enetic alteration of goethite. Magnetite is produced by metamorphism of iron oxide or by generation of hydrocarbons (Young, 1993, p. 468). These results progressively destroy the concentric fabric and increase the proportion of iron oxide.

This mineralogy has to work from the present diagenetic or post-diagenetic results backward to an original deposit. Today identifying these ooids is advanced by the use of X-ray diffraction, transmission and scanning microscopy, Mössbauer infra-red spectra, backscattered electron imagery, and electron microprobe analyses. Clues to the problem are helped by analyses such as those by Hughes (1989), Kearsley (1989), and Mücke (1994). In the Late Devonian Wadi Shatti ooids of central Libya (Turk et al., 1980, Fig. 16–27) the diagenetic and post-diagenetic results are illustrated, including siderite, magnetite, and maghemite.

Recent ooidal ironstones

Most of the Recent ferruginous green or brown granules are peloids, some of which are faecal pellets, such as the ones from the shelf off Trinidad, Venezuela, and Guiana of South America, the one from the Loch Etive in western Scotland, the ones from the shelf off Senegal, Guinea, Nigeria, and Gabon of Africa, and the one from the shelf off Sarawak (Odin, ed., 1988), as well as peloids from interdistributary area of the Mahakam Delta in eastern Kalimantan, Indonesia (Allen et al., 1979). So far only a few Recent sediments have yielded iron-rich ooids. These are described briefly.

Ooids accumulated in some sediments in the southernmost Lake Malawi in Malawi (Muller and Forstner, 1973). Geothermal springs erupt along the lake. The ooids were encountered in a grab sample. The surrounding sediments are sand and gravel. The ooids contain amorphous hydrous feric oxide and opal, commonly with a superficial shell of nontronite. The ooids chemical composition (%): Fe_2O_3 50.5, FeO 0.21, SiO_2 20.4, Al_2O_3 3.2, CaO 0.84, MgO 0.31, MnO 0.31, P_2O_5 0.82, TiO_2 0.15.

Ooids accumulated in shallow, brackish open water areas north of the Chari delta in southern Lake Chad in western Chad (Lemoalle and Dupont, 1973). The deposits are surrounded by mud. The brown ooids contain goethite and nontronite (Pedro et al., 1978). The average chemical composition (%): Fe_2O_3 34.5–49.5, SiO_2 33.0–45.2, Al_2O_3 1.75–4.0, CaO 1.18–1.69, MgO 1.05–1.69, MnO 0.11–0.40, TiO_2 0.09–0.23.

Ferric-rich ooids and peloids are deposited in a very shallow sea along the coast of Cape Mala Pascua in northern Venezuela (Kimberley, 1994). The region lies in an eastward fault zone in the coastal range. The pale green to brown ooids are enclosed in greenish mud. The ooids contain ferric silicate odinite-endmember berthierine. Their chemical composition (%): FeO 6.89–7.55, Fe_2O_3 16.22–23.49, SiO_2 25.70–29.72, Al_2O_3 4.76–5.04, CaO 1.97–8.72, MgO 10.89–12.97, MnO 0.02, P_2O_5 0.17–0.26, TiO_2 0.08–0.10.

Further research on these Recent iron-rich ooids and their origin is of primary significance.

Some problems of origins of ooidal ironstones

Time and space

Ooidal ironstones and their equivalents occur in all Phanerozoic periods. Yet some intervals exist that are noted for their conspicuous ferruginous accumulations (Strakhov, 1947; Van Houten and Bhattacharyya, 1982). Very significantly increased deposition of ooidal ironstones falls into (1) Ordovician and the subsequent part of Silurian, (2) Devonian, and (3) Jurassic-Cretaceous. On the other hand, long intervals also exist that are lacking major accumulations of ooidal ironstones. This applies especially to Carboniferous, Permian, and Triassic. Why? The rivers were steadily bringing iron from land into the aqueous basins and oceans, and the atmosphere and hydrosphere did not differ substantially from the preceding or succeeding periods. Neither organic life that witnessed such a notable expansion on land in Carboniferous time could have hardly been a sufficient reason for such a radical restriction of ferruginous deposition. The acid waters of extensive swamps should have provided conditions for enhanced leaching of iron from regoliths and subsequent transportation of iron into the depositional realms, but the content of CO_2 in the Carboniferous atmosphere (Berner, 1990) was low.

