Lower Ordovician ferriferous ooids from the Siljan district, Sweden

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In the lower Ordovician of the Siljan district, beds with ferriferous ooids occur at several localities. At Leskusänget they are particularly abundant and seem to represent a continuous series in the evolution of ooids, from superficial ooids in the lower part of the section to fully developed ooids near the top. The physical (length, thickness, nucleus size, number of laminae), chemical and mineralogical properties of these ooids were examined. The dominant mineral revealed by XRD from the cortex is goethite, but also quartz and a clay mineral, probably illite, were observed. This silicious material was found to form laminae alternating with the iron oxide matter.

The maximum ooid size was found to be approximately constant at about 2 mm throughout the section, but the size of the nuclei decreases almost continuously from the base to the top. The maximum number of laminae is about 40.

At Kårgärde, brown goethite and black chamosite ooids occur together in the same beds. Both contain several laminae, usually 40, or more. The silicious matter in the chamosite ooids also forms laminae, but these are not so well devoloped as in the goethitic ooids.

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Introduction

In an investigation of the lithogenesis and sea level changes in the Siljan district during the deposition of the high Lower Ordovician lower Kundan Stage, Hessland (1949b) presented extensive data on the vertical distribution of animal groups, algae, mineral particles and ooids from 18 outcrops. The data included the vertical distribution in the rock of calcium carbonate, iron, carbon, phosphorus, sulphur, magnesium, nitrogen and potassium. In the description of the ooids, petrographical methods were applied, but no XRD analyses were made and only two analyses of the chemical composition were reported. Hessland (1949a,b) also discussed the formation of limonite and chamositic ooids, and the origin of the iron.

Stratigraphy of the Ordovician sequence in the Siljan district was recently summarized by Jaanusson (1982b). The ooidiferous beds comprise the Hunderumian (Zone of *Asaphus expansus*) and lowermost Valastean substages of the Kundan stage. The boundary between the zones of *Didymograptus hirundo* and *D. "bifidus"*, that is, that between Arenig and Llanvirn in terms of the British sequence, is probably within the upper Hunderumian Substage (Jaanusson 1982a, Fig. 4). Jaanusson (1982b) emphasized that at about the base of the Valastean an important change in the facies of authigenic silicate minerals takes place all over the Baltoscandian region. In beds below that level the authigenic silicate, when present, is invariably glauconite, while above that level, it is mostly replaced by chamosite.

The ooids in the Siljan district are either chamositic or limonitic (goethitic); no hematite ooids have been observed so far. They are particularly abundant at Leskusänget and Kårgärde, but scattered, smaller ooids also occur elsewhere in the district (Silverberg, Gulleråsen, Rävanäs, Röjeråsvägen; Hessland 1949b). Leskussänget is the most important locality, not only for the abundance of ooids, but also because the section in the abandoned quarry shows an almost continuous series in the evolution of ooids, from superficial ooids in the lower part of the section to fully developed ooids near the top. The purpose of this study is to examine the physical, chemical and mineralogical properties of the ooids relative to the morphology and depositional environment. The chemical analyses of the rock provided by Hessland (1949b) are taken into account, supplemented by some additional analyses at selected levels.

A further reason for examining the Kårgärde section is that it includes some beds in which chamosite and limonite ooids occur together. Hessland (1949b) suggested fundamentally different modes of formation for these two types of ooids; according to him, the limonite ooids were of biogenic origin, whereas the chamositic ooids were chemical precipitates.

This paper is a contribution to the project "Noncarbonate Palaeozoic ooids in Baltoscandia: ultrastructure, mineralogy and chemical composition".

Materials and methods

In his study on the lithogenesis of the lower Kundan limestones in the Siljan District, Hessland (1949b) described two localities with ferriferous ooids: Leskusänget and Stenberg (Fig. 1). In both places, goethite (limonite) ooids are present in abundance, in Stenberg they are associated with minor amounts of black, chamositic ooids. The thickness of the ooidiferous beds at Leskusänget is about two metres, and in Stenberg less than one metre.

For this paper, samples were collected in 1986 and 1987 from Kundan ooidiferous beds in the abandoned quarry at Leskusänget and from the Kårgärde section. The latter is situated near Stenberg and was made available in 1976 (for a general description of the section, see Jaanusson 1982b, pp. 40-42).

