ISSN 0016-7029, Geochemistry International, 2007, Vol. 45, No. 3, pp. 235–246. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © A.Yu. Bychkov, O.E. Kikvadze, V.Yu. Lavrushin, V.N. Kuleshov, 2007, published in Geokhimiya, 2007, No. 3, pp. 269–281.

Physicochemical Model for the Generation of the Isotopic Composition of the Carbonate Travertine Produced by the Tokhana Spring, Mount Elbrus Area, Northern Caucasus

A. Yu. Bychkov[a], **O. E. Kikvadze**[b], **V. Yu. Lavrushin**[b], **and V. N. Kuleshov**[b]
[a] *Geological Faculty, Moscow State University, Leninskie gory, Moscow, 119899 Russia*
e-mail: bychkov@geol.msu.ru
[b] *Geological Institute (GIN), Russian Academy of Sciences, Pyzhevskii per. 7, Moscow, 109017 Russia*
e-mail; v_lavrushin@ginras.ru

Received July 19, 2005

Abstract—The isotopic composition of calcite from travertine deposits of the Tokhana-Verkhnii hot spring in the Elbrus area shows broad variations in $\delta^{13}C$ and $\delta^{18}O$ (from +3.8 to +16.3‰ and from +24.6 to +28.1‰, respectively). The $\delta^{13}C$ and $\delta^{18}O$ values increase toward the sole of the travertine dome. The isotopically heaviest carbonates ($\delta^{13}C$ of up to +16.3‰) were found near the bottom of the dome and composed ancient travertine, which are now not washed by mineral water. The scatter of the $\delta^{13}C$ values of the fresh sample is slightly narrower: from +3.8 to +10‰. Calculations indicate that all carbonates of the Tokhana dome were not in equilibrium with spontaneous carbon dioxide released by the spring ($\delta^{13}C_{CO_2} = -8‰$). To explain the generation of isotopically heavy travertine, a physicochemical model was developed for precipitation of Ca carbonates during the gradual degassing of the mineral water. The character of variations in the calculated $\delta^{13}C$ values (from +5.5 to +13‰) is in good agreement with the tendency in the variations of the $\delta^{13}C$ in the carbonate samples. The calculated and measured pH values are also consistent. Our results demonstrate that the isotopic composition of large travertine masses can be heterogeneous, and this should be taken into account during paleoclimatic and paleohydrogeological reconstruction.

DOI: 10.1134/S0016702907030032

INTRODUCTION

Travertine or calcareous sinter is a carbonate precipitated where groundwaters discharge. Travertine shows a diverse morphology, which is controlled by the character of water discharge, its temperature, composition, and many other factors [1]. Large travertine edifices often look like domes (travertine domes), whose volume can be as great as a few hundred or even a few thousand cubic meters.

Travertine is often formed by CO_2 mineralized or fresh waters that filtered through karstified carbonate rocks. Travertine is always produced in relation to the discharge of CO_2 waters in mobile belts. The isotopic composition of these carbonates is characterized by a broad range of $\delta^{13}C$ values, from –12.6 to +12.0‰ (PDB) and $\delta^{18}O$ from +5.2 to +28.0‰ (SMOW) [2–5]. The variations in $\delta^{13}C$ and $\delta^{18}O$ depend on the isotopic composition of the original CO_2 and H_2O, the deposition temperature of the carbonates, and the chemical composition of the mineral water. Carbonates with isotopically lighter C and O composition are more typical of high-temperature springs, such as in Kamchatka, Yellow Stone, Italy, etc.

In spite of the diversity of factors, it is generally reasonable to expect that the carbonate material precipitating from the mineral water of springs inherits the carbon and oxygen isotopic signatures of the parental aqueous solutions and spontaneous carbon dioxide. Because of this, travertine can be utilized for the reconstruction of the fluid regime of mountainous folded systems [2, 3].

However, the variability of the thermodynamic parameters under which carbonates are precipitated (temperature and chemical composition of the water), the isotopic characteristics of carbonates can also notably vary along the strike of a travertine dome. In addition to thermodynamic conditions, the isotopic composition of travertine can also possibly be controlled by other factors: photosynthesis, the destruction of organic matter, evaporation of the mineral water, etc.

Because of this, preparatorily to the use of the isotopic composition of carbonate travertines for various paleoreconstructions, it is necessary to assay the possible extent of the natural variations in the $\delta^{13}C$ and $\delta^{18}O$ of calcite in modern dome structures. If these variations are significant, it is interesting to estimate the volumes of precipitating carbonates of certain isotopic composition.

