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Hydrochemical data report from sampling of two deep abandoned hydrocarbon exploration wells, western Siberia, Russian Federation

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REPORT

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Title:
Hydrochemical data report from sampling of two deep abandoned hydrocarbon exploration wells: Byelii Yar and Parabel', Tomsk oblast', western Siberia, Russian Federation.

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Summary:

This report documents the hydrochemical analyses performed on water samples collected during a field expedition in August 2013 to two former hydrocarbon exploration boreholes (>2 km deep) in the West Siberian artesian megabasin. The sample sites were at Byelii Yar and at Goryachii Istochnik (near Parabel'), both in Tomsk oblast'. In neither case did the boreholes encounter significant hydrocarbon reserves; they currently overflow under artesian pressure at the surface and their geothermal water is used in simple spa resorts. In both cases, the waters are highly reducing; they contain H_2S and methane (CH_4) as dissolved gases, and do not contain detectable concentrations of sulphate and nitrate. Both waters are rich in barium (an indicator of sulphate reduction) and strontium (an indicator of long residence time).

The Byelii Yar borehole yields brackish water (mineralisation 1.8 g/L) of Na-Cl type. The water is rich in strontium and very poor in Ca and Mg. The water contains around 11.5 mg/L fluoride, rendering it unsuitable for human consumption on a regular basis. The Br/Cl ratio of the water suggests that the salt content is marine-derived (possibly marine connate water, or derived from a subsequent marine inundation). The water's salinity suggests only a 4-5% contribution of marine water, however. The stable isotope signature of the water indicates that the majority of the water is derived from direct or indirect recharge of meteoric water.

The Goryachii Istochnik borehole yields saline water (mineralisation 14 g/L) of Na-Cl-(Ca) type. The water is rich in strontium and very poor in Mg. The water contains around 120-130 µg/L arsenic, rendering it unsuitable for human consumption. The Br/Cl and Na/Cl ratios of the water suggest that the salt content is marine-derived (possibly marine connate water, or derived from a subsequent marine inundation). The water's salinity suggests a 40% contribution of marine water. The stable isotope signature of the water indicates that the marine-derived water is likely to have mixed with fresher water derived from direct or indirect recharge of meteoric water. The stable isotope signature has been somewhat enriched in ^{18}O, probably due to exchange with the aquifer matrix.

Keywords: Geochemistry	Hydrogeology	Drilled well
Groundwater quality	Oil	Microbiology
Stable isotopes	Geothermal energy	Data report

CONTENTS

1 INTRODUCTION

1.1 Previous studies and sampling activities

Tomsk State University (TGU) has long enjoyed an informal yet fruitful collaboration in the field of hydrochemistry with Norges geologiske undersøkelse (NGU) and Holymoor Consultancy (UK), now trading as D Banks Geoenvironmental Services. This collaboration initially supported a joint project between TGU and the Khakassian State Committee for Environmental Protection (SCEP) to produce the geological section of an "Environmental Atlas of Khakassia". This period of collaboration resulted in the following publications:

Banks, D., Parnachev, V.P., Frengstad, B., Holden, W., Karnachuk, O.V. & Vedernikov, A.A. (2004). The evolution of alkaline, saline ground- and surface waters in the southern Siberian steppes. **Applied Geochemistry** 19, 1905-1926.

Parnachev, V.P., Banks, D. & Berezovsky, A.Y. (1997). The anionic composition of groundwaters in extensional tectonic environments: the Shira Region, Khakassia, southern Siberia. **Norges geologiske undersøkelse Bulletin** 433, 62-63.

Parnachev, V.P., Khromikh, V.C., Kopilova, Y.G., Tanzibaev, M.G., Polozhii, A.V., Kurbatskii, V.I., Makarenko, N.A., Vidrina, S.N., Zarubina, R.F., Kallas, E.V., Kulizhskii, S.P., Naumova, E.G., Smetanina, I.V., Solovyeva, T.P. (1998a). *Otsenka sostoyaniya prirodnikh resursov i sozdanie ekologicheskovo atlasa territorii Respubliki Khakassia (Otchet ob itogakh vipolneniya khozdogovornikh rabot po teme No. 277 za 1997 god).* TGU/Tomsk 1998, 129 pp.

Parnachev, V.P., Khromikh, V.C., Kopilova, Y.G., Tanzibaev, M.G., Kurbatskii, V.I., Makarenko, N.A., Zarubina, R.F., Kulizhskii, S.P., Petrov, A.I., Smetanina, I.V., Panteleev, M.M., Sai, M.V., Arkhipov, A.L., Polekh, N.V. (1998b). *Otsenka sostoyaniya prirodnikh resursov i sozdanie ekologicheskovo atlasa territorii Respubliki Khakassia (Otchet ob itogakh vipolneniya khozdogovornikh rabot po teme No. 277 za pervoe polugodie 1998 goda).* TGU/Tomsk 1998, 120 pp.

Parnachev, V.P., Banks, D., Berezovsky, A.Y. & Garbe-Schönberg, D. (1999). Hydrochemical evolution of Na-SO_4-Cl groundwaters in a cold, semi-arid region of southern Siberia. **Hydrogeology Journal**, 7, 546-560.

Parnachev, V.P., Makarenko, N.A., Kopilova, Y.G., Tanzibaev, M.G., Kulizhskii, S.P., Petrov, A.I., Zarubina, R.F., Smetanina, I.V., Arkhipov, A.L., Arkhipova, N.V. (2000). *Otsenka sostoyaniya prirodnikh resursov i sozdanie ekologicheskovo atlasa territorii Respubliki Khakassia (Otchet ob itogakh vipolneniya khozdogovornikh rabot. po teme No. 277 za 1999 god).* TGU/Tomsk 2000, 142 pp.

and the following NGU Reports

Banks, D., Parnachev, V.P., Berezovsky, A.Y., & Garbe-Schönberg, D. (1998). The hydrochemistry of the Shira region, Republic of Khakassia, southern Siberia, Russian Federation - data report. **Nor. Geol. Unders. report** 98.090.

Banks, D., Parnachev, V.P., Frengstad, B., Holden, W., Karnachuk, O.V. & Vedernikov, A.A. (2001). The hydrogeochemistry of the Altaiskii, Askizskii,

Beiskii, Bogradskii, Shirinskii, Tashtipskii & Ust' Abakanskii Regions, Republic of Khakassia, Southern Siberia, Russian Federation, data report. **Nor. Geol. Unders. report** 2001.006, 45 pp. + appendices.

Banks, D., Parnachev, V.P., Frengstad, B., & Karnachuk, O.V. (2008). Hydrogeochemical data report: the sampling of selected locations in the Republic of Khakassia, Kuznetsk Alatau oblast' and Kemerovo oblast', Southern Siberia, Russian Federation. **Nor. Geol. Unders. report** 2008.013, 60 pp. + appendices.

In more recent years, the focus has been transferred to new projects: in particular, (i) a series of projects involving the characterisation of microbial communities in mine waters, mine wastes and oil boreholes, managed by Prof. Olga V. Karnachuk (Dept. of Plant Physiology and Biotechnology, Tomsk State University), and (ii) a new project between Professor Valerii P. Parnachev (Department of Dynamic Geology, TGU) and the Tomsk Oblast' Committee for Ecology, to produce an atlas and characterisation of water quality in Tomsk Oblast'. Results of this period of work have been presented in the following NGU Reports and publications:

Banks, D., Parnachev, V.P., Frengstad, B., & Karnachuk, O.V. (2008). Hydrogeochemical data report: the sampling of selected locations in the Republic of Khakassia, Kuznetsk Alatau oblast' and Kemerovo oblast', Southern Siberia, Russian Federation. **Nor. Geol. Unders. report** 2008.013, 60 pp. + appendices.

Karnachuk, O.V., Gerasimchuk, A.L., Banks, D., Frengstad, B., Stykon, G.A., Tikhonova, Z.L., Kaksonen, A., Puhakka, J., Yanenko, A.S. & Pimenov, N.V. (2009). Bacteria of the sulfur cycle in the sediments of gold mine tailings, Kuznetsk Basin, Russia (Бактерий цикла серы в осадках хвостохранилища добычи золота в кузбассе). **Microbiology** 78 (4), 483–491. Published in Russian in Mikrobiologiya, 78 (4), 535–544.

Banks, D., Parnachev, V.P., Karnachuk, O.V., Arkhipov, A.L., Gundersen, P. & Davis, J. (2011). Hydrogeochemical data report: the sampling of selected localities in Kemerovo oblast' and Tomsk oblast', Siberia, Russian Federation. **Nor. Geol. Unders. report** 2011.054, 69 pp. + appendices.

1.2 Sampling activities - August 2013

This report documents the most recent round of field work, in the period 23rd -30th August 2013, carried out by:

- Dr Yulia Frank and Ms Sofia Safaryan (Dept. of Plant Physiology and Biotechnology, Tomsk State University),
- Dr Vitalii V. Kadnikov (Bioengineering Centre of the Russian Academy of Sciences, Moscow),
- David Banks (University of Glasgow and D Banks Geoenvironmental Services, UK),

with the support of

- Prof. Olga V. Karnachuk (Dept. of Plant Physiology and Biotechnology, Tomsk State University), Sampling was carried out in two deep, abandoned, former oil exploration boreholes in the northern part of Tomsk Oblast', now taken into private ownership and developed as spas of varying degrees of sophistication. Both boreholes now produce brackish or saline warm groundwater under artesian (overflowing) head. The TGU Department of Plant Physiology and Biotechnology is currently engaged in a research project to characterise the microbiota of such wells.

During the sampling of August 2013, alkalinity, pH, Eh and temperature were measured in the field at both sites.

Field-filtered (0.45 μm) samples of water were returned to the United Kingdom for analysis by:

- Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at the British Geological Survey, Keyworth, Nottinghamshire.
- Ion Chromatography (IC) methods at the British Geological Survey, Keyworth, Nottinghamshire.
- ^{18}O and ^{2}H stable isotopic determinations at the laboratory of NERC Isotope Community Support Facility, Scottish Universities' Environmental Research Centre **(**SUERC), Rankine Avenue, East Kilbride, G75 0QF.

Dr Michael Watts and his staff at the British Geological Survey and Professor Adrian Boyce of SUERC / University of Glasgow are gratefully thanked for providing these analyses.

This report is intended to document the raw data produced during the study, together with a limited degree of interpretation. This raw data report will form the documentation basis for scientific papers interpreting the data collected during the study.

2 SAMPLING AND ANALYSIS ROUTINES: YEAR 2013

The sites sampled in August 2013 are detailed in Sections 3 and 4 of this Report.

2.1 Groundwater Sampling

Groundwater samples were taken at the wellhead from flowing artesian boreholes. Both boreholes were more or less continuously in use to feed spa / tourist facilities, and thus no "purging" was regarded as necessary.

In the case of water from Byelii Yar (see Section 3), the samples were taken from a branch of the pipe "tree" at the wellhead (see Figure 3.9). In the case of water from Goryachii Istochnik (see Section 4), samples were taken from a free-flowing rubber pipe leading directly from the (artesian) borehole head (Figure 4.2).

For each sample, the following aliquots were taken:

- 1 x 30 ml and 1 x 15 mL polyethene flasks, of water filtered at 0.45 μm, using a Millipore filter capsule and hand-held polypropene syringe. No acidification was carried out in the field. These samples were carried in baggage to the UK and delivered to the British Geological Survey. Except during periods of transport, samples were stored in the dark at c. 4°C. The 30 mL flask was used for ion chromatography analysis and the 15 mL flask for ICP-MS.
- 1 x 15 ml polyethene flask, completely filled with water filtered at 0.45 μm, using a Millipore filter capsule and hand-held polypropene syringe. Sample flask sealed additionally at neck with "Parafilm®" to hinder any leakage or evaporative losses. These samples were carried in baggage to the UK and delivered to SUERC. Except during periods of transport, samples were stored in the dark at c. 4°C.
- In some cases, a selection of samples for bacteriological analysis at TGU and additional chemical analysis at Russian organisations.

