Stable and noble gas isotopic study of thermal and groundwaters in northwestern Hokkaido, Japan and the occurrence of geopressured fluids

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Thermal and groundwaters are distributed along the west coast and in the inland region of Northwestern Hokkaido, Japan. The waters in the latter group have relatively high temperatures. Stable (D, O) and noble gas isotopic compositions of 23 thermal and groundwaters were analyzed to investigate their origins. The Cl concentrations vary from 45 to 19,300 mg/L and the δD values are in the range of -90 to -8‰ . The δD – $\delta^{18}O$ plots show a linear relationship which can be explained by a simple mixing of local meteoric waters and altered sea water, with oxygen isotopic shift of 5‰ . However, a δD –Cl plot shows that there is also a contribution of an additional water component of different origin. This 3rd component has a δD value of -20‰ and Cl concentration of 6,000 mg/L. Multivariate statistical analysis of the observed chemical and isotopic compositions using the code M3 (M; multivariate mixing and mass balance) also supports the view that the Toyotomi thermal water has the composition closest to that of the 3rd groundwater component. This component is regarded as a geopressured fluid.

The $^3\text{He}/^4\text{He}$ ratios in these waters are in the range of $(0.1\text{--}5) \times 10^{-6}$, which indicate contributions of both mantle and crustal He to the thermal and groundwaters in the studied area. The Toyotomi thermal water has a $^3\text{He}/^4\text{He}$ ratio of 5.5×10^{-7} , and a high $^3\text{He}/^{20}\text{Ne}$ ratio (~ 700). These results indicate a crustal He input with a small amount of mantle-derived He and imply that the 3rd groundwater component is of deep origin. On the basis of isotopic and chemical compositions, 5 of 23 samples studied groundwater and thermal waters are contributed by a geopressured fluid component. The results show that geopressured fluids with a δD value of -20‰ and Cl concentration of 6,000 mg/L are widely distributed in northwestern Hokkaido.

Keywords: geopressured fluid, hydrogen isotope, oxygen isotope, helium isotope, Hokkaido

INTRODUCTION

One of Professor Hitoshi Sakai's contributions to earth sciences was the identification of several groups of thermal waters in Japan, based on their isotopic and chemical compositions. He employed isotopic data to constrain the origin of Arima and coastal type waters (Sakai and Matsubaya, 1974, 1976) and also applied these data to interpret the origins and evolution of Kuroko ore forming fluids (Hattori and Sakai, 1979). In these papers, it was also recognized that the isotopic composition of fossil sea water differed from that of the original sea water

owing to interaction with the surrounding rocks. In several areas, fossil sea water was found to have $\delta^{18}O$ values of $+5$ to $+8\text{‰}$ due to the oxygen isotopic shift caused by the interaction, but to retain almost the same Cl concentration as fresh sea water (e.g., Sakai and Matsubaya, 1974; Mizukami *et al.*, 1977; Shibata *et al.*, 2005).

At depths below *ca.* 2 km in sedimentary regions associated with oil and/or natural gas, formation waters tend to be geopressured fluid with pressures between hydrostatic and lithostatic values (e.g., Myers, 1968; Jones, 1970; Oki *et al.*, 1999; Xu *et al.*, 2006). The δD and $\delta^{18}O$ data show that most geopressured fluid can be explained as a mixture of fossil sea water and local meteoric water, with an oxygen isotope shift due to rock-water interaction. Recently, fluids that have oilfield-like characteristic, with unusually high δD (-20‰) and low Cl concentrations (*ca.* 6,000 mg/L) have been observed along faults in the Horonobe area (Ishii *et al.*, 2006). These fluids might have originated as a mixture between sea water and

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Fig. 1. Localities of water and gas sampled. Geological map was quoted from Geological Survey of Japan (2002). Sample numbers correspond to those in Tables 1 and 3.

local meteoric water and then undergone compositional changes during diagenesis. However, the detailed mechanism responsible for the apparent D enrichment and Cl depletion of the fluids are presently unclear. One possibility is that mixing occurred between connate water and water produced by dehydration. Possible candidate dehydration reactions during progressive burial are the transition from opal A to C and/or transformation of smectite to illite with or without heating.

In mud volcanoes, formations created by geo-excreted liquids and gases, overpressured multiphase pore fluids (water and dissolved gases, mainly methane) are also rec-

ognized and are located mostly above strike-slip faults. The sediment is fluidized by rapid advection of pore fluids through the sedimentary mass along a conduit fault (Brown, 1990). Although chemical and isotopic studies of the expelled fluids are very scarce, this type of fluid might originate at least partly in dehydration in a subduction zone. The main dehydration process is thought to be a transition from smectite to illite similar to that for geopressured fluids observed in sedimentary basins (e.g., Shih, 1967; Sokolov *et al.*, 1968; Valyaev *et al.*, 1985; Dia *et al.*, 1995, 1999; Bechtel *et al.*, 2000).

He, Ne and Ar isotopic ratios and concentrations of

noble gases in groundwaters in Japan have been analyzed and give us the information of their origin and formation process (e.g., Sano and Wakita, 1985, 1988; Umeda *et al.*, 2006; Sano and Nakajima, 2008; Morikawa *et al.*, 2008). In the studied area, the He and Ne isotopic ratios were analyzed for groundwaters in Horonobe (Nagao *et al.*, 2003) and three thermal waters in northern Hokkaido (Sano and Wakita, 1985). These results show that the R/Ra is less than 0.2 (where R and Ra are the sample and atmospheric $^3\text{He}/^4\text{He}$ ratios (1.39×10^{-6}), respectively) and the $^4\text{He}/^{20}\text{Ne}$ ratio of 1000 and that most of He and Ne are of deep origin.

The aim of the present study is to research the distribution of geopressed fluid with high δD and low Cl concentration near the Horonobe area, Hokkaido, and to compare the characteristics of these waters with their rare gas isotopic compositions as well as other published data.

