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GEOCHEMISTRY

Participation of Microorganisms in the Formation of Travertines and Sapropelite Kerogen in Sediments of Thermal Carbonic Waters in the Baikal Rift Zone

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The geomicrobiological study of travertine sediments from hot springs of nitrogen sodium–sulfate waters in the Baikal rift zone demonstrated the decisive role of cyanobacterial mats in their formation [1]. At the same time, the mechanism of decompression formation without the participation of microorganisms is assumed for travertines that are widespread in the East Sayan terrain of hot and cold carbonic waters [2].

Our investigations in the Arshan Spring area show that travertine is also accumulated from thermal carbonic sulfate–hydrocarbonate calcic waters with the participation of microorganisms. Bacteria also participated in large accumulations of humus–sapropelite organic matter, including coal seams associated with travertines.

Springs and associated travertine terrains are localized on the northern slope of the Tunka depression in the Arshan reverse strike-slip fault zone that experienced three recent pulses of seismic shear strain (1315–1745, 7091–7385, 10 386–11 187 yr ago) [3]. The age range of travertine bodies (0–35 000 yr) [2] overlaps datings obtained for activation epochs of the Arshan segment of the Tunka thermoactive fault (heat flux 146 mW/m^2 [4]). However, culminations of travertine formation lack correlation with and are substantially older or younger than seismic deformation events (Table 1). Young (~800 yr) travertine deposits are also found [3].

Carbonic groundwater was repeatedly drilled in the Arshan resort area (>30 boreholes) to depths exceeding 750 m. The yield of water (2.6–1210 m^3/day) correlated with borehole depth and was maximal at the mouth of the deepest (772 m) borehole [5].

The chemical composition and properties of carbonic waters from the Arshan Spring are as follows [2, 5]: T = 7–44°C; pH = 6.1–6.6; TDS 2.0–4.5 g/l; HCO_3^- = 1500–2623 mg/l; SO_4^{2-} = 330–900 mg/l; Cl^- = 35.0–68.1 mg/l; F^- = 0.6–2.0 mg/l; SiO_2 = 40–96 mg/l; humins up to 2.7 mg/l; bitumen up to 7.9 mg/l; and CO_2 = 7–11 mg/l. Among cations, Ca^{2+}, Mg^{2+}, and Na^+ are dominant (600–654, 143.5–146.0, and 177.0–229.1 mg/l, respectively). CO_2 dominates among freely released gases (≥99%). Groundwater of the Tunka artesian basin, which feeds the Arshan Spring, has a strong head and elevated temperature (200–300°C or more) at the Tunka depression basement. This water is allegedly a product of the interaction between carbonate rocks of the Irkut Formation and infiltration waters [6]. According to geophysical studies and data on the composition of inclusions in basalts [7], tectonic zones of the depression basement include mafic–ultramafic rocks that strongly influenced the composition of thermal carbonic waters, resulting in high concentrations of Ni, Co, Zn, and Pb [8], as well as Mg.

The oldest travertines in the Kyngyrga River valley form thick (10–30 m or more) and extended (100–200 m) horizontal bodies (figure). They are related to the hydrothermal–metasomatic transformation of brecciated pegmatites and schists in the Precambrian basement of the depression and sedimentary–hydrothermal lithogenesis superimposed on terrace sediments of the Kyngyrga River. The dolomite content is 70–93%. Table 2 presents associated minerals. The fine-grained dolomitic matrix hosts bacterial gel-like to cryptogranular organogenic–clayey–ore microaggregates. They occur as rod-shaped (1.0 × 0.05–0.1 mm) and globular (up to 0.08 mm across) varieties in some places.