2.2 Field Measurements

Field determinations included:

- determination of alkalinity (by average of multiple determinations, typically three determinations) using a standard solution of 0.05 N HCl, prepared by TGU's Department for Plant Physiology and Biotechnology, an indicator comprising Hach bremocresol green / methyl red powder portioned in foil pillows (with an end point, in the region 4.3 to 4.6, depending on the alkalinity value, giving a measure of t-alkalinity), and a sampling syringe / container from the AquaMerck 11109 alkalinity test kit. This arrangement was due to strict air carriage regulations prohibiting carriage of acid and indicators in flammable organic solutions by aircraft from the UK.

- pH, Eh and temperature (T) using TGU Department for Plant Physiology and Biotechnology's Hanna Instruments HI8314 pH meter, regularly calibrated against solutions of known pH around 4, 7 or 10 as appropriate. Measurements were manually corrected for drift (assumed to be linear with time) on the basis of daily calibrations. The pH value was automatically temperature-compensated by the meter.

2.3 Analysis at British Geological Survey

Samples (for each sample 1 x 15 mL and 1 x 30 mL aliquot of filtered water) were transported by David Banks to the laboratory of the British Geological Survey at Keyworth, Nottingham. Prior to analysis, samples were stored in a refrigerator at around +4°C, except for brief periods of transport.

Appendix 1 contains the analytical report documentation from the British Geological Survey.

The 15 mL flasks were used for ICP-MS analysis. The samples were acidified with 1% v/v HNO_3 and 0.5% v/v HCl prior to analysis. Due to their salinity, the Byelii Yar samples were diluted by a factor of 5x prior to analysis and the Goryachii Istochnik samples (Parabel) by a factor of 25x. These dilution factors are reflected in the cited detection limits.

The 30 mL sample was used, following appropriate dilution, dependent on salinity, for the ion chromatography determination.

3 BYELII YAR (БЕЛЫЙ ЯР) - BOREHOLE 1-R

3.1 Location and Hydrogeology

The hydrocarbon borehole 1-R (1-P in Russian)) is located on Sovkhoznaya Street (ул. Совхозная) in the town of Byelii Yar (Белый Яр) in Tomsk oblast’ of Western Siberia at approximate coordinates 58.4496°N 85.0279°E. The borehole is located in a pump house on the south bank of the River Ket’ (a tributary of the Ob’) some 150 m from the river and at a ground elevation of c. 84 m asl.

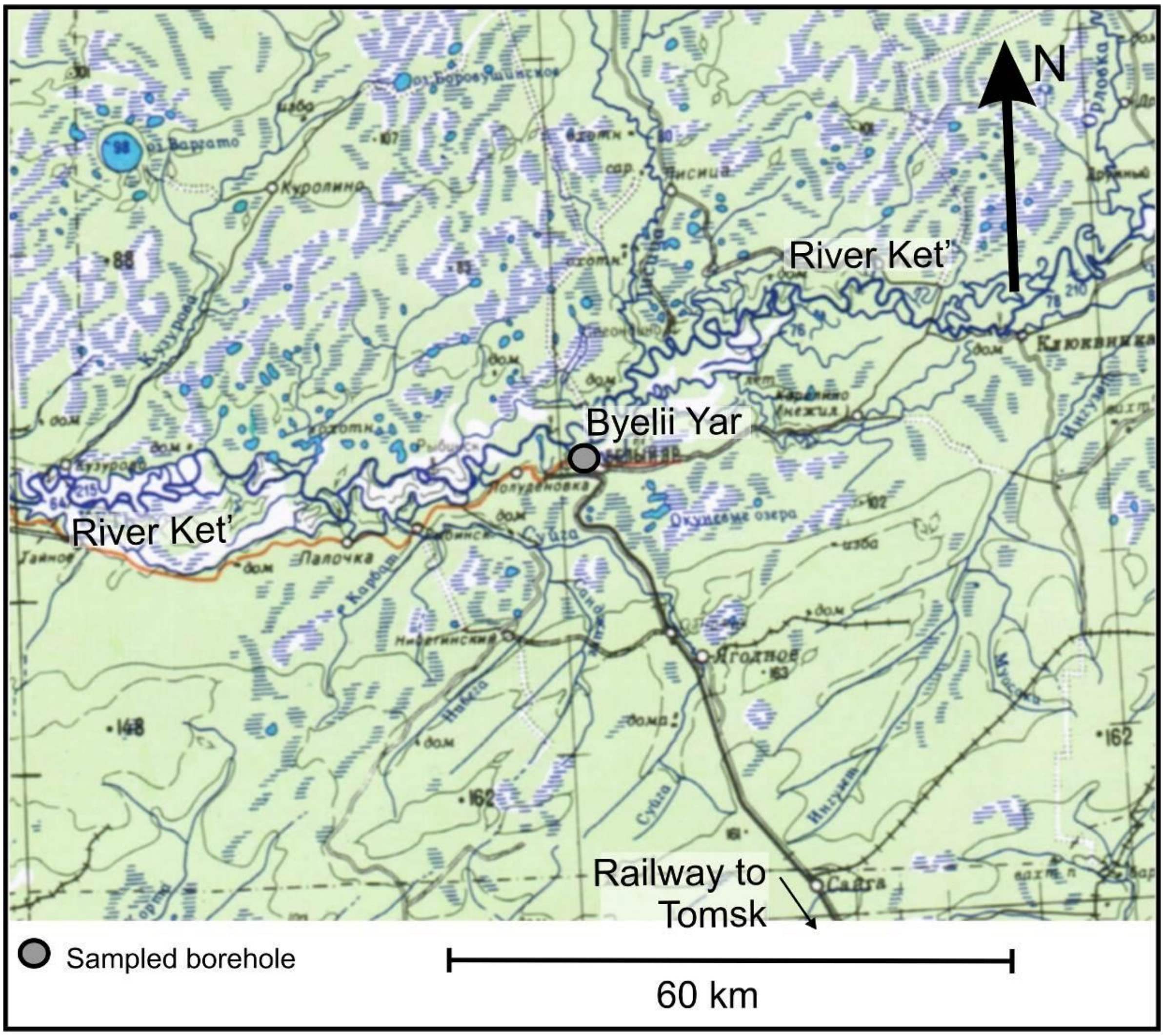

Figure 3.1. Location of the sampled Byelii Yar borehole.

The borehole was drilled at 22 to 10 inch diameter between September 1961 and September 1962 to 2.56 km depth (Винниченко, undated). Various strings of casing were set, ranging from an 18” diameter surface guidance pipe and 14” conductor casing, down to a final string of 5” diameter casing in the productive horizons.

The site is located in the West Siberian artesian megabasin, a huge synclinal structure containing large thicknesses of Mesozoic, Tertiary and Quaternary sediments (sands, silts, clays of varying degrees of lithification), overlying Palaeozoic basement, and roughly coinciding with the drainage basin of today's river Ob'. The borehole penetrated some 25 m of Quaternary sediments, followed by Palaeogene sediments (Nekrasovskaya suite) down to 170 m depth. This was succeeded by a Danian-Cretaceous sedimentary sequence down to 2186 m depth and a Jurassic sequence to 2505 m. At 2505 m, the borehole entered Palaeozoic basement, comprising sedimentary rocks to 2534 m and thereafter basalts to 2563 m (Figure 3.2).

Following completion, the borehole was tested by a bottom-up casing perforation method, whereby successive sections of casing were perforated and pressure/flow tested. After testing, the section was sealed by cement and a new section perforated higher up. The final recorded tested interval was from 1997 to 2005 m in the Hauterivian-Barremian (i.e. early Cretaceous) sedimentary rocks of the Ilekskaya Suite (with a cement seal having been emplaced up to 2172 m depth). Assuming no further perforation or testing was subsequently undertaken, the water overflowing from the borehole today should be derived from an aquifer horizon in this depth interval. The total static head measured at the time of testing (1962) was 4.37 atm. (45.2 m of freshwater equivalent head). There is some documentary evidence that water pressures have declined since the date of drilling.

The artesian flow was determined at various wellhead pressures, resulting in the diagrams in Figure 3.3. The specific capacity of the tested interval was typically in the region of 12 m^3/d flow per m drawdown in equivalent freshwater head.

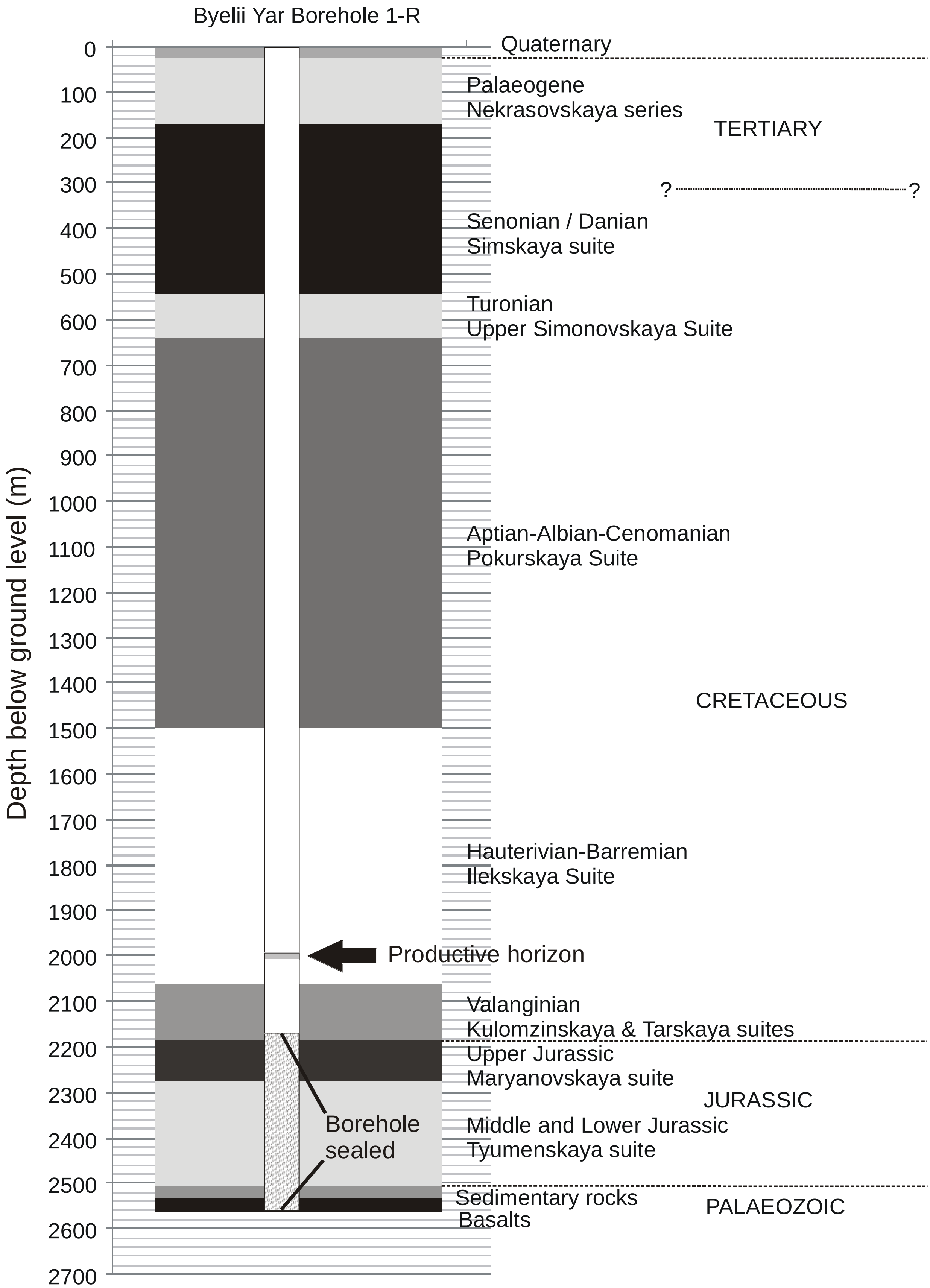

Figure 3.2. The stratigraphy of the Byelii Yar 1-R borehole.

