Short communication

BaMn[CO$_3$]$_2$ – a previously unrecognized double carbonate in low-temperature environments: Structural, spectroscopic, and textural tools for future identification

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ABSTRACT

Following a tentative evidence for the occurrence of low-temperature barium manganese(II) carbonates in brackish sediments of the Baltic Sea, a stoichiometric double carbonate, BaMn[CO$_3$]$_2$, was synthesized from aqueous solutions at ambient temperature for the first time. Here we report the results of a multi-method approach, including scanning electron microscopy (SEM–EDX) investigations, the chemical composition, and, in particular, the diagnostic powder X-ray diffraction pattern, as well as diagnostic parts of the FT infrared absorption and Raman spectra for future identification of this new carbonate in low-temperature environments, like brackish sediments.

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1. Introduction

BaMn[CO$_3$]$_2$, a stoichiometric anhydrous double carbonate was synthesized by Chang (1964) at high temperature and pressure (500 °C; 15 kbar) earlier. The authors mentioned isotypy to norsethite, BaMg[CO$_3$]$_2$. So far, the natural occurrence of BaMn[CO$_3$]$_2$ has been described from a metamorphic location only (Hirowatari and Fukuoka, 1988). More recently, however, a Mn-rich norsethite (Ba(Mg,Mn)[CO$_3$]$_2$) was described from a hydrothermal ore deposit (Zidarov et al., 2009), suggesting that there is a solid-solution behavior between pure norsethite and the still unnamed BaMn double carbonate. During ongoing investigations on the low-temperature biogeochemical cycles of barium and manganese,

we found tentative evidence for the occurrence of a previously unknown Ba–Mn carbonate by SEM (scanning electron microscopy) and EDX (energy-dispersive X-ray micro-analyses) analyses as well as by field-emission spectroscopy (FESM). First evidences came from sediments of anoxic sediments of the euxinic brackish Landsort Deep, west-central Baltic Sea (Fig. 1). These surface sediments are particularly rich in manganese and host a number of manganese(II)- and barium-bearing minerals like Ca-bearing rhodochrosite, manganese sulfides, and barite (e.g., Suess, 1979; Jakobsen and Postma, 1989; Lepland and Stevens, 1998; Lepland et al., 2000). Due to the low salinity bottom waters and microbial sulfate reduction, dissolved sulfate is already depleted close to the surface of brackish sediments (Fig. 2). As a consequence, barite derived from the water column may become physico-chemically unstable leading to the accumulation of dissolved barium in the pore waters (Fig. 2; Torres et al., 1996; Lepland et al., 2000). In addition, the microbial activity leading to the oxidation of organic
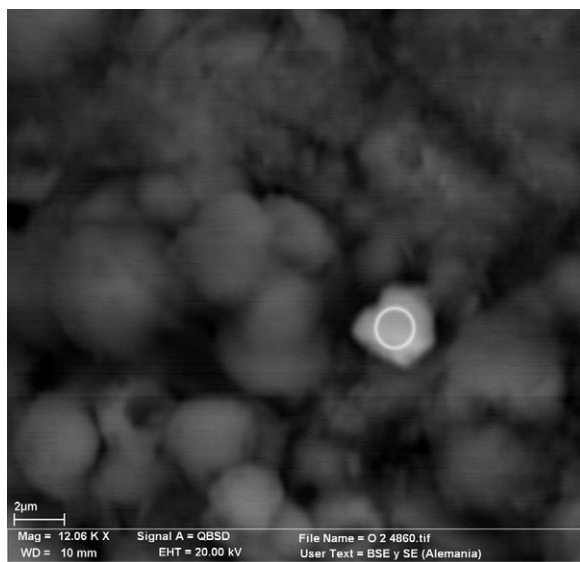
Fig. 1. FESM picture (BS mode) of part of a natural surface sediment core recovered of the anoxic Landsort deep, west-central Baltic Sea (IOW core 336870-2-1; 58.13°N and 18.13°E; 450 m water depth). Analysis at the given spot gave dominantly Ba and Mn signals. Minor elements found were Si, Ca, Al, K, Cl, and Fe(?). Further measurements on Ba- and Mn-rich particles at other parts of the sediment samples showed variable S contents indicating the closeness of authigenic BaMn carbonate formation with sedimentary barites.