OUTLINE OF GEOLOGY AT SAMPLING SITES

The studied region is located in the northwestern Hokkaido (Fig. 1), which is divided by Mesozoic rocks into west and east zones (Geological Survey of Hokkaido, 1992). The west zone consists of late Jurassic to Cretaceous rocks, comprising of mainly greenstones, cherts, siliceous mudstones, and so on. This zone includes serpentine and mafic igneous rocks, which have been metamorphosed to form high-pressure metamorphic rocks. The east zone is mainly composed of homogeneous Cretaceous lithologies with fine-grained turbidite and melange facies. The Paleogene system is distributed in the western part of the Paleozoic–Mesozoic Group, and includes the main coal fields of Hokkaido, which are aligned from south to north. There are older volcanoes, which formed during the Pliocene–Middle Pleistocene and newer ones formed in the early Pleistocene–late Pleistocene. Large thickness of felsic pyroclastic flow deposits are distributed in the central Hokkaido area. Marine argillaceous sediments of Late Miocene age are widely distributed in the northern part of the central basin (Tempoku–Haboro). These sediments consist of diatomite, porcellanite and siliceous shale and are divided, in ascending order, into the Wakkanai and Koetoi Formations based on lithology; the former is composed mainly of hard shale, while the latter is mainly composed of diatomite and diatomaceous mudstone.

In the northern Hokkaido siliceous Neogene rocks are cut by the Omagari Fault and deformed by an anticline that began to grow between 2.2 and 1.0 Ma, possibly due to the beginning of active tectonism in and around this area (Ishii *et al.*, 2006a). The Omagari Fault is surrounded by a fault zone, about 120 m wide, that consists mainly of the damage zone, and is relatively permeable. A magnetotelluric survey showed several high-resistivity

zones, one of which corresponds to the Omagari Fault as inferred from reflection seismic surveys. The high-resistivity zones are correlated with bodies of low-salinity water, which suggests that meteoric water has infiltrated through the permeable Omagari Fault zone (Ishii *et al.*, 2006b).

In Hokkaido, there are many occurrences of thermal water with a temperature of higher than 25°C. These waters are mainly distributed within high heat flow zones corresponding to an extension of the Tohoku–Japan Arc in the western Hokkaido and to the southwestern end of the Kuril Arc in the central-eastern Hokkaido. These zones coincide, for the most part, with the distribution of Quaternary volcanoes. No active volcanoes occur in the studied area.

SAMPLE COLLECTION AND ANALYTICAL PROCEDURES

Details of sampling sites are provided in Table 1. Samples of water from near the coast (No. 1 to 10) were obtained from wells, with depths of 371 to 1807 m. This region is widely underlain by marine argillaceous sediments of Late Miocene age, which consist of diatomite, porcellanite and siliceous shale. Almost all the waters from the wells occur in the sedimentary rocks. The other waters from inland were collected from hot springs, wells, and closed coal mines. In the area, pre-Tertiary sediments are present and locally contain coal-bearing strata.

In the present paper, water samples are grouped as thermal waters (>25°C) and groundwaters (<25°C) on the basis of the outlet temperature. The maximum temperature is 49.9°C in Sample No. 2 (Tomamae). Water samples were collected in plastic bottles (1 L volume) from 30th August to 2nd September 2004. The sampling points are shown in Table 1 and Fig. 1. Sampling bottles used for the noble gas study were made of a low He-permeability glass containing Pb. Each bottle had an internal volume of about 50 cm³ and high-vacuum stop-cocks were attached to both ends. Water was introduced directly into each glass bottle from the sampled water source through plastic tubing to avoid air contamination. After through rinsing with flowing water, the stop-cocks were closed. At several sampling sites, as shown in Table 1, we collected free gases that were separated from waters using the same type of glass bottle.

Dissolved ion concentrations were measured with conventional methods. The major anions Cl and SO₄ in filtered water samples were analyzed with a Dionex DX-120 ion chromatograph using an IonPac As14 column. Alkalinity was determined using standard titration with HCl. Cations were analyzed with ICP-MS and ICP-AES at the Naka Energy Research Laboratory, Energy Project and Technology Center, Mitsubishi Materials Corpora-

Table 1. Sample descriptions

Sample No.	Type*	Locality	Sample site	Geology	Rock type	Depth of well (m)	Screen depth** (m)
1	1	Hamamasu	well	Pv, Ps	pyroxene andesite with quartz	1200	700–1188
2	2	Tomamae	well	Ms	sandstone and mudstone	1400	831–1388
3	2	Haboro	well	Ms	sandstone and mudstone	1043	881–1043
4	2	Syosanbetsu	well	Ms	conglomerate, sandstone, mudstone, and sandy siltstone	1501	1004–1489
5	3	Enbetsu E-6	well	Ms	sandstone, mudstone, and mudstone with conglomerate	371	240–371
6	2	Teshio	well	Ms	alternation of sandstone and mudstone, and alternation of siltstone and shale	1807	944–1801
7	3	Horonobe TC-1	well	Ms	sandstone with conglomerate, mudstone, and hard shale	1502	1093–1236
8	3	Toyotomi R-4	well	Ms	sandstone with conglomerate, mudstone, and hard shale	959	1257–1501
9	3	Hamatonbetsu	well	Ms	sandstone, shale, green rocks and siliceous sandstone	1073	720–938
10	1	Esashi	well	Ms	tuff	1608	830–850
11	2	Nakagawa	well	PTs	conglomerate, sandstone, and shale	51	870–1072
12	1	Bifuka	well	Ps	sandstone and mudstone	502	1079–1585
13	1	Shibetsu	hot spring	Ps, Ms	tuff, sandstone, and siltstone		39–50
14	1	Shimokawa	hot spring	Ps, Ms	conglomerate, sandstone, and mudstone		324–489
15	1	Fukagawa	well	Ps	alternation of sandstone and siltstone		
16	1	Takikawa	well	Ps, Ms	conglomerate, and mudstone		
17	1	Utashinai	closed coal mine	PTs	sandstone and mudstone		
18	3	Ashibetsu	well	PTs	alternation of conglomerate, sandstone and siltstone, and shale	1003	491–997
19	1	Ashibetsu-shi	closed coal mine	PTs	sandstone, mudstone and coal seam		
20	1	Ashibetsu-kuni	hot spring	PTs	sandstone, mudstone and coal seam		
21	2	Ashibetsu-well	well	PTs	sandstone and mudstone		
22	1	Naie	closed coal mine	PTs	sandstone and mudstone with coaly shale	300	30–190
23	1	Mikasa	closed coal mine	PTs	sandstone and mudstone		
River water							
R1		Tonbetsu	N45°04.69' E142°19.82'				
R2		Teshio	N44°48.26' E142°04.19'				
R3		Sorachi	N43°31.40' E142°11.56'				