The ooids in the samples were isolated and enriched in two ways, mechanically by crushing and hand-picking, and by chemical disaggregation with acetic acid. The details of the method were given in Sturesson (1986, 1988). The composition of the fine fraction of the rock (<0.063 mm) in the residue not dissolved at the chemical disaggregation was determined separately by wet-sieving.

The chemical analyses of the ooids were made by flame atomic absorption spectrometry (Sturesson 1987), but also EDX and the electron microprobe have been employed for the identification of minerals under the SEM. Phosphate was determined colorimetrically using the yellow phospho-vanadomolybdate complex at 430 nm. In order to minimize the effect of the chemistry and size of the nucleus, only chemically disaggregated ooids were used for the analysis. After chemical disaggregation the XRD of the ooids revealed that the carbonate fraction of the ooids, mainly the nucleus, had been removed completely. The results in Table 1 therefore refer only to ooid cortex and non-carbonate material in the nucleus, not to the whole ooid.

The effect on the chemical composition of the ooids by the acetic acid treatment was tested separately at one level. The content of calcium decreased to about 40 percent of the amount in the mechani-



Figure 1. Siljan district. Map showing the location of the outcrops mentioned in the text. Redrawn from Jaanusson (1982b).

cally disaggregated ooids; other elements increased in various amounts. Fifteen samples of 0.100 to 0.150 g were taken. The X-ray powder diffraction analysis of the ooid material was made as described in Sturesson (1986); diffractograms were made on carbonate-free material for each level in the section. After boiling the ooids in concentrated HCl/HNO₃, fragile white rounded grains remained, which were analysed separately.

The carbonate content of the ooids was determined as loss of weight when mechanically disaggregated ooids had been treated with acetic acid (10 %). For the measurement of the ooid shape the relation between the size of the nucleus and that of the ooid, 50 to 80 of the largest ooids from each bed were selected. It is assumed that the largest, mature ooids are the most representative for the hydrodynamic conditions in which the bed was formed. The ooids from each level were mounted, embedded in epoxy resin and sectioned through the centre so that the maximal length (L) and minimal thickness (T) of the ooid could be measured under the microscope. The size of the nucleus (N) was also measured and the ooid factor was determined for each ooid as L-N/L.

The carbonate content of the rock was determined as the loss of weight after treatment with acetic acid. No further chemical analyses were made on the rock matrix: the results given by Hessland (1949b) have been employed for the discussion.