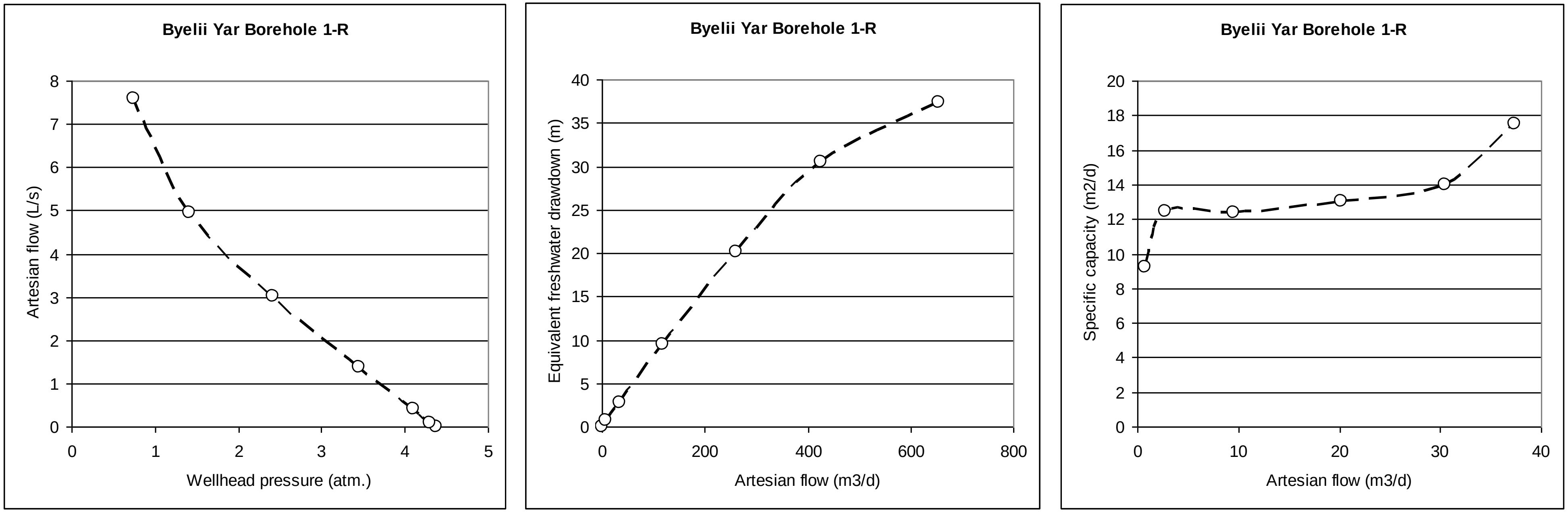

Figure 3.3. The hydraulic characteristics of the tested section from 1997 to 2005 m depth, with wellhead pressure (in atmospheres, and converted to m equivalent freshwater head) related to artesian flow at wellhead.
Data derived from that cited in well completion report.

At present, water from the borehole is available to a number of local users, via a closed wellhead "tree" of connections. The wellhead pressure thus decreases as more users access water from the wellhead. Thus, the wellhead pressure is inversely related to water flow.

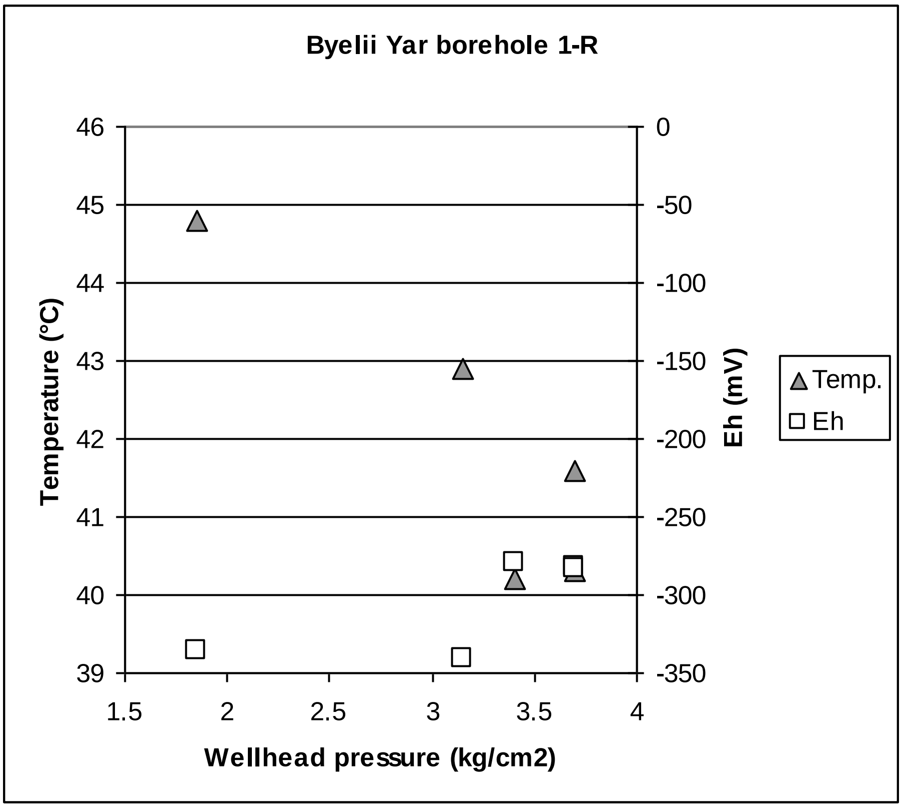

Figure 3.4. The relationship between wellhead pressure, water temperature and water redox potential (Eh) in August 2013.

Older data suggest that, at the time of drilling, the water temperature was around 45-48°C. It will be seen (Figure 3.4) that, in 2013, water temperature increases as flow (use) increases (i.e. as wellhead pressure decreases): this is because water is travelling more rapidly up the borehole axis and thus losing less heat by conduction to the cool strata in the borehole wall. There is also a tendency for redox potential to decrease if flow increases (rapid flow, less opportunity for oxidation). Thus, the samples and measurements taken at lowest wellhead pressure are more likely to be most representative of downhole conditions. In August 2013, field measurements taken at the wellhead suggested:

- Water temperature of up to 44.8°C
- Eh of down to -340 mV
- pH of around 8.2
- t-alkalinity of 4.7 meq/L

3.2 Previous Water Analyses

A water analysis from a sample of 15th October 2000, stated that the water was without colour or precipitate, with an H_2S smell and a weak salty taste. The following components were recorded:

Parameter	**Value / Concentration**
Mineralisation M	1.81 g/L
pH	7.92
Temperature	41°C
Chloride (Cl^-)	873.3 mg/L
Bicarbonate (HCO_3^-)	113.2 mg/L
Sulphate ($SO_4^=$)	5.15 mg/L
Nitrate (NO_3^-)	Not detectable
Fluoride (F^-)	11.2 mg/L
Bromine (Br)	2.2 mg/L
$Na^+ + K^+$	644.23 mg/L
Ammonium (NH_4^+)	1.05 mg/L
Metasilicic acid (H_2SiO_3)	43.25 mg/L
Boric acid (H_3BO_3)	14.0 mg/L
Phenol index	0.0013 mg/L
Permanganate oxidability	1.94 mg O_2/L

Overall Kurlov formula $M_{1.8} \frac{Cl_{86}(HCO_3 + CO_3)_{13}(SO_4)_1}{(Na+K)_{98}Ca_2} pH\ 7.92$

Table 3.1. Determination water quality of Byelii Yar borehole 1-R, based on a sample taken 15th October 2000, and reported in "Заключение о составе и качестве воды скважины Р-1 (п. Белый Яр, Томская область). 15.12.2000. Томского НИИ Курортологии и Физиологии” *[Conclusion on composition and quality of water from the well R-1 (Byelii Yar, Tomsk oblast’), dated 15 December 2000, Tomsk Research Institute for Balneology and Physiology]*.

The water quality reported in this 2000 analysis is very similar to that reported from this field study, with the exception of the alkalinity, which may reflect the difference between a field (2013) and a laboratory (2000) determination.

3.3 Dissolved gases

The groundwater from Byelii Yar borehole contains dissolved hydrogen sulphide gas. The contents were measured twice, by Dr Yulia Frank (Tomsk State University) using the methylene blue colorimetric technique, and found to be as follows:

- dissolved H_2S = 0.64 ± 0.35 mg/L (sampled in August 2013)

- dissolved H_2S = 0.88 ± 0.23 mg/L (sampled in August 2014)

On exposure to atmospheric pressure, the groundwater also exsolves bubbles of gas, which were collected in an inverted glass flask in August 2013 by Dr Vitalii Kadnikov, (bioengineering centre of the Russian Academy of Sciences - Центр "Биоинженерия" РАН) and analysed for volumetric composition at the laboratory of Dr Nikolai Pimenov (Vinogradsky Institute of Microbiology, RAS, Moscow):

Preliminary data on gas composition	**% (volume percent)**
Methane (CH_4)	60.2
Nitrogen (N_2)	32
Oxygen (O_2)	6.9
Helium (He)	0.7
Carbon monoxide (CO)	0.2

Table 3.2. Determination of composition of exsolved gas from the water of Byelii Yar 1-R borehole, as sampled in August 2013.

It can thus be stated that the groundwater in the Byelii Yar borehole contains significant contents of hydrogen sulphide and methane and is derived from a highly reducing methanogenic environment. The content of oxygen measured in the gas is puzzling in this context, but may simply represent atmospheric contamination during gas sampling or sample transport (the oxygen to nitrogen ratio is 0.22, slightly lower than the 0.27 ratio in atmospheric air).

3.4 Hydrogeochemistry

In addition to the field measurements mentioned above, in August 2013, samples of water were taken from a sampling line at the well-head. Four sets of samples were taken at regular intervals over a 32 hour period (11.00 am and 19.45 pm on 23/8/13; 11.00 am and 19.00 pm on 24/8/13, named ByY001 to 004 respectively). For each sample, three aliquots were taken, field filtered at 0.45 µm, using a hand-held syringe, into clean new polyethene sample flasks:

- aliquot for analysis by ICP-MS methods at the British Geological Survey, Keyworth, UK (15 mL)
- aliquot for analysis of anions by ion chromatography methods at the British Geological Survey, Keyworth, UK (30 mL)
- aliquot for analysis of ^{18}O and ^{2}H stable isotopes at the Scottish Universities' isotope facility at SUERC, East Kilbride, UK (15 mL)

Of these samples, the last (ByY004) was taken at the time of lowest wellhead pressure (greatest flow) and is thus most likely to be representative.

The ion balance error for all four analyses was <1.5%, which indicates extremely good analytical quality. The water analyses from all four samples were found to be very similar: Figure 4 is a pie diagram representing the milliequivalent composition of the water. It will be seen that the water is dominated by sodium as a cation, and chloride as an anion, with a modest component (4.7 meq/L) of bicarbonate alkalinity.