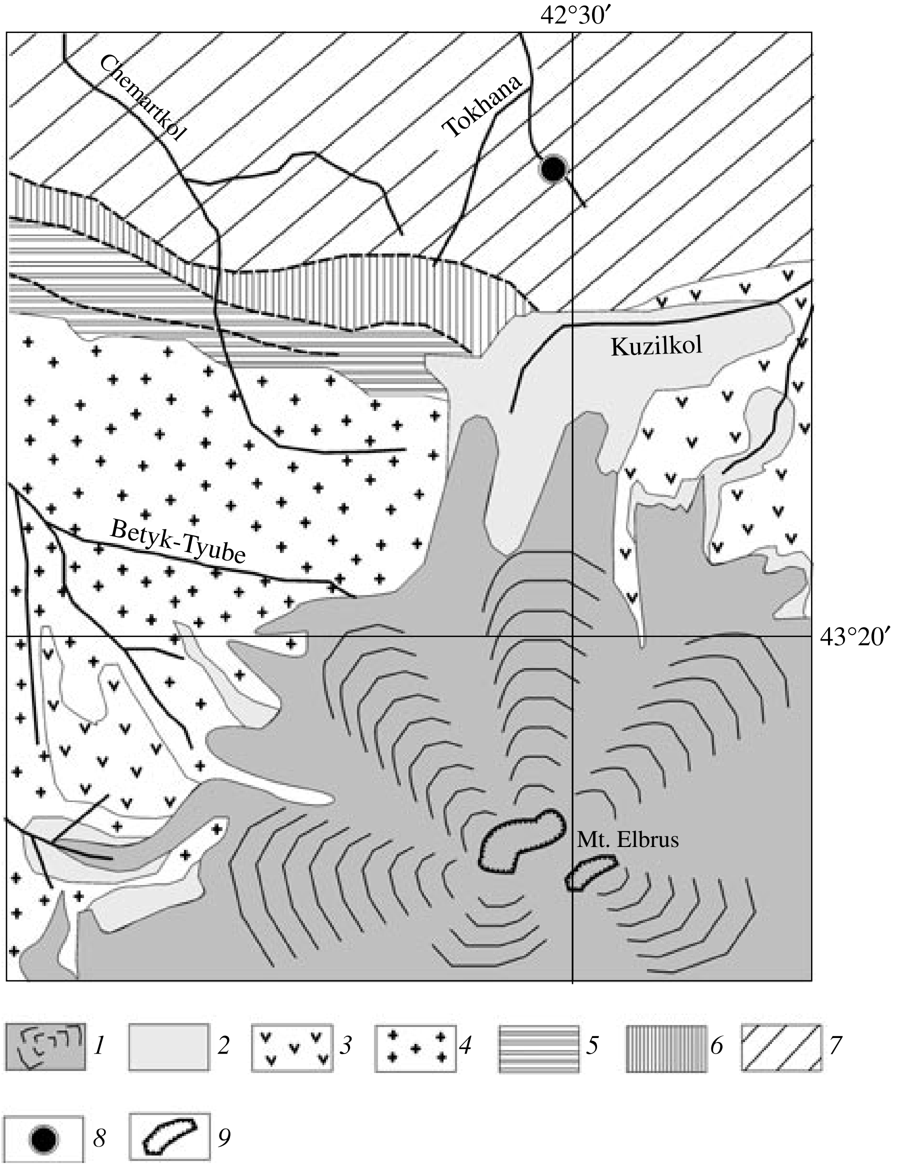

Fig. 1. Schematic geological map of the setting of the Tokhana-Verkhnii spring. (*1*) Glaciers; (*2*) loose Quaternary deposits (sand and gravel); (*3*) Late Pleistocene and Holocene andesite and andesite–dacite lavas; (*4*) Late Paleozoic granites; (*5*) Early Paleozoic quartz–chlorite, quartz–sericite, and quartz–chlorite–sericite schists; (*6*) Early and Middle Devonian diabases, quartz porphyries, siliceous shales, and variegated phyllites; (*7*) Early Carboniferous sandstones, clay shales, conglomerates and volcanic rocks; (*8*) Tokhana CO_2 spring; (*9*) Mount Elbrus fumarole field (according to [6]).

Our research was aimed at developing an isotopic–chemical model for the origin of travertine deposits and to compare the observed and simulated compositions of the water and calcite. To solve these problems, we examined the travertine dome of the Tokhana-Verkhnii CO_2 spring in the headwaters of Tokhana Brook in the area of Mount Elbrus, Northern Caucasus (Fig. 1).

MATERIALS AND METHODS

Almost all travertine deposits in the Greater Caucasus are related to the discharge areas of CO_2 waters. The northern slope of the Greater Caucasus is known to host about 30 travertine domes. Most of them are small, and their area usually does not exceed a few dozen or a few hundred square meters. The largest travertine domes are known in the vicinity of Pyatigorsk (on the slopes of Mount Mashuk), in the Elbrus area (Tokhana-Verkhnii and Verkhne-Baksan springs), in the area of Kazbek volcano (Verkhnii-Karmadon springs), and at the Kislye (Pkhiya) springs in the headwaters of the Bol'shaya Laba River. Almost all travertine-precipitating sources are cold. The exceptions are the springs of Verkhnii Karmadon, North Ossetiya, and the Proval spring in the town of Pyatigorsk, which precipitate carbonates from waters with a temperature of 55–60°C. All springs depositing travertine discharge at mountain slopes a few dozen meter above the thalwegs.

The travertine dome of the Tokhana-Verkhnii spring in the Northern Caucasus seems to be the largest of the modern edifices. Because of this, it is selected for our research. The Tokhana-Verkhnii spring is located 13–15 km north of Elbrus volcano (43° 28′ 7.1″ N, 42° 26′ 34.2″ E, $h = 2710$ m; Fig. 1). The reader can find its description in the catalogue of carbon dioxide springs in the Northern Caucasus (spring no. 43) [6].

The spring is hosted by the Pshekish–Tyrnyauz suture zone of sublatitudinal trend. The zone is of tectonic nature and separates Early Paleozoic crystalline massifs of granites and gneisses (which underlie the volcanic edifice of Mount Elbrus) and complicatedly tectonized Devonian, Carboniferous, and Permian volcanic and sedimentary complexes (Fig. 1). The Tokhana-Verkhnii spring is spatially restricted to the volcanic–sedimentary deposits of Early Carboniferous age (tuff–sandstones and tuff–siltstone).

The spring was thoroughly examined in July of 2001. Preparatorily to this, reconnaissance sampling of travertine, water, and gases was conducted in July of 1998. The pH was measured in the water flow at various distances from the source accurate to no worse than 0.1 pH unit. Simultaneously we measured the temperature of the water by an electronic thermometer accurate to 0.1°C. The air temperature during the sampling varied from 18 to 20°C.

Water samples for chemical analysis were stored in plastic bottles. The samples were taken at the discharge site and downstream from it. The chemical composition of water was analyzed by conventional techniques.

Samples of spontaneous gases released at the discharge site of the spring at the surface were collected in glass bottles using the displacement technique. The gases were analyzed in the laboratory on a KRISTALL 2000 M gas chromatographer by the method of absolute calibration, with Ar as the carrier gas.

Travertine samples were collected from the dome surface at various distances from the water discharge site. For our isotopic study, we tried to collect carbonate samples from the uppermost (fresh) crusts, although sometimes analyses were conducted on massive old travertine. The samples were decomposed by the conventional technique in H_3PO_4 [7]. The measurements of isotopic composition were conducted on a MI-1201V mass spectrometer. The precision of replicate $\delta^{13}C$ and $\delta^{18}O$ measurements was no worse than 0.25‰. The $\delta^{13}C$ values are listed in ‰ relative to the PDB standard, and the $\delta^{18}O$ values are presented relative to SMOW.

Structure of the Travertine Dome of the Tokhana-Verkhnii Spring

The Tokhana-Verkhnii spring (which will be referred to below as Tokhana) empties into the right-hand bank of the Tokhana Brook valley (in the headwaters of the Khudes River), some 150 m above the valley thalweg. The slope with the spring faces west. The mineral water flow rate is 2.0–2.5 l/s. The spring periodically releases gases. The main gryphon is accompanied by a few minor mineral springs (at a distances of 5–10 m from the main one), whose flow rates are negligibly low. All mineral water merges into a single creek, which flows down the valley slope for 400–450 m to the site where it empties into the Tokhana River. No other mineral water springs were found anywhere down the slope.

Travertine covers a stripe on the slope ~350 m long and no less than100 m wide. The maximum thickness of the travertine deposits is likely no less than 5–10 m. Old travertine deposits occur within 100–200 m north of the modern spring.

The chemistry, morphology, and mineralogy of the mineral matter precepitating from the water, i.e., along the strike of the travertine edifice, can be subdivided into four zones.

(1) Zone of limonitization in the vicinity of the spring and trends for no more than 20 m. No travertine is formed in this zone, and the only mineralization precipitating here is iron hydroxides, which color boulders and filaments of green algae into a brown color. Calcium carbonates are formed in this zone only sporadically on the surface of boulders above the water level. The carbonates are formed as thin calc–alga crusts a few millimeters thick.

(2) Zone of limonitization and the initial accumulation of carbonates. Carbonates start to precipitate on the spring bottom only at a distance of more than 20 m from the well. The first carbonate precipitates are loose (are easily crumbled by hands). They are strongly limonitized (are brown) and poorly crystalline. The thickness of these precipitates is no more than 5–10 cm. This is the zone of initial travertine formation and covers the spring bed segment at 20–40 m from the well.

(3) Zone of active $CaCO_3$ precipitation, which begins at a distance of 40–50 m from the spring and extends for 150–200 m. The thickness of the carbonate deposits reaches a maximum. The sinter carbonate textures are clearly zoned, and the travertine itself is very firm. The content of iron oxides decreases, and the travertine acquires yellowish and pinkish tints. The mineral water flows through this zone as a broad current on the slopes of the dome, which has a wavy surface resembling ripples.

