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**CHEMICAL AND MINERALOGICAL COMPOSITION OF HOLOCENE  
SIDERITIC MICRO-CONCRETIONS FROM THE GUADIANA  
ESTUARY, SOUTHERN PORTUGAL**

**Abstract:** Early-diagenetic siderite micro-concretions occur within the Holocene sediments in the estuary of Guadiana river at a depth of about 41 m in the transitional, fluvial-estuarine facies. They show regular compositional variation with regard to the ratio of Mg, Mn and Ca compounds. XRD-patterns do not show the presence of discrete carbonate phases pointing out to very tiny dimensions of carbonate crystals, which are smaller than the domains of coherent scattering of X-Rays. The "impure" chemical composition of the studied concretions points to their crystallization from marine waters rather than from the fluvial ones.

**Keywords:** siderite, concretions, Guadiana, estuary, XRD

INTRODUCTION

Siderite is an authigenic mineral in sedimentary rocks (*e.g.* Mozley, 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 (1989) 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. We describe here a layer rich in micro-concretions of siderite belonging to the transitional facies between the fluvial (higher energetic) and estuarine (lower energetic) depositional environments observed during the process of infilling of the Pleistocene paleovalley of Guadiana River. The maximum thickness of the sediments accumulated in this estuary since the Last Glacial Maximum (LGM) reaches 80 meters which is the highest value in the Gulf of Cádiz (Dabrio *et al.* 2000), with the rate of deposition varying from 8.5 mm/year until middle Holocene to 20 mm afterwards.

Fifteen sediment samples 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 fraction appeared to be best compromise between the 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. The heavy fraction yields were in the range 0.4-7.4 wt%. Density fractions were used to prepare polished thin sections of grains submerged in "Araldite" resin. To concentrate siderite for obtaining better XRD powder patterns was carried out further magnetic separation of the heavy fraction. The

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chemical identification was carried out by microprobe “JEOL 840A” equipped with “Noran” energy-dispersive 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” equipped with the position-sensitive wide-angle detector “Inel” was used to obtain quality spectra from 3 mm<sup>3</sup> aliquots of samples.

#### MINERAL AND CHEMICAL COMPOSITION

In the studied profiles of three boreholes CM1, CM3 and CM5, the mineral composition of the sandy fraction is quite homogenous with regard to the dominating quartz and feldspar grains accompanied by lithoclasts of fine-grained clastic rocks. The composition of a few weight per cent of the sediments, remaining after subtraction of low density fraction, is more variable both in kind of minerals and in their relative abundance. The main mineral components of the heavy fraction are tourmalines, amphiboles, pyroxenes, garnets, staurolite, andalusite, carbonates and Fe-oxides.

The siderite-bearing layer occurs at a depth of 40.95 m below the surface in the drilling core of the CM5 borehole, located at about 7 kilometers from the mouth of estuary. This sample is relatively poor in heavy components, which represent only 0.6 wt% of the total sample mass. Siderite micro-concretions constitute about 5% of the heavy fraction, have the sizes of 100-200 µm, and can be divided into 4 groups, basing on morphological and chemical features (Wilamowski, Boski 2005). They are characterized by chemical zoning from the center towards the rim. In the micro-concretions having the most complex structure, four compositional zones can be distinguished starting from the core (Table 1):

- nucleus with cationic ratio Fe:Mg close to 1:1,
- irregular and thin zone enriched in Mn up to 37 atom %,
- main body of concretionary siderite containing about 15 atom % of Ca and Mn,
- regular thin rim composed of Fe-Ca-Mg carbonate.

In the graphic projection, analyses of sub-samples belonging to different zones plot in markedly different fields (Fig. 1) pointing out to the phenomenon of stepwise change in conditions of their growth. If so, one can expect the occurrence of discrete carbonate phases instead of gradual change in chemical composition. As different carbonate phases can be distinguished by means of X-ray diffraction, this tool can be used to verify this hypothesis. However, in the experimental XRD-powder patterns (Fig. 2), in the regions of expected diagnostic reflections 104 of carbonate phases there occur only very tiny discrete reflections, underlain by broad bands resulting from continuous change in d-spacings, which can be attributed to gradual change in carbonate compositions. The left-side asymmetry of the reflection 2.808 points out to the occurrence of Fe-carbonates of different chemical compositions. For comparison, the projections of early diagenetic siderites studied by Mozley (1989) are shown in the Fig. 1 as fields marked by diagonal lines. According to Mozley, siderites

Table 1. Mean chemical composition in the micro-concretions of siderites.

