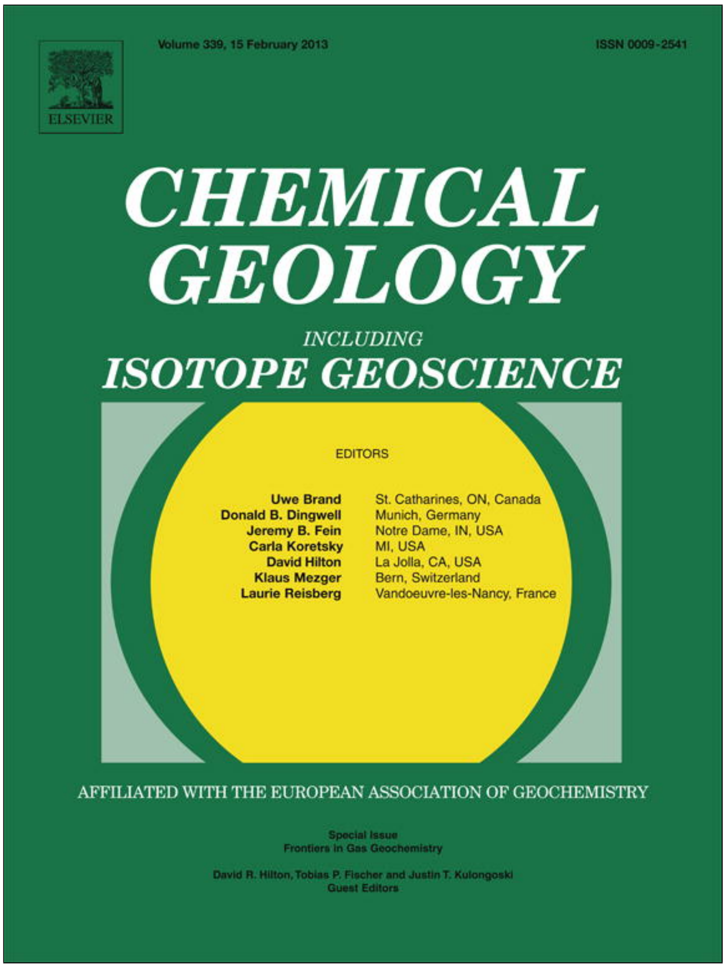
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He, Ar, C and N isotopes in thermal springs of the Chukotka Peninsula: Geochemical evidence of the recent rifting in the north-eastern Asia

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ABSTRACT

Thermal springs with water temperatures up to 97 °C were sampled in the Chukotka Peninsula of the north-eastern Asia on the area of ~60,000 km^2. He and Ar isotope ratios in bubbling gases were measured in 30 samples of from 23 spring groups. $^3He/^4He = R$ values vary in the range of $(20.2 \div 172) \times 10^{-8} = (0.14 \div 1.23) R_{atm}$. The over-atmospheric $^{40}Ar/^{36}Ar$ ratio values were found out in 18 groups. The compositions of gas phase were determined in 26 groups. In 16 of them N_2 content exceeds 90 vol.%. at $\delta^{15}N$ values = (0.0 ÷ +4.5) ‰. CO_2 contents vary from <1 to 95 vol.% and $\delta^{13}C_{CO_2}$ values determined in 19 samples vary from −20.4 to −4.4‰. In several samples $\delta^{13}C$ values were also measured in methane and ethane.

Geochemical specificity of gases was revealed in Kolyuchin–Mechigmen Zone (KMZ) of the Peninsula. The zone coincides with the trough of NW–SE strike that dissected the Precambrian basement of this part of the Chukotka–Seward microcontinent during the Triassic phase of tectonic activation. The latest re-activation of KMZ resulted in its subsidence during Quaternary, seismic activity and basic volcanism. The KMZ gases contain maximal contribution of light (mantle-derived) ^3He and carbon dioxide whereas this CO_2, and associated non-atmospheric N_2 and Ar are all enriched by heavy isotopes (^{13}C, ^{40}Ar, and ^{15}N, respectively). The waters of these springs are characterized by the highest reservoir temperatures estimated by solute geothermometers. These features are related to upwelling of mantle-derived melt supplying into the crust ^3He-enriched helium and thermal energy stimulating rock metamorphism.

1. Introduction

The Chukotka Peninsula (ChP) of ~58,000 km^2 in area is the easternmost margin of the Eurasia continent. It is washed by the Chukchi and Bering seas of the Arctic and Pacific oceans, respectively, and is separated from Alaska (Seward Peninsula) by the Bering Strait. The Chukotka Peninsula is situated in the zone of the gapless distribution of permafrost, and mean annual temperatures are negative everywhere. Another geothermal feature of the Peninsula is the abundance of thermal springs. Discharge of these springs is one of the manifestations of geothermal activity along with volcanism and background conductive heat flow.

Thermal springs are known in the Peninsula from the 18th century. In 1779 Cossack Ivan Kobelev discovered Senyavin Springs on its south-eastern coastal zone, and in winter 1791–92 Anton Batakov, the navigator of Joseph Billings' expedition, noted thermal springs in its northern part (Glotova, 1972). There is no information on any visits to the ChP thermal springs in the 19th century. In 1909–1910 the expedition of Russian Academy of Sciences visited Mechigmen Springs, and in 1934–1935 the researchers from Arctic Institute inspected Mechigmen, Senyavin and four other spring groups (Golovachov, 1937). Ivanov (1960) reported the chemical compositions of several springs studied in 1955. Some springs were described in the course of geological surveys in 1960–1980th, and Chaplin, Dezhnev and Kukun' springs were drilled (Suvorova, 1972; Karaseva, 1976; Karaseva and Safargaliev, 1986). The chemical compositions of fluids issued in the springs studied were determined showing the predominance of nitrogen in gas phase and sodium chloride among dissolved solids. Because of Cl–Na composition some researchers attributed marine genesis to spring waters, although isotopic composition of both H_2O and gases from thermal springs remained unknown.

In 2002–2004 most of the springs in the Chukotka Peninsula were sampled by the research team of the RAS Geological Institute (GIN RAS) to study features of chemical and isotopic composition of thermal fluids in different domains of the Peninsula. To this collection were added several samples collected by A. Kievskii (2006) during the inspection of the ChP springs in 2004–2005 and presented to us for analysis. The data related to H_2O isotopes in superficial and thermal

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waters were published (Polyak et al., 2008). This paper presented basically the data on spring gases.

Fig. 1 shows location of springs sampled in the different domains of the Chukotka Peninsula. Most of springs located in the northern parts of the Peninsula (the north-western and north-eastern domains, NWD and NED, respectively) are colder than those in the southern domain (SD). In the central domain (KMZ) the most southern springs (groups 6 and 8 in Fig. 1) are also warmer than the others. In winter, thermal waters discharging on the earth surface create chrystocrenes mapped in group 5 (Karaseva and Safargaliev, 1986) and many other places.

Water temperatures in the sampled springs vary from 97 °C to 3 °C. In this regard it is worth to remind the old remark by Keilhak (1912) who fairly supposed that in the areas with a mean annual temperature equal to 0 °C (and lower, as it is in the ChP) the springs with water temperature even 1 °C should be considered as thermal springs. Their discharge is accompanied by an advective heat efflux adding to conductive heat losses. Some of such low-temperature springs of the Chukotka Peninsula contain a noticeable quantity of dissolved solids as well as gases differing in composition from atmospheric air.

Location of thermal springs and isotopic composition of species contained in issued fluids (gases, first of all) show local and regional features of geological structure of the area and source reservoirs for different species. Our investigations were aimed mainly at revealing abyssal (mantle-derived?) components in the spring gases. Isotopic composition of helium is the only unequivocal indicator in this regard, as it became to know due to the pioneer works by Aldrich and Nier (1948), Clarke et al. (1969), Mamyrin et al. (1969), and a great number of following investigations.

These investigations showed that the ratio of $^3He/^4He = R$ varies in geological objects (rocks, minerals, fluids) in the range of several orders of magnitude depending on the contents of genetically different components. One of them is the radiogenic helium produced in terrestrial matter by U and Th decays and reaction $n + {}^6Li$. Radiogenic crustal helium originating at the Clarke contents of the parent elements is characterized by $R_{CR} = \sim 10^{-8}$ (Tolstikhin and Drubetskoy, 1975; Mamyrin and Tolstikhin, 1984) conforming well with the mean value for gases from Precambrian platforms of the FSU, $R_{Pcm} = (2 \pm 1) \times 10^{-8}$ (Polyak and Tolstikhin, 1985). Another component is primordial helium with $R_{PRIM} \sim 10^{-4}$ captured by the Earth during its accretion. Such helium was kept partially up to now in the earth mantle (Clarke et al., 1969; Mamyrin et al., 1969). That is why in helium from basalts and smokers of mid-ocean ridges $R_{MORB} = (1.15 \pm 0.1) \times 10^{-5}$ (Marty and Tolstikhin, 1998), whereas in “hot spots” (mantle plumes, like Hawaii, Iceland, etc.) this ratio R_{HS} is further enhanced (Craig and Lupton, 1978; Breddam et al., 2000; and others). At present, in the atmosphere $R_a \approx 1.4 \times 10^{-6}$ (Mamyrin et al., 1970), and this value is often used as normalizing parameter: $R_{MORB} = 8.2R_a$, $R_{Pcm} = 0.014R_a$, etc.

Helium enriched in ^3He is delivered into the crust along with mantle-derived melts (Polyak et al., 1981; Polyak and Tolstikhin, 1985; O'Nions and Oxburgh, 1988). Gerling (1957) showed that helium eventually escapes from rocks into subsurface fluids, where R is averaged in compliance with the contributions of all helium sources, and the resultant mean value is a quasi-stationary background characteristic of the particular tectonic unit.

