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Methane-rich thermal and mineral waters of the Avachinsky Depression, Kamchatka

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ABSTRACT

Wells up to 3000 m deep at the foot of the active volcanoes Koryaksky and Avachinsky within the Avachinsky Depression revealed a basin of saline waters (up to 22 g/l), methane-rich gas (CH_4 up to 75 vol% in dry gas) with a temperature up to about 70 °C in the western part of the explored area (Ketkino Field) and colder ones - to the east, closer to the Pacific coast. This article presents data on the chemical composition including trace elements, and isotopic compositions of these waters that include δD and $\delta^{18}O$ of waters, $^{87}Sr/^{86}Sr$ of the dissolved Sr, $^{3}He/^{4}He$, $\delta^{13}C$ of CH_4 and CO_2 in gases, and $\delta^{34}S$ of the dissolved H_2S and SO_4. The composition of the waters is sodium chloride, with very low contents of sulfate and magnesium in waters of the western section of the basin, high calcium (up to 960 ppm), and unusually high concentrations of strontium (up to 54 ppm). The N_2/Ar ratio is generally 2–3 times higher than in the air, i.e. non-atmospheric nitrogen is present. A distinctive geochemical feature of the basin is the significant difference between $\delta^{13}C$–CH_4 and $^{87}Sr/^{86}Sr$ in the thermal Ketkino fluids comparing to colder fluids of other parts of the basin, despite the practically identical composition of waters and gases. Possible scenarios of water-rock interaction responsible for the chemical composition of waters are discussed.

1. Introduction

The Kamchatka Peninsula is known as to host many hydrothermal systems and a variety of types of thermal and mineral waters (Trukhin, 2003; Taran, 2009 and references therein). Most systems are associated with individual volcanoes or volcanic centers, as well as with volcanic-tectonic structures. There are high-temperature "boiling" hydrothermal systems with boiling springs and steam vents on the surface, where drilling has opened fluids with temperatures above 300 °C, as well as hydrothermal systems with temperatures at depths accessible to drilling below 100 °C. Examples of such contrasting systems are Mutnovskaya and Paratunskaya, the closest (70 and 30 km to south, respectively) to the capital of Kamchatka, Petropavlovsk-Kamchatsky (Taran and Pilipenko, 1984; Trukhin, 2003). Thermal waters of these systems in Kamchatka, as a rule, have low mineralization, less than 3 g/l, accompanied by CO_2- or N_2-enriched gases and are characterized by chloride-sulfate to sulfate-chloride anionic composition. Thermal highly mineralized waters (up to 15 g/l) with free methane gas and hydrogen sulfide are found only in the south of Western Kamchatka, where magmatic bodies of the Eastern Volcanic Belt of Kamchatka are embedded in sedimentary oil and gas-bearing rocks: these are Savansky and Golyginsky springs and the Koshelevskaya hydrothermal system (Beskrovny and Lobkov, 1977; Pisareva, 1987; Trukhin, 2003; Taran, 2009). In the east of Kamchatka, cold Ca–Na–Cl waters with a mineralization up to 30 g/l were tapped by the prospecting wells at Bogachevskaya area, on the current territory of the Kronotsky Reserve, drilled in the 1940s in search of oil (Kudryavtseva, 1973).

In the late 1960s, at the foot of the Koryaksky volcano, near the extrusion formation "Height 202.0″ in the upper part of the Pinacheva River, near the warm (11 °C) springs, the GK-1P well was drilled, which brought to the surface mineralized water (about 10 g/l) with gas of mainly methane composition. In the late 1980s, not far from the GK-1P well, an exploration of thermal waters was carried out, initiated due to the existence of large areas of non-freezing streams and lakes here,

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indicating a hidden discharge of thermal waters. Wells drilled in this area, near the village of Ketkino (Fig. 1) brought to the surface highly mineralized water (up to 22 g/l) with a temperature at depth of 1000 m up to 80 °C, in the free gas of which methane prevails and hydrogen sulfide is present. The Ketkino thermal water is currently being used for balneological purposes. At about the same time, several deep wells were drilled to the east of Ketkino field (wells R-2 and R-3, Radygino area), as well as the G-1 well in Petropavlovsk-Kamchatsky itself (Fig. 1, Table 1). These wells also opened mineralized waters with free gas of mainly methane composition, but cold, with water temperature <30 °C at 1500 m deep. The first published data on the composition of water and gas of these wells can be found in Kiryukhin et al. (2017). Kopylova et al. (2018) presented detailed hydrochemical data for several of these wells included in the network for searching for hydrochemical earthquake precursors. The data of well testing in 1980–1990, including the chemical composition of water and gas were presented in technical unpublished reports of the Paratunka Hydrogeological Expedition. These reports contain also descriptions of the lithology of sections based on the results of the study of well cores later presented in detail by Pozdeyev (2003).

The purpose of this paper is to collect and to present all available data on the geochemistry of highly mineralized waters of the area (Kiryukhin et al., 2017; Kopylova et al., 2018). Our own data consist of the chemical and isotopic composition of waters from most of the drilled wells including trace elements, isotopic composition of the dissolved strontium and sulfur (H_2S and SO_4) as well as chemical and isotopic composition of free gases that include $^3He/^4He$ and isotopic composition of carbon of CH_4 and CO_2. We characterize these waters using standard geochemical methods and try to find out the features of their formation.

Table 1
Information about wells of the Avachinsky depression (Taran et al., 2021)

Well n°.	Location		Year of drilling	Depth, m	t°C/depth (M)/Q (l/s)	Head t, °C
	Lat N	Long E				
K-01	53°16′55″	158°21′34″	1991	2322	July 76, 1688/6	69.5
N°23	53°16′48″	158°21′28″	1986	341	58.8/340/4.5	58.2
K-2	53°17′00″	158°22′28″	1987	1295	March 67, 1196/1	49.0
K-4a	53°16′21″	158°21′24″	1988	1641	January 85, 1620/2	73.0
K-5	53°16′01″	158°23′14″	1988	1506	January 66, 1430/1.5	49.3
K-6	53°17′08″	158°20′42″	1990	1513	March 60, 1512/0.5	55.5
K-8	53°15′56″	158°22′13″	1989	1529	April 76, 1515/2	66.0
GK-1P	53°17′07″	158°24′34″	1969	1261	May 53, 1230/0.1	21.0
Z-5	53°16′56″	158°23′53″	1989	502	28.6/502/0.2	24.0
E-1	53°15′50″	158°28′37″	1984	3003	June 74, 3000/0	6.8
G-1	53°02′47″	158°39′47″	1987	2542	60.0/2542/0.01	11
R-3	53°08′39″	158°59′02″	1992	1503	33.0/1500/1.5	5.4
R-2	53°05′27″	158°56′03″	1993	1504	August 29, 1443/0	7.5

2. Geological and hydrological settings

A generalized geological map of the area that includes the Avachinsky Depression based on the geological survey of 1980–1990 (Sheymovich, 2000) is shown in Fig. 1. The map also shows the positions of the tested wells, the coordinates of which and some other parameters are given in Table 1. There are several models of the deep structure of the Avachinsky Depression based on data from geological surveys (Sheymovich, 2000) and instrumental geophysical measurements (Moroz and Gontovaya, 2003; Popruzhenko, Aprelkov, 1987). A

