ISSN 0016-7029, Geochemistry International, 2007, Vol. 45, No. 11, pp. 1131–1143. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © E.O. Dubinina, I.V. Chernyshev, N.S. Bortnikov, A.Yu. Lein, A.M. Sagalevich, Yu.V. Gol'tsman, E.D. Bairova, A.V. Mokhov, 2007, published in Geokhimiya, 2007, No. 11, pp. 1223–1236.

Isotopic–Geochemical Characteristics of the Lost City Hydrothermal Field

E. O. Dubinina[a], I. V. Chernyshev[a], N. S. Bortnikov[a], A. Yu. Lein[b], A. M. Sagalevich[b], Yu. V. Gol'tsman[a], E. D. Bairova[a], and A. V. Mokhov[a]

[a] *Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences, Staromonetnyi per. 35, Moscow, 109017 Russia*
e-mail: delta@igem.ru
[b] *Shirshov Institute of Oceanology, Russian Academy of Sciences, Nakhimovskii pr. 36, Moscow, 117991 Russia*

Received May 25, 2006

Abstract—The isotopic (δD, $\delta^{18}O$, $\delta^{13}C$, and $^{87}Sr/^{86}Sr$) and geochemical characteristics of hydrothermal solutions from the Mid-Atlantic Ridge and the material of brucite–carbonate chimneys at the Lost City hydrothermal field at 30°N, MAR, were examined to assay the role of the major factors controlling the genesis of the fluid and hydrothermal chimneys of the Lost City field. The values of δD and $\delta^{18}O$ in fluid samples indicates that solutions at the Lost City field were produced during the serpentinization of basement ultramafic rocks at temperatures higher than 200°C and at relatively low fluid/rock ratios (<1). The active role of serpentinization processes in the genesis of the Lost City fluid also follows from the results of the electron-microscopic studying of the material of hydrothermal chimneys at this field. The isotopic ($\delta^{18}O$, $\delta^{13}C$, and $^{87}Sr/^{86}Sr$) and geochemical (Sr/Ca and REE) signatures indicate that, before its submarine discharging at the Lost City field, the fluid filtered through already cold altered outer zones of the Atlantis Massif and cooled via conductive heat loss. During this stage, the fluid could partly dissolve previously deposited carbonates in veins cutting serpentinite at the upper levels of the Atlantis Massif and the carbonate cement of sedimentary breccias underlying the hydrothermal chimneys. Because of this, the age of modern hydrothermal activity at the Lost City field can be much younger than 25 ka.

DOI: 10.1134/S0016702907110067

INTRODUCTION

The long-term studying of hydrothermal activity related to seafloor spreading indicates that most of the currently known zones of hydrothermal activity in the Pacific and Indian oceans, the Red Sea, and the North Atlantic Ocean [1–3] is genetically related to basaltic magmatism. In convective cells developing thereby, seawater penetrating into the newly formed oceanic crust is transformed into a high-temperature (up to 400°C) acidic (pH 2–4) fluid, which can form sulfide mineralization. It is particularly interesting to examine hydrothermal processes occurring along the slow-spreading Mid-Atlantic Ridge (MAR). Not only active sulfide edifices (so-called black smokers) were detected along the MAR (at the Logachev, Rainbow, and Ashadze hydrothermal fields) but also carbonate edifices spatially related to serpentinized peridotites, which were discovered five years ago at the Lost City field [4]. The discovery of these hydrothermal vents indicates that convective cells developing in spreading zones are of an unusual type and are related not to a magmatic energy source but to some other sources of heat, perhaps, generated by exothermic reactions of olivine serpentinization. Data obtained at the Lost City hydrothermal field may be crucial for solving the problem of the energy and material source for such cells.

The Lost City field is situated 15 km off a spreading zone and rests on a fairly old (1.5 Ma) basement [4]. The field was determined to contain unusual barren brucite–carbonate mineralization, which was deposited by highly alkaline (pH 9–9.8) low-temperature (40–95°C) solutions. The discharge rate of the fluid is relatively low, and, according to [5], the solutions reach their discharge sites via diffusion mechanisms. The Na and Cl concentrations in the Lost City fluid are close to those in seawater, but this fluid is twice richer in Ca and bears notable amounts of dissolved gases: methane and hydrogen [4–6].

As at any other oceanic hydrothermal field, the original source of fluid at Lost City was seawater, which filtered through the oceanic crust via a network of fractures and faults. At a slow spreading velocity, which is typical of the territory, the scale of the deep circulation of the solutions is fairly high, and the solutions themselves show evidence of their active interaction with seafloor rocks [1]. Now all researchers of the Lost City hydrothermal field [4–10] admit its links with the serpentinization of ultramafic rocks. The two main hypotheses put forth to account for the genesis of hydrothermal fluid at Lost City are as follows. The proponents of one of them regard the Lost City solution as a result of mixing of a hot fluid produced by peridotite serpentinization (this fluid is enriched in gases, such as H_2, CH_4, CO_2, and H_2S, in the course of gas separation) with cold ambient water in the subsurface biosphere (where microbial processes take place, including the active reduction of the sulfate ion on hydrogen by archea sulfate-reducing microorganisms [6–8]). The other hypothesis is underlain by the results of thermodynamic simulations of serpentinization processes and mixing with seawater. These simulations have demonstrated that the fluid produced in the course of serpentinization can account for the mineralogical features of hydrothermal chimneys at Lost City during its mixing with bottom oceanic water, but the serpentinization process should have proceeded at significant temperatures (close to 300°C), while the mixing occurred at temperatures no higher than 150°C [9, 10]. The aforementioned authors believed that these processes were separated by a stage of the conductive cooling of the fluid without its mixing with seawater. Both hypotheses fail, however, to explain several issues in the genesis of the Lost City hydrothermal solution.

Heat balance calculations and geochemical simulations [10] for the Lost City field indicate that the temperature regime of the hydrothermal solutions cannot be explained only by the heat of the exothermal reaction of serpentine hydration. The comparison of the results of these calculations and geochemical data led the authors to conclude that the Lost City fluid is of more complicated genesis and could (at a low spreading velocity) reach deep lithospheric levels before discharging at the seafloor.

Although some issues remain uncertain as of yet, all researchers of the Lost City field reached a consensus on the necessity of the further detailed examination of both the fluid phase at the field and its precipitation products. The field is still poorly examined because, on the one hand, it was discovered quite recently and, on the other, is hard to reach. It was described only in a few pioneering papers presenting natural observations [4–7] and some results of geochemical and thermodynamic simulations and heat balance calculations [9, 10]. Disputable issues in the genesis of the fluid very unusual for submarine hydrothermal systems can be settled with the aid of isotopic data, which are, however, still scarce [5, 7].

This paper reports the results of our isotopic–geochemical study of hydrothermal deposits at Lost City and fluids from hydrothermal fields at the Mid-Atlantic Ridge. The samples were collected during 9 of the R/V *Akademik Mstislav Keldysh* in 2002. One of the tasks of our research, along with obtaining new isotopic–geochemical data on the Lost City field, was the numerical evaluation (based on isotopic evidence) of the main processes that formed the Lost City deposits: serpentinization, conductive cooling of the fluid, and its mixing with seawater. In the course of this research, we examined not only the mineral material of chimneys at Lost City but also hydrothermal fluid samples from this field and from some other nearby fields at the Mid-Atlantic Ridge: Rainbow and Lucky Strike, which lie between 20 and 40°N.

Solution samples were collected at Lost City near the top of the 60-m Poseidon chimney. The fluid venting from the central part of this structure resembles a drinking fountain 10–12 cm high and approximately 3 cm in diameter.

GENERAL CHARACTERIZATION OF THE LOST CITY HYDROTHERMAL FIELD

The Lost City hydrothermal field at 30° N lies at a depth of 750–850 m, 15 km from the intersection point of the Mid-Atlantic Ridge (MAR) with a transform fault in the upper part of the southern slope of the Atlantis Massif, which consists of strongly deformed serpentinite and metagabbro with numerous carbonate veins and veinlets. The upper part of the massif is unconformably overlain by sedimentary breccias, pelagic limestones, and brecciated fragments of hydrothermal deposits cemented by lithified carbonate sediments. The carbonate deposits and the lithified cement of the breccias is foraminiferan sand with well-preserved subtropical faunal remnants [4].