Fluids in regions of Phanerozoic magmatism contain helium with R values intermediate between R_{MORB} and R_{CR} [Polyak et al., 1979; Polyak and Tolstikhin, 1985]. In the Chukotka Peninsula, magmatic

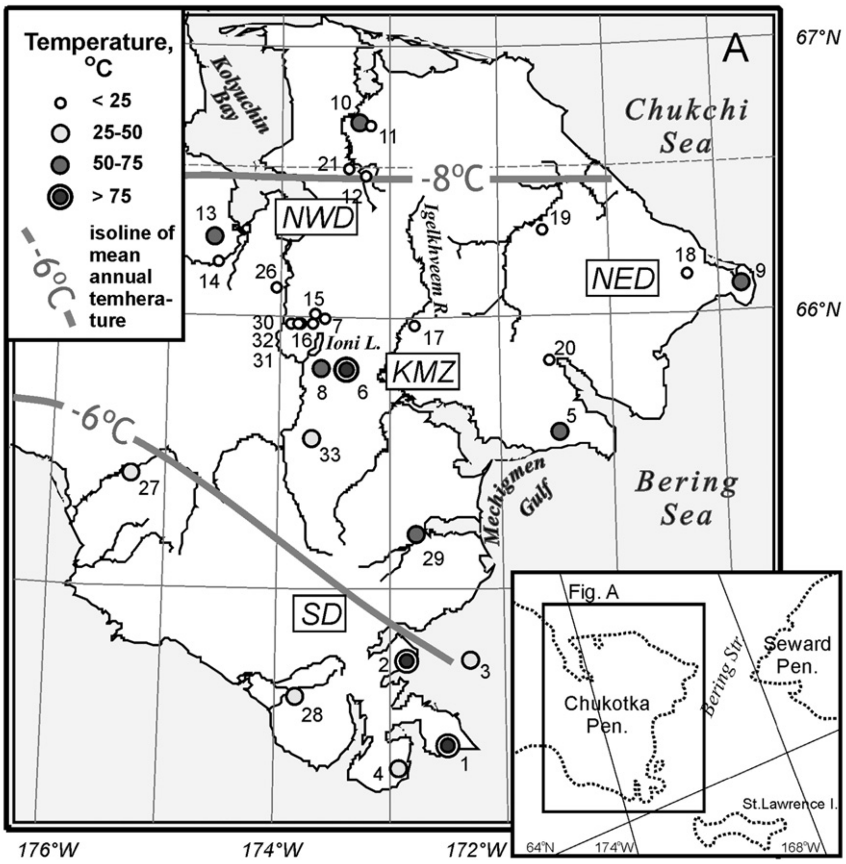

Fig. 1. Location of thermal spring groups in the Chukotka Peninsula. Groups are numbered according to the left column of Table 1. Different domains are noted by abbreviations SD (southern), NWD (north-western), NED (north-eastern), and KMZ (Kolyuchin–Mechigmen Zone).

reactivation occurred repeatedly in time and discretely in space. Therefore, our investigation was aimed to search for indications of this activity recorded in the isotopic composition of helium in subsurface fluids from various areas of the Peninsula.

This work continues the investigations of regional features of helium isotope composition in subsurface fluids. The investigations began from the studies of He composition in fluids from Kurile island arc (Devirts et al., 1971), Kamchatka (Kamenskii et al., 1976), Iceland (Kononov et al., 1974; Polyak et al., 1976) and some other hot spots (Craig and Lupton, 1978, and other), Italy (Polyak et al., 1981), Japan (Nagao et al., 1981), Mexico (Polyak et al., 1982), and Czechia (Polyak et al., 1985). Since then, in these and other regions tens and hundreds R measurements were made in various free-circulated subsurface fluids (stratal waters, mineral and thermal springs, geothermal systems, hydrocarbon deposits, gases of active volcanoes including mud volcanoes). The results of these measurements were reported in many publications.

The areas studied in detail in this regard and situated relatively close to the area of our research are the Japanese island arc (Sano et al., 1982; Sano and Wakita, 1985; Marty et al., 1989; Sano and Nakajima, 2008; and references herein) and the Kuril–Kamchatka region (Rozhkov and Verkhovskiy, 1990; Taran, 2009). Such studies were carried out in the Aleutian arc (Poreda and Craig, 1989; Symonds et al., 2003), as well as in Alaska, where 14 measurements in gases from mud volcanoes showed R values lying in the range of $(0.75 \div 4.1)R_a$ and 2 measurements in fumarole gas from the Wrangel volcano gave R values equal to 6.0 and $6.1R_a$ (Motyka et al., 1989). The comparison of the Alaska data with those obtained in Chukotka and presented below is beyond the scope of this article and can become an object for further investigations.

2. Geological setting

The Chukotka Peninsula is a fragment of the Late Mesozoic active margin and is related to the north-eastern flank of the Okhotsk–Chukotka volcanic belt superimposed on the western part of the ancient Chukotka–Seward microcontinent (Akinin and Apt, 1994, Akinin et al., 2008; Belyi, 1995, 1997, 2008; Kryukov, 1980, 1987; Zhulanova, 1990; Vladimirtseva et al., 2001, and others). The reviews of some of the above-cited and other Russian works are presented in Amato et al. (2003), Natal'in et al. (1999), Nokleberg et al. (1994, 2005), and see reference therein. Generalized tectonic pattern of the Peninsula is shown in Fig. 2 and similar to maps published in (Nokleberg et al., 1994; Natal'in et al., 1999, Fig. 2).

The area under study underwent several phases of tectonic-thermal re-activation. The oldest rocks outcropped in the Peninsula are the metamorphites of 2565 ± 150 Ma in the Rb–Sr age (Kotlyar et al., 2001). Precambrian basement is overlain with Paleozoic sedimentary cover undergone locally greenschist metamorphism in the 430–262 Ma (Vladimirtseva et al., 2001). The next phase of re-activation in the area under study took place during Early Mezozoic. This phase resulted in gabbro-dolerite intrusions and many normal faults in the zone extended from Kolyuchin Bay to Mechigmen Gulf (Kryukov, 1980). Igel'khveem–Lorino Fracture Zone of NW–SE strike is considered to be the largest of these deformations (Vladimirtseva et al., 2001). The basic intrusions are localized within Triassic terrigenous sequence and were dated by the only U–Pb determination of 252 Ma (Ledneva et al., 2009). These structural and sedimentological features of Kolyuchin–Mechigmen Zone (hereafter, KMZ) led to the suggestion on the coincidences of KMZ with pre-Jurassic trough which was be considered as *graben-syncline of rift type called Mechigmen Rift Zone* (Belyi, 1995, p. 52–53). This concept is supported by Imaev et al. (2000) who suggested that faults bounded KMZ are riftogenic.

The new large-scale phase of tectonic-thermal re-activation was manifested in this area in the Upper Cretaceous when it created the Okhotsk–Chukotka volcanic belt which masked the former structural pattern of the Peninsula. The belt studied in many details by Belyi (1977, 2008) is composed mainly by acid and intermediate lavas and comagmatic intrusions.

During Cenozoic the area under study was re-activated evidently more than once. The most known of the manifestations of its magmatic activation are Enmelen volcanoes situated on the south of the Peninsula. Between 3.9 and 10.7 Ma these volcanoes produce alkaline basalts which are the most ultramafic rocks in the Bering Volcanic Province including both the Chukotka Peninsula and Alaska (Akinin and Apt, 1994). As known, Neogene–Quaternary basic volcanism was sporadically manifested in many other areas of the North-Eastern Asia and surrounding aquatories (Patton and Csejtey, 1980; Fedorov, 2006; Akinin et al., 2008). Besides Enmelen volcanoes, the Cenozoic basalts were also found in the other parts of the ChP. The oldest of them are alkaline basalts with K–Ar age of 54–60 Ma outcropped in the valley of Igel'khveem River (Smirnov and Kondrat'ev, 2009). Basalt flows and dikes found in the other parts of the Peninsula remain undated. Somewhere they were related to Tunguveem Formation spread to the west of the area under study and attributed to Miocene from biostratigraphical data, whereas other similar manifestations are supposed from substituted data to be of Quaternary age (Kryukov, 1980).

In Bering Province the Cenozoic basalt volcanism was manifested not only on land but also in St. Lawrence Island as Kookooligits Mts. volcano active from 1.46 to 0.24 Ma ago (Patton and Csejtey, 1980). This island is situated ~80 km from the south-eastern end of the Chukotka Peninsula (Chaplino Cape) on KMZ strike and the youngest basalts in KMZ could be of similar age.

As known, KMZ is traced by positive Bouguer anomalies (Sazhina, 1968). On the one hand, we cannot exclude that this feature of the gravity field in KMZ is related to Cenozoic magmatism. On the other, however, this feature could be caused by gabbroid plutonism accompanying formation of the rift-like graben in Triassic.

Unlike of gravity anomalies, high seismicity is unequivocal proof of its present-day geodynamic activation of the Chukotka Peninsula. During the last 70 years of in 20th century, more than 100 seismic events took place in KMZ including six earthquakes with magnitudes from 5.0 up to 6.9 (Imaev et al., 2000). Fujita et al. (2002) discerned the Kolyuchin Gulf–Eastern Chukotka zone considered as "*a western extension of the rift system of Seward Peninsula*" (Fujita et al., 2002, p. 259), "*extensional in nature*" and "*the most active and enigmatic of the zones of Chukotka*" (Fujita et al., 2002, p. 264). Within this zone these researchers outlined "proposed rift areas" (Fig. 3A).

One more expression of the geodynamic activity is the intensity (velocity and amplitude) of tectonic movements. During Late Cenozoic, these movements have created the depressions along KMZ where the thickness of Quaternary sediments alone amounted locally up to 130 m (Vladimirtseva et al., 2001). According to Senin et al. (1989), in the Chukchi and Bering seas the ramified graben-rift system appeared in the Mezozoic–Early Cenozoic and was re-activated in the Late Cenozoic (Fig. 3B). The northern segments of this system are studied intensively in a frame of the Joint Russian American Long-term Census of the Arctic (RUSALCA) initiated in 2003 (Astakhov et al., 2010, and others). As a result, the Chukchi graben was mapped in the sea from Herald Trench to Kolyuchin Bay (Fig. 3C). The graben is continuated on the land as KMZ where we hope to find out specific features in chemical and isotope composition of hydrothermal gases.

3. Methods

Samples of spring waters collected in plastic containers were filtered (through a filter 0.45 μm) and were conserved by HNO_3 65%. Cl and HCO_3 concentrations were estimated from routine titration. Contents of Na, K, Ca, Mg and S (with following recalculation as SO_4) were determined by ICP-AES, whereas ICP-MS was used for Li. TDS value presents the sum of concentrations of major components

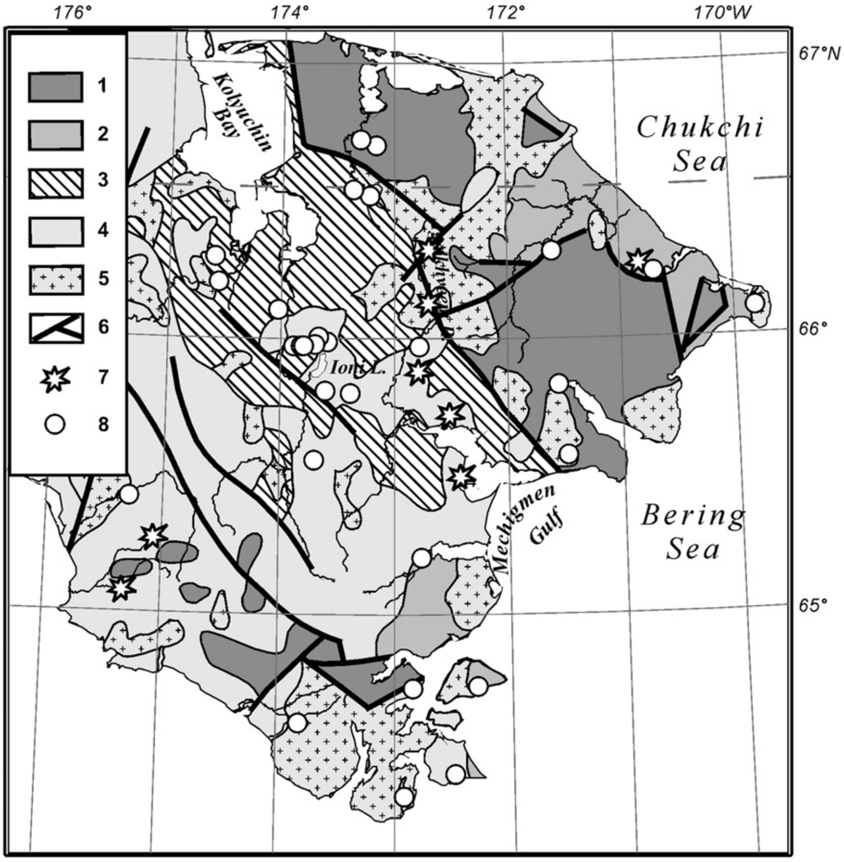

Fig. 2. Tectonic sketch of the Chukotka Peninsula according to Zhulanova (1990), simplified. (1–2) Chukotka–Seward microcontinent: (1) Pcm basement, (2) Pz cover; (3) P–T Kolyuchin–Mechigmen Zone (KMZ); (4–5) Upper Cretaceous Okhotsk–Chukotka superimposed volcano-plutonic belt: (4) lavas and tuffs and (5) granitoids; (6) faults, (7) Cenozoic volcanics according to Romanova and Zhukova (1970), Kryukov (1980, 1987), Akinin and Apt (1994), Akinin et al. (2008), and others, and (8) thermal springs.

of chemical composition of spring water. The results obtained are presented in Table 1 together with the information on sampling site positions, sample indexes, and some other details.

