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**Autor:** Gehring, Andreas U.  
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# A microchemical study of iron ooids

By ANDREAS U. GEHRING<sup>1)</sup>

## ABSTRACT

Iron ooids were investigated using optical microscopy, scanning electron microscopy and energy dispersive spectrometry. Goethitic ooids showing a typical concentric array of different chemical phases were subjected to microprobe analysis. The mode of formation of these ooids is explained by a two step model. In contrast iron ooids which show a relatively homogeneous distribution of the main elements cannot be classified by a unique process of formation.

## ZUSAMMENFASSUNG

Eisenoide wurden mit dem Durchlichtmikroskop, Raster-Elektronenmikroskop und einem energiedispersiven Röntgenanalysator untersucht. Vor allem goethitische Ooide, die aus unterschiedlichen chemischen Phasen in konzentrischer Anordnung aufgebaut sind, wurden mit der Mikrosonde analysiert. Für die Bildung dieser Ooide wird ein Modell vorgeschlagen. Eisenoide mit einer relativ homogenen Verteilung der wichtigsten Elemente lassen sich nicht in einem einheitlichen Bildungsmodell zusammenfassen.

## Introduction

Microchemical investigations of iron ooids have been rather sparse. Recent examples include BHATTACHARYYA & KAKIMOTO (1982), ROHRLICH (1974) and HALBACH (1968).

In general, iron ooids can be divided in two groups according to their mineral composition. One group contains chamositic (clay-iron oxide-rich) ooids, the other goethitic (iron oxy-hydroxide) and haematitic (iron oxide) ooids. Some iron ooids consist of alternating goethitic and chamositic laminae.

The aim of this paper is to report microchemical data of both types of ooids in order to establish a correlation between the chemical properties and the mode of formation.

## Samples

The samples of iron ooids for the present study were collected from several classic European localities ranging in age from the early Jurassic (Toarcian) to the late Jurassic (Oxfordian) (see Table). The following summaries impart aspects from each locality:

1. The samples were taken from iron-oolitic sediments from the middle/upper Jurassic boundary of the Jura region in northern Switzerland (GYGI 1969; ZIEGLER 1962). The

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<sup>1)</sup> Geologisches Institut, ETH-Zentrum, CH-8092 Zürich.

beds are often highly condensed, with a very rich ammonite fauna, and contain a variable percentage of clay-iron oxide-rich and/or ferric oxy-hydroxide ooids set in a micritic matrix. These beds are characterized by hardgrounds, hiatuses and reworking.

2. Iron ooids from the south coast of England occur together with carbonate-rich, iron-hydroxide concretions ("snuff boxes") (GATRALL et al. 1972) in a stratigraphically condensed bed. The iron ooids are goethitic in a calcareous or marly matrix.
3. Ooids from southern Germany, Luxemburg and Northamptonshire (England) were collected in disused, open pits. All these deposits can be described as minette-type ore, consisting characteristically of clay-iron oxide-rich or iron oxy-hydroxide, iron oxide ooids set in a sideritic-chamositic, calcareous, marly or sandy matrix (c.f. THEIN 1975; HALLAM 1966; URBAN 1966). The sedimentary structures of the different deposits often display a cyclic pattern, which can be explained by transgression and regression or by migration of sand waves of a slowly prograding shoreline (TEYSSEN 1984).
4. Samples from W. Scotland derive from the Raasay ironstone (kindly provided by D. Martill, University of Leicester).

Table: *Sample locations and pertinent field description references.*

No.	Stage	Locality	References
1	Calloviaian/Oxfordian	Northeastern Switzerland Northeastern Switzerland	GYGI (1969): profiles No., 33,51 ZIEGLER (1962): profile No. VI/94
2	Aalenian/Bajocian	Southern England Westbay, Dorset	GATRALL et al. (1972)
3	Aalenian	Southern Germany Kahlenfeld, Ringsheim	URBAN (1966)
	Toarcian/Aalenian	Luxemburg Hunnegfeld, Niedercorn	THEIN (1975); TEYSSEN (1984)
	Toarcian/Aalenian	Northamptonshire, England Cowthick quarry, Corby	TAYLOR (1951); HALLAM (1966)
4	Toarcian	Western Scotland Dun Strath Elogl, Skye	Collection University Leicester, spec. 255575

## Methods

Thin sections were first examined by light microscopy. After polishing, the same thin sections were analyzed as follows with a JEOL JSM 840:

a) ordinary scanning electron microscopy (SEM);

b) X-ray scanning photography with an energy dispersive spectrometer system (EDS) connected to the SEM (EDAX). X-ray area scans show the distribution of atomic constituents in the observed field and therefore yielding element distribution images.

