GALLIUM AND GERMANIUM DISTRIBUTON IN GEOTHERMAL WATER

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ABSTRACT

The geochemistry of gallium and germanium was studied in geothermal waters from the low-temperature fields in the Southern Lowlands and the Geysir high-temperature field in Iceland. Germanium concentrations in waters with temperatures below 225°C were in the range <0.05-24 ppb whereas those of gallium lie in the range of <0.01-21 ppb. Both elements show positive relationships with temperature, in particular Ge. Based on aqueous speciation studies, the dominant forms of Ge and Ga in the water are $H_4GeO_4^0$ and $Ga(OH)_4^-$, respectively, but $H_3GeO_4^-$ and $Ga(OH)_3^0$ are also important. The mobility of Ge relative to Si and of Ga relative to Al is much higher than the respective primary rock ratios. The cause of this is considered to be either non-stoichiometric dissolution of the primary basalt rock-forming minerals with respect to Ge and Si and Ga and Al and/or exchange of Ge into silicates and Ga into aluminium silicates in ratios that differ from those of fresh basalt. An example of such an exchange is given for Si and Ge.

INTRODUCTION

Gallium and germanium are trace elements in geothermal waters. They are positioned below Al and Si in the Periodic Table and exhibit many similar chemical properties. Germanium is enriched in geothermal water and some non-thermal groundwater relative to the ocean and river water. Only 0.06 ppb Ge are present in oceanic water (Burton et al., 1959). By contrast, Ge concentrations reported for geothermal waters are much higher, or between 2 and 30 ppb for Icelandic geothermal waters (Arnórsson, 1984), 0.4-43.8 ppb for geothermal waters in Japan (Uzumasa et al., 1959), 2-20 ppb in Vichy, France (Criaud and Fouillac, 1986) and on the Juan de Fuca Ridge they lie in the range 10.9-18.9 ppb (Mortlock et al., 1993). Much less data are available on Ga concentrations in geothermal waters. The values, however, seem to be lower compared to Ge. Gallium concentrations in geothermal waters at Broadlands and Wairakei, New Zealand, were estimated to be ~0.6 and ~0.2 ppb, respectively (Goguel, 1988) and in some Japanese geothermal waters values between 0.11 and 72 ppb have been reported (Uzumasa and Nasu, 1960).

The purpose of this study is to establish the distribution of Ga and Ge in geothermal waters from the Southern Lowlands in Iceland and to delineate the processes that may control the concentrations of these trace elements in these waters. The study is based on analyses of 72 samples of thermal waters from the Southern Lowlands and the Geysir high-temperature field and 22 samples of cold ground and surface waters, collected and analysed by Arnórsson and co-workers in 2002-2005. The cold waters mostly have temperatures below 10°C whereas the thermal waters are from slightly above ambient to >200°C. The waters from the Southern Lowlands are associated with basaltic rock formations, but in the Geysir field both basaltic and silicic volcanics outcrops.

GEOLOGICAL SETTINGS

Iceland is located on the North-Atlantic Ridge that separates the North-American and Eurasian plates (Vink, 1984). The volcanic succession pile of Iceland can be divided into four zones based on the age of the rocks: the Upper Tertiary flood basalt formations which are older than 3.1 m.y., the Upper Pliocene and Lower Pleistocene grey basalt formation, which are between 0.7 and 3.1 m.y., the Upper Pleistocene palagonite (hyaloclastite) formation that is younger than 0.7 m.y., and Postglacial lavas which formed during the last 9,000 to 13,000 years (Saemundsson, 1979).

Geothermal systems in Iceland have been divided into two groups, high-temperature fields (volcanic geothermal systems) and low-temperature fields (non-volcanic systems). The high-temperature fields are located within the active zone of volcanism and rifting and temperatures exceed 200°C at less than 1000 m depth. The low-temperature fields are widely distributed in Quaternary and Tertiary formations and have much lower temperatures, less than 150°C in the uppermost 1000 metres (Arnórsson et al., 2008).

In the Southern Lowlands, low-temperature activity is widespread, and sometimes divided into three distinct areas (Arnórsson, 1995). It mostly occurs to the north of an east-west running zone of intense seismic activity (Einarsson,

1991) (Figures 1). Hot springs are typically associated with young fractures. The Geysir field, which is of the high-temperature type, is located in the northernmost part of the Southern Lowlands. Great Geysir of Haukadalur is in the area, one of the more famous geysers in the world (Barth, 1940). The bedrock in the Southern Lowlands is basaltic, for the most part lavas, pillow lavas and hyaloclastite of Quaternary age. They are overlain in places by sediments formed at the end of the last glaciation and in early Holocene times. The same types of rocks outcrop in the Geysir field, i.e. hyaloclastites, in addition to relatively abundant rhyolites (Arnórsson, 1985).