All gas samples represent bubbling gases. They were collected in 220 cm^3 glass containers by routine water–gas displacement technique. Concentrations of N_2, CH_4, CO_2, O_2 and He in gases from 26 spring groups were determined using gas chromatograph Crystall-2000M with Ar as a gas-carrier and are given in Table 2. Noble as isotope abundances were also measured in the Geological Institute of the RAS Kola Scientific Center (GI RAS KSC, Apatity, RF), Isotopic Research Center of All-Russia Geological Institute (VSEGEI Enterprise, St. Petersburg, RF) and Laboratory of Fluid Isotope Geology of the St. Petersburg State University (SPbGU, RF). In total, $^3He/^4He$, $^{40}Ar/^{36}Ar$, $^{38}Ar/^{36}Ar$ and $^4He/^{20}Ne$ ratios were measured in 30 samples from 23 spring groups.

Isotope measurements were carried out using mass spectrometers: Micromass VG 5400 and MI-1201-IG. Sensitivity of the latter for He is

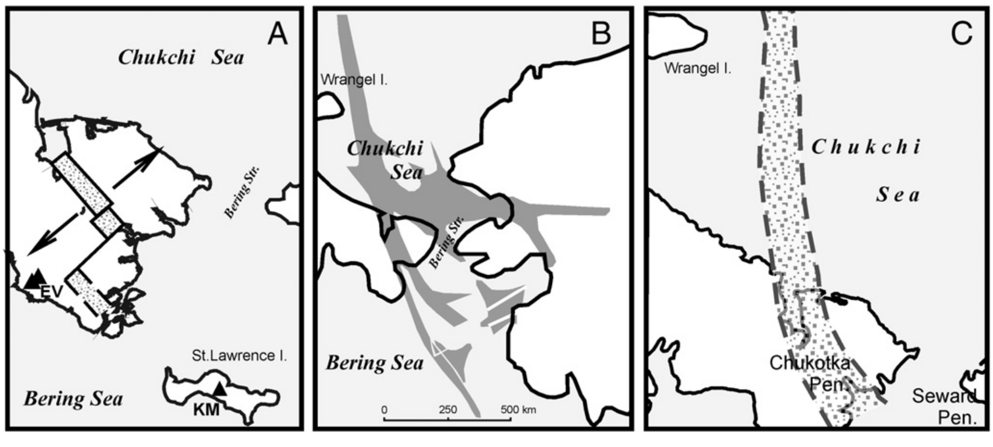

Fig. 3. Manifestations of recent rifting in the Arctic–Pacific conjugation zone. (A) The proposed rift areas in the Chukotka Peninsula according to Fujita et al. (2002, Fig. 8), simplified. Black triangles note N_2-Q volcanoes (EN, Enmelen group; KM, Kookooligits Mts.). Arrows show approximate relative motions. (B) The shaded zone marks the position of the Mz–Cz graben-rift systems in the Chukchi–Bering seas according to Senin et al. (1989). (C) The position of the neotectonic Chukchi graben according to Astakhov et al. (2010). See comments in the text.

Table 1
Locations, temperatures and chemical compositions of waters from the Chukotka springs.

Spring group ##	Coordinates		Sample index	Spring groups, sampling sites	T, °C	pH	TDS g/L	Concentrations,								
	N	W						Na^+ mg/L	K^+ mg/L	Ca^{2+} mg/L	Mg^{2+} mg/L	Li^+ 10^{-3} mg/L	Cl mg/L	SO_4^{2-} mg/L	HCO_3^- mg/L	SiO_2 mg/L
Southern domain (SD)																
1	64°25′	172°30′		Chaplino group												
1	64°25′	172°30′	1a	East subgroup, flowing well	87.5	8.6	19.28	4284	99	2192	0.95	2675	11,630	197	122	76.9
1	64°25′	172°30′	1b	East subgroup, spring	67.8	8.0	18.95	4205	111	2146	0.94	2747	10,990	178	98	59.3
1	64°25′	172°30′	1c	West subgroup, spring	65.3	7.2	17.96	4052	101	2016	0.82	2470	10,780	166	14.6	57.1
1	64°26′	172°31′	1d	Distant subgroup, spring	79.0	6.3	18.98	4160	107	2163	0.88	2620	10,990	179	14.6	63.5
2	64°44′	172°51′		Senyavin group												
2	64°44′	172°51′	2a	Spring 1	77.7	8.6	1.47	365	11	76	0.10	528	717	55	49	58.2
2	64°44′	172°51′	2b	Spring 2	78.7	8.6	1.5	354	10	82	0.09	504	717	56	29	59.3
3	64°45′	172°18′	3a	Arakamchechen group, spring	37.4	8.4	1.47	456	9	66	0.55	413	730	73	34	31.5
4	64°21′	172°56′	4a	Kivak group, spring in swimming pool	43.1	8.2	4.78	1050	16	789	0.40	796	2610	48	22	32.1
27	65°25′	173°18′	27a	Verkhne–Nunyamo group, spring 4	35.6	7.7	1.7	412	12	134	0.20	571	994	11	55	30.4
28	64°37′	173°49′	28a	Sineveem group, spring 6	43.0	5.8	8.5	1717	27	1241	3.29	842	5254	56	24	28.9
29	65°12′	172°47′	29a	Getlyangen group, spring 1	42.5	7.0	4.1	585	30	109	0.36	957	2343	33	37	50.8
Kolyuchin–Mechigmen Zone (KMZ)																
5	65°35′	171°29′		Kukun' group												
5	65°35′	171°29′	5a	Spring 1 captured in concrete cube	60.0	7.0	5.23	1447	68	254	1.16	3560	2590	57	81	82.6
5	65°35′	171°29′	5c	Spring 2	52.5	7.4	4.03	1118	61	279	0.99	3297	2120	50	73	69.5
6	65°48′	173°24′		Mechigmen group												
6	65°48′	173°24′	6a	Spring1	89.7	7.1	3.93	1255	72	94	1.81	5011	2050	70	190	130
6	65°48′	173°24′	6c	Spring 2	64.3	6.9	4.08	1273	65	98	1.86	4723	2100	70	217	126.2
7	66°00′	173°36′		Grandmouther glasses group												
7	66°00′	173°36′	7a	Northern spring at the top of the dome	20.1	6.5	9.26	1849	108	899	152.52	3961	3860	166	1928	21.8
7	66°00′	173°36′	7b	Northern spring at the top of the dome	20.8	6.3	9.58	1910	132	937	158.37	4650	4260	297	1810	31.3
7	66°00′	173°36′	7c	Southern spring at the top of the dome	13.7	6.7	9.15	1934	118	928	115.10	4237	4080	190	1897	23.1
8	65°49′	173°27′	8b	Tuman group, southern subgroup, spring	55.1	7.2	3.4	1127	60	100	2.83	3495	1710	65	207	100.6
15	66°01′	173°41′		Ynpyn group (Olen'i group)												
15	66°01′	173°41′	15a	Saline lake	15.2	7.6	8.53	1401	102	97	649.68	3424	3900	202	1420	3.3
15	66°01′	173°41′	15b	Spring 1	18.3	7.0		1519	67	152	629.98	3706		222		n.d.
16	65°59′	173°42′	16b	Arenyshkan group, spring 6	5.2	6.8	7.72	1884	92	880	151.57	4894	3834	320	1220	12.8
17	65°58′	172°47′		Nel'pygen group												
17	65°58′	172°47′	17a	Spring 1	3.1	6.6	6.87	1292	53	392	307.98	4923	2410	197	2460	23.9
30	65°59′	173°54′	30a	Stupenchat group, spring 1	11.4	6.5	5.5	775	51	410	66.71	2045	3578	122	1269	28.7
31	65°58′	173°49′	31a	Ioni gaseous group, spring 1	5.3	6.4	7.3	1766	82	898	211.41	4331	4217	234	1159	74.0
32	65° 59′	173° 50′	32и	Ioni mineral group, ист. 3	5.0	6.4	7.1	1321	84	772	125.24	4351	3578	252	1196	58.8
33	65°34′	173°42′	33a	Pechingtan group, spring 6	28.2	7.5	1.9	524	21	43	0.52	1362	994	1	122	53.6
26	66°06′	174°02′	26a	Krug group, spring 3	4.1	7.4	9.55	2242	115	7814	13.97	7457	5733	62	170.8	55.1
North-Western Domain (NWD)																
10	66°43′	173°18′	10a	Neshkan group, southern subgroup, spring	51.8	6.1	37.14	12,457	526	3328	24.77	18,049	22,400	0.8	122	110.7
11	66°42′	173°10′	11a	Teyuk group, spring 1	6.5	6.3	17.64	4275	182	1597	17.42	7143	9900	1.6	79	20.0
12	66°31′	173°14′	12a	Kub group, spring 1	7.2	7.1	4.48	927	79	160	37.99	3194	2490	12	550	48.5
13	66°19′	174°37′	13a	Vytkhyt group, spring 1	64.9	6.5	3.45	742	43	253	1.19	2522	1780	38	330	60.9
14	66°12′	174°34′	14a	Orange group, spring 1	14.0	6.4	36.23	6924	326	5289	67.11	10,007	20,950	157	232	92.5
21	66°33′	173°22′	21a	Levo-Tynyn group, spring 1	21.1	6.9	2.8	416	21	228	5.29	1555	1416	24	156	25.1
North-Eastern Domain (NWD)																
9	66°06′	169°49′	9b	Dezhnev group, central well	60.1	7.8	19.76	5527	205	1541	2.32	13,431	11,350	84	24	22.7
18	66°08′	170°17′	18a	Pykenlun group, spring 2	4.0	7.5	2.5	529	17	160	73.69	536	1349	34	171	7.4
19	66°19′	171°36′	19a	Танатап, ист. 2	4.7	n.d.	0.08	3.7	1.1	27	6.05	3.0	12.8	4.4	104	3.9
20	66°50′	171°34′	20a	Mamkin group, spring 1	11.8	n.d.	0.04	1.9	0.2	6.3	0.61	n.d.	7.0	1.6	37	2.9
Sea water (Horne, 1969)							35	10,760	387	413	1294		19,353	2712	142	

$(3–5)\times10^{-5}$ A/Torr. The resolution is $\approx$1000 allowing HD-^{3}He duplet to be completely separated. The total blanks of ^{4}He in the ampoule breaker, inlet line and mass-spectrometer chamber are 1×10^{-10} cm^3 STP. Reproducibility of isotope analysis (1σ) depending on the measured isotopic ratios is: 25, 10, and 3% for ^{3}He/^{4}He ~ 10^{-8}, ~10^{-7}, and ~10^{-6}, respectively; 20, 10, and 3%, for ^{4}He/^{20}Ne ~ 10^4, ~10^2, and 1, respectively; reproducibility of measurement of ^{4}He and ^{40}Ar concentrations is ±5% (1σ).