Source of iron

The source of iron has usually been sought in the weathering processes upon land, especially in tropical climate and the subsequent introduction of iron by rivers into seas and oceans, mostly in the adsorbed form (adhering to clay and other particles) or as colloidal suspensions. In the present writers' opinion only a small portion of iron can be ascribed to hydrotherms issuing upon the ocean bottoms or to submarine weathering and leaching of basic lavas and their pyroclastics. Opposite view is held by Kimberley (1989) who assumes that iron formations are attributable to submarine exhalations of fluids and the origin of ooidal ironstones specifically is attributed by him to hypersaline fluids which have risen to marine bottom along deep faults. According to Stakhovitch (1986), the iron of European Mesozoic and Cenozoic ooidal ironstones had been brought by hydrothermal ore-bearing solutions rising during the active phase of continental rifting.

Some authors seek the source of iron in the sediments underlying the ooidal ironstones (for example Aldinger, 1957; Lipayeva and Pavlov, 1986). The interstitial solutions enclosed in the underlying sediments (for example in petroliferous basins; Pavlov, 1989) rose to the sediment/water interface where their iron became bound in the ironstone. According to Borchert (1964), iron had been leached out from sediments in a "CO_2-zone" situated between a near-surface oxygenated zone and the deeper lying H_2S-zone.

The conspicuous and frequent association of ooidal ironstones with black shales may be an indication of some genetic relationship of ooidal ironstones with anoxia (for example Van Houten and Arthur, 1989). The microbial and other diagenetic processes affecting the clayey sediment, rich in organic matter and deposited in deltas, lagoons, and stagnant anoxic basins, lead to mobilization of iron – i.e. to the transformation of insoluble Fe^{3+} constituents to Fe^{2+} solutes. Under specific conditions, especially when coupled with upwelling, iron could have even been transported from relatively deep areas of anoxic sedimentation to the sites where generation of ooidal ironstones may have taken place. According to this hypothesis (Petránek, 1991) the anoxic sediments could have acted as very important sources and temporary storage sites of huge quantities of iron.

Origin of ooids

The actual origin of ferruginous ooids is a subject of long-lasting discussion. The initial view, namely that the ooidal ironstones formed by metasomatic ferruginization of ooidal limestones (Cayeux, 1909; Kimberley, 1979) is untenable, although in restricted extent the ferruginization of carbonate particles took place. The earlier concept of ooids growing in the state of suspension, in an agitated, high-energy aqueous environment, by precipitation of mineral substances upon suspended mineral grains, finds less and less support. According to the prevailing view the ferruginous ooids grew (1) upon the marine bottom, at the water/sediment interface (a) by concentric growth (addition, precipitation) of mineral matter, frequently upon heterogeneous nuclei, (b) by mechanical accretion of the snowball type, by rolling on the sea floor, or (2) by intrasedimentary growth inside the sediment at shallow depth below the water/sediment interface (a) as early diagenetic micro-concretions or (b) by replacement or addition of iron to peloids. Another problem still to be solved is whether these ooids grew from solutes, colloidal solutions or gels.

The growth of ooids could have been significantly promoted or even caused by microorganisms such as bacteria, primitive algae and the like. Traces of microbial activity in ooids have been reported for some time, but the extent of microbiotic processes and their role in ooid formation deserve further research.

As shown, different views exist concerning the origin of ooids but they deal mostly with physical aspects of ooid growth. Much less attention is being paid to chemical prerequisites for the particular ooid generation. The principal question is whether the needed iron in the generating environment existed in the form of a true solute (only Fe^{2+}, mainly as bicarbonate, can migrate as a true solute but can survive only in an oxygen-free reducing environment) or as dispersed colloidal particles or as various complex constituents (for instance soluble humates).

