POLSKIE TOWARZYSTWO MINERALOGICZNE – PRACE SPECJALNE
MINERALOGICAL SOCIETY OF POLAND – SPECIAL PAPERS
Zeszyt 26, 2005; Volume 26, 2005

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MICROBIAL MEDIATED CRYSTALLIZATION OF CARBONATES IN HOLOCENE SEDIMENTS IN THE GUADIANA ESTUARY, SOUTHERN PORTUGAL: MICRO-CONCRETIONS OF SIDERITE

Abstract: The siderite micro-concretions grown on detrital Fe-Mg-carbonate nuclei in the column of Holocene sediments. Their earliest parts are enriched in Mn that is in accordance with the sequence of precipitation of carbonates associated with bacteria-mediated oxidation of organic matter. The outermost layer is enriched in Ca that may stem from the change in pore-water chemistry.

Keywords: carbonate, siderite, concretions, estuary, Guadiana

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 diagenetic concretion's growth starting from its center towards the rim (Mozley 1989). This association seems to be associated with microbial respiration of organic matter producing the depth related Eh gradient within the shallowly buried sediments (*e.g.* Curtis *et al*. 1986, Wilkinson *et al*. 2000). Experimental studies of Mortimer, Coleman (1997) confirmed the crucial role of Fe-reducing bacteria in determining the composition of authigenic siderite.

Fine to medium quartz sands are dominant in large portions of the sedimentary infill of the Guadiana paleovalley near its mouth. In the profile, the sediments present intercalation of terrigenic and marine-brackish inputs (Boski *et al*. 2002). The siderite-bearing layer does not differ from other layers by the content of sandy material, and its siderite concentration is as low as 0.3 wt per mil. The process of siderite neoformation either was spatially extraneous and the siderite micro-concretions were then transported and deposited together with the main load of sand, or more likely took place *in situ* concurrently with the "normal" sandy sedimentation. In the Fig. 1 is shown the example of concretion with the most complex compositions. It reveals the presence of the irregular zone enriched in Mn, which is adjacent to the core. The boundary of the body part (dark) containing Fe and Mg well resembles the grain shape. Spatial distributions of Fe, Ca, Mg and Mn are shown in Fig. 2.

The zoning of siderite micro-concretions suggests their complex origin (Wilamowski, Boski 2005a). More or less angular core parts of intermediate composition siderite-magnesite are in sharp contrast to spherical coatings that present the outer parts of siderite micro-concretions. The core parts were likely deposited as sediment particles before the onset of the concretion's growth inside the sediment. Giant fields of Holocene carbonate concretions has recently been discovered in the Gulf of Cádiz at a depth of 1000 m (Mata *et al*. 2005), being one of possible sources of carbonate detritus which could serve as nuclei of the studied siderite micro-concretions. The micro-concretions start to grow from the core by

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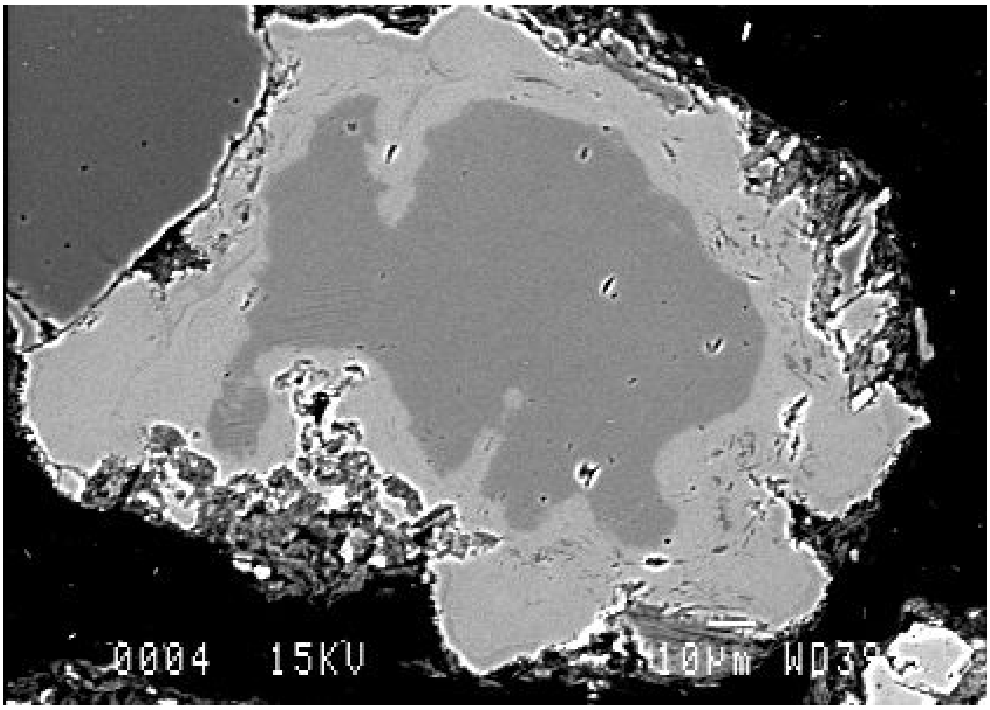

Fig. 1. Back-scatter electron image of multi-phase siderite micro-concretion.

coating the nucleus by newly precipitated siderite. In the course of growing, the relative proportions of main cations changed regularly (Wilamowski, Boski 2005b). Assuming the growth from center to rim, the time succession of chemical components 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. Oxidation of organic matter in the sediment column after burial seems to be responsible for remobilization of cations to concentrate in secondary phases, like Fe-carbonates. After the consumption of free oxygen by aerobic bacteria, the next oxidants of organic matter in the fresh-water environment would be Mn^{4+} and Fe^{3+}, which are derived from soil profiles. From these two cations, the Mn^{4+}-cation would be preferentially reduced because of greater energy production per mole of organic carbon oxidized (Froelich *et al*. 1979). The observed chemical zonation is consistent with this model as concerns spatial distribution of Mn and Fe. The outermost rim of the micro-concretions recorded the last change in growth conditions. It is characterized by precipitation of Ca-rich siderite with Ca-contents up to 29 atom %. Such Ca-rich siderites are not stable at low temperatures because of divergent ionic radii of divalent Fe and Ca. They do not form solid solutions but separate phases. In the case of low temperature crystallization, the co-precipitation of Ca-rich and Fe-rich carbonates is probable. The micritic nature of siderite concretions (Curtis *et al*. 1986) seems to favor precipitation of tiny carbonate crystals differing in composition with each other.