*Ground water and thermal water are divided into 3 types (see text).

**No casing between these depths.

Pv, Pliocene volcanic rocks; Ps, Pliocene sedimentary rocks; Ms, Miocene sedimentary rocks; PTs, Pre-Tertiary sedimentary rocks.

Table 2. Chemical and isotopic compositions of water samples. Sample numbers correspond to those in Fig. 1

Sample No.	Type*	Temp. (°C)	EC (S/m)	pH	ORP (mV)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	NH ₄ (mg/L)	Cl (mg/L)
1	1	41.8	1.42	7.98	-282	127	5	0	90		414
2	2	49.9	4.69	7.00	-218	10210	60	77	605	37	16770
3	2	33.4	2.93	7.15	-168	5810	104	176	805	34	11015
4	2	24.5	2.39	7.63	-178	5283	84	42	127	33	8295
5	3	31.7	2.72	7.14	-195	5550	38	28	663	17	9950
6	2	33.3	4.86	7.30	-118	11463	663	123	94	337	17527
7	3	11.4	3.41	6.77	-122	7415	235	117	153		11022
8	3	29.7	1.99	7.24	-131	4455	32	30	79	46	6075
9	3	46.4	0.95	7.92	-140	2206	31	1	1	12	1906
10	1	41.5	0.21	7.75	8	211	4	0	202		45
11	2	28.2	4.69	7.23	207	8677	24	20	3347	25	19347
12	1	20.5	0.09	8.05	15	190	4	2	12		179
13	1	11.6	0.03	8.22	154	51	3	2	5		26
14	1	14.2	0.18	6.14	33	207	21	108	75	1	117
15	1	15.4	0.02	7.56	-5	38	3	2	6		24
16	1	30.3	0.19	7.33	-176	290	13	19	60	3	463
17	1	18.4	0.34	7.24	-145	847	12	16	9	3	251
18	3	15.8	2.54	7.00	-122	5630	31	28	354	8	9020
19	1	10.3	0.17	7.20	-180	293	8	37	27		64
20	1	13.2	0.40	7.16	-175	897	11	25	25	3	476
21	2	11.2	2.11	8.51	-228	4910	25	24	40	9	7060
22	1	11.7	0.12	7.85	-158	278	5	13	5	1	8
23	1	14.7	0.10	7.28	-133	163	7	17	27		20

Sample No.	Type*	SO ₄ (mg/L)	HCO ₃ (mg/L)	F (mg/L)	Br (mg/L)	I (mg/L)	T-Fe (mg/L)	SiO ₂ (mg/L)	Mn (mg/L)	δD (‰)	δ ¹⁸ O (‰)
1	1	27	27		1		0.01	31	0.01	-68.2	-10.8
2	2	1	278		33	27	5.80	33	0.39	-23.0	1.9
3	2	4	128	1.8	29	16	1.00	75	0.06	-40.2	-3.1
4	2	3	521	0.4	28	10	5.80	52	0.19	-35.1	-1.7
5	3	2	198	2.2	24	21	12	33	0.37	-18.6	5.6
6	2	2	3565		153	79	1.20	75	0.03	-14.2	2.1
7	3	3	3721	0.2	81	25	1.20	69	0.01	-23.4	4.7
8	3	2	1943	1.0	17	13	0.71	22	0.01	-23.4	3.1
9	3	4	2519	12.1	6		0.06	27	0.01	-41.9	-0.3
10	1	981	26	4.2			0.05	23	0.01	-82.1	-12.5
11	2	2	78	1.6	43	37	0.23	4	0.10	-8.1	5.7
12	1	1	206	1.4	0		0.23	32	0.02	-79.4	-11.4
13	1	3	105	0.1	0		0.10	43	0.04	-80.4	-12.2
14	1		1129			0	1.80	82	0.01	-84.5	-12.2
15	1	3	96				0.07	61	0.01	-80.0	-12.3
16	1	14	287	0.7	1		0.08	87	0.13	-82.3	-11.8
17	1	5	2050				0.01	14	0.01	-73.8	-11.3
18	3	3	766	4.2	7	16	13	15	0.09	-21.4	5.3
19	1	100	925	0.8			0.01	9	0.01	-76.7	-11.6
20	1	147	1840	2.0			0.01	10	0.04	-71.8	-10.0
21	2	3	985	1.8	16	8	0.51	15	0.01	-64.8	-5.5
22	1	5	879	0.4			0.01	13	0.01	-73.4	-11.4
23	1	7	666	0.3			0.01	11	0.01	-70.4	-11.1

*Ground water and thermal water are divided into 3 types (see text).