Clayey–sandy–pebbly terrace sediments enclose horizontal lenses (0.2 × 1.5 m) of black sooty

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Table 1. Chemical composition of travertines from the Arshan Spring of carbonic waters (wt %)

Travertine variety	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O
Dolomitic travertine developed after incoherent terrace sediments and pegmatites	0.60	0.05	0.70	0.04	0.20	0.01	20.60	30.86	0.06
	<0.10	0.02	<0.10	–	0.16	0.01	21.78	31.00	0.03
	18.40	0.10	1.30	0.55	0.24	0.05	13.03	27.46	0.03
	28.80	0.47	8.50	2.07	2.08	0.08	13.20	23.40	0.17
Aragonitic–calcitic travertine developed after incoherent riverbed sediments of the Kyngyrga River (with relicts of dolomitic varieties)	<0.10	0.02	<0.10	0.67	0.30	0.02	0.59	55.30	0.10
	<0.10	<0.02	<0.10	0.80	0.18	0.02	0.56	55.30	0.10
	1.20	0.03	0.40	0.68	0.20	0.02	1.19	53.05	0.15
	0.40	0.02	<0.10	0.29	0.08	0.02	0.90	54.50	0.12
	0.30	<0.02	0.10	0.28	0.20	0.03	0.75	54.40	0.12
	1.20	0.04	0.40	3.01	0.36	0.03	0.73	52.00	0.15
Aragonitic–calcitic travertine developed after iron chutes, tubes, and wood fragments	0.30	0.02	<0.10	0.62	0.20	0.03	0.80	54.87	0.11
	0.10	<0.02	<0.10	0.92	0.16	0.03	0.75	54.10	0.11
	4.50	0.07	1.10	4.80	0.44	0.05	0.92	48.10	0.20
	2.50	0.04	0.30	1.96	0.16	0.05	0.08	52.30	0.17

Travertine variety	K_2O	P_2O_5	L.O.I.	Total	CO_2	F	$S_{sulfide}$	$S_{sulfate}$	Assumed age, yr
Dolomitic travertine developed after incoherent terrace sediments and pegmatites	0.04	<0.05	45.56	99.72	44.08	0.02	–	ÒÎ.	≥35 360
	0.02	<0.05	47.00	100.02	45.37	<0.01	–	ÒÎ.	
	0.19	0.52	38.19	100.06	33.33	<0.01	–	0.07	
	0.29	0.11	20.23	99.40	15.62	–	<0.01	0.02	
Aragonitic–calcitic travertine developed after incoherent riverbed sediments of the Kyngyrga River (with relicts of dolomitic varieties)	0.03	<0.05	42.25	99.28	40.10	0.15	–	0.84	35 360–17 240 [2]
	0.03	<0.05	42.56	99.55	40.53	0.16	–	0.80	
	0.09	<0.05	42.36	99.37	39.35	0.17	0.01	0.56	
	0.04	<0.05	43.17	99.54	39.78	0.15	0.01	0.53	
	0.03	<0.05	43.24	99.45	39.57	0.18	0.03	0.61	
	0.06	<0.05	41.48	99.46	38.06	0.18	–	0.68	
Aragonitic–calcitic travertine developed after iron chutes, tubes, and wood fragments	0.03	<0.05	42.84	99.82	40.10	0.18	–	0.65	0–50
	0.04	<0.05	43.02	99.23	40.10	0.16	–	0.63	
	0.14	0.05	39.25	99.62	33.98	0.16	–	0.03	
	0.09	<0.05	41.88	99.53	38.71	0.19	–	0.57	

Note: Analyst V.A. Ivanova, Geological Institute, Ulan-Ude.

sapropelites (10–15% of organic matter) with inclusions of dolomitic travertine crusts. Larger dolomite–sapropelite aggregates are observed in several natural outcrops of brecciated pegmatites along the Kyngyrga River bank. It is evident that Quaternary “buried soils and humus loams” [3], which locally grade into coal and sometimes associate with travertine bodies, are genetically similar to numerous thin coal seams in the Paleogene–Neogene Tankhoi Formation enriched in carbonate material [9]. The Tankhoi Formation contains abundant round clots (0.5–2.5 mm) of pelitomorphic material composed of round cells (0.0*n* mm) with a dark rim and light-colored matter in the internal zone. One can also see biomorphic rod-shaped structures [9]. These features imply active participation of microorganisms in sedimentary–hydrothermal processes during the formation of the Paleogene–Neogene sequence in the Tunka depression (primarily, its coal seams and carbonate section).