According to radiocarbon data, hydrothermal activity at the Lost City field was dated at approximately 30 ka [5]. At the same time, the radiocarbon age of the carbonate material of the hydrothermal chimneys broadly varies from 0 to 25 ka. The carbonate material in the basement of the stratigraphic succession (pelagic limestone, carbonate material of breccias, and veinlets in serpentinites) is older and varies within a narrower range: from 25 to 34 ka. The age of calcite veinlets in fracture zones in gabbro and serpentinites is the least variable and amounts to approximately 32 ka.

The hydrothermal field itself consists of vertical chimneys and towers of variable morphology and height. Some of them resemble thin pinnacles 3–5 m high and up to 20 cm in diameter, and others are large columnar structures, often having flat tops, up to 60 m high and 10 m in diameter. Some edifices are still active, while others are inactive. The active edifices are washed by shimmering waters, which ascent along the outer walls and seep and vent from the flat tops and escarps of the edifices [6]. Our research was conducted on the material of brucite–carbonate deposits sampled at a large active chimney.

ANALYTICAL TECHNIQUES AND RESULTS

A representative 2- to 5-g portion of each sample of the carbonate–brucite material was homogenized by grinding and used for all further chemical and isotopic analyses. The Sr isotopic analysis, atomic absorption

Table 1. Mineral composition of samples (X-ray powder diffraction data) and their description

Sample no.	Mineral composition	Material description
68-M2/5	Aragonite + (calcite)	Coral fragments in carbonate sand near the bottom of a chimney
67-M1-1/3	Brucite + calcite + aragonite	Top of a chimney. White porous rocks with a dense bluish crust
65-M2-2/3	Aragonite + brucite	Snow-white porous fans of crystals on the flat top of a chimney
64-M1-7/2	Aragonite + calcite	Top of an edifice, a zone of active seeping. Gray porous rocks, outer zone of the chimney
71-M2-1	Calcite + aragonite + brucite	Top of an edifice, a zone of active seeping. Sugar white rock
68-M2-4/2	Brucite + aragonite + calcite	Top of an edifice, a zone of active seeping. Sugar white rock
71-M2-4	Brucite + aragonite + calcite	Top of an edifice, a zone of active seeping. Sugarlike crystal aggregates
68-M2-2A	Aragonite + calcite	Top of an edifice, a zone of active seeping. Sugar white rock with a gray porous crust

analysis, and ICP-MS analysis were conducted on the same aliquots of the dissolved samples.

The mineral composition of the samples was determined by E.V. Koporulina using X-ray powder diffraction on a RIGAKU D/Max-2200 diffractometer at the Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM), Russian Academy of Sciences. The results obtained (Table 1) confirm that the major rock-forming minerals in hydrothermal chimneys at Lost City are aragonite, calcite, and brucite.

The concentrations of the major elements of the material (Ca, Mg, Sr, and Ba) were determined by atomic absorption at the Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, analyst L.F. Kartashova. Analyses for trace elements and REE were carried out by ICP-MS at the same institute, analyst S.A. Gorbacheva.

The Sr isotopic composition was determined on a Micromass Sector-54 thermoionization mass spectrometer, with ionization in single-filament mode on oxidized Ta [11]. The error of the measured $^{87}Sr/^{86}Sr$ isotopic ratios did not exceed ±0.0025% (2σ).

The O, C, and H isotopic composition was determined by mass spectrometry (IRMS) on a DELTA^{plus} Finnigan apparatus. The standards were the NBS-19 carbonate standard and the NBS-28 silicate standard. Samples of the carbonate constituent were prepared by classic decomposition methods in orthophosphoric acid.

Samples containing brucite were analyzed for the oxygen isotopic composition of the mineral. Brucite was separated from the carbonate matrix by treatment with diluted HCl at room temperature. The reaction was conducted on an object glass under a microscope in order to make it possible to visually observe the process. Upon the completion of the reaction, brucite crystals were further dissolved for a while to get rid of the possible admixture of isotopically heavy oxygen in carbonates. The material thus obtained was washed with distilled water and then dried at 120°C. The samples were then prepared using the classic fluorination technique commonly applied to silicates [12]. However, measurements indicate that the $\delta^{18}O$ value was reliably determined only in two of the samples, with the rest of them first yielding unrealistically high ^{18}O values, which indicated that the brucite was incompletely separated from carbonate material and that these data cannot be considered reliable. The oxygen, carbon, and strontium isotopic composition of our brucite–carbonate samples from the Lost City vent field is reported in Table 2.

The oxygen isotopic composition of fluid phases was analyzed by the quick method of isotopic equilibration in syringes [13]. The total error of this technique amounted to ±0.2‰. Fluid samples were analyses for hydrogen isotopic composition on a H/D instrument (ThermoQuest, Finnigan) by means of water decomposition on metallic chrome at a temperature of 800°C [13, 14]. The maximum error of the δD values was ±0.2 ‰. All examined samples of hydrothermal solutions were mixed aboard the research vessel with 5% HCl to pH 2.5, because these samples were initially intended for analysis for metals. The acidification of the solution samples slightly modified their oxygen and hydrogen isotopic composition. However, these parameters of the solutions were interesting in the context of our research and were corrected to minimize the aforementioned acidification effect. The corrections pertained mostly to the hydrogen isotopic system, because the difference between the hydrogen isotopic compositions of the solutions with the "oceanic" composition and the aqueous component of the acid prepared using deionized tap water was quite significant. The corrections were made with $\delta D = -57$ ‰ and $\delta^{18}O = -8.4$ ‰ for the aqueous component of the acid, and the added amount of the acid was known. Table 3 presents the results of the measurements together with the corrected values.

Table 2. Oxygen, carbon, and strontium isotopic composition of carbonate-brucite material from the Lost City field

Sample no.	$^{87}Sr/^{86}Sr$	Carbonate material			Brucite
		$\delta^{13}C_{PDB}$, ‰	$\delta^{18}O_{PDB}$, ‰	$\delta^{18}O_{SMOW}$, ‰	$\delta^{18}O_{SMOW}$, ‰
68-M2/5	0.709172 ± 16	0.22	2.96	33.96	–
68-M2-2A	0.708944 ± 17	1.92	5.50	36.58	–
64-M1-7/2	0.709042 ± 14	2.07	4.61	35.66	–
65-M2-2/3	0.709176 ± 13	1.49	4.29	35.33	–
71-M2-1	0.708607 ± 16	1.87	4.11	35.14	4.4
71-M2-4	0.707864 ± 17	0.79	3.16	34.17	–
68-M2-4/2	0.707408 ± 17	0.43	3.43	34.45	–
67-M1-1/3	0.706891 ± 16	0.79	0.51	31.44	–1.0

Table 3. Oxygen and hydrogen isotopic composition of MAR hydrothermal solutions

Vent field	Measured values		Corrected for acidification		Recalculated to end member C(Mg) = 0		Description
	δD, ‰	$\delta^{18}O$, ‰	δD, ‰	$\delta^{18}O$, ‰	δD, ‰	$\delta^{18}O$, ‰	
Lucky Strike	–2.4	0.4	–1.3	0.5	–4.0	1.6	Hot fluid, zone of black smokers
	–1.9	0.3	–0.8	0.5	–2.1	1.3	
Rainbow	–1.6	0.4	–0.5	0.6	–1.3	1.5	Hot fluid with suspended black material
	–0.3	0.6	0.9	0.8	4.5	4.2	
Lost City	–2.3	0.4	–0.1	0.8	(–1.1) –0.7	(7.0) 4.5	Warm water at the top of a chimney
	–1.2	0.4	0	0.5	(–0.5) –0.3	(6.7) 4.3	

Note: Numerals in parentheses are recalculations to the end member of the Lost City fluid for C(Mg) = 0; numerals without parentheses–t_0C(Mg) = 19 mmol/l, because this Mg concentration is thought to have been typical of the original fluid component at Lost City.

