MARINE ARAGONITE-OOIDS AND BRACKISH MG-CALCITE-OOIDS IN "NEOGENE"-PLEISTOCENE CYCLES OF THE SECTION OF THE CANAL OF CORINTH, GREECE

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ABSTRACT

This case study picks up the old problem of sedimentology concerning the genesis of aragonitic versus radial calcitic ooids. On the Isthmus of Corinth ooids occur within a neogene/quaternary sequence of strata built of cylces of glacialeustatic origin. Ooids with aragonitic cortices (replaced by secondary isometric calcite) are limited to marine levels whereas radial Mg-calcitic cortices (often replaced by Fe-calcite) occur in periods of lacustrine-brackish environments. The two types of primary ooids in this case are attributed to a change in the Mg/Ca-ratio of the aquatic system. Finally the results of this case study are discussed in regard to the changes of ooid composition throughout the Phanerozoic.

KEY WORDS: Ooids, aragonite, magnesian calcite, Pliocene, Pleistocene, cycles, Canal of Corinth

1. INTRODUCTION

Since SORBY (1879) sedimentologists are engaged in the study of genesis, composition and diagenesis of carbonate ooids (recent overviews or compilations: SIMONE (1981) and RICHTER (1983). Since the Precambrian carbonate ooids are abundant in shallow marine deposits of temperate latitudes and are often described in detail, but nevertheless their generation is not totally clear up to now (actual discussion: OPDYKE & WILKINSON (1990) on phanerozoic ooids in general). Even experiments did not result in distinct rules (DAVIES et al. 1978 versus FERGUSON et al. 1978) as the transferability of results at least to the marine environment stays questionable (RICHTER 1983; p. 95). Further more the importance of microorganisms is still in discussion (REITNER et al. 1997).

This case study is up to show regularities between primary ooid composition (aragonitic versus Mgcalcitic) and their respective depositional environment in the "neogenic" cycles in the study area described by NEUSER et al. (1982). The results are compared to the changes of primary aragonitic and radial-Mgcalcitic ooidcortices within the Phanerozoic. The depositonal environments of the "neogene"-quaternary cycles in the section of the canal of Corinth are well known since the work of NEUSER et al. (1982). As this sequence of strata at nearly 38° northern latidude represents one of the most northern outcrops of quaternary ooids in a marine environment (compare Tab. 1 in OPDYKE & WILKINSON (1990), the composition of the ooids should sensitively react on changes of the environment.

2. STUDY AREA AND SEQUENCE OF STRATA

The "Neogene"-Quaternary sequence of strata at the Isthmus of Corinth is tapped by the canal which was finished in 1892. The canal connects the Saronic Gulf to the Gulf of Corinth (Fig. 1). Complete geological profiles were done by FUCHS (1988), v. FREYBERG (1973) and NEUSER et al. (1982). The section of the canal reveals the complicated geological history of the Isthmus by showing the

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synsedimentary tectonic events and fast changes in facies. NEUSER et al. (1982). first succeeded in presenting a cylcic structuration of the deposits and proved a correlation of the Pleistocene cycles from the NW-area across the domed, poorly exposed central part to the SE-area. More recent investigations of COLLIER (1990) follow the correlations of v.FREYBERG (1973), which, however, are only in part correct as inventory and significance of nonmarine intercalations on both sides of the "central high" ("Scheiderócken", v. FREYBERG 1973) are not correctly identified (e.g. the brackish-niveau at the top of cycle C, see below).



Fig. 1: Geographic situation of the Canal of Corinth. When the sea level is eustatically lowered for about 100 m below the present level, four large basins are resulting between Peloponnese and Euboea: I = Corinth basin, II = Saronic basin, III = Patras basin. IV = Euboea basin. Note that the coast lines of the glacial basins have changed due to neotectonic activation. Hatched area: water depth < 100 m. Redrawn after RICHTER 1984.