In addition, semiquantitative electron microprobe analysis (EMA; type: SEMQ ARL) was performed on selected ooids.

Mechanically isolated ooids were pulverized and subsequently analyzed as methanol based smear slides using an X-ray powder diffractometer (XRD) (Philips X-ray generator PW 1130/00/60, 40 kW, 25 mA; proportional detector probe 1965/20/30) in order to determine the crystalline mineral composition.

### Results and discussion

Under the light microscope the iron ooids display a shell-like, concentric structure (Fig. 1a). The shape of the goethitic ooids examined is greatly influenced by the form of the nucleus. The nuclei can be of various origin e.g. fossil fragments, quartz grains or other iron ooids. In contrast chamositic ooids often display an indistinct nucleus and frequently exhibit nonconcentric, diagenetic changes, e.g. shrinkage or textures. For example, chamosite commonly transforms into siderite (see TAYLOR 1951, p. 81). Such chemical and physical changes are rare in goethitic ooids.

In general, the distribution of the main elements (Fe, Al, Si) in chamositic ooids is rather homogeneous, but can be inhomogeneous as a consequence of diagenetic or weathering processes. Recent chamositic pellets from Loch Etive (Scotland) show a less homogeneous distribution of Al and Si. This lack of homogeneity can be explained in terms of their mode of formation (ROHRLICH 1974). According to BHATTACHARYYA (1983) chamosite is produced mainly by a transformation process whereby detrital kaolinite accumulates Fe and releases Al and Si. The degree of alternation of the detrital precursor influences the elemental distribution.

Goethitic ooids from the minette-type ore of Luxemburg and southern Germany commonly consist of a fine-grained mixture of different mineralogical phases, for in-