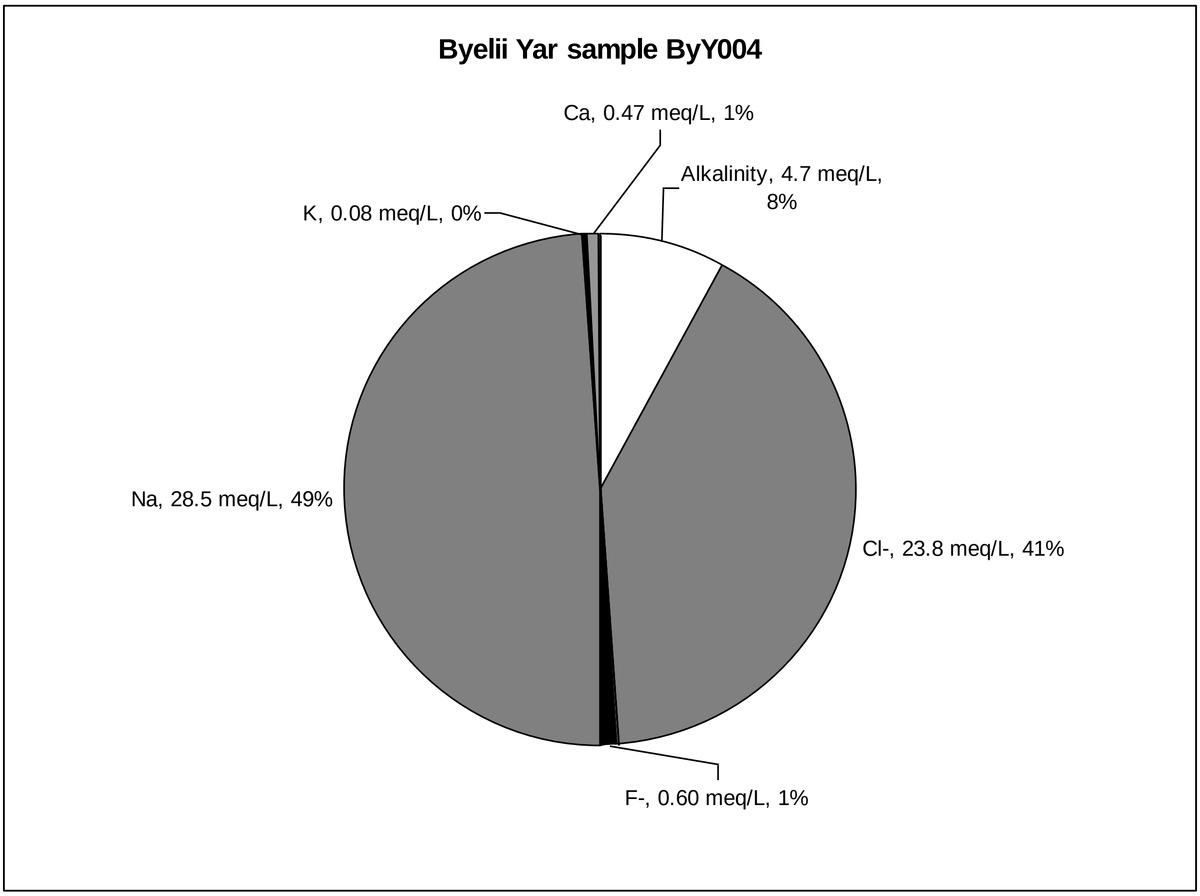

Figure 3.5. Pie diagram representing the meq/L composition of water from the Byelii Yar borehole (sample ByY004, at 19:00 on 24/8/13).

The highly reducing nature of the water is reflected in:

- concentrations of $SO_4^{=}$ and nitrate (NO_3^-) below analytical detection limit (<5 mg/L and <3 mg/L respectively)
- the water's low Eh (c. -340 mV)
- the odour of H_2S gas in the water
- the elevated concentration of barium (around 0.227 mg/L in ByY004)
- the negligible uranium concentrations (U is very poorly soluble under reducing conditions); much lower, in fact, than the thorium concentrations.

Sample No.			ByY001	ByY002	ByY003	ByY004
BGS sample reference		**Detection limit**	13273-0001	13273-0002	13273-0003	13273-0004
Date of sampling			23/08/2013	23/08/2013	24/08/2013	24/08/2013
Time	Local		11:00	19:45	11:00	19:00
Field determinations						
Wellhead pressure	kg/cm2		3.3-3.5	3.1-3.2	3.7	1.7-2.0
pH			7.92	8.06	8.25	8.21
Eh	mV		-279	-341	-283	-336
T	°C		40.2	42.9	41.6	44.8
t-Alk 1	meq/L		4.6	4.9	4.6	4.8
t-Alk 2	meq/L		4.8	4.8	4.7	4.7
t-Alk 3	meq/L		4.8	4.6	4.8	4.7
t-alkalinity	meq/L		4.7	4.8	4.7	4.7
Anions by ion chromatography						
Cl^-	mg/L		844	832	830	843
SO_4^{2-}	mg/L	**5**	<5	<5	<5	<5
NO_3^-	mg/L	**3**	<3	<3	<3	<3
Br^-	mg/L		3.10	3.07	3.25	3.04
F^-	mg/L		11.7	11.4	11.6	11.5
Major and minor cations by ICP-MS						
Na	mg/L	**0.4**	661	633	639	656
Mg	mg/L	**0.03**	0.14	0.13	0.13	0.14
Ca	mg/L	**0.5**	9.7	9.0	8.9	9.4
K	mg/L	**0.04**	3.02	2.94	2.93	3.14
Mn	µg/L	**0.2**	9.4	9.0	8.6	8.3
Fe	µg/L	**1**	119	128	105	97
Sr	µg/L	**2**	1011	961	946	1003
Ba	µg/L	**0.1**	224	229	220	227
Li	µg/L	**2**	49	43	46	46
Other significant elements						
Al	µg/L	**1**	13	13	12	14
Si	µg/L	**50**	12726	13074	13007	12853
P	mg/L	**0.01**	<0.01	<0.01	<0.01	<0.01
S	mg/L	**1**	2	2	2	2
B	µg/L	**18**	2337	2077	2284	2274
Trace elements						
Ag	µg/L	**0.05**	<0.05	<0.05	<0.05	<0.05
As	µg/L	**0.02**	0.54	0.55	0.42	0.48
Be	µg/L	**0.01**	0.01	0.01	<0.01	0.02
Cd	µg/L	**0.02**	<0.02	<0.02	<0.02	0.03
Co	µg/L	**0.02**	<0.02	<0.02	<0.02	<0.02
Cr	µg/L	**0.05**	<0.05	<0.05	<0.05	<0.05
Cs	µg/L	**0.005**	0.461	0.437	0.453	0.467
Cu	µg/L	**0.4**	<0.4	<0.4	<0.4	0.5
Ga	µg/L	**0.2**	0.3	0.3	0.3	0.3
Hf	µg/L	**0.01**	0.06	0.04	0.03	0.03
Mo	µg/L	**0.03**	3.38	3.21	3.39	3.43
Nb	µg/L	**0.02**	<0.02	<0.02	<0.02	<0.02
Ni	µg/L	**0.1**	<0.1	<0.1	<0.1	0.1
Pb	µg/L	**0.03**	<0.03	<0.03	<0.03	<0.03
Rb	µg/L	**0.01**	3.96	3.94	3.88	3.94
Sb	µg/L	**0.005**	0.007	0.009	0.007	0.007
Se	µg/L	**0.1**	<0.1	<0.1	<0.1	<0.1
Sn	µg/L	**0.02**	<0.02	<0.02	<0.02	<0.02
Ta	µg/L	**0.02**	0.09	0.08	0.06	0.06
Th	µg/L	**0.005**	0.056	0.040	0.031	0.023

Ti	µg/L	**0.05**	<0.05	<0.05	0.09	0.24
Tl	µg/L	**0.02**	<0.02	<0.02	<0.02	<0.02
U	µg/L	**0.007**	<0.007	<0.007	<0.007	<0.007
V	µg/L	**0.2**	<0.2	<0.2	<0.2	0.3
W	µg/L	**0.05**	4.27	3.87	4.15	4.10
Zn	µg/L	**0.5**	0.8	1.3	0.6	<0.5
Zr	µg/L	**0.05**	0.06	<0.05	<0.05	<0.05
Rare Earth Elements						
Y	µg/L	**0.005**	0.017	0.017	0.015	0.014
La	µg/L	**0.002**	0.005	0.005	0.004	0.004
Ce	µg/L	**0.003**	<0.003	0.004	<0.003	<0.003
Pr	µg/L	**0.003**	<0.003	<0.003	<0.003	<0.003
Nd	µg/L	**0.05**	<0.05	<0.05	<0.05	<0.05
Sm	µg/L	**0.003**	<0.003	<0.003	0.003	<0.003
Eu	µg/L	**0.002**	<0.002	<0.002	<0.002	<0.002
Tb	µg/L	**0.002**	<0.002	<0.002	<0.002	<0.002
Gd	µg/L	**0.002**	<0.002	<0.002	<0.002	<0.002
Dy	µg/L	**0.003**	<0.003	<0.003	<0.003	<0.003
Ho	µg/L	**0.002**	<0.002	<0.002	<0.002	<0.002
Er	µg/L	**0.002**	0.002	<0.002	<0.002	<0.002
Tm	µg/L	**0.002**	<0.002	<0.002	<0.002	<0.002
Yb	µg/L	**0.002**	<0.002	0.003	<0.002	0.003
Lu	µg/L	**0.002**	<0.002	<0.002	<0.002	<0.002

Table 3.3. Inorganic chemical analysis of water from Byelii Yar 1-R borehole, analysed by ICP-MS and ion chromatography techniques at the British Geological Survey, Keyworth, UK. Note that three determinations of alkalinity were made in the field (pale script), resulting in an average.

Concentrations of iron and manganese were, however, rather modest at around 100 µg/L and 9 µg/L, respectively, presumably being suppressed by the high pH of the water and the excessive sulphide concentrations.

The total mineralization of the water can be estimated by summing chloride, sodium and bicarbonate = 1.8 g/L, which coincides well with previously reported analyses from the borehole.

Calcium and magnesium are almost absent from the water (Ca around 9 mg/L). It is likely that these have been removed by precipitation of calcite / dolomite in a high-pH, bicarbonate-rich environment. Simulation using PHREEQC Interactive software confirms that the waters are approximately saturated with respect to calcium carbonate. .Magnesium/strontium mass ratios are extremely low (c. 0.14), suggesting that strontium has accumulated strongly during a prolonged residence time, while magnesium has been depleted. The molar ratio of Na/Cl^- is around 1.2, suggesting that there has been some accumulation of sodium in the water from hydrolysis of feldspars and other silicates (or conceivably from ion exchange).

Bromide occurs at just over 3 mg/L in the water, with a chloride to bromide mass ratio of around 270. This is very close to seawater (288) and suggests that the groundwater’s salinity may have its origin in relict ocean water.

Fluoride concentrations are rather high at c. 11.5 mg/L (relative to the WHO guide limit of 1.5 mg/L) suggesting that water from this well should not be regularly used for human consumption. The high fluoride concentrations are likely due to prolonged residence time in a low-calcium, alkaline environment where anion exchange or dissolution of fluoride-containing minerals can allow fluoride to accumulate in the water without a fluorite (CaF_2) saturation ceiling being breached. Simulation using PHREEQC Interactive software confirms that the waters are approximately saturated with respect to fluorite.

As regards other components of health significance: arsenic concentrations are relatively low (c. 0.5 µg/L), as are those of most heavy metals (presumed to be suppressed by the high pH and sulphide concentrations). Uranium concentrations are below detection limit and (unusually) thorium concentrations exceed those of uranium. This is likely to reflect the highly reducing nature of the water, in which uranium is almost insoluble Tungsten occurs at around 4 µg/L: this is an element known to accumulate in high pH groundwaters (Frengstad et al. 2001).

Silicon is present at concentrations of around 13 mg/L (around 27.5 mg/L as SiO_2), while boron reaches relatively high concentrations of c. 2.2 mg/L (around 13 mg/L as H_3BO_3).

