

Appendix A

DIAGENESIS OF IRON-RICH ROCKS

(Illustrated by the Role of Diagenesis in Oolitic Iron Ores)

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INTRODUCTION-DEFINITIONS

Because of its abundance in the earth's crust, iron is one of the major constituents of rocks and is always present, in varying quantities, in sedimentary formations. The diagenetic evolution, however, may be related to iron-phase changes only in iron-rich rocks. This is particularly true in sedimentary iron ores. It should be kept in mind, however, that the term "ore" is restricted here to iron formations that are economically minable, which implies meeting requirements such as location, thickness, and grade. Iron-rich rocks have more widespread distribution through geological scale and on the earth's surface than ores.

A major difficulty arises when an attempt is made to assign a definite sedimentary origin to ores. It is not sufficient for an iron formation to be interbedded in sedimentary rocks in order to assign a sedimentary origin to iron, because it may be introduced either by solution through replacement of host rocks (substitution type of iron deposits) or through magmatic injection (Kiruna type). The difficulty in assigning an unquestionable sedimentary origin in such cases is the fact that mineralogical changes that occur in iron-rich rocks are so destructive of pre-existent textures and structures that the various stages of evolution cannot be recognized.

Iron ores of sedimentary origin have many different physical and chemical properties and have been found in all types of rocks and from all stages of sedimentary evolution. Classically, four fundamental categories, which are presented in order of importance below, may easily be distinguished:

(1) The Lake Superior ore type, including low-grade banded ores, B.H.Q. taconites, etc., i.e., different iron-bearing formations (James, 1955); (2) the oolitic ores, with very varied parageneses; (3) the glauconitic ores; (4) the sphaerosiderite ores.

The stages of evolution undergone by the sedimentary iron ores before reaching the present state are numerous and varied. Attempts have always been made to understand the mode of formation by also trying to explain the apparent anomaly of the iron mineralization. The diversity of the proposed classifications reflects the complexity of the phenomena. If one attempts to distinguish the role of the main sedimentary processes and in

particular the role of diagenesis, however, it is necessary to study all the stages of transformation.

Many authors working mainly on considerably modified pre-Hercynian ores have often denied all possible effects of diagenesis, even of epigenesis. They explained the mineral associations solely by the processes of syngenetic precipitation during deposition. Taking into consideration the present state of knowledge, however, it is impossible to ignore diagenesis. It is an extremely important process, particularly in the case of iron, an element the chemical behavior of which varies greatly according to its ionic state. (See discussions in Grubb, 1971; Dimroth and Chauvel, 1973; Tsu-Ming Han, 1968.)

At present, after tremendous amount of studies, the ores of *Lake Superior type*, which are generally called "iron-formations", have still not been clearly related to the original state of deposition that remains conjectural. (See discussions and references in James, 1955; Gross, 1965.) The main contribution is in relative mineralogical changes that may be observed through morphological transformations and justified by mineral equilibria. To date, however, no complete balance from depositional to post-diagenetic stage has been determined for any one of those ores.

The importance of *sphaerosiderites* is mainly historical, because these ores were the mainstay of the British iron industry during the 19th century; but no new exploitation seems likely at present. Diagenetic segregation of the siderite from diffused material in clays appears to be the most common present interpretation (Williams et al., 1954; Kazakov, 1957).

The *glauconite iron* ore deposits that could possibly be exploited are very rare; however, the frequent occurrence of these ores has led to some research. The problems in this case are similar to those of the *oolitic ores* as they have many common features. These are mainly: (1) texture, (2) nature of associated minerals, and (3) depositional environment. The great peculiarity of these ores is that glauconite is of primary origin, and several hypotheses have been proposed to explain this. The oldest involves the activity of Foraminifera. Also the frequent association of glauconite with biotite led to the hypothesis that glauconite is a weathering product of biotite. Some Soviet authors assigned a diagenetic origin to this mineral in a slightly oxidizing environment (Krotov, 1952; Kazakov, 1957; also see Hower, 1961).