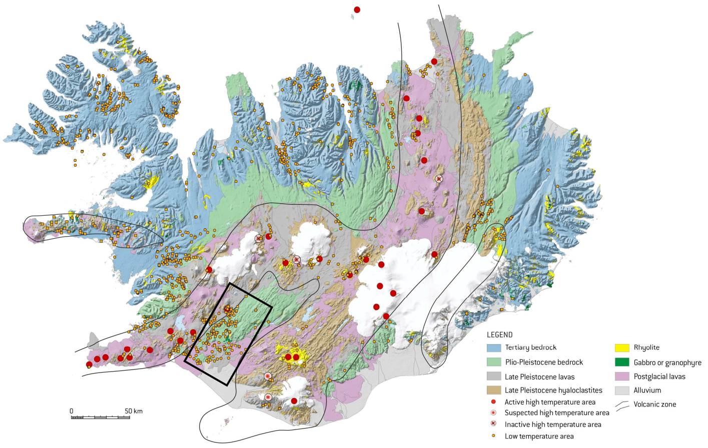

FIGURE 1: A geological map of Iceland with geothermal areas (modified from ISOR database)

SAMPLING AND ANALYTICAL METHODS

The present study is based on data on the chemical composition of 91 samples of ground and geothermal waters from the Southern Lowlands and the Geyser geothermal field (Figure 2). Of these, 66 are of geothermal waters from springs and wells and 25 are non-thermal groundwater, also from springs and wells. The data constitute a part of an unpublished database of the Institute of Earth Science of the University of Iceland, the University of Akureyri and Iceland GeoSurvey. The samples from the Southern Lowlands were collected and analysed in 2002-2005, whereas the samples from the Geysir geothermal field were collected and analysed in 2001. The samples were collected and analysed by Stefán Arnórsson and co-workers. The results for elements relevant for the present study are shown in Table 1.

The samples were collected and treated according to the procedures described by Arnórsson et al. (2002) and Arnórsson and Óskarsson (2007). The samples were filtered on-site through a 0.2 µm acetate cellulose membrane followed by acidification by 1 ml Suprapur HNO_3 (Merck) to a 100 ml sample. Aluminium, Ga, Ge and Si, as well as a number of other major and trace elements, were determined by ICP-MS, ICP-OES and ion chromatography. The detection limit for

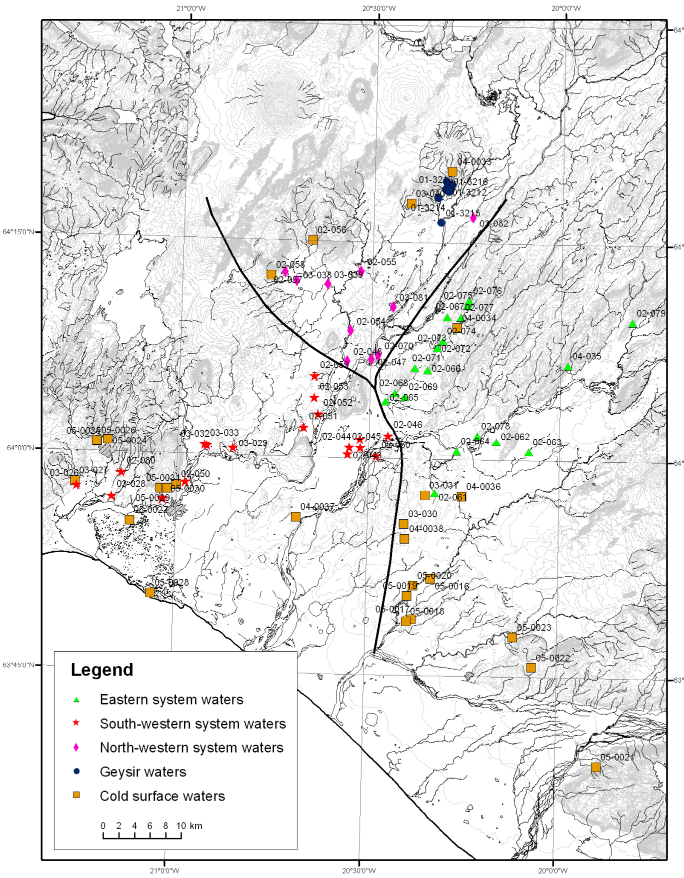

FIGURE 2: A map of the Southern Lowlands of Iceland showing sample locations and the division of the low-temperature activity into three fields; The Geysir high-temperature field is located at the northern periphery of the area

Ge and Ga are ~0.01 and ~0.05 ppb, respectively.

AQUEOUS SPECIATION

Thermodynamic data

To quantify and understand the Ga and Ge accumulation in geothermal waters requires knowledge of the thermodynamic properties of important aqueous Ga and Ge species. The most important aqueous Ge species are germanic acid ($H_4GeO_4^0$) and its dissociation products ($H_3GeO_4^-$ and $H_2GeO_4^{2-}$).

TABLE 1: The concentrations of SiO2, Al, Ga and Ge in cold groundwater and geothermal waters from the Southern Lowlands and the Geysir high-temperature field; also shown are measured surface temperature , and silica and Na/K geothermometer temperatures.

