Secondary carbonates in edaphic components of ecosystems

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Abstract. The paper considers some examples of secondary carbonates in edaphic ecosystem components (soils, river and lake bottom sediments, suspensions). In addition to calcite, more soluble and less stable polymorphic modifications of calcite vaterite and aragonite, which are important precursors of carbonate-forming systems, are diagnosed. Microforms of vaterite are formed in presence of low molecular weight amino acids. In turn, microforms of aragonite are associated with extremely high salinity of water. According to the nonclassical mesocrystal concept, stability of vaterite and aragonite in situ is explained by the formation of mesocrystals – hierarchically organized superstructures from nanocrystals. The mesocrystal concept may be an important key to understanding the micro- and macroaggregates in soils.

1. Introduction
Calcium carbonate is an important component of the edaphic components of ecosystems (soils, river and lake sediments, suspensions). The main attention of scientists was and is being paid to geochemical confinement, processes of formation, content and morphology of calcite, the most thermodynamically stable polymorphic modification of calcium carbonate [1]. Climate, i.e. precipitation and temperature, is suggested as the main controlling factor for formation and localization of calcite in soils. Accumulation of calcite near the soil surface is common for arid and semi-arid zones. Calcite can be accumulated in soils in a wide range of temperatures from very hot conditions in hot deserts of Asia to cold climatic zones such as tundra and Antarctic Dry Valleys. The calcite formation in the river and lake waters and, accordingly, in the bottom sediments is also a characteristic process of arid and semi-arid zones [2]. Due to the prevalence of evaporation over precipitation, surface waters (rivers and lakes) are oversaturated by Ca2+ and CO32− that leads to the formation and precipitation of CaCO3 in bottom sediments. In the humid zone, in contrast, CaCO3, as a relatively highly soluble compound, is in a state of undersaturation in the surface waters. Therefore, it is not accumulated either in alluvium or in bottom sediments.

Two other polymorphic modifications of calcium carbonate, aragonite and vaterite, as less thermodynamically stable and more soluble than calcite [3], are found in natural setting much rare
(except for their biogenic formations) and are much less studied. Aragonite only occasionally occurs in the soil profile [4]. In lake sediments, aragonite is more common. Vaterite is thought to be metastable under all known conditions and has a higher solubility than the other CaCO$_3$ polymorphs, calcite and aragonite. Although vaterite was precipitated inorganically in the laboratory, it was originally thought not to occur as a naturally forming mineral [5]. Natural occurrences of vaterite are largely associated with organic tissue, gallstones, urinary calculi and microbial biscuits.

The goal of this work is to study the manifestations and stability of polymorphic modifications of calcium carbonate (calcite, aragonite and vaterite) in river suspensions and bottom sediments of rivers and lakes of different natural zones.

2. Objects and methods

The study was focused on the river (the Jordan River, Jordan, site 1) and lake (the Grand Salt Lake, USA, site 2) bottom sediments of semi-arid and humid zones (the Simmy River, Far East, Russia, sites 3 and 4). Additionally, ice cores were studied (the Amur River, Khabarovsk, Far East, Russia, site 5). The major methods were particle size distribution, bulk chemical analysis and scanning electron microscopy (SEM). For comparison, SEM methods also were used to analyze peat deposits (the interfluve of the Kiya and Khor rivers, Amur River basin, site 6), and soil samples that we had studied earlier (Gobi Desert, Mongolia, site 7; Central Anatolia, Turkey, site 8) [6–8]. The peat samples were kindly provided by M. A. Klimin and A. Yu. Peskov (Far East Branch of RAS, Khabarovsk, Russia). The sampling sites are briefly characterized in table 1.

| N | Site Description | Edaphic component of ecosystem |
|---|------------------|--------------------------------|
| 1 | The Jordan River, near Al-Maghtas ruins, 31°50'13"N 35°32'47"E | bottom sediments |
| 2 | The Great Salt Lake, USA the endorheic lake with salinity 5–27 %, 40°43'04"N 112°13'58"W | bottom sediments |
| 3 | The Simmy River (Amur river basin), Russia the downstream, near the Bolon Lake 49°42'23"N 136°16'53"E | bottom sediments |
| 4 | Ibid the upstream 49°30'21" N 136°01'34" E | bottom sediments |
| 5 | The Amur River, Russia the Middle Amur, near Khabarovsk city 48°36'18" N 135°02'24" E | ice core, moderately hummocky ice |
| 6 | The interfluve of the Kiya and Khor rivers (Amur river basin), Russia The Kiya lowland peat deposit, 47°50' N 135°40' E | peat stratum |
| 7 | The alluvial plain, Gobi Desert, Mongolia near Züün Saihan ridge, 43°33'17"N 104°06'57"E | soil (Endosalic Calcisols Yermic) |
| 8 | The alluvial plain, Central Anatolia, Turkey Experimental field in Çumra district, drip irrigation, 37°33'52" N 32°45'48" E | soil (Calcic Haploxerept) |