New categories probably will be added to this list. For example, personal observations convinced the author (Bubenicek, 1968) that in Kiruna ores many residual features may be explained by sedimentary processes, and that the actual state reached by this iron ore may be explained through metamorphic phenomena applied to a sedimentary formation. In the same way, the substitution type of iron ore, which is well illustrated by the Ouenza deposit in Algeria, leads one to believe in replacement of calcareous formation by

ferruginous brines at early stages of diagenesis.

The brief general survey presented here shows that the research is not sufficiently advanced to allow a satisfactory definition of the diagenetic history of the iron ore deposits, except for the oolitic ores. All possible evolutionary stages may be noted in the latter ores, which occur in all formations from the Precambrian up to the Lower Quaternary and through various stages of evolution between syngeneses and metamorphism. These stages have been studied in detail by Bubenicek (1968).

HISTORICAL REVIEW OF LITERATURE ON DIAGENESIS IN OOLITIC IRON ORES

In earlier publications on oolitic iron deposits, emphasis was placed on the process of diagenesis in the formation of the deposits, i.e., the concentration of the iron. Thus, numerous hypotheses have been proposed, involving mineralizing solutions and the replacement of pre-existing rocks. As a result of progressive accumulation of new data, however, it was concluded that the concentration of iron in a deposit is a phenomenon related to differentiations antedating the deposits. Many different genetical schemes have, therefore, appeared to explain the existing textures.

The role assigned to different processes by various authors varies a great deal and depends largely on which observational scheme is regarded as decisive. The different theories may be classified as follows:

(I) Iron has been concentrated and deposited during diagenesis. The iron (and silica) has been brought in by mineralizing solutions of various origins (marine, submarine, thermal springs, compactional fluids, etc.), with replacement of oolitic and calcareous detritus by iron solutions containing SiO_2 and Fe (Castano and Garrels, 1950).

(1) Without reworking phenomena: the different minerals were directly formed during the replacement processes (Arend, 1933).

(2) With reworking phenomena: the different mineralogical types were formed by oxidation during the reworking process (Cayeux, 1909, 1922; Deverin, 1945).

(II) Iron ore deposits resulted from a sedimentary differentiation process predating the deposit, i.e., predating sedimentation.

(1) With direct precipitation of iron along with other components at the bottom of the sedimentary basin.

(a) Direct formation of different iron ore minerals during precipitation. Formation of oolites in situ as a result of diagenesis. The mineralogical distribution depended on the distance from the shore line (Poustovalov, 1940; Caillère and Kraut, 1954, 1956; Braun, 1963; Petranek, 1964).

(b) Formation of oolites in situ in minerals having low iron content

(e.g., chlorite). Formation of limonite due to oxidation during a reworking stage, with detrital deposition of oxidized oolites. The siderite is considered by some authors to be of diagenetic origin (Berg, 1924, 1944; Hallimond, 1925; Bichelonne and Angot, 1939; Taylor, 1949; Krotov, 1952; Bushinsky, 1956. Without details: Braconnier, 1833).

(2) Formation of oolites in dynamic conditions before deposition.

(a) The oolites were formed directly from various mineralogical types of iron minerals prior to deposition: (i) as part of primary cement (Borchert, 1952); (ii) alone: cement or a few minerals only being of diagenetic origin (Popov, 1955; Tochilin, 1956; Courty, 1959, 1961; Formosova, 1959; Dunham, 1960; Teodorovich, 1961).

(b) The oolites are of an oxidized nature; different reduced iron minerals present are the result of diagenetic processes (Brown, 1943; Harder, 1951, 1957; Correns, 1952; Kolbe, 1958; Bubenicek, 1961, 1963).

These various hypotheses reflect the treading of a new path of research, as new data were obtained. Every genetic theory, however, should not only give an explanation of the facts, but also allow practical conclusions and inferences to be drawn. A brief review of the present knowledge on this subject is presented below.