Sample No.	Location	Coordinates	t_{meas}/°C	t_{NaK}/°C	t_{cal}/°C	SiO$_2$ ppm	Al ppb	Ga ppb	Ge ppb
01-3201	Geysir	64.31387/-20.29934	87.0	197	233	533.9	742.0	9.10	21.40
01-3202	Blesi	64.31352/-20.30140	87.5	188	230.7	517.3	300.0	7.94	21.10
01-3203	Ótherrishola	64.31208/-20.30237	98.0	188	230.5	519.0	243.0	13.00	20.30
01-3204	Litli-Geysir	64.31180/-20.30126	93.0	143	214.4	416.1	394.0	20.50	23.60
01-3205	Litli-Strokkur	64.31115/-20.30230	88.0	141	207.3	364.7	156.0	14.90	17.90
01-3206	Smidur	64.31057/-20.30184	99.0	142	204	358.5	165.0	20.90	17.50
01-3207	Konungshver	64.31386/-20.30186	95.0	184	226.2	488.9	386.0	10.30	21.30
01-3208	Helludalur 1	64.32171/-20.30826	30.1	187	81.1	62.7	8.8	0.11	2.05
01-3209	Laugarfell west	64.31280/-20.31019	38.8	155	101.4	88.5	8.0	0.06	2.62
01-3210	"82-015"	64.31833/-20.30478	26.0	155	72.3	51.7	11.7	0.21	1.25
01-3211	Spring by Beiná	64.31793/-20.29345	19.6	161	39.2	24.6	7.2	0.14	0.17
01-3212	Laugarfell east	64.31390/-20.30607	97.5	132	208.1	373.8	564.0	19.90	18.10
01-3213	Strokkur	64.31269/-20.30095	86.0	156	214.2	416.7	543.0	14.90	22.80
01-3214	Nedridalur 1	64.30280/-20.33033	65.2	256	142.2	176.2	11.7	0.12	7.45
01-3215	Múli 1	64.27408/-20.32108	48.0	196	123	126.3	5.6	0.05	2.99
01-3216	Nyihver	64.31039/-20.30155	98.0	144	210.2	392.4	525.0	20.70	21.60
02-041	Blesastadir		69.0	74	70	66.7	48.2	2.22	2.20
02-042	Brautarholt	64:01.3137/20:31.3048	68.8	82	74	64.7	43.2	2.81	2.18
02-043	Brjánsstadir	64:00.2642/20:33.1877	63.9	137	117	125.1	3.6	0.11	2.41
02-044	Hlemmiskeid	64:00.7290/20:32.9498	68.5	87	64	67.3	71.5	3.55	1.48
02-045	Húsatóttir	64:01.5925/20:31.2093	73.5	87	66	68.1	51.9	2.96	2.26
02-046	Reykir, Skeid	64:02.6440/20:26.9037	68.3	85	75	64.7	41.3	2.38	3.37
02-047	Laugarás	64:06.8750/20:29.4882	97.3	108	98	110.4	120.0	4.98	6.21
02-048	Thorlákshver	64:06.7325/20:33.6703	97.0	104	109	104.6	109.0	3.92	6.73
02-050	Ingólfsfjall	63:57.8318/20:59.9705	3.8	133	12	13.1	14.8	0.45	<0.05
02-051	Vatnsendi	64:02.0740/20:40.2103	80.0	129	117	136.6	28.6	1.03	6.29
02-052	Hamrar	64:03:008720:37.9740	48.0	102	81	63.6	1.7	0.04	1.65
02-053	Sólheimar	64:04.1362/20:38.6425	79.0	110	107	96.5	16.3	1.63	6.82
02-054	Spóastadir	64:08.8410/20:33.2123	76.4	106	102	100.5	25.6	1.22	9.30
02-055	Sydri-Reykir	64:12.9550/20:31.7545	98.6	140	145	183.5	325.0	5.57	9.17
02-056	Ljósuár	64:15.0405/20:39.5447	4.3	137	-2	13.3	31.8	1.05	0.07
02-057	Laugarvatn I	64:12.8182/20:43.7842	97.0	136	118	140.0	139.0	3.84	6.70
02-058	Laugarvatn II	64:12.5493/20:45.9553	4.8	133	10	15.6	20.3	1.06	0.05
02-059	Kringla	64:05.6357/20:38.7160	81.3	103	86	83.3	66.1	2.95	8.15
02-060	Kaldárholt	64:00.1680/20:28.7383	62.4	71	57	51.9	35.8	1.90	1.06
02-061	Skammbeinsstadir	63:57.7073/20:19.4503	50.6	60	33	76.6	187.0	10.30	1.80
02-062	Hvammur, Skardsfjall	64:01.3134/20:09.8485	57.0	79	54	71.6	143.0	6.42	1.32
02-063	Stóri-Klofi	64:00.6440/20:04.7430	54.6	74	46	61.5	57.8	3.30	0.54
02-064	Flagbjarnarholt	64:00.5940/20:16.0819	60.4	69	49	71.4	146.0	8.45	2.69
02-065	Ósabakki	64:03.9940/20:27.4518	60.0	81	67	68.9	37.5	2.55	5.05
02-066	Midfell	64:06.1992/20:20.9337	62.0	80	96	91.9	11.9	0.85	5.25
02-067	Kópsvatn	64:09.9104/20:18.0108	94.0	122	133	156.6	64.3	2.66	8.84
02-068	Sydra-Langholt	64:04.5701/20:26.0099	64.2	91	78	69.3	45.3	2.46	4.95
02-069	Birtingaholt	64:04.3251/20:24.4410	61.0	88	73	69.9	26.0	1.87	5.18