3.5 Stable Isotopes

In parallel with the four samples of groundwater, taken in August 2013 for chemical analysis, four x 15 mL aliquots (ByY001F to ByY004F), filtered at 0.45µm using a hand-held syringe and filter capsule, were also taken for stable isotope analysis. A duplicate of sample ByY001F was taken for quality assurance purposes. During storage and transport the HDPE bottles were sealed with 'Parafilm®'. The samples were analysed by Prof. Adrian Boyce's laboratory at the Scottish Universities Environmental Research Centre (SUERC), where the results shown in Table 3.4 were obtained (see also Figure 3.6).

When plotted on an ^{18}O vs. ^{2}H plot (Figure 3.6), the Byelii Yar samples fall very slightly to the right of the global meteoric water line (GMWL). This suggests that the water is essentially derived from meteoric recharge, with the isotopic signature slightly modified by ^{18}O exchange with the aquifer matrix in a mildly geothermal environment (or possibly by admixture with a minor component of connate marine water).

Sample no.	$d^{18}O$ VSMOW	d^2H SMOW	d^2H SMOW (repeat analysis)
	‰	‰	‰
ByY001F	-15.3	-128	
ByY001F	-15.3		
ByY001F dup	-15.5	-129	
ByY001F dup	-15.4		
ByY002F	-15.4	-119	–113
ByY002F	-15.4		
ByY003F	-15.3	-127	
ByY003F	-15.4		
ByY004F	-15.5	-129	
ByY004F	-15.4		

Table 3.4. Stable isotope analysis of water from Byelii Yar 1-R borehole, analysed by mass spectrometry techniques at SUERC, East Kilbride, UK.

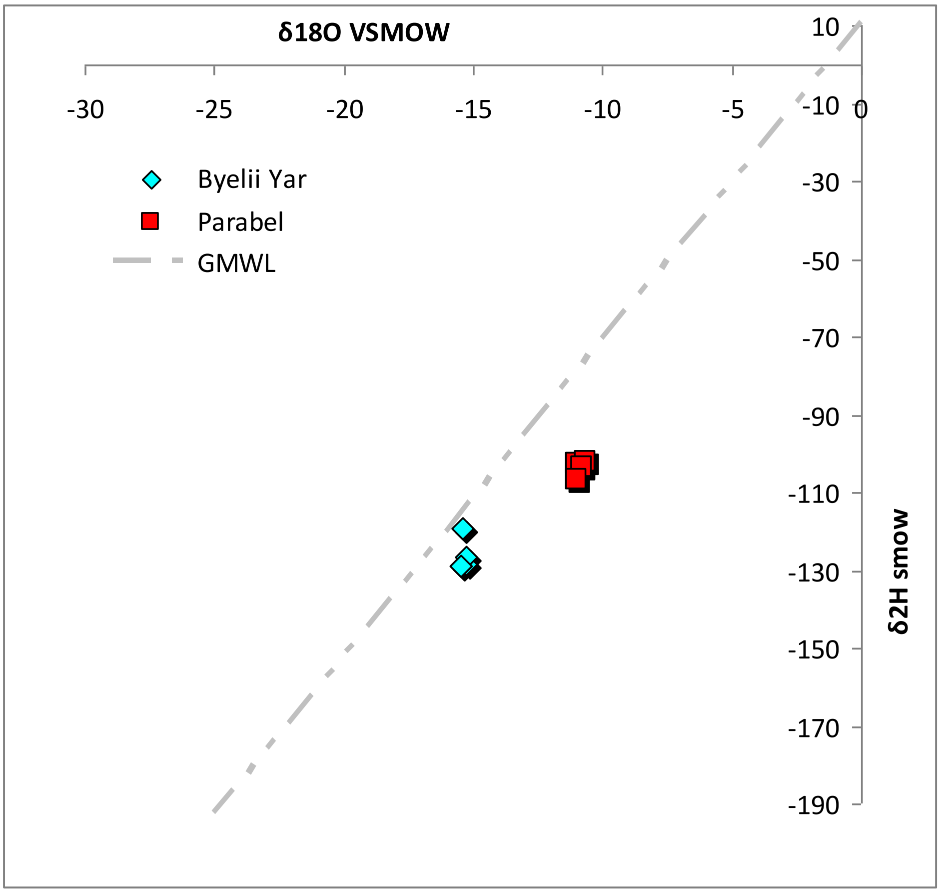

Figure 3.6. Plot of ^{18}O vs. ^2H for the Byelii Yar 1-R groundwater samples (blue), compared with similar samples from the deeper, hotter Goryachii Istochnik borehole 3-R (red), near Parabel', also in Tomsk oblast' (Chapter 4). The global meteoric water line (GMWL), defined as $\delta^2H = 8.13 * \delta^{18}O + 10.8$, is also shown.

3.6 Russian Sources of Information

Винниченко Н.Н. (undated) Выкопировка из паспорта скв. 1-Р (приложение 6) (Extract from ecological passport for borehole 1-R - Annex 6)

Волкова Т.К. (1994) Справка о регистрации водозаборной скважины. Letter dated 4/8/94 from the Committee for Natural Resources of Tomsk oblast'.

Шинкаренкоб В.П. (undated). Экспертное заключение о геолого-гидрогеологических условиах участка лицензирования (приложение 6) (Expert conclusions about geological/hydrogeological conditions for the purpose of licensing - Annex 8).

Томского НИИ Курортологии и Физиологии (2000). Заключение о составе и качестве воды скважины Р-1 (п. Белый Яр, Томская область). 15.12.2000.

Figure 3.7. River Ket' at Byelii Yar (Photo by David Banks)

Figure 3.8. Well-house for the Byelii Yar 1-R borehole (Photo by David Banks)

Figure 3.9. Wellhead of the Byelii Yar 1-R borehole (Photo by David Banks)

Figure 3.10. Dr Vitalii Kadnikov and Dr Yulia Frank sampling the Byelii Yar 1-R borehole (Photo by David Banks)

4 GORYACHII ISTOCHNIK (ГОРЯЧИЙ ИСТОЧНИК) BOREHOLE, NEAR PARABEL' (ПАРАБЕЛЬ) - - BOREHOLE 3-R

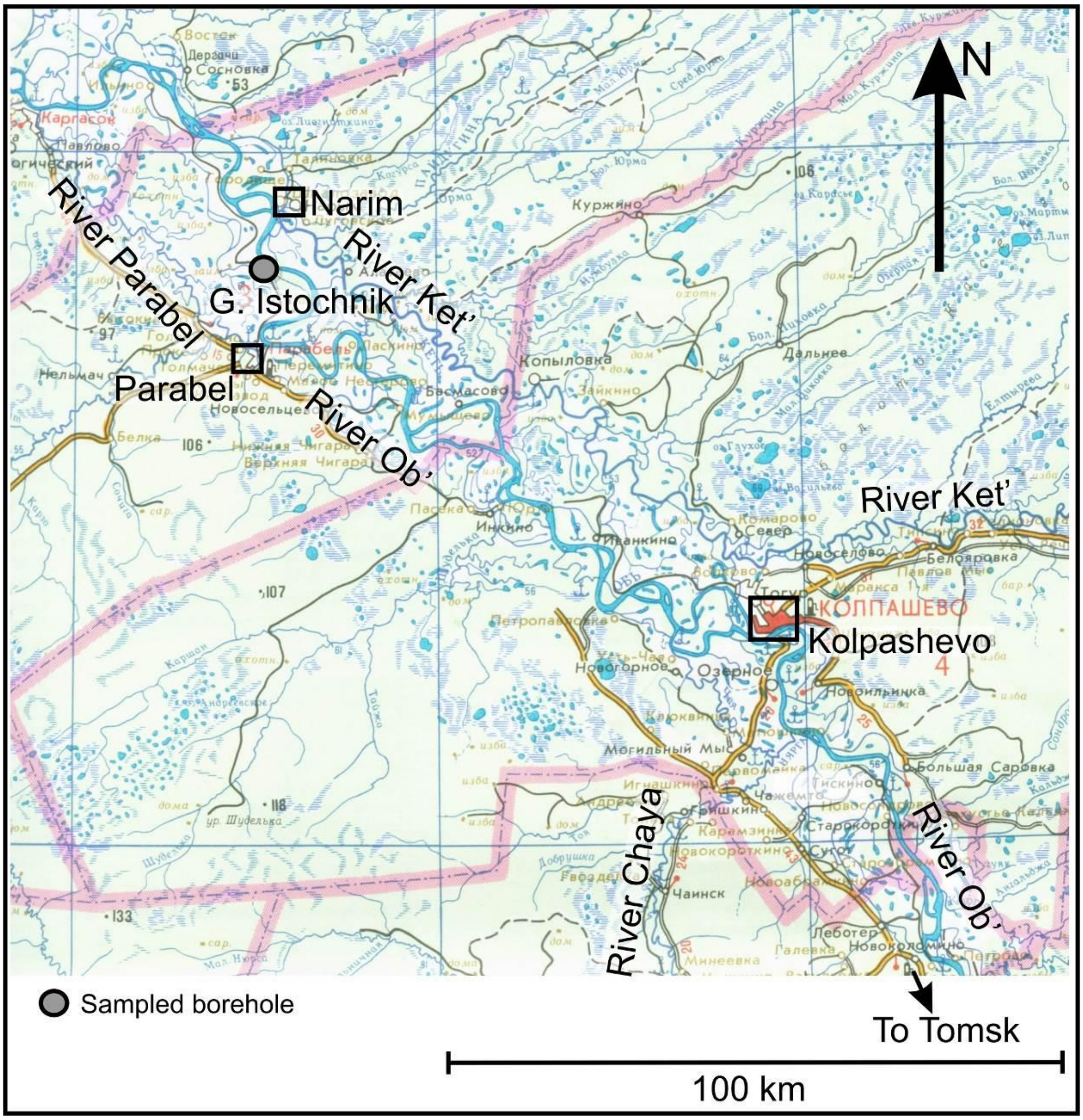

Figure 4.1. Location of the sampled Goryachii Istochnik (Chistii Yar) borehole.

4.1 Location and Hydrogeology

The hydrocarbon borehole 3-R (3-P in Russian) is located at the spa resort of Goryachii Istochnik (Горячий Источник - simply meaning "hot spring"), located in an isolated spot on the west bank of the River Ob', between the towns of Parabel' (Парабель) and Narim (Нарым) in Tomsk oblast' of Western Siberia. The spa resort is alternatively named Chistii Yar (Чистый Яр - meaning "clean steep bank"). The borehole is at approximate coordinates 58.8348°N 81.5019°E. The borehole is located in the open air around 690 m south-west of the River Ob', on its left bank, and at a ground elevation of c. 53 m asl (as estimated from Google Earth - the Soviet borehole log gives the well top as 57.74 m asl).

The borehole was reportedly drilled in around 1957 and, like the borehole at Byelii Yar, encountered no exploitable hydrocarbon resources.

Figure 4.2. Wellhead of the Goryachii Istochnik 3-R borehole (Photo by David Banks, August 2013)

The well currently feeds a modest, rather isolated, tourist spa resort of several wooden cabins, a handful of indoor and outdoor wooden baths and river bathing in an abandoned meander of the Ob'. The surrounding area forms the boggy flood plain of the Ob'. The borehole's steel well casing protrudes from the ground and is highly corroded. The water has a strong smell of H_2S and the gas bubbles emerging from the water are flammable (methane - CH_4). The water flow rate was estimated at c. 0.2 to 0.3 L/s in 2010 (Banks et al. 2011); however, in 2013, the total flow used for all purposes at the whole spa facility was estimated as possibly as high as 2-3 L/s, judging from the waste water effluent stream.

As at Byelii Yar, the site is located in the West Siberian artesian megabasin, a huge synclinal structure containing large thicknesses of Mesozoic, Tertiary and Quaternary sediments (sands, silts, clays of varying degrees of lithification), overlying Palaeozoic basement, and roughly coinciding with the drainage basin of today's river Ob'.

Figure 4.3. Baths fed by borehole 3-R at Goryachii Istochnik, looking over the Ob' flood plain towards the Ob' (Photo by David Banks).