Control measurements of the ^{3}He/^{4}He ratio in two samples were made in Istituto Nazionale di Geofisica e Vulcanologia (INGV, Palermo, Italy) using GVI-Helix SFT mass-spectrometer. The results of these measurements are in a good agreement with those obtained in Russia.

Because of possible air contamination, measured value of the ^{3}He/^{4}He = R_{meas} was corrected (using ^{4}He/^{20}Ne ratio) applying the equation (Nagao et al., 1979; Giggenbach et al., 1993): $R_{corr} = [R_{meas}(^4He/^{20}Ne)_{meas} - R_{atm}(^4He/^{20}Ne)_{ATM}]/[(^4He/^{20}Ne)_{meas} - (^4He/^{20}Ne)_{atm}]$.

Table 2
Water temperatures, TDS contents, and gas phase composition from the Chukotka thermal springs.

Spring group ##	Sample index	Sampling year	T, °C	TDS, g/L	Concentration, vol.%						
					Chromatography					Mass-spectr.	
					CO_2	N_2	CH_4	O_2	He	He	Ar
Southern domain (SD)											
1	1a	2002	87.5	19.28	0.07	94.07	1.2	0.05	0.296	0.28	1.5
1	1b	2002	67.8	18.95	0.14	93.6	0.89	0.6	n.d.	n.d.	n.d.
1	1c	2002	65.3	17.96	0.05	94.1	0.97	0.15	n.d.	n.d.	n.d.
1	1d	2002	79	18.98	0.05	93.4	1.19	0.44	n.d.	n.d.	n.d.
2	2a	2002	77.7	1.47	0.07	97.9	0.13	0.06	n.d.	n.d.	n.d.
2	2b	2002	78.7	1.5	0.05	98	0.13	0.13	0.11	0.1	1.7
3	3a	2002	37.4	1.47	0.02	95.9	0.0002	3.02	0.043	0.04	1.3
4	4a	2002	43.1	4.78	0.07	96.8	0.0003	2.42	0.106	0.096	1.3
27	27a	2005	35.6	1.1	0.1	91.5	0.00001	3.5	n.d.	0.15	1.03
28	28a	2005	43	8.5	0.2	93.6	0.00004	2.3	n.d.	0.15	1.37
29	29a	2005	42.5	2.7	1.1	80.9	0.00005	12.4	n.d.	0.13	1.26
Kolyuchin–Mechigmen Zone											
5	5a	2002	60	5.23	1.04	96.4	0.78	0.57	0.199	0.17	0.94
5	5b	2004	56.5	4.6	1.37	96.9	0.83	0.29	n.d.	0.18	1.33
5	5c	2002	52.5	4.03	0.66	97.5	0.54	0.25	n.d.	n.d.	n.d.
6	6a	2002	89.7	3.93	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6	6b	2002	97	n.d.	57.63	40.1	0.84	0.85	0.246	0. 420	0.88
6	6c	2002	64.3	4.08	29.34	69.3	1.38	0.1	n.d.	n.d.	n.d.
7	7a	2002	20.1	9.26	92.63	3.4	0.0015	0.13	0.023	0.02	0.02
7	7b	2004	20.8	9.58	92.49	5.2	0.0027	0.15	n.d.	0.052	0.09
7	7c	2002	13.7	9.15	92	3.7	0.0016	0.38	0.021	n.d.	n.d.
7	7d	2004	17.9	9.38	94.59	3.3	0.0019	0.33	n.d.	0.024	0.08
8	8b	2002	55.1	3.4	4.89	93.6	0.0038	1	0.433	0.4	1.2
15	15a	2004	15.2	8.53	79.81	19.69	0.028	0.91	0.13	0.13	0.19
15	15b	2005	18.3	7.6	65.5	34.4	0.033	0.4	n.d.	0.16	0.16
16	16b	2005	5.2	8.2	37.4	59.5	0.02	0.2	n.d.	0.44	0.66
17	17a	2004	6.6	6.87	60.13	39.79	0.0047	0.12	0.39	0.44	0.37
17	17b	2005	3.1	7.9	72.8	22.3	0.0064	0.1	n.d.	0.18	0.31
30	30a	2005	11.4	6.6	33.2	65.5	0.028	0.2	n.d.	0.68	0.58
31	31a	2005	5.3	8.2	34.7	61.1	0.012	0.1	n.d.	n.d.	n.d.
32	32a	2005	5	7.8	25.4	71.6	0.011	0.8	n.d.	n.d.	n.d.
33	33a	2005	28.2	1.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
26	26a	2004	4.1	9.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
North-Western Domain (NWD)											
10	10a	2004	51.8	37.14	9.07	80.88	7.18	0.021	1.13	1.15	1.04
11	11a	2004	6.5	17.64	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
12	12a	2004	7.2	4.48	8.48	90.22	0.0026	0.026	0.74	0.750	1.01
13	13a	2004	64.9	3.45	1.38	94.41	0.23	0.37	0.4	0.370	1.66
14	14a	2004	14	36.23	8.35	89	0.037	0.1	1.75	1.7	0.77
21	21a	2004	21.1	2.1	0.6	91.5	0.0009	7.4	n.d.	n.d.	n.d.
North-Eastern Domain (NED)											
9	9b	2002	60.1	19.76	0.05	94.6	1.04	0.012	0.305	0.3	1.4
18	18a	2004	4	2.4	1.1	93.6	0.0004	6.9	0.08	0.078	0.89
19	19a	2004	4.7	0.08	1.1	89.4	0.0026	11.5	0	0.008	0.9
20	20a	2004	11.8	0.05	0.6	82.2	0.00001	17.2	0	0.006	0.79
22	22a	2004	15.6	6.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
23	23a	2004	7.2	5.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
24	24a	2004	13.8	0.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
25	25a	2004	4.1	2.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Notes: n.d. — not determined.

Isotope compositions of carbon (relative to PDB standard) and nitrogen (relative to air nitrogen) were measured by DELTA^{plus}XL (Thermo Finnigan) mass spectrometer following to IRM-MS technique in VSEGEI Enterprize lab. The reproducibility of gas isotope composition was equal 0.1–0.2‰. Control measurements of the $\delta^{15}N$ value in 8 samples were made in INGV lab by means of the same DELTA^{plus}XL (Thermo Finnigan) mass spectrometer connected to a chromatograph, as described in Eberhard et al. (1994). The results of measurements made in different labs are in a good agreement.

Besides, in water from the Chukotka Peninsula springs the values of δD and $\delta^{18}O$ (relative to SMOW standard) were measured in RAS Institute of ore deposit geology (RAS IGEM, Moscow); these results were discussed in detail elsewhere (Polyak et al., 2008).

The results of isotopic measurements and their analytical errors are shown in Table 3. They indicated regular spatial variations of chemical and isotopic compositions of thermal fluids and revealed their features in the zone, stretched out from the Kolyuchin Bay on the north-west up to Mechigmen Gulf on the south-east of the Peninsula.

4. Chemical composition of spring waters

The total content of dissolved solids, TDS, in the spring waters varies in a very wide range: in most cases, from 50–80 ppm up to ~20,000 ppm (Table 1). Moreover, in groups 10 and 14 TDS values to (36–37) × 10^3 ppm exceed the salinity of sea water, TDS_{sw} = 35,000 ppm (Horne, 1969). The compositions of spring waters are rather uniform differing

Table 3
Isotopes of He, Ar, N and C in the Chukotka thermal fluids.