TABLE 1: Continued

02-070	Audsholt, Bisk.	64:07.1811/20:28.7419	84.1	102	87	91.0	106.0	4.85	3.84
02-071	Ásatún	64:06.3328/20:22.9470	82.4	98	102	93.4	51.8	2.38	5.33
02-072	Flúdir	64:07.7525/20:19.4240	95.2	111	128	137.6	90.4	3.55	6.93
02-073	Flúdir	64:07.7530/20:19.4070	99.8	119	127	155.0	103.0	3.77	7.07
02-074	Vadmálahver	64:08.2195/20:18.5758	99.3	116	133	147.7	143.0	4.05	7.13
02-075	Thórarinsstadir	64:10.7200/20:14.7742	98.9	125	133	174.3	233.0	6.10	10.50
02-076	Laugar, Hrun	64:11.0508/20:14.5958	98.4	146	172	278.5	315.0	4.96	14.10
02-077	Reykjadalur	64:09.8834/20:15.8153	97.8	119	119	138.3	119.0	4.09	7.45
02-078	Thjórsárholt	64:01.6751/20:12.9245	63.2	90	56	70.2	175.0	7.89	2.15
02-079	Thjórsardalur	64:09.6914/19:48.6926	67.5	98	50	60.0	18.4	1.34	7.41
02-080	Gljúfurholt	63:58.5928/21:08.6710	82.1	128	118	116.9	63.7	1.50	5.91
03-026	Thóroddstadir, Ölfus, 1	63:57.6230/21:15.6159	120.0	124	122	129.4	93.4	1.23	9.40
03-027	Thóroddstadir, Ölfus	63:57.8611/21:15.9083	4.7	192	21	15.7	16.4	0.07	0.005
03-028	Audsholt, Ölfus, 1	63:56.9405/21:10.0430	59.5	73	55	50.7	52.3	1.84	4.85
03-029	Vadnes, 1	64:00.5292/20:51.2214	73.8	84	72	80.9	86.4	2.65	2.21
03-030	Laugaland, Holt	63:55.5150/20:24.1664	4.6	192	47	29.0	2.3	<0.005	0.014
03-031	Skammbeinsstadir	63:57.4965/20:20.9695	5.1	202	43	27.0	3.5	0.014	0.013
03-032	Öndverdarnes, 27	64:00.6458/20:55.3309	83.8	105	90	88.1	52.9	1.67	2.09
03-033	Öndverdarnes, 18	64:00.6994/20:55.6627	72.0	100	85	72.3	32.1	1.26	1.41
03-038	Útey	64:12.2125/20:41.9244	90.2	124	113	133.1	74.1	2.89	10.30
03-039	Austurey 1	64:12.0392/20:36.9789	88.2	104	93	103.9	125.0	3.06	9.77
03-040	Bjarnarfell water supply	64:17.7149/20:24.0784	6.7	144	31	22.5	15.5	0.24	0.22
03-081	Reykholt, 1	64:10.5379/20:26.5587	133.0	128	145	173.0	188.0	4.87	10.60
03-082	Gýgjarhólskot, 1	64:16.8487/20:14.2051	22.7	138	47	37.7	12.4	0.20	0.23
04-031	Árbaer	63:56.8582/21:02.0727	59.9	83	62	59.7	101.0	1.99	1.75
04-032	Árbaer	63:56.8410/21;02.0771	59.7	83	62	59.5	114.0	2.05	1.60
04-033	Haukadalur	64:20.0035/20:17.6668	5.9	162	24	17.5	16.9	0.16	0.08
04-034	Flúdir	64:09.1498/20:16.3752	6.7	230	51	31.9	6.4	<0.005	0.02
04-035	Ásólfsstadir, 1	64:06.6545/19:58.7788	51.6	70	68	79.1	34.3	0.835	4.36
04-036	Laekjarbotnar, Land	63:57.4585/20:15.2132	5.3	162	37	22.9	7.9	0.037	0.03
04-037	Urridafoss	63:55.8115/20:41.1091	4.4	205	44	27.4	4.3	<0.005	0.02
04-038	Bjálmholt	63:54.4677/20:23.9866	5.5	174	48	30.1	4.6	0.012	0.04
05-019	Hella	63:50.5288/20.23.4507	5.0	237	49	30.6	1.7	<0.005	0.007
05-020	Hella	63:51.2504/20:22.5616	7.0	212	47	29.1	2.4	<0.005	0.004
05-023	Hvolsvöllur	63:47.8123/20:06.8407	3.8	196	27	17.8	6.6	0.040	0.002
05-024	Hveragerdi	64:00.8208/21:10.9586	11.1	238	33	20.7	1.8	<0.005	0.009
05-025	Hveragerdi	64:00.6758/21:12.6596	6.6	173	21	15.3	9.4	0.052	0.055
05-026	Hveragerdi	64:00.7022/21:12.7003	6.6	174	19	14.6	10.0	0.052	0.040
05-027	Kaldadarnes	63:55.2541/21:07.1673	5.8	205	42	25.9	0.6	<0.005	0.011
05-028	Stokkseyri	63:50.2814/21:03.5478	9.0	181	31	22.4	1.5	<0.005	<0.001
05-029	Selfoss 1	63:57.5389/21:02.4961	4.0	127	18	13.9	13.3	0.247	0.020
05-030	Selfoss 2	63:57.5478/21:01.6121	3.6	117	19	14.2	10.3	0.196	0.017
05-031	Selfoss 3	63:57.5626/21:01.3249	3.4	129	13	13.8	15.3	0.203	0.016

Experimental data on the first dissociation constant of germanic acid were summarised by Wood and Samson (2006). The data show considerable discrepancies. For this study the data of Pokrovski and Schott (1998) were selected. They are summarised in Table 2. Experimental data on the second dissociation constant of germanic acid is available at 25°C only. They indicate that the $H_2GeO_4^{2-}$ species only occurs in significant concentrations at pH above 12, meaning that this species is not expected to contribute significantly to the total germanium concentration in the water considered for the present study. This species was, therefore, ignored and it was assumed that practically all aqueous germanium occurs as $H_4GeO_4^0$ and $H_3GeO_4^-$. The most important Gallium species are Ga^{3+}, $GaOH^{2+}$, $Ga(OH)_2^+$ and $Ga(OH)_4^-$ (Wood and Samson, 2006). The thermodynamic properties of the Ga species were selected from Wood and Samson (2006) and Shock et al. (1997).