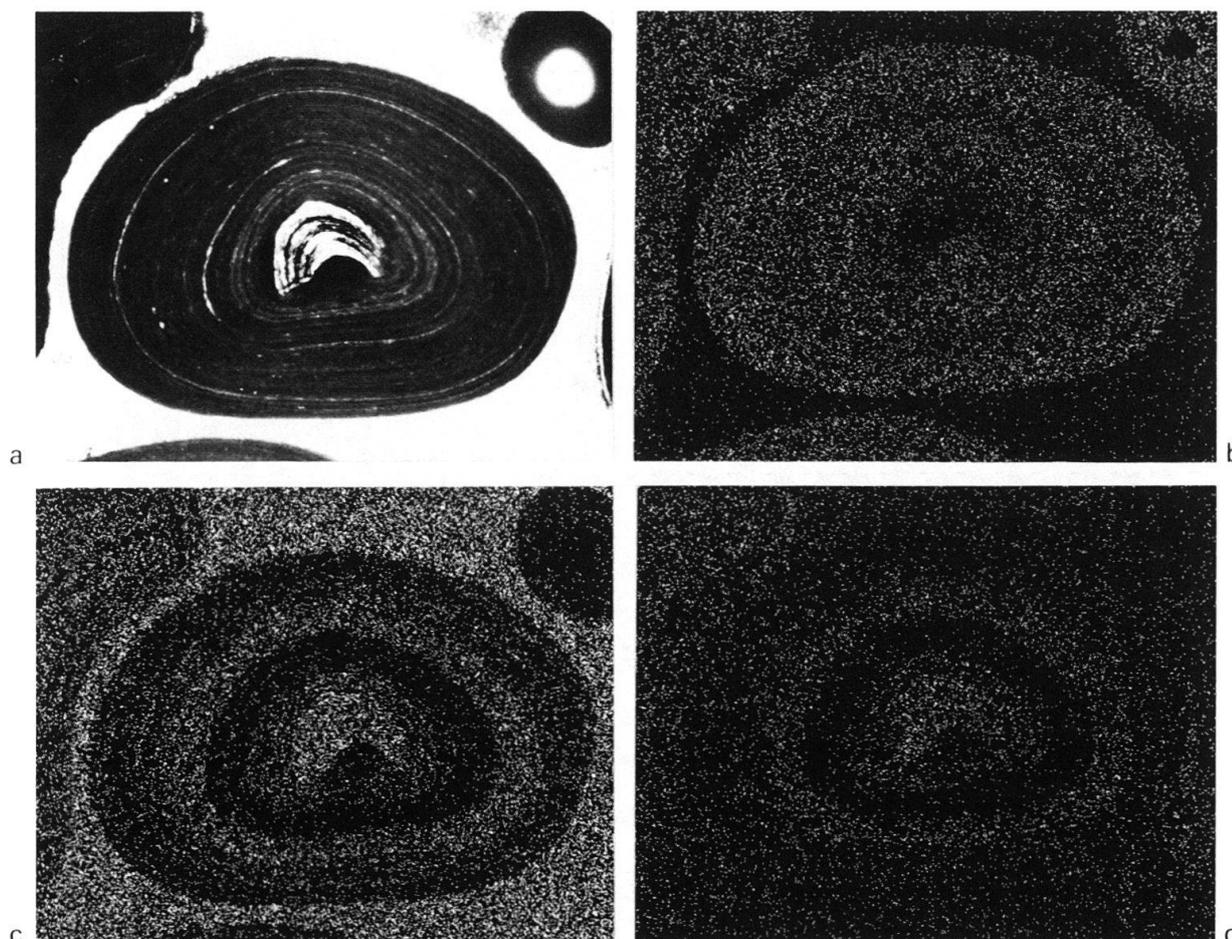


Fig. 1. a: Photomicrograph of a goethitic ooid in a micritic matrix showing a small nucleus (fossil fragment) and thick oolitic coating.  $\times 45$ . b-d: Element distribution images of the specimen shown in a: with b: Fe, c: Ca and d: P.