(4) Zone where carbonate precipitation terminates. Near the lower boundary of the dome at ~300–350 m from the spring, the water current again composes a creek, which partly erodes the travertine. The bottom of the brook hosts alga colonies, whose surface is colored

Table 1. Chemical composition of water of the Tokhana-Verkhnii spring

Sample	Sampling year	Distance from the spring, m	T, °C	pH	Eh, mV	Mineralization, g/l	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	H_4SiO_4	CO_2, g/l
14/98	1998	0	6.7	6.13	–25	1.81	6.6	0.7	414	33.1	915	7.1	436	28	0.43
14/01	2001	0	6.6	6.27	40	1.79	5.7	0.5	408	36.5	933	10.6	398	25.6	1.19
14-5/01	2001	75	8.9	8.03	–	1.29	6.0	0.6	279	35.3	555	7.1	407	19.2	–
14-10/01	2001	150	15.9	8.04	–	1.11	6.0	0.4	237	36.5	408	5.3	415	28.8	–
14-15/01	2001	~300	18.2	8.02	–	1.07	6.1	0.4	233	32.8	390	5.3	407	17.6	–

in green. Practically no carbonate precipitates occur at the brook bottom. The base of the dome is covered with flaky carbonate fragments and small travertine platelets. Large blocks of very firm carbonate of dark gray color (old travertine) locally protrude from the talus.

The travertine edifice exhibits complicated relations between its chemogenic and biogenic constituents. The chemogenic rocks of cold springs are mostly various carbonates and iron oxides, and their biogenic component consists of diatomic shells and colonies of green–blue algae. The travertine deposits contain biogenic remnants practically everywhere.

Mineralogically, the carbonate of the travertine edifice is dominated by calcite of variable crystallinity. Away from the well, the sizes of calcite crystals increase and reach a maximum in the lower part of the dome.

The rock samples sometimes contain aragonite, which can be readily identified by X-ray diffraction techniques. This mineral is found only in the upper part of the zone of carbonate precipitation (at ~20–40 m from the spring, in zone 2). Aragonite forms aggregates of small acicular, sometimes radiating crystals, which fill pores in the loose carbonate–limonite deposits. Its concentration is low, no higher than 1–2% of the overall $CaCO_3$ mass. No aragonite was found in the central part of the travertine edifice (zones 3 and 4).

CHEMICAL COMPOSITION OF WATER AND SPONTANEOUS GASES

The water of the Tokhana spring has a mineralization of 1.8 g/l, which is dominated by the Ca^{2+} and HCO_3^- ions (Table 1). The concentrations of Na^+, K^+, and Mg^{2+} are low, and those of SO_4^{2-} are high (~400 g/l), which is more than two to three times higher than the sulfate concentrations of other springs in the Elbrus area. The waters of this spring are likely contributed by waters from the oxidation zone of some sulfide deposits, which are situated not far from the area, in the slopes of the Frontal Range. The comparison of the chemical composition of the waters in 1960 [6], 1998, and 2001 (Table 1, nos. 14/98 and 14/01) indicates that this composition practically does not vary with time.

When discharged at the surface, the mineral water has a temperature of 6.7°C and pH 6.27 and is gradually heated to 18°C (ambient air temperature) on the surface of the travertine dome. The pH of the water simultaneously also increases and is stabilized at ~8.0 (Fig. 2) at a distance of approximately 40–50 m from the well. This spatially coincides with the onset of the active precipitation of Ca carbonates (boundary between zones 2 and 3).

The processes of Ca carbonate precipitation affect the chemical composition of the water, and the Ca^{2+} and HCO_3^- concentrations in the spring decrease by almost a factor of two at ~300 m from the well (Table 1, sample 14-15/01).

The spring spontaneously outgases. The CO_2 fraction in the released spontaneous gas is 32–49 vol % (Table 2), with the rest accounted for mostly by N_2. The $\delta^{13}C$ of the CO_2 is –8.0‰.

ISOTOPIC COMPOSITION OF CARBONATE TRAVERTINE

The carbon and oxygen isotopic composition of the carbonates at various distances from the discharge site are reported in Table 3. The $\delta^{13}C$ and $\delta^{18}O$ values vary from +3.8 to +16.3 and from +24.6 to +28.1‰, respectively. The $\delta^{13}C$ values systematically increase downstream (Fig. 3), with this tendency violated only by the first sample (14-2/01), which has a high $\delta^{13}C$ value of +9.2‰. This sample represents not the travertine (as the rest of the samples) but alga–carbonate sinter that grows on the surface of boulders near the discharge site of the mineral water (zone 1, a zone where iron hydroxides precipitate).

The isotopically heaviest carbonates ($\delta^{13}C$ as high as +16‰) are formed in the lower part of the dome (zone 4). In our samples, all of them represent "old" travertine (Table 3, samples 14-1/01 and 14a/98), which are now not washed by the mineral water stream (these are single rock blocks projecting over the carbonate rock talus at the bottom of the dome). The scatter of the $\delta^{13}C$ values of the fresh samples is somewhat narrower: from +3.8 to +10‰ (Fig. 3), but the value of +10‰ still seems to not correspond to the final formation stages of the modern travertine, because the mineral water stream extends further down the slope. Because of this, the maximum values of $\delta^{13}C$ from +12.7 to +16.3‰ obtained for the old travertine can likely be correlated with the closing stages of carbonate deposition.

Hence, the scatter of the $\delta^{13}C$ ($CaCO_3$) values for a single dome edifice is as significant as 12‰, with isotopically heavy carbonates ($\delta^{13}C$ of up to +16‰) precipitating near the bottom of the dome.

Calculations indicate that none of the carbonates of the Tokhana dome are in equilibrium with the spontaneously released $\delta^{13}C = -8.0$‰, because the equilibrium value for carbonate at a temperature of 20°C should be close to 0‰.

The values of $\delta^{18}O$ of the carbonates precipitating now from the mineral water is 24.6–25.9‰. The oxygen isotopic composition of the old travertine is slightly different: $\delta^{18}O = 27.3$–28.1‰ (Fig. 4).

The analysis of relations between the $\delta^{18}O$ and $\delta^{13}C$ values of the carbonates indicates that they are positively correlated and define a trend resembling a mixing line (Fig. 5). However, this situation does not imply any mixing because the only CO_2 source in the system is the CO_2 of the mineral water.

Correspondingly, this trend and the precipitation of isotopically heavy carbonates can be controlled by other factors:

(1) fractionation of isotopes during water degassing at the surface;

(2) activity of microorganisms; and

(3) variations in the $\delta^{13}C$ of the spontaneous CO_2 with time.

The mechanisms responsible for variations in the isotopic composition of carbonates under the effect of these factors are different. For example, the fractionation of isotopes is pronounced the most conspicuously during the partial degassing of CO_2 waters at the surface. Mineral waters do not degas instantaneously, but during a certain time. The dissolved CO_2 is thereby enriched in the heavy carbon isotopes. This process is partly compensated by the precipitation of $CaCO_3$, which preferably accommodates the heavy carbon isotope. However, the tendency in the variations of the $\delta^{13}C$ of the calcite precipitating during the degassing of CO_2 waters is controlled, first of all, by the proportions of the masses of the CO_2 released to the atmosphere and deposited $CaCO_3$. According to [8], a correlation between the $\delta^{13}C$ and $\delta^{18}O$ of the travertine (Fig. 3) and the variability of its isotopic signatures could result from the isotopic fractionation in the gas–water–calcite system.

