

Háskóli Íslands
Raunvísindadeild



HÁSKÓLI ÍSLANDS

**Aquatic geochemistry of barium
in basaltic terrain, Iceland**

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Abstract

The present study focuses on barium, its objective being to quantify the processes that control its concentration in ground waters in the basaltic environment in Iceland. It is based on over 300 samples. The concentrations of Ba in ground waters and <150°C waters from low-temperature geothermal fields in Iceland are highly variable, ranging from <0.01 ppb to about 300 ppb. The average Ba concentration in selected Icelandic basalts is 75 ppm. Aqueous Ba concentrations increase with increasing chloride content of the water. Barium occurs largely as free Ba^{+2} ion, being over 98% in two-thirds of the samples analyzed and always >92%. All waters are strongly witherite under-saturated. Most of the sampled waters are also barite under-saturated. Yet waters with chloride concentrations above 100 ppm tend to be close to saturation as are some waters of mixed cold- and geothermal water origin. In these waters samples barite solubility controls aqueous Ba concentrations. A correlation is observed between the activities of Ba^{+2} versus K^+ . It is known that Ba substitutes for K in K-bearing rock-forming minerals due to the similar size of the Ba^{+2} and K^+ ions. It is considered that aqueous Ba concentrations in barite under-saturated waters are controlled by exchange equilibria between Ba^{+2} and K^+ in secondary K-bearing minerals or possibly by adsorption of Ba^{+2} onto clay mineral surfaces where it competes with K^+ and other ions. Neither was a correlation found between Ba concentration and temperature nor Ba concentration and pH of the samples. Calculations in this study show a clear order in the relative mobilities of the cations of interest. Their mobility is in this order: $\text{Na} > \text{K} > \text{Ca} > \text{Ba} > \text{Mg} > \text{Sr}$.

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1. Introduction

Knowledge of the aquatic geochemistry of trace elements is of importance because they may affect water quality and improve understanding of water–rock interaction processes. Further, their role in biology is important. Some trace elements may be used as tracers for hydrological studies and some are toxic to biota. Depending on their chemical properties and the extent of water–rock–soil interaction, the concentrations of trace elements in natural waters may be controlled by precipitation reactions or they may be conservative, i.e. their aqueous concentrations are determined by their availability to the water (e.g. Ellis and Sewell, 1963; Giggenbach, 1991; Arnórsson and Andrésdóttir, 1995; Smedley and Kinniburgh, 2002). Data on trace elements in river waters provide information on their fluxes to the ocean and on denudation rates (e.g. Edmond et al., 1995; Allégre et al., 1996; Gíslason et al., 1996; Gaillardet et al., 1997). The essential role of barium in biology has been known for a long time (Kojola et al., 1978).

Barium is widely distributed in common rock types. It belongs to the alkaline earth group of elements, chemically resembling calcium in some respects. Due to the similar size of Ba^{+2} and K^+ barium typically follows potassium, both in natural waters and rock-forming minerals. Thus barium is concentrated in feldspars where it substitutes for potassium. Elemental barium is never found in nature as the metal oxidizes very easily upon contact with air or water. The most common barium minerals in nature are barium sulfate, BaSO_4 (barite) and to a lesser extent barium carbonate, BaCO_3 (witherite).

Chemical weathering of crustal rocks is one of the principal processes controlling the geochemical cycle of elements at the Earth's surface. Chemical weathering consumes atmospheric and/or endogenous carbon dioxide and extracts metals from the rocks, which in turn are released to rivers and shallow ground waters and finally discharged into the ocean (Garrels and MacKenzie, 1971). Among rocks of volcanic origin, basalts are particularly sensitive to chemical erosion (Berner and Berner, 1996). Therefore, basaltic systems are useful to investigate the partitioning of chemical elements during weathering.

Hydrothermally mineralized, barite-containing veins are relatively common in crustal rocks. Barite is sparingly soluble ($\log K_{sp} = -9.96$, Blount, 1977; Bishop, 1988), its precipitation and dissolution may affect the distribution of barium in surface waters as well as in crustal fluids. Mixing of barium-rich hydrothermal fluids with sulfate-rich meteoric or ocean fluids can produce solutions supersaturated with respect to barite and result in its precipitation. In oceanic waters, the uptake and regeneration of barium has also been related to phytoplankton activity and possibly to the passive precipitation of barite in supersaturated biogenic environments (Dehairs et al., 1992; Dymond et al., 1919; Falkner et al., 1993). Barite in marine sediments is remobilized by biological reduction (Torres et al., 1996). Barite is one of the commonest and most intractable scales formed in oil and gas wells, usually as a result of the mixing of injected and formation waters (Hall, 1995). The oil industry routinely uses large quantities of chemical crystal growth inhibitors to control barite scale formation.

Some experimental work has been published concerning the partitioning of Ba^{+2} into calcite. According to Pingitore and Eastman (1984) the upper limit for the ideal solid solution of $Ba-CaCO_3$ would be a 2 molar percentage of Ba into the calcite lattice, whereas the investigations Tesoriero and Pankow, (1996) report values around 1%.

The present study focuses on the element barium, its objective being to quantify the processes that control its concentration in surface- and ground waters in the basaltic environment in Iceland. It is based on over 300 samples of ground waters from wells in very many areas in the country and of geothermal well discharges from all of Iceland's low-temperature systems. These data provide an understanding of the dissolution and mobility of barium during chemical weathering and hydrothermal alteration of the basalts. The water samples were analyzed for the major elements and selected trace elements. Extensive data are available for major elements in basaltic rocks of Iceland and for some trace elements. This permits assessment of the mobility of barium relative to other elements in the basaltic environment, such as the alkaline and the alkaline earths elements (Na, K, Ca, Mg and Sr), both in the surface (weathering) and sub-surface (geothermal) environments.

2. Analytical methods and data handling

2.1. Sampling and analytical methods

Arnórsson et al. (2002) give details of the methods used to collect and treat water samples. Specifically, for the trace element analysis, including Ba, the samples were filtered on site through 0.2 µl acetate cellulose membrane followed by acidification by 1 ml Suprapure nitric acid (E. Merck 100441) to 100 ml sample. Barium was determined in a total of 308 water samples by high resolution ICP mass spectrometry at Analytica in Sweden (Table 1). The detection limit for Ba is 0.01 ppb.

Table 1. Chemical analysis of waters in Iceland. Concentrations are in ppm or ppb as indicated.