The sequence of stata in the canal section covering the >100 m thick, lacustrine-brackish Corinthian Marl is subdivided into eight cycles (Fig. 2 and 3). A strong discordance between the 2, and 3, cycles is regarded as the lithostratigraphic boundary between Tertiary and Quaternary (N1, N2 = "Neogene", A-F = Pleistocene). Based upon the determination of foraminifera, Cycles N2 and A are classified as Upper Pliocene to Old Tertiary (kindly written information of Prof. Meulenkamp/Utrecht). Investigations of RΦMMELT-DOLL (1990) on ostracods put the Pliocene/Pleistocene boundary between N1 and N2. Cycles D, E and F contain a fauna including *Strombus bubonius*, which proves their Tyrrhenian age (D and E = Paleotyrrhenian, F = Eutyrrhenian; NEUSER et al. 1982). This is also according to U/Th datings of corals by COLLIER (1990): cycle B = 311800 a, cycle E = 205200 a (our cycle naming).

West of the highest point of the canal section ("central high", approx. 80 m above present sea level), coinciding with a horst-structure due to tectonic activities in the Pliocene and Pleistocene, the Pleistocene cycles reflect a change of marine and lacustrine-brackish periods grading to a coastal facies towards the "central high".

East of this Ridge intercalations of soils (terra rossa and reworked red soils, partly with calcretes) are corresponding to the lacustrine-brackish deposits NW of it. The cylces are made up by a lower marine part (with foraminifera, echinoids, corals) and an upper nonmarine part (with Dreisseniida, Limnocardia, Characea, lacustrine-brackish ostracods and gastropods, and additional calcretes east of the "central high").





The cyclicity is attributed to the well-known climatic changes in the youngest Cenozoic with the nonmarine parts representing the so-called glacials (in this area a relatively warm climate as is indicated by redsoils with calcretes). In these times the world sea level was lower than today resulting in an emersion of the area east of the "central high" whereas the Gulf of Corinth west of it changed into a brackish lake (compare to Fig. 1) cut off the sea by a barrier at Patras and the "central high" at the Isthmus of Corinth (RICHTER et al., 1970) at 1970 at 19

After RICHTER et al. (1979) the modern depth of the swell at Patras of about 40 m is due to erosion and tectonical drawdown and probably was much less in the Late Pleistocene. This theory is supported by seismic profiles in the swell area of Patras from 1931 which verify an extensional tectonic being active still in the Holocene (BROOKS & FERENTINOS 1984).

Additionally PIPER & PANAGOS (1979) also assume an eustatically influenced variation of marine and nonmarine Quaternary stages in the Gulf of Patras located W of the Gulf of Corinth. Lacustrinebrackish conditions in glacial times are also known from the basin facies of the Gulf of Corinth, as HEEZEN et.al. (1966, p. 295) mention brackish organisms at low drilling depths within the Gulf of Corinth.

A lake limited to the outline of the Gulf of Corinth, however, only applies to Pleistocene glacials. The prevailing nonmarine sections of the Neogene consisting of lacustrine-brackish sediments extend all over the Isthmus and the first marine ingressions (cycles N 1 and N2) cover an area of still much larger extension (NEUSER et al. 1982).

3. TYPES OF OOIDS AND THEIR DISTRIBUTION

Regardless of the environment, calcareous ooids are assigned to five fundamental types, based upon primary and secondary structures of the cortex (compare RICHTER 1983): (a) tangential, (b) radial, (c) random, (d) oomoldic, and (e) in situ calcitized. Up to now type a is known to be primary; type b and c may be primary and secondary in regard to their chemical and mineralogical compositon; type d and e are only secondary, especially after primary aragonitc composition of the cortices.

In this study it is useful to differentiate ooids by their primary mineralogical composition (aragonite versus Mg-calcite), as this clarifies the relation to the marine respectively lacustrine-brackish environment. We will only discuss ooids of the cycles N1, N2 and A-E, as the Late Pleistocene cycle F only occurs in isolated minor outcrops with no connection to the terrace sediments of the canal section.

3.1. ARAGONITIC OOIDS

In the canal section oolites bearing aragonitic ooids are restricted to the marine parts of the pleistocene cycles B-E (compare Fig. 3). Occasional aragonitic ooids in the marine layers of cycles N2 and A at least indicate aragonitic ooid generation in the cycles around the lithostratigraphic boundary of the Plio-Pleistocene. Aragonitic ooids are not restricted to a special position in a marine section: they may be intercalated at the base (cycles B and D of the NW canal section), in the center (cycle B of the SE canal section), and at the top of the marine sequences as well (cycle C of the SE canal section and Cycle E in the whole canal area).