RESULTS AND DISCUSSION

Hydrothermal MAR Solutions: The Role of Serpentinization Processes

Table 3 and Fig. 1 summarize the $\delta^{18}O$ and δD values obtained on fluid phase samples from a number of MAR vent fields. The isotopic data indicate that the oxygen and hydrogen isotopic composition of solutions sampled at Lost City is close to that of solutions from the nearby Rainbow and Lucky Strike vent fields in MAR (Fig. 1). All of the samples exhibit slightly heavier oxygen isotopic composition than SMOW and small negative values of δD (Fig. 1,Table 3) (except one sample from the Rainbow field). The $\delta^{18}O$ and δD values are correlated, and this arrangement of the data points in Fig. 1 likely suggests a temperature evolution of a fluid system genetically linked to seawater. The more significant variations in the hydrogen isotopic composition (approximately one order of magnitude greater than the scatter of the $\delta^{18}O$ values) are characteristic of the evolution of originally compositionally similar fluids at various temperatures. However, the extrapolation of the original $\delta^{18}O$ and δD values to a zero Mg concentration (end member) indicates that the Lost City fluid differs from the fluids of the neighboring vent fields. The results of the calculations are presented in Table 3 and Fig. 1. The data points shown for the Lost City solutions are recalculated not only to a zero Mg concentration but also to the Mg concentration in the end member (equal to 19 mmol/l), because it is thought [4] that the original fluid in Lost City contains up to 19 mmol/l Mg. As can be readily seen, the values calculated for Lost City with an extrapolation to C(Mg) = 0 are higher than the universally adopted value of $\delta^{18}O$ for seafloor rocks (basalts and ultramafic rocks), which is shown in Fig. 1 as a range from 5.5 to 6.5‰. We believe that these unrealistic values once again testify to the presence of own Mg in the end member of the hydrothermal component of the Lost City fluid.

In order to analyze the role of interaction processes between seawater and ultrabasic rocks when the hydrothermal solutions are formed, in Fig. 1 we plotted the line of the serpentine isotopic composition in equilibrium with seawater (0; 0) at temperatures from 175 to 300°C (the line was calculated by the equations developed by Sakai and Tsutsumi [15] and Zheng [16]). As can be seen in Fig. 1, the calculated compositions of solutions from the Rainbow and Lucky Strike fields extrapolated to the end member are shifted toward the equilibrium line of serpentine and seawater. The end-

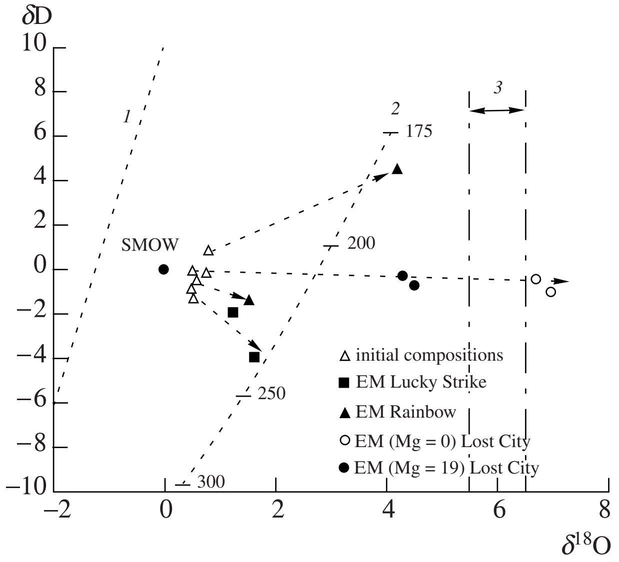

Fig. 1. Hydrogen and oxygen isotopic composition of MAR hydrothermal solutions. Original solutions are measured δD and $\delta^{18}O$ values corrected for acidification; EM are compositions recalculated to the end member for each point; *1* is the line of meteoric waters, *2* is a line calculated according to [15, 16] for the isotopic composition of serpentine in equilibrium with seawater at various temperatures (numerals show the temperatures, °C), and *3* is the oxygen isotopic composition range measured in seafloor silicate rocks (tholeiitic basalts and ultrabasic rocks).

member data points for the Lost City fluid plot at much higher $\delta^{18}O$ values without any significant change in δD, a fact suggesting that the solutions interacted with silicate rocks at elevated temperatures.

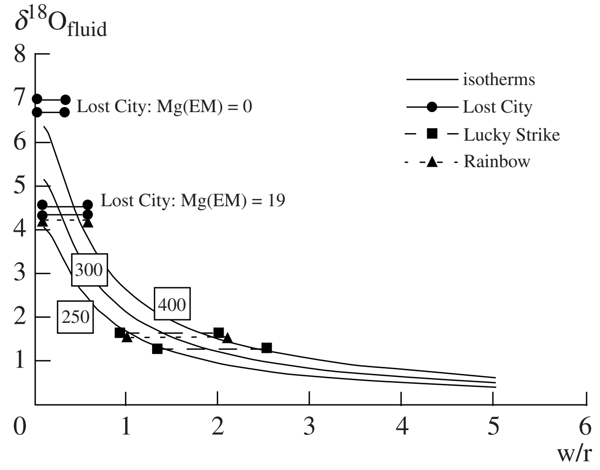

Fig. 2. Calculated isotherms for $\delta^{18}O$ variations in fluid, according to the model [17], depending on the water/rock ratio during serpentinization of a rock consisting of olivine with a "primary" oxygen isotopic composition ($\delta^{18}O$ = 5.5‰) at temperatures from 250 to 400°C (numerals near isotherms). Shown in the calculated field are the compositions of MAR fluids recalculated to the end member C(Mg) = 0 and C(Mg) = 19 mmol/l for Lost City.

The data presented above can be explained as follows. Serpentinization at the strong predominance of the fluid mass over that of the rocks (fluid-dominated regime of isotopic exchange) should result in an isotopic composition of the serpentine corresponding to serpentine–seawater equilibrium at this temperature. The further interaction of the fluid with the altered rocks should result in an isotopic composition of the fluid in the range between the composition of seawater and serpentine in equilibrium with it, depending on the degree of isotopic equilibration, which is controlled by the filtration velocity of the fluid and its temperature. However, the fraction of unequilibrated fluid with isotopic parameters of seawater cannot be identified when the end member is calculated, which results in an arrangement of the data points for MAR hydrothermal fluids along the equilibrium line of serpentine and seawater. The Lost City field shows the effect of the "original" oxygen isotopic parameters of the basement ultrabasic rocks at the neutral behavior of the hydrogen isotopic system. This suggests that the process of rock serpentinization in the basement of the Lost City field should have proceeded under conditions notably different from those of a fluid-dominanted regime of isotopic exchange. The constancy of the hydrogen isotopic composition that results in a horizontal shift in the diagram of Fig. 1 is quite expectable in this situation, because the only hydrogen-bearing phase able to exchange with hydrothermal fluid is serpentine, which was produced with the participation of seawater. Consequently, the hydrogen isotopic system behaves neutrally, while the oxygen isotopic system reflects the evolution of the interaction of the hydrothermal solution and rock.

The behavior of the oxygen isotopic system enabled us to assay the scale of this interaction. Figure 2 displays the calculated trajectories of the changes in the isotopic composition of the fluid that participated in serpentinization of olivine with "primary" oxygen isotopic signatures ($\delta^{18}O = 5.5‰$) depending on variations in the water/rock ratio. The calculations were conducted according to the model [17] with regard for the inflow of ^{18}O into the fluid from dissolving olivine of constant isotopic composition and the incorporation of ^{18}O into the crystallizing serpentine, a process resulting in a gradual change in the isotopic composition of the fluid with the progress of the serpentinization reaction. Although we neglected water incorporation into the serpentine structure in our calculations, this simplification was justified when the major tendencies in the behavior of fluids were identified at the MAR and Lost City. The position of the $\delta^{18}O$ of the Lost City fluid extrapolated to the end member relative to the calculated lines indicates that the extrapolation to the zero value also yields an unrealistically low water/rock ratio. The values extrapolated to 19 mmol/l of Mg lead to water/rock ratios less than one for a broad temperature range from 250 to 400°C. Except only one data point of the Rainbow fluid, all other data fall within the region of higher water/rock ratios: from 1 to 2.5 for the afore-

