Micro-scale sideritic concretions in Holocene sediments of Guadiana estuary, Southern Portugal: their structure, composition and origin

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Abstract: Most sedimentological studies focussed so far on concretions in centimeter-scale. Authors described micrometer-scale concretions found within the Holocene sediments in the estuary of Guadiana River at a depth of about 41 m in the transitional, fluvial-estuarine facies. The concretions show internal zoning in micro-scale, pointing to their complex origin. Four types of concretions were distinguished by morphological, mineralogical and chemical features, showing a regular variation in the ratio of Mg, Mn and Ca compounds. Fe-carbonate concretions precipitated on detrital Fe-Mg nuclei. The innermost parts are enriched in Mn in accordance with the sequence of precipitation of carbonates associated with bacteria-mediated oxidation of organic matter. The outermost layer is enriched in Ca. XRD-patterns proved the occurrence of discrete carbonate phases.

Keywords: Siderite, Concretions, Estuarine sediment, Guadiana River, Holocene.

1. Introduction

The carbonate micro-concretions of diameter about 100-200 μm, found in Holocene sediments of Guadiana River, are predominantly of sideritic composition. Siderite is an authigenic mineral in sedimentary rocks (e.g. Mozley and Carothers, 1992). It usually forms concretions, which precipitated within the pore-spaces of sediments after deposition (Curtis et al., 1986). The strongly varying chemical compositions of siderite concretions are governed both by pore-water origin and by microbial influence. Mozley (1989a) showed that early diagenetic siderites from marine environments are “impure” containing considerable amounts of Mg and Ca, and never approaching end-member siderite compositions, while siderites from fresh-water environments often attain end-member composition. Concretionary siderite often reveals variation in chemical composition from the center to the outer edge. This variation is attributed to the changes in physical and chemical conditions in course of the concretion’s growth starting from its center towards the rim (Mozley, 1989b), and is associated with the depth-controlled microbial processes within the shallowly buried sediments (e.g. Curtis et al., 1986; Wilkinson et al., 2000). Experimental studies of Mortimer and Coleman (1997) confirmed the crucial role of Fe-reducing bacteria in determining the composition of authigenic siderite. In the studied micro-concretions one can observe very similar regular compositional variations in micrometer-scale, as those well known in commonly occurring centimeter-size carbonate concretions (e.g. Mata et al., 2005; Wilkinson et al., 2000). The aim of this work is to draw sedimentologist’s attention to microscopic-scale sideritic concretions, which may considerably contribute to understanding of the geological processes occurring in sediments.

2. Geological setting

Guadiana is one of the major rivers on the Iberian Peninsula discharging to the Atlantic Ocean. Late Pleistocene sandy sediments containing a siderite-enriched layer belong to the estuarine infill of Guadiana Pleistocene paleovalley. The present estuarine palaeovalley was formed as a narrow channel excavated into the fractured Carboniferous shale substratum by fluvial incision, during the Pleistocene marine lowstands (Morales, 1997). As a consequence, the channel reached in its deepest parts the depth of about 80 m below the present MSL (Boski et al., 2008). Such a deep erosion could occur during the Last Glacial Maximum, when the sea level was ca. 120 m lower than present (Hernández-Molina et al., 1994), and is quite unique when compared to other estuaries in Gulf of Cádiz reported by Dabrio et al., 2000. The borehole site referred in this paper lies close the...
Beliche rivulet – Guadiana River confluence, within the reaches of the present estuary of Guadiana.

The site is situated in a distance of about 9 kilometers from the present estuary river mouth and within the intertidal range of extensive salt marshes, which are developed on the accreted sediments on both sides of the infilled estuary and are covered by halophytic plants: Spartina densiflora, Spartina maritima, Atriplex spp. and Salicornia patula.

The borehole profile embraces the time span of the last 13000 years corresponding to ca. 48.5 m sedimentary sequence deposited on top of a fluvial gravel bed dating back to the past marine lowstands of undermined age. The entire sequence has a very well established depth-age model, which reflects the rate of sea-level rise and the creation of accommodation space for the sediments. Indeed from 13000 cal yrs BP until ca 7500 cal yrs BP the sediments accumulated at a rate of ca 7 mm/yr and afterwards with a rate of ca 1.3 mm until present. (Boski et al., 2008). The lower rate of sediment accumulation due to the lack of accommodation space led to the accretion of the Guadiana Delta which is now subject to the changes imposed by lower sediment delivery from the river due to the damming and coastal protection structures (Sampath et al., 2008).