The temperature dependence of the equilibrium constants for Ga and Ge species was calculated from the following equation, using the data in Table 1 (see Arnórsson et al., 1982):

$$\log K = 0.0523 \times \Delta_r S° + (33.043\ \Delta_r S° - 0.2185\ \Delta_r H°)/T + 0.623 \times 10^{-6} \times \Delta_r S° \times T^2$$

In the above equation, $\Delta_r S$ and $\Delta_r H$ represent the entropy and enthalpy of the respective reaction at 25°C, and T is in Kelvin. The resulting dissociational reactions are summarised in Table 2.

TABLE 2: Thermodynamic data used in the present study

Reaction	$\Delta_r S°(T_r)$ (cal/mol.K)	$\Delta_r H°(T_r)$ (cal/mol)	Log K(Tr)	Log K (T)
$GaOH^{2+} = Ga^{3+} + OH^-$	-20.33	9153.6	-11.85	$-1.063-2671.9 / T-12.666\times10^{-6}\times T^2$
$Ga(OH)_2^+ = GaOH^{2+} + OH^-$	-22.24	6104.1	-9.34	$-1.163-2069.36 / T-13.86\times10^{-6}\times T^2$
$Ga(OH)_3 = Ga(OH)_2^+ + OH^-$	-44.86	-340.0	-9.56	$-2.346-1409.50 / T- 27.95\times10^{-6}\times T^2$
$Ga(OH)_4^- = Ga(OH)_3 + OH^-$	-3.52	12975.5	-9.91	$-0.184-2951.58 / T-2.19\times10^{-6}\times T^2$
$H_4GeO_4 = H_3GeO_4^- + H^+$	-20.69	6500		

Speciation calculation

Calculation of the aqueous speciation distribution was carried out with the aid of the WATCH programme, version 2.3 (Arnórsson et al., 1982; Bjarnason, 1994). For a selected temperature, the programme calculates individual aqueous species activities, activity coefficients and selected mineral activity products as well as mineral solubility constants for the same minerals. This involved simultaneous solution of mass balance and mass action equations. Gallium and Ge are not included in the database of the WATCH program but were added to the calculation routine for the present work. The species included were $H_4GeO_4^0$ and $H_3GeO_4^-$ for germanium, and Ga^{3+}, $GaOH^{2+}$, $Ga(OH)_2^+$, $Ga(OH)_3$ and $Ga(OH)_4^-$ for gallium. The hydrolysis reactions for the respective species are given in Table 2. The activity coefficient is obtained from the Debye-Hückel equation:

$$-\log \gamma_i = \frac{A z_i^2 \sqrt{I}}{1 + B \mathring{a}_i \sqrt{I}}$$

where γ_i is the activity coefficient, A and B are temperature and pressure dependent solvent parameters, z_i is the species charge and I is ionic strength given by:

$$I = 0.5\ \Sigma m_i z_i^2$$

where m_i represents concentration in moles/kg.

The speciation calculations were solved by combining the equilibrium constants (Table 2) and the mass equations for Ge and Ga given by

$$m_{Ge} = m_{H_4GeO_4^0} + m_{H_3GeO_4}$$

and

$$m_{\mathrm{Ga}} = m_{\mathrm{Ga}^{3+}} + m_{\mathrm{GaOH}^{+2}} + m_{\mathrm{Ga(OH)}_2^+} + m_{\mathrm{Ga(OH)}_3^0} + m_{\mathrm{Ga(OH)}_4^-}$$

These calculations need selection of a specific temperature. For the present work, chalcedony geothermometer temperatures, as computed by the WATCH program, were used as the selected reference temperature in the low-temperature areas of the Southern Lowlands as well as for the mixed waters in the Geysir field, whereas quartz equilibrium temperatures were used for reference for boiling hot springs for Geysir (Table 1). Measured temperatures were used for reference for non-thermal waters.

GERMANIUM AND GALLIUM DISTRIBUTION IN WATERS

The concentrations of Ga and Ge in all the water samples considered for the present study are given in Table 1 together with the concentrations of Si and Al. Gallium was detected in all but 8 cold spring samples and Ge in all but 2 samples, also of non-thermal waters. The Ge concentrations in the geothermal waters were between 0.17 and 24 ppb but in the non-thermal waters they were generally below or close to the detection limits, the highest Ge concentrations in these waters being 0.22 ppb. The Ge concentrations increased with increasing temperature (Figure 3). Accordingly, the samples from the Geysir geothermal field have the highest Ge concentrations. In the Southern Lowlands low-temperature areas the Ge concentrations showed complete overlap between the three recognized geothermal systems. Most samples had 1-10 ppb Ge.