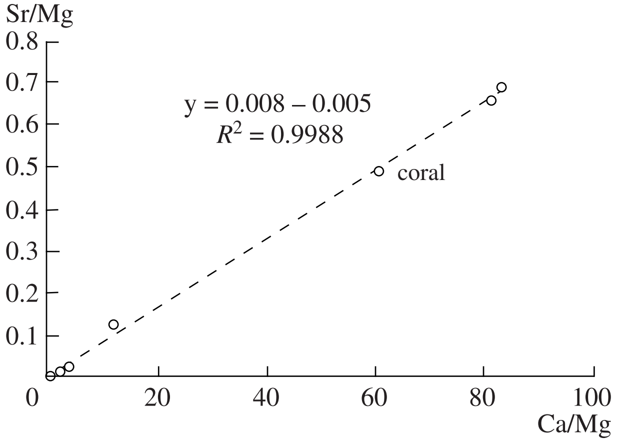

Fig. 3. Correlation between the Sr/Mg and Ca/Mg ratios in whole-rock samples of the carbonate–brucite material composing Lost City chimneys. The data point named coral corresponds to a sample of biogenic genesis (sample 68-M2/5).

mentioned temperature range. The data shown in Fig. 2 are consistent with the conclusions [10], which were drawn based on the simulation of the heat balance and geochemical parameters of the Lost City fluid and solid material, that the serpentinization process took place at approximately 270°C at a low fluid/rock ratio.

The clearly pronounced relations between the Lost City hydrothermal solutions and the serpentinization process of the ultrabasic basement rocks are also confirmed by the chemistry of gases dissolved in the fluid: the occurrence of methane and hydrogen is typical of hydration reactions and iron oxidation in olivine in the presence of H_2O and HCO_3^- [9]. The authors of the publication quoted above noted that serpentinization at low water/rock ratios may give rise to a highly alkaline fluid with methane and hydrogen.

It is also worth mentioning that the low water/rock ratio is in conflict with the fact that the Na, K, and Cl concentrations in the Lost City fluid are practically identical to those in seawater. In other words, water consumption during olivine hydration should have increased the concentrations of these elements in the residual fluid. This discrepancy calls for resolution and still remains a matter of discussion. It may only be noted that the behavior of the elements depends not only on the composition of the altered ultrabasic rocks but also on the conditions of the alteration process. Moreover, since the system was not closed, slow fluid filtration through already-altered (serpentinized) rocks toward the submarine discharge zone could be associated with changes in the salt composition of the fluid. As was mentioned in [1], significant variations in the Na, K, and Cl concentrations in oceanic hydrothermal solutions are most commonly indicative not of interaction with oceanic rocks but of the phase separation of the fluid.

However, there are still no facts confirming that the Lost City fluid has undergone its phase separation at depth. Phase separation was identified in the MAR for high-temperature hydrothermal solutions related to serpentinites (at the Logachev and Rainbow fields [18]). The Lost City field however is characterized by low temperatures. Then, phase separation should be associated with the redistribution of both hydrogen and oxygen isotopes between phases, with the hydrogen isotopic system of the fluid affected more strongly by this process than the oxygen isotopic system. However, two fluid samples from Lost City with practically equal Mg concentrations (and, consequently, equally mixed with the bottom water) showed almost identical hydrogen isotopic compositions but a notable oxygen isotopic shift. And at the and, the concentrations of Na and Cl (two major components that are actively redistributed during phase separation) in the Lost City fluid are at the level typical of seawater. Thus, the isotopic characteristics of the Lost City fluid currently cannot be regarded as resulting from the phase separation of the fluid and should have been controlled mostly by the process of serpentinization at low fluid/rock ratios and temperatures of at least 200°C.

Carbonate–Brucite Material Composing Chimneys at the Lost City Field

1. Role of serpentinization processes. The mineralogy of the carbonate–brucite material of hydrothermal chimneys at Lost City allowed us to consider their major-element composition within the framework of the Ca–Mg–Sr three-cation system, with the Ca/Mg and Sr/Mg molar ratios in bulk-rock samples showing strong linear correlations (Fig. 3). The correlation between the Ca and Sr concentrations (which are not normalized to Mg) is weaker, a fact suggesting that Mg acted as a diluting component and that Sr is strongly related to the carbonate phase of the samples, while Mg is related to brucite.

The carbonate constituent of all samples consists of a mixture of calcite and aragonite. Pure aragonite with the minimum brucite content was found only in a sample of fan-shaped crystals from the top of a large chimney (65-M2-2/3). A coral sample (68-M2/5) is also strongly dominated by aragonite and bears a minor calcite admixture. These two samples are characterized by the highest $^{87}Sr/^{86}Sr$ ratio, whose value corresponds to the average isotopic ratio of modern seawater (0.70916 [19]). This is quite natural for a coral sample, but the "oceanic" Sr isotopic ratio of the aragonite of obviously inorganic genesis led us to the conclusion that the Sr concentration in the original hydrothermal solution was low.

In all other samples, their carbonate constituent consists of a mixture of aragonite and calcite, usually with the predominance of the former. The $^{87}Sr/^{86}Sr$ isotopic ratio of these samples ranges from 0.709 (brucite-free samples) to 0.7069 and increases with increasing brucite and calcite percentages in these samples. It is commonly thought [4, 5] that diagenetic alterations of the calcite–aragonite–brucite association under conditions typical of seawater should result in brucite dissolution and a decrease in the aragonite content in the carbonate component of the sample. With regard for these data, it is natural to hypothesize that the brucite-free samples (68-M2-2A and 64-M1-7/2) should be characterized by the longest histories of their interaction with seawater after crystallization. This is corroborated by their chondrite-normalized LREE patterns (Fig. 4): the samples with brucite are noted for low REE concentrations, even those of LREE. The concentration of HREE are not shown because they were below the detection limit of the analytical technique without preliminary enrichment. The most significant enrichment in LREE was identified in the coral sample, and both of the brucite-free samples occupy an intermediate position closer to the coral sample. The latter two samples also display a negative Ce anomaly, which is typical of the products of the processes of interaction with seawater.

Thus, it can be seen that the source of REE and Sr for the carbonate–brucite material of Lost City chimneys was solutions with a $^{87}Sr/^{86}Sr$ ratio much lower than that in seawater, REE spectra close to the chondritic one, and with low Sr and REE concentrations. This fact is in good agreement with the idea that the Lost City fluid actively interacted with ultrabasic rocks during their serpentinization. High degrees of interaction at low fluid/rock ratios could result in the loss of the original seawater REE signatures, and consequently, the configuration of the REE patterns became closely similar to that of primitive rocks during initial serpentinization stages. The gradual enrichment of the brucite-free samples in LREE could take place after the deposition of the chimney material due to seawater interaction during initial diagenesis.

The role of serpentinization processes is also confirmed by electron-microscopic studies of a sample with the highest brucite content (67-M1-1/3). Figure 5 displays images of various parts of this sample. As could be expected, the material of the sample contains all three major phases: calcite, aragonite, and brucite. The sample shows, however, the following rhythmical zoning: (i) an outermost zone of radiating columnar brucite crystals (Fig. 5a); (ii) calcite–aragonite–brucite zone (Fig. 5b), (iii) a pure aragonite zone (Fig. 5c); (iv) calcite–aragonite–brucite zone; (v) aragonite-free zone of euhedral calcite crystals and clusters of brucite crystals (Fig. 5d); (vi) calcite–aragonite–brucite zone; and (vii) a monomineralic brucite zone of large aggregates of flaky crystals. The morphology of the crystals and their position in all zones suggest that the carbonate and brucite crystallized simultaneously in zones of mixed composition. Aragonite crystals often "grow through" brucite grains (Fig. 5e), which indicates that aragonite in this material is slightly younger than brucite. The aforementioned zoning shows not sharp boundaries, and its zones grade into one another. However, the fact of the occurrence of this zoning is consistent with the results of thermodynamic simulations [9, 10]. Model calculations indicate that the mixing of warm fluid (which participated in the serpentinization process at 200–300°C and underwent conductive cooling to at least 150°C) with cold seawater with increasing percentage of the latter should lead to a decrease in the brucite percentage in the material of the chimneys and a gradual increase in the percentage of the carbonate phase. The arrival of fresh solution portions could bring about the development of new zoning in the same sample, as is seen in our sample, showing a number of rhythms within 1-cm distance.