Diagenetically unmodified aragonitic ooids of the canal area like the recent ooid cortices of the Bahamas (e.g. FABRICIUS 1977), are composed of cryptocrystalline granules and rods of 0.5 to 2 mm size. Thin section observations with crossed polars and I-compensator show that most of these ooids are positive pseudouniaxial, verifying the tangential orientation of the aragonite crystals. Layers with radial orientation of the aragonite crystals are rare among the ooids of the canal area, however, they are abundant in the Pleistocene ooids of the hills of Kira Wrissi (1-2 km south of the SE canal section, RICHTER 1983, p. 94).

Following LOREAU & PURSER (1973), FRIEDMAN et al. (1973) and LOREAU (1982), radial aragonitic ooids are indicative of low degrees of water turbulence. But this interpretation seems not to be conclusive: on one hand the largest outcrop of oolite in the Isthmus area, the above mentioned hills of Kira Wrissi with its large ripple layering, is composed of tangential and radial aragonite ooids with up to 5 mm in diameter. On the other hand pure tangential-aragonitic crusts are observed in the interior of coronas of small sea urchins of a Holocene oolite from Neapolis (South Peloponnese, RICHTER 1983 - Fig., 2B).



Fig. 3: Distribution of ooid types in the cycles of the Canal of Corinth. NW = west of the "central high", SE = east of hte "central high".

The radial and tangential oriented aragonite layers of the ooids of the Isthmus of Corinth exhibit the same anomally low birefringence presented by ooids of Bahama-type (tangential aragonitic cortices). Birefringence measurements of ooids from the Bahamas resp. Persian Gulf (ILLING 1954 and LOREAU & PURSER, 1973) only vary between 0.030-0.035 instead of 0.155 (thickness of thin section: 25-30 mm). The reason lor this low birefringence is attributed to high microporosity (loose packing of the rods) and variability in orientation of the crystallites in the plane of the laminae (statistically tangential).

Oolites with diagenetically changed primary aragonitic ooids occur in the marine sections of Cycles B to E. Here, oomoldic and in situ calcitized ooids (FRIEDMAN 1964) are the basic types, whose transformation cannot be put down to different hydrological influences, because they occur side by side in cycle B (SE-Canal) as well as in cycle E (NW and SE Canal). This is explained as follows: after the deposition of the oolitic layers the whole set of strata was drowned at the end of a cycle and aragonite was completely dissolved in the vadose zone. However, the in situ calcitized ooids suggest phreatic microlenses

within the vadose environment.

Another diagenetical effect observed on the studied ooids is a micritic to microsparitic calcitization of the primary aragonitic cortices, where transitions to the oomoldic and in situ calcitized types occur as well (RICHTER 1983). This kind of calcitization nucleates in the micropores between the aragonitic rods which are replaced as well in the progress of diagenesis. Finally, this diagenesis is concluded by low-Mg calcitic micritic to microsparitic ooids.

The carbonate-referred concentration of Sr in these oolites varies between 1000 and 4000 ppm which coincides with concentrations found in comparable oolites of Paleotyrrhenian age (last but one interglacial) from the Perachora-peninsula NW of the Canal of Corinth (HERFORTH & RICHTER 1979). Due to diagenetic effects like solution and/or calcitization of aragonitic cortices, the Sr-concentration is too low compared to 8500-11000 ppm in unchanged aragonitic ooids of the marine environment (Tab. 9 in RICHTER 1979; Tab. 1 in: BRAND & VEIZER 1983). However, referring to aragonite, the Sr-concentrations still reach values >7000 ppm.