Sample no.	Location	Temp. °C	pH in situ	Na ppm	Cl ppm	K ppm	Mg ppm	Ca ppm	Sr ppb	Ba ppb
02-001	Seltjarnarnes, 12	108	7,35	592,9	1820,0	12,97	0,5024	581,70	2430,0	61,00
02-002	Húsafell, 2	61,2	8,94	80,6	34,4	0,59	0,0066	5,59	19,4	0,31
02-003	Gardur	5,92	9,12	25,1	2,2	1,57	4,5600	7,61	7,6	0,31
02-004	Hverfjallsgjá	6	8,81	20,1	5,0	1,78	6,8959	11,83	13,9	0,55
02-005	Grjótagjá	47,4	7,77	77,5	16,9	7,27	2,9943	12,79	15,6	2,50
02-006	Helgavogur	25,7	7,88	56,5	10,4	4,94	5,8220	24,92	33,0	1,82
02-007	SWN-1	55,7	9,30	42,8	15,0	0,77	0,0036	2,84	5,6	0,09
02-008	Gardsvík	8,4	9,62	19,4	7,3	<0,5	0,3394	3,59	1,7	<0,01
02-009	Húsafell, 2	61,9	8,83	78,4	34,1	0,87	0,0032	5,32	19,9	0,12
02-010	Húsafell /h-1 Teitsgr.	76,7	8,53	88,0	35,9	1,58	0,0020	4,69	28,6	0,19
02-011	Húsafell-kalt	3,4	8,21	7,5	5,7	0,52	1,4840	3,54	4,9	0,07
02-012	Kirkjuból	28,3	9,72	58,1	15,7	<0,5	0,0026	2,24	0,6	<0,01
02-013	Kirkjuból-kalt	7,8	7,21	12,0	16,3	1,11	4,1338	8,04	13,5	0,16
02-014	Heilsulind-Þverfell	4,1	9,39	11,6	8,9	<0,5	1,6977	5,45	1,5	0,03
02-015	Volgipollur-Thverf.	18,9	10,34	29,7	10,0	<0,5	0,0040	2,45	0,4	<0,01
02-016	Englandshver	87,3	8,33	72,7	17,5	2,09	0,0431	2,52	2,0	0,06
02-017	Krosslaug	43	9,13	68,3	24,5	0,90	0,0052	3,35	1,8	0,03
02-018	Áslaugar	73,8	8,97	49,3	10,3	0,99	0,0029	1,71	2,9	0,29
02-019	Hægindi	99,6	8,22	85,5	33,5	3,47	0,0032	2,70	6,6	0,12
02-020	Hýrumelur	99,6	8,42	80,7	33,4	2,37	0,0022	2,43	4,3	0,16
02-021	Reykholts	134,6	8,03	81,8	33,1	3,60	0,0017	2,16	7,5	0,46
02-022	Deildartunguhver	100,2	8,38	75,8	35,3	2,04	0,0018	3,06	10,5	0,29
02-023	N-Reykir	99,9	8,39	80,8	33,5	2,34	0,0016	2,27	3,3	0,16
02-024	Úlfssadir	50	8,68	72,5	25,2	1,39	0,0091	1,14	2,3	0,24
02-025	Hurdarbak	100,1	8,35	77,1	33,8	2,07	0,0016	2,77	6,6	0,25
02-026	Kópareykir	97	8,17	84,5	35,9	3,08	0,0050	2,33	6,5	0,28
02-027	Runnar	81	8,64	82,9	50,3	2,28	0,0058	2,85	3,8	0,49
02-028	SN-04	104,6	7,24	611,6	1890,0	13,17	0,2815	540,49	2300,0	67,00
02-029	SN-05	98,8	7,28	508,2	1400,0	10,64	0,2771	354,01	1310,0	29,60
02-030	L_-10	104,1	8,61	55,1	13,3	1,41	<0,0010	2,06	12,0	0,21
02-031	Vaglir	4	7,06	5,0	5,6	1,02	2,6378	6,28	10,7	0,44
02-032	HJ-19	85,7	9,00	55,5	10,9	1,06	0,0012	1,79	12,4	0,09
02-033	GYN-7	60,5	9,18	45,9	11,3	0,66	<0,0010	2,45	10,6	0,12
02-034	RNW-7	75,7	8,86	53,4	11,7	1,05	<0,0010	3,65	21,1	0,45
02-035	HN-10	83,4	8,80	45,6	8,1	0,84	0,0014	3,45	16,9	0,14
02-036	BN-1	90,5	8,66	54,2	11,9	1,23	0,0022	4,32	28,3	0,76
02-037	LJ-5	94,4	8,26	52,4	12,5	1,19	<0,0010	2,85	19,9	0,50
02-038	TN-4	81,4	8,83	56,0	15,8	0,89	<0,0010	3,71	20,6	0,18
02-039	Glerárdalslindir	3,05	7,74	4,3	3,1	0,55	1,1048	7,11	10,6	0,10
02-040	Hesjuvallalindir	2,9		4,5	2,3	2,90	0,7283	4,84	4,5	0,03
02-041	Blesastadir	69	8,72	356,1	527,0	3,98	0,0045	35,76	42,3	0,96
02-042	Brautarholt	68,8	8,54	155,4	193,0	2,10	0,0034	14,35	14,4	0,29
02-043	Brjánsstadir	63,9	8,30	256,7	334,0	10,61	0,0150	11,22	17,1	2,11
02-044	Hlemmiskeid	68,5	8,94	153,2	173,0	2,31	0,0013	10,18	8,4	0,45
02-045	Húsatóttir	73,5	8,84	152,3	177,0	2,29	0,0010	12,69	12,0	0,22
02-046	Reykir, Skeid	68,3	8,53	103,3	105,0	1,50	0,0043	8,12	24,1	0,17

Table 1. (Continued)