Assuming the *in situ* gradual growth embracing the change from Mn- to Ca-rich siderite, late precipitation of Ca-rich phase might have been promoted by the change in pore water chemistry. A higher activity of Ca^{+2} ions may happen in response to floods as shown

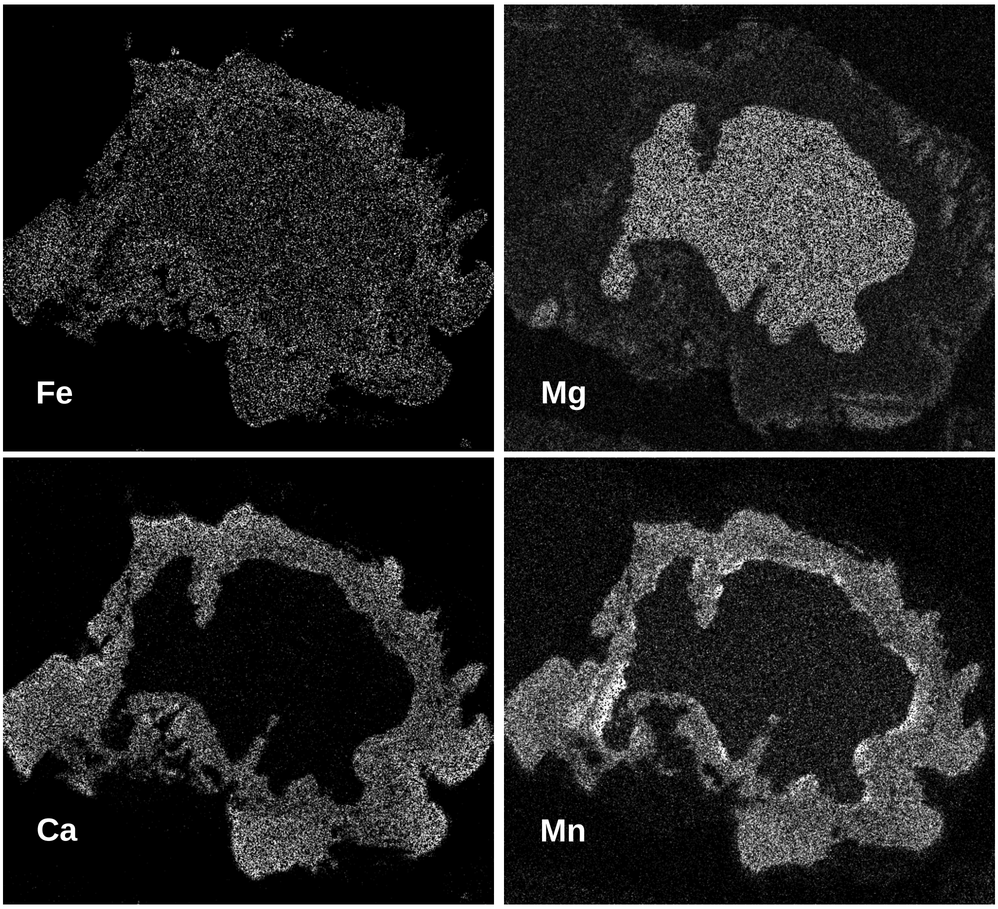

Fig. 2. X-Ray maps of cation distribution in the micro-concretion showed in BSE-image in Fig. 1.

in Holocene deposits from Boina-Arade estuary (*e.g.* Wilamowski, Boski 2004) or as result of the skeletal carbonate dissolution in the low pH porewaters

Other explanation of the late change in composition is mechanical remobilisation and redeposition of sediment into environment characterized by higher supply with Ca^{2+}-cations, resulting in growth of Fe-Ca carbonate phase. Although the concretions' morphologies do not show mechanical damage, which likely could take place during erosion, transport and redeposition, the knowledge about isotopic composition of carbonate carbon in inner and outer parts of concretions might help proving one of these hypotheses. Once buried, the siderite precipitation starts just below the millimeter thick oxydation zone (Curtis *et al.* 1986) as was evidenced by high Mn contents of early precipitates. Upon absence of SO_4^{2-} in predominantly fresh-water diagenetic environment, the carbonate in the early precipitation zones should consume the isotopically light C produced as CO_2 during bacteria-mediated reduction of Mn^{4+} and Fe^{3+} according to "MnR" and partly "FeR" reactions (Coleman 1985). In turn, the late precipitates of carbonates should utilize the isotopically heavy CO_2-carbon produced during the methanogenesis in the "Me" zone. Therefore, in a single precipitation sequence, the isotopically heavier C is expected to constitute the late zones than the early ones. The expected differences in the values $\delta^{13}C$

between the inner and outer parts of the studied concretions would be as great as 40 per mil (Coleman, Raiswell 1993). The determination of isotopic composition will be the next step of our investigations on siderite micro-concretions. The data presented here are part of regular article (Boski *et al.* 2005), which is in preparation.

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