$BaMn[CO_3]_2$ is of general interest for carbonate geochemistry, because of its isotypy to norsethite the structural relation to the structure type of dolomite (see below). $BaMn[CO_3]_2$ was synthesized under similar conditions as described for norsethite (Lippmann, 1973; Böttcher, 2000). However, the wide-spread formation of dolomite at low temperatures is still not fully understood (Morrow and Ricketts, 1986; Vasconcelos et al., 1995; Alonso-Zarza and Martin-Pérez, 2008).

The characteristic compositional, and textural features, the powder X-ray diffraction patterns, infrared absorption bands and (micro-)Raman frequency shift data are presented. This analytical frame should encourage the search for this double carbonate in natural low-temperature environments, as for instance brackish-marine sediments, and it should be used as a tool (among others) to understand its actual role in the coupled geochemical cycles of carbon, barium, manganese, and sulfur.

2. Materials and methods

$BaMn[CO_3]_2$ was synthesized at ambient temperature (21 ± 1°C; 1 atm total pressure) from aqueous solutions of 0.17 M barium/manganese(II) chloride and 0.28 M sodium bicarbonate. De-ionized water in a DURAN glass bottle was deoxygenated by inert gas (N_2) and p.a. grade chemicals were subsequently dissolved in the solution under a continuous stream of nitrogen gas. Mother solution and precipitate were allowed to react for 10 days in a closed bottle. Final pH was measured with an ion-selective electrode (Mettler Toledo InLab Basics electrode; Schott handy lab pH11 pH meter). Afterwards, the solids were separated from the mother fluids via membrane filtration (cellulose acetate; 0.45 μm diameter), washed with deionized water, and dried in an oven at 60°C. SEM analysis showed that the crystal sizes were below 10 μm (Fig. 3). An aliquot of the aqueous solution was acidified (p.a. grade HNO_3) and the concentrations of dissolved cations were measured after appropriate dilution by ICP-OES (Thermo, iCAP 6300 Duo). In the successful experiments with an initial molar Ba/Mn ratio of 0.4, the final solutions contained Ba in excess with respect to Mn (final Ba/Mn ratio ≈ 16), and the final pH was 5.9. Under these conditions, the double carbonate was the dominant phase accompanied by some "rhodochrosite" (artificial compounds with the same composition and crystal structure as a mineral are indicated by the apostrophized mineral name throughout the paper). At initial Ba/Mn ratios exceeding 6.4, "witherite" was the dominant phase with very minor double carbonate. In parallel experiments with solutions containing also Mg, norsethite was found as an additional reaction product. In
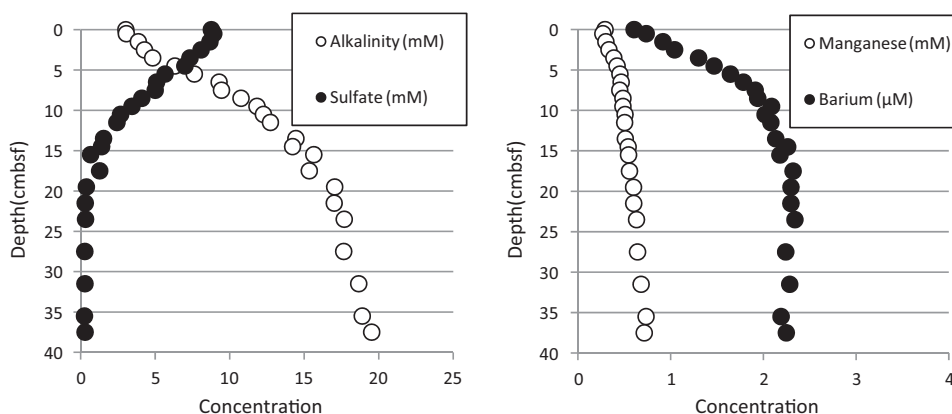
matter and the reduction of manganese(III/IV) oxides leads to an accumulation of dissolved inorganic carbonate and divalent manganese (Fig. 2). Here we give experimental evidence, that these conditions may provide the physico–chemical environment for the formation of authigenic barium–manganese(II) carbonates. Up to now, the low-temperature geochemistry of the system Ba–Mn–S–C was only discussed in terms of manganese(III,IV) oxides, Mn(II) carbonate (rhodochrosite), barium sulfate (barite), and barium carbonate (witherite) (e.g., Church, 1979; Jakobsen and Postma, 1989; Torres et al., 1996; Lepland and Stevens, 1998; Lepland et al., 2000; Riedinger et al., 2006). In the present study, we report on the synthesis and characterization of the Ba–Mn double carbonate $BaMn[CO_3]_2$, synthesized under ambient conditions from relatively low concentrated aqueous solutions without biological catalysis and within reasonable times. This double carbonate provides a new phase that may limit the concentrations of dissolved Ba^{2+} and Mn^{2+} in suboxic and anoxic aquatic low-temperature environments. Besides its proxy potential for low-sulfate environments,