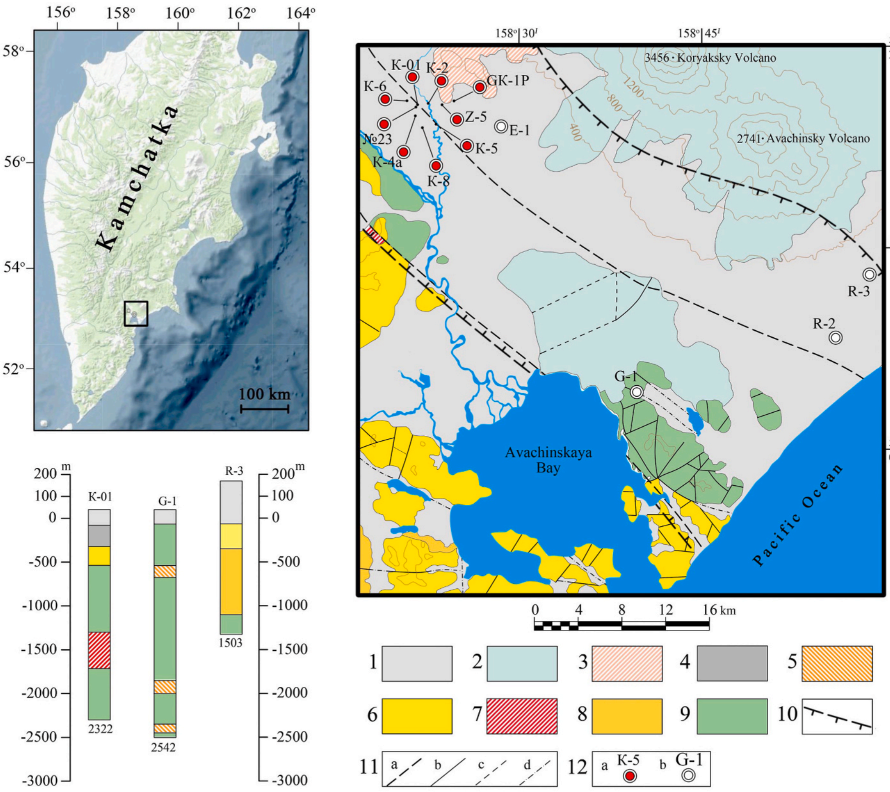

Fig. 1. Sketch geological map of the study area. According to Sheymovich (2000) and Pozdeyev (2003). Also are shown the geographic position of the Avachinsky depression on the Kamchatka map and well columns for 3 wells of different locations.
1. Different types of Pleistocene - Holocene alluvial, marine and delta deposits; 2 – Pleistocene - Holocene lava flows, tuffs, pyroclastic and volcanoclastic rocks; 3 – Middle - Upper Pleistocene volcanogenic and subvolcanic rocks; 4 – Lower – Upper Pleistocene sandstones, argillites, clays, breccia, gravelites; 5 – Middle Miocene volcanogenic and terrigenous formation; 6 - volcanogenic and volcanogenic-terrigenous formations (andesites, basalts, basaltic andesites, tuffs, tuff sandstones, ignimbrites; subvolcanic bodies); 7 – Miocene-Pliocene intrusive bodies; 8 – Eocene - Miocene sedimentary tuffs; 9 – Late Cretaceous metamorphic Nikolskaya formation; 10 – accepted boundaries of the Avachinsky depression (according to Pozdeyev, 2003); 11 – faults; 12 – well and its number: (a) Ketkino and Pinachevo wells, (b) “parametric” wells (see text).

common idea presents the Avachinsky Depression as a graben-like structure extending from the Pacific coast in a NW direction (Fig. 1) at a distance of about 75 km (Pozdeyev, 2003). Paleotectonic reconstructions demonstrate very complex relationships of rock complexes of different ages in the east of Kamchatka (Konstantinovskaya, 2003; Shapiro, 1987), however, in the case of the Avachinsky Depression, sections from prospecting and exploration wells (Fig. 1, Table 1) allow us to judge its structure quite definitely to depths of 2000–3000 m. According to the results of drilling wells, the base of the depression is the Upper Cretaceous strongly dislocated metamorphosed volcanogenic sedimentary rocks of the Nikolskaya Formation. The depression itself is composed of relatively poorly dislocated volcanogenic sedimentary deposits, whose age varies from the Middle Eocene - Oligocene to Miocene – Pliocene, overlain by loose Quaternary volcanogenic sediments. The hydrogeological conditions of the area under consideration are summarized by Manukhin and Pavlova (2011). From the point of view of hydrogeology, there are two main complexes at depth. The upper part of the section combines quaternary loose and volcanogenic deposits into a single aquifer complex. This is a zone of intensive water exchange, with water recharge zones on the slopes of nearby volcanoes and volcanic ridges (Fig. 1). Zones of tectonic fracturing in the Upper Cretaceous metamorphosed sedimentary rocks at the base of the Avachinsky Depression provide storage and pathways for mineral groundwater transport. These mineral groundwaters in the Upper Cretaceous formations, within the boundaries of the Avachinsky Depression, are tapped by almost all wells drilled in the area from 500 to 3000 m below surface. However, the highest groundwater temperatures are recorded in the local area, called Ketkino Field of thermomineral waters (Fig. 1). The discharge of the wells of the Ketkino Field is low, from 1 to 4.5 l/s (Table 1). Well E1 and wells from Radygino area R-2 and R-3 are closed and have very low or no (E1 and R-2) discharge through the valves attached to the heads of wells. The “urban” well G-1 has a vanishingly low flow rate of several milliliters per second (Kopylova et al., 2018).

3. Methods

Measurements of the physico-chemical parameters of the waters of the tested wells (pH and temperature, conductivity) were carried out directly at the sampling points. Gas samples were taken using a plastic funnel, a syringe, and a three-way valve into glass flasks with septa by the displacement method. The samples were analyzed by gas chromatography (Chromatec-Kritsall-5000) using thermal conductivity detector and two packed columns (molecular sieves and Porapak-Q) for determination of He, H_2, O_2, N_2, Ar, CH_4 and CO_2, and a Porapak Q column with flame ionization detector for determination of light hydrocarbons. The concentrations of main cations and anions (Na, K, Ca, Mg, F, Cl, SO_4) in water samples were determined by ion chromatography (METRHOM-801), atomic absorption (Sr) and wet chemistry (HCO_3, H_2S, SiO_2). The analysis for trace elements and B was carried out by ICP-MS technique. Samples for the isotopic composition of sulfur of the dissolved H_2S were prepared in the laboratory by precipitation of CdS from 1 L of an aqueous sample with a 10% solution of cadmium acetate. For the isotopic composition of sulfur in dissolved sulfate, $BaSO_4$ was precipitated out of the water sample using 10% solution of $BaCl_2$. Isotopic compositions of water ($\delta^{18}O$ and δD), dissolved hydrogen sulfide sulfur ($\delta^{34}S$–H_2S) and sulfate ($\delta^{34}S$ – SO_4), as well as carbon in CH_4 and CO_2 in free gas ($\delta^{13}C$–CH_4 and $\delta^{13}C$–CO_2) were analyzed at the Geological Institute of the Russian Academy of Sciences using a gas chromatography-mass spectrometric combined method on Finnigan Delta Plus XP continuous-flow equipment IRMS. Isotopic composition of the dissolved Sr was determined also at the Geological Institute of the Russian Academy of Sciences using a methodology described in Bujakaite et al. (2020).

The isotopic composition of water is given in per mil relative to the V-SMOW standard (average oceanic water). The isotopic composition of carbon is in per mil relative to V-PDB (belemnite of Cretaceous deposits), and the isotopic composition of sulfur is in per mil relative to V-CDT (troilite of Diablo Canyon). The isotopic composition of helium and the He/Ne ratio were measured at the Vernadski Institute of Geochemistry of the Russian Academy of Sciences according Rozhkov and Verchovsky (1990), using MI-9302 mass-spectrometer. He isotopic ratio $^3He/^4He$ is expressed in Ra units where Ra = $(^3He/^4He)_{meas}/(^3He/^4He)_{air}$, and $(^3He/^4He)_{air} = 1.39 \times 10^{-6}$ (Mamyrin et al., 1970).

4. Results

4.1. Chemical and isotopic composition of water

Table 1 shows data for the wells sampled in this study. The data include coordinates, depths, years of drilling, temperatures measured at the bottoms and wellheads and flow rates. Positions of the wells can be seen in Fig. 1. All 6 wells with “K-#” and well N°23 are drilled within Ketkino Field and discharge gas-saturated, bubbling thermal waters with temperature from 40 to 73 °C (K-4) at the head. The well GK1-P is drilled close to Ketkino Field and discharges warm water (21 °C) with a similar to the Ketkino wells composition. Four so-called “parametric” deep wells were drilled outside of this area (Fig. 1 and Table 1, wells E−1, G-1, R-2 and R-3). These wells also tapped mineralized gas-rich waters with methane as the main component in the free gas, but the water temperatures turned out to be low (Table 1).