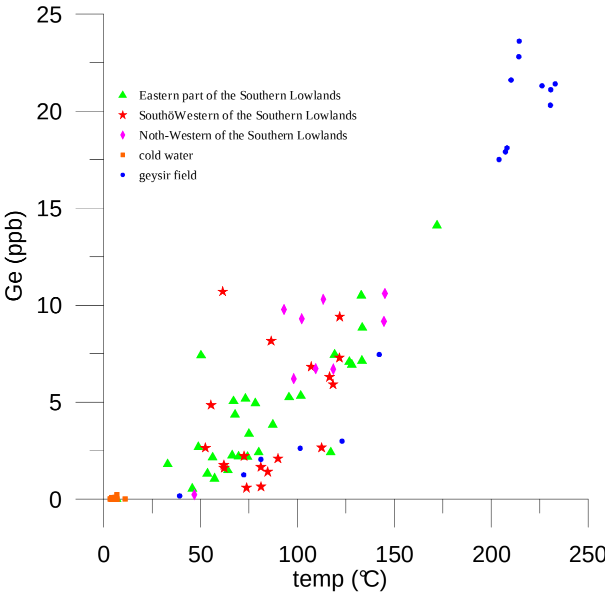

FIGURE 3: Germanium concentrations in geothermal waters as a function of aquifer temperature. For the high-temperature waters of the Geysir field, this temperature was taken to be representedby the quartz geothermometer but for the mixed waters in this field as well as in thelow-temperature systems by the chalcedony geothermometer. For non-thermal groundwaters the measured temperature was used for reference.

The Ga concentrations in the geothermal waters ranged between 0.04 and 21 ppb. In the Southern Lowlands, they were, however, mostly between 1 and 5 ppb. Non-thermal groundwaters contained less Ga, the highest concentration being 1 ppb while a third did not contain detectable Ga (<0.005 ppb). The Ga concentrations increased with increasing temperature (Figure 4). The Ga concentrations in waters from the Southern Lowlands generally registered between 0.5 and 3 ppb. A considerable range in the concentration range was observed for samples from boiling hot springs in the Geysir area. This was considered a result of mixing between non-thermal waters containing low Ga concentrations and deep geothermal waters containing elevated Ga concentrations. In warm waters from the Geysir field that contain a large cold water component. Ga concentrations were very low.

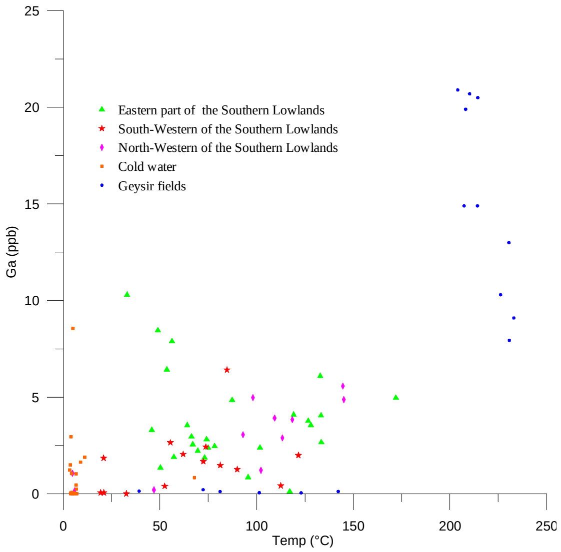

FIGURE 4: Gallium concentrations as a function of temperature; for selection of aquifer temperature see Figure 3

The results of the aqueous speciation calculations indicate that the dominant Ge species is $H_4GeO_4^0$, whereas the dominant Ga species is $Ga(OH)_4^-$. Germanium and Ga show similar chemical behaviour as Si and Al, respectively. The predominant species of Ge and Ga are tetra-coordinated hydroxy complexes, just like for Si and Al or $H_4SiO_4^0$ and $Al(OH)_4^-$. The ratios of $H_4GeO_4^0$ / $H_4SiO_4^0$ and $Ga(OH)_4^-$ / $Al(OH)_4^-$ are plotted against temperature in Figures 5 and 6. From Figure 5 it is seen that the ratio $H_4GeO_4^0$ / $H_4SiO_4^0$ increased with increasing temperature. This suggests that the chemical behaviour may not be exactly the same. Silicade was incorporated into smectites, zeolites and chalcedony at temperatures below about 150°C, whereas at higher temperatures it could also enter quartz, chlorite, epidote, prehnite and some other silicates. The observed variation in the $H_4GeO_4^0$ / $H_4SiO_4^0$ ratio with temperature might possibly be caused by its incorporation into different minerals and their rates of formation. Germanium has an ionic radius of 0.53 Å which is somewhat larger than that of Si (0.39 Å). This limits substitution of Ge for Si in silicate minerals, and the mineral structure is more compact. For the primary minerals of basalt, it was demonstrated by Harris (1954) that substitution of Ge for Si is easiest in olivine (iron silicate), less so in pyroxene (chain-silicate) and least in the plagioclase (framework silicate). The increase in the $H_4GeO_4^0$ / $H_4SiO_4^0$ ratios with rising temperature may thus be explained by the fact that hydrothermal minerals forming at high temperature have a more compact or rigid crystal structure than the secondary minerals formed at lower temperatures. However, the extent of the water-rock interaction would have the same effect; the more particular water has precipitated secondary or hydrothermal minerals, the higher the $H_4GeO_4^0$ / $H_4SiO_4^0$ ratio. It is to be expected that the higher the temperature a particular geothermal water has attained, the more extensive the water-rock interaction.