Spring group ##	Sample index	He, vol.%	$^4He/^{20}Ne$	$^3He/^4He$, 10^{-8}		R_{corr}/R_{ATM}[a]	Ar, vol.%	$^{38}Ar/^{36}Ar$	$^{40}Ar/^{36}Ar$		Ar_{rad}/Ar, %	$^4He/^{40}Ar_{rad}$	N_2/Ar_{ATM}	$\delta^{15}N$	$\delta^{13}C_{PDB}$, ‰, CH_4	$\delta^{13}C_{PDB}$, ‰, C_2H_6	$\delta^{13}C_{PDB}$, ‰, CO_2	Lab[b]
				Meas.	Corr.			Meas.	Meas.	Corr.[c]								
Southern Domain (SD)																		
1	1a	0.28	287	30.5	30	0.21	1.5	n.d.	310	n.d.	4.7	4.2	66	1	−24.5	−32.7	−13.9	1, 2
1	1e	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.88	−18.9	n.d.	−10.7	2, 3
2	2a	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.9	n.d.	n.d.	n.d.	2
2	2b	0.1	47	26.7	27	0.19	1.7	n.d.	294	n.d.	0	n.d.	57	n.d.	n.d.	n.d.	n.d.	1
3	3a	0.04	33	44.4	44	0.31	1.3	n.d.	302	n.d.	2.2	1.5	75	0.09	n.d.	n.d.	n.d.	1, 3
4	4a	0.096	83	20.2	20	0.14	1.3	n.d.	306	n.d.	3.4	2.2	77	0.25	n.d.	n.d.	n.d.	1, 3
27	27a	0.15	112	35.7	35	0.25	1.03	0.1878	297.7	302	2.2	6.8	91	0.1	n.d.	n.d.	−20.4	2
28	28a	0.15	19	40.5	39	0.28	1.37	0.1871	294.8	298	0.8	14	69	0.5	n.d.	n.d.	−13.6	2
29	29a	0.13	2800	51	51	0.36	1.26	0.1873	297.1	299	1.1	8.7	65	0.4	n.d.	n.d.	−19.7	2
Kolyuchin–Mechigmen Zone (KMZ)																		
5	5a	0.17	137	51.3	51	0.36	0.94	n.d.	300	n.d.	1.5	12	104	n.d.	−24.6	−32.4	−11	1, 2
5	5b	0.18	24	80	80	0.57	1.33	0.1868	289.8	294	0	n.d.	73	0.4	n.d.	n.d.	n.d.	2
5	5e	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.31	n.d.	n.d.	n.d.	3
6	6a	n.d.	13	51.7	52	0.37	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3
6	6b	0.42	722	53.8	54	0.39	0.88	n.d.	316	n.d.	6.5	7.4	49	1.8	−35.1	−38.9	−4.4	1, 2
6	6c	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2	−34.4	−38.5	−6.1	2
7	7a	0.02	651	65.5	66	0.47	0.02	n.d.	290	n.d.	0	n.d.	165	0	n.d.	n.d.	n.d.	1, 3
7	7b	0.052	630	65.2	65	0.46	0.09	0.1862	297.1	303	2.5	26	58	n.d.	n.d.	n.d.	−5.6	2
7	7c	n.d.	75	55.8	56	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3
7	7d	0.024	400	62.9	63	0.45	0.08	0.1862	294.2	300	1.5	20	40	n.d.	n.d.	n.d.	n.d.	2
8	8b	0.4	213	55.5	56	0.4	1.2	n.d.	304	n.d.	2.8	12	80	0.86	n.d.	n.d.	n.d.	1, 3
15	15a	0.13	3220	88	88	0.63	0.19	0.1846	299.9	311	5	14	109	n.d.	n.d.	n.d.	n.d.	2
15	15b	0.16	250	92.6	93	0.66	0.16	0.1874	321.2	323	8.5	12	235	4.5	n.d.	n.d.	−6	2
16	16b	0.44	130	46.9	47	0.34	0.66	0.1873	302.3	305	3.1	22	93	2.2	n.d.	n.d.	−8.2	2
17	17a	0.44	5330	172	172	1.23	0.37	0.1877	322.4	324	8.8	15	118	n.d.	n.d.	n.d.	−8.4	2
17	17b	0.18	225	166	166	1.19	0.31	0.188	322.3	322	8.2	7.8	78	3.6	n.d.	n.d.	−9	2
30	30a	0.68	990	52.6	53	0.38	0.58	0.1886	304.7	303	2.5	48	116	2	n.d.	n.d.	−8.2	2
North-Western Domain (NWD)																		
10	10a	1.15	3640	44.9	45	0.32	1.04	0.1868	303.2	307	3.8	31	81	2.8	−36.3	−42.2	−7.2	2
12	12a	0.75	2800	51	51	0.36	1.01	0.1873	297	299	1.2	62	90	n.d.	n.d.	n.d.	−11.7	2
13	13a	0.37	1480	28	28	0.2	1.66	0.1875	295.1	297	0.5	44	57	1.6	−51.4	n.d.	−17.4	2
14	14a	1.7	8060	30.4	30	0.21	0.77	0.1876	306.1	307	3.8	61	120	n.d.	n.d.	n.d.	−12	2
North-Eastern Domain (NED)																		
9	9b	0.3	292	42	42	0.3	1.4	n.d.	296	n.d.	n.d.	n.d.	68	0.95	−36.1	−35.9	−18.8	1, 2, 3
18	18a	0.078	51	78	77	0.55	0.89	0.1877	292.3	293	0	n.d.	104	n.d.	n.d.	n.d.	n.d.	2
19	19a	0.008	4.95	57	52	0.37	0.9	0.1873	291.9	294	0	n.d.	99	n.d.	n.d.	n.d.	n.d.	2
20	20a	0.006	0.64	118.5	98	0.7	0.79	0.1872	292.4	295	0	n.d.	103	n.d.	n.d.	n.d.	n.d.	2
ATM		0.00052	0.317	140		0.93	0.1880		295.5			84	0					
ASW 5 °C		0.00018	0.25	140		1.71	0.1880		295.5			38				−7	[d]	

Notes.
[a] $R_{ATM} = 140 \times 10^{-8}$.
[b] Labs: (1) GI KNC RAN, (2) VSEGEI, and (3) INGV.
[c] $^{40}Ar/^{36}Ar$ was corrected from $\delta^{38}Ar$.
[d] Kipfer et al. (2002).

from that of sea water. As in the latter, Cl^- predominates among anions, but the secondary component is HCO_3^- (its content is enhanced in the KMZ springs), whereas SO_4^{2-} content is very low. Like in sea water, Na^+ prevails among the cations, and Ca^{++} is the subordinate component. However, the absolute Ca^{++} abundances (in ppm) are often noticeably higher than those in sea water and correlate positively with TDS values. It is observed both in the springs where $TDS > TDS_{sw}$ and others (groups 1, 4, 7, 9, 16). On the contrary, Mg^{++} content is almost negligible and increases only in KMZ springs enriched in HCO_3^- ion.

In terms of chemical composition the spring waters are qualitatively similar to brines contained in deep aquifers of sedimentary basins. This suggests that spring waters including those with maximal TDS values could result from mixing such brines with low-mineralized infiltration waters near the surface. At the same time, the increased TDS values can be of cryogenic nature: they could be resulted from transformation of subsurface water during permafrost development that causes the partial freezing of solutions and the increasing of salinity in residual liquid (Tolstikhin, 1941, and others). Therefore, up to now the origin of the over-marine TDS values in the Chukotka Peninsula springs remains obscure.

As a whole, TDS values do not correlate with water temperatures (Fig. 4). As in the case of temperature, chemical composition of dissolved solids and their quantity show no lateral trends, i.e. correlation with neither distance of springs from the sea (Fig. 5) nor geological setting. However, the data on chemical composition of subsurface waters make it possible to estimate their reservoir temperatures (temperatures at unknown depth where they are heated and enriched in dissolved solids) using empirical correlation relationships between the concentration of some components called hydrochemical or solute geothermometers (Fournier and Trusdell, 1973; Giggenbach, 1988; and others). The Na/K and Na/Li geothermometers, $T\ ^\circ C = 777/[\log(Na/K) + 0.7] - 273.15$ (Fouillac and Michard, 1981), and $T\ ^\circ C = 1000/[\log(Na/Li) - 0.14] - 273$ (Kharaka and Mariner, 1989) showed the best convergence of such indirect estimates for the Chukotka Peninsula springs. These estimates show regional differences in temperature of hydrothermal reservoirs located in different parts of the Peninsula. In the northern domains these estimates are too scarce for definite inferences. At the same time, as Fig. 6 suggests, the calculated reservoir temperatures in the southern domain (SD) are noticeably lower than those in KMZ. The specificity of KMZ is also evident in the features of gases discharging in thermal springs.

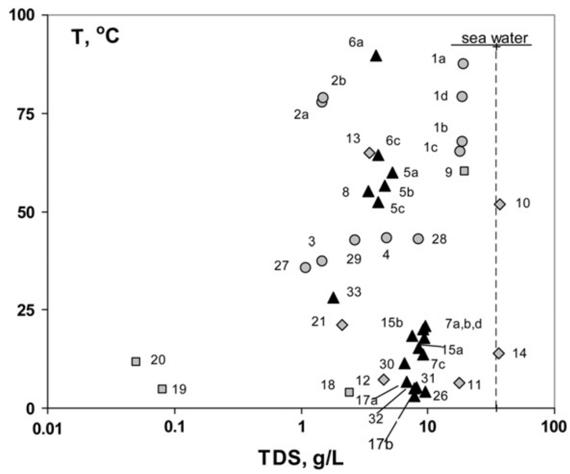

Fig. 4. The plot of TDS vs. spring water temperatures from different domains of the Chukotka Peninsula: KMZ (triangles), SD (dots), NWD (diamonds), and NED (squares). Data points correspond to spring groups numbered as Table 1.

5. Carbon dioxide

5.1. CO_2 content in gas phase

In most cases N_2 predominates in the gas phase: its concentration exceeds 50 vol.% in 22 groups and exceeds 90 vol.% in 16 groups (Table 1). The residual is mainly CO_2. CO_2 concentrations in the gas phase correlate with neither spring temperatures, nor TDS. However, heightened CO_2 contents distinguish the KMZ springs (Fig. 7A). Spring gases from 8 groups of this zone contain more than 25 vol.% of carbon dioxide, in three groups CO_2 content exceeds 70 vol.% and amounts up to 95 vol.% in group 7.

CO_2 is the main component of volcanic emanations; hence, it could trace hidden magmatic activity. CO_2 origin in the KMZ and other springs is clarified by isotope studies.

5.2. CO_2 isotopic composition

$\delta^{13}C$ values in CO_2 (measured in 18 samples, see Table 2) vary in a great range from −20.4 to −4.4‰ and probably reflect mixing two genetic components. The low $\delta^{13}C_{CO_2}$ values are observed in N_2-rich gases of springs located outside KMZ (Figs. 7B and 8). The only $\delta^{13}C_{CO_2}$ value in the north-eastern domain is equal to −18.8‰, the mean $\delta^{13}C_{CO_2}$ values in gases from southern and north-western domains are higher (−15.7 and −12.1‰, respectively). The probable source of this CO_2 is oxidizing sedimentary organic matter containing carbon with $\delta^{13}C \sim -25$‰. On the contrary, KMZ gases enriched in CO_2 show the maximal $\delta^{13}C_{CO_2}$ values amounting up to −4.4‰ in the hottest Mechigmen Springs (group 6). These "heaviest" $\delta^{13}C_{CO_2}$ values are similar to those in volcanic gases and correspond to the mantle carbon isotope composition (Galimov, 1968; Faure and Mensing, 2005). At the same time, source of "heavy" CO_2 could also be crustal carbonate matter too. In any case, isotopic data suggest that KMZ gases are enriched in the most hypogene carbon dioxide.