3.2. MG-CALCITIC OOIDS

Oolites with radial-calcitic coated grains are intercalated within the non-marine Corinthian Marl (bedrock of N 1) and the non-marine parts of the cycles N 1, N 2, A, B and C (Fig. 3) of the canal incision. In contrast to the aragonite ooids described before, the cortices of these ooids show no anomalous double refraction in thin sections, which prooves a compact carbonate composition of the laminae. Radial structured Fe-calcitic ooids of brackisch origin from the "*Ingressionsfolge*" (Ingression Member) of the uppermost Corinthian Marl have already been discussed by RICHTER (1980). The Fe-calcitic composition as well as structure are interpreted tollowing RICHTER & F α CHTBAUER (1978) as a structure-preserving transformation of primarily Mg-calcitic ooids in an iron-rich reducing pore water environment. Fe-calcitic ooids with a radially-fibrous cortex are present in the Neogene of the Isthmus of Corinth since approx. 25 ma, determined by the age of a dacitic intercalation (RICHTER et al. 1982). In the canal incision these Fe-calcitic ooids can be observed in the upper Corinthian Marl in the Neogene cycles N1 as well as N2 and in the Middle Pleistocene cycle C. The ooids of cycle C are of particular interest because they are composed and structured differently in the north-western and south-eastern part of the Isthmus (see Fig. 3), reflecting divergenting histories of development on both sides of the eastern rise of the Corinthian Gulf:

(a) In the northwestern canal incision at the former street bridge the nonmarine section of cycle C is composed of an arenitic base with Limnocardiae (Neopseudocatillus catilloides), Dreisseniidae as well as abundant fragments of Charophycea (especially oogones). This set is topped by oolitic layers with radial-fibrous Fe-calcitic ooids. Minor amounts of radial-calcitic and mikritic ooids also occur in the base and some of the radial-calcitic ooids from the top show tangential-aragonitic ooids as nucleus. The oolitic level is covered by a conglomerate with Ostreae, which represents the marine section of cycle D here. More to the west this conglomerate is carrying typical fauna of the Tyrrhenian in the Mediterranean region. For the first time in the sequence of strata Strombus bubonius, an invaded gastropod from the West African coasts, was found in the sediments.

(b) In the southeastern canal incision a conglomeratic layer with Dreisseniidae and oolitic matrix overlies the marine section of cycle C, where the cortices of the ooids are oriented tangential-aragonitic. The upper part of this layer and the overlying oolites also contain Limnocardiae (among them: Neopseudocatillus catilloides). The coated grains composing the oolites mostly show a twofold cortex: An internal tangential-aragonitic part is wrapped by radial-calcitic laminae. Chemical staining of the thin section after LINDHOLM & FINKELMAN (1972) reveals no Fe²⁺ in the calcite lattice and X-ray diffraction analyses show MgCO₃-contents of 4.0-5.5 mol-%. Finally, cycle C at this location is completed by a thick red soil containing calcretes at the base and frequently pebbles as well as Helicidae in the upper alluvial part. It is topped horder box of base and other West African fauna (Natica lactea, Conus testudinarius, large

specimens of Spondylus gaederopus).

(c) History of development: Due to the lowering of the sea level after the warm period of cycle C (marine section) the Corinthian Gulf becomes more and more brackish. The initial eastern rise is located east of the Isthmus of Corinth, prooved by the occurrence of Limnocardiae and Dreisseniidae in the south-eastern canal incision. With increasing freshening of the basin a change in composition and structure of the cortices of the ooids is recorded. Starting with tangentially-aragonitic laminae, the ooids are switching to radial-fibrous laminae made up by Mg-calcite. MgCO₃-contents of 4.0-5.5 Mol-% in the calcite of ooids of the eastern incision are very probably primary and are not due to a transformation of high-Mg calcite into Mg-poorer calcite.

Paddings of Rivularia haematites from contemporaneous brackish reefs at the Perachora peninsula northwest of the Isthmus of Corinth show comparable Mg-contents. They show, however, a Mn-dependent zonation (differently luminescing layers) which would be erased when transformed from high-Mg-calcite to Mg-poorer calcite (RICHTER & ZINKERNAGEL 1981).

In the northwestern canal incision the cortices of the ooids have been Fe-calcitized in a reducing Feemphasized pore environment while preserving the original structure. This is put down to a missing terrestrial episode in this part of the Isthmus.