PRESENT KNOWLEDGE OF THE DIAGENESIS OF OOLITIC FORMS OF ORES—CONDITIONS OF DEPOSITION

The data available at present leads one to believe that the sedimentary differentiation of iron is due to two main processes. The first one, of a pedological nature, is associated with the evolution of the continent. The second process takes place in the basin itself, where iron is precipitated and oolites are formed.

It appears that there is no direct relation between the influx of iron and the evolution of the basin. Because of the oolitic form, iron is deposited together with various detrital grains, mainly quartz grains or fragments of various shells. At this stage the last possible concentration of the iron takes place by variation of the relative proportions of detrital particles.

Consequently, there are deposits exhibiting primary structures of current-bedding and cross-bedding, which reflect current effects. In clay muds, penecontemporaneous deformation features, such as slumping and animal burrowing, are common. The conditions of deposition are such that the iron-bearing oolites contain the most oxidized form of iron (Fe^{3+}) in association with oxides of aluminium, phosphorus, and manganese.

The constant composition of the material precipitated in the oolitic envelopes (limonite) and the fact that generally in almost all known oolitic

iron deposits subsequent changes did not lead to the subtraction or addition of major components, allow a preliminary interpretation of the chemical composition of these ores.

Some conclusions can be drawn on the basis of the almost constant amounts of Al_2O_3 and P, along with the dominant iron, especially in the original limonite: (1) In the case of non-clay ores, Al_2O_3 and phosphorus contents¹ are proportional to the amount of iron (the more common $\text{Al}_2\text{O}_3/\text{Fe}$ ratio is 0.10–0.12 in Recent deposits and 0.05 in Paleozoic deposits). This is valid for all the iron contents, which depend on the degree of original dilution with quartz grains or calcite from shell debris; (2) An excessive amount of Al_2O_3 indicates clay ores.

DIAGENETIC EVOLUTION

Limits of diagenesis

When discussing diagenesis, it is always necessary to define the limits of this process, because of lack of agreement among various authors. The present author assigns to diagenesis all the processes which act on the sediment after the end of mechanical movements of the particles², whether during deposition or in seeking a mechanical stability through slumping, and in a milieu having lost all direct relation to the medium of precipitation. Thus, on the one hand diagenesis can start in fine clay sediments that are only a few millimeters thick, whereas in very permeable sands circulation of water coming from the water–sediment interface can preserve syngenetic conditions over a long period of time.

Generally, cessation of the mechanical movement of the particles involves isolation of interstitial solutions. The communication between the depositional environment and these solutions exists only through diffusion or by very slow circulation which depends on the permeability of the sediment and on possible ionic composition and charge differences. Circulation occurs on the beaches where the water of waves returns to the sea through the deposited sand³. When the exchange of matter with exterior is low, the

¹ For the whole ore body, taking into consideration the whole thickness of a layer, and not only sections where segregation phenomena could be involved.

² It should be kept in mind, however, that the “compactional diagenesis” involving movement of particles is very important. (Editorial comment.)

³ Cementation and/or solution occurring as a result of this process is considered as part of diagenesis by many authors. (Editorial comment.)

“closed milieu” conditions of evolution are approached.

The end of diagenesis is more difficult to establish. The present writer places it at the beginning of epigenesis, when hydrated minerals are transformed into less hydrated forms (e.g., limonite to hematite and silicates to micas) with compaction of the rock and loss of its permeability.

It is between these limits, in fact, that the oolitic iron ores acquire the essential characteristics of their mineralogical facies. Other transformations, however, may occur beyond this point as has been shown for metamorphosed ores, e.g., for hematite and magnetite type ores (see Bubenicek, 1965).

Role of diagenesis in the paragenesis of iron-bearing minerals

Nature of the diagenetic environment. The diagenetic environment mainly consists of two phases: (1) solid phase: the detrital sedimentary phase where the dominant iron-bearing components are present in the most oxidized forms; (2) liquid phase: the pore solutions filling the pore spaces between the grains or the micropores and microfractures of these particles.