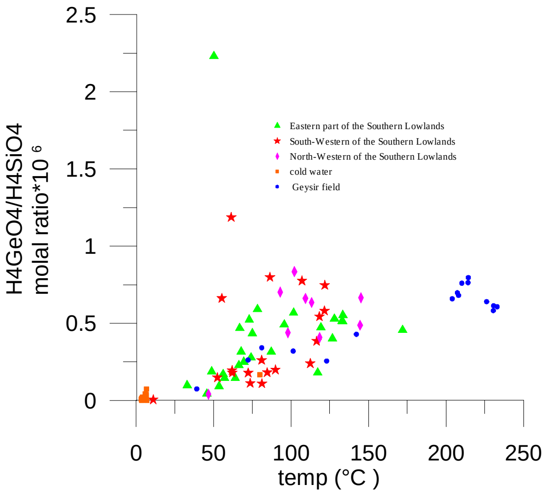

FIGURE 5: H_4GeO_4/H_4SiO_4 species ratios versus aquifer temperature in geothermal waters in the Southern Lowlands and the Geysir field; for selection of aquifer temperature see Figure 3

The $Ga(OH)_4^-$ / $Al(OH)_4^-$ activity ratio is shown in Figure 6 as a function of temperature. No temperature variations were observed. Instead, significant differences were observed for this ratio at any temperature between the three main low-temperature geothermal systems of the Southern Lowlands. In the Geysir field, the ratio was very low for warm waters that contained a large cold groundwater component. For the hot springs, the ratios were highly variable, largely caused by the removal of Al from the solution. Gallium concentrations were near-constant in these waters. The reasons for this may be the same as for Ge and Si. Gallium has an ionic radius of 0.62 Å whereas that of Al is 0.50 Å. Evidently the mineral that removes Al from the hot spring waters at the Geysir field does not consume Ga. Thus, $Ga(OH)_4^-$ / $Al(OH)_4^-$ activity ratios may be much affected by which mineral precipitates from the solution and its rate of formation as well as the extent of water-rock interaction. The distribution of the $Ga(OH)_4^-$ / $Al(OH)_4^-$ ratios between the different low-temperature geothermal systems in the Southern Lowlands may be the consequence of the formation of different hydrothermal minerals in different systems, likely zeolites and/or clay minerals.

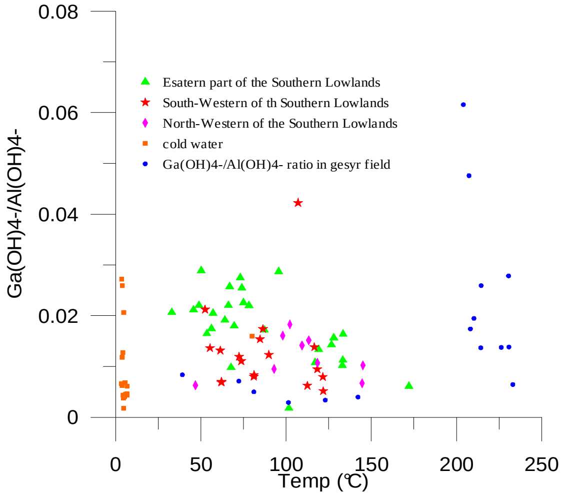

FIGURE 6: $Ga(OH)_4^-$ / $Al(OH)_4^-$ species ratios versus aquifer temperature in geothermal waters in the Southern Lowlands and the Geysir field; for selection of aquifer temperature see Figure 3

MOBILITY AND SATURATION OF GERMANIUM AND GALLIUM IN GEOTHERMAL WATERS

The mobility of one element relative to another may be used to gain insight into its geochemical behaviour. The concentration of $H_4GeO_4^0$ vs. $H_4SiO_4^0$ is shown in Figure 7. In addition, the Ge/SiO_2 ratio in basaltic rocks is shown (line). This line was obtained from data on Ge in selected Icelandic basalts as given by Arnórsson (1984) and assuming its SiO_2 content to be 50%. The $H_4GeO_4^0$ concentrations in the waters relative to $H_4SiO_4^0$ are much higher than the average Ge/SiO_2 ratio of basalt. This indicates that Ge is more mobile than Si by a factor of about 20. This does not, however, imply that Ge is mobile. The cause of the high mobility of Ge as compared to Si likely is its non-stoichiometric substitution for Si into secondary minerals due to its larger size. By the terminology of Goldschmidt, Ge is permitted into the structure of silicates where it replaces silica, but the substitution is not free.

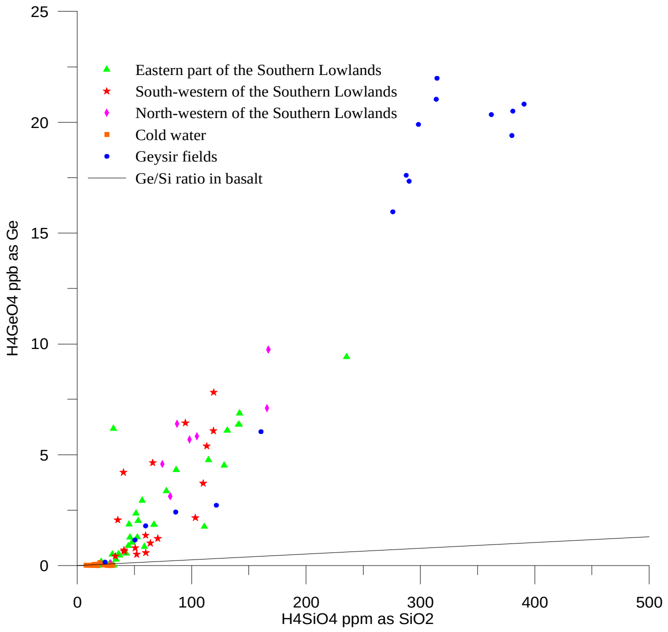

FIGURE 7: The relationship between Ge and Si in geothermal waters in the low-temperature field of the Southern Lowlands of Iceland and the Geysir field; the black line represents the Ge/Si ratio in basalts