Fig. 2. Pore water profiles of selected geochemical parameters from a short sediment core recovered from the euxinic brackish Landsort Deep, west-central Baltic Sea (IOW core 342390-2-1; 58.58°N and 18.23°E; 441 m water depth), close to the site that gave first evidence for the occurrence of an authigenic BaMn carbonate. cmbsf: cm below surface. Data are taken from Winde (2009).
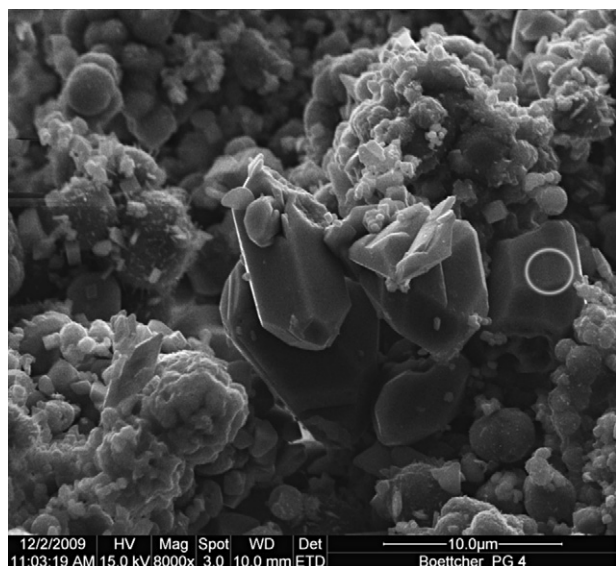
Fig. 3. SEM–EDX analyses of BaMn[CO$_3$]$_2$ synthesised at 21 °C. EDX analysis at the indicated spot gave an atomic Ba/(Ba + Mn) ratio of 0.48. No further elements besides O and C were observed. Other measurements confirmed the essentially ideal 1:1 stoichiometry of cations in the double carbonate. Spherical precipitates in the background are precipitated "rhodochrosite".

scanning microscopy (LEO, Carl zeiss, mod. GEMINI–1530) was carried out at the analytical unit of the University of Granada (CIC), Spain.

The solid phases were characterized by X-ray powder diffraction (Siemens D 5000 X-ray goniometer with Ni-filtered Cu$_{K\alpha}$ radiation). Calibration of peak positions (Table 1) was carried out for one sample by the addition of synthetic ZnO as an internal standard. One X-ray powder pattern of an admixture of MnCO$_3$ and BaMn[CO$_3$]$_2$ was taken with a Philips PW3710 diffractometer (Cu$_{K\alpha}$ radiation, 2Θ range 3–90°, step size 0.02°, step time 1 s) and refined by Rietveld method (Program TOPAS. Version 3.0, Brucker AXS Inc., Karlsruhe, Germany, 1999).

The FTIR spectra were measured at ambient conditions with a Mattson 3000 type FTIR spectrometer between 4000 and 400 cm^{-1} using specimens with grain sizes <2 μm, embedded in KBr. 2.5, 5 and 10 mg samples were mixed in an agate mortar with 1 g KBr. Pellets were obtained under vacuum at a pressure of 7.5 tons/cm^2 (Böttcher et al., 1997).