Sample no.	Location	Temp. °C	pH in situ	Na ppm	Cl ppm	K ppm	Mg ppm	Ca ppm	Sr ppb	Ba ppb
02-047	Laugarás	97,3	8,49	82,9	49,2	1,97	0,0099	3,76	12,6	0,12
02-048	Thorlákshver	97	7,76	81,3	52,3	1,80	0,0024	3,80	12,2	0,15
02-049	Laugarbakkar	55,4	9,04	68,5	53,6	0,51	0,0019	2,36	2,0	0,04
02-050	Ingólfssfjall	3,8	9,39	13,1	10,6	<0,5	0,8589	6,17	1,0	<0,01
02-051	Vatnsendi	80	8,45	138,6	139,0	4,98	0,0032	3,85	5,1	0,14
02-052	Hamrar	48	8,23	238,7	339,0	5,10	0,7288	25,64	43,0	2,44
02-053	Sólheimar	79	7,38	162,6	199,0	4,05	0,0154	13,24	72,5	1,50
02-054	Spóastadir	76,4	8,30	84,0	48,9	1,94	0,0084	3,92	11,1	0,04
02-055	Syðri-Reykir	98,6	7,95	89,9	46,4	3,88	0,0016	2,06	10,8	0,09
02-056	Ljósúár	4,3	10,21	12,1	4,4	<0,5	0,0415	2,28	0,2	<0,01
02-057	Laugarvatn I	97	8,31	75,1	33,9	3,04	0,0026	2,96	15,4	0,08
02-058	Laugarvatn II	4,8	9,92	13,0	6,6	<0,5	0,2997	3,95	1,1	<0,01
02-059	Kringla	81,3	8,48	92,4	77,7	2,01	0,0032	5,92	57,8	0,33
02-060	Kaldárholt	62,4	8,86	172,9	234,0	1,78	0,0047	16,56	34,2	0,21
02-061	Skammbeinsstadir	50,6	9,85	66,0	18,0	<0,5	0,0032	1,92	0,8	0,04
02-062	Hvammur, Skardsfjall	57	9,39	63,3	15,3	0,79	0,0071	2,05	1,8	0,07
02-063	Stóri-Klofi	54,6	9,44	68,1	19,1	0,75	0,0011	4,74	3,6	0,05
02-064	Flaggbjarnarholt	60,4	9,43	58,1	15,8	0,57	<0,0010	2,20	4,2	0,06
02-065	Ósabakki	60	9,02	72,9	46,4	0,96	0,0049	5,70	17,6	0,23
02-066	Midfell	62	8,54	63,0	22,4	0,81	0,0027	3,18	3,0	0,10
02-067	Kópsvatn	94	7,97	85,9	36,0	2,73	0,0040	3,49	28,2	0,31
02-068	Syðra-Langholt	64,2	8,60	58,2	24,6	0,98	0,0018	2,83	20,3	0,09
02-069	Birtingaholt	61	8,86	60,9	28,5	0,94	0,0180	3,04	21,0	0,18
02-070	Audsholt, Bisk.	84,1	8,60	68,9	34,7	1,46	0,0010	3,18	5,4	0,06
02-071	Ásatún	82,4	7,97	61,6	22,4	1,21	0,0037	2,40	2,0	0,03
02-072	Flúdir	95,2	7,64	75,2	23,8	1,93	0,0016	1,72	2,0	0,16
02-073	Flúdir	99,8	8,23	78,2	24,4	2,32	0,0012	1,27	1,2	0,14
02-074	Vadmálahver	99,3	7,56	79,0	24,9	2,23	0,0023	1,93	3,2	0,09
02-075	Thórarinsstadir	98,9	8,30	89,1	27,2	2,96	0,0017	1,59	4,5	0,17
02-076	Laugar, Hrun	98,4	8,18	119,9	35,1	5,74	0,0014	1,40	3,0	0,12
02-077	Reykjadalur	97,8	8,24	78,8	24,9	2,33	0,0027	2,14	6,7	0,22
02-078	Thjórsárholt	63,2	9,25	56,9	14,9	0,92	<0,0010	2,31	1,5	0,02
02-079	Thjórsardalur	67,5	8,00	122,4	78,9	2,39	0,0136	53,21	568,0	1,62
02-080	Gljúfurholt	82,1	7,57	112,1	78,9	3,98	0,0236	3,06	3,8	0,32
02-081	Stykkishólmur, 01	86,2	6,73	671,1	2980,0	13,53	0,4400	1019,71	5630,0	107,00
02-082	Reykholar, 1	82,5	8,53	56,8	26,6	2,19	0,0018	2,26	11,8	0,07
02-083	Siglufjördur, 11	71,6	8,97	43,3	9,0	0,87	0,0010	1,47	2,2	0,04
02-084	Ólafsfjördur, 4	67	9,29	38,2	8,6	0,74	<0,0010	2,48	8,1	0,04
02-085	Ólafsfjördur, 12	56,3	9,46	34,1	7,6	0,69	<0,0010	1,82	1,6	0,02
02-086	Dalvík, 10	64,5	9,40	48,6	9,3	0,81	<0,0010	1,93	1,7	0,02
02-087	Árskógsströnd, 29	73,4	9,17	54,7	13,9	1,17	<0,0010	2,02	8,6	0,05
02-088	Hrísey, 10	76,7	8,01	236,2	500,0	4,53	<0,0010	90,23	167,0	1,12
02-089	Urridavatn, 8	75,6	8,63	66,3	42,4	1,12	0,0019	6,99	36,5	0,15
02-090	Eskifjördur, 1	76,3	7,71	262,6	393,0	4,16	0,0110	101,50	580,0	5,85
03-001	Ellidaársaedi, 39	89,7	8,01	42,6	21,2	0,97	0,0055	2,67	23,7	0,48
03-002	Ellidaársaedi, 23	89,2	8,57	44,7	23,2	1,06	0,0060	2,50	18,4	0,21

Table 1. (Continued)

Sample no.	Location	Temp. °C	pH in situ	Na ppm	Cl ppm	K ppm	Mg ppm	Ca ppm	Sr ppb	Ba ppb
03-003	Laugarnessvaedi, 15	128	8,14	68,7	54,6	2,56	0,0041	4,04	35,5	2,66
03-004	Laugarnessvaedi, 9	124	7,26	75,1	66,3	2,89	<0.002	4,89	45,5	0,86
03-005	Laugarnessvaedi, 19	127,3	8,21	52,5	28,5	1,80	0,0020	2,36	22,1	0,51
03-006	Laugarnessvaedi, 35	123,8	7,36	69,8	57,7	2,40	0,0023	3,61	23,0	0,88
03-007	Reykjahlíð, 39	92,1	8,69	48,1	13,0	1,05	0,0021	1,95	22,2	0,26
03-008	Reykjahlíð, 29	92,9	8,45	48,3	13,2	1,05	0,0037	1,81	26,9	0,51
03-009	Reykjahlíð, 37	100,3	8,34	50,7	18,0	1,25	<0.002	2,69	28,7	0,55
03-010	Reykjahlíð, 5	78,7	8,78	44,6	13,4	0,78	0,0021	2,09	13,9	0,12
03-011	Reykir. Mos., 16	99,7	8,51	47,0	16,2	1,19	0,0055	2,24	13,9	0,13
03-012	Reykir. Mos., 30	74,3	8,52	42,0	14,5	0,70	0,0070	2,65	4,4	0,04
03-013	Reykir. Mos., 23	69,8	8,89	34,8	13,8	<0.50	0,0030	2,54	8,0	0,05
03-014	Reykir. Mos., 9	79,3	8,81	35,3	14,8	<0.50	0,0065	2,73	12,9	0,10
03-015	Reykir. Mos., 20	91,5	8,60	42,7	16,2	0,87	0,0021	2,45	18,2	0,11
03-016	Reykir. Mos., 15	86,2	8,64	39,4	14,8	0,70	0,0029	2,29	10,5	0,08
03-017	Gvendarbrunnar, 21	4	9,44	10,9	10,7	<0.50	1,1230	4,16	4,2	0,22
03-018	Gvendarbrunnar, 20	3,7	9,45	10,2	10,6	<0.50	1,1661	3,95	4,2	0,21
03-019	Jadar, 4	4	9,84	10,8	10,0	<0.50	0,8326	4,41	2,6	0,05
03-020	Jadar, 3	4,5	9,78	11,1	10,1	<0.50	0,8145	4,39	2,5	0,03
03-021	Millulaekur, 13	4,1	9,64	9,7	9,9	<0.50	0,8114	5,02	0,6	0,01
03-022	Kriki, 5	4,1	9,66	8,6	9,1	<0.50	0,9549	5,12	2,9	0,08
03-023	Kriki, 1	3,9	9,61	8,6	9,2	<0.50	0,9113	5,11	2,6	0,07
03-024	Millulaekur, 14	4,2	9,65	10,0	10,0	<0.50	0,8310	5,02	1,5	0,03
03-025	Kjalarnes	5,1	8,94	6,1	9,5	<0.50	1,9771	19,29	39,5	0,09
03-026	Thóroddstadir, Ölfus, 1	120	7,67	271,8	370,0	8,89	0,0222	20,82	77,5	1,77
03-027	Thóroddstadir, Ölfus	4,7	8,92	8,9	9,6	0,80	2,1444	5,56	11,4	0,13
03-028	Audsholt, Ölfus, 1	59,5	8,92	148,5	186,0	1,59	0,0046	16,46	20,9	0,10
03-029	Vadnes, 1	73,8	8,91	100,2	80,7	1,41	<0.0020	7,13	8,5	0,17
03-030	Laugaland, Holt	4,6	7,01	9,5	10,2	0,85	4,6685	9,86	12,7	0,11
03-031	Skammbeinsstadir	5,1	7,39	21,6	10,8	2,18	7,6118	20,42	40,1	0,17
03-032	Öndverdarnes, 27	83,8	8,42	150,7	183,0	3,41	0,0050	12,81	17,3	0,37
03-033	Öndverdarnes, 18	72	8,27	125,9	148,0	2,55	0,0044	11,41	14,8	0,13
03-034	Vik in Mýrdalur, a	4,7	9,45	13,9	14,7	1,01	0,9464	7,94	23,3	0,02
03-035	Vik in Mýrdalur, b	5,2	7,85	13,3	14,0	0,75	3,0927	11,14	23,3	0,04
03-036	Skógar, 1	53	8,60	147,8	93,1	1,34	0,0126	2,29	17,1	0,51
03-037	Skógar, water supply	5,5	7,77	10,7	9,7	1,47	3,2507	5,44	23,2	0,33
03-038	Útey	90,2	8,42	81,3	46,7	2,67	0,0335	4,72	17,0	0,26
03-039	Austurey 1	88,2	8,61	76,9	47,4	1,69	0,0024	3,06	11,2	0,12
03-040	Bjarnarfell w. supp. Reykholt	6,7	9,42	11,5	5,8	0,53	1,0716	5,10	4,1	0,08
03-041	Húsafell	2,74	9,81	6,0	4,2	<0.50	0,8517	3,30	2,0	0,03
03-042	Gardsá	18,81	9,82	53,6	19,0	0,46	0,0075	5,08	4,8	0,04
03-043	Grísaarlindir	2,8	8,04	3,4	2,4	0,77	1,3853	5,42	9,7	0,12
03-044	Selbót undir Haus	3,98	7,73	8,1	5,1	<0.50	1,3339	5,16	0,8	0,04
03-045	Borhola ofan Öngulsstada	5,35	7,56	8,1	5,5	<0.50	1,3776	5,29	0,8	0,02
03-046	Hólsgerdi	40,7	9,33	81,1	38,8	1,49	0,0355	5,76	7,5	0,16
03-047	Reykholar, Hólslind	4,56	7,07	11,2	17,8	<0.50	1,5496	7,29	1,9	0,06
03-048	Höllustaðir	61,07	9,03	57,3	26,1	0,97	<0.0020	2,71	6,4	0,06