Only in the basal unit (48.5 m – 40.5 m), the sediments consist of sand- silt intercalation and reflect the environment evolving from fluvial to estuarine. The remaining overlying units are monotonously silty up to the surface and were deposited in the mud flat – saltmarsh environment as indicated by foraminifera and bivalve fauna. The conditions of sheltered embayment, formed at the confluence of Beliche Rivulet and main estuarine channel, were responsible for an apparently uninterrupted, low energy deposition and a remarkably linear depth – age model which served for plotting the first regional sea-level rise curve (Delgado et al., 2008).

3. Materials and methods

The borehole CM5, whose site was placed within the upper reaches of the intertidal zone, was carried out with a WIRTH B0 drilling rig using bentonite slurry and steel casing in order to avoid the collapse of the borehole walls. The borehole mouth was assumed to have elevation of 0 m above the mean sea level. The core barrel was equipped with plastic 6” corelinetm (Rocbore Ltd) tube which optimized the recovery of sediment to an average of 80% on a volume basis. The cores were further sectioned in two halves, one for immediate sampling and the other for archiving.

Apart from CM5, there were also analyzed samples from two other boreholes: CM1 and CM3, located in a distance of 5 – 7 km from CM5 down the valley. All boreholes were drilled within the estuarine sediments, and samples were taken from horizons showing high magnetic susceptibility within the profiles. According to Rey et al. (2005), magnetic susceptibility may reveal diagenetic remobilization/enrichment of sediments in redox sensitive metallic elements like iron (Fe) or manganese (Mn). Nevertheless, elevated magnetic susceptibility may also point to the concentration of detrital Fe-rich minerals. Accordingly, fourteen samples were taken, spanning the depths from 5.3 m to 47.3 m. They were separated in size fractions by sieving without any pretreatment, and the sandy fraction 0.12 – 0.22 mm was taken for further experiments. This size fraction appeared to be best compromise between the maximum size and monomineral composition of grains. The mineral compositions were identified by three methods: transmission light microscopy, electron microprobe and X-Ray powder diffraction. Samples were subjected to separation into density fractions by using of bromoform CHBr 3 (density 2.88 g/cm 3). The heavy density fraction yields were in the range 0.4 – 7.4 wt%. Magnetic separation of a heavy density fraction was carried out using the Frantz Isodynamic® Separator Model L-1 to concentrate siderite for obtaining better XRD powder patterns. Density fractions were used to prepare polished thin sections of grains submerged in araldite-type resin.

The chemical identification was carried out by microprobe “JEOL 840A” equipped with “Noran” energy-dispersive (EDS) detector using accelerating voltage 15 kV. X-Ray powder diffraction patterns were recorded by the transmission technique using the powdered samples placed in capillaries of the internal diameter 0.5 mm. The diffractometer “CGR” with the Co-X-Ray tube, operating at 40 kV and 35 mA, equipped with the monochromator and the position-sensitive wide-angle detector “Inel” was used to record good quality spectra from powder samples of the bulk volume less than 1 mm3, exposure time 18 hours.

4. Mineral composition of the sediment

Siderite was identified in 2 samples out of 14, but only in one sample, CM5 40.95 m below the surface, it forms a a quantitatively significant population. In the second sample, CM3 32.7 m, there were found three grains only. In the studied profiles, the mineral composition of the infill is quite homogenous, with dominating quartz and feldspar grains accompanied by lithoclasts of fine-grained clastic rocks. According to Boski et al. (2008), the clay fraction comprises in decreasing order: illite, interstratified illite-chlorite, interstratified illite-vermiculite and kaolinite, interstratified illite-smectite. After subtraction of a low-density fraction, the remaining part (a few % wt.) showed variable composition, both in kind of minerals and in their relative abundances. The main mineral...
components of the heavy-density fraction are tourmalines, amphiboles, pyroxenes, garnets, staurolite, andalusite, carbonates and Fe-oxides.

The siderite-bearing layer in the CM5 profile does not differ from other layers by the ratio of sandy material and is relatively poor in high-density components, which represent only 0.6 wt% of the total sample mass. Siderite grains constitute about 5% of the high-density fraction, therefore, the amount of siderite in the sediment is only about 300 ppm. So sparsely distributed minute grains of siderite were only to be found by means of SEM identification of the high-density fraction.

5. Compositional variety of micro-concretions

Siderite-like carbonate grains are round in shape, and in back-scatter electron images often show presence of cracks. The cracks appear to be the effect of a deep relief of the grain’s surface, and the voids are usually filled by fine sediment particles, mainly clay minerals. The pronounced ratio of interstratified clay minerals in the sediment may suggest, that early diagenetic processes have already set on. Nevertheless, interstratified clay minerals could also be linked to pedogenetic and transport processes.