During the exploration of Ketkino Field more than a hundred samples of water and gas were selected and analyzed. Table 2 shows concentrations of main dissolved species, water isotopic composition and isotopic composition of dissolved H_2S, SO_4, and Sr. The samples collected after 2018 have been collected and analyzed as a part of this study. Other compositions are single results from the technical reports of the Kamchatkan Hydrogeological Survey, most close to average compositions. Data for wells E−1 and G-1 are from the work of Kopylova et al. (2018).

Table 3 shows data on the composition of trace elements in the water of some wells. Some trace elements can serve as indicators of the water-rock interaction. Therefore, their concentrations are presented in Table 2. For wells GK-1P and G-1, data on trace elements are taken from the work of Kopylova et al. (2018).

Wells of the Ketkino Field, including the GK-1P, the G-1 well located about 30 km south-east, in the urban area of Petropavlovsk-Kamchatsky town, as well as wells R-2 and R-3 drilled 10–15 km to the east (Fig. 1), discharge to the surface waters similar in composition. These are highly mineralized waters (8–20 g/l) of the sodium chloride type with an increased calcium content (Table 2). These waters differ in the temperature at well heads and in the ratios of some minor components. Only the wells of Ketkino Field discharge thermal waters to the surface (up to 73 °C). In the same waters, very low concentrations of sulfate and magnesium were determined (below 10 mg/l and 2 mg/l, respectively) and very high – up to 54 mg/l – strontium concentration (Table 2). Thus, we can talk about a regional basin of mineral waters of deep formation with a local heat source beneath the Ketkino Field.

The isotopic composition of the groundwaters of the region depends on the altitude above sea level of the water recharge zones, but on average is close to the values of δD = −120‰ and $\delta^{18}O$ = −16‰ (V-SMOW), which corresponds to the recharge zones at altitudes of ~2000 m (Cheshko, 1994). Water from wells is noticeably isotopically heavier and approaches meteoric water in isotopic composition for wells discharging water with lower salinity (Fig. 2 a,b; Table 2, wells K-6, Z-5). This trend can be attributed to the mixing between meteoric water and seawater (with a positive oxygen isotopic shift), and it is also visible on a graph of δD vs chloride (Fig. 2b). It should be noted here that the point δD-Cl for the “town” well G-1 somewhat fall out of the general trend.

Strontium isotopic ratios, $^{87}Sr/^{86}Sr$, measured in waters (Table 2), despite similarly high concentrations of Sr in waters of all wells, are characterized by two distinct groups of values: in a narrow range of 0.7035–0.7037 in hot waters from wells of the Ketkino Field, and in a

Table 2
Chemical (mg/l) and isotopic composition of water (δD, $\delta^{18}O$), sulfur of dissolved H_2S and SO_4, and $^{87}Sr/^{86}Sr$ of the dissolved Sr. Empty cells mean no data.

Well	Ketkino field							Pinachevo			Town	Radygino	
	K-01	K-2	K-4a	K-5	K-6	K-8	N°23	GK-1P	Z-5	E-1[a]	G-1[a]	R-2	R-3
Year of sampling	2020	2018	1992	2020	2019	1993	2019	2021	2021	1984	2021	1992	2021
t°C sampling	55	38	69	49	43	61	57	17	24		11	7.5	5.4
pH	7.52	8.2	8.44	8.1	8.76	8.4	8.31	7.55	7.07	11	9.1	8.16	7.55
SiO_2	79	89	35	41	62	32	91	39	60.9		2	31	42
NH_4	6.4		7.2	2.5	2.7	7.1	10	2.8	2.0	7.0	8.9	18	30
Na	3539	2710	3276	3220	1354	3288	2683	2830	1360	3072	4040	3680	6667
K	188	98	105	84	26	96	98	95	71	60	48	43	167
Ca	970	500	650	678	190	693	419	960	197	952	221	485	679
Mg	2.1	1.8	0.9	0.5	0.1	2.9	3.2	40	42	16	32	172	234
Cl	7264	5106	6385	5988	2414	6413	4894	5886	2655	6013	7510	6901	12331
SO_4	173	1.7	37	21	2.4	13	1.0	0.1	2.6	114	43	16	2.4
HCO_3	127	52	35	50	30	39	55	163	123	80	73	275	144
F	1.8	–	1.6	1.5	1.6	2.0		0.24	0.28	0.7	3.8	0.2	0.0
B	24	20	25	31	12	23	19	10	16		21	34	20
Sr	51	49	54	52	28	54	37	54	15		14		36
H_2S(p-p)	32	6.5	36	9.0	<1	32	0.5	10					0.2
Li	2.3	1.5	1.9	1.9	0.8	2.6	1.6	0.8	0.29		3.2	0.8	0.8
Rb		0.14		0.14			1.4	0.06	0.056		0.06		0.06
Cs		0.03		0.04			0.04	0.009	0.004		0.03		0.006
Fe		0.034		0.016			0.05	0.33	0.53		0.14		8.03
Al		0.10		0.056			0.2	0.007	0.057		0.15		0.34
Ba	3	2.3		5.0			2.7	12	2.2		0.7		5.7
δD	−68	−80[b)]	−74[c)]	−67	−114[d)]		−77	−96[c)]	−130		−34		−40
$\delta^{18}O$	−4.7	−9.1[b)]	−7.1[c)]	−5.2	−14[d)]		−8.7	−11.2[c)]	−16.8		1.1		−3.4
$\delta^{34}S–H_2S$	+15.4			+8.5									
$\delta^{34}S–SO_4$	+26.4												
87Sr/86Sr		0.70354		0.70371			0.70369	0.70541			0.70570		0.70563

Data of: [a)] Kopylova et al. (2018); [b)] Cheshko (1994); [c)] Taran et al. (1997); [d)] Kiryukhin et al., 2017.

range of 0.7051–0.7057 in the warm water of the GK-1P well and in colder waters of the eastern part of the basin, in wells G-1 and R-3.

The isotopic composition of the dissolved sulfate of the K-01 well, the only one of the Ketkino wells, with a relatively high concentration of SO_4 (about 150 mg/l, Table .2), is noticeably heavier compared to seawater sulfate (+26.3‰ vs ~ +21‰).

4.2. Gas composition

The compositions of gases, as well as the compositions of waters, are very similar for all wells. It is a methane-nitrogen gas with a very low CO_2 content (<0.5 vol %), with hydrogen sulfide (mainly in dissolved form) and relatively high (mainly above 0.02 vol%, Table 4) helium concentrations. A high proportion of non-atmospheric nitrogen can also be considered a characteristic feature, since the N_2/Ar ratio in most samples significantly exceeds the air ratio of 83.6. The isotopic ratios of helium measured in gases from wells K-23, GK-P1 and G-1 (Table 4) exceed the atmospheric ratio ($2Ra < R < 4Ra$) but lower than typical for Kamchatka “volcanic” values that are in the range of 7 - 8Ra (Rozhkov and Verchovsky, 1990; Taran, 2009).

Concentrations of C_{2+} hydrocarbons, i.e., heavier methane homologues up to C_4 (ethane, propane, butanes) are very low with a C_1/C_{2+} ratio to ~ 35,000. Typical ratio C_1/C_{2+} for the methane homologues in hydrothermal gases is < 100 (e.g., Taran and Giggenbach, 2003). The isotopic composition of the CO_2 carbon measured in a gas sample from the K-01 well shows a low value of $\delta^{13}C–CO_2 = −21‰$. The isotopic composition of methane carbon, $\delta^{13}C–CH_4$, for all samples from wells in the Ketkino Field varies in a narrow range from −34‰ to −39‰ (Table 4). Methane from the GK-1P well is characterized by significantly isotopically lighter carbon ($\delta^{13}C–CH_4 = −57.5‰$). The same is observed for the well R-3, where $\delta^{13}C–CH_4 = −58.8‰$ (measured as −61‰ by Kiryukhin et al., 2017) and $\delta^{13}C–CO_2$ as low as −50‰ (Table 4).