6. Helium

6.1. He content

Helium concentration, [He], varies in N_2-rich gases within 4 orders of magnitude, from 60–80 ppm in the NE domain (groups 20 and 19) to 11,500–17,000 ppm in the NW domain (groups 10 and 14, respectively). The highest He contents in gases from groups 10 and 14 are accompanied by over-marine TDS values (see above) and enhanced

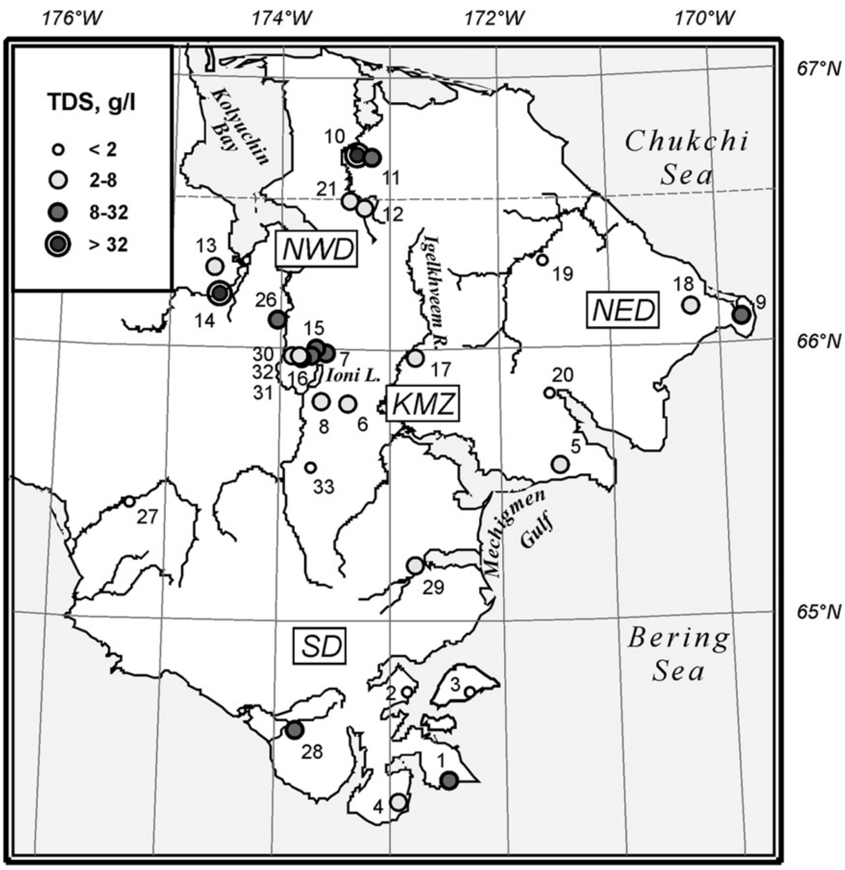

Fig. 5. The spatial variations of TDS values in waters from the Chukotka Peninsula springs.

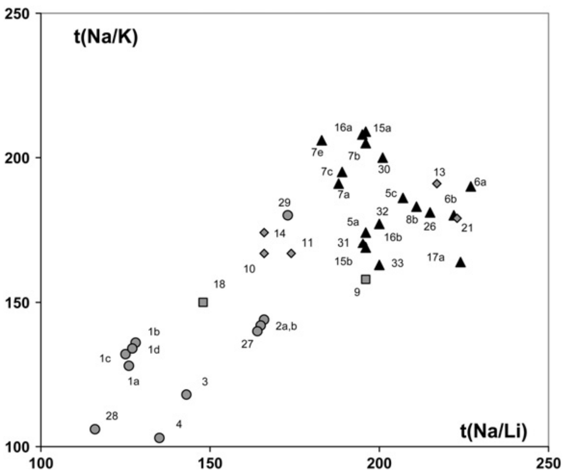

Fig. 6. The reservoir temperatures estimated by Na/K and Na/Li geothermometers in the different domains of the Chukotka Peninsula. Symbols and data point numeration as in Fig. 4.

[CO_2] contents, 9.07 and 8.35 vol.%, respectively (Table 2); besides, gas from group 10 is distinguished by maximal [CH_4] = 7.18 vol.%. These features of spring waters from NW domain indicate a very long residence of these waters in volatile-poor rocks (I.N. Tolstikhin, personal comment).

In the predominately CO_2-rich KMZ gases He concentration varies from 419 to 8600 ppm (3560 ppm in average). In N_2-rich gases from the southern domain of the Peninsula the mean [He] is noticeably lower (1350 ppm). The regional differences observed in He content calls for further special investigation.

6.2. He isotopic composition

Helium isotopes were studied in 23 spring groups. The $^4He/^{20}Ne$ values (4.95–8060) indicate a negligible admixture of atmospheric He in spring gases, so the correction of the measured R values for air contamination approaches the experimental error or below. The only exception is a sample from group 20 with $^4He/^{20}Ne = 0.64$, where R corrected is ~20% lower than R measured.

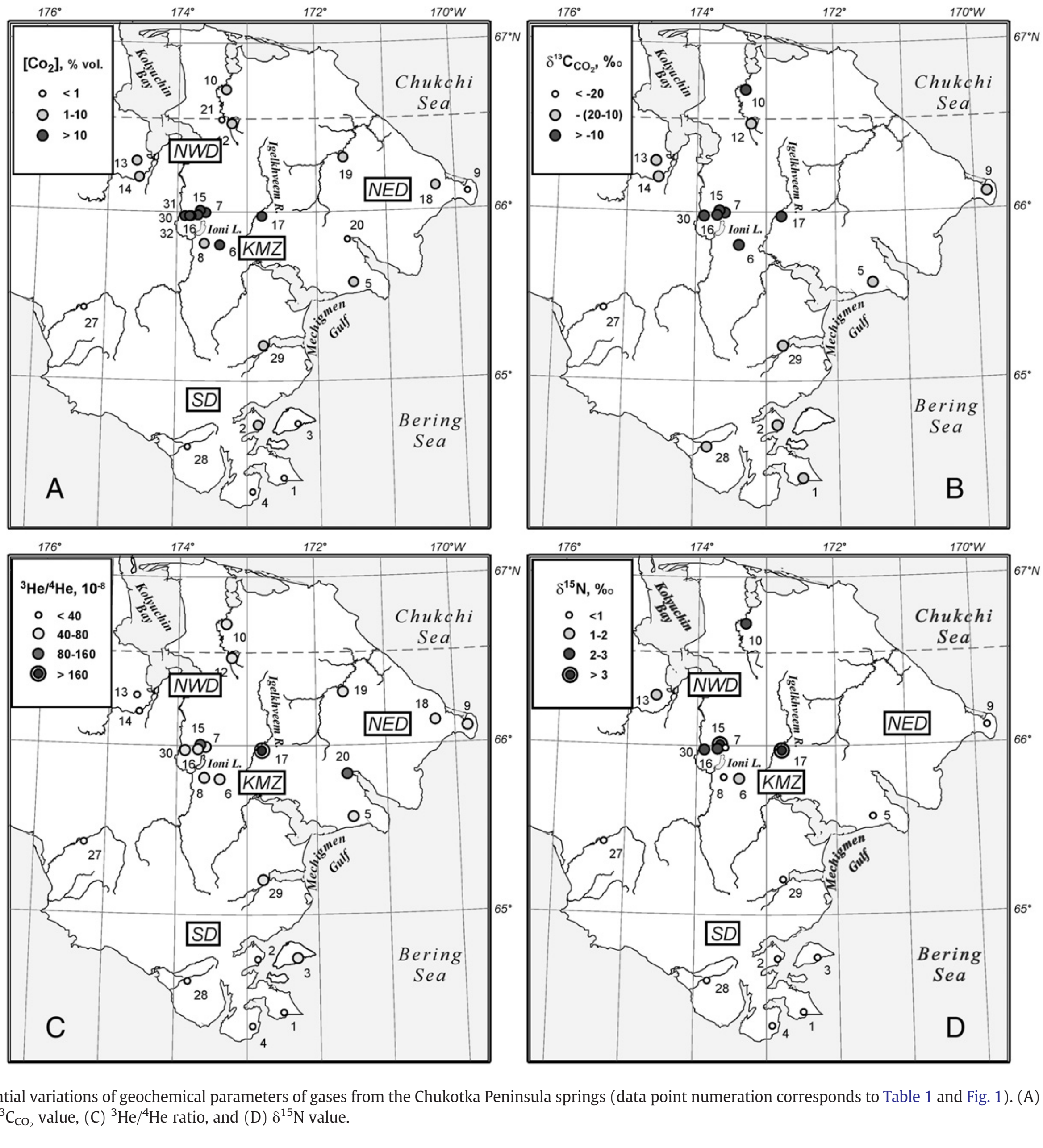

Fig. 7. The spatial variations of geochemical parameters of gases from the Chukotka Peninsula springs (data point numeration corresponds to Table 1 and Fig. 1). (A) Concentration of CO_2, (B) $\delta^{13}C_{CO_2}$ value, (C) $^3He/^4He$ ratio, and (D) $\delta^{15}N$ value.

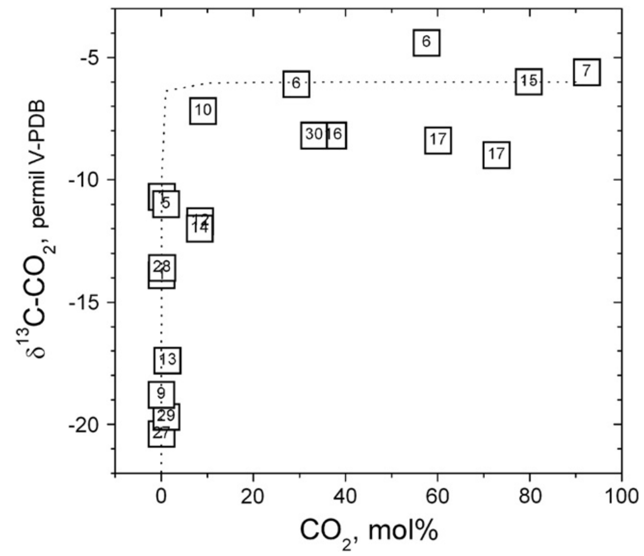

Fig. 8. Plot of $\delta^{13}C_{CO_2}$ and the measured concentration of CO_2 in gases from the Chukotka Peninsula springs. A dotted line shows mixing with a suggested sedimentary end-member (CO_2 = 0.02 vol.%; $\delta^{13}C$ = −25‰) and "deep" CO_2 with $\delta^{13}C$ = −6‰ (numbers in symbols as in Table 1).

Helium isotope ratios indicate contributions of mantle-derived He and radiogenic crustal He in all samples (Fig. 9). The R values vary from $20.2\times10^{-8}=0.14R_a$ in spring with water temperature of 79.7 °C (group 2) to $172\times10^{-8}=1.23R_a$ in the coldest (~3 °C) spring (group 17). Nevertheless, there is no general correlation between the R values and temperatures. The extreme R values mentioned above correspond to contribution of MORB-like helium at 2.2% and 14%, respectively, and canonic radiogenic helium produced in the crust and prevailing in the samples. The repeated sampling of the same springs in groups 5, 7, 15 and 17 revealed that the $^3He/^4He$ value is almost constant in time. Hence, the R values in different groups indicate spatial variations of He isotope composition in the Chukotka Peninsula springs (Fig. 7C) rather than temporal fluctuations.

The mean R values in different domains of the Peninsula reveal a regular character of these variations. In the southern domain, the contribution of mantle-derived He in spring gases is quite noticeable: here $R_{mean}=35.2\times10^{-8}=0.25R_a$ is identical to that determined in fluids from the continental crust activated in the Late Cretaceous (Polyak and Tolstikhin, 1985). This inference agrees with the same age of Okhotsk–Chukotka volcano-plutonic belt (Belyi, 2008). Similar R values are observed in springs located to the west from Kolyuchin Bay.

In two other groups of the same NW domain the R values are higher: $(45\text{–}51)\times10^{-8}=(0.32\text{–}0.36)R_a$. In the NE domain composed of Pz and Pcm rocks, they are increasing further to $98\times10^{-8}=0.7R_a$ indicating re-activation of the domain by mantle-derived intrusions.