These solutions are at first identical to those of the sedimentation environment (e.g., sea water). They are, therefore, rich in salts, organic matter and organisms of all kinds. As a result of lack of oxygen, the environment becomes progressively more reducing. This is usually associated with a notable change of pH through temporary acidification (see Bubenicek, 1964).

The diagenetic environment has a certain oxidation-reduction potential and capacity, which is a function of the quantity of the confined organic matter or its possible renewal through slow movements of solutions. At a given pH, there are organisms which are able to live under reducing conditions, in particular the sulfate-reducing bacteria. Furthermore, interstitial solutions contain an important reserve of a variety of different ions in variable concentrations. A new diagenetic environment is established more or less rapidly at various depths in the deposit, depending on the type of material and other conditions.

In order to define these ideas more accurately, one has to consider the level at which $Eh = 0$ with respect to the depositional interface:

(1) If the level at which $Eh = 0$ is within the sediment, its depth will depend on the conditions given above. In this case the changes in the sediment will be of a diagenetic nature.

(2) If the level at which $Eh = 0$ is above the top of the water-sediment interface, deposition of products by direct precipitation from solution could occur. In this case one may only apply the term syngeneses, as defined by sedimentologists.

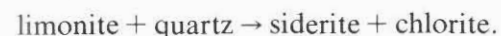
Nature of the transformations. The passage from one environment to another, having different physicochemical characteristics, results in a reorganization of the chemical elements in order to establish a new and more stable equilibrium. The previously-formed minerals become unstable and new minerals are precipitated in a stable form, accompanied by exchange of chemical elements (addition or subtraction) with the interstitial solutions.

The formation possibilities of the principal iron minerals were discussed by Garrels (1961), who defined the theoretical conditions of their stability (Fig. A-1). Although, theoretical, these diagrams show that all pH-Eh variations involve crossing of stability boundaries which occurs during diagenesis. The following should be noted, however:

(1) These diagrams should be expanded by adding areas where the mineral species can exist in a metastable state.

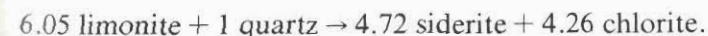
(2) The stability diagrams only give an imperfect picture of the reactions, because on assuming the existence of a closed environment the concentrations would vary in accordance with the displacement of the reactions. Consequently, threshold to other reactions would appear (Fig. A-2).

Main transformations. The main reactions which can occur, as already suspected on studying many deposits, have been confirmed by studies of the Lorraine iron ore deposits. The first fundamental reaction for the non-clay ores is:



The determination of the relative proportions of siderite and chlorite is made possible by the invariance of Al_2O_3 and iron contents and by the knowledge of the Al_2O_3/Fe ratio in the original limonite. This ratio is equal to 7/52 in the case of the Lorraine limonite.

It seems that this ratio is applicable to all Lorraine-type oolitic iron ores. Taking the average chemical composition of the phases given in Table A-I the reaction becomes:



These values only represent the first attempt to roughly estimate the proportions of the constituents. In this reaction, the retained constituents are Al_2O_3 , Fe, SiO_2 , Mn, and P; MgO and S are added, whereas H_2O is subtracted. The origin of the CO_2 is open to discussion; however, pyrite forms in the siliceous sediments where calcite is not abundant. This would suggest that at least this CO_2 is derived from the calcite, and that there would be a corresponding loss of CaO with the gradual destruction of the calcium carbonate.