Figure 4.4. Bathing at Goryachii Istochnik, in an abandoned meander of the Ob' (Photo by David Banks).

The borehole penetrated a little less than 30 m of Quaternary sediments, followed by Palaeogene sediments down to 182 m depth. This was succeeded by a Cretaceous sedimentary sequence down to 2250 m depth and a Jurassic sequence to 2600 m. At 2600 m, the borehole entered Palaeozoic basement, comprising monzonite and granite.

Wellhead = 57.74 m asl		
Age	**Description**	**Depth of base (m below well-head)**
Quaternary	Sand with clay	30
Palaeogene Pg_3	Grey silts with interbedded clays	102
Palaeogene Pg_{2-3}	Dark green clay with interbedded sands	176
	Dark grey sand with interbedded pebbles	182
Cretaceous Cr_2	Grey silts	240
	Grey micaceous clay	360
	Iron-rich dark grey sandstone	376
	Grey-green sand	420
Cretaceous Cr_1	Grey micaceous clay	457
	Grey sand	600
	Grey clay with interbedded sand	674
	Coarse-grained micaceous sand	700
	Grey clay with interbedded sand	836
	Clay with sandstone	1020
	Grey clay with occasional interbedded sandstone	1120
	Grey calcareous sandstones	1362
	Dark green clay with interbedded sandstone	1486
	Clay / mudstone	1760
	Clay	2050
	Clay with interbedded sandstone	2140
	Clay/ mudstone with interbedded sandstone	2194
	Dark grey clay with interbedded sandstone	2250
Jurassic	Grey clay with interbedded sandstone	2330
	Alternating mudstones and sandstones	2600
Palaeozoic Pz	Monzonite and granite	2609

Table 4.1. The stratigraphy of borehole 3-R at Goryachii Istochnik, according to Soviet records. For depth below ground level, a few metres should be subtracted.

It is uncertain where the water is stratigraphically derived from, although a depth in excess of 2000 m must be suspected, given a water temperature of around 50°C.

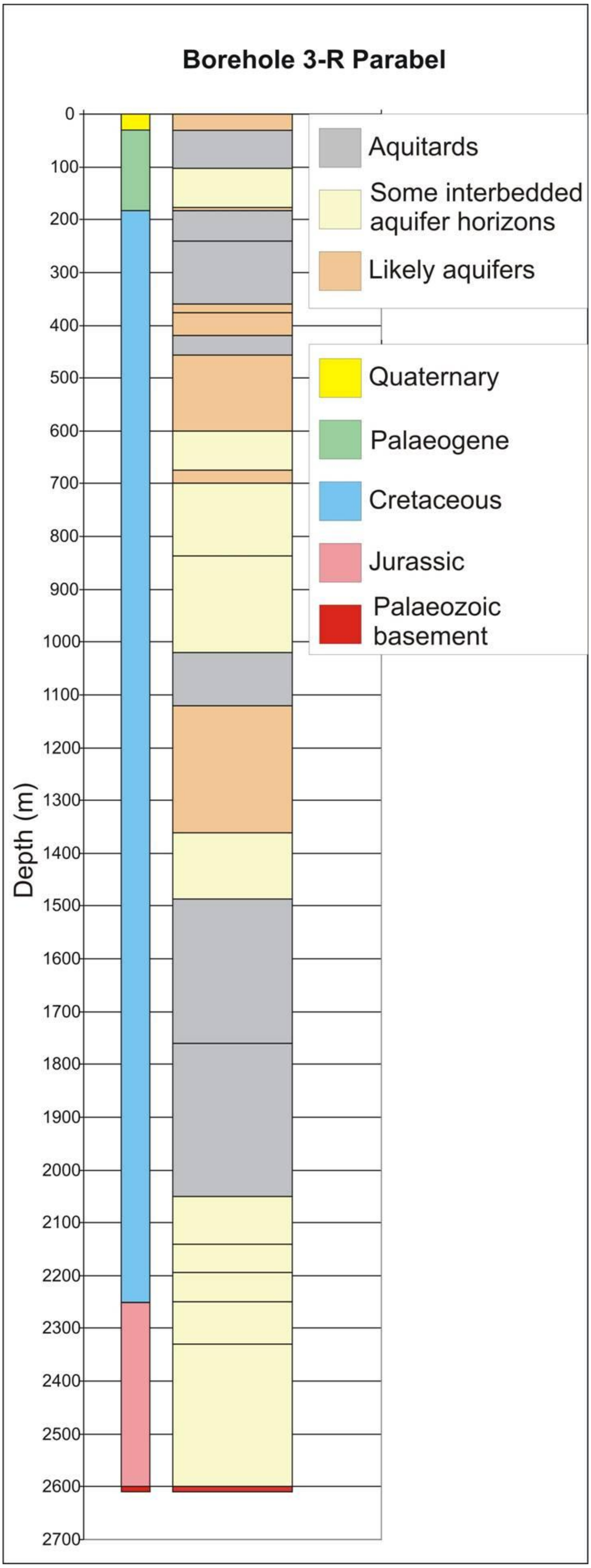

Figure 4.5. The stratigraphy of the Goryachii Istochnik 3-R borehole in metres below wellhead datum.

A number of analyses were made throughout the spring and summer of 1974 by the Tomsk Institute of Kurortology and the Tomsk Institute of Medicine. The analyses read as follows:

Parameter	**Units**	**February 1974**	**April 1974**	**May 1974**	**September 1974**
Iodine (I)	mg/L*	1.2	0.9	1.4	-
Bromine (Br)	mg/L*	-	3.0	6.0	3.0
H_2SiO_3	mg/L*	56.6	60.6	59.3	57.5
Si (calculated)	mg/L*	20.4	21.8	21.3	20.7
H_2S	mg/L*	-	5.3	3.4	6.8
Fluoride (F)	mg/L*	2.8	3.0	2.2	2.4
pH		7.55	7.5	7.6	7.25
Temp.	°C	53.0	53.0	53.0	53.0
Mineralization	g/L	13.4	14.3	13.0	13.5
Major ion content	meq/L %*	$\frac{Cl_{98}}{Na_{73}Ca_{25}}$	$\frac{Cl_{99}}{Na_{70}Ca_{25}}$	$\frac{Cl_{97}}{Na_{73}Ca_{26}}$	$\frac{Cl_{99}}{Na_{78}Ca_{20}}$

* = presumed units

Overall Kurlov formula $H_2S\ 0.00516\ M\ 13.5\ \frac{Cl_{98}}{Na_{74}Ca_{24}}\ pH\ 7.5\ T\ 53°C$

Table 4.2. The hydrochemistry of water from the Goryachii Istochnik 3-R borehole, according to analyses made in 1974 by the Tomsk Institute of Kurortology and the Tomsk Institute of Medicine (after Banks et al. 2011)**.**

Another official analysis, dated 2006, was made by the Tomsk Scientific Research Institute for Kurortology and Physiotherapy (Томский Научно-исследовательский Институт Курортологии и Физиотерапии). The analysis found a total mineralization of 16.7 g/L. The temperature was reported as 68°C and the pH as 7.38. The major ion composition is given as a Kurlov Formula:

$$H_2SiO_3\ 0.169\ M\ 16.7\ \frac{Cl_{99}HCO3_1}{(Na+K)_{77}Ca_{21}Mg_2}\ pH\ 7.38\ T\ 68°C$$

In other words, the water is a NaCl brine with subsidiary Ca.

The well was sampled by Tomsk State University in 2010, and the results of this sampling are presented in full by Banks et al. (2011). The borehole was re-sampled in August 2013, and the results are presented here. In August 2013, field measurements taken at the wellhead suggested:

- Water temperature of around 50°C (i.e. slightly hotter than Byelii Yar)

- Eh of down to -298 mV, but typically c. -280 mV
- pH of around 7.3 (i.e. slightly less alkaline than Byelii Yar)
- t-alkalinity of around 3.1 meq/L (i.e. slightly less alkaline than Byelii Yar)

Notes on field pH determination and alkalinity titration at Goryachii Istochnik borehole: the pH reading from the electrode stabilised very slowly. Also, the indicator colour change at the alkalinity titration end point was very slow, especially when a larger quantity of indicator was used (sample Par001). For the last three determinations (samples Par002, Par003 and Par004), a smaller amount of indicator was used and the colour change was clearer. Nevertheless, for the cited values in Table 4.3, a pale purple-pink end point was selected. For a bright pink end-point, add an extra 0.3 meq/L to the last three sampling rounds (Par002, Par003 and Par004). The sensitivity of the alkalinity test is only 0.3 meq/L (size of one drop of titrating acid).

4.2 Hydrogeochemistry

In addition to the field measurements mentioned above, in August 2013, samples of water were taken from a sampling line at the well-head. Four samples were taken at regular intervals over a c.18 hour period (20:20 pm on 29/8/13; 02:15 am, 08.40 am and 14.55 pm on 30/8/13, named Par001 to Par004 respectively). For each sample, three aliquots were taken, field filtered at 0.45 μm, using a hand-held syringe, into clean new polyethene sample flasks:

- aliquot for analysis by ICP-MS methods at the British Geological Survey, Keyworth, UK (15 mL)
- aliquot for analysis of anions by ion chromatography methods at the British Geological Survey, Keyworth, UK (30 mL)
- aliquot for analysis of ^{18}O and ^{2}H stable isotopes at the Scottish Universities' isotope facility at SUERC, East Kilbride, UK (15 mL), sealed with Parafilm®.

The ion balance error for all four analyses varied between 1.1 and 6.1%, which indicates relatively good analytical quality. In all cases, there was a slight anion deficit, suggesting that other anionic species may be present in the water which have not been taken account of in the ion balance calculation (e.g. silicates). The water analyses from all four samples were found to be very similar: Figure 4.6 is a pie diagram representing the milliequivalent composition of the water. It will be seen that the water is dominated by sodium as a cation, and chloride as an anion, with subsidiary calcium and a very modest component (around 3 meq/L) of bicarbonate alkalinity.

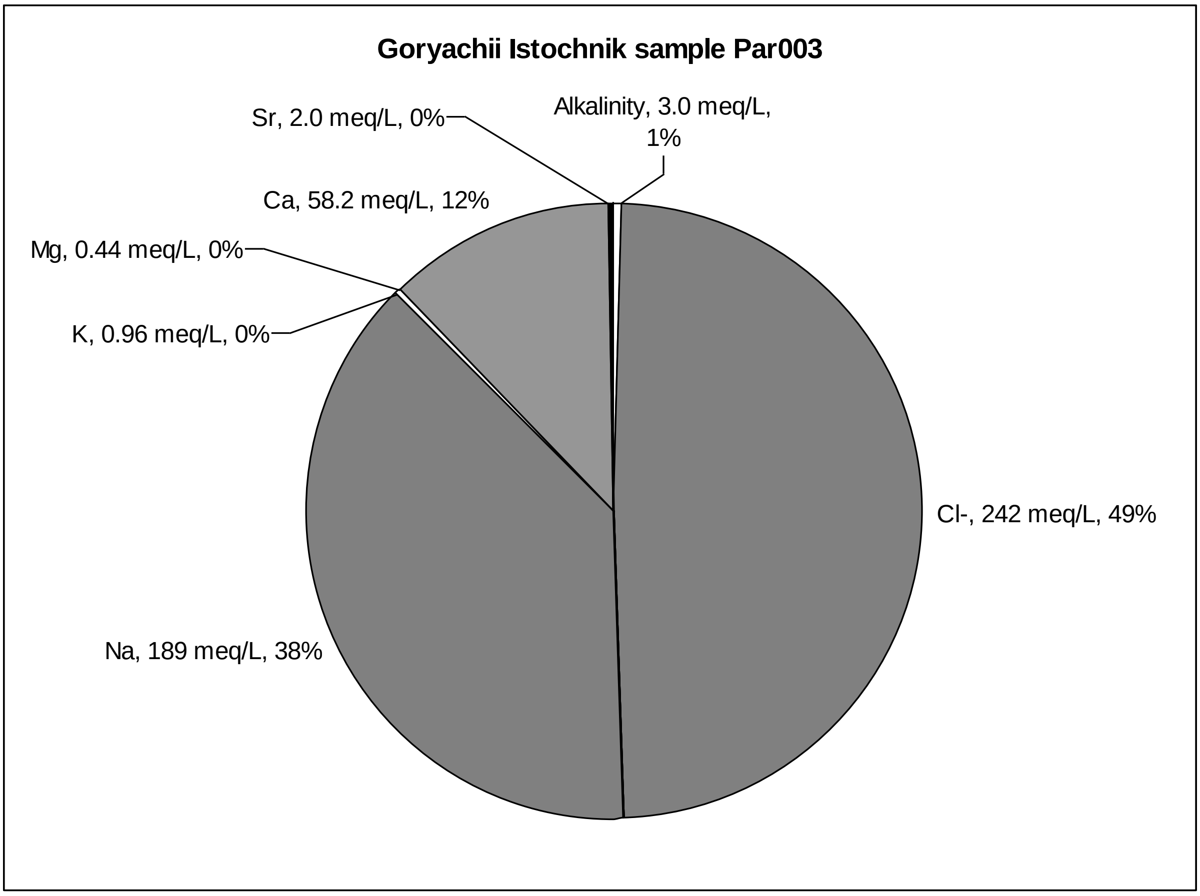

Figure 4.6. Pie diagram representing the meq/L composition of water from the Goryachii Istochnik 3-R borehole (sample Par003, at 08:40 on 30/8/13).