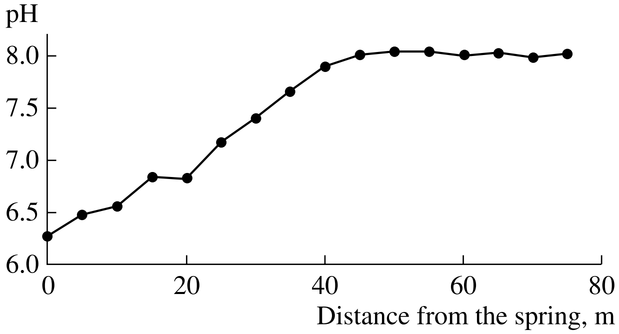

Fig. 2. Systematic variations in pH in the mineral water stream of the Tokhana spring.

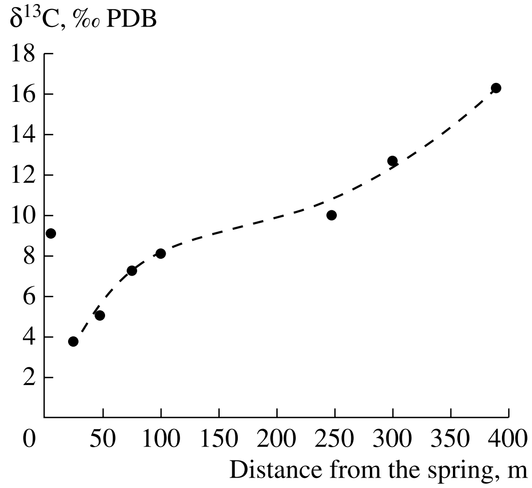

Fig. 3. Systematic variations in the $\delta^{13}C$ of carbonates along the strike of the Tokhana travertine dome.

Theoretically, the isotopic composition of carbonates precipitating from water is also affected by the activity of blue–green algae, which are widespread on the surface of the travertine. The photosynthesis process results in the preferable consumption of CO_2 with the light carbon isotope by plants. The CO_2 remaining

Table 2. Chemical composition (vol %) of spontaneous gases of the Tokhana-Verkhnii spring

Sample	Sampling year	CH_4	CO_2	O_2	N_2	Total
14/98	1998	0.22	32.14	1.04	63.77	97.19
14/01	2001	0.13	48.82	0.78	49.10	98.83

Table 3. Isotopic composition of carbonate travertine of the Tokhana-Verkhnii spring, Mount Elbrus area, Northern Caucasus

Sample*	Sample description	Distance from the spring, m	$\delta^{13}C$‰, PDB	$\delta^{18}O$‰, SMOW
14-2/01	Fresh thin carbonate–alga crusts (sinter) on boulders	3–5	+9.2	+25.9
14-3/01	Fresh travertine, whole-rock sample	25	+3.8	+25.0
14-4/01	Upper layer of fresh travertine	50	+5.0	+24.6
14-5/01	Upper layer of fresh travertine	75	+7.4	+25.2
14-6/01	Upper layer of fresh travertine	250	+10.0	+25.8
14-1/01	Old travertine from the bottom of the dome	~300	+12.7	+28.1
14/98	Massive fresh travertine, whole-rock sample	~100	+8.1	+25.5 +26.0
14a/98	Block of old massive travertine from the bottom of the dome	~400	+16.3	+28.1
14a/98	Block of old massive travertine from the bottom of the dome (duplicate sample)	~400	+16.2	+27.3

Note: * The numerals 98 and 01 in sample numbers correspond to the sampling years 1998 and 2001, respectively).

in the water should thereby be enriched in the heavy carbon isotope.

The idea that the isotopic composition of spontaneous CO_2 varies with time seems to be hardly plausible, because the $\delta^{13}C$ of CO_2 in other springs in the Mount Elbrus area varies within a relatively narrow range (from –6 to –10‰) [9]. These variations cannot be responsible for the observed variations in the carbon

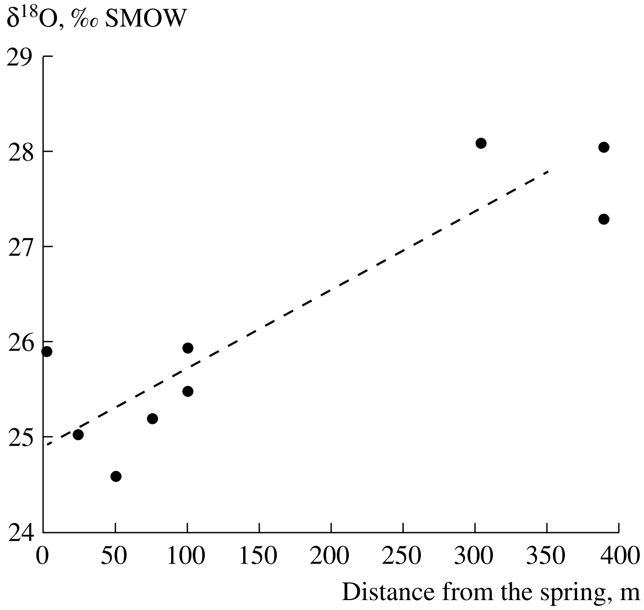

Fig. 4. Systematic variations in the $\delta^{18}O$ of carbonates along the strike of the Tokhana travertine dome.

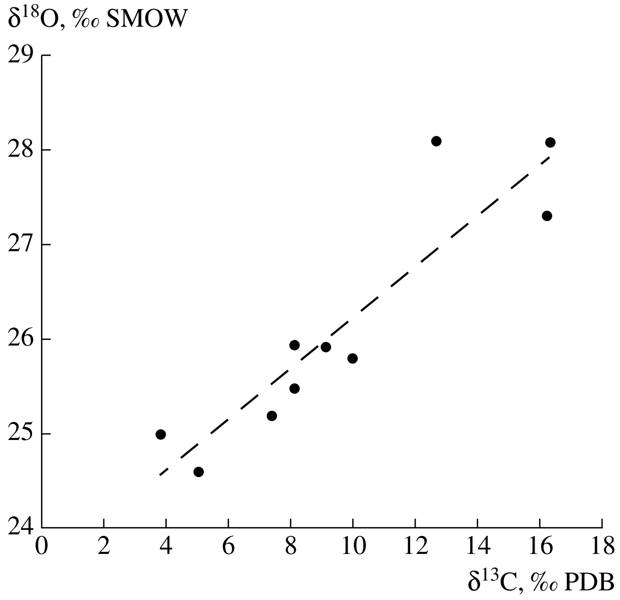

Fig. 5. Correlation between the $\delta^{18}O$ and $\delta^{13}C$ of the travertine of the Tokhana spring.

isotopic composition of the calcite. At a temperature of 20°C, these gases can be in equilibrium with carbonates having $\delta^{13}C$ values from –2 to +2‰.

