

# Modern carbonate formation in low-mineralized flowing waters

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**Abstract.** Continental carbonate formation in low-mineralized flowing waters of temperate latitude is rare phenomenon. Taking this into account a study was conducted of crustate and stalactite-like authigenic calcite aggregates formed in the thalwegs of the ravines of the Volga Upland. According to chemical and isotopic analysis, modern carbonates are formed from poorly mineralized, meteoric waters of medium hardness, hydrocarbonate-magnesium-calcium hydrochemical type. It has been established that newly formed carbonate aggregates are characterized by the predominance of lightweight carbon and oxygen in the crystal structure. The osmotic hypothesis of the formation of lime-calcite aggregates is proposed.

## 1 Introduction

Modern carbonate formation in flowing freshwater, of temperate latitudes is a relatively rare phenomenon in nature. The concentration of ions in water, insufficient for sedimentation of salts of carbonic acid, in the majority leads to the fact that in the valleys of streams and rivers not precipitation, but dissolution of carbonate minerals prevail. Therefore, all finds of authigenic freshwater carbonates are of scientific interest.

On the territory of Tatarstan Republic, manifestations of freshwater carbonate-genesis were found in the streams of the Ilyinsky and Monastyrsky ravines located within the Tetyushsky district. Geographically, the territory belongs to the eastern slope of the Volga Upland, steeply descending to the Volga River. The study site is located on the Pre-Volga physiographic province, characterized by a predominance of the temperate continental climate of mid-latitudes. The rainfall here varies from 460 to 600 mm per year.

## 2 Object

Ilyinsky and Monastery ravines are linear erosional relief forms, elongated in a sublatitudinal direction. The length of the Ilyinsky ravine is about 700 m, Monastyrsky - about 1300 m. The tops of both ravines are directed towards the Volga-Sviyazhsky watershed, their base line of erosion is the valley of the Volga River. The Ilyinsky ravine is

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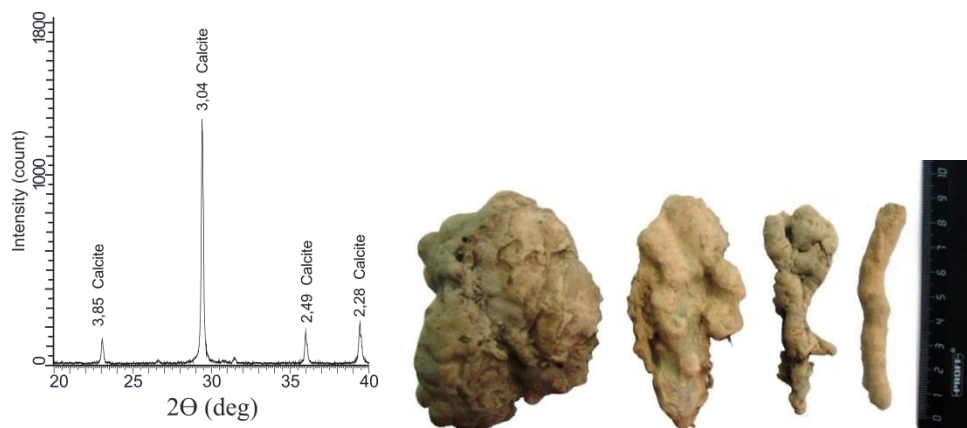
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characterized by a straightened thalweg, the absence of branch, longitudinal profile with a stepped bottom, high steep walls (75-85°), in which the grass cover is completely absent. The Monastic ravine has an extensive network of branches, more flat bottom without sharp hypsometric difference in elevation, which area is heavily wooded and turfed. Judging by the morphological features of the ravines, the first one belongs to relatively young systems, intensively developing. The second one is rather old and corresponds to the stage of flattening.

Both ravines denude the primary rocks of the Biarmian series of the Urzhumian stage of the Permian system. In the lower part of ravines edges are exposed red-brown and greenish-gray dolomite marls; in the upper part there is a similar altered marls and light gray dolomites with lenses of dark brown alluvial sandstones. The apparent thickness of the Permian layers is about 80 m [1,2]

In the left edges of both ravines there are numerous discharges of groundwater related to the aquifer of the locally water-tight stratum of the Urzhumian carbonate-terrigenous complex ( $R_{2ur}$ ) in the intervals of absolute elevations of 53.0-165.0 m. Groundwater drains middle and upper parts aquifers of Elyinsky and Monastyrsky ravines. Groundwater outlets of the Urzhumian stage sections are multi-tiered and located one above the other with a gap of 2-5 m. The aquifers are composed of fractured dolomites and dolomite marls. In places of discharge, the flow rates range from 2.5 to 10.5 l/min. Numerous of descending springs are merging and form permanent streams at the bottom of the ravines, in which the average flow velocity is about 1.8 m/s. In these streams, on bar formation and at base of waterfalls ledges were discovered local "foci" of modern carbonate formation.