Table 1. (Continued)

Sample no.	Location	Temp. °C	pH in situ	Na ppm	Cl ppm	K ppm	Mg ppm	Ca ppm	Sr ppb	Ba ppb
03-049	Laugaland	56,08	9,04	50,2	26,0	1,10	0,0038	2,93	4,7	0,10
03-050	Djúpidalur	44,23	9,23	41,8	16,2	0,74	<0,002	2,67	16,9	0,08
03-051	Flókalundur	38,34	9,77	22,8	12,3	<0,50	<0,002	2,40	0,5	0,02
03-052	Krosslaug	39,81	9,67	33,4	20,3	<0,50	0,0017	2,50	1,2	0,08
03-053	Patreksfjörður, neðra vatnsból	2,75	8,36	7,9	13,5	<0,50	1,2893	2,64	6,1	0,17
03-054	Patreksfjörður, efra vatnsból	2,88	8,48	6,9	11,8	0,57	0,9442	2,62	5,2	0,14
03-055	Litli-Laugardalur	47	9,13	29,1	14,5	0,54	0,0054	2,05	1,0	0,02
03-056	Sveinseyri, borhola 3	19,85	9,60	16,5	13,9	0,50	0,1517	1,85	0,7	0,04
03-057	Patreksfjörður, volgt	19,9	9,61	23,1	19,3	<0,50	0,0507	1,65	1,3	0,12
03-058	Drangsnes, heitt	61,1	8,70	133,6	187,0	1,71	0,0032	17,48	60,4	0,44
03-059	Drangsnes, kalt	4,88	7,79	20,6	32,3	0,45	2,9929	15,96	7,4	0,13
03-060	Reykjavík í fjöru	18,2	10,05	22,4	14,7	<0,50	0,0107	2,59	0,3	0,01
03-061	Gvendarlaug við Klíku	40,24	9,51	29,8	16,2	<0,50	0,0050	2,52	0,9	0,02
03-062	Nauteyri, syðsta borhola	42,3	9,44	34,8	19,4	<0,50	0,0045	1,67	0,4	0,04
03-063	Laugaból	40,05	9,35	49,5	47,3	0,63	0,0213	4,28	1,9	0,04
03-064	Reykjanes ofan sundlaugar	87,1	7,83	300,4	756,0	4,99	0,0301	186,05	445,0	9,78
03-065	Reykjanes á hlaði skóla	93,5	7,27	301,4	755,0	5,02	0,0275	191,58	451,0	10,50
03-066	Kleifar	11,57	9,58	14,4	11,7	1,23	0,0426	0,56	0,8	0,07
03-067	Hvítanes í fjöru	29,55	9,40	29,7	24,2	1,24	0,1811	3,16	2,5	0,06
03-068	Bolungarvík, efra vatnsból	8,03	7,50	8,3	14,0	<0,50	1,5960	2,26	8,5	0,10
03-069	Ísafjörur við göng	3,28	9,27	7,8	13,4	0,74	1,0208	2,88	4,2	0,47
03-070	Suðureyri, borhola 2	64,13	8,87	93,2	84,0	0,88	0,0154	10,26	7,8	0,07
03-071	Bolungarvík, úr krana	8,99	7,45	8,1	13,7	<0,50	1,6333	2,35	8,5	0,08
03-072	Tungudalur	34,18	9,29	101,4	74,0	1,22	0,0048	2,23	3,4	0,10
03-073	Hestfjarðarbotn	25,39	9,77	20,2	11,4	<0,50	0,0050	0,61	0,2	0,02
03-074	Laugaból, minni laug	42,81	9,40	33,2	20,4	0,47	0,0061	1,39	0,3	0,01
03-075	Hörgshlíð	48,84	9,37	30,7	18,2	<0,50	0,0060	2,84	1,0	0,02
03-076	Kelda	43,33	9,42	35,2	20,0	0,53	0,0132	2,38	0,7	0,02
03-077	Heydalur	44,3	9,51	36,2	18,0	<0,50	0,0562	1,41	0,5	0,02
03-078	Bjarnastaðalaug, í fjöru	47,3	9,02	31,1	26,0	0,52	0,0116	4,82	1,6	0,03
03-079	Eyri	19,4	9,82	22,2	14,1	<0,50	0,1575	2,93	0,4	0,02
03-080	NV í Hrísalísi	33,49	10,01	34,0	4,5	<0,50	0,0144	1,43	0,4	0,02
03-081	Reykholts, 1	133	7,28	116,0	77,1	4,11	<0,002	2,44	14,2	1,23
03-082	Gýgjarhólskot, 1	22,7	9,40	35,6	8,9	1,50	0,1898	3,51	6,4	0,24
03-083	Laugaland, 4	97	8,76	84,6	39,7	1,58	0,0117	2,51	6,9	0,17
03-084	Kaldárholt, 36	66,9	9,44	64,3	20,0	0,64	<0,002	2,63	15,5	0,14
03-085	Thorleifskot, 10	65,5	7,89	123,1	161,0	2,75	0,1189	20,33	87,5	0,46
03-086	Thorleifskot, 12	114,5	7,74	278,1	354,0	9,40	0,0037	28,15	274,0	3,93
03-087	Thorleifskot, 13	73,7	7,71	150,6	215,0	3,51	0,0838	24,42	86,1	0,60
03-088	Bakki, 1	112	7,67	405,7	643,0	16,67	0,0088	62,36	416,0	5,32
03-089	Hjallakrókur, 1	98,8	7,76	314,1	493,0	10,33	0,0132	46,68	216,0	2,49
03-090	Vogar, water supply,	5	7,78	91,2	179,0	2,37	14,4931	16,86	67,9	0,78
03-091	Gjá in Lágum	5	7,76	33,7	66,9	1,35	6,9542	7,63	27,5	0,46
03-092	Hafnir, water supply, 2	5,5	7,40	187,0	328,0	6,00	20,6520	12,99	130,0	1,38
03-093	Gjá in Lágum, 100	5,7	7,77	33,8	70,6	1,44	7,5243	8,40	28,5	0,53
03-094	Laugabakkar, 3	97	8,11	148,6	143,0	3,34	0,0108	23,10	113,0	2,82