| Level M | Resid. o/o | Ca ppm | Mg ppm | Mn ppm | Zn ppm | Fe o/o | Al o/o | Ti o/o | P ₂ O ₅ o/o | N |
|------------|---------------|-----------|-------------|------------|-----------|-----------|-----------|-----------|--------------------------------------|----|
| LESKU | SÄNGET | | | | | | | | | |
| +0.30 | 11.4 | 550 | 8087 | 337 | 175 | 42.7 | 2.52 | 0.71 | 1.36 | 7 |
| | | 174 | 418 | 5.6 | 8.6 | 0.6 | 0.05 | 0.03 | 0.11 | |
| +0.45 | 13.1 | 738 | 8985 | 342 | 153 | 38.4 | 2.88 | 0.68 | 1.15 | 6 |
| +0.65 | 11.3 | 383 | 233 7667 | 311 | 132 | 41.8 | 2 37 | 0.03 | 1.01 | 8 |
| 10.05 | 11.5 | 48 | 303 | 5.2 | 2.3 | 0.8 | 0.04 | 0.07 | 0.07 | 0 |
| +0.70 | 12.6 | 362 | 7610 | 310 | 131 | 40.4 | 2.35 | 0.68 | 1.13 | 4 |
| | | 30 | 113 | 2.1 | 2.4 | 0.3 | 0.05 | 0.01 | 0.04 | _ |
| +1.00 | 10.0 | 308 | 6295 | 364 | 137 | 43.7 | 2.22 | 0.55 | 1.14 | 7 |
| 1 1 25 | 0.4 | 24 | 261 | 14 | 4.5 | 2.0 | 0.06 | 0.01 | 0.03 | 7 |
| +1.25 | 9.4 | 5/4 | 0541 | 3/0 | 231 | 40.2 | 2.20 | 0.50 | 1.22 | / |
| +1.30 | 91 | 375 | 7062 | 336 | 133 | 41.4 | 2 22 | 0.01 | 1 17 | 7 |
| 11.50 | | 32 | 87 | 5.8 | 1.7 | 3.0 | 0.04 | 0.01 | 0.02 | , |
| +1.50 | 9.2 | 481 | 6916 | 391 | 296 | 43.1 | 2.18 | 0.72 | 1.27 | 7 |
| | | 37 | 81 | 9.0 | 7.2 | 2.9 | 0.04 | 0.10 | 0.13 | |
| +1.70 | 14.8 | 723 | 6779 | 370 | 265 | 44.3 | 2.22 | 0.76 | 1.38 | 7 |
| . 2 00 | 15 7 | 66 | 141 | 3.9 | 2.9 | 0.6 | 0.05 | 0.03 | 0.08 | - |
| +2.00 | 15.7 | 14897 | 6003 | 284 | 1899 | 39.1 | 2.04 | 0.15 | 2.53 | 1 |
| +2.20 | 173 | 20048 | 539 8770 | 7.0 777 | 50 118 | 34.0 | 2 01 | 0.11 | 0.20 | 7 |
| 1 2.20 | 17.5 | 20948 | 334 | 15.5 | 34 | 0.6 | 0.08 | 0.37 | 0.28 | / |
| +2.50 | 13.2 | 15767 | 7032 | 296 | 1277 | 40.2 | 2.39 | 0.28 | 3.06 | 7 |
| | | 1079 | 536 | 7.6 | 44 | 0.9 | 0.09 | 0.19 | 0.17 | |
| KÅRGÅ | ÄRDE | | | | | | | | | |
| Brown | 11.3 | 1104 | 6593 | 299 | 118 | 44.5 | 2.62 | 0.71 | 1.13 | 14 |
| | | 200 | 382 | 5.9 | 2.3 | 1.6 | 0.17 | 0.04 | 0.10 | |
| Black | 21.0 | 8513 | 18843 | 240 | 165 | 22.5 | 6.81 | 0.17 | 5.13 | 8 |
| | | 522 | 621 | 9.6 | 23 | 0.8 | 0.25 | 0.04 | 0.32 | |

| Table 1. | The chemical | composition of | the ooid | cortex. Mean | values and s | standard d | eviations are | given fo | or each le | evel. |
|----------|--------------|----------------|----------|--------------|--------------|------------|---------------|----------|------------|-------|
| | | | | | | | | | | |

Microscopy

SEM studies were made on both polished and broken surfaces of mechanically disaggregated ooids. For the etchings the following media and times were used: 0.02 M EDTA and 2 % acetic acid from one hour to three days (to remove carbonate) 10 % cold acetic acid and HCl up to three hours (to etch the phosphate), and a hot concentrated HCl/HNO₃ for a few hours (to remove the iron oxide). Altogether, more than 200 ooids were examined by these methods.

Results

Physical parameters, mineralogical and chemical composition

At Leskusänget, at the base of the Holen Limestone

(Kundan Stage), the rock changes in colour from red to gray via a discontinuity surface stained by a diffuse goethitic crust. The upper boundary of the red limestone was used as a reference level; in the text, levels above the reference are given in metres and with a positive sign.

In the lower part of the section (below +1 m), the coated grains consist entirely of iron-stained echinoderm fragments with a thin crust of limonite including goethite (Fig. 2A). Microprobe analysis of the crust also reveals the presence of Si and Al. These superficial ooids are the largest in the sequence with a maximum length of about 2 mm; they are not flattened as are the normal ooids (Figs. 2 and 3). From +1 to about +1,5 m, the crinoids still form ooid nuclei, but also other shell fragments, such as trilobites etc., are common. The amount of unidentified nuclear material increases upwards and over +1,7m, only about 10 percent can be classified. At this level, the lamination in the cortex also becomes



Figure 2. Ooids from the Leskusänget section. A. Superficial ooid from 0.3 m. Length 1.3 mm. Arrows point to the thin lamination. B. Ooid from 1.0 m. The ooids at this level are elongated due to the shape of the nucleus and different growth rates. Length 2 mm. C. Ooid from level 1.3 m. with bored nucleus. Picture length = 1.4 mm. D. SEM picture of the filaments in C. E and F. Ooids from level 2.0 m. Note the coarser laminae at this level and the higher ooid factor. Distorted ooids occur mainly in the uppermost part of the section, but they are not common.

poor; the thinnest lamina can seldom be distinguished (Fig. 2E).