The KMZ springs show the highest $R_{mean}=72.6\times10^{-8}=0.52R_a$. The maximal $R=172\times10^{-8}=1.23R_a$ was measured, as noted above, in springs of group 17 situated near to one of the manifestations of Late Cenozoic basalts mapped by Kryukov (1980). These springs are situated along the same latitude (~65°59′) together with other CO_2-rich springs having the high R values (groups 7, 15, 16, 30) and thus probably indicate a deep fault. The epicenters of weak earthquakes are grouped along the same latitude, as shown in Fujita et al. (2002, Fig. 6a). Along the KMZ strike, the R values decrease both to the north-west and the south-east of the maximum seen in group 17. Such a linear trend in changeability of the R values is typical feature of continental rift zones (Polyak, 2004).

Therefore helium isotopic signatures of the ChP thermal springs reflects more than one phase of mantle He supply into the crust of the Precambrian Chukotka–Seward microcontinent. He–Sr isotope correlations in products of recent volcanic and hydrothermal activity in Italy (Polyak et al., 1981), Indonesia (Hilton and Craig, 1989), and in other places indicate that silicate melts can act as mantle He carriers. Therefore, the phases of He supply from the mantle into the crust should be identified with impulses of magmatic activity. Helium isotopic composition in springs from the southern domain of the Peninsula, as noted above, agrees well with the Late Cretaceous age of Okhotsk–Chukotka volcano-plutonic belt. However, the higher R values in other springs indicate the later thermal activation. The maximum R values in gases imply that the latest (Cenozoic) intrusions of mantle magmas into the Peninsula crust took place within KMZ. The Pliocene activity of Enmelen volcanoes and the Quaternary volcanism on St. Lawrence Island envisage a young (N_2-Q?) age of some undated basalts manifested sporadically within KMZ. It should be noted that spring groups 1–4 with the lowest R values are situated more than ~300 km from Enmelen volcanoes but group 28 with similar composition of helium is located nearer to them (~50 km). In the latter case, the low R values seem to indicate a relatively small size of a volcanic chamber but the direct data on this matter are not available.

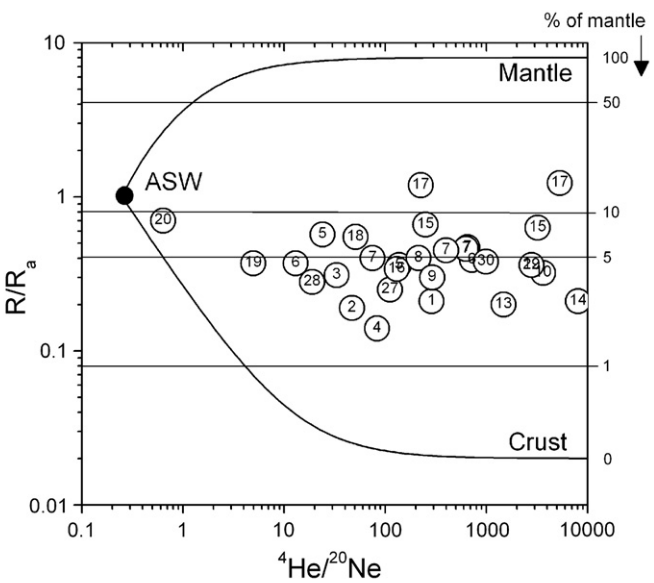

Fig. 9. He–Ne diagram for gases from the Chukotka Peninsula springs (numbers in symbols as in Table 1). See text for discussion.

7. Argon

7.1. Ar content

Ar concentration, [Ar], in the ChP gases varies from 0.02 vol.% to 1.7 vol.% In six CO_2-rich springs of KMZ [Ar] does not exceed 0.88 vol.% (on average, 0.52 vol.%), but in two N_2-rich springs (groups 5 and 8) it amounts to 1.20–1.33 vol.% The latter values are similar to those in the N_2-rich springs from the southern domain where [Ar] = (1.03 ÷ 1.70) vol.% with an average value of 1.35 vol.%. In the springs located in NW and NE domains, [Ar] = (0.77 — 1.40) vol.%.

The data reported show that in some samples the Ar content (mostly, of atmospheric origin, as it is shown below) is higher than that in the atmosphere. It partly results from enrichment of subsurface waters in atmospheric Ar as compared with less soluble N_2 at the contact air–water. The following formation of free gas phase in underground waters was evidently very quick as judged from isotopic data considered below.

7.2. Ar isotopic composition

Isotope analysis of argon made it possible to identify and to calculate the fraction of atmospheric Ar and to assess the contribution of other gases of the same origin. Atmospheric Ar is dominated in spring gases of the Chukotka Peninsula: $^{40}Ar/^{36}Ar$ ratios in the samples studied do not differ much from that inherent atmosphere (295.5). In order to identify deep radiogenic component of Ar ($^{40}Ar_{rad} = Ar^*$) in this situation, it is necessary exclude the possible influence of Ar isotope fractionation. The presence of three stable isotopes of argon allows controlling this possibility: the relative deviation of $^{40}Ar/^{36}Ar$ ratio in a sample from that in air has to exceed almost twice the deviation of the ratio of atmospheric Ar isotopes ($^{38}Ar/^{36}Ar$). However, such measurements are extremely rare, although they are useful because of the possible association of magnitude of the isotope effect and the rate of degassing of ground water.

The measurements of $^{40}Ar/^{36}Ar$ ratio showed locally some enrichment of gases in ^{36}Ar as compared with atmospheric air. This enrichment indicates Ar isotope fractionation during the degassing of subsurface waters that distorts the $^{40}Ar/^{36}Ar$ ratio in fluids. This conclusion is supported by measurements of $^{38}Ar/^{36}Ar$ ratio in 19 samples: 18 of them showed an enrichment of gases in ^{36}Ar at the mean values of $^{38}Ar/^{36}Ar = 0.1874$, that is 0.3% lower than that in atmosphere (0.1880). Such a feature of the studied fluids evidently indicates their non-equilibrium degassing of subsurface waters because of high velocity of the process.

In KMZ, CO_2-rich gases from groups 5 and 7 (in the latter CO_2 content approaches 95 vol.%) distinguish by the minimal values of $^{38}Ar/^{36}Ar$ ratio those are 1.0–1.8% lower than that in atmosphere. Evidently, in these places the velocity of free gas phase formation should be maximal (possibly, corresponding to boiling up of subsurface waters).

Ar isotope fractionation leads to anomalous ratios of atmogenic ^{38}Ar and ^{36}Ar isotopes and distorts the $^{40}Ar/^{36}Ar$ values used to estimate the contribution of excess radiogenic argon $^{40}Ar_{rad}$. In order to exclude fractionation effect, the measured $^{40}Ar/^{36}Ar$ values should be corrected according to the following equation: $(^{40}Ar/^{36}Ar)_{corr} = (^{40}Ar/^{36}Ar)_{meas} \times (1 + \Delta)$, where $\Delta = -2\delta^{38}Ar$; $\delta^{38}Ar = [(^{38}Ar/^{36}Ar)_{meas}/(^{38}Ar/^{36}Ar)_{atm}] - 1$. After this procedure we obtained the $^{40}Ar/^{36}Ar$ values close to the atmospheric one (295.5), or slightly higher.

The over-atmospheric values of $^{40}Ar/^{36}Ar$ ratio were found out in 18 of 23 spring groups. A contribution of excess $^{40}Ar_{rad}$ varies from 0 to 8.8% of total Ar. In the north-eastern domain this contribution was not observed. In the north-western and southern domains the $^{40}Ar_{rad}$ contribution locally amounts up to 3.8–4.8% [Ar], respectively, and amounts up to the highest values in the KMZ gases, where the mean value of $^{40}Ar/^{36}Ar = 308.8$ and the maximum amounts to 322.4. The latter was measured in gases from Nel'pygen Springs (group 17) together with the highest value of $^3He/^4He = 1.72 \times 10^{-6} = 1.23R_a$ noted in Section 6.2. Therefore the $^{40}Ar/^{36}Ar$ values indicate locally the presence of some admixture of non-atmospheric Ar.

The absolute dominance of atmospheric components is typical for near-surface aquifers where discharging fluids are contaminated by air gases to the greatest extent. An increase in the fraction of excess (radiogenic) Ar indicates higher temperatures (and, therefore, more complete degassing) of rocks supplying $^{40}Ar_{rad}$ in subsurface fluids.

It is interesting to compare the isotopic compositions of argon and helium in the same samples. This comparison is graphically made in Fig. 10. The plot is based on the measured values of $^{40}Ar/^{36}Ar$ without considering isotope fractionation. The distribution of data points seems to reveal two trends. The first trend reflects mixing air component (ASW) and crustal gases with low values of R and high values of $^{40}Ar/^{36}Ar$, corresponding to gases discharging out of KMZ. The second one shows the enrichment of crustal gases in radiogenic argon and helium mantle. This statistically significant trend was observed only in gases KMZ.

7.3. $^4He/^{40}Ar_{rad}$ ratio

$^4He/^{40}Ar_{rad}$ ratio has been considered as genetic criterion long ago. The values of this ratio were determined in 280 natural gas field of the former Soviet Union (Voronov et al., 1974). It has been found that this ratio varies in a wide range (average value is close to 12) and is different in tectonic units of different age. The analysis of different correlations and model calculations showed that the main cause of $^4He/^{40}Ar_{rad}$ variations is the difference of temperature degassing of source rocks. In the range of 60–300 °C typical of sedimentary sequences, the calculated $^4He/^{40}Ar_{rad}$ ratio values vary from 40 to 7. Their scattering results from strong difference in He and Ar loss from rocks at different temperatures (at low temperature, Ar escapes from source rocks less intensively than He).

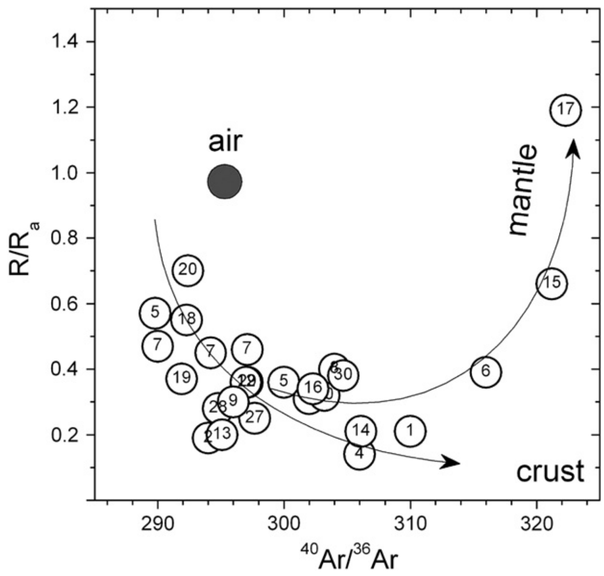

Fig. 10. The plot R/Ra vs. $^{40}Ar/^{36}Ar$ for gases from the Chukotka Peninsula springs (numbers in symbols as in Table 1). See text for discussion.