Table 3. Chemical and isotopic compositions of river water samples. Sample numbers correspond to those in Fig. 1

Sample No.	Temp. (°C)	EC (S/m)	pH	ORP (mV)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	HCO ₃ (mg/L)	F (mg/L)	T-Fe (mg/L)	SiO ₂ (mg/L)	Mn (mg/L)	δD (‰)	$\delta^{18}O$ (‰)
R1	18.2	0.02	7.33	20	8	1	8	9	9	7	78	0.1	0.10	8	0.01	-70.1	-10.7
R2	18.2	0.08	7.77	35	9	1	2	7	8	9	65	0.1	0.42	16	0.02	-74.3	-11.2
R3	18.6	0.01	8.39	-24	9	2	3	11	8	16	46	0.1	0.44	21	0.05	-79.8	-11.8

Table 4. Isotopic ratios of He, Ne and Ar in waters and gases collected from the northern part of Hokkaido. Sample numbers correspond to those in Fig. 1

Sample No. in Fig. 1	Type*	Gas/Water	$^4\text{He}/^{20}\text{Ne}$	$^3\text{He}/^4\text{He}$ (10^{-6})	$^{20}\text{Ne}/^{22}\text{Ne}$	$^{21}\text{Ne}/^{22}\text{Ne}$	$^{38}\text{Ar}/^{36}\text{Ar}$	$^{40}\text{Ar}/^{36}\text{Ar}$
1	1	W	55.9	5.302 ± 0.075	9.801 ± 0.007	0.02909 ± 0.00010	0.19022 ± 0.00041	305.01 ± 0.59
2	2	G	1830	2.346 ± 0.079	9.911 ± 0.010	0.03034 ± 0.00039	0.18780 ± 0.00081	464.40 ± 0.47
2	2	G	6.09	2.410 ± 0.030	9.820 ± 0.020	0.02900 ± 0.00010	0.18780 ± 0.00050	297.90 ± 0.50
3	2	G	684	1.425 ± 0.030	9.865 ± 0.015	0.02960 ± 0.00032	0.18771 ± 0.00070	363.89 ± 0.62
3	2	G	246	1.440 ± 0.020	9.880 ± 0.020	0.02940 ± 0.00010	0.18740 ± 0.00060	315.70 ± 0.50
5	3	G	3090	1.984 ± 0.061	9.841 ± 0.019	0.03113 ± 0.00030	0.18844 ± 0.00071	503.36 ± 0.77
5	3	G	274	1.960 ± 0.040	9.700 ± 0.040	0.02910 ± 0.00040	0.18740 ± 0.00050	348.50 ± 0.30
6	2	G	31.2	0.398 ± 0.022	9.916 ± 0.011	0.02924 ± 0.00020	0.18688 ± 0.00036	294.39 ± 0.38
7	3	G	178	0.110 ± 0.010	9.945 ± 0.011	0.02935 ± 0.00014	0.18772 ± 0.00053	299.54 ± 0.44
8	3	G	723	0.529 ± 0.012	9.952 ± 0.017	0.02987 ± 0.00015	0.18767 ± 0.00067	350.77 ± 0.37
8	3	G	519	0.563 ± 0.010	9.920 ± 0.020	0.03240 ± 0.00010	0.18770 ± 0.00090	333.40 ± 0.50
9	3	G	3760	0.927 ± 0.039	9.856 ± 0.023	0.03089 ± 0.00046	0.18761 ± 0.00045	424.90 ± 0.61
13	1	G	8.77	1.379 ± 0.035	9.821 ± 0.008	0.02903 ± 0.00010	0.18771 ± 0.00071	295.16 ± 0.46
14	1	G	29.9	2.074 ± 0.047	9.818 ± 0.008	0.02900 ± 0.00011	0.18789 ± 0.00051	300.89 ± 0.49
16	1	W	52.5	3.920 ± 0.090	9.804 ± 0.008	0.02897 ± 0.00012	0.18820 ± 0.00055	299.99 ± 0.42
17	1	W	2.79	1.520 ± 0.070	9.796 ± 0.006	0.02911 ± 0.00006	0.19010 ± 0.00040	302.48 ± 0.36
18	3	G	2470	2.460 ± 0.080	9.826 ± 0.006	0.03050 ± 0.00010	0.18856 ± 0.00029	442.68 ± 0.71
19	1	W	19.1	2.570 ± 0.050	9.810 ± 0.005	0.02901 ± 0.00007	0.18728 ± 0.00089	295.78 ± 0.40
21	2	G	0.529	1.034 ± 0.022	9.802 ± 0.007	0.02896 ± 0.00009	0.18778 ± 0.00060	295.30 ± 0.34
22	1	G	4.83	0.145 ± 0.012	9.808 ± 0.010	0.02899 ± 0.00013	0.18787 ± 0.00036	297.86 ± 0.64
23	1	W	1.98	0.265 ± 0.020	9.804 ± 0.007	0.02900 ± 0.00009	0.18775 ± 0.00064	295.88 ± 0.38

*Ground water and thermal water are divided into 3 types (see text).

Table 5. Concentrations of noble gases and elemental abundance ratios normalized to ^{36}Ar . Sample numbers correspond to those in Fig. 1

