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BaMn[CO3]2 – a previously unrecognized double carbonate in brackish sediments: Characterization and possible biogeochemical implications

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BaMn[CO3]2, a double carbonate that has been described from one metamorphic natural location (Hirowatari & Fukuoka, 1988), was only synthesized by Chang (1964) at high temperature and pressure. Its occurrence as a new mineral, however, has not been approved by IMA, so far (Jambor & Grew, 1991). We found first evidence for the possible formation of BaMn carbonates in a low-temperature natural environment from detailed SEM-EDAX and FEM investigations in anoxic brackish sediments recovered from the Landsort Deep, Baltic Sea. Samples were obtained with a multi-corer applied from research vessel P. Penck. These brackish sediments are particular rich in manganese. Dissolved sulfate was already depleted in the top 20 cm due to microbial sulfate reduction, and the water column provides biogenic barites that are dissolved in the sulfate-depleted sediments. We present a first report on the room-temperature synthesis of BaMn[CO3]2 from aqueous solution. The experiments are part of ongoing investigations on the low temperature (bio) geochemistry of barium in the natural barium cycle. The double carbonate, with minor co-occurrence of Ba-containing manganese(II) carbonate, was characterized by powder X-ray diffraction, SEM-EDAX, Raman and FTIR spectroscopy. Due to the similarity of tentative powder X-ray data and the spectroscopic results with BaMg[CO3]2 we suggest a structure similar to the mineral norsethite (Effenberger and Zemann, 1985; Chang, 1964).

The low-temperature formation of BaMn[CO3]2 is of particular biogeochemical interest because it is an indicator for low-sulfate suboxic depositional environments. In addition, the anhydrous double carbonate is an analogue to the mineral dolomite (CaMg[CO3]2), whose wide-spread occurrence in low-temperature sedimentary environments is still not fully understood. It should be noted, that significant solid-solution incorporation of divalent Mn into the crystals of precipitated witherite and Ba into the lattice of rhodochrosite were observed. This metastable SS-AS behavior requires further detailed investigation. Current research seeks to further investigate the thermodynamics and kinetics leading to the low-temperature formation of BaMn[CO3]2.

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