In strike-slip deformation zones, some amorphous organic matter of dolomitic travertines (up to 10%) is transformed into graphite. Small (0.01–0.03 mm) graphite flakes are confined to newly formed thin (up to 1–5 mm) quartz veinlets. The heavier carbon isotopic composition of the bacterial biomass (Table 3) is related to the influence of two processes: (i) accumulation of calcite in the course of life activity of bacteria (its content amounts to 14.18% in bacterial mats of the

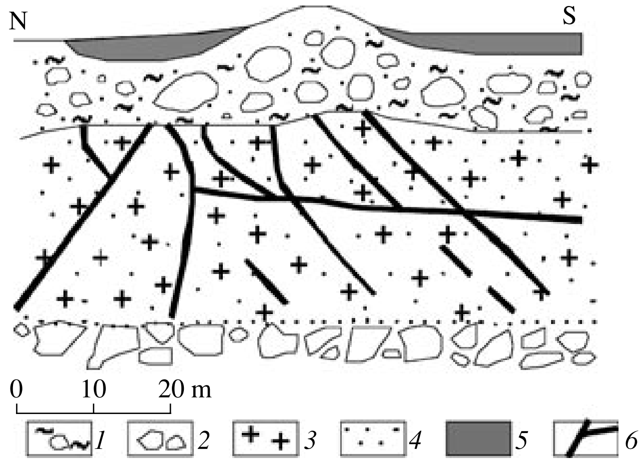
Garga Spring [10] and 18–27% in the organic matter from travertines of the Arshan Spring); (ii) processes of dynamometamorphism.

Aragonite–calcite travertines (Table 4) that are younger than their dolomitic varieties form small (up to 10 × 5 m), thin (1–30 cm) bodies in discharge areas of hot (43–44°C) waters.

Rubbly–pebbly sediments of the riverbed represent a main substrate for development of stratified travertine domes. One of the domes includes eight successive microlaminae (10 mm thick in total) composed of structureless siliceous, carbonate, siliceous–carbonate, and siliceous–clayey–carbonate matter.

Siliceous–smectite–calcite laminae contain abundant rods of lithified microorganisms (approximately 0.1%, on average) that form small accumulations at boundaries between calcite and smectite aggregates. Some rod-shaped bacteria are replaced by transparent fibrous smectite with simultaneous formation of a siliceous envelope around them. In the course of metabolism, bacteria probably decompose smectite and produce a shell of amorphous silica around bacterial cells. Simultaneously, ore elements are released from the organic matrix and concentrated in pyrite, magnetite, ilmenite, and galena. Another part of bacteria is replaced by pelitomorphic carbonaceous ore matter with a rim of iron hydroxides.

Calcic travertines are enriched in heavy isotopes of carbon ($\delta^{13}C$ = 3.2–6.1‰) and, particularly, oxygen ($\delta^{18}O$ = 10.4–12.9‰). Such isotopic values are usually characteristic of Precambrian metasedimentary carbonate rocks (dolomites, dolomitic crystalline schists, and calcareous and dolomitic marbles) with stromatolitic buildups and a high content of C_{org}.



Dolomitic travertines in rubbly–pebbly terrace sediments and block plagioclase pegmatites (sketch of the outcrop fragment in northern outskirts of the Arshan resort). (*1*) Terrace sediments; (*2*) rubbly talus; (*3*) pegmatites; (*4*) stringer–disseminated travertines developed after pegmatites and travertine crusts on riverbed sediments; (*5*) almost continuous banded travertine body; (*6*) large tectonic fractures filled with sooty carbonaceous sapropelite.