The ooid factor (Fig. 3) shows clearly an almost continuous increase in the cortex to nuclear ratio throughout the section, and simultaneously there is a slight decrease in the maximum ooid length from about 2 to 1.5 mm (Fig. 3). Between 1.3 and 2.0 m, the roundness of the ooids is as best; according to Pettijohn's roundness index (Pettijohn 1975), they are rounded to well rounded. The sorting of the ooids is generally poor in the whole section; the range of ooid length is from about 0.2 mm up to their maximum length of about 2 mm.

The decrease of the carbonate in the ooids at about 1.0 m indicates a transition from dominant superficial ooids to normal ooids (Fig. 3).

Mineralogy. – The mineralogical compositon of the ooid cortex is practically the same throughout the whole section. The X-ray diffractograms show peaks



Figure 3. Some physical parameters describing the properties of the ooids from the Leskusänget section and the black chamosite ooids from Kårgärde. T/L is a plot of the shortest to the longest axis. L_{max} is the mean of the ten largest true ooids in the sample. The ooid factor illustrates the relation between the cortex thickness and the ooid size. The carbonate content in the ooids is given from 1.0 m to illustrate the transition from superficial ooids to true ooids. Horizontal bars show the confidence interval for p=0.05.

which can be attributed mainly to goethite (Fig. 4). The white silicious material in the ooids, which occurs as a residue after the acid digestion, contains both quartz and a clay mineral, probably illite (Fig. 4). The high background in XRD between 20 and 30 degrees indicates also the presence of non-crystalline silica. Some of this could have been formed by the decomposition of clay minerals by the hot acid. The silicious material was detected only in the cortex of the ooids, where it forms separate laminae (Fig. 5F). This fact can partly explain the larger quantities of insoluble residue in the ooids in the upper half of the section; there the cortex is thicker as shown by the ooid factor.

Chemical composition. – The chemical composition of the rock material given by Hessland (1949b) (Fig. 6) is based on whole rock analysis, *i.e.* the ooids are included, and the data must therefore be interpreted with care. The maximum peak on the iron

curve, for instance, corresponds to a bed with a particularly high quantity of ooids. The values are consequently not always representative of the sedimentary matrix, and for the interpretation of the genetic environment these pitfalls have to be considered.

There are variations in the rock chemistry, however, which must be related to the matrix proper. Hessland (1949b) reported high phosphate values, 0.8 and 0.9 percent respectively, at two levels, +1and +2 m. The lower peak coincides with other maxima; also potassium, carbon and nitrogen have their highest values here, which could be an indication of an organogenic origin. At the upper peak only carbon seems to follow, and all other elements have low concentrations. The highest quantities of ooids seem to occur at, or after, these maxima. Hessland also found a correspondence between phosphorus and animal frequency in this part of the section, and a reciprocal correspondence between phosphate and algal frequency.



Figure 4. X-ray diffractograms of A. the ooid cortex from three selected levels at Leskusänget: a = +0.3, b = +1.7 and c = +2.5 meters, and B. the corresponding insoluble residues. The diffractograms in A were made at 1.2 deg/min. and those in B at 2.4 deg/min.

The phosphate in the ooids is constant in the lower beds, but displays a significant peak in the upper part of the section (Fig. 7). This increase coincides with a similar increase in calcium, aluminium and zinc, but also in the insoluble silicious fraction. Simultaneously there is a decrease in iron, manganese and titanium. In the uppermost sample of the section (+2.5 m) the ooids appear to contain traces of chamosite. These facts indicate that there may be a transition from a limonitic ooid composition in the lower part of the section towards a more chamosite in the upper reaches, but the environmental conditions necessary for the formation of true chamosite content in the ooids up to +1.7 m is not matched by a corresponding content in calcium, and the presence of any apatite-type mineral is therefore excluded. EDX-analysis of the filaments in the nucleus reveals no calcium, only iron and phosphate, but no peak in the XRD can be referred to an iron phosphate. The presence of phosphatic filaments is probably not sufficient to explain the phosphate content. Phosphate is present in the cortex, but its distribution is uncertain. Above +2 m however, the calcium is in stoichiometric relation to the phosphate, and faint traces of an apatite mineral can be observed in XRD (Fig. 4A).