Sample No. in Fig. 1	Type*	Gas/Water	^4He	^{20}Ne	^{36}Ar	^{40}Ar	^{84}Kr	^{132}Xe	$^4\text{He}/^{36}\text{Ar}$	$^{20}\text{Ne}/^{36}\text{Ar}$	$^{84}\text{Kr}/^{36}\text{Ar}$	$^{132}\text{Xe}/^{36}\text{Ar}$
Gas sample (ppm) Water sample ($10^{-9} \text{ cm}^3\text{STP/g water}$)												
1	1	W	10800	194	789	869000	205	16.7	13.689	0.246	0.2601	0.0212
2	2	G	70.5	0.0386	0.269	125	0.0137	0.00124	262	0.144	0.0508	0.00461
2	2	G	39.6	6.50	6.56	1950	0.138	0.00715	6.04	0.991	0.0210	0.00109
3	2	G	38.8	0.0567	0.196	91.3	0.0108	0.00110	198	0.289	0.0550	0.00561
3	2	G	46.3	0.188	0.538	169	0.0220	0.00232	86.1	0.349	0.0409	0.00431
5	3	G	37.1	0.0120	0.0894	45.0	0.00441	0.000407	414	0.134	0.0493	0.00455
5	3	G	39.4	0.144	0.326	113	0.0183	0.000994	121	0.442	0.0561	0.00305
6	2	G	1.06	0.0340	0.0902	26.5	0.00727	0.000666	11.8	0.377	0.0807	0.00739
7	3	G	4.84	0.0272	0.143	42.8	0.0143	0.00240	33.9	0.190	0.1001	0.0168
8	3	G	11.3	0.0156	0.0712	25.0	0.00362	0.000408	158	0.219	0.0509	0.00573
8	3	G	11.0	0.0212	0.0780	26.0	0.00403	0.000617	141	0.272	0.0517	0.00791
9	3	G	127	0.0336	0.248	106	0.0134	0.00139	509	0.135	0.0539	0.00557
13	1	G	83.8	9.56	23.0	6800	0.559	0.0767	3.64	0.415	0.0243	0.00333
14	1	G	4.74	0.159	2.28	687	0.100	0.00749	2.08	0.070	0.0436	0.00328
16	1	W	14300	272	1690	506000	69.5	6.22	8.46	0.161	0.0411	0.00368
17	1	W	81.7	29.3	254	76700	19.4	1.21	0.322	0.116	0.0766	0.00477
18	3	G	208	0.0842	0.749	332	0.0316	0.00107	278	0.112	0.0422	0.00143
19	1	W	3950	208	777	230000	27.6	0.882	5.08	0.268	0.0355	0.00114
21	2	G	8.22	15.5	18.3	5420	0.400	0.0198	0.448	0.847	0.0218	0.00108
22	1	G	9.21	1.91	5.92	1760	0.160	0.00673	1.56	0.322	0.0270	0.00114
23	1	W	391	197	933	783000	102	23.7	0.419	0.212	0.1090	0.0254

*Ground water and thermal water are divided into 3 types (see text).

tion.

The O- and H-isotopic measurements were performed at the Analytical Center, Mitsubishi Materials Techno Corporation. Oxygen isotope ratios were determined by the CO₂ equilibration method (Epstein and Mayeda, 1953). The D isotopic values were determined by the method of Coleman *et al.* (1982). The $\delta^{18}\text{O}$ and δD values are reported relative to V-SMOW with an analytical precision of 0.1‰ and 1‰, respectively.

Noble gas isotopic compositions and concentrations were measured in the Laboratory for Earthquake Chemistry, The University of Tokyo. Noble gases dissolved in the water samples were extracted using an all metal Toepler pump system. This system is basically the same as conventional ones made of glass (Steele, 1909; Dalton, 1935; Thielens and Malfait, 1965), but has been specially designed and constructed to measure water samples with low concentration of noble gases. A greatly reduced blank, especially for He, is a great advantage of this metal Toepler pump compared to the conventional ones, which can allow atmospheric He to permeate into the vacuum line through glass. Dissolved gases were extracted from the water samples under vacuum and transferred into the noble gas purification line of a mass spectrometry system. Blank levels for the Toepler pump and the purification line were 1.2×10^{-10} (^4He), 3.0×10^{-10} (^{20}Ne), 3.3×10^{-10} (^{36}Ar), 9.8×10^{-12} (^{84}Kr) and 6.3×10^{-13} (^{132}Xe), all in units of cm³STP. These blank levels are several orders of magnitude lower than the amounts of noble gases extracted from the water samples. The noble gases extracted from the water samples and those from the gas samples were purified by two Ti–Zr getters heated at about 800°C and separated into three fractions He, Ne and Ar–Kr–Xe, i.e., Ar, Kr and Xe were separated from He and Ne by adsorbing them on a charcoal trap cooled by liquid nitrogen. Then Ne was separated from He by adsorbing Ne onto a sintered stainless steel trap cryogenically cooled to a temperature of 15 K.

The He, Ne and Ar isotopic ratios and absolute abundances of all noble gases (He, Ne, Ar, ^{84}Kr and ^{132}Xe) were measured on a modified VG5400 (MS-III) noble gas mass spectrometer. Sensitivities and mass discrimination correction factors of the mass spectrometer system were determined by measuring known amounts of atmosphere with the same procedures that were applied for the samples. The discrimination factor for $^3\text{He}/^4\text{He}$ was determined by measuring the HESJ (He Standard of Japan) with $^3\text{He}/^4\text{He} = (28.88 \pm 0.14) \times 10^{-6}$ (Matsuda *et al.*, 2002). Experimental uncertainties for the noble gas concentrations were estimated to be about 5–15%, based on the reproducibility of measurements of the standard gas and ambiguity in the gas reduction procedure. Errors on the isotopic ratios in Table 4 are one standard deviation, including uncertainties for mass discrimination.

Fig. 2. δD vs. $\delta^{18}\text{O}$ plots of water samples. The solid line is Meteoric Water Line defined by Craig (1961).

RESULTS AND DISCUSSION

The chemical and isotopic compositions of water samples are shown in Tables 2, 3, 4 and 5, where the sample numbers correspond to those in Figs. 1 through 10. The symbols (cross, circle and square) in these figures correspond to the three groups as discussed below.