The highly reducing nature of the water is reflected in:

- concentrations of $SO_4^{=}$ and nitrate (NO_3^-) below detection limit (<25 mg/L and <15 mg/L respectively). The sulphur concentration, as measured by ICP-MS is also <12 mg/L.
- the water's low Eh (c. -280 to -300 mV)
- the odour of H_2S gas in the water and the previously demonstrated presence of methane in flammable quantities (Banks et al. 2011).
- the highly elevated concentration of barium (around 17 mg/L)

Concentrations of iron and manganese were, however, rather modest at around c. 80 µg/L and c. 340 µg/L, respectively, presumably being suppressed by the high pH of the water and the excessive sulphide concentrations.

The water as a whole is far more saline than at Byelii Yar, however, with a total ion content of around 460 meq/L, as opposed to c. 58 meq/L at Byelii Yar.

Sample No.			Par001F	Par002F	Par003F	Par004F
BGS sample reference		**Detection limit**	**13223-0005**	**13223-0006**	**13223-0007**	**13223-0008**
Date of sampling			29/08/2013	30/08/2013	30/08/2013	30/08/2013
Time	Local		20:20	02:15	08:40	14:55
Field determinations						
pH			7.24	7.39	7.30	7.39
Eh	mV		-256	-282	-283	-298
T	°C		49.9	50.0	50.0	50.0
t-Alk 1	meq/L		2.5 to 3.8	3.3	3.0	2.9
t-Alk 2	meq/L		3.0 to 3.6	3.2	3.0	3.0
t-Alk 3	meq/L		3.0 to 3.4	3.2	3.0	2.9
t-Alk 4	meq/L		3.2 to 3.6	3.0 to 3.3		
t-alkalinity	meq/L		3.4	3.2	3.0	2.9
Anions by ion chromatography						
Cl^-	mg/L		7481	7659	8562	7545
SO_4^{2-}	mg/L	**25**	<25	<25	<25	<25
NO_3^-	mg/L	**15**	<15	<15	<15	<15
Br^-	mg/L		28.4	27.9	32.7	27.9
F^-	mg/L	**2.5**	<2.5	<2.5	<2.5	<2.5
Major and minor cations by ICP-MS						
Na	mg/L	**5**	4053	4272	4339	4222
Mg	mg/L	**0.3**	5.1	5.3	5.4	5.2
Ca	mg/L	**6**	1104	1153	1166	1147
K	mg/L	**0.5**	35.7	37.3	37.4	36.7
Mn	µg/L	**1**	326	341	348	345
Fe	µg/L	**4**	72	89	78	84
Sr	µg/L	**13**	81378	86488	86377	84475
Ba	µg/L	**0.3**	17939	17156	16757	17600
Li	µg/L	**14**	724	691	657	666
Other significant elements						
Al	µg/L	**4**	<4	<4	<4	9
Si	µg/L	**64**	17959	20063	19835	19337
P	mg/L	**0.06**	<0.06	<0.06	<0.06	<0.06
S	mg/L	**12**	<12	<12	<12	<12
B	µg/L	**223**	11172	10834	10237	10343
Trace elements						
Ag	µg/L	**0.3**	<0.3	<0.3	<0.3	<0.3
As	µg/L	**0.2**	133	126	126	130
Be	µg/L	**0.03**	0.09	0.03	0.06	<0.03
Cd	µg/L	**0.3**	<0.3	<0.3	<0.3	<0.3
Co	µg/L	**0.2**	<0.2	<0.2	<0.2	<0.2
Cr	µg/L	**0.2**	<0.2	0.5	<0.2	<0.2
Cs	µg/L	**0.04**	15.2	16.0	15.4	15.6
Cu	µg/L	**3**	<3	<3	<3	<3
Ga	µg/L	**2**	<2	<2	<2	<2
Hf	µg/L	**0.03**	<0.03	<0.03	0.03	0.03
Mo	µg/L	**0.2**	1.0	1.0	0.8	0.9
Nb	µg/L	**0.07**	<0.07	<0.07	<0.07	<0.07
Ni	µg/L	**0.2**	<0.2	0.3	<0.2	<0.2
Pb	µg/L	**0.4**	<0.4	<0.4	<0.4	<0.4
Rb	µg/L	**0.05**	63.2	60.7	59.6	61.6
Sb	µg/L	**0.008**	0.246	0.249	0.248	0.272
Se	µg/L	**0.2**	<0.2	<0.2	0.3	<0.2
Sn	µg/L	**0.09**	<0.09	<0.09	<0.09	<0.09
Ta	µg/L	**0.2**	<0.2	<0.2	<0.2	<0.2
Th	µg/L	**0.06**	0.08	<0.06	<0.06	0.06

Ti	µg/L	**0.6**	<0.6	<0.6	<0.6	<0.6
Tl	µg/L	**0.2**	<0.2	0.2	<0.2	<0.2
U	µg/L	**0.08**	<0.08	<0.08	<0.08	<0.08
V	µg/L	**2**	<2	<2	<2	<2
W	µg/L	**0.2**	1.34	1.35	1.25	1.31
Zn	µg/L	**2**	9	9	10	12
Zr	µg/L	**0.06**	<0.06	<0.06	<0.06	<0.06
Rare Earth Elements						
Y	µg/L	**0.03**	0.57	0.63	0.57	0.60
La	µg/L	**0.02**	0.17	0.21	0.19	0.19
Ce	µg/L	**0.04**	<0.04	<0.04	<0.04	<0.04
Pr	µg/L	**0.03**	<0.03	<0.03	<0.03	<0.03
Nd	µg/L	**0.6**	<0.6	<0.6	<0.6	<0.6
Sm	µg/L	**0.03**	0.11	0.07	0.12	0.09
Eu	µg/L	**0.02**	<0.02	<0.02	0.05	0.03
Tb	µg/L	**0.009**	<0.009	<0.009	<0.009	<0.009
Gd	µg/L	**0.02**	<0.02	<0.02	<0.02	<0.02
Dy	µg/L	**0.03**	<0.03	<0.03	<0.03	<0.03
Ho	µg/L	**0.01**	<0.01	<0.01	<0.01	<0.01
Er	µg/L	**0.02**	<0.02	<0.02	<0.02	<0.02
Tm	µg/L	**0.007**	0.008	<0.007	<0.007	<0.007
Yb	µg/L	**0.02**	0.05	0.07	0.04	0.05
Lu	µg/L	**0.01**	0.02	0.02	0.02	0.02

Table 4.3. Inorganic chemical analysis of water from Goryachii Istochnik 3-R borehole, analysed by ICP-MS and ion chromatography techniques at the British Geological Survey, Keyworth, UK. Note that three or four determinations of alkalinity were made in the field (pale script), resulting in an average.

The total mineralization of the water can be estimated by summing chloride, sodium, bicarbonate and calcium = 12.8 to 14.2 g/L, which coincides well with previously reported analyses from the well.

In contrast to Byelii Yar (Chapter 3), calcium is present in the water at a high concentration of 1.1 to 1.2 g/L, while magnesium is almost absent from the water (Mg around 5 mg/L). Simulation using PHREEQC Interactive software confirms that the waters are somewhat supersaturated with respect to calcite and approximately saturated with respect to dolomite and strontianite. Magnesium/strontium mass ratios are extremely low (c. 0.06), and even lower than Byelii Yar (c. 0.14), suggesting that strontium (up to 86 mg/L at Goryachii Istochnik) has accumulated strongly during a prolonged residence time, while magnesium has been depleted, possibly by dolomitisation. The molar ratio of Na/Cl^- is between 0.78 and 0.86, which is almost identical to modern sea water (0.86).

The sodium content of 4.05 - 4.34 g/L and the chloride content of 7.48 - 8.56 g/L suggests that the water could represent a mixture of fresh meteoric recharge water with around 40% marine water (which could be original connate marine sedimentary water, or be derived from a subsequent marine inundation of the terrain).

Bromide occurs at 28-33 mg/L in the water, with a chloride to bromide mass ratio of around 262-275. This is very close to seawater (288) and suggests that the groundwater's salinity may have its origin in relict ocean water.

Fluoride concentrations are less than the analytical detection limit (<2.5 mg/L) at Goryachii Istochnik; i.e., much lower than at Byelii Yar (11.5 mg/L). The lower fluoride at Goryachii Istochnik reflects the rather high calcium concentration, which places a fluorite (CaF_2) saturation ceiling on the accumulation of fluoride. Simulation using PHREEQC Interactive software confirms that a fluoride content of <2.5 mg/L could result in fluorite saturation.

As regards other components of health significance: arsenic concentrations are very high at 130 µg/L (in stark contrast to c. 0.5 µg/L at Byelii Yar). This fully supports the analyses of 2010, carried out at the laboratory of the Geological Survey of Norway, which found 120 µg/L - Banks et al. 2011). The water from Goryachii Istochnik should thus not be used for regular human consumption, on the grounds of its arsenic concentration.

In the water of Goryachii Istochnik, concentrations of most heavy metals (except barium - see above) are low and are presumed to be suppressed by the high pH and sulphide concentrations.

As at Byelii Yar, uranium concentrations are below detection limit while one sample exhibits a detectable thorium concentration. This is likely to reflect the highly reducing nature of the water, in which uranium is almost insoluble. Tungsten occurs at around 1.3 µg/L: this is an element known to accumulate in high pH groundwaters.

Silicon is present at concentrations of around 18-20 mg/L (around 38-43 mg/L as SiO_2). This is higher than at Byelii Yar and may reflect the higher solubility of silica at higher downhole temperatures. Boron reaches rather high concentrations of 10-11 mg/L.

4.3 Stable Isotopes

In parallel with the four samples of groundwater, taken in August 2013 for chemical analysis, four x 15 mL aliquots (Par001F to BPar004F), filtered at 0.45µm using a hand-held syringe and filter capsule, were also taken for stable isotope analysis. During storage and transport the HDPE bottles were sealed with 'Parafilm®'. The samples were analysed by Prof. Adrian Boyce's laboratory at the Scottish Universities Environmental Research Centre (SUERC), where the following results were obtained (Table 4.4, see also Figure 3.6):

Sample no.	**d^{18}O VSMOW**	**d^{2}H SMOW**
	‰	**‰**
Par001F	-11.0	-103
Par001F	-11.0	
Par002F	-10.6	-102
Par002F	-10.8	
Par003F	-10.8	-104
Par003F	-10.8	
Par004F	-11.0	-107
Par004F	-10.8	

Table 4.4. Stable isotope analysis of water from Goryachii Istochnik 3-R borehole, analysed by mass spectrometry techniques at SUERC, East Kilbride, UK.