Microorganisms are highly diverse in microbial mats and sediments of the Zhoigon carbonic spring in the East Sayan province, where calcitic travertines contain abundant lithified films of bacterial mats. Microscopic study of the mucous ocherous sediment accumulated in mat near the discharge area of this spring revealed the presence of abundant filamentous ferruginous bacteria close to *Leptothrix* sp. and *Gallionella* sp. associated with cyanobacterial mats. Cyanobacteria include dominant *Phormidium tenue* and subordinate *Phormidium valderiae* f. *pseudovalderianum* and *Oscillatoria tenuis* f. *woronichiana.*

Table 2. Genetic typification of mineral and bacterial organomineral associations in the examined dolomitic travertine bodies

Characteristics of travertines	Genetic types of mineral associations		
	low-temperature hydrothermal–metasomatic	sedimentary–hydrothermal	dynamometamorphic
Morphology and setting of bodies	Strata-bound bodies of breccia and stockwork zones developed after Precambrian brecciated pegmatites and crystalline schists	Lenticular bodies and crusts on fragments of different rock fragments in Quaternary incoherent sediments	Veinlets in bodies of early brecciated travertines
Associations:			
abiogenic	Dolomite, calcite, quartz, glassy spherical particles of microscoria	The same	Graphite, quartz
of biogenic organomineral aggregates	Amorphous silica, smectite, hydromicas, hematite, pyrite, sphalerite		
Role of microorganisms in rock and mineral formation	Transformation of the component composition and alkalinity (up to pH ≥ 8) of thermal carbonic waters due to assimilation of dissolved CO_2 by autotrophic organisms; decomposition of organic matter from buried bacterial biomass by sulfate-reducing organisms, resulting in dolomite crystallization. Formation of gel-type organogenic, ore, and mineral microaggregates that serve as centers of dolomite crystallization		

Table 3. Isotopic composition (‰) of biogenic carbon from dolomitic travertines of the Arshan mineral spring of carbonic waters

Sample characteristics	$\delta^{13}C$
Green algae from the quarry basin in terrace sediments	–22.8
Dispersed coal-type carbonaceous matter from banded travertines in terrace rubbles and pebbles	–25.6
Sooty coal-type carbonaceous matter from stringer–disseminated travertines formed after pegmatites	–15.5
The same from travertine crusts formed after pegmatites	–13.0
The same from late veinlet accumulations developed after mylonitized, silicified, and dolomitized ("travertinized") pegmatites	–10.5
Flagellar structures of amorphous carbonaceous matter partly transformed into graphite from brecciated travertines formed after pegmatites	–8.1

Note: Analyst T.A. Velivetskaya, Analytical Center of the Far East Geological Institute, Vladivostok.

Table 4. Brief characteristics of the examined aragonitic–calcitic travertines (sedimentary–hydrothermal genetic type)

Characteristics of travertines	
Morphology and setting of bodies	Domes, blanket deposits, and crusts on fragments of different rocks, woods, and tubes
Associations:	
abiogenic	Calcite, aragonite, dolomite, gypsum, quartz, tourmaline, spherical microscoria particles (glassy and metallic)
of biogenic organomineral aggregates	Siliceous matter, amorphous carbonate, smectite, kaolinite, hydromicas, iron hydroxides, boehmite, phosphosiderite, hematite, ilmenite, magnetite, pyrite, galena
Role of microorganisms in rock and mineral formation	Differentiation and transformation of the primary composition of water by cyanobacteria and iron bacteria (sulfate reduction, deposition of iron hydroxides); destruction of organic matter by proteolytic microorganisms. Formation of gel-type organogenic, ore, and mineral aggregates that served as centers of aragonite and calcite crystallization

The abundance of microorganisms cultivated on the medium with peptone, sucrose, and cellulose was determined for travertine samples from the Arshan Spring. The number of bacteria from the proteolytic and saccharolytic groups amounted to 100 and 1000 cells/ml, respectively. Bacteria cultivated on the peptone medium formed endospores and occurred as rod-shaped cells.

Thus, diverse physiological bacteria groups in the microbial community of carbonic waters in the Tunka hydrothermal system played an important role in the formation of carbonate rocks and sapropelite kerogen (ranging from humus to coal) during the Cenozoic.

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