δD and $\delta^{18}\text{O}$

The δD and $\delta^{18}\text{O}$ values of water samples are shown in Fig. 2. Half of the samples plot along the meteoric water line (e.g., Craig, 1961; Dansgaard, 1964) and are of meteoric origin (type 1, as shown by cross symbols). In contrast, the others have a good correlation between δD and $\delta^{18}\text{O}$ values and may be a mixture of meteoric water and fossil sea water that is enriched in ^{18}O ($\delta^{18}\text{O} = \text{ca. } +6\text{‰}$). The δD –Cl and $\delta^{18}\text{O}$ –Cl relationships (Fig. 3) show that some of the samples (type 2, square symbols) are plotting along and above the mixing lines between meteoric and fresh sea water, respectively. These results support the view mentioned above. In contrast, 5 samples (type 3, circle symbols; No. 5, 7, 8, 9 and 18) are away from this mixing line. This means that these samples contain a 3rd water component of different origin having a δD value of ca. -20‰ and Cl concentration of ca. 6,000 mg/L as discussed below. Figure 3 also shows the $\delta^{18}\text{O}$ –Cl relationship which demonstrates that the type 3 waters have higher $\delta^{18}\text{O}$ values than those of type 2 waters, which results from water–rock interaction under long residence time and/or high rock/water ratio.

Sample No. 8, one of the fluids having the characteristics of the 3rd component, was collected at Horonobe. More than 180 water samples from this site have been analyzed for their chemical and isotopic compositions as part of the Horonobe Underground Research Laboratory (Horonobe URL) project (e.g., Hama *et al.*, 2007). Their

Fig. 3. (a) δD vs. Cl and (b) $\delta^{18}O$ vs. Cl diagrams.

results show that the groundwaters are divided into two types; Na–HCO₃ type water in the shallower part of the sedimentary formations and Na–Cl type saline water in the deeper part of the sedimentary formations. Water-rock interactions and mixing are considered to be the dominant evolution processes of the groundwater. However, the Na–Cl type waters have unusually high δD values and low Cl concentrations of -20 to -30‰ and 5,000 to 6,000 mg/L, respectively (Ishii *et al.*, 2006), similar to those of sample No. 8 in the present study. These results indicate that groundwater with a high proportion of the 3rd component is widely distributed in the deeper part of this area in the Wakkanai Formation. The enrichment factor (ΔD) is defined as the difference between δD that a sample would have if it originated by simple dilution of current sea water by local meteoric water (using the Cl content of the sample to estimate the degree of dilution), and the observed δD of the sample (Ishii *et al.*, 2006). The ΔD increases up to 45‰ at depths below -500 m, where opal A changes to opal CT. At this depth, the H₂O⁺ contents in the rocks decreases by 2 wt% (Ishii *et al.*, 2006).

The groundwater and thermal water samples studied are divided into 3 groups on the basis of their isotopic and chemical compositions; type 1 (sample Nos. 1, 10, 12 to 17, 19, 20, 22 and 23) mostly of meteoric origin, type 2 (Nos. 2, 3, 4, 6, 11 and 21) which is a mixture of local meteoric water and fossil sea water, and type 3 (Nos. 5, 7, 8, 9 and 18) which is a mixture of meteoric water, fossil sea water and deep groundwater (geopressed fluid). There is no good correlation between their types and outlet temperatures. In Figs. 2 to 10, water samples of types 1, 2 and 3 are expressed by symbols of cross, circle and square, respectively. The geopressed

(overpressured) fluid is defined as formation water with pressure between hydrostatic and lithostatic conditions, which is typically distributed below *ca.* 2 km depth in sedimentary rocks associated with oil and/or natural gas (e.g., Myers, 1968; Jones, 1970; Capuano, 1990, 1992; Oki *et al.*, 1999; Xu *et al.*, 2006).

Chemical composition

Concentrations of some major chemical constituents of water samples are plotted against Cl concentrations in Fig. 4. The broken line in the figure represents mixing between meteoric water and unmodified sea water. The Na concentrations of the water samples plot along this mixing line. The K, Mg and SO₄ plot lower than the line. These characteristics are independent of the temperature and are similar to those that have been reported for groundwaters from various localities around the world, such as in the Seikan tunnel in Japan (e.g., Mizukami *et al.*, 1977), Frio Formation in U.S.A. (Land, 1995), and Aspö in Sweden (Laaksoharju, 1990; Laaksoharju *et al.*, 2008). These studies have attributed the observed chemical characteristics to water-rock interaction and mixing processes. It is noted that the HCO₃ concentrations are much higher than those of the mixing line in Fig. 4 and that samples with high HCO₃ concentrations have low Ca concentrations. The saturation indices of water samples with respect to calcite were calculated from the observed chemical compositions in Table 2 by using the chemical modeling code, PHREEQ-C (Parkhurst and Appelo, 1999). The saturation indices (S.I.) are expressed as follows;

$$S.I. = \log(Q/K),$$

Fig. 4. Correlation diagrams for some chemical constituents plotted against Cl concentration.

Fig. 5. M3 modelling of hydrogeochemical data for the northern Hokkaido area. The three end members are shown.

where Q and K are the activity product and solubility product for Ca^{2+} and CO_3^{2-} , respectively. The calculations show that most water samples are under-saturated (S.I. = $-1.74 \sim -0.13$) with respect to calcite except for sample Nos. 6 (S.I. = 0.13) and 21 (S.I. = 0.31). Sample No. 11 has the highest Ca concentration (3,347 mg/L) of all samples studied, where the Cl concentration (19,347 mg/L) is almost the same as that of unmodified sea water. The S.I. of calcite for this sample was -0.19 . Taking into account the fact that the solubility of calcite decreases with increasing temperature, most water samples studied are thought to have been saturated with respect to calcite, but become under-saturated due to decrease in temperature during their ascent to the surface. The temperatures at which the waters are saturated with respect to calcite are calculated to be 50 to 150°C , which are higher than the observed temperature.