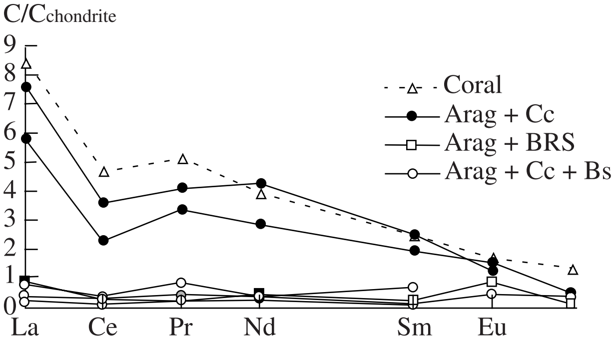

Fig. 4. Chondrite-normalized LREE patters of carbonate–brucite material from the Lost City field.

The inner zones of the sample, which are dominated by brucite, contain aggregates of acicular chrysotile, a serpentine variety, crystals (Fig. 5f). Serpentine was not detected in the pure aragonite zone of the sample and in the outermost brucite zone (crusts). Crystallization from the fluid during its mixing with cold seawater likely involved the crystallization of residual dissolved serpentine together with the major phases, first of all, brucite. The occurrence of minor serpentine amounts was predicted based on the simulation results of the mineral-forming processes during the progressive mixing of the Lost City fluid with seawater [10].

2. The role of fluid mixing with seawater. The role played by the mixing of warm hydrothermal fluids with seawater as the main factor controlling the crystallization sequence of minerals at Lost City chimneys was quantitatively evaluated by means of thermodynamic simulations in [9, 10]. The authors of these simulations did not, however, consider the behavior of oxygen and carbon isotopes and the $^{87}Sr/^{86}Sr$ isotopic ratio, i.e., the major isotopic systems of carbonate associations.

The quantitative evaluation of isotopic fractionation duirng the mixing process of the Lost City hydrothermal fluid and seawater is quite difficult because of the different behavior of various isotopic system in the course of this process. In mineral material, only its Sr isotopic system, which is insensitive to temperature and pH variations, provides information on the proportions of the two mixing solutions, because no Sr isotopic fractionation takes place between a solution and min-

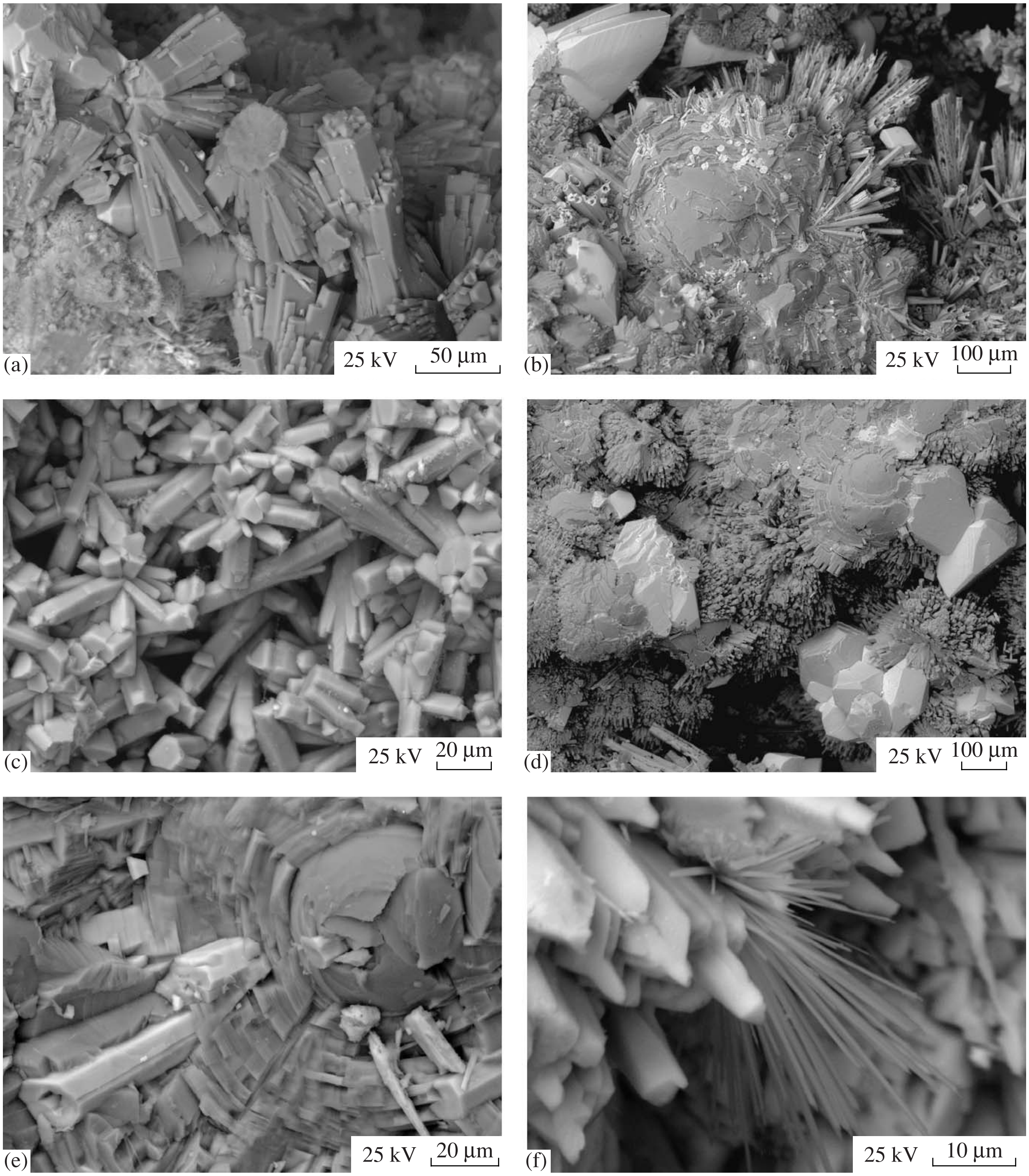

Fig. 5. Electron microscopic images of material from various zones of sample 67-M1-1/3: (a) an outermost monomineralic brucite zone; (b) typical image of the Cc–Ar–Bru three-mineral zone, aragonite is contained in this zone in the form of tubular crystals, brucite occurs as flaky spherical aggregates, and calcite forms large equant crystals; (c) monomineralic aragonite zone; (d) calcite–brucite zone; (e) aragonite crystals growing through the core of an aggregate of flaky brucite crystals; (f) aggregate of thin acicular lizardite crystals.

eral. For the oxygen isotopic system of carbonate, a significant role is played by the temperature, source of isotope, and the degree of isotopic equilibrium between the carbonate ion and solution (these values can be smaller than 100% at high pH [20, 21]). The isotopic system should have behaved fairly unusually during the precipitation of carbonates from highly alkaline solutions of the Lost City vent field. The carbon isotopic

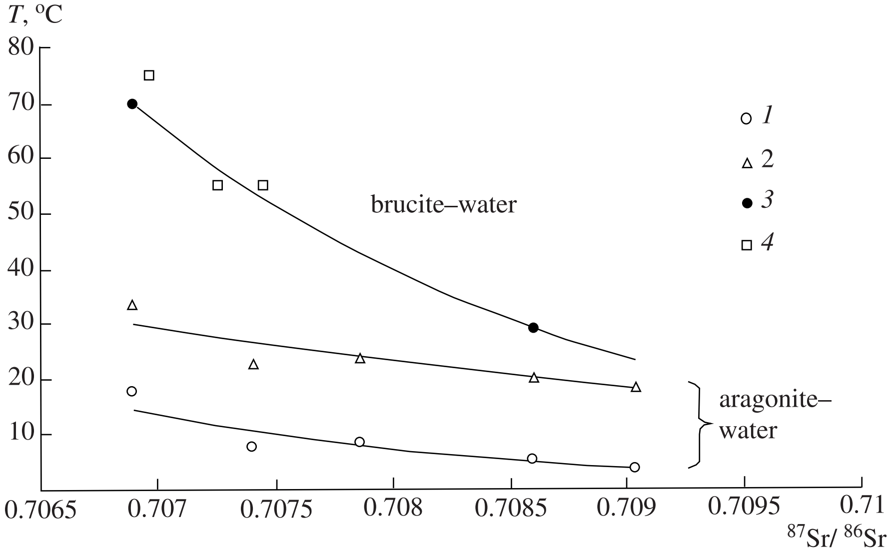

Fig. 6. Correlation between the fluid temperature and the $^{87}Sr/^{86}Sr$ ratio. (*1*, *2*) Temperature calculated by the aragonite–water equilibrium for the $\delta^{18}O$ range from (*1*) seawater to (*2*) extrapolated end member fluid of the Lost City field; (*3*) temperature calculated by the brucite–seawater equilibrium; (*4*) direct measurements of the Sr isotopic composition and temperature of the fluid [5].

composition of the carbonates should be less sensitive to temperature variations, because the carbonate ion is almost completely removed from the solution at high pH.