	Rim	Body	Mn-rich	Core
Si	0.18	0.13	0.09	0.06
Fe <sup>+2</sup>	27.53	30.22	19.57	26.47
Mn	1.82	5.71	17.07	1.18
Mg	1.64	1.42	0.97	11.80
Ca	9.32	4.86	5.59	0.60
Total	40.49	42.34	43.29	40.10
#Fe <sup>+2</sup>	0.60	0.66	0.42	0.48
#Mn <sup>+2</sup>	0.04	0.13	0.37	0.02
#Mg <sup>+2</sup>	0.08	0.06	0.05	0.48
#Ca <sup>+2</sup>	0.28	0.15	0.17	0.02

belonging to marine and fresh-water environments differ chemically. Their projection points occupy somehow different fields in the diagram, however, the fields partly overlap. In general, the marine siderites contain more Mg and Ca than the fresh-water ones. Nevertheless, the chemical variability of the studied micro-concretions is by far greater than the one noticed by Mozley, and there is no clear relationship in the observed trends to neither marine nor fresh-water environments of Mozley (*op.cit.*).

## DISCUSSION

The ideal solid-solution between Mg- and Fe-carbonate was proven 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 change of chemical composition. The angular positions of the mentioned discrete reflections are, however, not characteristic of end-member carbonate compositions, but they rather can be assigned to general compositional zoning (Table 1). They also could be attributed to the intermediate compositions within the non-ideal mixing series of Ca-Fe carbonates. In this compositional series, the occurrence of broad bands instead of discrete, well-defined reflections, might result from the mixture of sub-micritic Ca- and Fe-carbonate crystals which are smaller than the domains of coherent scattering of X-Rays. According to Mozley (*op. cit.*), the “impure” chemical composition of the studied micro-concretions may be linked to crystallization from the marine waters rather than from the fluvial ones. The occasional input of brackish waters into the estuary was proven by the occurrence of brackish microfauna in the sediments. It is very likely that the sandy layers underlying directly the discussed layer bearing micro-concretions of siderite may well be the pathway of infiltration of fresh water carrying the dissolved iron, which subsequently is making up the siderite micro-concretions growing in pore-spaces of sediment. The data presented here are

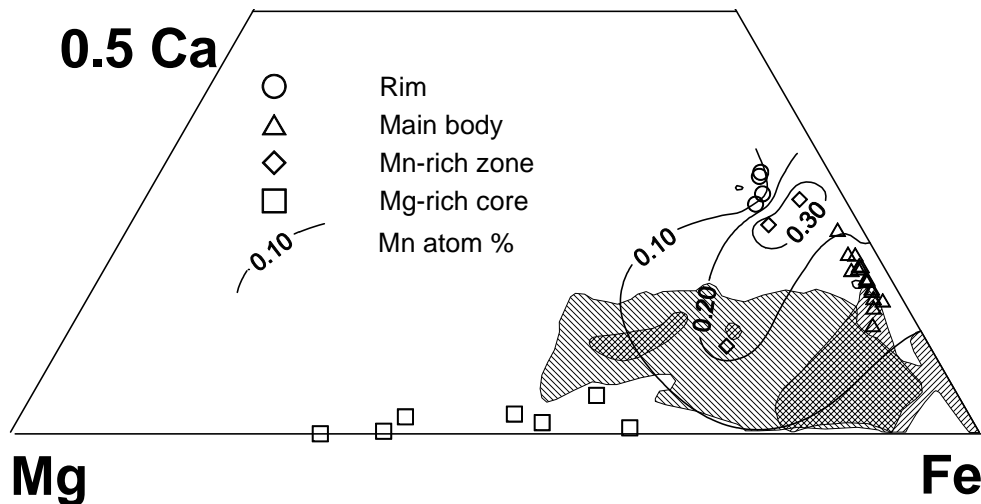


Fig. 1. Chemical compositions in atom % of four different compositional zones in siderite micro-concretions presented in the semi-ternary diagram in four-component system. For the purpose of the triangle presentation, compositions were normalized to 100 with regard to three variables: Ca, Mg and Fe, and the true Mn-contents were presented as isolines. The actual Ca, Mg and Fe-contents can be read out directly from the triangle after subtraction of Mn-contents. For reference, fields of siderites representing two distinct depositional environments are shown, marked by diagonal lines (according to Mozley 1989): marine – direction NW-SE and fresh water – NE-SW.