The isotopic composition of the H_2S sulfur in wells K-01 and K-5 ($\delta^{34}S$ = +8.5‰ and +15.4‰) is significantly enriched with a heavy isotope compared to hydrogen sulfide from steam vents and from wells of high-temperature hydrothermal systems, for example, the Mutnovsky geothermal region ($\delta^{34}S–H_2S$ ~ 0‰, Zelensky and Taran, 2011).

5. Discussion

5.1. Systematics of waters of the Avachinsky Depression

Sodium chloride waters with a mineralization similar to that of the studied waters, with a high content of calcium and a low content of sulfate, in some cases can be considered as dilute brines - typical continental groundwater that often accompany oil and gas horizons (Krainov et al., 2004; Shvartsev, 1998). According to terminology of these authors, there are two main types of brines: (1) infiltration brines formed because of the dissolution of rocks and minerals of halogen formations, for example, deposits of potassium salts, and (2) sedimentogenic chloride solutions, which are also called formation waters formed due to the accumulation of seawater in buried marine sediments and subsequent dilution with low-salinity waters of upper aquifers (e.g., Kharaka and Thordsen, 1992; Krainov et al., 2004). Thus, it can be assumed that the mineral water uncovered by wells within the Avachinsky Depression are partially diluted sedimentary marine water of Late Cretaceous and possibly later deposits, which is consistent with geological and tectonic reconstructions about the Late Cretaceous marginal seas of Eastern Kamchatka (Konstantinovskaya, 2003; Shapiro, 1987) that implies a long period of sedimentation. Therefore, the points of the water compositions of all wells on the Na vs Cl plot fall on one straight line with a slope corresponding to mixing between meteoric and seawater (Fig. 3a). The waters are significantly enriched with calcium compared to seawater. The corresponding Ca–Cl graph (Fig. 3b) shows different trends for the Ketkino and Radygino wells R-2 and R-3, which may be due to different conditions of water-rock interaction in different

Table 3

Trace elements in waters from wells of the Ketkino field. Concentrations in ppb. Analyses for wells GK-1P and G-1 are taken from Kopylova et al. (2018).

	N°23	K-2	K-5	GK-1P	G-1
Be	0.14	0.24	0.35	0.07	0.07
Sc	0.07	0.09	0.09	0.5	0.4
Ti	13.3	<3	<3	2.5	0.45
V	1.5	<0.02	<0.02	17	16
Cr	<2	<2	<2	0.6	0.3
Mn	46	67	15	752	33
Co	0.19	<0.03	<0.03	0.04	0.03
Ni	<1	<1	<1	2.5	1.5
Cu	<5	<5	<5	0.65	4.7
Zn	8.8	<1	<1	3.5	45
Ga	0.12	0.09	0.13	0.15	0.2
Ge	4.1	4.0	5.5	1.0	1.2
As	15	1.1	0.4	35	1.8
Se	<0.5	<0.5	<0.5	13	8
Br	10260	10380	12980		
Y	0.38	0.33	0.49	0.22	0.08
Zr	0.44	0.05	0.06	0.08	0.01
Nb	0.06	<0.01	<0.01	0.25	0.13
Mo	0.19	2.3	0.36	0.48	45
Ag	<0.05	<0.05	<0.05	0.25	0.13
Cd	1.2	0.05	2.9	0.01	0.17
Sn	0.26	<0.2	<0.2	0.02	0.3
Sb	0.2	0.2	0.1	0.13	0.4
Te	0.2	0.2	0.6	0.38	0.01
I	5116	4100	8640		
∑REE	0.5	<0.4	<04	0.2	0.4
Hf	0.01	<0.01	<0.01		
Ta	<0.03	<0.03	<0.03		
W	1.0	1.4	1.3	0.5	0.51
Re	<0.03	<0.03	<0.03		
Tl	0.95	0.10	0.05	0.5	1.3
Pb	3.3	<0.2	<0.2	0.32	1.8
Th	<0.03	<0.03	<0.03	0.25	0.13
U	<0.03	<0.03	<0.03	0.01	0.03

parts of the basin. The water of some Ketkino wells, as already noted, is also characterized by extremely low concentrations of sulfate and magnesium (<10 ppm, Table 2).

The formation (sedimentogenic) character of the waters is also confirmed by their isotopic composition (Fig. 2a and b). Infiltration brines, as a rule, have a light isotopic composition of water since they are formed due to the dissolution of salts by infiltrated (paleo)meteoric waters (e.g., Frape et al., 1984). The formation waters are similar in isotopic composition to the buried seawater, sometimes partially evaporated (Kharaka and Thordsen, 1992). A good visible correlation between δD and chloride content (except G-1 well, Fig. 2b) also suggests that water of the wells of the Avachinsky Depression is buried seawater, diluted to varying degrees by groundwater and modified (metamorphosed) due to interaction with rocks. The presence of a noticeable positive isotopic oxygen shift (Fig. 2a) may indicate a low water-rock ratio in the aquifer or partial evaporation of seawater in marine sediments before mixing with shallow water (Kharaka and Thordsen, 1992). The changes should include, first, very high absolute (up to 57 mg/l), and relative concentrations of strontium, with a weight ratio of Ca/Sr up to 10 (Table 2). In seawater, this ratio is about 50. High strontium concentrations and low Ca/Sr ratios are characteristic of continental brines (Krainov et al., 2004; Kharaka et al., 1987). However, the waters of the Avachinsky Depression cannot be called brines. These are highly mineralized waters with a salinity below the salinity of seawater (<35 g/l). Another situation occurs with the relationship between Ca and Sr (Fig. 4). Similar to the Ca vs Cl plot (Fig. 3b), there are two different trends: a clearly expressed "Ketkino line" and points for Radygino water with relatively lower Sr concentrations. The general enrichment in Ca and Sr of formation waters relative to seawater concentrations is the result of complex water-rock reactions of the ionic exchange. For example, Ca enrichment can be provided by dolomitization of calcite by Mg from seawater. Input of Sr can be a result of processes of leaching Sr from Ca-bearing minerals of sedimentary or hydrothermally altered rocks (e.g., DePaolo, 2006).

A discussion on the use of the Ca/Sr ratio as an indicator of the formation of the composition of waters can be found in the study by Peiffer et al. (2011, and references therein). In the cited article we discuss unusual hot waters (up to 80 °C), with high mineralization, up to 15 g/l, heated by magmatic bodies near the volcano El Chichon (Mexico), but formed in the upper part of the Cretaceous basement, within the limits of the oil and gas bearing zone, deeper than 2000 m from the surface. These waters are a rare example of an analogue to waters of the Avachinsky Depression with similar concentrations of Cl, Na, K, Ca and Sr and even with a close $^{87}Sr/^{86}Sr$ ratio.

Another example of the presence of springs discharging saline waters on slopes of active volcanoes is Mt. Etna, Sicily. Several groups of such springs with different salinities, up to 70 g/l and Na–Cl composition, are known there (Chiodini et al., 1996; Aiuppa et al., 2004). But the chemistry of these waters and associated gases and their isotopic indicators, including Sr isotope ratios (Pennisi et al., 2000), are different from waters of the Avachinsky Depression.

5.2. Trace elements

Due to the fact that the waters from the wells of the Avachinsky Depression are slightly alkaline, with a pH reaching 9, the metal content in these waters is very low, usually below tens of μg/l, often below the detection level (Table 3). The concentrations of indicator components (rare alkalis, Sr and Ba) are shown separately, in Table 2. At the same time, strontium, for the waters of the Avachinsky Depression, with concentrations >50 mg/l, can be considered a major component. The relative concentrations of Ca, Ba and Sr, as well as Li, Rb and Cs (Fig. 5a and b) are shown together with the composition areas for the mean crust, as well as for limestone for alkaline-earth elements (Wedepohl,

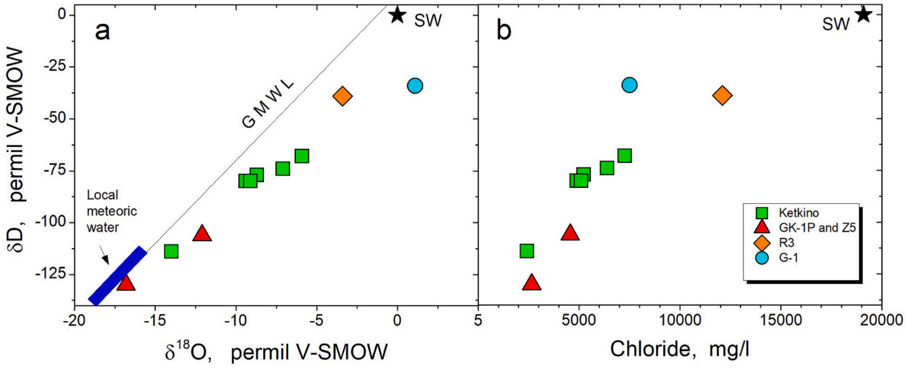

Fig. 2. *a*) The δD – $\delta^{18}O$ diagram for waters from wells of the Avachinsky depression. *b*) Relationship between chloride and δD (see text). Box A corresponds to the compositions of magmatic (Arc) water. GMWL – global meteoric water line; SW – seawater.