At Kårgärde, the brown ooids are almost entirely goethitic, whereas the black ooids consists of chamosite and a small amount of apatite (Fig. 8). The



Figure 5. SEM photographs of the laminae. A to C. Superficially coated echinoderm fragment from Leskusänget, +0.7 m. Microprobe analysis of the crust revealed only three elements: Fe, Al and Si. D. Similar thin sheath between laminae of goethite (limonite). E. Pores in cortex after etching with EDTA = removal of carbonate. The ooids in D and E are from the 2 m level. F. The insoluble residue in the cortex of a limonite ooid from level 1.7 m after treatment with hot concentrated HCl. Bar length is in A 100 and in E 50 microns; in B to E the length is 10 microns.

goethitic ooids have a chemical composition almost identical with the ooids in the Leskusänget profile up to about 1.7 m. The chemical composition of the black chamosite ooids at Kårgärde shows lower values for the iron and iron-related elements and higher amounts of chamosite related elements such as aluminium, magnesium and silicate (as insoluble residue). The phosphate concentration is also higher, its role in the ooid formation is unclear. The composition of the black Kårgärde ooids seems to be a continuation of the trend in the Leskusänget profile towards more chamositic ooids (see Fig. 7); also the physical parameters for the chamosite ooids (Fig. 3) support this trend.

The insoluble silicious matter in these ooids appear either as white laminae, as in the Leskusänget profile, or as a dense black substance.

Hessland also made spectral analysis of the ooids at two selected levels, +0.3 and +1.5 m approximately. These results coincide well with those obtained here, except for calcium, which is higher in Hessland's work, probably due to the presence of carbonate.



Figure 6. The chemistry of the rock at Leskusänget. The six curves to the right (N to Fe) are redrawn from Hessland (1949a).



Figure 7. The chemical composition of the ooid cortex for the Leskusänget section and the chamosite ooids from Kårgärde. The insoluble residue consists mainly of silica. The confidence interval (p=0.05) is given in some cases, but usually it is to small to be drawn at scale. The values given for Kårgärde refer to chamosite ooids.



Figure 8. X-ray diffractograms of A, the ooid cortex at Kårgärde, a = chamosite ooids, b = goethite ooids, and B, the corresponding insoluble residue.

SEM and light microscopy

Thin sections of typical ooids from selected levels at Leskusänget are shown in Fig. 2, and from Kårgärde in Fig. 9. The shape of the ooids is to some part determined by the shape of the nucleus, particularly in the lower part of the section where the ooids have a low ooid factor. The elongated shape of the larger ooids is due to a different net growth rate (Fig. 2B), probably caused by limited mobility. The ooids at both Leskusänget and Kårgärde are seldom broken or abraded, implying a rather tranquil environment for their formation and little transport thereafter. In the upper part of the section the ooid cortex seems to be more translucent due to incipient recrystallisation of the inner laminae (Fig. 2E). This process has in some rare cases caused the formation of distorted ooids (Fig. 2F); such 'spastoliths' are commonly associated with a chamositic composition.

The maximum number of laminae in the cortex of the largest ooids increase from a few in the superficial ooids at the base of the section to about 40 at +1.7 m, whereafter they are constant. At Kårgärde, both goethitic and chamositic ooids contain many laminae, usually 40 or more. At some levels, the fine lamination is obscured by recrystallisation and the original number of laminae could therefore have been higher.

The material in the nuclei of the Kårgärde ooids (Fig. 9) is varied; skeletal grains are common but also diffuse peloids occur, particularly in the black ooids. Complete recrystallisation of the nucleus has been observed in some cases (Fig. 9E–F). The inner cortex of many chamosite ooids consists of a pale green, translucent microcrystalline material where the fine lamination is indistinguishable (Fig. 9C). Under crossed nicols and with a gypsum plate however, the coloured cross reveals a tangential orientation of the crystallites (Fig. 9D).