Micro-Raman spectra were measured on single grains at ambient temperature and atmospheric pressure with a Horiba Jobin Yvon HR 800 UV micro-Raman spectrometer as described by Bendel and Schmidt (2008). The sample was excited using a 488 nm laser line from an Ar$^+$ laser, with 20 mW at the laser exit. The use of a holographic grating with 2400 grooves/mm and a CCD detector with 1024 × 256 pixels yielded a spectral dispersion better than 0.43 cm^{-1} per pixel. Raman spectra were collected in the range 100–1800 cm^{-1} with an acquisition time of 2 × 60 s for each spectral window. The Raman spectra were frequency corrected using silicon (Si band at 520.4 cm^{-1}), which was measured directly after the sample measurement. The absolute wave-number accuracy of the HR 800 UV system is ±0.5 cm^{-1}, the wave-number precision (±0.5 cm^{-1}) was determined from repeated measurements of the silicon standard against the Rayleigh line.

contrast to precipitation experiments from Mg-bearing bicarbonate solutions (e.g., Böttcher, 2000) no evidence was found for a temporal formation of hydrous or X-ray amorphous precipitates in the Mg-free solutions used in the present study.

SEM–EDX investigations were performed on a FEI Quanta 400 microscope connected with an EDAX-Genesis system. Sample powders were glued on Al stubs and covered by pure carbon (vacuum sputtered). Measurement parameters of the microscope system during analyses were: high vacuum; 15 kV electron beam; working distance: 10 mm; SE and BSE detector; variable enlargement. The X-ray microanalyses were performed by spot analyses on selected particles taking EDX-spectra (EDAX-Econ 4 detector), the identification and quantification of the elements was carried out after ZAF-correction considering a Ti-free sample. Field emission

3. Results and discussion

SEM–EDX analyses and the powder XRD pattern are presented in Figs. 3 and 4. SEM–EDX analysis confirm the existence of BaMn[CO$_3$]$_2$ with an essentially ideal 1:1 cationic stoichiometry (Fig. 3). Powder XRD patterns (Fig. 4) are very similar to previously

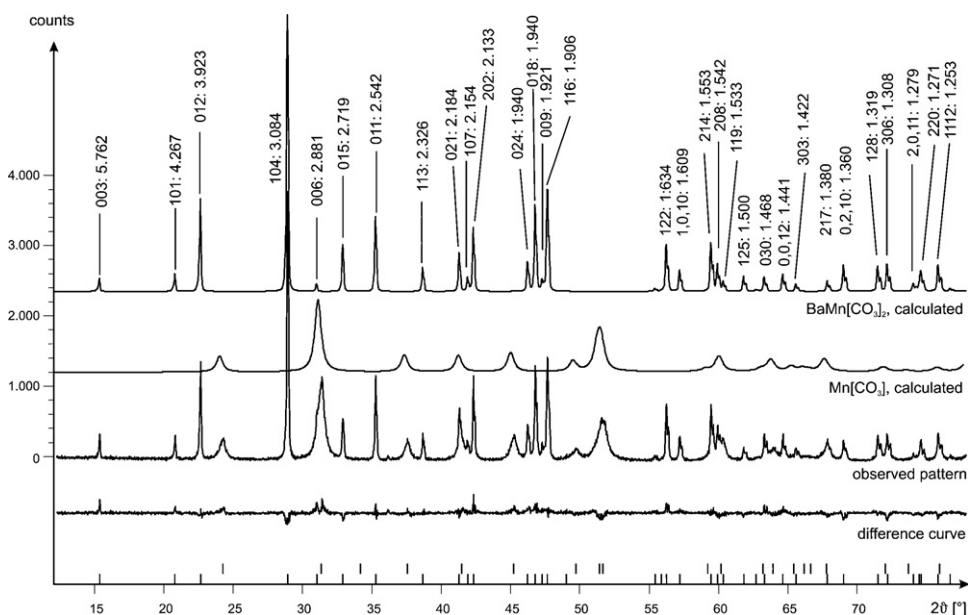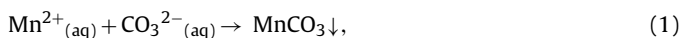**Fig. 4.** Powder X-ray patterns and Rietfeld refinement of synthetic BaMn[CO$_3$]$_2$ with co-precipitated "rhodochrosite". Modeled d-values may deviate slightly from the observed data given in Table 1.