Authigenic (diagenetic) carbonates found at the water edge of the Ilyinsky and Monastyrsky ravines brooks have various shape. Most often these are spindle-shaped stalactite-like growths of calcites light gray color (fig.1). In some cases, the crustate (coarse grain) forms of aggregates with well-pronounced layering prevail. An analysis of the localization features of different carbonate new growth morphotypes showed that crusts form on clay-argillaceous substrate, and stalactite-like aggregates - on plant roots. The carbonate crusts are characterized by peeling and botryoidal structure. That is due to the consistent growth of ones dense calcite layers on top of others. Between dense calcite layers are thinner puffs composed of loose microgranular calcite aggregates. Due to the interlayering of dense and loose growth membranes, the crustate aggregates are easily stratified into separate botryoidal parts. All carbonate crusts in the base are composed of interlacing hollow calcite tubules, like vessels, with a diameter of 0.05-0.2 mm. Judging by the morphology, these tubular aggregates are of biogenic origin. Stalactite-like carbonate new growths are characterized by a complex structure. In their central part a hollow canal or rhizome is traced, around which zonal-concentric calcite aggregates grow. In the longitudinal and transverse sections of stalactite-like new growths, growth zones in the form of layers growing on each other are clearly visible. Depending on the diameter of the aggregates in cross section fixed from 3 to 7 rings of growth.



**Fig. 1.** Isolation forms of authigenic calcite aggregates and their composition by X-ray data.

### 3 Results

The study of calcites isotopic composition of newly formed carbonate aggregates showed that, regardless of morphology, all of them are characterized by the predominance of lightweight carbon and oxygen in the crystal structure. The  $\delta^{13}\text{C}$  content varies in the range from -8.98‰ to -11.03‰, and  $\delta^{18}\text{O}$  varies from -9.51‰ to -10.10‰ (Table 1). If we look at the isotopic composition of Permian primary rocks, which are the source of ions for the formation of modern carbonates, it is seen, that both dolomite and dolomite marl are characterized by a higher content of heavy carbon ( $^{13}\text{C}$ ) and oxygen ( $^{18}\text{O}$ ). That is, modern authigenic carbonates do not fully inherit hydrocarbonate ions of primary and sedimentary rocks of middle Permian age, but are enriched in light isotopes due to oxygen and carbon fractionation in natural systems.

**Table 1.** The isotopic composition of newly formed carbonates and primary rocks in edges of the Monastery ravine.

Sample of carbonate rock, age	$\delta^{13}\text{C}$ , ‰	$\delta^{18}\text{O}$ , ‰
Calcite aggregate crust, Q <sub>IV</sub>	-10,40	-10,10
Stalactite-like calcite aggregate, Q <sub>IV</sub>	-11,03	-9,90
Stalactite-like calcite aggregate, Q <sub>IV</sub>	-10,23	-10,04
Stalactite-like calcite aggregate, Q <sub>IV</sub>	-8,98	-9,51
Dolomite, P <sub>2ur</sub>	-1,13	-3,77
Dolomite marl, P <sub>2ur</sub>	+0,40	+2,48

Taking into account the importance of the mineral formation environment for the authigenic calcites origin, a study of ground and surface waters composition was conducted one of the areas where new carbonates are forming. The Monastery ravine was chosen as the most accessible for sampling of well and spring waters. In order to assess the contribution groundwater to the composition of stream water flowing in the thalweg, spring's water was taken from the most high-output springs. One of the spring sources was located in the upper part of the ravine, the other - in the lower part. Also was made water samples from the stream itself at area of authigenic carbonates formation. Conducted studies of the samples showed underground and surface waters are characterize low TDS (Total dissolved solids). In their composition bicarbonate-ion predominates from anions, calcium and magnesium are main among cations (Table 2). Also sulfate and nitrates ions

are present as impurities. In terms of the ratio of the main anions and cations, all waters belong to magnesium-calcium hydrocarbonate type with medium hardness. The study of the isotopic composition of ground and surface waters showed that all of them are enriched with light isotopes of hydrogen and oxygen (Table 3). The distribution of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  relatively to the global meteoric water line (Meteoric Water Line, MWL) evidence about infiltration origin of analyzed ground and surface waters. On the graph, all points are clustered along the MWL. Comparing the obtained values of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of the Monastyrsky ravine stream waters (-12.96‰ and -92.14‰) with average annual values of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of atmospheric precipitation of the Russia European territory (-11.00 and -86.3‰), [3] can see that they are close in quantity. That is, the composition of surface waters in the thalweg of the ravine is formed with significant participation of atmospheric precipitation.