Figure 9. Ooids from Kårgärde. A. Goethitic ooid with a bored nucleus and a well preserved fine laminated cortex. B. Chamosite ooid with a skeletal grain as nucleus and alternating white bands of amorphous silica in the cortex. C and D. Chamosite ooid with a diffuse nucleus. The dark extinction cross in D (crossed nicols) indicates a tangential orientation of the minerals in the cortex. E and F. Goethite ooid with a recrystallized nucleus. Crossed nicols in F. Ooid length is 2.2 mm.

A purpose of the SEM study was to search for traces of algal activity in the formation of the ooid cortex. The presence of filaments in the carbonate nuclei was described by Hessland (1949a,b) and is shown in Fig. 2C-D. It can be seen that the filaments are of two kinds: thin (1 to 2 microns) unbranched, and thicker (5 to 6 microns) branched threads. Filaments of this kind have not been observed in the cortex so far. On EDTA etched

broken surfaces interlaminar porosity is common (Fig. 5E). The thickness of these irregular holes is about 2 to 5 micrometres, and they occur mainly in the central parts of the ooid, from the nucleus to the middle of the cortex. The origin of this porosity is unknown, but it could be remnants of an organic film, later replaced by carbonate; it can also be the original porosity of the grain.

Fig. 5A shows a thinly laminated coating of

goethite (limonite) on a crinoid fragment; a superficial ooid at 1.0 m level. The coating displays the features of a true ooidal lamina as abrasion on protruding parts and the filling of embayments. Each individual lamina is very thin, less than one micrometer (Fig. 5B-C). Similar thin sheaths have also been observed within the cortex of true ooids, between thicker laminae of platy crystals (Fig. 5D). The silicious laminae in the cortex shown in Fig. 5E demonstrate clearly that the ooids are formed by alternating laminae of iron oxides and silica. In the black ooids from Kårgärde these laminae are not so well developed.

Discussion

The matrix of the oolitic limestone is at both localities dominantly gray, which means that the iron is in the ferrous state. Hessland (1949b) reported almost one percent of organic carbon but a low content of sulphur; the sediment was, according to him, deposited in a stagnant environment with a low content of oxygen. The goethitic (limonite) ooids on the other hand are oxidized, even the chamositic ooids at Kårgärde contain laminae of oxidized material, and the cortex material must have been exposed to an environment with a higher Eh. Oolitic structure is generally indicative of deposition in a shallow, high-energy environment in well aerated water. These circumstances indicate that the ooids either were formed directly by ferric matter, or they were transported from an oxic environment to the site of deposition, or that they were oxidized by other means.

Hayes (1915) and Hessland (1949a) suggested that the limonite ooids were formed within a coating of enveloping algae, and that the oxygen was delivered during their photosynthesis. The results obtained in this investigation do not support such an interpretation for the formation of these ooids. The filaments observed are entirely restricted to the nucleus, and no signs of filaments have been detected in the cortex. Many bored skeletal fragments do have a coating of goethite (limonite), but they are never laminated, *i.e.* they are not ooids. Such fragments constitute only a fraction of the nuclei in the goethite (limonite) ooids, so this model is likely to be of minor importance. In a series of experiments, Loeppert & Hossner (1985) and Clarke et al. (1986) have demonstrated that precipitates of ferrihydrite on pure calcite, very similar to those observed on skeletal grains in this material, readily form under conditions that prevail in freshwater environments. The increased surface area caused by the algal borings must have favored such reactions.

Inherent in most ironstone formation is a rather high content, 1 to 2 percent, of phosphorus (James 1966, table 8,9), and in the Leskusänget section a high concentration of ooids coincides with high amounts of phosphate. The phosphate content within the ooids is generally much higher than in whole rock samples, particularly in the upper part of the section. Recent investigations on the behavior of goethite in lake- and sea-water and its role in the adsorption of other ions may shed new light on the role of phosphate in the formation of the ooids (Balistrieri & Murray 1981).

It is well established that the solubility of the ferric ion in oxic waters is extremely low, and that this ion is not the main form for ion transport in ventilated waters. The hydrated oxide (goethite), however, easily forms a colloid and may remain in suspension for long time, particularly if stabilized by a hydrophilic organic colloid (James 1966, Krauskopf 1967, Boyle et al. 1977). Carrol (1958) suggests a similar model, but here the iron colloid is transported as a coating on detrital clays.