It will be demonstrated below that the behavior of the carbon, oxygen, and strontium isotopic systems in the carbonate material of Lost City is undoubtedly controlled by the mixing of hydrothermal solutions with bottom seawater.

This can be illustrated, for example, by the temperature dependence of the precipitation of carbonates on the $^{87}Sr/^{86}Sr$ ratio (Fig. 6). Obviously, the Sr isotopic composition does not depend on temperature, but the Sr isotopic ratio is in this situation an indirect parameter reflecting the dilution of the warm hydrothermal solution by cold bottom seawater. At various Sr isotopic compositions and various compositions of the mixing solutions, these parameters should inevitably be correlated with each other, because the Sr isotopic ratio of the precipitating carbonate material should have been identical to that of the solution at the crystallization moment. Figure 6 displays the temperatures calculated from the aragonite–water oxygen isotopic equilibrium [22, 23] for samples in equilibrium with oceanic water and the isotopic composition of the end-member fluid (C(Mg) = 19 mmol/l). These variants of the calculations should overlap the whole range of the probable values, because the isotopic composition of the mixed solution could vary from the composition of seawater to that of the pure hydrothermal fluid at a given temperature range. Note that the Sr isotopic composition of the aragonite is related to its crystallization temperature, i.e., reflects the mixing process of the hydrothermal fluid (of less radiogenic Sr composition) with seawater. However, the estimates by the aragonite–water equilibrium yield underestimated crystallization temperature values compared to the known temperature of the Lost City. For comparison, Fig. 6 exhibits data of the direct measurements of the Sr isotopic composition and temperature of the Lost City fluid compiled from [5]. These data significantly differ from the temperatures calculated from the aragonite–water oxygen isotopic equilibria. The oxygen isotopic composition of brucite in two samples can be used to calculate the crystallization temperature of the mineral. This calculation was conducted by theoretical equations for oxygen isotope fractionation in the brucite–water system [16], and the results are displayed in Fig. 6. It is interesting that the results of the direct measurements of the temperature and Sr isotopic composition of the Lost City fluid published in [5] plot along the line obtained for the brucite–water equilibrium. This coincidence can be explained not only by brucite crystallization before (i.e., at a higher temperature) the carbonate phases but also by the fact that oxygen isotopic fractionation during brucite crystallization is principally different from fractionation in the carbonate system. During brucite crystallization, oxygen isotopic exchange involves only a water molecule, because the reaction forming brucite can be formally written as

$$Mg^{2+} + 2(OH)^- \longrightarrow Mg(OH)_2\downarrow.$$

During the crystallization of carbonates, oxygen isotopic equilibrium with water is reached according to a more complicated scheme, including an intermediate stage of isotopic exchange between the dissolved carbonate (bicarbonate) ion and water, as follows from the formal scheme of the reaction producing calcite

$$H_2O + Ca^{2+} + HCO_3^-(CO_3^{2-}) \longrightarrow CaCO_3\downarrow.$$

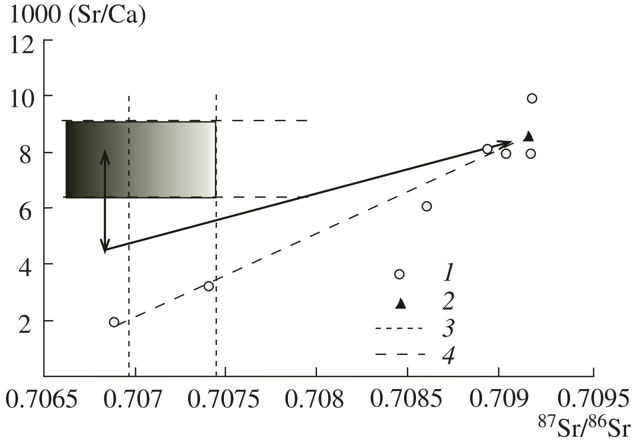

Fig. 7. Evolution of the Sr/Ca ratio of aragonite during the mixing of hydrothermal fluid with seawater. Along with (*1*) measured data on Lost City, the diagram also shows (*2*) seawater data point; (*3*) $^{87}Sr/^{86}Sr$ range measured in the Lost City hydrothermal solutions [5]; (*4*) range of the Sr/Ca ratio in hydrothermal solutions related to ultrabasic rocks [1]. The vertical arrow approximately corresponds to the Sr/Ca ratio of aragonite precipitating from the "original" fluid, and the continuation of the arrow corresponds to the evolution during mixing with seawater (see text).

If the carbonate system is far from isotopic equilibrium with water, the crystallization temperatures of aragonite can be systematically underestimated, for example, when seawater is not the only source of the carbonate (bicarbonate) ion. This is quite probable for Lost City, because the hydrothermal solutions of this system have high pH. Recent experimental data on the effect of the pH of the solution on the kinetics of establishing isotopic equilibrium in the carbonate system indicate that a solute carbonate species very slowly reaches isotopic equilibrium with water at pH higher than 7–8 [20, 21].

If the carbonate crystallized in oxygen isotopic equilibrium with the solution, the lower temperatures obtained by the aragonite–water equilibrium should be indicative of the later precipitation of the carbonate material than brucite. This is, however, in conflict with electron microscopic observations, according to which the samples contain zones with the simultaneous crystallization of aragonite and brucite. This discrepancy can be settled based on the results of further isotopic studies.

Inasmuch as the Sr isotopic system is the most reliable indicator of the mixing process, it is particularly important to elucidate the Sr concentrations in the end members: the Lost City hydrothermal solution and seawater. The Sr concentration and $^{87}Sr/^{86}Sr$ ratio are known for seawater but not for the Lost City fluid. Available data on three samples published in [5] were obtained for solutions that could have contained an admixture of oceanic water. To quantitatively assay these values, one has to know the Sr isotopic composition and concentration in the "original" Lost City fluid. We can only hypothesize that, if the Lost City fluid participated in the serpentinization of the ultrabasic rocks, the Sr concentration in this fluid should have been high, because the Sr content in the ultrabasic rocks was of the order of a few ppm. Nevertheless, the Sr concentration in the "original" Lost City fluid can be indirectly inferred from of the Sr/Ca ratio in the carbonates.

As is well known, the Sr/Ca ratio of seawater is constant and equal to 8.6 (mmol Sr/mol Ca), while this ratio of carbonates reflects this ratio of the ambient water, depends on temperature, and varies from one carbonate mineral species to another [24–27]. For example, the Sr/Ca partition coefficient for aragonite and solution at 25°C is close to 1, and that for calcite and solution is roughly one order of magnitude lower. The Sr/Ca ratios of brucite-bearing carbonate material at Lost City are either equal to or lower than the Sr/Ca ratio of seawater. The only exception is a sample of fans of aragonite crystals whose Sr/Ca = 9.9. Samples with Sr isotopic composition close to that of seawater also show Sr/Ca ratios similar to those of seawater, i.e., 8–8.1 (Fig. 7). However, a decrease in the $^{87}Sr/^{86}Sr$ ratio is associated with a linear decrease in the Sr/Ca ratio to 1.95. Figure 7 displays a region of the Sr/Ca ratio calculated from the Sr and Ca concentrations reported in the review [1] for ultrabasic-hosted fluid systems. The vertical lines constrain the range of the $^{87}Sr/^{86}Sr$ ratio measured in the Lost City fluid [5]. With regard for a possible seawater admixture in the fluid, the field that can correspond to the "original" Lost City fluid is shifted to the left, toward the lowest of the obtained $^{87}Sr/^{86}Sr$ values. According to experimental data on the Sr partitioning in the system of inorganic aragonite–water [26], the Sr/Ca ratio of this mineral in equilibrium with such an "original" fluid at the measured temperatures can range from 4.5 to 5. At mixing with seawater, a temperature decrease can give rise to an evolutionary trend marked with an arrow in Fig. 7. The incomplete coincidence of this sequence with the natural observations can be partly explained by the fact that the examined material is not pure aragonite, and a calcite admixture decreases the Sr/Ca ratio in the sample. However, the low Sr/Ca values obtained for the sample can be explained otherwise. First, the "original" fluid can contain not only less radiogenic Sr but also have a lower Sr/Ca ratio than that of seawater. Second, the aragonite percentage in the precipitated material can increase with time due to calcite and brucite dissolution in the course of early diagenesis, which is consistent with the data presented above for the REE composition of the material of Lost City chimneys. Both of these factors can equally probably affect the Sr/Ca ratio.

