., vol. 60, pp. 1-33.