Carbonates in the soils of the Aral Sea dried bottom

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Abstract. The paper considers the first stage of salt deposition, namely, the features of calcium carbonate formation in the soils (solonchak-like formations) of the Aral Sea dried bottom, its south-eastern part. The studied soils (sandy and silty-clay soils) are significantly saline and enriched with calcium carbonate. The content of only mollusk shells can reach 10–20%. The content of mineral CaCO₃ in the soils is quite uniform, its content varies by no more than an order of magnitude, which indicates relatively close conditions for its formation in soils with different particle size distribution. However, the types of aggregations of calcium carbonate (with a close size ca. 250 µm) and the mechanisms of their formation in the soils are different. In sandy soils, ooids (CaCO₃ cutans on the surface of sand-sized particles) are formed by the template mechanism. In silty-clay soils with a large number of crystallization centers (the predominant particle size is < 50 µm), the precipitation of calcium carbonate leads to the formation of CaCO₃ microaggregates from silty-clay particles. Separate crystallites and mesocrystals of calcium carbonate (up to 40 µm in size) are found singly.

1. Introduction

Investigation of relatively simple natural systems may contribute significantly to our understanding of more complex phenomena. In soil science, an example of such systems can be soils developed in extreme environments as soils of the Aral Sea (dried bottom). The Aral Sea is a large saline terminal lake situated in the arid and semi-arid Turanian Depression of Central Asia [1, 2]. The area is one of the world’s foremost natural laboratories in Holocene hydrology and landscape ecology. Palaeolimnological reconstruction of variability in water levels of the Aral Sea since 11,700 BP indicates a long history of alternating phase of regression and transgression, which have been attributed variously to climate, tectonic and anthropogenic forcing [3–5]. Over the past 60 year the Aral Sea has shrunk drastically, largely due water abstraction from the Amu Darya and Syr Darya rivers for land irrigation. These processes dominate in the shallow south-eastern part of the Aral Sea [6]. All regressions resulted in the deposition of the salts (carbonates and evaporites) by evaporation of the water. Our aim in this article is...
to study the first stage of salt deposition [7], namely, the features of calcium carbonate formation in the soils of the dried bottom of the Aral Sea.

2. Objects and methods

The study was focused on soils of dried bottom sediments in the south-eastern part of the Aral Sea. The sampling sites are shown on a schematic map (Figure 1). A brief description of selected physical and chemical properties of the soils is given in Table.

![Figure 1. A schematic map of sample site locations.](image)

The major methods were particle size composition, gross analysis and scanning electron microscopy (SEM). The SEM analysis was carried out using VEGA 3 LMH (TESCAN, Czech Republic). For the analysis, the samples, after removing the Mollusca shells, grinding and sieving through a 2-mm sieve, were prepared via pouring, Pt-spraying and magnification of up to 20,000. The X-max 80 energy-dispersive spectrometer (Oxford Instruments, UK) was used to analyze the elemental composition of the most representative regions. The particle size composition (without decomposition of carbonates) determined with the laser diffraction method on a particle size analyzer SALD-2300 (SHIMADZU, Japan). 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 and XRF analyses were carried out in the Analytical Centre at the Institute for Tectonics and Geophysics, FEB RAS, Khabarovsk.
3. Results and Discussion

The results of the chemical analysis showed that the soils of the dried bottom are significantly saline and enriched with calcium carbonate. And if salinity (estimation of soluble salts by electrical conductivity) in the studied series of soils varies by more than two orders of magnitude, then the content of calcium carbonate in soils is relatively constant. Its content varies by no more than an order of magnitude from 2 to 40% in terms of CaO, which indicates relatively close conditions of calcium carbonate precipitation.