Therefore, the $^4He/^{40}Ar_{rad}$ ratio can serve as an indirect indicator of subsurface temperatures. Minimal values of this ratio indicate a hotter environment stimulating loss of both radiogenic isotopes from parent rocks (Prasolov, 1990). In the Chukotka Peninsula gases the values of this ratio vary in a wide range. The gases with low $^4He/^{40}Ar_{rad}$ (<8) are observed in the southern domain, with the mean value of 6.2. In KMZ gases the mean $^4He/^{40}Ar_{rad}$ value was unexpectedly found to be higher. However, gases from both the coldest Nel'pygen springs (group 17, where $^3He/^4He$ and $^{40}Ar/^{36}Ar$ ratios are maximal), and the hottest Mechigmen springs (group 6) show the $^4He/^{40}Ar_{rad}$ values similar to those in the southern domain indicating the same degassing temperatures about ~500 °C according to Prasolov (1990). Keeping in mind the high concentrations of He in the ChP gases, an error of $^4He/^{40}Ar_{rad}$ estimations is unlikely.

8. Nitrogen

8.1. N_2 components

N_2/Ar_{atm} ratios in all of samples were found to be higher than those in ASW (~40). In a half of the springs sampled this ratio lies between those in ASW and the atmospheric value (84). These intermediate values reflect complicated processes of interaction of air bubbles with descending water flow in the recharge area, as well as solubility-controlled fractionation of N_2 and Ar during water degassing at recharge. Therefore N_2/Ar_{atm} ratios (even those exceeding the atmospheric value) could hardly be considered as a firm evidence of non-atmogenic N_2 contribution. Nevertheless, the values of $N_2/Ar_{atm} > 84$ were found in another half of the springs. Almost all of these springs are located in KMZ. As noted above, gases from these springs are enriched in carbon dioxide and statistically significant positive correlation between CO_2

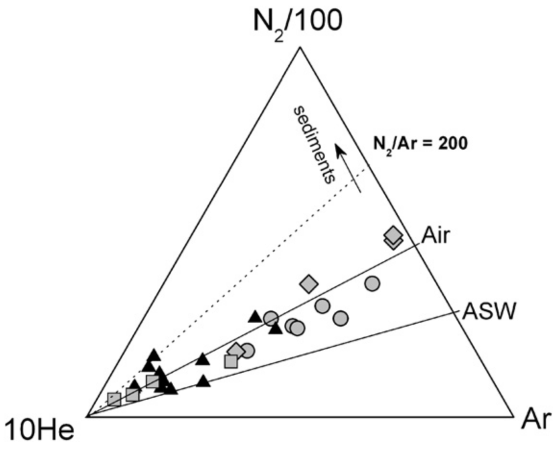

Fig. 11. N_2–He–Ar triangular plot (e.g., Giggenbach, 1996). Symbols as in Fig. 4, see text for further discussion.

and N_2/Ar_{atm} ratio is observed. This correlation is an argument in favor of non-atmospheric origin of N_2 excess in KMZ gases.

General N_2–He–Ar systematics of the ChP spring gases are plotted in Fig. 11. This diagram shows that the studied gases were formed from a He-rich end-member contaminated with air to variable extents. Some gases contain excess (sedimentary) besides atmogenic nitrogen consistent with the N_2/Ar ratios higher than the air value of 84. Distribution of compositional points on a triangular plot reflects neither differences in the predominant component of the gas (N_2 or CO_2), nor the peculiarities of the spring localization.

The most convincing evidence of the N_2 excess origin follows from isotopic data.

8.2. N_2 isotopic composition

In order to understand the N_2 sources its isotopic composition was measured in 18 spring groups (relative to the atmospheric standard, $\delta^{15}N_{atm} \equiv 0$). The $\delta^{15}N$ value in the ChP gases varies in the range of 0.0 to +4.5‰. Hence, the contribution of the mantle-derived nitrogen can be ruled out, since investigations of He, Ar and N_2 isotope systematics in gases from Kamchatka, Kuriles and other segments of the mobile belts allowed $\delta^{15}N \approx -6$‰ to be suggested for mantle-derived nitrogen (Prasolov et al., 1990). The same value of $\delta^{15}N_{man} = -5$‰ was proposed using $\delta^{15}N_{atm}$ vs. $^{40}Ar/^{36}Ar$ correlation in the MORB sample (Marty and Humbert, 1997).

Even lighter nitrogen with $\delta^{15}N = -15$‰ was found out in hydrothermal fluids of Iceland mantle plume (Inguaggiato et al., 2009). At the same time, hydrothermal gases from the Jalisco Block (Mexico), Volcano Isl. (Aeolian Arc), and Nisiros Isl. (Aegean arc) contain heavy nitrogen with $\delta^{15}N \approx +(4.5 \div 5)$‰ (Inguaggiato et al., 2004). In the cited paper, appearance of such nitrogen was attributed to thermal metamorphism of the continental crust. In this context it should be noted that N_2 of the similar isotopic composition ($\delta^{15}N \approx +5$‰) is often encountered in oil–gas pools (Prasolov et al., 1990). In any case, the N_2 isotopic composition together with the $N_2/^{40}Ar_{atm}$ ratio values (see Table 2) indicates dual origin of nitrogen in the ChP gases: one of its source reservoir is the atmosphere, the other is the crust.

The enhanced $\delta^{15}N$ values (in relation to atmospheric nitrogen) are grouped in KMZ (Fig. 7D). $\delta^{15}N$ values in the ChP springs correlate positively with both $^{40}Ar/^{36}Ar$ ratios (Fig. 12A) and $\delta^{13}C_{CO_2}$ values (Fig. 12B). This correlation suggests similar reasons for the enrichment of both gases in heavy isotopes and invites further investigations.

9. Hydrocarbons

Methane concentrations in bubbling gases vary from very low values of several ppmv to a relatively high value of 7.18% in a spring of the NW part of the peninsula (sample #10). Carbon isotopic composition in methane was determined in 8 samples. The $\delta^{13}C_{CH_4}$ values vary from −51‰ to −19‰. The isotopically heaviest methane was found in gases from the southern part of the Peninsula (−18.9‰, sample #1), whereas methane with $\delta^{13}C = -51$‰ was analyzed in the north-western part (sample #13). The range of the isotopic composition of CH_4 corresponds in general to a thermogenic source of hydrocarbons (e.g., Schoell, 1983). There is no correlation between isotopic composition of methane and its concentration, as well as with the isotopic composition of CO_2 (Table 3).

Six samples were used for determination of carbon isotopic composition in ethane. Values of $\delta^{13}C(C_2H_6)$, varying from −42.2 to −32.4‰, are isotopically lighter than those in co-existing methane, contrary to a common isotopic behavior of these two components in thermogenic hydrocarbons. Similar behavior has been observed in gases of Siberia, in some sites of Precambrian shields, in several oil–gas fields of China (Prasolov et al., 1990; Li et al., 2011). Such an inverse isotopic trend among light hydrocarbons is common for gases from serpentinite-hosted submarine springs and fumaroles and many authors attributed this trend as an indicator of abiogenic origin of hydrocarbons (Sherwood Lollar et al., 2002; Taran et al., 2010).

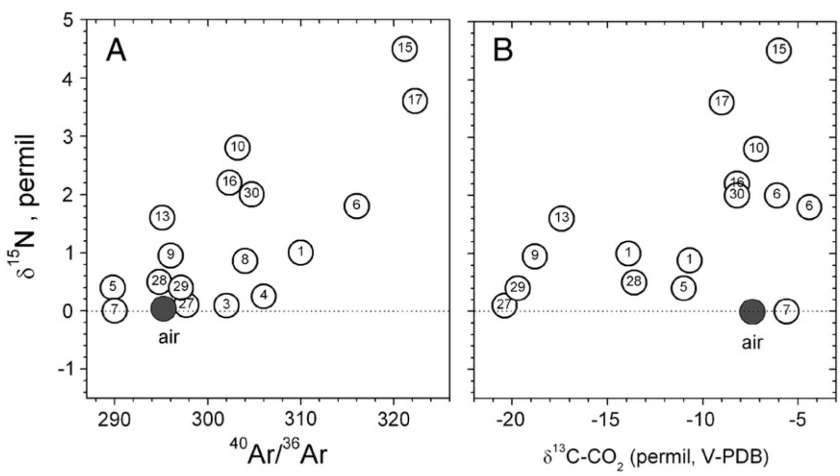

Fig. 12. The plots $\delta^{15}N$ versus $^{40}Ar/^{36}Ar$ (A) and $\delta^{15}N$ versus $\delta^{13}C_{CO_2}$ (B) for gases from the Chukotka Peninsula springs (numbers in symbols as in Table 1). A positive correlation can be seen on both plots indicating that positive values of $\delta^{15}N$ are associated with both more radiogenic Ar and isotopically heavier CO_2. See text for further discussion.

Prasolov (1990) was the first who explained this effect by mixing of gases from different sources (see also Jenden et al., 1993).

10. Conclusions

The main features of thermomineral springs discharged in the Kolyuchin–Mechigmen Zone, distinguish them from other springs of the Chukotka Peninsula:

- maximal enrichment in mantle-derived helium (up to 14% of the total He);
- enrichment of gas phase in carbon dioxide (CO_2 concentration amounts up to 95 vol.%);
- contribution of non-atmogenic nitrogen;
- enrichment of CO_2, Ar and N_2 in heavy isotopes;
- maximal reservoir temperatures estimated by solute geothermometers.

Specificity of KMZ is also manifested in isotopic composition of spring waters. It was studied and described in many detail in Polyak et al. (2008). This investigation showed that waters of the Chukotka Peninsula springs including those discharged in the immediate vicinity of the sea coasts differ sharply from the marine waters in D and ^{18}O contents: δD and $\delta^{18}O$ values in them vary in relation to SMOW from −134.2 to −92.5‰ and from −17.6 to −10.5‰, respectively. It is particularly remarkable that "lightest" waters ($\delta D < -120$‰) discharges in CO_2-enriched springs close to Ioni Lake in the KMZ center. In subsurface ices from the Chukotka permafrost sequences δD and $\delta^{18}O$ values decrease somewhere down to −223‰ and −29.2‰, respectively (Vasil'chuk and Kotlyakov, 2000). Therefore, melting of the permafrost could be a possible explanation for the enrichment of H_2O in light isotopes. This explanation appears to be plausible taking in mind the features of the spring gases considered above. If so, H_2O isotopic composition could be considered as one more indirect sign of higher thermal activity in the KMZ interior.

In total, these concerted features represent a consistent data system which can be interpreted as complex reflection of the Late Cenozoic upwelling of mantle-derived basic melts supplying into the crust helium enriched in ^3He and thermal energy that causes metamorphism of rocks and intensifies permafrost degradation. This inference is in agreement with geological and geophysical data on the recent geodynamic activity in the Chukotka Peninsula and neighbor ocean regions.

Acknowledgments

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