Table 4

Chemical (vol %) and isotopic ($^3He/^4He$, $\delta^{13}C$-CH_4 и$\delta^{13}C$-CO_2) compositions of free gas from wells of the Avachinsky depression. (*) – from Rozhkov and Verchovsky (1990); (**) –from Kiryukhin et al. (2017).

Well	K-01	K-2	K-4A	K-5	K-6	K-8	N°23	GK-1P	Z-5	G-1	R-3
Year	1992	2020	1992	2020	1992	2020	2020	2020	2021	2021	2021
He	0.033	0.029	0.027	0.036	0.021	0.036	0.022	0.031	0.032	0.005	0.013
H_2		0.002	0.008			0.002	0.005	0.041	0.0001	0.0002	0.0017
CO_2	1.27	0.07	0.43	1.1	3.35	0.014	0.02	0.22	0.09	0.88	0.023
H_2S						0.25					
N_2	19.2	21.5	28.2	28.9	36.2	21.2	17.1	19.4	21.7	57.1	35.0
Ar	0.036	0.056	0.09	0.08	0.33	0.056	0.053	0.15	0.19	0.18	0.07
CH_4	80.5	78.0	70.2	69.9	60.1	77.7	82.6	80.0	73.7	25.3	62.9
C_2H_6		0.25		0.11	0.11	0.14	0.09	0.033	0.011	0.014	0.0018
C3H8		0.0026		0.0021			0.0015	0.0005		0.001	0.000
$\sum C_4H_{10}$		0.00013		0.00003			0.00007	0.00003		0.0005	
C_2H_4											
C_3H_6				0.0017				1e-6		0.0002	
C_1/C_{2+}		312		680	520	555	901	2390	6700	1829	35000
$\delta^{13}C$–CH_4		−39.5		−36.3		−37	−39.3	−57.5	−56	−57	−58.8
$\delta^{13}C$–CO_2		−21									−50**
$^3He/^4He$ (R/Ra)*		3.7						2.6		3.1	
$^4He/^{20}Ne$		365						73		205	
N_2/Ar	530	378	313	361	110	379	323	129	115	312	500

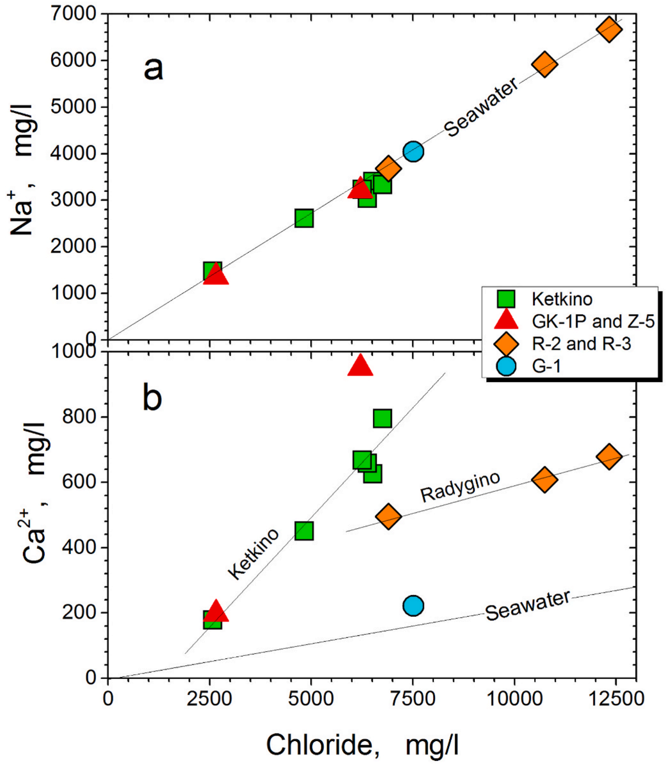

Fig. 3. Systematics of waters from wells of the Avachnsky depression based on relationship between chloride, sodium (*a*) and calcium (*b*).

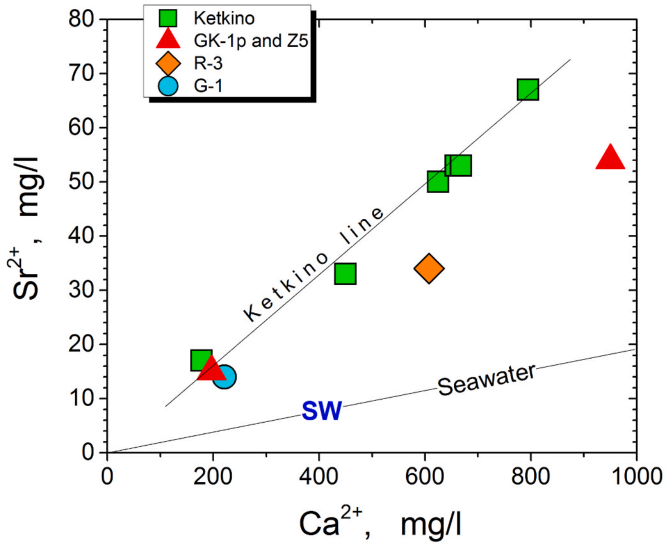

Fig. 4. Relationship between calcium and strontium in waters of deep wells of the Avachinsky depression. SW – seawater composition.

1995). In addition, in Fig. 5a the compositions of rare alkalis in the thermal waters of Kamchatka are shown, according to Arsanova (1974).

We did not find systematic data on the contents of Sr and Ba in the thermal waters of Kamchatka. The geochemistry of strontium and barium in continental brines was considered in sufficient detail decades ago by Shvartsev (1973) (see also Krainov et al., 2004). According to these authors, the source of strontium in brines is typically carbonate rocks, and the source of barium is silicates. Therefore, the Sr/Ba ratio can vary significantly in different lithologies as it can be seen in Fig. 5b on the ternary Ca–50Sr–100Ba diagram. The composition points for the waters of the Avachinsky Depression lie close to the composition area of the average crust (Wedepohl, 1995).

Water from the wells of the Avachinsky depression is also characterized by relatively high concentrations of bromine and iodine – up to 12 mg/l and up to 9 mg/l, respectively (Table 3). The geochemistry of bromine and iodine in formation waters is discussed in sufficient detail in the monograph (Krainov et al., 2004). The main source of the bromide ion is buried, partially evaporated seawater, and the source of iodine is organic matter of marine origin. In other words, the content of such indicator components as bromine and iodine indicates the marine origin of the mineral waters of the Avachinsky Depression. It should be noted that Cl/Br ratio in water from all wells is near two times higher than in seawater (~600 vs 297).