Following Arnórsson (1984), an exchange equilibrium between Ge and Si involving solid SiO_2 (chalcedony or quartz) may be defined as $H_4GeO_4^0 / H_4SiO_4^0 = X_{SiO2}$ where X represents the mole fraction of the subscribed species (quartz). At equilibrium with respect to $SiO_2(s)$ we have $H_4GeO_4^0 = = H_4SiO_4^0 \times X_{SiO2} \times K_{SiO2}$ where $K_{SiO2}(s)$ is the solubility of quartz or chalcedony as a function of temperature. Geothermal waters in Iceland are known to be undersaturated with respect to germanium oxide (Arnórsson, 1984). However, exchange with other minerals like quartz or chalcedony containing up to 10 ppm Ge may explain the Ge concentrations in the waters at >100°C. For waters of the present study a similar trend was observed (Figure 8). A very good agreement was observed suggesting that the possible exchange of reactions between Ge and Si in minerals like chalcedony might explain the geochemical behaviour of Ge.

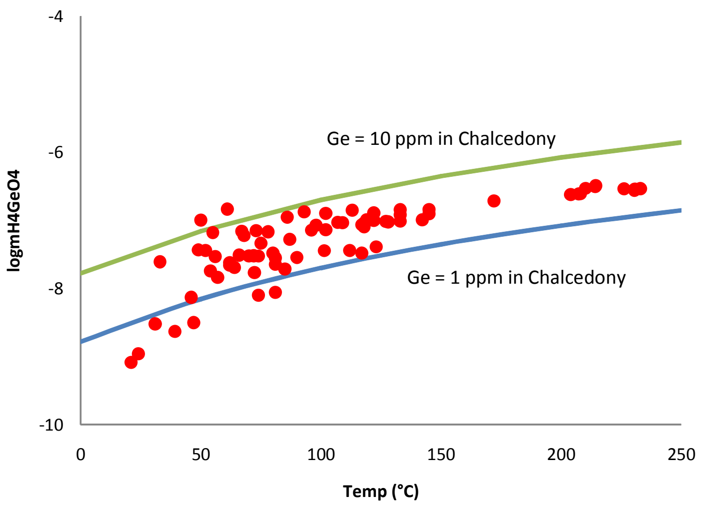

FIGURE 8: Saturation state with respect to chalcedony assuming 1-10 ppm Ge; the solubility constant for chalcedony was selected from Arnórsson et al. (1982)

The mobility of Ga compared to Al is shown in Figure 9. A similar trend as for Ge and Si was observed: Ga had a higher mobility than Al. The cause for this may be the same as for Ge, non-stoichiometric dissolution of the primary rock-forming minerals or exchange of Ga with Al into secondary minerals in proportions other than those found in the unaltered rock. Aluminium is incorporated into many secondary aluminium silicates. Therefore, assigning a particular mineral or ratio may be difficult to assess the trace impurities of Ga in secondary minerals containing Al.

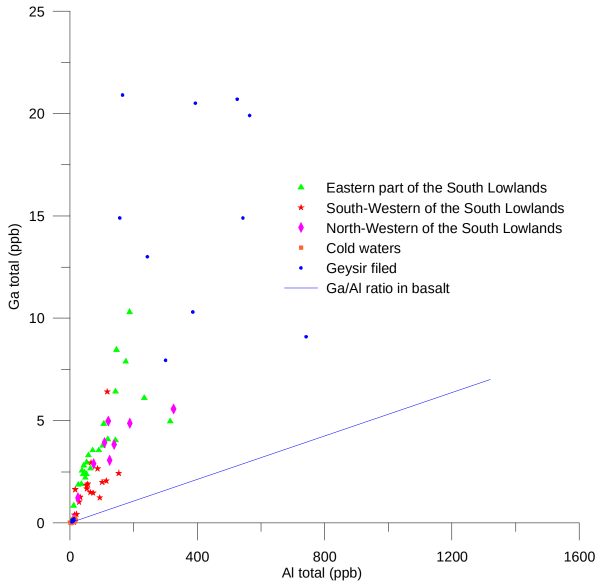

FIGURE 9: The relationship between Ga and Al in geothermal waters on the Southern Lowlands and the Geysir field; the black line represents the average Ga/Al ratio in basalt

SUMMARY AND CONCLUSIONS

The geochemistry of gallium and germanium was studied in geothermal waters in the low-temperature fields of the Southern Lowlands in Iceland and the Geysir high-temperature field. Germanium concentrations in water samples ranged between <0.05 and 24 ppb but those of gallium the ranged between <0.01 and 21 ppb. Germanium showed a good positive correlation with temperature whereas for gallium it was poor.

The mobility of Ge was studied relative to Si. The two elements showed very similar chemical behaviour. Germanium was observed to be 20 times more mobile than Si for the samples considered for this study. The cause is considered to be either non-stoichiometric rock dissolution or incorporation of Ge into Si containing secondary minerals with a molal exchange ratio that differs from that of the fresh basalt. An example of Ge exchange for Si into chalcedony indicated that Ge concentrations between 1 and 10 ppm in chalcedony matched the observed Ge concentrations. Similar trends were observed for Ga relative to Al, i.e. Ga showed much higher mobility than Al relative to primary rock composition.

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