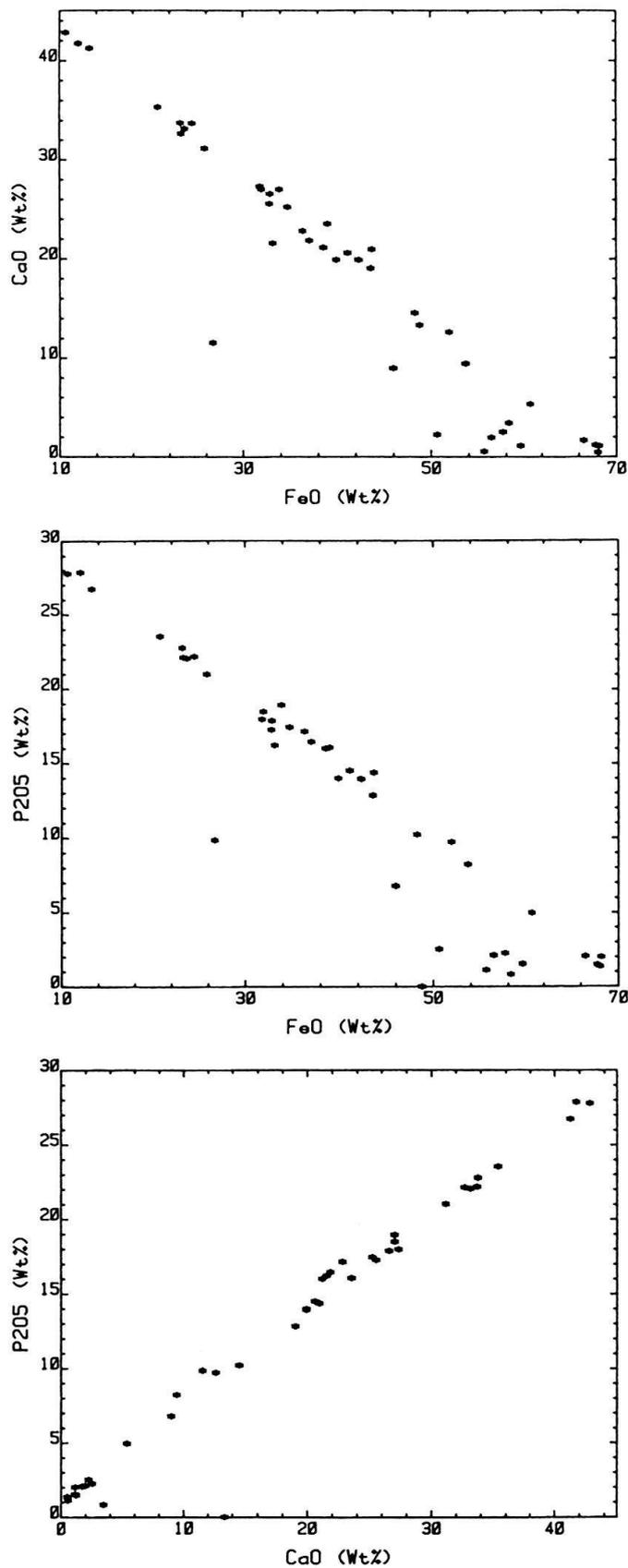


Fig. 2. Electron microprobe analysis of a goethitic ooid. Fe, Ca and P concentrations (the three principal elements) as determined from their oxide form are plotted as weight percentages (wt %) of a total analysis.

stance goethite, haematite, iron phosphate and kaolinite (JONOT et al. 1968; URBAN 1966; BUBENICEK 1961). The main elements are distributed more or less evenly. The resolution of the EDAX method is insufficient to analyze individual minerals in these ultrafine-grained mixtures. As a consequence the measured elements cannot be correlated with specific chemical phases. XRD-data indicate that goethitic ooids from southern England and northern Switzerland mainly consist of a single iron phase: FeOOH. The distribution images of the main elements (Fe, Ca, P) show a concentric pattern (Fig. 1b–d). Fe is clearly dominating in the sheath, Ca and P are enriched in areas concentric to the nucleus. Measurements with the EMA along a profile from the periphery to the nucleus of an ooid demonstrate the relationship between the different elements (Fig. 2). The width of analysis of the EMA beam (2–5  $\mu\text{m}$ ), however, does not allow for the determination of a small size (< 2  $\mu\text{m}$ ) of an individual lamina. As a consequence of the limited resolution of the EMA, the data obtained (Fig. 2a–c) reflect values from several chemical phases. Fe correlates negatively with respect to Ca and P, which correlate positively to each other. This indicates that the Fe-concentration is low in areas of high Ca- and P-concentration. Therefore Ca and P are probably elements of the same compound. In fact, apatite occurs in X-ray diffraction patterns subordinate to dominant goethite.

### Model

In the following section, the microchemical data for the goethitic type of ooids is used in a model for their genesis. In goethitic ooids, concomitant appearance of chemically different phases arranged in a concentric array, may be indicative of the mode of the formation assuming that concentric laminae results from discrete growth periods.

The following, schematic two-step model is proposed (see Fig. 3):

1. The sediment is the main source of the iron. In anoxic sediments iron in its soluble form  $[\text{Fe}^{2+}]$  migrates to the sediment-water interface. Above the interface microorganisms and other organic matter create locally reducing zones within this generally oxidizing environment (KRAUSKOPF 1979). In these zones iron remains mobile and can thus adsorb to an inorganic surface (e.g.  $\text{SiO}_2$ , silicates) (DALANG 1977). Due to a shift from locally reducing to oxidizing conditions, iron precipitates as amorphous FeOOH, which subsequently ages to  $\alpha$ -FeOOH. Under oxidizing conditions, the  $\text{Fe}^{2+}$ -concentration is low and the  $\text{Fe}^{3+}$ -concentration is negligible (STUMM & LEE 1961).
2. During a second stage an apatite is formed on the goethite-rich surface. There are two possibilities: first, direct chemisorption of the phosphate on the FeOOH-surface (IIa) (STUMM & MORGAN 1981), second, apatite formation passing through an intermediate calcitic phase (IIb). In the latter case calcite nucleates directly on the FeOOH-surface or on an organic film, e.g. algae (KUNZ 1983). An alternation of calcite with apatite was described by LECKIE & STUMM (1970) and is mainly a function of the pH and the soluble phosphate. A complete transformation is time dependent.

The two process steps above are repeated during the formation of a concentric ooid.