It is also well established that in a sediment, strong adsorption of phosphate occurs on iron oxyhydroxides (Krom & Berner 1980, 1984, Sholkowitz & Copland 1982, Lucotte & D'Anglejan 1983). In anoxic waters the adsorption capacity decreases (50:1) and the phosphate is released; some phosphate is also released when the oxy-hydroxide crystallizes (Krom & Berner (1980). Carrit & Goodgal (1954) and Jitts (1959) have demonstated experimentally that this adsorption is inhibited by electrolytes and organic matter. The optimum pH for phosphate adsorption was found to be between 5 and 7. If it is assumed that ferrihydrite in colloidal form is one agent in the formation of the ooids, then the high phosphate content can be explained.

Next to the iron minerals, silica is the most common compound in the ooid cortex. James (1966) reports concentrations from 5 to 25 % in limonitic, and about 7 to 50 % SiO₂ in chamositic ironstones of various ages. In this material, the SiO₂ is about 9 to 17 % in the goethitic ooids, and over 20 % in the chamosite ooids at Kårgärde. Similar result was obtained for ooids of corresponding age at Byrum, Öland (Sturesson 1988). Alternating shells of chamosite and goethite in chamosite ooids is a common feature, and a similar lamination of goethite and silica in goethite ooids (Fig. 5E) clearly indicates that the silicious matter plays an active role also in the formation of the goethitic ooid cortex.

The ooids from Lake Chad described by Lemoalle & Dupont (1973) have a similar silicious framework together with goethite laminae. The chemical composition of the ooids has much in common with those described here, except for SiO_2 . In

the Lake Chad ooids the nucleus is composed of clay, which gives a higher content of silica. The authors give clear evidence of the recent age and a freshwater to brackish origin of these ooids; they also suggest a formation by co-precipitation of iron oxide and silica from a colloidal clay system. For the formation of the chamosite ooids Hessland (1949b) suggests a similar model; here the lamination is due to an alternating deposition of silica and ferric oxide colloids, caused by the opposite charge of the substances. He also emphasized the importance of a low electrolyte content in the water for the process.

In laboratory experiments simulating early diagenetic conditions, Bhattacharyya (1983) studied the transformation of detrital kaolinite to chamosite (berthierine). It was shown that in a reducing environment (pH=7, Eh = -250 to -350 mV) a progressive transformation of kaolinite to berthierine took place within about a year. The transformation did not occur in the absence of magnesium. Modern deposits of chamosite have been reported from shallow-marine environments (Porrenga 1965, 1967), brackish-cold water sediments (Rohrlich et al. 1969, Rohrlich 1974). A freshwater origin of chamosite in Triassic coal measures of Japan has been reported by Iijima & Matsumoto (1982). Evidently, chamosite is a mineral that can be formed under a variety of condition; its occurrence in ooid laminae, however, puts some constraints upon the genetic environments.

The origin of ferriferous ooids has been discussed in numerous papers, and a summary of the present state of knowledge is given by Maynard (1983). The presence of similar silicious frameworks in the two kinds of ooids described here, and the progressive development of the goethitic ooids towards chamosite in the Leskusänget section, indicate that in the Siljan district, the ooids were formed by essentially similar processes. There is a growing body of facts in favour of a colloidal origin of the ooid laminae, which necessitates a low electrolyte content in the water, *i.e.* freshwater or brackish water. The flocculation of iron is salinity-dependent up to about 15 %, and it is a rather rapid process. Sholkovitz (1976) demonstrated experimentally that 30 minutes after the mixing of river water with seawater most of the iron had flocculated.

One possible precursor to the chamosite is a kaolinite colloid; the iron for the transformation could have been transported as a coating on the clay. Depending on the bottom conditions, either chamosite or goethite was formed in early diagenetic reactions; the lamination in the ooid cortex could be due to a change of the colloid surface charge during these reactions. The details of these processes are to a large extent still unkown, but will probably include adsorption of various ions to surfaces of colloids, influence of organic matter on colloid stability in various environments, flocculation of colloids by electrolytes etc., and are now the object of further studies.

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