It is possible to quantify the effect of isotopic fractionation during the precipitation of Ca carbonates under the assumption that all of the observed variations in the carbon isotopic composition of travertine within the dome were caused by physicochemical processes in the system atmosphere–mineral water–solid precipitate. If this hypothesis is valid, the $\delta^{13}C$ variations of the calcite should be consistent in scale and direction with the thermodynamic model, otherwise the isotopic composition of the travertine is controlled by other processes, for example, the activity of microorganisms. The role of the blue–green algae can then be determined by other methods.

PHYSICOCHEMICAL MODEL FOR THE GENESIS OF TRAVERTINE

The calculations of the carbonate equilibrium and calcite solubility are now a routine operation in any course of the thermodynamics of natural processes. The diversity of models proposed for the precipitation of calcite still do not include a model of the partial degassing of solutions during their interaction with atmospheric air. At the same time, heterogenization models for hydrothermal systems indicate that systematic degassing and the subsequent release of the gas phase can result in isotopic depletion and significant effects [10, 11].

The simulations were conducted for the H–C–O–N–Na–K–Ca–Mg–Cl–S ten-component system with a gas phase, which is characterized by the ideal mixing of the molecular species (H_2O, CO_2, and N_2). The aqueous solution was assumed to be potentially able to contain 36 aqueous species and one solid phase (calcite). The equilibria were calculated by the HCh program complex [12], the thermodynamic characteristics of all components were borrowed from the UNITHERM thermodynamic database integrated in this program complex. Previously we conducted the verification of these data for carbonate systems. Independent numerical simulations indicate that these data make it possible to predict calcite solubility accurate to 20% at temperatures below 100°C [13].

In the literature, a method was proposed for the thermodynamic simulations of physicochemical systems by the HCh computer program [14–17]. The independent components of the system selected in this case are not elements but isotopes, and thermodynamic properties are calculated for each chemical compound with a given isotope. The HCh program complex does not involve a database of thermodynamic characteristics of isotopic–chemical systems, which causes certain difficulties in the calculations, particularly, at various temperatures. We decided to attack our problem using the simpler method of Omoto [18]. According to this technique, the calculations are conducted in two stages: first, the chemical equilibrium and the concentrations of compounds participating in isotopic exchange are simulated, and, second, the known concentrations are used to calculate the equilibrium distribution of isotopes between the compounds based on balance and isotopic-exchange equations. This approach can be utilized because the influence of the isotopic distribution on the chemical equilibrium is relatively insignificant. The temperature function of the isotopic distribution coefficients was calculated by the equation

$$1000 \ln \alpha = A(10^6 T^{-2}) + B. \qquad (1)$$

The coefficients A and B for the H_2CO_3–CO_2, HCO_3^-–CO_2, and HCO_3^-–$CaCO_3$ were compiled from [19]. The values of these coefficients for various temperatures are listed in Table 4.

The degassing of mineral waters can be visualized as interaction with air in successive states of the system, with the gas phase renewed at each step. This approach is generally equivalent to the method of flow-through stepwise reactors, which was developed for simulating water–rock interactions [17]. In the first reactor R_0, the equilibrium of the original mineral water and spontaneous gas (50% CO_2, 50% N_2) is calculated (Table 1) at a spring temperature of 7°C and a pressure of 1 atm. No saturation with respect to calcite is reached, because no carbonate minerals occur in the gryphon. The composition of reactor R_1 is calculated for 1 liter of water from reactor R_0 and 1 liter of atmospheric air. The composition of the air is specified in the model by N_2 with a low CO_2 concentration (0.01 mol %). Inasmuch as we did not simulate redox reactions, the model did not take oxygen into account. The equilibrium composition of the liquid was then transferred into reactor R_2, and equilibrium with the newly supplied air portion was simulated. A scheme of the simulations is presented in Fig. 6. The model included 14 reactors. As was demonstrated by preliminary simulations, this is enough for the practically complete degassing of the solution and precipitation of calcite, so that the complex of the solution varies after this only insignificantly.

The main dynamic parameter of this model is the interaction coefficient of air and mineral solution volumes (A/S). This coefficient depends on numerous factors (depth of the flow, flow velocity, stirring of the current, wind velocity, etc.). Because it seems to be impossible to evaluate this parameter, we assumed it to be equal to one for each reactor, which allowed us to subdivide the degassing process into a reasonable number of individual simulations. The integral value of the Σ A/S ratio is equal to 14, i.e., 1 l of the solution eventually interacts with 14 l of air (14 1-l portions). The integral Σ A/S ratio should vary for individual flows and be prone to generally increase with time and with increasing distance from the spring.

The model considers the following three variants of the temperature regimes of water degassing:

Table 4. Isotopic fractionation coefficients of carbon used in the simulations [19]

T,°C	1000 ln(α)		
	$H_2CO_{3(sol)}$–$CO_{2(gas)}$	$HCO^-_{3(sol)}$ – $CO_{2(gas)}$	$HCO^-_{3(sol)}$ – $CaCO_{3(sol)}$
0	–0.82	10.24	2.17
5	–0.82	9.72	2.13
10	–0.82	9.22	2.08
15	–0.82	8.75	2.04
20	–0.83	8.30	2.01

(1) a temperature decrease from 7 to 0°C (the temperature in each subsequent reactor is decreased by 0.5°C), which corresponds to the winter period of time;

(2) a temperature increase from 7 to 20°C (the temperature in each subsequent reactor is increased by 0.1°C), which corresponds to the summer thermal regime; and

(3) a constant temperature (7°C in each reactor), which corresponds to the autumn period of time.

SIMULATION RESULTS

The simulation results demonstrate that the mineral water of the spring in equilibrium with spontaneous gas is not saturated with respect to calcite. The predominant aqueous carbon-bearing species is carbonic acid, and the pH of the solution is equal to 5.7. The most important results of the simulations can be considered using the example of the model for the summer temperature regime (Fig. 7). During exchange with air and an increase in the integral A/S ratio, the concentration of dissolved carbonic acid rapidly decreases. At the fourth step of the simulations (A/S = 4), the concentrations of H_2CO_3 and HCO_3^- in the solution become equal, and then the predominant species is HCO_3^-; the pH simultaneously increases. At the sixth step (A/S = 6), the solution reaches saturation with respect to calcite, and travertine starts precipitating according to the reaction:

$$\begin{aligned} Ca^{2+} + 2HCO_3^- = {} & CaCO_3(\text{calcite})\downarrow \\ & + H_2O + CO_2\uparrow. \end{aligned} \tag{2}$$

The maximum amounts of carbonate precipitate in reactors 7–11 (A/S = 7–11) (Fig. 7b). By reactor 14, degassing becomes weak, and calcite precipitates mostly because of water evaporation. The pH of the solution is thereby stabilized at 7.4–7.5.

The simulation results can be tested by their comparison with measured pH values (Figs. 7a and 2, respectively). The calculated pH values are slight underestimates compared to the measured values, which can be caused by the fact that the measured solutions were already partly degassed. In general, the calculated and measured data are in good agreement and make it possible to assay the integral Σ A/S ratio as a function of distance from the spring. For the spring in question, Σ A/S = 14 is reached at a distance of approximately 200 m. Hence, our model is generally able to adequately describe the degassing dynamics of the mineral water flow.