5.3. *Solute geothermometry*

As already noted, thermal water of Ketkino wells is significantly depleted of magnesium. Very low magnesium contents in thermal

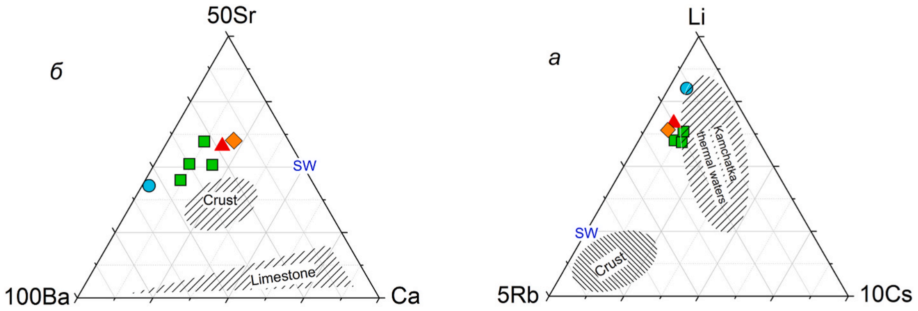

Fig. 5. (*a*) Relative concentrations of Li, Rb, Cs and (*b*) Ca, Sr, Ba in waters from wells of the Avachinsky depression. SW - seawater composition. Shaded areas are the compositions of characteristic reservoirs (see text for details). For symbols see Fig. 2.

waters, as a rule, indicate a high temperature of formation. Giggenbach (1988) proposed the so-called magnesium geothermometer based on the equilibrium between the solution and a set of minerals characteristic of the propylite facies alteration (K-feldspar, chlorite, muscovite, quartz/chalcedony):

$$t°C\ (K\text{–}Mg) = 4410/(14 - \log(K^2/Mg)) - 273, \quad (1)$$

where elements denote their concentrations in solution in mg/l. On the other hand, the equilibrium temperature at depth can be estimated using the Na–K geothermometer:

$$t°C\ (Na\text{–}K) = 1390/(1.75 + \log(Na/K)) - 273, \quad (2)$$

Constructed in the same work on the equilibrium of a solution with a pair of albite-K-feldspar (see also discussion by Fournier, 1990). Waters from deep wells of high-temperature hydrothermal systems, such as Mutnovsky in Kamchatka, are in equilibrium with the rock, and therefore the temperatures calculated using these two geothermometers are close. In most cases, the composition of hot spring waters show Na–K temperatures significantly higher than K–Mg temperatures, which is associated with the rate of equilibration: in the K–Mg system, it is attained much faster than in the Na–K system, i.e. as the water rises to the surface and the temperature drops, magnesium quickly passes into solution from the host rocks, and the Na/K ratio does not have time to change much. These considerations formed the basis of the widely used the Giggenbach ternary plot (Giggenbach, 1988) "K - Na/100 - $Mg^{1/2}$", which can be otherwise represented by a rectangular log-log plot log (Na/K) vs log (K^2/Mg), (Fig. 6). The graph shows that the points of the water compositions from the Ketkino wells lie close to the line of "full equilibrium" between 140 and 180 °C. The points for the remaining wells fall into the region of "partial equilibrium" at lower temperatures. Thus, it can be argued that in the area of Ketkino Field, the regional sedimentogenic waters are locally heated to a temperature at least of ~160 °C. The heat source is most likely an intrusive formation associated with magmatic plumbing systems of Koryaksky and Avacha volcanoes. At what depth this intrusion is located and to what depth the aquifer is extended - these questions remain unanswered for the time being. What is interesting is that the Mg–Li geothermometer of Kharaka and Mariner (1989) derived for formation waters (concentrations in mg/l):

$$t_{Mg\text{-}Li} = 2200/(\log(Mg^{1/2}/Li) + 5.47) - 273 \quad (3)$$

Gives for Ketkino wells a similar temperature range of 140–160 °C, and much lower for other waters, within a range of 50–70 °C.

The temperature of about 160 °C of the productive zone of the Ketkino Field can be confirmed in another way – by calculating the so-called saturation indices for potential minerals that can precipitate from the solution at different temperatures. The saturation index is defined as:

$$SI = \log(Q/K) \quad (4)$$

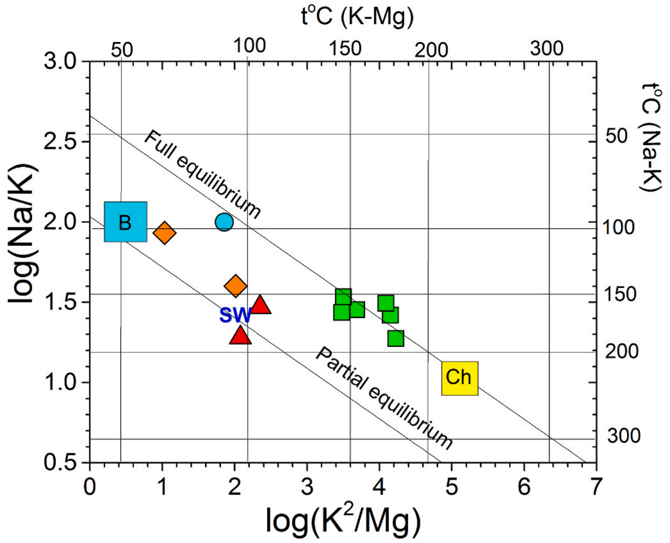

Fig. 6. The Na–K–Mg diagram for waters of the Avachinsky depression. Modified from Giggenbach (1988). Symbols as in Fig. 2. SW – seawater; Ch – spring near El Chichon (Peiffer et al., 2011); B – water from wells of the Bogachevsky area (Kudryavtseva, 1973), see text for details.

Where Q is the product of ion activities in a solution of a given composition, and K is the theoretical product of solubility for a given mineral. At SI = 0, the solution is saturated with respect to this mineral. At SI < 0, it is undersaturated and at SI > 0, it is supersaturated. The calculation was carried out using the SOLVEQ program (Reed and Spycher, 1984) with the updated SOLTHERM (Soltherm.H06-June 06, Reed and Palandri, 2006) thermodynamic data set, for the composition of the deep K-01 well having a bottom hole temperature of about 80 °C (Table 1). The calculation was possible because aluminum and iron were analyzed (Table 2). The results are shown in Fig. 7. It follows from the figure that the water of the K-01 well is in equilibrium with a set of the most typical hydrothermal minerals (aluminosilicates) at a temperature of about 150 °C, i.e. in a temperature range already estimated using the Giggenbach diagram (Fig. 6). Thus, two simple independent thermodynamic estimates can serve as a sufficiently convincing argument in favor of the existence in the area of Ketkino Field at some depth of the water horizon with a temperature of at least 150 °C. Interestingly, iron-containing minerals, mainly oxides, show an equilibrium temperature close to the temperature recorded at the bottom of wells (Fig. 7b). Apparently, this has something to do with the material of the casing of wells. It should also be added that the water from the K-01 well, regardless of temperature, is supersaturated with respect to pyrite (FeS_2), barite ($BaSO_4$), strontianite ($SrCO_3$) and celestine ($SrSO_4$).

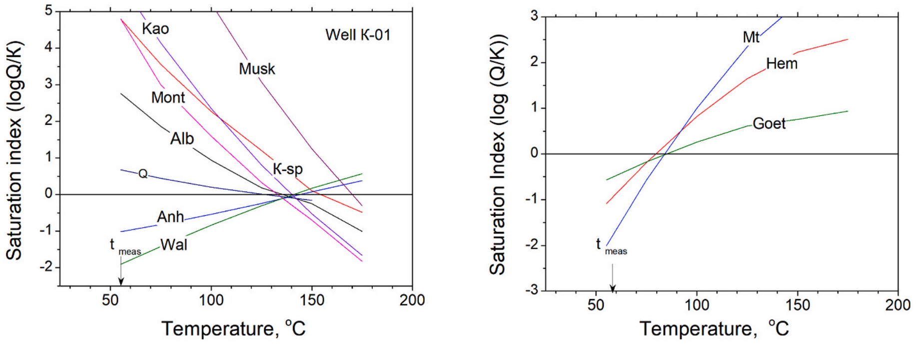

Fig. 7. Saturation indices for the solution of well # K-01 vs. temperature. Abbreviations: Musk – muscovite; Kaol – kaolinite; K-Sp – K-Spar; Mont – Na-montmorillonite; Alb – albite; Q – quartz; Anh– anhydrite; Wal – wollastonite; Mt – magnetite; Hem – hematite; Gt – goethite. t_{meas} is the measured temperature at the well bottom (Table 1).