### Conclusions

The chemical composition of an iron ooid may give clues to the mode of their formation. The concentric crusts of mineralogically different phases reflect changes in

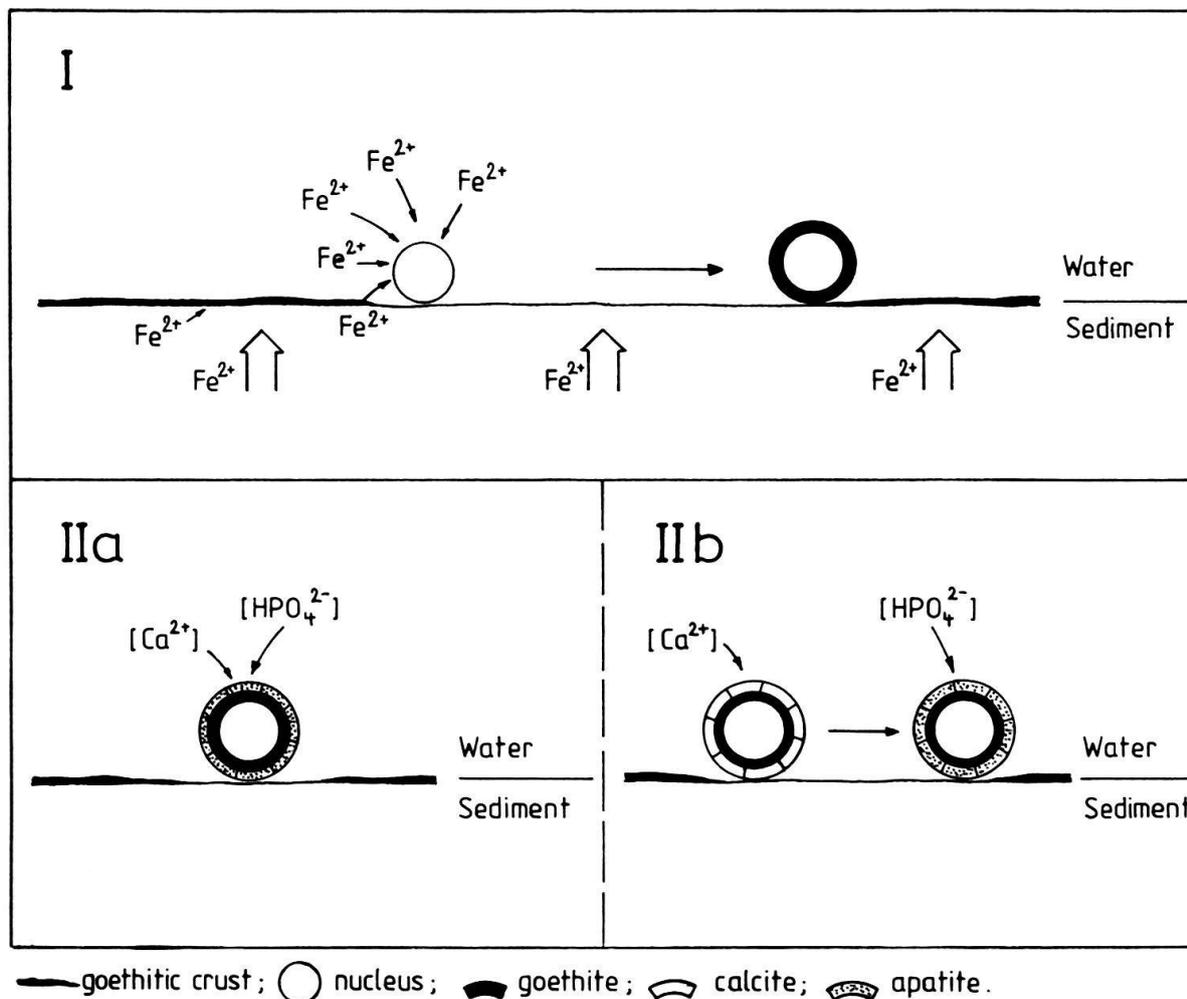


Fig. 3. Elements of a two-step iron ooid model.

ambient chemical conditions during the genesis. Ooids displaying these changes are associated with condensed deposits and/or hardgrounds. Both of these formed in predominantly aerobic environments. This study further suggests, that goethitic ooids were mainly produced through chemisorption processes.

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