Iron incorporation and ferruginization as well as other forms of mineralization of various sedimentary substances and particles are of considerable importance for understanding the generation of ferruginous ooids. In this respect much attention is being paid to clay minerals, namely along three lines: (1) natural synthesis of iron layer silicates in different sedimentary environments, (2) transformation of non-iron-bearing phyllosilicates into iron-bearing ones (ferruginization of argillaceous muds), and (3) the role of iron-rich, green, trioctahedral clay minerals of warm seas as possible precursors of later ooidal minerals (for example Bhattacharyya, 1983; Harder, 1978, 1989; Odin, 1988; Odin and others, 1988; Van Houten and Purucker, 1984). These problems are closely connected with the detailed elucidation of berthierine generation. What physico-chemical conditions determined the growth and occurrence of berthierine? Was it precipitated from a gel or solute? Is it a product of transformation of a mixture of kaolinite with hydrous ferric oxide or was it generated by complex synthesis of silicic, ferric and aluminous substances? Is it a product of transformation of peloidal substances such as faecal pellets? What were the conditions of generation of berthierine ooids versus berthierine cement which is cementing ooids of varied composition?

All theories explaining the origin and growth of ferruginous ooids must comply with the observed fact that ooids are commonly built of alternate ferric oxide and berthierine-rich sheaths of submicroscopoic thickness (Bhattacharyya and Crerar, 1993). Can such common alternation of ferric and ferrous sheaths be derived from high frequency changes of oxidation-reduction potential? Or were these changes less frequent and the growth of ooids must have been very slow and long-lasting process? As the ooids were often thoroughly reworked and redistributed, their growth interrupted and renewed again, and as the ooidal ironstones often represent condensed sequences, it is difficult to assess the real age of ooids in terms of growth rate.

Site of generation versus site of deposition

All genetic interpretations necessitate a careful distinction between the site of ooid generation and the site of their deposition. These two sites may be identical, but they frequently differ. The loose, shallow marine ooids were namely very sensitive to all sea level oscillations, were easily eroded, reworked, and redeposited as evidenced by their common wear and fracturing, their conspicuous sorting or sometimes observed occurrence in the form of well sorted ooidal bars paralleling the coasts.

Deposition of ooidal ironstones in epicontinental conditions, not far from the coastline, gives rise to an uncommon idea of ooids having been formed on land and only later introduced into the marine environment. Siehl and Thein (1989) maintain the view that the ferruginous ooids originated on land in the course of lateritic weathering and were subsequently freed from soils, transported, sorted and finally deposited in the marine environment. Supporting the pedogenic hypothesis would be a frequent existence of ooidal ironstones laid down in lacustrine and fluvial environment. To the authors' knowledge one of the very few undoubtful fluviatile deposits is known in southwestern Kazakhstan (Formozova, 1959), in the northern vicinity of the Aral Lake.

Thanks to the Russian participants of the IGCP Project 277 who organized in 1992 an excursion to the Aral Lake region – forbidden to foreigners until recently – both present authors had the priviledge to be among the first four foreign geologists ever to see the local Late Oligocene deposits of marine, deltaic, and fluviatile origin.

The local fluviatile deposits are secondary accumulations of loose, very fine and well sorted goethite ooids laid down in river beds and derived from destruction of nearby, not yet lithified sediments enclosing ferruginous ooids and their deposits. Similarly the possibility of reworking of ferruginous ooids from unlithified earlier sediments is to be taken in consideration when interpreting the lacustrine and deltaic occurrences. Recent and subrecent ferruginous ooids have been reported for example from African lakes Chad and Malawi, Gulf of Guinea, from Mahakam Delta in Kalimantan, and off the northern coast of South America.

Diagenetic transformation and neoformation

Any study of mineral constituents must be closely connected with the study of diagenetic processes. There exists an omnipresent question – what was the original constitution of ooids? Were they of ferrous nature, that is reduced, containing minerals with essentially bivalent iron such as berthierine, or were they of ferric nature containing predominantly trivalent iron as hydrous ferric oxide? The state of iron represents a very useful tool for deciphering the oxidation potential, and this applies to both primary and neoformed minerals constituting the ferruginous ooids (mainly goethite, hematite, iron phyllosilicates, siderite, and magnetite). At an early stage some of these minerals must had been hydrous and very sensitive to changes of oxidation potential. They may have repeatedly changed their oxidic or reduced nature in response to changing depositional and environmental conditions such as reworking, redeposition, effects of oxygenated open shallow water, reductive effects of both anoxic waters in local deeps and microbial activity and organic carbon enclosed in argillaceous sediments burying the ooids.