Table 1. (Continued)

Sample no.	Location	Temp. °C	pH in situ	Na ppm	Cl ppm	K ppm	Mg ppm	Ca ppm	Sr ppb	Ba ppb
03-095	Reykir, Reykjabraut, 12	75	8,78	66,3	8,5	1,75	0,0033	2,81	40,5	0,11
03-096	Varmahlíð, 3	91	8,58	76,4	27,5	1,82	0,0028	1,68	7,1	0,11
03-097	Saudárkrókur, 12	70,6	9,03	58,2	23,0	0,80	0,0017	3,64	18,8	0,09
03-098	Saudárkrókur, 13	68,8	9,12	53,8	18,4	0,73	0,0017	3,25	16,7	0,11
03-099	Laugar, Reykjadalur, 2	65,3	9,39	48,3	4,8	<0,50	<0,002	2,05	0,9	0,03
03-100	Fagridalur in Mýrdal	6,1	9,77	36,4	13,6	1,69	0,0704	2,15	9,0	0,08
03-101	Hrísey, water supply, 11	66,05	9,03	66,0	37,9	1,07	<0,002	6,56	74,9	0,74
03-102	Vaðstakksheiði	2,85	7,15	6,4	8,9	0,80	1,1165	1,40	6,2	1,98
03-103	Ólafsvík	3,66	7,75	5,9	8,2	0,78	1,3435	1,90	5,3	0,13
03-104	Grundarfjörður	10,57	6,85	4,8	6,0	<0,50	1,0365	1,98	8,1	0,65
03-105	Vatnsból v. Svelgsá, Stykkish.	2,89	7,50	5,6	7,0	0,66	1,8325	2,57	9,8	0,49
03-106	Borholur á Seleyri, Borgarnes	6,5	6,86	5,9	6,3	<0,50	1,4690	5,51	9,7	0,06
03-107	Lindir 1+2 Háumelum, Borgarn	4,96	8,05	7,4	9,7	<0,50	2,1058	21,63	25,7	0,07
03-108	Berjadalsá, Akranes	5	7,37	10,4	13,3	<0,50	2,0484	5,43	2,7	0,05
03-109	Gröf	83	8,05	112,5	55,2	3,31	0,0057	7,38	46,9	0,37
03-110	Búdardalur inntak vatnsv.	4	7,93	6,9	11,4	<0,50	1,4602	5,29	6,2	0,17
03-111	Skógrskot	19	9,56	50,3	21,9	<0,50	0,0130	1,43	0,9	0,04
03-112	Húsavíkurhöfdi h-1	53	8,02	827,1	1760,0	26,24	0,0146	237,46	850,0	1,98
03-113	Kalt vatnsból Húsavík	4,98	8,77	12,4	13,0	<0,50	1,4384	5,33	3,7	0,04
03-114	Hafralækjarskóli	72	9,11	57,0	9,5	0,59	<0,002	2,04	1,6	0,08
03-115	Hólmi, Botnsdal	5,2	0,02	29,8	5,7	<0,50	0,0050	7,57	1,7	0,01
03-116	Grímsstadir	3,26	9,88	19,5	3,5	0,85	0,5594	2,06	2,9	0,04
03-117	Nedstifoss, Botnsdal	16,05	11,06	43,0	4,7	<0,50	0,0018	4,84	1,4	0,01
03-118	NV í Svartahrygg	8,6	10,39	21,9	7,2	<0,50	0,0785	3,26	0,4	0,01
03-119	Austaraselslindir	4,2	7,63	8,8	3,1	1,13	6,3949	10,50	10,4	0,46
03-120	Hrísey, water supply, 11	6,8	8,59	19,0	23,7	<0,50	0,9342	10,68	2,1	0,03
04-001	Fannardalur	4,7	6,95	3,9	3,9	0,17	1,0339	2,77	1,6	0,01
04-002	Eskifjördur	3,5	8,63	4,9	4,5	0,09	0,8008	3,68	0,8	<0,01
04-003	Reyðarfjördur	4,7	7,22	3,9	2,6	0,22	1,2187	2,93	2,9	<0,01
04-004	Seyðisfjördur	8,4	7,26	2,1	1,4	0,14	0,6234	1,37	2,4	0,02
04-005	Fellabær	5,1	7,14	4,2	4,4	0,29	2,1393	4,52	4,9	0,04
04-006	Egilsstadir	4,5	6,58	5,6	7,1	0,44	3,9328	9,06	5,3	0,05
04-007	Vopnafjördur	3,7	7,44	5,4	4,8	0,18	1,4241	5,16	4,5	0,02
04-008	Blönduós	5,6	7,17	13,9	24,0	1,05	6,0484	12,20	8,5	0,10
04-009	Skagaströnd	7	7,42	9,2	17,7	0,26	3,0051	13,86	10,7	0,16
04-010	Hvammstangi	5,4	8,08	7,3	10,5	0,33	1,3659	11,58	7,7	0,09
04-011	Bordeyri	5,2	6,72	13,7	20,3	0,59	4,5541	9,35	5,0	0,19
04-012	Unadsdalur	20,5	9,36	15,8	20,0	0,18	0,1444	3,10	0,8	<0,01
04-013	Tyrdilmýri	13,7	10,22	26,9	18,8	0,19	0,0223	2,67	0,5	<0,01
04-014	Laugaland	50,2	9,31	38,9	27,1	0,30	0,0123	2,45	1,0	<0,01
04-015	Húsafell	4,1	9,81	5,7	2,8	0,27	0,5698	2,62	1,5	0,03
04-016	Dynjandi	27,9	10,13	35,4	17,2	0,16	0,0175	1,59	0,4	0,01
04-017	Laugaból, Arnarf.	42,8	9,60	52,8	39,6	0,38	0,0019	2,48	1,2	<0,01
04-018	Laugaból, kalt	3,5	7,15	9,3	13,0	0,23	1,4893	3,69	0,9	0,02
04-019	Reykjarfjördur	55	9,20	27,7	19,0	0,30	0,0509	1,35	1,3	0,02
04-020	Lysuhóll, hola1	45	6,14	417,7	85,8	30,57	27,2382	99,66	418,0	69,50