The chemical and isotopic compositions of the waters were subjected to multivariate statistical analysis using the code M3 (multivariate mixing and mass-balance calculations), as described in Laaksoharju *et al.* (1999a, b). This statistical analysis shows that the water samples studied look as a mixture of three end members of meteoric water, fresh sea water and altered sea water (corresponding to sample No. 11) (Fig. 5). In Fig. 5, the type 3 groundwaters (circle) are plotted in the middle field between these end members and can not be explained by mixing of meteoric water, fresh sea water and altered sea water. As mentioned before, the sample No. 8 has the highest ΔD value and low Cl concentration among the type 3 waters (Fig. 3). These features may imply that sample No. 8 groundwater is another end member. According to these results, the type 1 groundwaters are of meteoric origin and the type 2 samples are mixtures of meteoric water, fresh sea water and fossil sea water enriched in ^{18}O . The type 3 groundwaters are recognized to be mix-

Fig. 6. $^3\text{He}/^4\text{He}$ vs. $^3\text{He}/^{20}\text{Ne}$ plot of water and gas samples. The solid curves show mixing lines between Air and MORB, and Air and Crust, respectively.

tures of geopressured fluid represented by sample No. 8 and meteoric water, fresh sea water and fossil sea water. Sample No. 11 has an unusual high Ca concentration (Fig. 4). Such Ca-rich waters are reported to occur in the submarine volcanogenic Kunnui formation about 200 m below the sea floor in the shafts of the Seikan Undersea Tunnel between Honshu and southern Hokkaido, between zero and 4 km off shore (Mizukami *et al.*, 1977). The concentration of Cl of the waters was reported to range from 700 to 17,500 mg/L, close to the concentration in seawater, whereas Ca concentration varies from 530 to 3100 mg/L. In these samples, concentrations of HCO_3^- are lower than 60 mg/L. The chemical characteristics of sample No. 11, i.e., high Ca concentration, low HCO_3^- concentration and Cl concentration close to that of sea water, are interpreted to indicate fossil sea water as reported elsewhere (e.g., Land, 1995).

Rare gas isotopes

Figure 6 shows a plot for $^3\text{He}/^4\text{He}$ versus $^4\text{He}/^{20}\text{Ne}$ ratios. All gas and dissolved gas samples except for Nos. 21, 22 and 23 gave medium values between the MORB-AIR and CRUST-AIR mixing lines. There is no clear difference in $^3\text{He}/^4\text{He}$ ratios between all types. This means that these gases come from both magmatic and radiogenic sources, where the proportion of MORB component in the samples is calculated to be ca. 20%, assuming that the MORB gas has a $^3\text{He}/^4\text{He}$ ratio of 11×10^{-6} and that of CRUST gas of 1×10^{-8} . It is noted that the range of $^4\text{He}/^{20}\text{Ne}$ ratios of type 3 samples is higher than that of type 1, while that of type 2 overlaps with types 1 and 3 except for sample No. 21. Sample Nos. 21, 22 and 23 are plotted along the CRUST-AIR mixing lines and are of radiogenic origin. In all the samples, two samples 1 and 16 of type 1 have the highest $^3\text{He}/^4\text{He}$ ratios, suggesting a large contribution of magmatic gas.

Fig. 7. $^3\text{He}/^4\text{He}$ vs. $^{21}\text{Ne}/^{22}\text{Ne}$ plot of water and gas samples.

Fig. 8. $^3\text{He}/^4\text{He}$ vs. $^{40}\text{Ar}/^{36}\text{Ar}$ plot of water and gas samples. The rectangle drawn by broken lines shows the composition range of groundwaters in the Horoman area reported by Nagao *et al.* (2003).

Groundwater samples of type 1 are of meteoric origin as mentioned before and have both He and Ne from MORB and radiogenic components (Fig. 6). This means that deep sourced He and Ne are added in these samples because the concentrations of He and Ne in meteoric water is low and easily changed by the addition of other sourced He and Ne.

It is noted that $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios in samples of type 1 are plotted around air and those in the other types have increasing of $^{21}\text{Ne}/^{22}\text{Ne}$ ratios with decreasing of $^{20}\text{Ne}/^{22}\text{Ne}$ ratios (Fig. 7). This means that both of

Fig. 9. $^{40}\text{Ar}/^{36}\text{Ar}$ vs. $^{21}\text{Ne}/^{22}\text{Ne}$ plot of water and gas samples.

Fig. 10. $^3\text{He}/^4\text{He}$ vs. HCO_3^- concentration in water samples.

Ne from MORB and nucleogenic sources is added to types 1 and 2. Also noted is that type 1 samples have almost atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ value of 296 with variable $^3\text{He}/^4\text{He}$ ratios (Fig. 8). This indicates that there is no contribution of nucleogenic Ar to these samples. In contrast, types 2 and 3 samples have higher $^{40}\text{Ar}/^{36}\text{Ar}$ ratios than the air value. Of the samples collected, the highest $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of about 500 were observed in sample No. 5 (type 3 groundwater). This means that the groundwaters are relatively older than type 1 waters. Nagao *et al.* (2003) reported $^3\text{He}/^4\text{He}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios (the rectangle drawn by broken lines in Fig. 8) of groundwaters collected from wells HDB 3 to 5 at 200~520 m depth in the Horonobe area to be 0.4~3.1 and 297~303, respectively. From the δD and $\delta^{18}\text{O}$ values of pore water from cores in these wells, the waters are defined as types 1 and 2 as mentioned before (Teramoto *et al.*, 2006; Hama *et al.*, 2007). These results demonstrate that high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are not observed in the groundwaters at shallow depth (*ca.* 500 m) but observable in samples issuing from the fractures. A good correlation between $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios is observed (Fig. 9) except for one of two No. 8

samples. Note that this sample exhibited a high $^{21}\text{Ne}/^{22}\text{Ne}$ ratio away from the other samples (Fig. 7). In Fig. 9, type 1 samples plot around air. This demonstrates that types 2 and 3 samples are contributed by gases from nucleogenic sources.

Groundwaters and thermal waters are characterized by high CO_2 concentrations as mentioned before. Figure 10 shows that HCO_3^- concentration (total dissolved CO_2 such as H_2CO_3 , HCO_3^- , and CO_3^{2-} are converted as HCO_3^-) in the water samples increases with decreasing $^3\text{He}/^4\text{He}$ ratios except for sample Nos. 21, 22 and 23 which have no MORB derived He and Ne and almost constant CO_2 concentration. This result implies that the CO_2 of types 2 and 3 samples might come from both deep sources and sediments because the He, Ne and Ar isotopes indicate the addition of MORB and nucleogenic sources.