The particle size composition (without decomposition of carbonates) determined with the laser diffraction method on a particle size analyzer SALD-2300 (SHIMADZU, Japan). Before the analysis of bottom sediments on the SALD-2300 (flow cell), a water suspension of the test sample (~0.5 to 1 g depending on the suspension absorption) was treated with ultrasound (built-in disperser for sample homogenization) [9]. The contents of selected chemical elements were determined via the X-ray fluorescence method (XRF) (Pioneer S4, Bruker AXS, Germany), using the silicate technique. The SEM analysis was carried out using VEGA 3 LMH (TESCAN, Czech Republic). For the analysis, the samples, after grinding and sieving through a 2-mm sieve, were prepared via pouring, Pt-spraying and...
magnification of up to 20,000. In addition, carbon spraying was used to visualize the formation of clay-calcite ultramicro-aggregates on the surface of micro-aggregates (sample 8). A backscattered electron detector (BSE detector) was used for the analysis of phases with a high atomic number. When images are acquired using a BSE detector, phases with a high average atomic number are reflected in contrast more vividly than those with a lower atomic number. The X-max 80 energy-dispersive spectrometer (Oxford Instruments, UK) was used to analyze the elemental composition of the most representative regions. The SEM and XRF analyses were carried out in the Analytical Centre at the Institute for Tectonics and Geophysics, FEB RAS, Khabarovsky.

3. Results and discussion
According to the bulk chemical analysis, the change in the calcium content and, accordingly, carbonates in sediments does not contradict the climatic zonality of their distribution: high calcium content in the sediments of the semi-arid zone and much less in those of the humid zone (table 2). Highly dispersed bottom sediments of the Jordan River are characterized by extremely high calcium content (more than 40% CaO from the total composition). Lake-river sediments of the Simmy River (downstream) have a close particle size composition (the predominance of silt). But since the basin of the Simmy River is located in the humid zone, and in addition, the processes of physical weathering prevail in the territory (as a result of deep freezing of soils), which is confirmed by the particle size distribution (PSD) data of the upstream river bottom sediments, the calcium content is almost two orders of magnitude lower.

Table 2. Some physical and chemical properties of sediments.

| No | Bulk chemical composition, % | Particle size distribution, fractions a, % | Jordan River |
|----|-----------------------------|------------------------------------------|--------------|
|    | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | Na₃O | K₂O | Sr b | <2  | 2–20 | 20–50 | 50–200 | 200–2000 |
| 1  | 29.7 | 5.7 | 7.0 | 45.1 | 6.1 | 1.3 | 1.4 | 2831 | 12.3 | 63.1 | 15.8 | 9.9 | 0 |
| 2  | 55.2 | 2.9 | 19.7 | 16.4 | 2.6 | 0.6 | 1.4 | 854 | 0 | 0 | 0.1 | 32.9 | 67.0 |
| 3  | 70.0 | 16.4 | 5.1 | 0.7 | 1.4 | 2.4 | 2.7 | 192 | 7.0 | 48.0 | 27.1 | 17.9 | 0 |
| 4  | 76.4 | 12.7 | 2.5 | 0.7 | 0.8 | 3.2 | 2.8 | 170 | 0 | 4.1 | 3.3 | 56.6 | 36.1 |
| 5  | – | – | – | – | – | – | – | – | 0 | 0 | 0 | 0.1 | 99.9 |
|    | a | size fractions in µm; | | b | content in mg/kg; | | c | 43–52 cm ice layer; dash – no data. |

In the Amur ice cores calcium carbonate was detected only in 43–52 cm layer. Most likely, CaCO₃ is formed in the layer during freezing of river water, since it contains the highest concentrations of bicarbonate ion HCO₃⁻ at the end of the freeze-up (up to 60–80 mg/L). Calcium carbonate is represented by particles up to 100–200 µm in size. Most of them are poorly and moderately crystallized. But there are also spherical shaped particles of CaCO₃ (figure 1a). Similar formations were found in precipitates forming at a supraglacial sulfur spring, in Borup Fiord Pass, northern Ellesmere Island, Canadian High Arctic [10]. Vaterite found at the site was characterized by 2 to 10 µm rounded to spherical shaped particles (comprising smaller 0.5 to 2 µm spheres) as both individuals and in chainlike
structures. The morphology of the particles and similar conditions for their formation allow us sufficient confidence to assume that is vaterite.

Since vaterite was not diagnosed in the bottom sediments of the Middle Amur, but was found in ice cores, we tried to assess the possibility of its formation in the sediments of the Lower Amur. The Simmy River (the Amur River basin) was chosen for this. It is almost a degree to the north, it is much colder there, winters are lightly snowy and soils freeze up to 160 cm. As SEM and EDS analyzes showed, bottom sediments of the Simmy River are characterized by a relatively high content of sphene \( \text{CaTiSiO}_5 \). However, \( \text{CaCO}_3 \) was diagnosed only in the lake-river sediments (site 3, downstream of the river) in the form of rare cauliflower-shaped agglomerates up to 5 \( \mu \text{m} \) in size.