However, according to the particle size distribution and SEM data, the studied series of samples is clearly subdivided into two subgroups: sand and silty-clay deposits. Figure 2 shows the extreme members of the series both in particle size (figure 2a, c) and in the content of Na₂SO₄ and CaCO₃ (figure 2b, d respectively). Significantly smaller compared to the particle size distribution in the case of deposits of the Lazarev Strait is associated with an extremely high content of sodium salts (48% in terms of Na₂O), and the formation of salt microaggregates. Vice versa, the predominance of the sand fraction 50–200 µm in size in the sediment composition of site 2 (peak with a maximum of 140 µm) is caused by aggregation of silty-clay particles with CaCO₃ (the content of CaCO₃ is more than 40% in terms of CaO, the loss of heat reaches ca. 30%).

In sandy deposits (sites 5–10, Lazarev Strait), CaCO₃ precipitation occurs mainly on the surface of quartz grains with the formation of ooids of varying degrees of stability and grain coating (figure 3a–d). Depending on the mineralization conditions (site Lazarev Strait), further successive crystallization of sulfate and sodium chloride may occur (figure 3a). In silty-clay deposits (sites 1–3), CaCO₃ precipitation occurs mainly on the surface of clay and silt particles with the formation of microaggregates (figure 3e) up to 250 µm in size. Only at an extremely high concentration of CaCO₃ (site 2) was the formation of separate CaCO₃ mesocrystals (figure 3f and 3g) observed, which is associated with constrained crystallization conditions [8]. The size of the diagnosed mesocrystals does not exceed 10–15 µm. A rhombohedral calcite crystal measuring ca. 40 µm was diagnosed singly (figure 3h).

| Site, depth (cm) | EC (mScm⁻¹) | LH (%) | Gross composition (%) | Particle size composition (µm), % |
|-----------------|-------------|--------|-----------------------|-----------------------------------|
| Site Lazarev Strait | 65.9 | 16.3 | SiO₂ | CaO | MgO | Na₂O | S | <2 | 2–50 | 50–1000 |
| 1 | 0–10 | 19.6 | 16.3 | 44.6 | 11.6 | 4.7 | 6.9 | 0.7 | 7.8 | 76.1 | 16.1 |
| 2 | 0–10 | 10.1 | 27.7 | 23.5 | 40.7 | 2.0 | 1.9 | 0.9 | 3.8 | 36.0 | 60.2 |
| 3 | 0–10 | 21.1 | 10.2 | 51.3 | 9.8 | 3.8 | 10.2 | 4.7 | 0 | 15.5 | 84.5 |
| 4 | 0–10 | 18.3 | 17.7 | 40.3 | 15.2 | 4.9 | 5.1 | 1.4 | 7.3 | 81.1 | 11.6 |
| 5 | 0–10 | 2.3 | 11.3 | 55.6 | 14.6 | 1.7 | 1.8 | 0.6 | 0 | 7.8 | 92.2 |
| 6 | 0–10 | 23.0 | 10.4 | 58.6 | 8.6 | 3.5 | 10.2 | 3.7 | 0 | 1.6 | 98.4 |
| 7 | 0–10 | 10.9 | 16.8 | 43.4 | 18.9 | 2.7 | 4.0 | 1.4 | 6.3 | 30.9 | 62.8 |
| 8 | 0–10 | 1.7 | 12.6 | 54.9 | 17.3 | 0.5 | 0.8 | 1.6 | 0 | 0 | 100 |
| 9 | 0–10 | 0.8 | 2.4 | 84.1 | 2.1 | 0.8 | 2.6 | 0.1 | 0 | 0.3 | 99.7 |
| *0 | 0–10 | 4.7 | 10.8 | 50.4 | 15.1 | 1.1 | 2.2 | 4.4 | 4.3 | 93.7 |
| 0–10 | 1.5 | 7.6 | 49.4 | 9.2 | 0.5 | 1.6 | 0.4 | 0 | 0 | 100 |
| 0–10 | 20–30 | 0.5 | 7.2 | 71.5 | 9.0 | 0.5 | 1.4 | 0.1 | 0 | 0 | 100 |
| 10 | 0–10 | 8.8 | 9.9 | 62.8 | 10.6 | 2.8 | 2.8 | 2.4 | 0 | 15.1 | 84.9 |
| 10 | 0–10 | 1.2 | 2.9 | 90.9 | 3.0 | 1.0 | 1.3 | 0 | 0 | 1.2 | 98.8 |
| 10 | 0–10 | 4.4 | 12.6 | 51.2 | 12.7 | 3.5 | 3.1 | 0.3 | 59.3 | 36.9 |