Depending on the initial quartz/limonite ratio, the first threshold would

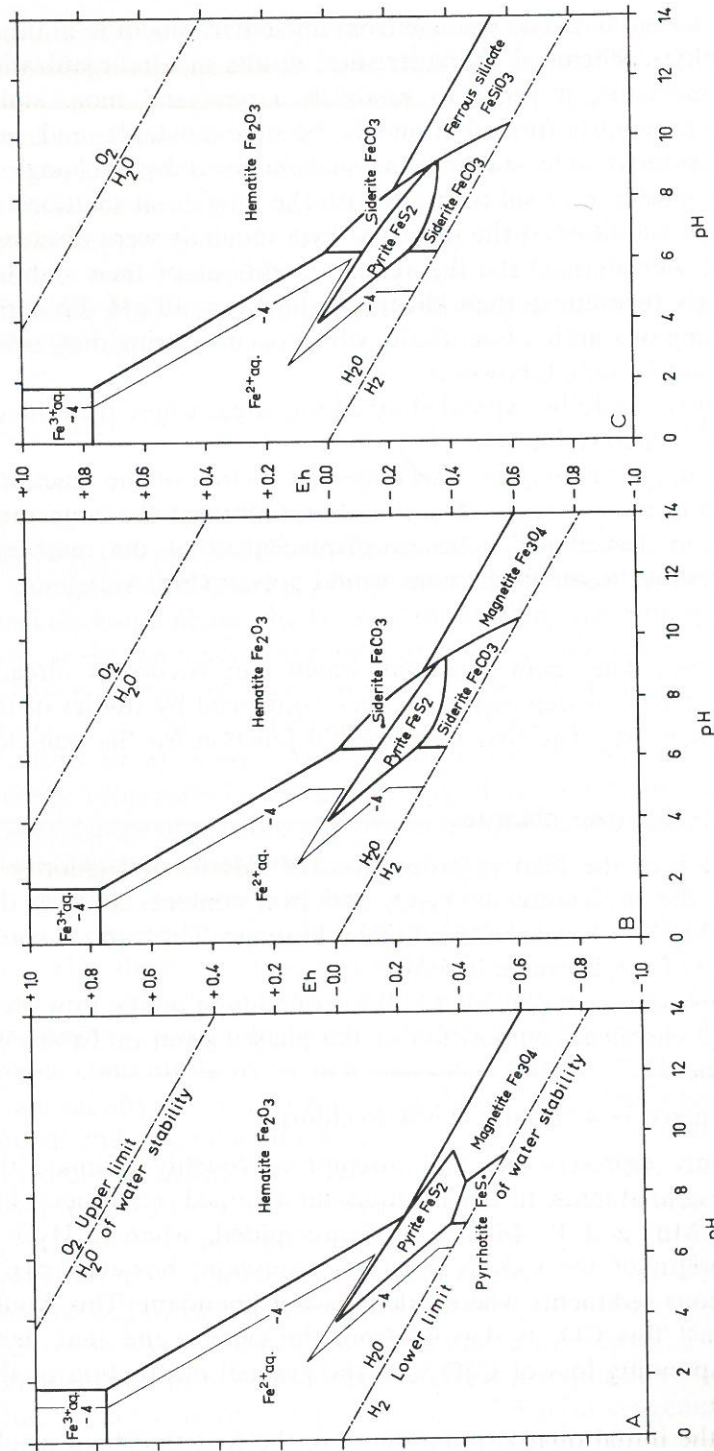


Fig. A-1. Stability diagrams of the main iron minerals under various experimental conditions; $T = 25^{\circ}\text{C}$; $p = 1 \text{ atm}$. (After GARRELS, 1961.)
 A. Absence of silica and CO_2 , $\Sigma S = 10^{-6}$.
 B. Absence of silica, $\Sigma \text{CO}_2 = 10^{-2}$, $\Sigma S = 10^{-6}$.
 C. Presence of silica, $\Sigma \text{CO}_2 = 10^{-2}$, $\Sigma S = 10^{-6}$.