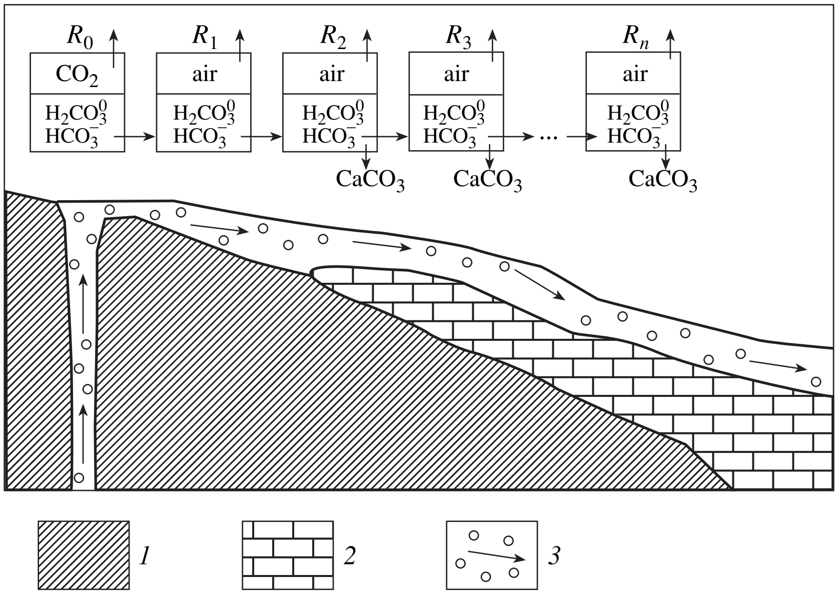

Fig. 6. Physicochemical model for the development of a travertine dome. (*1*) Host rocks; (*2*) travertine precipitates; (3) water flow.

The assumed initial value was the composition of spontaneous CO_2 of the spring with $\delta^{13}C = -8.0‰$. In simulating equilibria of the solution and spontaneous gas in the spring, the isotopic composition of all aqueous carbon species was determined relative to free CO_2 according to the isotopic fractionation coefficients at 7°C. The carbon isotopic composition of solution was calculated based on our model for the concentrations of carbon-bearing species by the equation

$$\delta^{13}C_{\Sigma}^{R_{n-1}} = \delta^{13}C^{R_n}_{HCO_3^-}\chi_{HCO_3^-} + \delta^{13}C^{R_n}_{H_2CO_3}\chi_{H_2CO_3} + \delta^{13}C^{R_n}_{CaCO_3}\chi_{CaCO_3} + \delta^{13}C^{R_n}_{CO_2}\chi_{CO_2}, \quad (3)$$

where $\delta^{13}C_{\Sigma}^{R_{n-1}}$ is the carbon isotopic composition of the liquid phase in the previous reactor; R_{n-1}, $\delta^{13}C_i^{R_n}$, and χ_i are the carbon isotopic composition and the mole fraction of a given carbon species among all carbon species.

The value of $\delta^{13}C_{\Sigma}^{R_{n-1}}$ was then calculated as

$$\delta^{13}C_{\Sigma}^{R_{n-1}} = \delta^{13}C^{R_n}_{HCO_3^-}\chi'_{HCO_3^-} + \delta^{13}C^{R_n}_{H_2CO_3}\chi'_{H_2CO_3}, \quad (4)$$

where χ'_i – is the mole fraction of the carbon species in the aqueous solution. The calculations were then repeated for the next reactor by Eq. (3).

The carbon isotopic composition calculated for its predominant species for the summer temperature regime is shown in Fig. 7. During the early degassing stages, $\delta^{13}C$ of dissolved CO_2 slightly decreases due to the losses of isotopically heavy CO_2 to the gas phase. The contribution of this effect is generally insignificant, but successive fractionation results in a decrease in the $\delta^{13}C$ of CO_2 to –9‰. When the excess CO_2 is mostly degassed, the predominant aqueous carbon species at A/S = 5 becomes the hydrocarbonate ion. The fractionation coefficient of carbon isotopes between the hydrocarbonate ion and gaseous carbon dioxide is significant, and the gas phase is richer in the light isotope. The $\delta^{13}C$ of hydrocarbonate starts to increase in the liquid because of the degassing of the solution. Calcite begins precipitating starting at step 6, and its $\delta^{13}C$ systematically increases with degassing. Calcite precipitation depletes the solution in the heavy carbon isotope, but this cannot counterbalance the release of the light isotope with gaseous CO_2. As the water degasses and carbonates precipitate, their $\delta^{13}C$ gradually increase from +5.5 in reactor 1 to +13‰ in the last reactor. The variation character of the calculated $\delta^{13}C$ values is in good agreement with the tendency toward an increase in the measured $\delta^{13}C$ values in carbonate samples taken near the bottom of the dome.

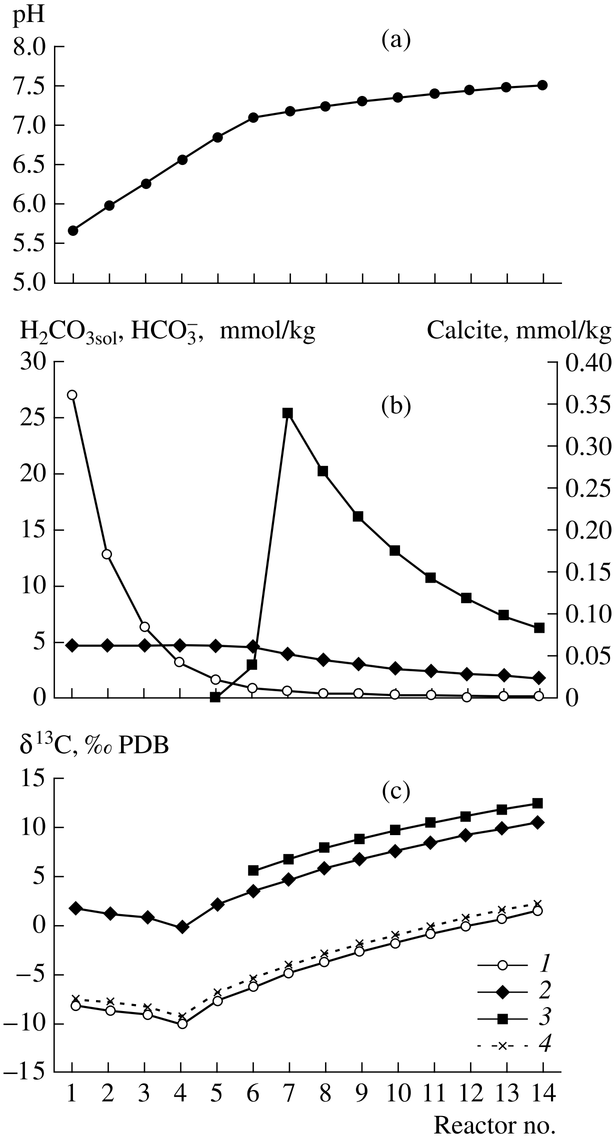

Fig. 7. Simulation results of mineral water degassing in the summer temperature regime: (a) pH of the solution; (b) concentrations of predominant aqueous carbon species and the amount of precipitating calcite; (c) isotopic composition of predominant aqueous carbon species (*1*—H_2CO_3; *2*—HCO_3^-; *3*—calcite; *4*—CO_2).