Table 1
Most diagnostic d_{hkl} values (relative intensity in brackets), FTIR absorption bands and Raman shift data.
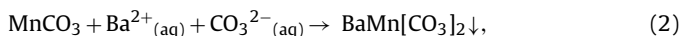
XRD	d_{hkl} value (Å)	4.282 (20), 3.924 (60), 3.085 (100), 2.719 (25), 2.542 (35), 2.133 (25), 1.940 (20), 1.906 (30)
FTIR	(cm^{-1})	696.5 (v4), 867 (v2), 1436 (v3), 1096 (v1)
Raman	(cm^{-1})	124, 251 (T, L), 697 (v4), 1097 (v1), 1735/1738(2*v2)

published data for the double carbonate with the same chemical composition but synthesized under high-temperature and high-pressure conditions (Chang, 1964). The investigated samples were found to be associated with "rhodochrosite" (Fig. 4). SEM analyses (Fig. 3) showed that the synthesized double carbonate, in contrast to "rhodochrosite", occurs with different textures and morphologies, mostly forming solid-phase aggregates with single crystals up to 10 μm in diameter. For some crystals a rhombohedral shape could be observed indicating trigonal symmetry (Fig. 3). The co-precipitating "rhodochrosite", occurred as spherical aggregates of very small micro-crystals as was also found for rhodochrosite in early-diagenetic precipitates in brackish sediments (Suess, 1979; Lepland and Stevens, 1998).
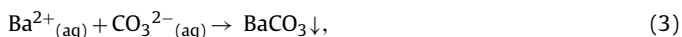
From the actual synthesis and based on the solubilities of the end-member carbonates (e.g., Morse et al., 2007), as well as according to previous observations on BaMg[CO$_3$]$_2$ formations (Lippmann, 1973; Hood et al., 1974; Böttcher, 2000), we suggest two replacement scenarios for the formation pathways depending on initial aqueous Ba/Mn ratios:
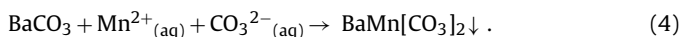
$$Mn^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)} \rightarrow MnCO_3\downarrow, \tag{1}$$

and

$$MnCO_3 + Ba^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)} \rightarrow BaMn[CO_3]_2\downarrow, \tag{2}$$

or

$$Ba^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)} \rightarrow BaCO_3\downarrow, \tag{3}$$

and

$$BaCO_3 + Mn^{2+}{}_{(aq)} + CO_3{}^{2-}{}_{(aq)} \rightarrow BaMn[CO_3]_2\downarrow. \tag{4}$$

Also a direct precipitation of the double carbonate from the aqueous solutions cannot be ruled out. The pathways depend on the initial boundary conditions (e.g., Ba/Mn ratios). Böttcher (2000) described for experiments on carbonate precipitation from mixed Mg-bearing solutions the alteration of an X-ray amorphous gel to crystalline BaMg[CO$_3$]$_2$. A physico-chemical reaction path analysis is part of a planned later communication.

The powder X-ray diffraction pattern (Fig. 4) shows sharp reflections for BaMn[CO$_3$]$_2$ indicating a well crystallized and ordered crystal structure. Isotypy with norsethite, BaMg[CO$_3$]$_2$ (Effenberger and Zemann, 1985; Secco and Lavina, 1999) was proved by a Rietveld refinement. As expected from the ionic radii (Shannon, 1976) of the ions $Mg^{2+[6]}$ (0.72 Å) and $Mn^{2+[6]}$ (0.83 Å) the unit cell is larger when compared with norsethite; consequently the respective peaks (Table 1) are shifted to smaller 2Θ values in BaMn[CO$_3$]$_2$. Unit-cell parameters of norsethite (space group $R\bar{3}m$) reported by the above mentioned authors are practically the same: $a = 5.021(1)$ Å, $c = 16.768(4)$ Å; those of BaMn[CO$_3$]$_2$ are increased to $a = 5.0844(8)$ Å and $c = 17.287(4)$ Å if space group $R\bar{3}m$ is considered. The diffractogram is consistent with that reported for the compound synthesized by Chang (1964) under high-temperature and high-pressure conditions. The bond distances $Ba^{[12]}-O = 2.959(2)$ Å and $C^{[3]}-O = 1.275(4)$ Å agree within limits of error in BaMn[CO$_3$]$_2$ and norsethite; $Mg^{[6]}-O = 2.060(2)$ Å in norsethite and $Mn^{[6]}-O = 2.161(4)$ Å in BaMn[CO$_3$]$_2$ reflect the distinct ionic radii. In contrast to the double carbonate, the peaks for the co-precipitated "rhodochrosite" are much broader, indicating smaller crystal sizes and/or a less ordered atomic arrangement as well as some variation in the chemical composition. The cell