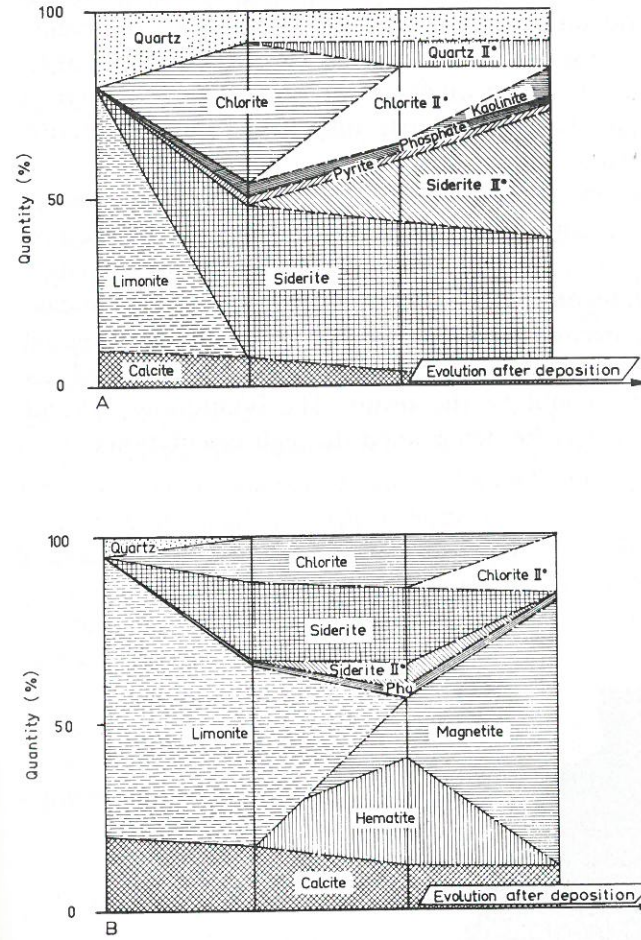


Fig. A-2. Diagrams of the evolution of limonite-quartz-calcite ores during diagenetic reduction. These ores have not undergone metamorphism. Lorraine, France; central Great Britain; Jurassic deposits of Germany, etc. (After Bubenicek, 1963.) A. Evolution when quartz is in excess. B. Evolution when limonite is in excess.

TABLE A-I

Chemical composition of the iron-bearing phases of the minette of Lorraine

	Fe	SiO ₂	CaO	MgO	Al ₂ O ₃	P	H ₂ O
Limonite	52.0	4.0	0.5	1.2	6.0	0.7	11.5
Chlorite	31.9	29.1	1.5	6.5	9.9	0.2	10.9
Siderite	37.7	—	5.3	5.6	—	—	39.2

appear when one of these components had been completely consumed in the reaction forming chlorite and siderite. New transformations then intervene: (1) In the case of excess of the limonite, there is formation of hematite, siderite and then magnetite. (2) When quartz is present in excess, there is destruction of the first generation of chlorite and formation of siderite, chlorite, and secondary quartz.

Equilibrium is reached when the limonite/quartz ratio becomes equal to 6.05. The various parageneses and their evolutionary relationships are presented diagrammatically in Fig. A-2. The limonite and the quartz transformations as a result of fundamental reduction reaction can cease in the case of exhaustion of reducing agent or of one or the other of the original components. If in the initial stage these two components are consumed, an excess of quartz or limonite would be the result. The boundaries beyond which new parageneses occur may be determined through calculations.



Fig. A-3. Calcite concretions. There is a continuity of the laminae between the concretion and the inter-concretionary ore. The inflection of laminae along contact with the two margins indicates a settling of the inter-concretionary ore material and increase in volume of the concretions during the process of CaCO_3 displacement; $\times 0.25$.

Role of diagenesis in modifying structures

As noted earlier, the primary and fundamental structures within the oolitic iron ores are current-bedding (most common) and contorted structures. Diagenesis can modify these structures in two different ways:

(1) By the general volume shrinkage due to the formation of more compact new minerals. This is followed quite frequently by the development of upright cracks, which can be filled mechanically.

(2) By change in the distribution of components (Fig. A-3), usually by segregation of some primary component (e.g., calcite) or of components produced during diagenesis (e.g., siderite and pyrite). These segregation phenomena correspond to the reorganization of the constituents, in order to reach a greater degree of stability. As Ramberg (1952) pointed out, due to surface-energy differences, the free energy of concretion material is lower when the material is concentrated than when it is dispersed. As the stability of a mineral increases with a decrease of free energy, this phenomenon is frequent for minor components (Seibold, 1955; Pettijohn, 1956).