Table 1. (Continued)

Sample no.	Location	Temp. °C	pH in situ	Na ppm	Cl ppm	K ppm	Mg ppm	Ca ppm	Sr ppb	Ba ppb
04-021	Ölkelda	8,1	6,46	297,7	137,5	14,32	34,0740	155,37	515,0	24,00
04-022	Miðhraun A	3,4	7,27	5,3	7,6	0,58	1,4671	2,10	7,4	0,39
04-023	Miðhraun V	3,5	7,31	5,3	7,4	0,61	1,5036	2,00	7,0	0,48
04-024	Eiðhús H-7	100,8	6,86	695,5	2136,3	20,34	0,1960	484,03	2130,0	43,80
04-025	Siglufjördur, Hvanneyrarskál	5,2	6,85	8,0	13,5	0,30	1,9509	5,35	4,2	0,04
04-026	Thingeyrar h-14	20,4	9,28	109,6	89,8	0,62	0,0178	22,28	9,6	0,08
04-027	Sigríðarstaðir	60,6	8,75	85,7	81,2	1,56	0,0029	11,99	74,3	0,51
04-028	Sólbakki	5,6	6,98	11,6	21,0	0,75	4,8331	15,54	28,7	0,13
04-029	Bær H-01	52,8	9,07	80,3	46,7	1,91	0,0023	2,60	9,4	0,50
04-030	Eiðhús H-11	98	6,62	692,0	2132,6	19,86	0,2565	488,48	2050,0	38,60
04-031	Árbaer	59,9	8,98	52,0	26,5	0,72	0,0073	1,81	1,5	0,07
04-032	Árbaer	59,7	8,98	52,0	25,4	0,72	0,0047	1,81	1,5	0,15
04-033	Haukadalur	5,9	9,15	8,2	5,5	0,49	1,4994	6,40	5,3	0,11
04-034	Flúdir	6,7	7,06	9,4	8,3	1,27	5,0222	9,43	34,8	0,09
04-035	Ásólfssadir, 1	51,6	9,27	76,0	29,7	0,75	0,0090	3,48	6,5	0,09
04-036	Laekjarbotnar, Land	5,3	7,95	16,6	9,1	1,00	2,7506	6,12	16,6	0,42
04-037	Urridafoss	4,4	7,02	11,9	13,8	1,24	6,6753	9,95	26,5	0,72
04-038	Bjálmholt	5,5	7,36	22,1	11,8	1,58	6,3594	14,73	28,7	0,06
04-039	Thorvaldseyri	63,5	8,13	256,1	89,7	3,12	0,0507	3,89	52,8	4,15
04-040	Seljavallir, 1	65,6	7,77	187,7	33,1	2,84	0,3075	8,40	139,0	4,57
04-041	Raufarfell, 1	51,9	8,66	211,0	114,0	1,80	0,1362	2,57	23,1	1,24
04-042	Kirkjubaejkraustur	6,1	7,94	9,5	4,9	0,58	3,6740	7,79	12,3	0,30
04-043	Skaftafell	8,6	7,17	8,5	7,1	0,61	3,3480	14,23	14,2	0,07
04-044	Mýrar	5,3	8,07	5,2	4,8	0,12	2,0190	12,04	5,6	0,04
04-045	Höfn	5,6	7,51	5,8	6,3	0,35	3,0776	12,51	29,7	0,20
04-046	Búlandsdalur	7,1	7,32	4,4	1,4	0,16	0,9323	3,57	2,6	0,04
04-047	Breiddalsvík	3,6	7,42	4,8	3,9	0,34	1,2439	4,56	2,6	0,11
04-048	Stöðvarfjördur	6,6	7,31	5,5	4,6	0,39	3,3561	11,11	19,7	0,34
04-049	Fáskrúdsfjördur	8,2	6,57	3,9	2,0	0,32	1,4807	3,40	5,1	0,08
04-050	Hnappavellir	4	8,19	7,9	6,6	1,34	2,1920	4,39	13,8	0,93
04-051	Kjarnholt	71,6	6,66	283,7	80,7	20,16	0,9008	9,42	29,4	3,86
04-052	Sýrfell	7,4	7,44	68,0	156,9	2,51	10,1246	8,25	46,0	1,16
04-053	Sýrfell	8,1	7,38	57,6	131,3	2,14	8,8661	7,53	39,8	0,65
04-054	Hreðavatn	6,2	7,31	7,1	9,7	0,39	1,6540	3,27	3220,0	174,00
04-055	Berserkseyri	75,8	6,37	703,3	2018,5	18,20	15,1873	391,04	5,3	<0,2
04-056	Kjalvarstarðir	89,5	8,30	84,2	41,1	2,73	0,0096	2,15	7,2	0,50
04-057	Hveravellir	128	8,11	57,8	14,2	2,27	0,0020	1,69	6,1	0,79
05-001	Gautlönd GL-01	65,6	9,52	55,8	10,8	0,62	0,0014	1,91	1,7	0,07
05-002	Stóru Tjarnir, ST-07	66,2	9,03	53,8	19,5	0,87	0,0017	2,44	4,4	0,11
05-003	Brún, Reykjadal BR-03	53,8	10,14	62,5	7,5	0,60	0,0003	2,68	1,1	0,29
05-004	GYN-7	61	9,18	49,4	12,9	0,54	0,0009	2,60	11,4	0,10
05-005	Glerá	1,1	7,77	6,4	11,0	0,49	2,1947	6,53	11,9	0,37
05-006	Kaldárbotnar A	3,4	9,25	9,3	10,9	0,59	1,8627	4,59	4,2	0,06
05-007	Kaldárbotnar B	3,4	9,25	8,9	10,9	0,58	2,0549	4,59	4,4	0,07
05-008	Kaldárbotnar D	3,4	8,81	8,6	10,9	0,60	2,5693	4,73	4,8	0,07
05-009	Kaldárbotnar L-1	3,4	9,05	9,8	10,8	0,58	1,6875	4,61	3,9	0,06

Table 1. (Continued)