The south-eastern region of the studied area had freshwater influences only at the beginning of the glacial episode between the marine sections of cycles C and D. Here, the remaining glacial cycle is dominated by meteoric-vadose conditions with formation of soils and calcretes, while the northwestern part of the Isthmus area connected to the lake of Corinth remained covered by water. A continuous freshening of this lake is documented by Mg-calcitic ooids, indicative of brackish-phreatic conditions. Fe-calcitized ooids are more probably due to a meteoric-phreatic origin near the ancient coast. Finally, an eustatic sea level rise again caused a marine flooding of both sides of the Isthmus region (base of cycle D = Paleotyrrhenian = Mindel-Riss interglacial).

A wide-spread and well-exposed oolite with radially calcitic coated grains contemporaneous to the brackish level of cycle C occurs at the western end of the Perachora peninsula between lake Vouliagmeni and Cape Hiròon (path incision at the Roman cistern). After RICHTER (1984, p. 161) the ooids are composed of Mg_{3.5}-calcite. Locally these oolites were indurated during the marine flooding of the Paleotyrrhenian to beachrock with calcite cement. This Mg_{13.15}-calcite cement is diagenetically unchanged until recent.

In other places the radially calcitic cortices are wrapped by tangentially aragonitic laminae. There are a lot additional examples of tangentially aragonitic and/or radially calcitic ooids and corresponding environments on sites along the south coast of the Gulf of Corinth. Here, Quaternary coast terraces are influenced by a marine/brackisch cyclicity resulting in a complex lithological and diagenetic pattern (RICHTER & SEDAT 1983, SEDAT 1986).

5. CONCLUSIONS AND DISCUSSION

(1) In the Neogene/Quaternary sequence of strata of the Isthmus of Corinth the occurrence of aragonitic ooids is tied to marine sections, whereas Mg-calcitic ooids occur in limnic-brackish sections which is indicated by the accompanying fauna and/or flora associations. As it is located at a latitude of 38°, it is considered to be one of the northernmost Late Cainozoic occurrences of marine ooids of the world, which is valid also for Phanerozoic formations (OPDYKE & WILKINSON 1990). So, for instance, the formerly aragonitic ooids of the "Schaumkalkzone" from the Anisian of the Elm Ridge (E Braunschweig; No. 17 in Tab. 2 by RICHTER 1983) are deposited between latitudes of 35° and 40° as one of the northernmost Triassic occurrences of this type.

(2) Composition and structure of the aragonitic cortices correspond to the ooids at the Bahamas and/or the Persian Gulf of Holocene age (rods and granules of 0.5-2 mm, >7000 ppm Sr, tangentially - radially less abundant - arranged crywholdig Bibicoonki "Oboopdoroed dig in interfection of the content of the microsparitic coated grains appear as secondary types. The chemical composition (Sr-content) of modern ooids of the Bahama-type is closely coinciding with other aragonitic marine precipitates (RICHTER 1979 - Tab. 9) but as the aragonite of the laminae is not confined by crystal boundaries, an organic influence on the growth of these ooids seems to be probable (FABRICIUS 1977).

(3) The radially-structured Mg-calcitic ooids primarily consist of calcite with up to 5.5 Mol-% MgCO₃ and secondarily of Fe-calcite. The primary composition agrees with contemporaneously formed paddings of Rivularia haematites with preserved mineralogical/chemical growth zonation. The common occurrence of radially calcitic ooids and calcified blue-green algae is also known from older formations. So, both radialcalcitic ooids and stromatolites occur in the slightly hypersaline playa lake of the Lower Buntsandstein of north Germany (PAUL 1982). Additionally, these radially structured coated grains consist of Mg-calcite because of their primarily Fe-calcitic composition (RICHTER 1980).

(4) The limnic-brackish $Mg_{4.5.5}$ -calcitic ooids of the Isthmus take a mediating role between marine high-Mg calcitic ooids (e.g. 11-13 Mol-% MgCO₃ after MILLIMAN & BARRETTO 1975) and likewise radially structured low-Mg calcitic cavepearls (among others HAHNE et al. 1968). This emphasizes the importance of the Mg/Ca-ratio of the water with regard to the composition radially calcitic ooids. Regarding experiments on Mg-calcite by F\u00e4CHTBAUER & HARDIE (1980) our Mg-calcitic ooids point out a significantly lower Mg/Ca-ratio of the water (2:1 versus 5:1) compared to a normal marine environment.