5.4. Sr isotopes

Sr isotope ratio in thermal waters is an effective indicator of the rock origin of the aquifers, trajectories of the water flow and mixing of fluids. Effective exchange of Sr between rock and water is a well-known process, and sophisticated models exist that combine many factors including diffusion and kinetics of dissolution and precipitation of minerals for explaining the observed variations of $^{87}Sr/^{86}Sr$ in natural waters (e.g., DePaolo, 2006). It is generally the case when Sr isotopic ratios in thermal waters are close to the ratios in the host rocks. For Kamchatkan thermal waters this has been first shown decades ago by Vinogradov and Vakin (1983).

As was mentioned above, despite a very similar chemical composition of waters from the Avachinsky Depression, isotopic composition of the dissolved Sr is divided into two groups of waters: (i) thermal waters from wells of the Ketkino Field with $^{87}Sr/^{86}Sr$ between 0.70354 and 0.70371 and (ii) colder waters from other wells, including well GK-1P located close to the Ketkino field (Table 2, Fig. 1), with $^{87}Sr/^{86}Sr$ between 0.70541 and 0.70563. In other words, Ketkino Sr is from volcanic rocks ($^{87}Sr/^{86}Sr$ for the Avacha and Koryaksky volcanoes eruptive products vary between 0.7033 and 0.7035, e.g., Kepezhinskas et al., 1997), and Sr of colder waters from other wells most probably is a mixture of volcanic Sr and Sr from the buried seawater (0.7092) or crustal rocks (>0.7100). Therefore, waters from the Ketkino Field have a long-term contact with pure igneous rocks, i.e., the aquifer tapped by the wells consists of products of the eruptions and intrusive bodies of the Koryaksky-Avacha volcanic group. The zone supplying the hot aquifer with mineralized, sediment-associated water in this case is located deeper. Cold and more mineralized water from the eastern deep wells G-1, R-2 and R-3 probably represents this seawater-bearing brine buried in the Cretaceous sediments underlying the depression. This, so-called Nikolskaya Late Cretaceous - Paleogene Formation, according to Pozdeyev (2003) consists of a complex combination of volcanogenic sediments, siltstones, sandstones and carbonates of marine origin and intrusive bodies of later ages cutting or feeling this stratum. The Sr isotope ratios of ~0.7056 of waters indicate that the aquifers are composed more of volcanogenic rocks but with a significant proportion of marine sediments. It can be seen in Fig. 8 where $^{87}Sr/^{86}Sr$ values are plotted vs Ca/Sr weight ratio. The radiogenic endmember can be either seawater (Ca/Sr = 52) or more radiogenic crustal Sr from the old metamorphic basement (Ca/Sr ~ 100, mean crust), while “volcanic” endmenber is represented by quite unusual composition with Ca/Sr ratio <10. Interesting that saline waters around Mt. Etna are characterized by the higher Ca/Sr ratio >30, and $^{87}Sr/^{86}Sr$ close to the seawater ratio (0.7089, Pennisi et al., 2000).

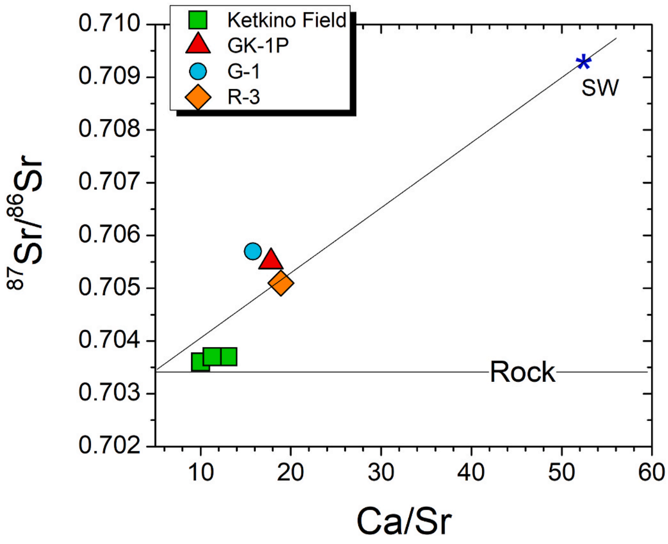

Fig. 8. $^{87}Sr/^{86}Sr$ ratios vs Ca/Sr weight ratios for well waters of Avachinsky Depression.

5.5. Formation of the gas composition

As already was noted, a characteristic feature of gases from all the considered wells of the Avachinsky Depression, except for the predominant methane content, is the high relative content of the non-atmospheric nitrogen. This is shown in the ternary diagram proposed by Giggenbach (1991) in Fig. 9. The N_2/Ar ratio in some gases is above 500, i.e., more than 80% of the nitrogen in these gases is not of atmospheric origin. The source of nitrogen and argon in the gases of thermal waters is mainly air dissolved in the meteoric water that feeds the system. But some of the nitrogen may enter the water from the host rocks, and some may have a deeper origin, i.e., come from deeper horizons of the crust or even from the mantle (Prasolov, 1990). The most probable source of non-atmospheric nitrogen in the mineral waters of the Avachinsky Depression is the same as the source of methane, namely, organic matter buried together with marine sediments. It is also worth noting relatively high concentrations of helium in gases. Several determination of the isotopic composition of helium in the wells of the Avachinsky depression, taken from Rozhkov and Verchovsky (1990), showed a fairly high proportion of mantle helium in those gases where these ratios were measured (Table 4). The highest value, 3.7Ra (Ra – air ratio, 1.4×10^{-6}) was obtained for the Ketkino well K-2. A little lower, 2.6Ra, was obtained for the Pinachevo GK-1P well, drilled close to Ketkino Field and closer to the Koryaksky volcano (Fig. 1). However, high $^{3}He/^{4}He$ ratio of 3.1Ra was also noted in the “urban” well G-1,

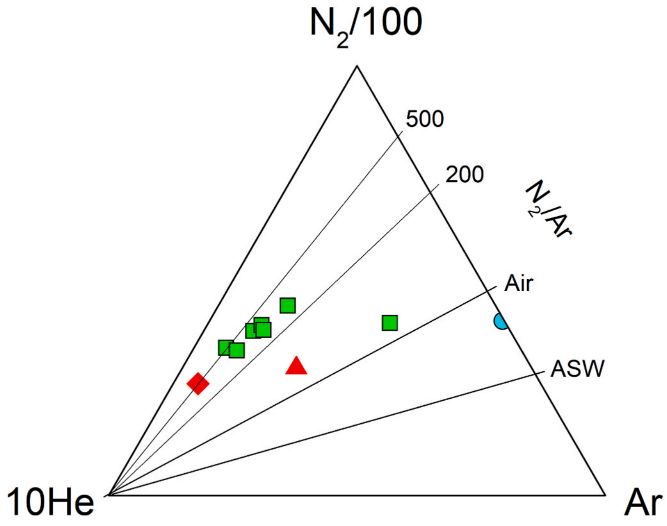

Fig. 9. Ternary diagram for relative concentrations of helium, argon and nitrogen (Giggenbach, 1991) in wells of the Avachinsky depression. Symbols as in Fig. 2.

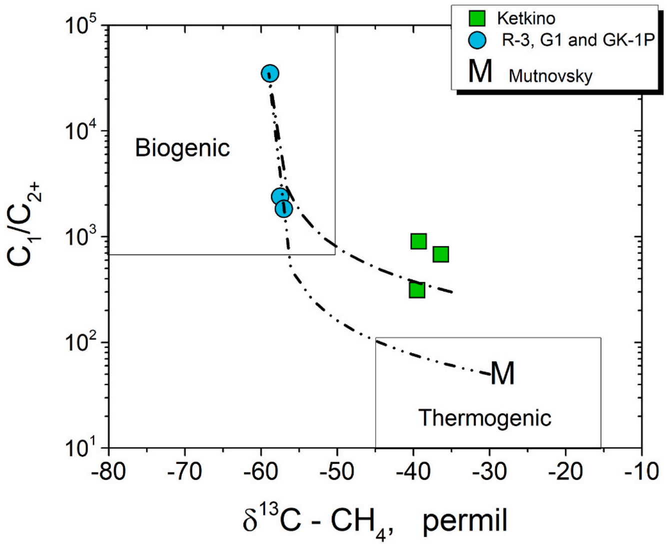

Fig. 10. The C_1/C_{2+} vs $\delta^{13}C$–CH_4 diagram (from Whiticar, 1999). Gases from wells of the Avachinsky Depression are divided in two groups: thermogenic and biogenic. Two mixing lines are shown: R-3 gas with thermogenic gas from Mutnovsky (M) geothermal field, and R-3 gas with Ketkino field gas. See text for details.

drilled 30 km to the southeast. These data indicate a sufficiently high permeability (deep faults, fracturing) of the crust beneath the Avachinsky Depression, which allows magmatic helium to rise to relatively shallow aquifers. Therefore, part of nitrogen can be of magmatic origin with typical for subduction zones high N_2/Ar ratios (e.g., Giggenbach, 1991; Zelenski and Taran, 2011).