Sample no.	Location	Temp. °C	pH in situ	Na ppm	Cl ppm	K ppm	Mg ppm	Ca ppm	Sr ppb	Ba ppb
05-010	Kaldárbotnar L-2	3,4	9,22	9,2	10,8	0,58	1,8398	4,56	4,2	0,11
05-011	Dýjakrókar 3	4,3	9,33	17,2	18,9	0,30	0,6903	7,63	0,9	<0,01
05-012	Dýjakrókar 2	4,3	9,28	16,3	18,7	0,31	0,8159	7,27	1,1	0,01
05-013	Hvalstöd 2	130	7,89	85,4	36,2	3,69	0,0019	3,62	37,4	0,20
05-014	Ferstikla 1	100	8,04	105,2	81,9	2,04	0,0050	8,24	74,6	0,27
05-015	Hvammsvík	62,3	8,50	101,5	75,1	2,47	0,0131	7,17	65,8	0,15
05-016	Hella	4,9	7,80	11,3	13,8	0,96	5,7986	9,73	36,8	0,05
05-017	Selalaekur N	4,9	8,52	11,8	15,8	0,95	6,0229	9,81	31,1	0,14
05-018	Selalaekur S	4,9	8,13	17,1	20,3	1,48	12,0287	20,00	71,7	0,23
05-019	Hella	5	7,18	14,1	14,8	2,04	9,3560	16,77	69,1	0,21
05-020	Hella	7	7,38	14,5	13,6	1,62	10,9473	18,75	73,8	0,08
05-021	Sydsta Mörk	3,2	8,48	7,5	7,4	1,38	3,0877	3,36	9,6	0,09
05-022	Vesturlandeyjar	5,6	8,23	13,2	13,0	1,15	5,7037	15,15	54,7	0,03
05-023	Hvolsvöllur	3,8	8,20	11,2	11,5	1,06	3,8675	6,56	22,0	0,13
05-024	Hveragerði	11,1	7,59	7,7	9,9	1,12	5,6312	12,51	20,4	0,12
05-025	Hveragerði	6,6	8,07	9,5	15,1	0,67	2,3738	6,02	12,0	0,20
05-026	Hveragerði	6,6	8,00	8,9	16,3	0,64	2,5007	6,13	11,8	0,14
05-027	Kaldadarnes	5,8	6,99	10,2	16,0	1,06	6,3261	6,59	23,4	0,55
05-028	Stokkseyri	9	9,33	10,1	13,1	0,79	3,5307	6,09	8,4	0,19
05-029	Selfoss 1	4	7,44	9,6	10,7	0,33	0,6033	5,64	1,8	0,02
05-030	Selfoss 2	3,6	7,60	10,5	11,4	0,30	0,4310	6,06	0,7	<0,01
05-031	Selfoss 3	3,4	9,50	9,7	10,1	0,35	0,6741	5,62	2,2	0,01
05-032	Laugarbakkar lb-02	51,8	9,41	62,3	64,0	0,57	0,0060	2,41	4,4	0,05
05-033	Laugarbakkar LB-23	55,8	8,61	67,7	53,2	0,91	0,0798	4,54	11,7	0,11
05-034	Midengi ME-12	53,8	6,17	324,0	380,1	16,20	178,9858	141,79	301,0	6,06
05-035	Eskifjörður ES-02A	80,8	8,20	298,1	467,2	3,63	0,0123	102,93	589,0	4,82
05-036	Minni Vatnsleysa MV-05	5,6	7,94	112,2	278,2	3,40	17,5309	18,16	111,0	0,94
05-037	Kálfstjörn	7,7	7,68	99,6	239,7	2,93	14,2854	17,86	97,3	1,17
05-038	Vogar VH-06	6,1	7,54	98,6	249,5	2,60	16,9438	18,30	77,8	1,06
05-039	Lambagjá	7,8	7,53	1127,7	2100,0	62,96	91,4183	101,99	893,0	9,38
05-040	Stadur ST-08	83,9	6,63	10625,0	23175,3	288,21	101,3695	1934,49	13600,0	302,00
05-041	Laekjarbotnar	4,6	9,15	13,4	19,5	0,30	0,8471	4,14	2,8	0,12

3. Environmental toxicology of barium

Barium poisoning to humans is uncommon and usually due to accidental contamination of food sources or suicidal ingestion. The water-soluble barium salts (acetate, chloride, hydroxide, nitrate, sulfide) are highly toxic, whereas the insoluble barium sulfate and carbonate are nontoxic because they are not absorbed from the gastrointestinal canal. Soluble barium salts are found in depilatories, fireworks and rodenticides and are used in manufacture of glass and in dyeing textiles. Barium sulfide and polysulfide may also produce hydrogen sulfide toxicity.

The mechanism of toxicity: Barium poisoning is characterized by profound hypokalemia leading to respiratory and cardiac arrest. The mechanism for the rapid onset of severe hypokalemia is not known: Studies have excluded adrenergic stimulation. It has been proposed that barium ions have a direct action on muscle cell potassium permeability, which stimulates smooth, striated, and cardiac muscles, resulting in peristalsis, arterial hypertension, muscle twitching, and cardiac arrhythmias (Olson et al., 1998).

Toxic dose: The minimum oral toxic dose of soluble barium salts is undetermined but may be as low as 200 mg. Lethal doses range between 1-30 g for various barium salts because absorption is influenced by gastric pH and foods high in sulfate (Olson et al., 1998).

Clinical presentation: Within minutes to a few hours after ingestion, victims develop profound hypokalemia and skeletal muscle weakness progressing to flaccid paralysis of the limb and respiratory muscles. Ventricular arrhythmias also occur. Gastroenteritis with severe watery diarrhea, impaired visual accommodation, and central nervous system depression are sometimes present. More often, patients remain conscious even when severely intoxicated.

Diagnosis: Diagnosis is based on a history of exposure, accompanied by rapidly progressive hypokalemia and muscle weakness (Olson et al., 1998).

4. Aqueous speciation of barium

4.1. Speciation calculations

A survey of the literature revealed chemical thermodynamic data on $\Delta G_{f,i}^\circ$, $\Delta H_{f,i}^\circ$ and S_i° for the following barium species at 25°C and 1 bar: Ba^{+2} (Shock et al., 1997), $BaOH^+$, $BaCl^+$, BaF^+ , $BaCO_3^0$ (Sverjensky et al., 1997) and $BaSO_4^0$ (Ryzhenko et al., 1971). From these data and thermodynamic data on OH^- , Cl^- , F^- , SO_4^{2-} and CO_3^{2-} dissociation constants for Ba-ion pairs have been calculated at 25°C and 1 bar (Table 2). We have:

$$\Delta G_r^\circ = \nu \Delta G_{f,i}^\circ \quad (1)$$

$$\Delta H_r^\circ = \nu \Delta H_{f,i}^\circ \quad (2)$$

and

$$\Delta S_r^\circ = \nu S_i^\circ \quad (3)$$

where ν stands for the respective stoichiometric coefficients, being positive for products and negative for reactants. The relationship between ΔG_r° and the logarithm of the dissociation (equilibrium) constant is given by

$$\log K = \frac{-\Delta G_r^\circ}{RT \ln(10)} \quad (4)$$

where R is the gas constant and T is the temperature in Kelvin.