**Table 2.** The chemical composition of ground and surface waters of the Monastery ravine. (use capital letter L in mg/L).

Main elements	well spring in upper part	well spring in lower part	Stream in thalweg
	content of major elements, mg/L		
$\text{Ca}^{2+}$	107,83	99,00	73,78
$\text{Mg}^{2+}$	18,25	22,74	19,57
$\text{Na}^+$	2,95	2,96	4,84
$\text{K}^+$	0,06	0,11	1,74
$\text{HCO}_3^-$	445,45	463,75	305,10
$\text{SO}_4^{2-}$	8,41	9,19	8,49
$\text{Cl}^-$	1,11	1,65	1,57
$\text{NO}_2$	0,09	0,00	0,04
$\text{NO}_3$	2,46	0,01	5,11
Mineralization (TDS)	586,61	599,41	420,24
hardness, $\text{mg}^*\text{eqv/L}$	6,88	6,81	5,29
pH	7,37	7,81	7,65
T, °C	8,0	7,0	8-9

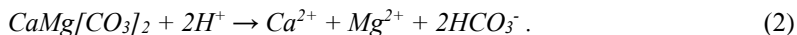
**Table 3.** Oxygen and hydrogen isotopic value of ground and surface waters of the Monastery ravine.

Sampling point in ravine	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	Genetic Type of water
well spring in upper part	-12,41	-84,59	Infiltration
well spring in lower part	-13,01	-87,62	Infiltration
Stream in thalweg	-12,96	-92,14	Infiltration

## 4 Discussion

Analysis of the chemical composition of underground and surface meteoric waters shows that all of them are undersaturated with respect to calcite (calcite starts to precipitate at  $\text{TDS} > 600 \text{ mg/L}$  and  $\text{pH} > 7.3$ ) [4]. Therefore, the formation of limestone aggregates with their participation under normal conditions is impossible. Having and possible concentration of dissolved  $\text{CO}_2$  of about  $0.8 \text{ mg/L}$ , all analyzed meteoric waters analyzed are aggressive with respect to carbonate rocks. This is confirmed by the presence in their composition of relatively high calcium and magnesium concentrations, formed during the reactions:





The explanation of the carbonate formation process in low-mineralized, flowing, cold waters of ravine thalweg streams can show areas of new forming calcite aggregates localization. Recall that modern sinter and cortical aggregates are associated with to plants roots and clay-loamy sediments. Both those and other base places of mineral formation have common features - the presence of thin and micro-pore channels and the ability to accumulate low concentrations of dissolved mineral matter. Apparently, a subcapillary pore, which makes thin tubes, serve as a place for concentration of dissolved in water some  $Ca^{2+}$  ions, which is facilitated by the osmotic pressure on the one hand, and the sorption activity of clay minerals on the other. The way directional movement of moisture due to the difference in capillary pressures and concentration gradients create the necessary conditions for the continuous influx of  $Ca^{2+}$  ions to the “root-air” and “clay-air” boundaries. Pellicular moisture enriched in  $HCO_3^-$  on surfaces of roots and clay-loam sediments, make conditions to processes of carbonate formation here by the reaction:



Considering the presence of microbial mucus on wet roots and surface of a clay substrate, it can be assumed that in the processes of modern carbonate formation the colonies of aerobic microorganisms are also involved. This is supported by the presence of intertwining thin calcareous tubules in the sole of crustate diagenetic aggregates.

## 5 Conclusion

The result of the work may be the following conclusions and discussions. Modern calcite of new formed carbonate aggregates differs about primary sedimentary rocks by lighter composition of carbon and oxygen. The feed solution is infiltration water with more light isotopic composition, flowing through soils which containing organic matter and enriched with  $^{12}C$  compared to primary sedimentary rock.

Low mineralization of freshwaters causes the biotemogenic mechanism for the formation of modern calcite aggregates. The required amount of  $Ca^{2+}$  ions is supplied due to the osmotic pressure in the thin pores foundation of the carbonate formation. When interacting film water of the clay substrate with the  $HCO_3^-$  and microbial mucus, the  $Ca^{2+}$  ions form crystals of carbonic acid salts. Gradually growing together, crystals of calcite form cortical (crustate) and stalactite-like aggregates.

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