*Loss of heat
Our data indicate two mechanisms of calcium carbonate formation in the soils as a result of increasing evaporation of water, concentration of salt solution and subsequent drying of the Aral Sea bottom. First, with a small number of crystallization centers (sandy soils), the template mechanism of CaCO$_3$ crystallization is implemented with the formation of cutans of different degrees of stability and coating of sand grains. The formation of predominantly ooids may indicate the orientation of individual CaCO$_3$ crystals perpendicular to the grain surface. In turn, the stability and completeness of the coating with calcium carbonate of rounded quartz grains with a high degree of confidence allows us to assume the formation of aragonite, a polymorphic modification of calcite that is stable at a high salt content [9]. The process of formation of aragonite ooids is noted in the bottom sediments of Grand Salt Lake (USA) with extremely high salinity of water. Needle-like crystals of aragonite are “ideal” for their densest packing on the surface of sand grains and forming the radial structure of ooids. Analysis of Grand Salt Lake ooids showed that a similar mechanism is implemented on biological templates of similar shape and size (Artemia franciscana cysts, average size 200–250 µm). It is possible that the ooid shown in Figure 3d is also the result of CaCO$_3$ precipitation on some biological object. The size of Artemia cysts, which are widely represented in the waters of the Aral Sea, is suitable. Second, with large number of crystallization centers (silty-clay soils), the precipitation of calcium carbonate leads primarily formation separate clusters (rather not crystals), which bind clay and sand particles into microaggregates.

**Figure 2.** SEM images of sandy (a, b) and silty-clay soils (c, d): a – site 8, 20–30 cm (arrows – CaCO$_3$-ooids); b – site in Lazarev Strait, 0–10 cm (arrows – grains of sand size); c – site 3, 0–10 cm; d – site 2, 0–10 cm (SEM, BSE-detector).
Figure 3. SEM images of secondary carbonates of sandy (a–d, ooids) and silty-clay soils (e–h): a – site in Lazarev Strait, 0–10 cm; b and c – site 8, surface and 10–20 cm respectively; d – site 7, 0–10 cm; e – CaCO₃-clay microaggregate; f и g – mesocrystals of calcite and vaterite respectively, site 2, 0–10 cm; h – rhombohedral calcite, site 9, 10–15 cm (SEM, BSE-detector).
4. Conclusion
Using the methods of electron microscopy, gross and sedimentation analysis, the composition of the soils of the dried bottom of the Aral Sea, its south-eastern part was studied. It is shown that the soils of the dried bottom – sandy and silty-clay soils – are significantly saline and enriched with calcium carbonate. A distinctive feature of the studied soils is their relative uniformity in the content of the latter. In sandy soils, CaCO$_3$ was diagnosed as part of ooids, in silty-clay soils – as part of microaggregates. Crystallites and mesocrystals of calcium carbonate occur sporadically.

The data obtained indicate two mechanisms of calcium carbonate formation in the soils as a result of increasing evaporation of water, concentration of salt solution and subsequent drying of the Aral Sea bottom. With a small number of crystallization centers (sandy soils), the template mechanism of CaCO$_3$ crystallization is implemented with the formation of cutans of different degrees of stability and coating of sand grains.

With a large number of crystallization centers (silty-clay soils), precipitation of calcium carbonate leads primarily to nucleation (formation of separate clusters of calcium carbonate molecules) and the formation of microaggregates from silty-clay particles.

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