The variations in the $\delta^{13}C$ at various temperatures, which imitate seasonal variations in the air temperature (summer, winter, and autumn), are insignificant compared to the observed dynamic effects (Fig. 8). In general, a temperature decrease leads to an increase in the $\delta^{13}C$ of the carbonates. The isotopic compositions of carbonates precipitating "in summer" and "in winter" differ in the initial reactors by approximately 1‰ and gradually converge during later stages of the process (Fig. 8). This is explained by the fact that the temperature dependence of the fractionation is expressed mostly in the solubility of carbon dioxide in water. As the process evolves, the dynamic parameter (A/S) becomes predominant in all cases. Thus, the discharge of CO_2 mineral water can be associated with the precipitation of carbonates with broadly varying $\delta^{13}C$ values,

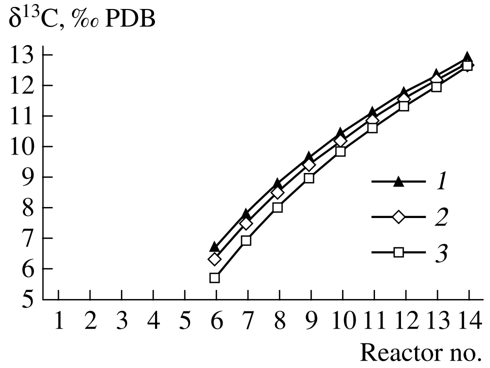

Fig. 8. Carbon isotopic composition of calcite calculated in models with different temperature regimes: (*1*) winter, (*2*) autumn, (*3*) summer.

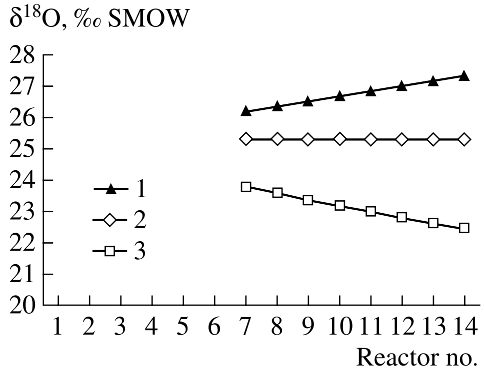

Fig. 9. Oxygen isotopic composition of calcite calculated in models with different temperature regimes: (*1*) winter, (*2*) autumn, (*3*) summer.

which are controlled, first of all, by the distance from the discharge site of the water.

The comparison of the variations in the $\delta^{13}C$ values with the volumes of precipitating calcite (Figs. 7b, c) demonstrates that the fractions of carbonates with different $\delta^{13}C$ vary within the travertine dome. Calcite with $\delta^{13}C$ from 7 to 11‰ accounts for 85% of the overall volume of the carbonate material. Carbonates with the minimum and maximum $\delta^{13}C$ values are produced in much lower amounts (2 and 23%, respectively). They are formed at the periphery of the travertine dome (near its upper and lower boundaries). Because of this, the probability that carbonates with intermediate $\delta^{13}C$ values (i.e., with a narrower variation range of $\delta^{13}C$) are preserved during the weathering of the travertine rocks is higher.

The oxygen isotopic composition of calcite calculated in the equilibrium model depends only on the temperature. The effect of degassing cannot modify the oxygen isotopic composition of the water, because only a very low amount of oxygen (<0.02%) leaves the solution together with carbon dioxide and water vapor. The calculation of the oxygen isotopic composition of calcite at various temperature regimes is displayed in Fig. 9. The temperature dependence of the isotopic exchange coefficient was borrowed from [20]. High-temperature (summer) regimes can produce isotopically light calcite ($\delta^{18}O$ 22.5–23.8‰), whereas calcite precipitating in winter is isotopically heavy ($\delta^{18}O$ 26.2–27.4‰). At the same time, the correlation between the carbon and oxygen isotopic compositions of the carbonates can also be explained by the absence of isotopic equilibrium between the water, calcite, and dissolved carbonate species. In this situation, degassing similarly shifts the carbon and oxygen isotopic compositions. However, quantitative estimates of the effect of this mechanism can be made only with regard for the reaction rates (which are still poorly known).

DISCUSSION

The results of our thermodynamic simulations indicate that the degassing of CO_2 waters in air lead to a systematic enrichment of the precipitating calcite in the heavy isotopes with increasing distance from the spring.

The range of the $\delta^{13}C$ values yielded by the model (from +5.5 to +13‰) agree in scale and general tendencies with the data of isotopic measurements in travertine samples: from +3.8 to +10‰ (or to +16‰ in old travertine) (Table 3, Figs. 4 and 7c).

In the model, the values of $\delta^{13}C$ (+5.5‰) in the first $CaCO_3$ portions are slightly higher than in natural calcite samples (+3.8‰). It is possible that this was caused by the water degassing parameters assumed in the model and the subdivision into elementary systems (reactors) for the simulations. It should also be noted that aragonite formation, which was noted to take place near the upper margin of the travertine dome, was not taken into account in our model. Aragonite is formed as a metastable phase due to certain kinetic preferences. Obviously, it is impossible to simulate the replacement of aragonite by calcite within the scope of an equilibrium model. Inasmuch as aragonite occurs in travertine deposits in subordinate amounts, we neglected its crystallization.

Our thermodynamic model is able to accurately enough describe the genesis of travertine. Our estimates can also be tested via the calculated pH values, which coincide with those measured in the naturally occurring waters (Figs. 2 and 7a).

In general, our model implies that the longer the segment where carbonates precipitate, the higher the $\delta^{13}C$ values of the $CaCO_3$ precipitating near the bottom of the travertine edifice. Judging from our simulation data and the $\delta^{13}C$ of travertine from the Tokhana dome, the linear rate of the increase in the $\delta^{13}C$ values can be as high as 3–4‰ per 100 m. Comparison with other springs corroborates with these evaluations.

Indeed, smaller travertine edifice (no longer than 100 m, such as Pkhiya, Verkhnii Baksan, Irik, and

Verkhnii Karmadon) show much narrower $\delta^{13}C$ variations, usually no more than 2–2.5‰.

Thus, the natural variations in the $\delta^{13}C$ values in travertine from large domes can reach at least 7–8‰ and, judging from measurements in natural samples, even 12‰. Because of this, it seems to be impossible to reproduce the original isotopic composition of the spontaneous CO_2 of ancient CO_2 springs on the basis of miscellaneous travertine fragments or unsystematically sampled fragments of large dome structures. The best results can be obtained by studying small (no larger than 100 m) travertine edifices. However, in this situation, it is also expedient to sample various portions of the edifice.

The oxygen isotopic composition is controlled by other mechanisms. Within the framework of our model, calcite with high $\delta^{18}O$ values can be formed only during water cooling in winter. In contrast to the carbon system, degassing almost does not affect the oxygen isotopic composition of the water (and, correspondingly, the carbonates precipitating from it). The increase in the $\delta^{18}O$ ($CaCO_3$) toward the bottom of the travertine dome (Fig. 5) can also be explained by other factors.