metrics of "rhodochrosite" obtained during the present investigation ($a = 4.786(3)$ Å, $c = 15.718(11)$ Å; space group $R\bar{3}m$) is somewhat larger as compared to the values published by Effenberger et al. (1981) for natural rhodochrosite ($a = 4.7682(2)$ Å, $c = 15.6354(8)$ Å) and by Maslen et al. (1995) for "rhodochrosite" synthesized under hydrothermal conditions ($a = 4.773(1)$ Å, $c = 15.642(1)$ Å). However, the bond distance $Mn^{[6]}-O = 2.193(2)$ Å found in "rhodochrosite" agrees with that found in rhodochrosite $Mn^{[6]}-O = 2.1900(5)$ Å (Effenberger et al., 1981). Additionally, SEM–EDX analyses indicate some minor incorporation of Ba^{2+} into the $MnCO_3$ structure, that, in analogy to calcite, may further lead to a distortion of the crystal lattice (Pingitore, 1986; Reeder et al., 1999). It should be noted, that the XRD pattern of BaMn[CO$_3$]$_2$ is similar to that reported for benstonite, $Ba_6Ca_6Mg(CO_3)_{13}$ (Effenberger, 1979), which may partly explain, why this phase has not been reported in natural low-temperature systems, so far. The five strongest reflections of benstonite and BaMn[CO$_3$]$_2$ are roughly at the same 2Θ angles and exhibit a similar intensity distribution.

The FTIR and Raman spectra of synthetic BaMn[CO$_3$]$_2$ are typical for a rhombehedral carbonate (White, 1974). The most diagnostic wave-numbers of infrared absorption bands and Raman shifts are compiled in Table 1. The assignment of infrared and Raman modes follows Bischoff et al. (1985) and White (1974). The fundamental $v1$, $v2$, $v3$ and $v4$ modes are found to be active in the FTIR spectrum of BaMn[CO$_3$]$_2$. Extra absorption bands are due to the presence of $MnCO_3$ as confirmed by SEM–EDX and XRD. The Raman spectrum carried out on samples of BaMn[CO$_3$]$_2$ shows the fundamental $v1$, and $v4$ modes, a 2^*v2 combination, and two broad lattice mode (Table 1). The $v2$ and $v3$ bands are too small to be recognized in complex natural samples (Schmidt et al., submitted).

More laboratory work is in progress and more field studies are needed to define the physico-chemical boundary conditions of the BaMn[CO$_3$]$_2$ formation in nature and its role in the coupled low-temperature biogeochemical element cycles of barium, manganese, carbon, and sulfur. We suggest that this newly discovered low-temperature phase may be involved in the partitioning of trace elements and C, O and Ba stable isotopes between aqueous solutions and solid phases (Böttcher and Dietzel, 2010; von Allmen et al., 2010). The present study provides the essential analytical tools for future (re-)search in natural low-temperature systems, as brackish-marine or lake sediments. Further experiments at 4 °C and 10 °C also succeeded in demonstrating the synthesis of the double carbonate (Neugebauer and Böttcher, unpublished), extending the formation range down to typical seafloor conditions. The dedication of BaMn[CO$_3$]$_2$ as a new mineral phase has hitherto not been approved by IMA (Jambor and Grew, 1991). However, based on the new findings and expected further reports on natural occurrences, this likely will have to be revised in the near future.

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