![Figure 1. SEM images of secondary carbonates: a – inclusions in the river ice (43–52 cm layer, site 5); b, c – toroid-shaped microforms from river bottom sediments (site 3 and site 1); d – aragonite ooid from lake bottom sediments (site 2); e – calcite porous mesocrystal (site 7); f – calcite ultra-microaggregates (arrow) on surface of microaggregate (site 8).](image)

In addition, unusual toroid-shaped microforms of \( \text{CaCO}_3 \), with internal diameter of 8–10 \( \mu \text{m} \) and cross-sectional radius of about 1 \( \mu \text{m} \), were determined (figure 1b). The similar toroid-shaped microforms
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1f microaggregation processes of clay minerals by pedogen coefficient (300 cm/day)

matter and the absence of aggregates of agronomical site 8 calcite in soils in the presence of clay minerals may lead to the formation of porous mesocrystals clay minerals can be seen as macrofold (matrix) and b facets along the c separate nano atoms/ions/molecules.

Makus Antonietti \[ 76x171 \]

Julian Banfield atom/ion/molecule

highlight aragonite ooids outside the "habitat" micritic particles <4 µm are also encountered. Apparently, this is the result of the destruction of transformations is not a direct solid phase reaction, but recrystallization of calcium carbonate through the formation of calcite began, leading to their destruction and a reduction of their size to 250–350 µm in size from micritic particles <4 µm are also encountered. In the bottom sediments of the lake. The content of CaO in the sample is high, more than 16%. Indeed, the sample contains multiple ooids for the most part of regular spherical shape up to 350–400 µm in size (figure 1d). As previously shown, these are aragonite formations. Ooids were found with both a perfectly smooth surface and ooids in which the processes of recrystallization and the formation of calcite began, leading to their destruction and a reduction of their size to 250–300 µm. The transformation is not a direct solid phase reaction, but recrystallization of calcium carbonate through the dissolution of aragonite and growth of calcite. Porous microaggregates up to 200 µm in size from micritic particles <4 µm are also encountered. Apparently, this is the result of the destruction of aragonite ooids outside the “habitat” – the salt water of the lake.

The data are clearly stacked in the new concept of crystallization – mesocrystal concept. This concept highlights nonclassical crystallization pathway toward single crystals besides the classical atom/ion/molecule-based mechanism. The pioneer work in this field was the study of R. Lee Penn and Julian Banfield [15]. First review and formalization of concepts were made by Helmut Cölfen and Makus Antonietti [16]. According to this concept, crystallization occurs as a result of the association of separate nanocrystallites (under the influence of steric constraints, the formation of mineral bridges, etc.) with the formation of hierarchically organized superstructures (porous aggregates of nanocrystals).

In the case of classical crystallization secondary calcite forms rhombohedral crystals. The crystal facets along the c-axis through oxygen atoms have a partial negative charge; the facets in plane the a- and b-axes due to calcium cations have a partial positive charge. In the presence of anionic polymers (matrix) calcite can form mesocrystals with the cube octahedron symmetry and mesocrystals with sixfold rotational symmetry from the individual rhombohedral nanocrystallites. In turn, the crystallites of clay minerals can be seen as macro-anions, their charge is offset by exchange cations. Crystallization of calcite in soils in the presence of clay minerals may lead to the formation of porous mesocrystals (figure 1e) as in Endosalic Calciolys Yermic of Mongolia (site 7). But the reverse process may happen, when the matrix is calcite. A similar case was marked by us in alluvial calcareous soils (Calcic Haploxerept, site 8). These soils with heavy granulometric composition (up to 50% of clay), low content of organic matter and the absence of aggregates of agronomically valuable sizes have unusually high filtration coefficient (300 cm/day) [7]. As demonstrated by scanning electron microscopy data, this is due to microaggregation processes of clay minerals by pedogenic calcite, which forms mineral bridges (figure 1f) in the structure of the porous mesocrystals [8].
4. Conclusion
In the edaphic components of ecosystems (soils, river and lake bottom sediments, suspensions), in addition to calcite, more soluble and less stable polymorphic modifications of calcite, vaterite and aragonite, which are important precursors of carbonate-forming systems, are diagnosed. Spherical shaped microforms of vaterite are formed in extra cold conditions (the ice cores of the Amur River, Russia). Toroid-shaped microforms of vaterite were first discovered in natural samples (peat deposits and river bottom sediments of the Amur River basin, and bottom sediments of the Jourdan River, Jordan). They are formed in presence of low molecular weight amino acids. In turn, microforms of aragonite are associated with extremely high salinity of water (bottom sediments of the Great Salt Lake, USA). According to the nonclassical mesocrystal concept, their stability in edaphic components of ecosystems is explained by the formation of hierarchically organized superstructures from nanocrystals.

The mesocrystal concept may be an important key to understanding the formation of not only secondary carbonates, but also micro- and macroaggregates in soils. Thus, crystallization of calcite in soils in the presence of clay minerals (macro-anion matrix) may lead to the formation of porous calcite mesocrystals as in Endosalic Calcisols Yermic of Mongolia. In turn, when the matrix is calcite, it forms mineral bridges in the structure of the porous mesocrystals from clay particles as in Calcic Haploxerupt of Turkey. However, there is still much to be learned about the forces guiding mesocrystal assembly and the exact formation mechanisms.

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