Differences in structure or texture can control the arrangement of the concretions, which may be scattered in beds rich in concretions or may be perfectly localized and rounded. The presence of center of preferential attraction and the role of the permeability in the emplacement of concretions and aggregates should also be considered. It must be noted that migration of components may appear to modify the above rules at the level of individual samples.

ROLE OF DIAGENESIS IN THE FORMATION OF TEXTURES

The final texture of the rock reflects all of the above described changes and also those which arise as a result of metamorphism and the effects of meteoric waters, which largely tend to destroy earlier textures. Nonetheless textural studies alone often enable one to determine the history of the physical and chemical reorganization of the components. Three groups of textures due to three fundamental processes may be distinguished:

(1) Filling textures (cementation textures) due to displacement of material at the time of segregation. At the actual time of crystallization an increase in volume frequently occurs. On the other hand, in impoverished zones physical reorganization is brought about by compaction, quite often with breaking of oolites or plastic deformation. There is frequently secondary growth in the zones of enrichment and also sometimes of saturation, especially in the case of quartz.

(2) Solution textures are frequently associated with corrosion textures, and

the disappearing minerals are clearly different from the new ones. The disappearance can take place in a progressive or alternating way, as in the case of the transformation of oolitic limonite into chlorite.

(3) Growth textures are the fundamental textures which distinguish the growth (by precipitation of whatever origin) of a mineral at a given point and include:

(a) Incrustation: cementation on all minerals; the pores may remain open or may be filled completely (the most common case for chlorite; Fig. A-4).

(b) Corrosion: with the new mineral filling up gaps left as a result of the disappearance of destabilized minerals (frequent for siderite corroding quartz grains; Fig. A-5).

(c) Authigenic (with euhedral shapes): the mineral crystallizes into euhedral shapes and forces away the surrounding material. Siderite crystals could develop crystalline faces against clay minerals, but would only adjust their shape to that of an oolite or its envelope. At the interface between the authigenic crystal and the surrounding material, the effect is comparable to that of corrosion. Siderite shows this very often against clay minerals and

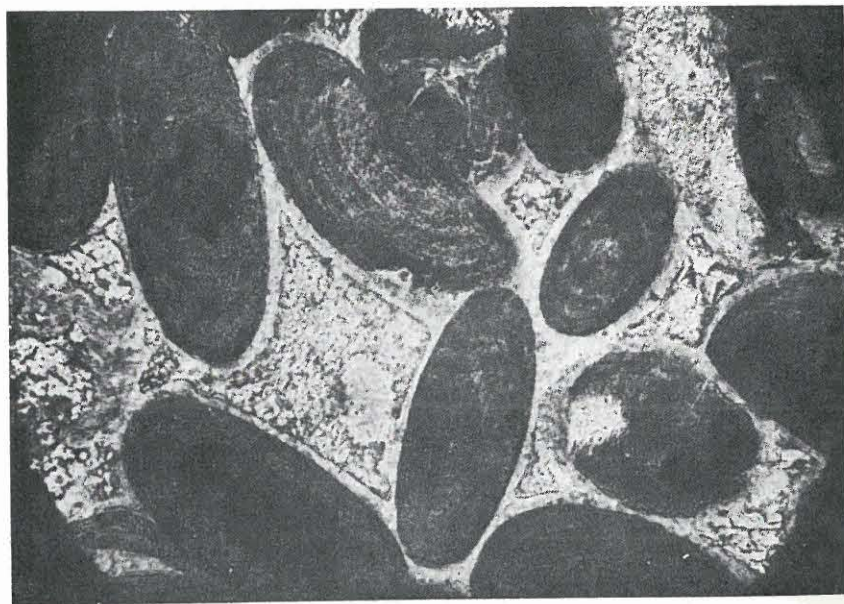


Fig. A-4. Development of chlorite from the limonite of oolites. Chlorite appears as a pellicular cement around the limonitic oolites. The advanced transformation of limonite into chlorite appears clearly on some oolites. Lorraine ore; grey bed=chlorite paragenesis; $\times 150$, natural transmitted light.