The studied micro-concretions show complex chemical compositions. As a rule, the carbonate grains have a thin outer rim, which is more calcic than the inner parts. The pool of carbonate micro-concretions can be subdivided into four morphological and compositional types:

In the simplest type 1, a round grain consists of two chemical zones: the internal part reveals a sideritic compositions with minor Mg and Mn contents and Ca-content of 15 – 20 mol%, and the thin rim ranging up to a few micrometers in thickness which contains up to 29 mol% of Ca-compound (Fig. 2a). Rarely, carbonate concretions may contain impurities included in course of their growth.

The second type of grains is less regular in shape, usually more elongated and sometimes showing a framboid-like internal structure which likely is an effect of aggregation of smaller grains (Fig. 2b). The complex carbonate grain contains more mineral impurities, caught in course of the growth of siderite concretion. The main extraneous phases are silicates and Fe-oxides. These impurities occur both inside particular siderite grains, and in interstitial space of the aggregate. Similarly to the type 1, the Ca-rich rim surrounds the whole aggregated grain, while the particular subgrains of the aggregated grain are not surrounded by this Ca-rich rim. It proves, that process of aggregation took place before the growth of Ca-rich rim.

The inner parts of the third type of grains resemble euhedral carbonate crystals with composition near to Fe:Mg=1:1. The outer parts are same as in the type 1, suggesting the subsequent concentrical growth. The boundaries of the core may exhibit relief. Its shape either presents the former erosion surface or is effect of the chemical reaction between both parts of the present grain (Fig. 2c). The relative sizes of the core part observed in cross-sections are strongly variable.

The most complex compositions show grains of the 4th type, which are similar to type 3 but reveal the presence of the irregular zone enriched in Mn, which is adjacent to the core. The boundary of the core part (dark) containing Fe and Mg well resembles the grain shape (Fig. 2d). The spatial distributions of Fe, Ca, Mg and Mn in the same carbonate grain are shown in Figure 3. The center-to-edge textural and geochemical trends are consistent with concentric growth. Four compositional zones can be distinguished starting from the core (Tab. 1):

1. Nucleus with cationic ratio Fe:Mg close to 1:1,
2. Irregular and thin inner zone enriched in Mn up to 37 mol%,
3. Main body of concretion siderite containing about 15 mol% Ca and Mn,
4. Regular thin rim composed of Fe-Ca-Mg carbonate.
6. Discussion

Projection points of sub-samples belonging to different zones plot in markedly different fields (Fig. 4), and are grouped in well-defined areas, pointing to the precipitation of separate carbonate phases under varying chemical conditions. In the experimental XRD pattern, the prominent peak of carbonates corresponding to the (104) crystal plane shows a complex structure, likely being a superposition of a few discrete reflections. Modeling of experimental profile was done using the WinFit computer program (Krumm, 1994, 1996) by fitting diffraction peaks of individual phases. A quite good matching of the calculated composite peak with the experimental one was obtained by fitting 5 peaks, computed by a Pearson VII function (Fig. 5).

Individual peaks likely stem from discrete carbonate phases having the chemical compositions governed by miscibility of end-member compositions. According to Reeder (1983), among rhombohedral carbonates the complete miscibility is attained between the following end-members: Fe-Mg, Fe-Mn, Mg-Mn. The ideal solid-solution between Mg- and Fe-carbonate was confirmed by Chai and Navrotsky (1996). These authors showed that the positions of X-Ray reflections, and the unit-cell parameters, gradually migrate along with the changing chemical composition. Bearing in mind, that the nuclei contain almost solely Mg-Fe carbonates in an average ratio 1:1 (Table 1, Fig. 4), the reflection peak 104 of the nuclei should have the intermediate position between end-member positions of rhodochrosite and syderite. Modeling of the diffraction profile disclosed the presence of such a reflection peak. It occupies the middle position among the fitted discrete peaks in the Fig. 5 and is relatively broad, which is in accordance with a big scatter of chemical analyses of the nuclei (Fig. 4). Identification of other discrete peaks is difficult, because they represent four-component solid solutions of carbonates. Owing to a much bigger ionic radius of Ca$^{2+}$ compared to other mentioned divalent cations, the solid solutions involving calcite are limited except at high temperatures. Nevertheless, at lower temperatures the metastable formations of these solid solutions are widespread (Reeder, op. cit.).