3. The role of fluid conductive cooling and the problem of the source of the carbonate material. As was mentioned above, in considering oxygen isotopic data on carbonate phases from Lost City chimneys that were produced by highly alkaline solutions, it is necessary to determine the degree of their isotopic equilibrium with seawater and solve the problem of the source of the carbonate ion. If this source was seawater alone, then, for example, the carbon isotopic composition of Lost City carbonates should not be correlated with the Sr isotopic composition. If the fluid contained carbonate ions that were not in equilibrium with seawater, then the rapid crystallization of the carbonates at high pH should have resulted in a correlation between their carbon (and, to a lesser degree, also oxygen) isotopic composition with the Sr isotopic composition. This is explained by temperature variations during the mixing of the fluid and seawater, and thus, the correlation between the $\delta^{18}O$ of the carbonates and the Sr isotopic composition should have also depended on the temperature. The carbon isotopic system is less sensitive to temperature variations and can thus more clearly reflect the mixing process of the two solutions containing carbonate species with various carbon isotopic composition.

Figures 8a and 8b display not only our own data but also those compiled from the literature [5], which also demonstrate that the samples having a Sr isotopic composition closest to that of seawater also have high $\delta^{18}O$ and $\delta^{13}C$ values. It is worth mentioning the good agreement between our results and the literature data, a fact highlighting the high homogeneity of the material and justifies the combined analysis of all available information.

The fact of the occurrence of these relations, particularly a correlation between $\delta^{13}C$ and the Sr isotopic composition, demonstrates that the dissolved carbonate species that participated in the precipitation of the Lost City material were borrowed not only from seawater alone. The correlation between the Sr and C isotopic composition (Fig. 8b) indicates that C of this source should have been characterized by low negative $\delta^{13}C$ values (when extrapolated to the "primitive" Sr isotopic composition, the $\delta^{13}C$ value ranges from –2 to –2.5‰). These values are very close to the carbon isotopic composition measured in calcite veins in the Atlantis serpentinites and gabbro: from –2 to –2.8 ‰ [5]. However, a simple extrapolation cannot yield "mantle" $\delta^{13}C$ values (from –4 to –8) or even lower typical of oceanic organic matter.

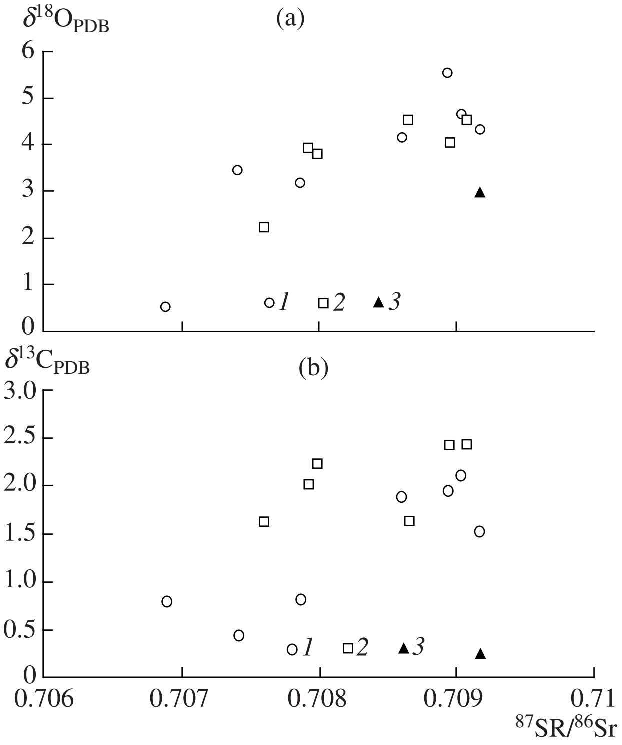

Fig. 8. Correlation between (a) Sr and O isotopic composition and (b) Sr and C isotopic composition for carbonates composing chimneys at Lost City: (*1*) this publication, (*2*) data from [5], and (*3*) our data on biogenic aragonite.

It is quite probable that the source of part of the complexes dissolved in the fluid was preexisting carbonate veins in the serpentinites, which dissolved in the course of fluid filtration through the already-cold serpentinized zone of the Atlantis Massif. As was mentioned above, the filtration of the Lost City fluid toward its discharge zone proceeded via the diffusion mechanism [5]. If the hyperbasite serpentinization front had penetrated deep levels of the Atlantis Massif during the activity period of the Lost City field, then the fluids ascending to the surface had to percolate through already cold and serpentinized rocks cut by numerous calcite veinlets. In the process of its filtration, the fluid cooled, possibly without any significant changes in its major-component complex other than an increase in the Ca concentration and a change in the isotopic composition of dissolved carbonate species due to the dissolution of preexisting carbonates. This period of time was likely characterized by the conductive cooling of the fluid, with its necessity for the development of carbonate–brucite chimneys at Lost City demonstrated by thermodynamic simulations [10]. Moreover, the unequilibrated dissolution of calcite by the filtering aqueous fluid could have maintained high alkalinity of the Lost City fluid and its elevated Ca concentration according to the reaction

$$H_2O + (CaCO_3)_s \longrightarrow Ca^{2+} + HCO_3^- + OH^-.$$

From this standpoint, it is interesting to recall the aforementioned fact that the carbon isotopic age of the Lost City carbonate chimneys [5] broadly varies, from an age close to that of the carbonate cement of the breccias and vein calcite in serpentinites to modern. In discussing these results, the authors of [5] suggested that the age of the chimney material can be bimodal, although the morphology of the chimneys does not provide evidence of any discreteness in the activity of the fluid system. The limited number of the samples does not provide any clue to the validation or invalidation of this conclusion. However, assuming that carbon was partly provided for the Lost City fluid by older carbonate material eliminates this contradiction, and this can, perhaps, mean that the activity age of the currently active hydrothermal system at Lost City is much younger than 25 ka.

CONCLUSIONS

The Lost City hydrothermal system obviously had a complicated evolutionary history, and available data are still insufficient for its complete documenting. Nevertheless, these data make it possible to briefly characterize some pivotal issues in the hydrothermal activity of the Lost City field.

(1) The serpentinization of ultrabasic rocks occurred in the Atlantis Massif at significant depths and temperatures higher than 200°C. The fluid/rock ratios during this process were low (<1).

(2) The serpentinizing fluid filtered toward its submarine discharge sites and zones through already altered and cold outer zones of the Atlantis Massif, which abounded in carbonate veins. Fluid filtered through already reworked zones likely simultaneously with cooling diminish. Its filtration could be also associated with the dissolution of the preexisting carbonate material (calcite veins in serpentinites at high levels of the Atlantis Massif and the carbonate cement of sedimentary breccias underlying the hydrothermal chimneys).

(3) At the boundary of the mixing of the already cold fluid and seawater, the material of the brucite–aragonite–calcite association precipitated and formed hydrothermal chimneys at the Lost City field. Brucite and calcite precipitation took place early during mixing with seawater, and an increase in the seawater fraction in the mixture was marked by an increase in the aragonite percentage in the material of the chimneys. Early diagenesis acted in a similar manner, and the material of the chimneys exhibits an increase in the aragonite percentage at the expense of dissolved brucite and calcite.