The hydrocarbon part of gases is mainly represented by methane and is characterized by high C_1/C_{2+} ratios. The main indicator of the origin of methane and hydrocarbons is the isotopic composition of carbon. Thermogenic methane is isotopically heavy and has $\delta^{13}C$ above −40% and, as a rule, $C_1/C_{2+} < 100$ (Procesi et al., 2019; Schoell, 1988; Taran and Giggenbach, 2003 and references in these works). Biogenic methane is significantly isotopically lighter, up to the values $\delta^{13}C$ of −80%, with much higher C_1/C_{2+} ratios ($>10^3$) than for thermogenic gases (Schoell, 1988; Whiticar, 1999). Methane of high-temperature hydrothermal systems of Kamchatka (Mutnovsky, Uzon-Geyser, etc.) has a thermogenic nature and is characterized by values $\delta^{13}C > -30\%$ with $C_1/C_{2+} < 50$ (Beskrovny and Lobkov, 1977; Zelensky and Taran, 2011; Taran, 1988). Our data on wells K-01, K-2, K-5 and N°23 and data on well K-2 (Kiryukhin et al., 2017) show that Ketkino Field methane has a "thermogenic" isotopic composition, with $\delta^{13}C$ from −36‰ to −39‰ but with much higher C_1/C_{2+} ratios than for thermogenic gases, up to 900 (Table 4). Methane from the R-3, G-1, GK-1P and Z-5 wells is characterized by a more "biogenic" composition with $\delta^{13}C$ from −56‰ to-59‰ (Kiryukhin et al. (2017) give $\delta^{13}C$–CH_4 for R-3 well a value of −61‰). and with very high C_1/C_{2+} of 35,000 in the R-3 well. Gas from Z-5, GK-1P and G-1 wells is characterized by intermediate C_1/C_{2+} values of 6800, 2900 and 1890, respectively (Table 4). All data are plotted in Fig. 10 together with two hypothetical mixing lines. The first one is between a "thermogenic" gas with $\delta^{13}C$–$CH_4 = -30‰$ and $C_1/C_{2+} = 50$ (point M in Fig. 10), like in geothermal wells of the Mutnovsly high-temperature geothermal field (Taran, 1988; Zelenski and Taran, 2011) and a "Radygino" gas from well R-3 with $\delta^{13}C$–$CH_4 = -59‰$ and $C_1/C_{2+} = 35{,}000$. The second line is for gases from the well R-3 and average data for the Ketkino Field (Table 4). Points for Radygino and Ketkino wells are plotted approximately on their mixing line, but the Ketkino points are plotted notably out of the mixing line between "classic" thermogenic high-temperature gas and biogenic gas from Radygino wells.

The source of gases, as was already mentioned, is most probably the organic matter of the Late Cretaceous - Paleogene sedimentary formation. It is not clear how different mechanisms of the methane generation (thermogenic and biogenic-bacterial) can produce a similar CH_4-rich gas within a common basin. On the other hand, it is not clear why CH_4-rich gases, similar in chemical composition within a common basin are characterized by so different isotopic composition of CH_4 and the C_1/C_{2+} ratios.

Methane of thermogenic origin and with high C_1/C_{2+} has been noted for hot (280 °C) gases from the seafloor vents of Okinawa Trough (Kawagaucci et al., 2013) and for coalbed gases in China (Li et al., 2018). Kawagaucci et al. (2013) believe that the apparent conflict between thermogenic signature for CH_4 and biogenic one for C_1/C_{2+} can be resolved if one accepts the thermal decomposition of C_{2+} hydrocarbons at high temperature and under highly reduced (?) conditions. On the other hand, the coalbed gases with a thermogenic $\delta^{13}C$–CH_4 and biogenic C_1/C_{2+} (high dryness) are characteristic for the high maturity coalbed gases (Li et al., 2018 and references therein). A general view based on a global dataset of isotopic and chemical data for natural gases can be found in Milkov and Etiope (2018).

For gases of the Avachinsky Depression this is an open problem. More data on the isotopic composition of carbon and hydrogen, including the isotopic composition of methane homologues and maybe clumped isotopes, are needed to understand the sources and mechanisms of the formation of methane and hydrocarbons in the depths of the Avachinsky Depression. On the other hand, data on the isotopic composition of sulfur of dissolved sulfate and hydrogen sulfide in water and gases of the Ketkino area (Table 2) indicate the so-called TSR mechanism of hydrogen sulfide formation (Kiyosu, 1980; Machel et al., 1995) - thermogenic sulfate reduction. If, with the biogenic sulfate reduction, sulfide sulfur turns out to be significantly lightened, up to −40% CDT, as it was studied in detail (Johnston et al., 2007) and shown, for example, for pyrites of Dvukhyurtochny springs in Kamchatka (Taran et al., 2020), then with thermogenic sulfate reduction, sulfide sulfur turns out to be isotopically heavy. In our case, hydrogen sulfide in wells K-01 and K-5 has $\delta^{34}S$ +8.5% and +15.4% and $\delta^{34}S$ of dissolved sulfate +26.4%, which is noticeably higher than the value for marine sulfate (∼+20%). Therefore, the isotopic composition of sulfur in the Ketkino wells, along with geothermometry, confirms the presence of a significantly warmed-up aquifer in this part of the Avachinsky depression. In addition to sulfate reduction, hydrogen sulfide can also participate in the reduction of CO_2 (carbonates) to methane, as indicated by the extremely isotopically light carbon of CO_2 (−21‰ and −50‰, Table 4, see also Milkov and Etiope, 2018). In any case more data are needed for $\delta^{34}S$ to evaluate the role of TSP in affecting hydrocarbon gas compositions.

6. Summary

Wells drilled within the Avachinsky Depression revealed mineral waters of marine genesis with a large amount of free gas enriched with methane. The compositions of water and gas are approximately the same throughout this regional basin of mineral waters. In the west of the basin, these waters are heated by shallow magmatic bodies. Thermal and cold waters differ in the isotopic composition of dissolved strontium, as well as methane carbon and C_1/C_{2+} ratios in gases. The problem of delineating the heat source for the thermal waters of the Ketkino Field is not really a problem because of the unconditional presence of cooling subvolcanic bodies in the vicinity of two highly active volcanoes Avacha and Koryaksky. The problem is a coexistence of a basin of waters characteristic for oil and gas structures and a typical volcanogenic basin of aquifers composed of magmatic rocks and heated by intrusive bodies at the base of active volcanoes, that drastically changes isotopic and chemical signatures of the initially typical formation waters.

To approach the solution of these problems from the point of view of geochemistry, it is necessary, in our opinion, to conduct an additional detailed isotope-geochemical study of solutions and gases. This study should include analyses of the isotopic composition of fluids from all wells: water, sulfur, dissolved sulfate and hydrogen sulfide, dissolved strontium, boron, carbon, nitrogen and hydrogen of methane and its homologues, clumped isotopes in methane, nitrogen, as well as isotopic composition of helium and argon. It is also necessary to conduct a parallel study of borehole fluids of the Bogachevskaya Field, ~300 km to the NE, also located close to active volcanoes and geothermal fields and known by its surface oil seepages, as well as thermal manifestations of the Tyushevsky Trough at Kronotsky accretional complex area with CH_4-rich gas vents, to understand the origin and potential of these unusual manifestations for Eastern Kamchatka in the complex.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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