The angular positions of the fitted discrete reflection peaks can likely be assigned to the observed compositional zoning. The nature of different width of the discrete reflection peaks can be explained both by different crystallinity of the corresponding carbonate phases, and by different sizes of domains coherently scattering X-Ray beams. Different crystallinity may be attributed to differences in water carbonate ion concentrations during the precipitation of a given compositional variety of a carbonate phase. Similarly, Bassinot et al. (2004) found a strong relationship between foraminifera calcite crystallinity and the bottom water saturation relative to calcite. Changes in concentrations of dissolved chemical compounds can likely occur in short-time scale, corresponding to periods in which different compositional zones of the studied microconcretions were formed. The rates of precipitation of carbonate concretions can be very high. Pye et al. (1990) showed, that up to 10 mm authigenic carbonate may precipitate in natural conditions within less than 2 years. Therefore, the tiny sizes of the studied microconcretions suggest that they might have crystallized in a very short time, implying both not perfect crystallinity, and small sizes of crystallites.

Both the lack of mechanical abrasion of micro-concretions and fillings of cracks from their surface by tiny particles of neoformed clay minerals, favour the in-situ crystallization. The intermediate composition siderite-magnesite, which often exhibits angular core parts, is in sharp contrast to more or less spherical coatings, which build the outer parts of siderite concretions. The core parts of the present siderite concretions likely were deposited as sediment particles, being nuclei of the concretion’s growth inside the sediment. Giant fields of Holocene carbonate concretions have been discovered in the Gulf of Cádiz at a depth of 1000 m (Mata et al., 2005). Thus shallower, shelf equivalents may be well candidate for the source of detritus remobilized and dragged across the shelf during the post-glacial transgression. Other possible sources of extraneous nuclei of a given carbonate composition can be associated with precipitation from saline ponds, developing in salt marshes during the spring tides and subject to rapid evaporation during hot, dry Mediterranean type summers (e.g. Boski et al., 2008). A similar process of precipitation of carbonates of various compositions, including magnesites, in the arid zone lakes on Iberian Peninsula, is described by Pérez et al. (2002).
Coating the nucleus with newly precipitated siderite occurs most likely in microenvironments where due to the dissilimilatory Fe(III) and Mn(IV) reduction a local supersaturation with respect to siderite is attained. The forming sequence of chemical components, recorded in the micro-concretions, was: Mn → Fe → Ca. The highest concentrations of Mn in central, i.e. the earliest parts of early diagenetic siderite concretions, were reported both from recent sediments (e.g. Choi et al., 2003) and from fossil diagenetic systems (e.g. Curtis et al., 1986). The latter authors postulate that Mn is enriched in those sub-samples, which formed very close to the sediment/water interface. Mn$^{2+}$-cation would be preferentially reduced over Fe$^{3+}$ because of greater energy production per mole of organic carbon oxidized (Froelich et al., 1979).

The outermost rim of the concretions recorded the last change in growth conditions. It is characterized by precipitation of a few micrometer layer of Ca-rich siderite with Ca-contents up to 29 mol%, which is metastable at low temperatures. Late precipitation of Ca-rich phase might have been promoted by the input of fresh waters. This could be achieved for example by an episode of flooding which, in case of Guadiana river, occur regularly and play a crucial role in the transfer of sediment from the estuary to the coastal ocean (Portela, 2006). In addition to irregular hydrological regime with the interannual variation of discharge as big as 100 to 1 (Bernardo, 2003), episodic floods were reported in Guadiana river in Recent (e.g. Aliotta et al., 2002), and they were also evidenced in Holocene deposits from Boina-Arade estuary (Wilamowski and Boski, 2004).

7. Conclusions

A complex structure of carbonate micro-concretions, sparsely occurring in Holocene deposits of Guadiana Valley near it’s estuary, evidences their multiphase origin.

Micro-concretions are chemically zoned. XRD-patterns prove the occurrence of a few discrete carbonate phases.

In most cases, concretional growth took place around a particle of carbonate of intermediate, magnesite-siderite composition. These ex-situ nuclei show various degrees of erosional rounding.

The subsequent crystallization of concretions reflects compositional changes of interstitial water, and phased precipitation within a sediment column, as described by Curtis et al., (1986): the very early coatings attached to the nucleus are enriched in Mn, the following coatings are composed of Fe-carbonate.

The outermost coatings are richer in Ca-carbonate. A possible mechanism, involving a shortage of Fe-source and a change in environmental parameters that resulted in precipitation of Ca-carbonate, was proposed.

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