(4) The ^{87}Sr/^{86}Sr isotopic ratio in the “original” Lost City fluid could be notably lower than that determined by measurements in the venting fluid, and the Sr/Ca ratio of this fluid could be lower than the range typical of ultrabasic-hosted hydrothermal systems.

(5) The occurrence of dissolved carbonate material from veins in the serpentinites and the cement of the sedimentary breccias in the hydrothermal fluid could its conductive the age of hydrothermal activity at the Lost City field significantly younger than 25 ka.

ACKNOWLEDGMENTS

The authors thank S.A. Silantyev for fruitful discussion of the manuscript.

This study was financially supported by the program “Fundamental Problems of Oceanology: Physics, Chemistry, Geology, and Ecology” of the Presidium of the Russian Academy of Sciences and by Fundamental Research Program 8 of the Division of Earth Sciences, Russian Academy of Sciences (project “Isotopic Fractionation of Light Elements in the System Mineral–Aqueous Fluid–Rock”).

REFERENCES

1. C. R. German and K. L. Von Damm, “Hydrothermal Processes,” in *Treatise in Geology. The Oceans and Marine Geochemistry*, Ed. by H. Elderfield (Elsevier. Amsterdam, 2003), Vol. 6, pp. 182–222.
2. W. S. Shanks III, “Stable Isotopes in Seafloor Hydrothermal Systems: Vent Fluids, Hydrothermal Deposits, Hydrothermal Alteration, and Microprobe Processes,” in *Stable Isotope Geochemistry*, Ed. by J. W. Valley and D. R. Cole, Rev. Mineral. Geochem. **43**, 469–525 (2001).
3. N. S. Bortnikov and I. V. Vikent’ev, “Modern Base Metal Sulfide Mineral Formation in the World Ocean,” Geol. Rudn. Mestorozhd. **47**, 16–50 (2005) [Geol. Ore Dep. **47**, 13–45 (2005)].
4. D. S. Kelley, J. A. Karson, D. K. Blackman, et al., “An Off-Axis Hydrothermal Vent Field near the Mid-Atlantic Ridge at 30°N,” Nature **412** (12), 145–149 (2001).
5. G. L. Fruh-Green, D. S. Kelley, S. M. Bernasconi, et al., “30 000 Years of Hydrothermal Activity at the Lost City Vent Field,” Science **301**, 495–498 (2003).
6. A. Yu. Lein, Yu. A. Bogdanov, A. M. Sagalevich, et al., “White Columns at Lost City”, Priroda, No. 12, 40–45 (2002).
7. A. Yu. Lein, Yu. A. Bogdanov, A. M. Sagalevich, et al., “A New Type of Hydrothermal Field in the Mid-Atlantic Ridge (Lost City Field, 30°N),” Dokl. Akad Nauk **394** (3), 380–383 (2004) [Dokl. Earth Sci. **394**, 92–96].
8. A. Yu. Lein, O. Yu. Bogdanova, Yu. A. Bogdanov, and L. O. Magazina, “Mineralogical–Geochemical Features of Authigenic Carbonates at the Seep and Hydrothermal Fields: Evidence from Black Sea Reefs and Chimneys of the Lost City Field,” Okeanologiya, 2006. (in press).
9. J. L. Palandri and M. H. Reed, “Geochemical Models of Metasomatism in Ultramafic Systems: Serpentinization, Rodingitization, and Sea Floor Carbonate Chimney Precipitation,” Geochim. Cosmochim. Acta **68** (5), 1115–1133 (2004).
10. D. E. Allen and W. E. Seyfried, Jr., “Serpentinization and Heat Generation: Constraints from the Lost City and Rainbow Hydrothermal Systems,” Geochem. Cosmochim. Acta **68** (6), 1347–1354 (2004).
11. I. V. Chernyshev, N. I. Serdyuk, D. Z. Zhuravlev, and Yu. A. Kostitsyn, *Precision of Strontium Isotope Analysis Using an Ionization Filament*, in *Mass Spectrometry and Isotopic Geology* (Nauka, Moscow, 1983), pp. 30–43 [in Russian].
12. T. W. Vennemann and H. S. Smith, “The Rate and Temperature of Reaction of ClF_3 with Silicate Minerals, and Their Relevance to Oxygen Isotope Analysis,” Chem. Geol **86**, 83–88 (1990).
13. A. S. Avdeenko and E. O. Dubinina, “Oxygen Isotopic Analysis of Water Using Equilibration with CO_2 in Single-Use Syringe,” in *Proceedings of 6th Vinogradov Symposium on Isotope Geochemistry* (Moscow, 2001), pp. 73–74 [in Russian].
14. V. Yu. Lavrushin, E. O. Dubinina, and A. S. Avdeenko, “Isotopic Composition of Oxygen and Hydrogen in Mud-Volcanic Waters from Taman (Russia) and Kakhetia (Eastern Georgia),” Litol. Polezn. Iskop. No. 2, 143–159 (2005) [Lithol. Mineral. Res. **40**, 123–137 (2005)].
15. H. Sakai and M. Tsutsumi, “D/H Fractionation Factors between Serpentine and Water at100° to 500°C and

2000 Bar Water Pressure and the D/H Ratios of the Natural Serpentines," Earth Planet. Sci. Lett. **40**, 231–242 (1978).

16. Y. F. Zheng, "Calculation of Oxygen Isotope Fractionation in Hydroxyl-Bearing Silicates," Earth. Plan. Sci. Lett. **120**, 247–263 (1993).
17. E. O. Dubinina and L. Z. Lakshtanov, "A Kinetic Model of Isotopic Exchange in Dissolution–Precipitation Processes," Geochim. Cosmochim. Acta **61** (11), 2265–2273 (1997).
18. N. S. Bortnikov, V. A. Simonov, and Yu. A. Bogdanov, "Fluid Inclusions in Minerals from Modern Sulfide Edifices: Physicochemical Conditions of the Formation and Evolution of Fluids," Geol. Rudn. Mestorozhd. **46** (1), 74–87 (2004) [Geol. Ore Dep. **46**, 64–75 (2004)].
19. H. Elderfield and A. Schultz, "Mid-Ocean Ridge Hydrothermal Fluxes and the Chemical Composition of the Ocean," Ann. Rev. Earth Planet. Sci. **24**, 191–224 (1996).
20. S.-T. Kim and J. R. O' Neil, "Equilibrium and Nonequilibrium Oxygen Isotope Effects in Synthetic Carbonates," Geochim. Cosmochim. Acta **61** (6), 3461–3475 (1997).
21. L. Z. Lakshtanov, E. O. Dubinina, and S. L. Stipp, "Experimental Study of Oxygen Isotope Exchange Between Calcite and Water," Geochim. Cosmochim. Acta **68**, A154 (2004).
22. Y. F. Zheng, "Oxygen Isotope Fractionation in Metal Monoxides," Mineral. Mag. **58A**, 1000–1001 (1994).
23. J. R. O' Neil, R. N. Clayton, and T. K. Mayeda, "Oxygen Isotope Fractionation in Divalent Metal Carbonates," J. Chem. Phys. **51** (12), 5547–5558 (1969).
24. K. K. Turekian and K. H. Wedepohl, "Distribution of the Elements in Some Major Units of the Earth's Crust," Geology **72**, 175–182 (1961).
25. J. A. Speer, "Crystal Chemistry and Phase Relations of Orthorhombic Carbonates," in *Carbonates: Mineralogy and Chemistry*, Ed. by R. J. Reeder, Rev. Mineral. **11**, 145–190 (Mineral. Soc. Am., Washington, 1985; Mir, Moscow, 1987), pp. 145–190.
26. D. J. J. Kinsman and H. D. Holland, "The Coprecipitation of Cations with $CaCO_3$—IV. The Coprecipitation of Sr^{+2} with Aragonite between 16° and 96°," Geochim. Cosmochim. Acta **33**, 1–17 (1969).
27. D. J. J. Kinsman, "Interpretation of Sr^{+2} Concentration in Carbonate Minerals and Rocks," J. Sed. Petrol. **39**, 486–508 (1969).