Occurrence of geopressured fluid

Geopressured (overpressured) fluid is defined as formation water with pressures between hydrostatic and lithostatic conditions as mentioned before. The δD and $\delta^{18}\text{O}$ data generally show that most of the geopressured fluids can be explained as a mixture of fossil sea water and local meteoric water with an oxygen isotope shift due to rock-water interaction. Several formation waters from oil fields have high Cl concentrations (up to 10 times of that of sea water; e.g., Birkle *et al.*, 2002) due to dissolution of salt deposits. Recently, geopressured fluids with unusually high δD (-20‰) and low Cl concentration (ca. 6,000 mg/L) have been observed along faults in several localities in Japan, e.g., Niigata (Oki *et al.*, 1999; Xu *et al.*, 2006), Horonobe (Ishii *et al.*, 2006), Mobara gas field (Maekawa *et al.*, 2006), and Miyazaki (Ohsawa and Ohi, personal comm.). Fluids in mud volcanoes in various part of the world also have such high δD (-20‰) and low Cl concentrations (e.g., Dia *et al.*, 1999).

Ishii *et al.* (2006) examined the isotopic and chemical compositions of formation waters in the Horonobe area, including sample No. 8 of the present study (Toyotomi Spa. associated with CH_4). This sample (Table 1) is thought to be a geopressured fluid that has ascended through the Ohmagari fault. The feature indicating marine environments of the geological formations suggests that this fluid may have been formed by sea water which underwent changes in isotopic and chemical compositions during diagenesis. Ishii *et al.* (2006) discussed the possibility that the isotopic change from 0 to -20‰ was caused by dehydration of opal A during the formation of opal C (2 wt% water can be released). The D/H fractionation factor between opal (amorphous silica) and water is -145‰ and -108‰ at 25°C and 50°C , respectively (Faure *et al.*, 2000). This mineralogical transition is observed in the sedimentary rocks at about -500 m depth, while the temperature is not clear but generally around 50°C (Ishii

et al., 2006). During transition of opal A to C, the δD value and Cl concentration of the connate water in the sedimentary rocks might be decreased due to dilution by dehydrated water from opal A. However, the observed isotopic and chemical compositions cannot be explained by this model because the total amount of water dehydrated from rocks is too small compared to that of the connate water due to the large porosity (35%). At greater depths, transition of smectite to illite is commonly observed (e.g., Bruce, 1984; Colten-Bradley, 1987). During this transition, the δD value and Cl concentration of the connate water become lower due to dilution by dehydrated water from smectite which has lower δD values (D/H isotopic fractionation between smectite and water is about -40‰ at 25°C ; Savin and Epstein, 1970; Lawrence and Taylor, 1971; Yeh and Epstein, 1978).

Primmer and Shaw (1991) analyzed the oxygen and hydrogen isotopic compositions of argillaceous rocks from a partly overpressured Tertiary sequence in an offshore well from the Texas Gulf Coast. They showed increasing illitization of illite-smectite rich formations with depth of burial and a general trend towards enrichment of D and depletion of ^{18}O with increasing illitization. By using D and O isotopic fractionation factors between smectite/illite-water (Yeh, 1980; Savin and Lee, 1988), they calculated the δD and $\delta^{18}\text{O}$ values of water in equilibrium with illite-smectite to be -15 to -40‰ and -1 to $+8\text{‰}$, respectively, similar to those of sample No. 8 in the present study. Hyeong and Capuano (2004) reported that δD values of water and clay in the normally pressured (lithostatic) and geopressured sections are different. In the normally pressured section (<2.6 km), δD of water is constant (-15‰), while δD of clay increases linearly from -59 to -43‰ with increasing depth. In contrast, in the geopressured section δD of water decreases linearly from -7 to -26‰ with increasing depth, while δD of clay is nearly constant (-36‰).

Yeh (1980) demonstrated membrane filtration as a fundamental process in depleting the deuterium content of the migrating fluid in sedimentary rocks. This effect would also deplete the ^{18}O content of the migrating fluid (Coplen and Hanshaw, 1973; Demir, 1988). Primmer and Shaw (1991) examined the membrane filtration for hydrogen isotope compositions of interlayer water and showed that the water giving rise to the overpressure is more enriched in ^{18}O than normally pressured pore water. They indicated that membrane filtration cannot satisfactorily explain the trends in the calculated isotopic composition of the water in the overpressured zones. According to these previous studies, the observed chemical and isotopic characteristics of waters with unusually high δD in this study may be explained by conversion (dehydration) of smectite to illite and isotopic equilibration between water and smectite/illite during diagenesis (e.g.,

Bechtel *et al.*, 2000). The low Cl concentration may result from dilution by dehydration water.

CONCLUSIONS

H, O and rare gas isotopic compositions were analyzed for groundwaters and thermal waters (maximum temperature is 49.9°C) in northwestern Hokkaido, Japan. The water samples can be divided into 3 types; type 1 is of meteoric origin, type 2 is a mixture of meteoric water and altered sea water (fossil sea water) and type 3 is a mixture of meteoric waters, altered sea waters and geopressured water. The geopressured fluids have a δD value of -20‰ and Cl concentration of 6,000 mg/L and are widely distributed in northwestern Hokkaido. The $^3\text{He}/^4\text{He}$ ratios of 5.5×10^{-7} with high $^3\text{He}/^{20}\text{Ne}$ ratio (~ 700) of type 3 samples indicate a crustal He input with a small amount of He derived from MORB source. In this paper, we could not confirm the occurrence of the geopressured fluids at depths and their geological environments. From the detailed study at Horonobe (sample No. 8), the geopressured fluids might have migrated along fractures from deep crustal source.

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