The very first changes could have resulted from the reworking of ooids. For example, the original berthierine ooids succumbed to oxidation in the well oxygenated, high-energy marine environment. Similarly, following the final deposition, the diagenetic processes could have completely obscured the initial nature of ooids. For instance, the hydroxidic Fe^{3+} of ooids could have been reduced and iron thus freed became bound in neoformed siderite impregnating both ooids and matrix. This process leads to simultaneous unveiling of the hitherto masked phyllosilicate constituents in seemingly pure hematite or goethite ooids (Petránek, 1964c). Thus, both oxygenated waters and reductive anoxic waters as well as reductive nature of the organic matter and sediment enclosing ooids, are the essential factors controlling the valence of iron. i.e. the mineral composition. The diagenetic transformation of ooids is sometimes of isochemical nature: despite changes in mineral composition the bulk of major as well as minor elements does not change essentially. The diagenetic and post-diagenetic processes, so profoundly affecting the ooidal ironstones, are numerous and complex. They include, among others, reduction of Fe^{3+} to Fe^{2+}, neoformation of Ca-phosphate, sideritization, neoformation of hematite, goethite, magnetite, berthierine cement, iron-rich carbonate cement, iron-poor carbonate cement, neoformation of pyrite and quartz (see e.g. Cotter 1992, Harder 1989, Petránek 1964a, c, 1988).

On the other hand, Stakhovitch (1986) denies the importance of diagenesis and explains both the vertical and horizontal changes of mineral composition within the orebodies by changes of temperature, Eh and pH of iron-bearing hydrothermal solutions; as a result, the ironstone deposits show in his view the same hypogene zonality as the post-magmatic ore deposits.

In the post-diagenetic period intense weathering as well as the descending meteoric waters may also considerably affect the composition of ooidal ironstones. According to Mücke (1994), the meteoric waters, enriched in iron by destruction of pyrite and/or marcasite in the overlying strata, are responsible for ferruginization of ooidal ironstones: ooids, originally of berthierine nature, are thus changed into goethite or hematite ooids. No doubt exists that neoformed goethite or hematite may obscure the phyllosilicate nature of many ooids but is it justified to consider all oxidic ooidal ironstones to be the products of ferruginization by meteoric waters?

Genetic relationship to transgressions or regressions

Majority of ooidal ironstones shows some relation to eustatic variations (for example, Young 1989b). Most of the ooidal deposits occur either toward the close of the regressive or in the earlier part of the transgressive phase of a sedimentary episode or cycle. As a result, two principally contradictory schools of thought exist, namely: (1) the ironstones are tied to regressions, or (2) the ironstones are tied to transgressions. It has to be noted that both views are supported by sufficient and indubitable stratigraphic evidence based on the position of concrete ooidal ironstones within a particular sedimentary sequence.

Although the retreating sea could have also generated environments favourable for the growth of ferruginous ooids not much probability exists that some characteristic and distinctive physico-chemical conditions specifically promoting the ferruginous deposition existed during the regressive phases. On the contrary, the ooidal ironstones laid down in shallow marine environments were very early affected by the retreat of the sea, became subjected to destructive wave activity and later, when subaerially exposed, were affected by erosion and denudation. Many of the exposed sediments were still insufficiently lithified and their ooids became released from the parent sediment, reworked, sorted and redeposited together with coarser clastic material of undoubtful regressive nature. The ooids may have undergone repeated reworking and may recur several times in the regressive suites. Thus, not only the regressions but also minor regressive episodes could have been decisive for the location of ferruginous ooids, but not indispensable for their growth.

In other cases the growth of ooids has been indubitably promoted by transgressions especially when extensive flooding affected a flat and low-lying land. Its regolith may have become an important source of iron as well anoxic sediments releasing iron solutes in the newly-formed marine depressions and local basins while the sites of detrital input were shifted faraway landward.

As the global rise and fall of sea level has been repeated with some degree of cyclicity during certain time intervals, the expression of cyclicity (Milankovitch patterns) had also been sought among ironstones in major sedimentary basins. Such cyclical patterns different in foredeep, or unstable craton, and in intracratonic basins have been reported by Van Houten (1986).