When plotted on an ^{18}O vs. ^{2}H plot (Figure 3.6), the Goryachii Istochnik (Parabel) samples fall to the right of the global meteoric water line (GMWL). This suggests that the water may partly be derived from meteoric recharge, but with the isotopic signature modified by ^{18}O exchange with the aquifer matrix in a mildly geothermal environment. The fact that the samples lie closer to the origin than the Byelii Yar samples may also suggest a greater component of connate marine water.

5 BRIEF COMPARISON AND CONCLUSIONS

5.1 Comparison

Table 5.1 highlights several key parameters describing the hydrochemistry of the groundwaters sampled from Byelii Yar and Goryachii Istochnik, based on samples ByY004F and Par002F (deemed to be the most representative of the samples taken), respectively.

Parameter	Unit	Modern Seawater (ppm)	Byelii Yar 1-R	Goryachii Istochnik 3-R
Temperature at wellhead	°C		44.8	50.0
pH			8.21	7.39
Eh	mV		-336	-282
t-alkalinity	meq/L	2.29 meq/kg	4.7	3.2
Na	mg/L	10784	656	4272
Mg	mg/L	1284	0.14	5.3
Ca	mg/L	412.1	9.4	1153
K	mg/L	399.1	3.14	37.3
Cl^-	mg/L	19352	843	7659
Br^-	mg/L	67.3	3.04	27.9
Sr	mg/L	7.9	1.00	86.5
Ba	mg/L		0.23	17.2
Li	µg/L	170	46	691
Rb	µg/L	120	3.94	60.7
B	mg/L	4.5 (4 to 5)	2.27	10.8
Ratios				
Mg/Ca	molar	5.14	0.024	0.0076
Sr/Ca	mass	0.0192	0.11	0.075
Mg/Sr	mass	163	0.14	0.061
Na/Cl^-	molar	0.86	1.20	0.86
Br^-/Cl^-	mass	288	277	275
K/Rb	mass	3326	798	615

Table 5.1. Comparison of hydrochemistry of groundwaters from Byelii Yar 1-R and Goryachii Istochnik 3-R. Seawater chemistry in ppm (or meq/kg for alkalinity) taken from Dickson & Goyet (1994). Rb in seawater from Smith et al. (1965). Li in seawater from Lenntech (2014). B in seawater from MBARI (2014) and Rakestraw & Mahncke (1935).

Table 5.2 estimates the proportion of marine water within the samples, to account for the salt content (based on current marine composition).

	Byelii Yar borehole 1-R			
	ByY001	**ByY002**	**ByY003**	**ByY004**
Cl^-	4%	4%	4%	4%
Na	6%	6%	6%	6%
Br^-	5%	5%	5%	5%
Rb	3%	3%	3%	3%
	Goryachii Istochnik borehole 3-R			
	Par001	**Par002**	**Par003**	**Par004**
Cl^-	39%	40%	44%	39%
Na	38%	40%	40%	39%
Br^-	42%	41%	49%	41%
Rb	53%	51%	50%	51%

Table 5.2. Percentage of marine water in samples to account for content of four potentially marine-related components. Seawater chemistry assumed to be Cl^- = 19.35 g/kg, Na = 10.78 g/kg, Br^- 67.3 mg/kg (Dickson & Goyet, 1994), Rb = 120 µg/kg (Smith et al. 1965).

5.2 Conclusions - Byelii Yar

The groundwater discharging from the Byelii Yar borehole is a brackish (mineralisation = 1.8 g/L) water, believed to be derived from early Cretaceous (Hauterivian-Barremian) Ilekskaya Suite strata in the depth interval 1997 to 2005 m bgl. The water contains dissolved methane and hydrogen sulphide gases and is highly reducing (Eh = c. -340 mV). The water temperature on discharge varies with discharge rate, but reaches 44.8°C. The pH is around 8.2.

The water's chemical composition is dominated by Na^+-Cl^- with a modest component of bicarbonate alkalinity. The Br/Cl ratio indicates that the groundwater's salinity is likely to be derived from marine salts (possibly original sedimentary "connate" water, or marine water that has intruded during a subsequent marine inundation). The water chemistry has been modified by prolonged residence at high pH (high strontium concentrations, some lithological Na-excess and removal of Ca and Mg by carbonate precipitation).

The salinity represents only 4-5% of marine salinity, however. Thus, although the water's salinity may be derived from marine salts, isotopic evidence suggests that the majority of the water itself is derived from direct or indirect infiltration of meteoric precipitation.

5.3 Conclusions - Goryachii Istochnik

The groundwater discharging from the Goryachii Istochnik borehole 3-R, near Parabel', is a saline (mineralisation up to 14 g/L) water, believed to be derived from Mesozoic sedimentary strata at least 2000 m bgl. The water contains dissolved methane and hydrogen sulphide gases and is highly reducing (Eh down to -298 mV). The water temperature on discharge is around 50°C. The pH is around 7.3.

The water's chemical composition is dominated by Na^+-Cl^- with subsidiary calcium. The Br/Cl and Na/Cl ratios suggest that the water's salinity is likely to be derived from marine salts (possibly original sedimentary "connate" water, or marine water that has intruded during a subsequent marine inundation). The salinity represents around 40% of modern marine salinity. Isotopic evidence suggests that the remainder of the water itself is derived from direct or indirect infiltration of meteoric precipitation.

The water chemistry and stable isotopic signature has been modified by prolonged residence at high pH and temperature (high strontium concentrations, and removal of Mg by immobilisation in carbonate).

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APPENDIX 1 - BGS ANALYTICAL PROTOCOL

Analytical Documentation from the British Geological Survey

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ANALYTICAL GEOCHEMISTRY LABORATORIES

ANALYSIS REPORT COVER NOTE

This report consists of a 2 page Analysis Report Cover Note and 3 pages of test data

Report Number:	13223/1	Customer Ref/Order No:	Siberian waters
Report Date:	16 October 2013	Sample(s) received on:	05 September 2013
Issue Status:	Complete	Analysis commenced on:	25 September 2013

Sample Details

All samples were received in good condition. The samples were acidified with 1% v/v HNO_3 and 0.5% v/v HCl before analysis by ICP-MS.

Unless previously agreed otherwise in writing, samples will be retained for six months from the date of issue of this report prior to disposal. Please contact the Laboratory if you wish to make alternative arrangements. This excludes any subcontracted analysis.

Analysis Details

Determinands	Test Method	Procedure	Notes
Ca, Mg, Na, K, Si, Ba, Sr, Mn, Total Fe, Li, Be, B, Al, Ti, V, Cr, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Pb, Th, U	ICP-MS	AG 2.3.18	UKAS
Total P, Total S, Ag	ICP-MS		N

Tests marked UKAS in the above table are included in the UKAS Accreditation Schedule for this Laboratory; those marked N are not. Tests marked S have been subcontracted to an outside laboratory who either hold (S1) or do not hold (S2) UKAS accreditation for the method concerned.

Due to high concentrations present in the samples the analysis was carried out at x5 dilution for samples 13223-0001 to 13223-0004 and at x25 dilution for samples 13223-0005 to 13223-0008. The reported detection limits reflect the dilutions used.

Because of limitations with the current software used for reporting data, the number of significant figures quoted in the attached table may not be representative of the actual uncertainty. Data should be considered accurate to no more than three significant figures.

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ANALYTICAL GEOCHEMISTRY LABORATORIES

ANALYSIS REPORT COVER NOTE

This report is issued under complete status. All analyses requested have been completed and results are issued with full compliance of data verification.

We would be pleased to receive any feedback you may have on the quality of our service.

Report authorised by: .... Date: ....

Dr Simon Chenery
Deputy Head of Inorganic Geochemistry

Opinions and interpretations expressed herein are outside the scope of UKAS accreditation. The BGS does not accept responsibility for the validity of methods used to obtain or preserve the samples provided to the Laboratory and does not accept liability for the consequences of any acts taken or omissions made on the basis of the analysis or advice or interpretation provided. The results given relate only to the items tested.

APPENDIX 2 - SOVIET DATA ON GORYACHII ISTOCHNIK BOREHOLE 3-R

ГЕОЛОГИЧЕСКИЙ РАЗРЕЗ СКВАЖИНЫ № 3-Р

абсолютная отметка устья
57,74 м

№№	ОПИСАНИЕ ПОРОД	геолог. возраст	Глубина, м от	до
1	2	3	4	5
1.	Песок с глиной	Q	00	30
2.	Алеврит серый с прослоями глины	Pg_3	30	102
3.	Глина темная зеленая с прослоями песка		102	176
4.	Песок темно-серый с прослоями гальки	Pg_{2-3}	176	182
5.	Алеврит серый		182	240
6.	Глина серая слюдистая		240	360
7.	Песчаник темно-серый ожелезненный		360	376
8.	Песок зелено-серый	Cr_2	376	420
9.	Глина серая слюдистая		420	457
10.	Песок серый		457	600
11.	Глина серая с прослоями песка		600	674
12.	Песок крупнозернистый слюдистый		674	700
13.	Глина серая с прослоями песка		700	836
14.	Глина с песчаником		836	1020
15.	Глина серая с редкими прослоями песчаника		1020	1120
16.	Песчаники серые известковистые		1120	1362
17.	Глина темно-зеленая с прослоями песчаника		1362	1486
18.	Глина аргиллитоподобная		1486	1760
19.	Глина		1760	2050

1	2	3	4	5
20.	Глина с прослоями песчаника		2050	2140
21.	Глина аргиллитоподобная с прослоями песчаника		2140	2194
22.	Глина темно-серая с прослоями песчаника	C_2	2194	2250
23.	Глина серая с прослоями песчаника	J_1	2250	2330
24.	Переслаивание аргиллитов и песчаников	J_{1-2}	2330	2600
25.	Монцонит и гранит	Pz	2600	2609

СРАВНИТЕЛЬНАЯ ХАРАКТЕРИСТИКА НЕКОТОРЫХ ФИЗИКО-ХИМИЧЕСКИХ ПОКАЗАТЕЛЕЙ ПАРАБЕЛЬСКОЙ ПОДЗЕМНОЙ ВОДЫ ПО СЕЗОНАМ 1974 г.

Местонахождение скважины п. Парабель

Организация проводившая анализ Томский НИИ курортологии
Томский мединститут

Дата анализа (месяц): В 1л. воды содержится, мг:	Февраль	Апрель	Июль	Сентябрь	Примечание допуст. расхожд. (А.А.Резников, 1970).
J	I,2	0,9	I,4	-	1 мг/л
Br	-	3,0	6,0	3,0	4%
H_2SiO_3	56,6	60,6	59,3	57,5	15 %
H_2S	– –	5,3	3,4	6,8	8%
F	2,8	3,0	2,2	2,4	15%
PH	7,55	7,5	7,6	7,25	0,1 pH
T°	53,0	53,0	53,0	53,0	–
M (г/л)	I3,4	I4,3	I3,0	I3,5	2%
Формула ионного состава	$\frac{Cl\,98}{Na\,73\,Ca\,25}$	$\frac{Cl\,99}{Na\,70\,Ca\,25}$	$\frac{Cl\,97}{Na\,73\,Ca\,26}$	$\frac{Cl\,99}{Na\,78\,Ca\,20}$	

(Формула М.Г.Курлова, усредн. зн.) $H_2S_{0,00516}\,M_{13,5}\,\frac{Cl\,98}{Na\,74\,Ca\,24}\,pH\,7,5\;T\,53$

Обозначения: - не обнаружено

– не определяли

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