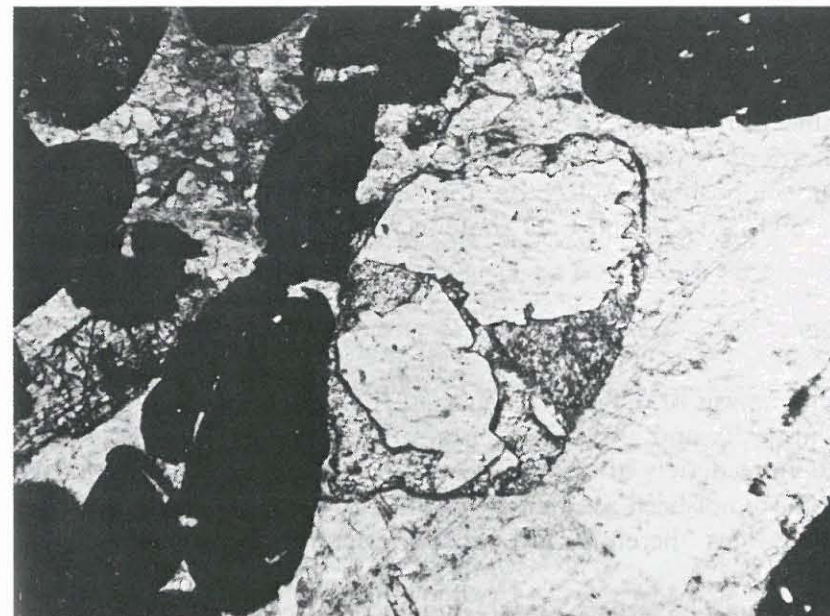


Fig. A-5. Corrosion of a quartz grain by siderite. The two residual areas of quartz show intended rounded outlines, and have the same optical orientation. The outlines of the quartz-siderite association preserve the shape of the detrital quartz grains; $\times 150$, natural transmitted light.

sometimes against calcite. In ores containing very small amounts of quartz, magnetite (euhedral grains) formed as a result of diagenetic reduction.

Effect of diagenesis on the chemical composition of ores

As indicated above, the diagenetic reactions which occur after deposition essentially do not involve exchange of the original Fe, Al_2O_3 , P and Mn in solid phase with interstitial solutions. At the most, the role of these solutions is to take part in displacements of material, which are considerable in the case of formation of concretions and slight in the case of authigenic mineral formation. It is different for other elements and compounds, which may indeed undergo exchange with solutions present in the pores of the rock. These include particularly MgO, H_2O , CO_2 , and CaO. The movements of these materials can considerably modify the mass relationships between the elements and greatly change the iron content of the ore. Thus, two ores with the same original iron content could be quite different if diagenesis affected them differently. In both cases, however, the relationships between the elements which were not exchanged will remain unaltered. This permits an

adequate comparison of different ores. In order to reduce them to identical conditions, it is advisable to compare them after an ignition loss test. The Fe^{2+}/Fe_{total} ratio is used to determine the evolutionary stage of the ore. In the case of the Lorraine ore, exact knowledge of the changes and of the minerals that are present, has permitted the calculation of the chemical and mineralogical compositions solely on the basis of the determination of Fe_{total} , Fe^{2+} , SiO_2 , Al_2O_3 , and CaO contents (Bubenicek, 1963).

CONCLUSIONS

The present analysis of the role of diagenesis in the formation of iron ores shows the complexity and also the intensity of the phenomena which affect the sediments immediately after their deposition. Many Mesozoic and Tertiary deposits have not been so intensely modified by epigenesis as the older formations and they, therefore, give a clear picture of the fundamental process of diagenesis.

All deposits which have been deeply buried or affected by an orogeny, and especially the older deposits, have been subjected to important modifications which frequently mask the earlier textures. It would appear, nevertheless, that the chemical characteristics established during diagenesis (particularly the reduction index Fe^{2+}/Fe_{total}) are preserved for a long time if the deposit has not been subjected to weathering, recent or ancient.

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