Input of clastics and redistribution

Restricted input of clastics has long been considered a prerequisite for deposition of chemical sediments of any kind. Recently this has been again emphasized by Bhattacharyya and Crerar (1993) conditioning the sedimentation of ooidal ironstones "during periods of lowest detrital input". However, the thickness and rate of deposition of stratigraphic equivalents of many ooidal ironstones do not correspond to periods of lowest detrital input. Similarly, condensed deposits of starved basins are not restricted to those periods. The dominant factor seems to be the local hydrodynamic conditions and especially the topographic relief of land and sea bottom, protecting the ooidal deposits from excessive dilution by clastics of any kind. This protection was of importance especially in the later evolutionary stage, when majority of ooids already existed and the ooids were being reworked (sorted, redistributed) and laid down. On the other hand, the site of ooid generation had not necessarily to be unusually impoverished in clastic material as evidenced by quartz and other clastic particles commonly occurring as nuclei of ooids.

Reworking of ooidal sediments in a shallow-water environment often leads to separation of ooids, their concentration and a very high degree of sorting. Such deposits may form elongated lenses subparallel to the coast, and sometimes laid down in shallow depressions protected by submarine elevations or sills from further destruction or dilution by input of clastic material. On the other hand, where the ooidal ironstone is less affected by redistribution and can be followed from the shallows basinward, a zonation of ironstone types may locally be observed. For instance, ironstone with concentrated hematite ooids leads to mottled type with clusters of hematite and partly leached (dehematized) ooids in a pelosiderite matrix and finally to argillaceous siderite enclosing dispersed, small and squeezed, spastolithic phyllosilicate (illite) ooids (Petránek, 1964c).

Ooidal ironstones and evolution of the Earth

We do not know very typical and major deposits of ooidal ironstones in Recent sediments. Their absence cannot be considered as unusual since through out the Phanerozoic time long intervals existed without any significant and extensive deposition of ooidal ironstones. Whatever evolution the Earth may have undergone during the Phanerozoic concerning the biosphere, atmosphere, hydrosphere, climate and tectonism, no marked and undisputable reflections of those evolutionary changes were sofar detected in the nature of ooidal ironstones. This should be borne in mind when considering the evolutionary background for the notable change in the deposition of iron at the Proterozoic-Phanerozoic transition, with general occurrence of banded iron formations in the Precambrian and of ooidal ironstones in the Phanerozoic sequences. The time boundary between the two is conventional and only approximate since banded iron formations are common in rocks older than $2x10^9$ years and rare among younger ones (Cloud, 1983). Disregarding ooidal precursors in Precambrian and occurrences of rare banded iron formations in Paleozoic, these two different kinds of ferruginous deposits in typical form almost exclude each other in terms of geological time. Though the change of the Precambrian to Phanerozoic ferruginous deposition is marked and provocative, no unequivocal and generally accepted explanation exists, despite all progress in our science. The enigma of differing depositional parameters steadily fascinates the researchers for both economic aspects involved and scientific attraction.

Evolutionary changes of the depositional environments led Formozova (1962) to assumption of a transition of the ferruginous sedimentation from original deep sea to shallow marine conditions in the course of geological history, namely around the Early/Late Paleozoic transition. This view had been opposed by Petránek (1964b) and the majority of typical ooidal ironstones is nowadays considered of shallow marine origin.

The seemingly erratic occurrences of ooidal ironstones in the Phanerozoic can have solely one explanation – ferruginous deposition could have taken place only as a result of interplay of several positive factors. Trying to explain the generation of ooidal ironstones by application of a single factor, such as salinity of the seawater, composition of the atmosphere and its content of carbon dioxide and oxygen, biotic evolution and interaction of specific organisms, availability of dissolved or precipitated iron compounds, climatic conditions both of seasonal or long-lasting and cyclical nature, unusual physico-chemical conditions, specific depth parameters of the marine environment, changes of diagenetic processes in dependence upon the depth of burial and nature of sediments enclosing the ooids, hydrothermal input of iron, tectonism, and the like, and the ensuing generalization are doomed to failure. The only possible way to solve this problem, or rather to arrive to several plausible hypotheses, is a careful analysis of a great amount of both descriptive (i.e. objective) and genetic or other interpretative data. The hope may be expressed that