(5) Only two types of the ooids with a multiphase cortex, being of special genetical interest (Precambrian - TUCKER 1984, Pennsylvanian - WILKINSON et al. 1984), could be observed in the Corinth region: a. Aragonitic cortices are wrapped by radially calcitic laminae documenting the change from marine to limnic-brackish conditions; b. Radially calcitic cortices are wrapped by aragonitic laminae showing the change from limnic-brackish to marine conditions.

A multiple mineralogical-chemical change of the laminae in the same ooid - like in modern ooids from the Baffin Bay (aragonite and $Mg_{12,4-14,4}$ -calcite after LAND et al. 1979) - could be observed in no case. This confirms a clearly separated change of environmental conditions - see point 1.

(6) The marine flooding of the glacial lake in the Gulf of Corinth during the interglacial sea level rise only took short time (see the evolution of ostracods, R Φ MMELT-DOLL 1990). This explains the envelope of aragonitic laminae around radially structured Mg_{3,5}-calcitic ooids. However, the change from marine to brackish conditions is combined with a slow freshening of the lake which is documented in a hiatus between aragonite ooids and their Mg_{4.5.5}-calcitic envelopes. Three explanations are given: a. The abundance of Mg-richer calcite laminae is very low and thus not significant in XRD-analyses; b. Mg-richer calcite has been diagenetically transformed to Mg-poorer calcite; c. In the transition phase no ooids have developed. As in the region of Corinth exclusively two-phase are observed (see point 5) we are favourably disposed to accept explanation c.

(7) The currently assumed dependence of the composition of marine ooids on changing pCO₂conditions, as assumed for the global changes during the Phanerozoic (pCO₂ < 10⁻³ atm + aragonite and Mg_{>8}-calcite, pCO₂ > 10⁻³ atm + Mg_{<8}-calcite and no aragonite; MACKENZIE & PIGOTT 1981, SANDBERG 1983) can be excluded for the Isthmus of Corinth, because such a rapid change in the composition of the atmosphere is not probable without human influence.

But the change of the Mg/Ca-ratio the waters significant for the composition the ooids in the marine/lacustrine cycles of the Isthmus of Corinth has the same effect as the pC0₂-change of the atmosphere on the global distribution of the ooid types during the Phanerozoic. Thus, our investigation may be regarded as a case study for the global change. The change in temperature of glacial and interglacial stages (5° for Greece - kind contribution of an anonymous reviewer) could be an additional effect resulting in different cortex compositions. However, recent Mg-calcitic ooids of the marine and lacustrine/brackish environment in comparable cool climates are not known. Additionally, in the Isthmus region also glacial stages are marked by red soils and calcretes being indicators for warm climates.

(8) The study of the change of ooid types in marine/lacustrine cycles clearly shows the importance of the primary composition Busication and Busication clearly reveals the weak point in the interpretation of the balance of the ooids in the Phanerozoic, for we know very little about the primary composition of radial-calcitic ooids of the past. Although the Fe-calcitic composition of many radially structured ooids of the Phanerozoic shows their formerly Mg-calcitic composition (RICHTER 1980), the exact amount of the primary Mg-content cannot be reconstructed exactly up to now. Additionally, a participation of lower organisms in building marine ooide is probable, as rods and granules without crystal surfaces indicate a diagenetically unaffected growth of aragonitic laminae, which makes an interpretation as a cement most probable. However, the exact primary composition of marine calcite cemente of past formations is still known very little. The compositions of primary marine Mg-calcitic cements (13 mol-% MgCO₃ - Mississippian/New Mexico - MEYERS & LOHMANN 1978, 15 mol-% MgCO₃ - upper Muschelkalk/North Germany - RICHTER 1984) are to be looked at as very promising attempts.

(9) As demonstrated before, the composition of ooids controlled by the environment in cycles of different order admits - somewhat speculatively - the following predictions:

• During the next glacial - as far as another glacial will come - the Gulf of Corinth will again develop to a fresh-water lake and will produce radial-calcitic ooids with 3-5.5 mol-% MgCO₃ at suitable places (flat bars).

• If the rise in CO_2 of the atmosphere induced by humans will continue, no more marine aragonitic ooids will develop. Instead, the corresponding ooids will have radially structured cortices of Mg_{e 8}

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