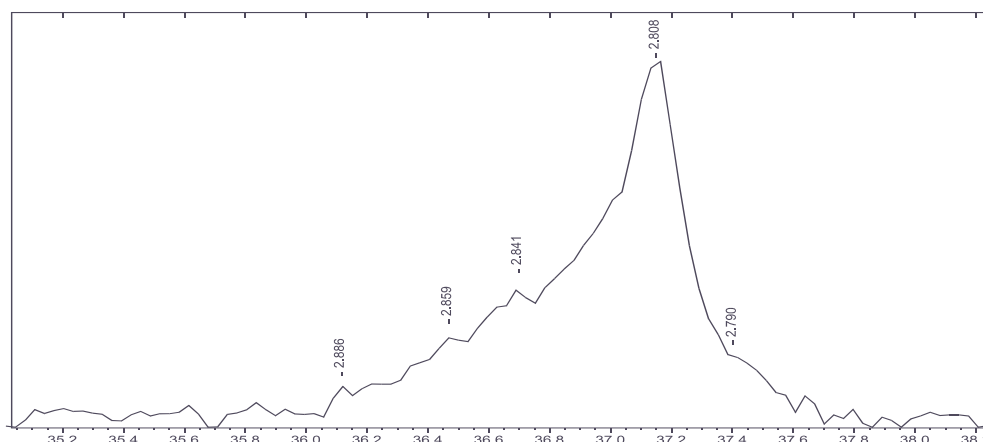


Fig. 2. The fragment of powder XRD-pattern of siderites around 104 reflection showing prevailing gradual change in composition over the mixture of discrete carbonate phases ( $\text{Co}_{\text{K}\alpha 1}$ ).

a part of a regular article (Boski *et al.* 2005), which is in preparation.

#### REFERENCES

- BOSKI T., CAMACHO S., WILAMOWSKI A., MOURA D., VEIGA-PIRES C., FLETCHER W. 2005: 13000 yr record of sediment infilling in Guadiana river estuary, S. Portugal. *Quat. Sci. Rev.* (in prep).
- CHAI L., NAVROTSKY A. 1996: Synthesis, characterization, and energetics of solid solution along the  $\text{CaMg}(\text{CO}_3)_2$ - $\text{CaFe}(\text{CO}_3)_2$  join, and implication for the stability of ordered  $\text{CaFe}(\text{CO}_3)_2$ . *Am. Mineral.*, 81, 1141-1147.
- CURTIS C.D., COLEMAN M.L., LOVE L.G. 1986: Pore water evolution during sediment burial from isotopic and mineral chemistry of calcite, dolomite and siderite concretions. *Geochim. Cosmochim. Acta*, 50, 2321-2334.
- DABRIO C.J., ZAZO C., GOY J.L., SIERRA F.J., BORJA F., LARIO J., GONZÁLEZ J.A., FLORES J.F. 2000: Depositional history of estuarine infill during the last postglacial transgression (Gulf of Cadiz, Southern Spain). *Marine Geol.*, 162, 381-404.
- MOZLEY P.S. 1989: Relation between depositional environment and the elemental composition of early diagenetic siderite. *Geology*, 17, 704-706.
- MOZLEY P.S., CAROTHERS W.W. 1992: Elemental and isotopic compositions of siderite in the Kuparuk Formation, Alaska: effect of microbial activity and water/sediment interaction on early pore-water chemistry. *J. Sed. Petrol.*, 62, 681-692.
- WILAMOWSKI A., BOSKI T. 2005: Four types of micro-concretions of siderite from the Guadiana estuary, Southern Portugal. *Pol. Tow. Mineral. Prace Spec.*, 25, 250-253.