The observed $\delta^{18}O$ isotopic effects can, theoretically, result from the activity of blue–green algae on the travertine surface (these algae preferably utilize the light oxygen isotope). Another factor that can yield analogous results could be water evaporation at the surface of the flow. Water evaporation could play a determining role in the middle part of the dome, where the active precipitation of $CaCO_3$ takes place. Mineral water broadly spreads there over the travertine surface. The width of the wet portion of the dome is there no less than 10–15 m, and the depth of the water current does not exceed 1–2 cm. Evidently, evaporation processes may play the leading role controlling the isotopic composition of the carbonate material under favorable weather conditions.

CONCLUSIONS

1. Isotopic measurements indicate that travertines from the Northern Caucasus may contain isotopically heavy calcite ($\delta^{13}C$ up to + 16‰). The $\delta^{13}C$ and $\delta^{18}O$ values increase away from the spring. The variations in the $\delta^{13}C$ ($CaCO_3$) values within the modern dome reach ~12‰, with an average $\delta^{13}C$ ($CaCO_3$) increase of ~3–4‰ per 100 m.

2. The thermodynamic model for travertine formation imitates the processes of carbon isotopic fractionation during the degassing of CO_2 waters at the surface. The variations in the calculated $\delta^{13}C$ ($CaCO_3$) values along the strike of the dome structure have a scale and trend analogous to those observed in nature. Thus, the reasons for the origin of isotopically heavy carbonate travertine do not necessarily include other factors, such as the activities of blue–green alga colonies.

3. Compared to the dynamic effects, seasonal temperature variations play a subordinate role in controlling the isotopic composition of carbonates in large dome structures. The significance of the seasonal factors increases, however, for small travertine structures, at which the contributions of dynamic and temperature effects of isotopic fractionation become comparable.

4. Our results demonstrate that the composition of travertine can significantly vary along the strikes of the structures. This should be taken into account in paleoclimatic and paleohydrogeological reconstructions. Our data also imply that it is generally unadvisable to conduct these reconstructions using unsystematically sampled fragments of ancient travertine, which can be sometimes found in talus and alluvial deposits. Even if the samples were collected at the central, well-preserved portions of dome structures, the natural variations in the isotopic composition of the carbonates caused by dynamic effects may be as great as 2.0–2.5‰ for carbon and 1.0–1.5‰ for oxygen.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project nos. 03-05-64696 and 06-05-65156) and the Program "Physical Geochemistry of Natural Processes" for the Support of Leading Research Schools.

REFERENCES

1. A. Pentecost, "The Quaternary Travertine Deposits of Europe and Asia Minor," Quat. Sci. Rev. **14**, 1005–1028 (1995).
2. S. I. Naboko, I. P. Lugovaya, and V. N. Zagnitko, "Carbon and Oxygen Isotopic Composition in Recent Travertines and Geyserites of Kamchatka," Mineral. Zh. **21** (5/6), 33–39 (1999).
3. C. Savelli and K. H. Wederpohl, "Geochimishe Untersuchengen an Sinterkalken (Travertinen)," Contrib. Mineral. Petrol. **21**, 238–256 (1969).
4. A. Navas, B.L. Valero-Garces, A. Delgado-Huertas, and N. Ratto, "Large ^{13}C Enrichment in Primary Carbonates from Andean Altiplano Lakes, Northwest Argentina," Earth Planet. Sci. Lett. **171**, 253–266 (1999).
5. J. E. Andrews, R. Riding, and P. F. Dennis, "The Stable Isotope Record of Environmental and Climatic Signals in Modern Terrestrial Microbial Carbonates from Europe," Palaeogeography, Palaeoclimatology, Palaeoecology **129**, 171–189 (1997).
6. *Carbon Dioxide Mineral Waters in the Northern Caucasus*, Ed. by I. Ya. Panteleeva (izd-vo AN SSSR, Moscow, 1963) [in Russian].
7. J. M. McCrea, "On the Isotope Chemistry of Carbonates and Paleotemperature Scale," J. Chem. Phys. **18**, 849–857 (1950).
8. C. H. Hendy, "The Isotopic Geochemistry of Speleothems.—I. The Calculation of the Effects of Different Modes of Formation on the Isotopic Composition of Speleothems and Their Applicability as Palaeoclimatic

Indicators," Geochim. Cosmochim. Acta **35**, 801–824 (1971).

9. *Geodynamics, Seismotectonics, and Volcanism of the Northern Caucasus*, Ed. by N. P. Laverov (OIFZ RAN, Moscow, 2001) [in Russian].
10. S. S. Matveeva and A. Yu. Bychkov, "Carbon Isotope Fractionation in Fluids during the Formation of the Spokoinoe Wolframite Deposit," Dokl. Akad. Nauk **381**, 403–405 (2001) [Dokl. Earth Sci. **381A**, 1057–1060 (2001)].
11. S. S. Matveeva, M. Yu. Spasennykh, T. M. Sushchevskaya, et al., "Geochemical Model of the Formation of the Spokoininsk Tungsten Deposit (Eastern Transbaikal Region, Russia)," Geol. Rudn. Mestorozhd. **44**, 125–147 (2002) [Geol. Ore Dep. **44**, 111–131 (2002)].
12. Yu. V. Shvarov and E. Bastrakov, "HCh: A Software Package for Geochemical Equilibrium Modelling. User's Guide," in *Australian Geological Survey Organization* (Canberra, 1999).
13. V. P. Il'chenko, T. V. Levshenko, A. Yu. Bychkov, and V. S. Goncharov, *Salt Accumulation during Exploitation of Gas and Gas condensate Deposits* (IRTs Gazprom, Moscow, 1999) [in Russian].
14. L. N. Bannikova and B. N. Ryzhenko, "Carbon and Sulfur Isotopic Ratio in the Products of Redox Reactions under Hydrothermal Conditions (System CH_4–Na_2SO_4–NaCl–H_2O)," Geokhimiya, No. 9, 1268–1281 (1984).
15. L. N. Bannikova, D. V. Grichuk, and B. N. Ryzhenko, "Calculations of Chemical and Isotopic Equilibria in the C–H–O System and Their Application to the Study of Redox Reactions under Hydrothermal Conditions," Geokhimiya, No. 3, 416–428 (1987).
16. D. V. Grichuk, "Isotopic–Chemical Thermodynamic Model of Hydrothermal Systems," Dokl. Akad. Nauk SSSR **298** (5), 1222–1225 (1988).
17. D. V. Grichuk, *Thermodynamic Models of Submarine Hydrothermal Systems* (Nauchnyi Mir, Moscow, 2000) [in Russian].
18. H. Ohmoto, "Systematic of Sulfur and Carbon Isotopes in Hydrothermal Ore Deposits," Econ. Geol. **65** (5), 551–578 (1972).
19. P. Deines, D. Langmuir, and R. S. Harmon, "Stable Carbon Isotope Ratios and the Existence of a Gas Phase in the Evolution of Carbonate Ground Waters," Geochim. Cosmochim. Acta **38**, 1147–1164 (1974).
20. I. Friedman and J. R. O'Neil, "Complication stable isotope fractionation factors of geochemical interest. Data of Geochemistry," US. Geol. Surv. Prof. Pap., No. 440-KK (1977).