Table 2. Chemical thermodynamic data on aqueous Ba-species at 25°C and 1 bar

Compound	Reaction	ΔG°_f cal/mole	ΔH°_f cal/mole	ΔS°_f cal/mole K	ΔG°_r cal/mole	ΔH°_r cal/mole	ΔS°_r cal/mole	$\log K_{25^\circ C}$
Ba^{+2}		-134030	-128500	2.3				
BaOH^+		-172300	-175900	27.5				
BaCl^+		-164730	-165323	24.0				
BaF^+		-201120	-206510	5.5				
BaSO_4		-311860	-306070	19.42				
BaCO_3		-263830	-285850	16.0				
OH^-		-37595	-54977	-2.56				
Cl^-		-31378	-39933	13.56				
F^-		-67340	-80150	-3.15				
SO_4^{-2}		-177930	-217400	4.5				
CO_3^{-2}		-126191	-161385	-11.95				
	$\text{BaOH}^+ = \text{Ba}^{+2} + \text{OH}^-$				675	-7577	-27.76	-0.1183
	$\text{BaCl}^+ = \text{Ba}^{+2} + \text{Cl}^-$				-678	-3110	-8.14	0.1188
	$\text{BaF}^+ = \text{Ba}^{+2} + \text{F}^-$				-250	-2140	-6.35	0.0438
	$\text{BaSO}_4 = \text{Ba}^{+2} + \text{SO}_4^{-2}$				-100	-3863	-12.62	0.0175
	$\text{BaCO}_3 = \text{Ba}^{+2} + \text{CO}_3^{-2}$				3609	-4035	-25,65	-0.6323

The temperature dependence of the dissociation constants has been predicted by the electrostatic approach of Helgeson (1967) following the procedure given by Arnórsson et al. (1982) using

$$\log K = 0.0523 \cdot \Delta S_r^\circ + \frac{1}{T} (33.043 \cdot \Delta S_r^\circ - 0.2185 \cdot \Delta H_r^\circ) + 0.623 \cdot 10^{-6} \Delta S_r^\circ \cdot T^2 \quad (5)$$

where T is in Kelvin and ΔS_r° and ΔH_r° in cal mole⁻¹ K⁻¹ and cal mole⁻¹, respectively. The respective temperature equations for dissociational equilibria involving Ba-species are shown in table 3.

Table 3

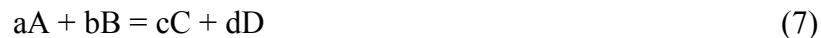
Dissociation equations for the barium species	The temperature dependence of the dissociation constants
$BaOH^+ = Ba^{+2} + OH^-$	$\log K_T = -1.451848 + \frac{738.30082}{T} - 0.00001729448 \cdot T^2$
$BaCl^+ = Ba^{+2} + Cl^-$	$\log K_T = -0.425722 + \frac{410.56498}{T} - 0.00000507122 \cdot T^2$
$BaF^+ = Ba^{+2} + F^-$	$\log K_T = -0.332105 + \frac{257.76695}{T} - 0.00000395605 \cdot T^2$
$BaSO_4^0 = Ba^{+2} + SO_4^{-2}$	$\log K_T = -0.660026 + \frac{427.06284}{T} - 0.00000786226 \cdot T^2$
$BaCO_3^0 = Ba^{+2} + CO_3^{-2}$	$\log K_T = -1.341495 + \frac{34.09455}{T} - 0.00001597995 \cdot T^2$

The WATCH speciation program (Arnórsson et al., 1982), version 2.3 (Bjarnason, 2004) was used to calculate major species distribution and pH. A special supplement was added to WATCH for calculating Ba-species distribution. The WATCH speciation program calculates individual species activities of major components and H⁺ at a selected temperature. The program also provides data on solubility constants for selected common weathering and hydrothermal minerals. From the species activity calculations, mineral activity products are derived. Comparison between these activity products and the mineral solubility constants permits evaluation of the state of saturation of the water with respect to these minerals. From the thermodynamic expression for chemical equilibrium we have

$$\Delta G_r = \Delta G_r^\circ + RT\ln(Q) \quad (6)$$

where ΔG_r stands for the Gibbs energy of reaction, ΔG_r° the standard Gibbs energy of

reaction and Q is the activity product. R is the gas constant (8.314472) and T temperature in K. For a general reaction



where a, b, c and d represent stoichiometric constants and A, B, C and D products and reactants, Q is given by

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (8)$$

Brackets represent activity of the enclosed species. From equation (4) we have

$$\Delta G_r^\circ = -RT\ln(K) \quad (9)$$

so

$$\Delta G_r = -RT\ln(K) + RT\ln(Q) \quad (10)$$

At equilibrium $\Delta G_r = 0$ so $K = Q$. It is common to express $\ln(Q/K)$ as saturation index (SI). When a mineral-solution reaction is expressed in such a way that the mineral is written as reactant (on the left hand side) and aqueous species as products, $SI > 0$ for a supersaturated solution and $SI < 0$ for an under-saturated solution.

The solubility constants for the commonly occurring Ba-mineral, barite and witherite have been calculated from the thermodynamic data on the minerals, as given by Robie and Hemingway (1995) and those on Ba^{+2} , SO_4^{-2} and CO_3^{-2} from Shock et al. (1997).

5. Barium in primary basalt minerals

Limited data are available on the Ba content of Icelandic basalts. For the present study we used data on Ba concentrations in Tertiary tholeiitic basalts in Skagafjörður in north Iceland: The average concentration of Ba in 32 samples is 75 ppm. Based on data of barium in primary basalt mineral, the barium of the Skagafjörður basalts will be concentrated in the plagioclase where it replaces minor potassium.

The Skagafjördur basalts are almost exclusively lava flows forming a flood basalt sequence of as much as 7 km thickness (Jóhannesson, 1991). The basalt lavas are fine-grained due to rapid cooling, typically with occasional plagioclase phenocrysts and rare olivine phenocrysts. The mineralogy of groundmass is characterized by a preponderance of calcic plagioclase feldspar and pyroxene. Fe-Ti-oxides are invariably present, being titano-magnetite. Olivine is most often absent.

6. Barium concentration in water samples

The concentrations of Ba in water samples range from <0.01 ppb to 302 ppb. Of the 308 samples Ba was not detected in 15 samples (< 0.01 ppb), 113 samples had Ba of < 0.1 ppb, 116 samples have Ba concentrations of 0.1 – 0.5 ppb and 10 samples had Ba > 10 ppb. The average Ba concentration of samples with detectable concentration was 3.6 ppb.

Non-thermal ground waters show the whole range of the observed Ba concentration variation. For the thermal waters no relationship is observed between Ba concentrations and temperature (Figs. 1a and 1b). Also there is no correlation between Ba concentrations and in situ pH (Fig. 2). At each pH, the whole range of Ba concentrations are observed. The term in situ pH, as used here, refers to the pH of the waters at well discharge temperatures as calculated by the WATCH speciation program from the measured pH value around room temperature. Arnórsson et al. (2002) provide detailed account of the calculation procedure.

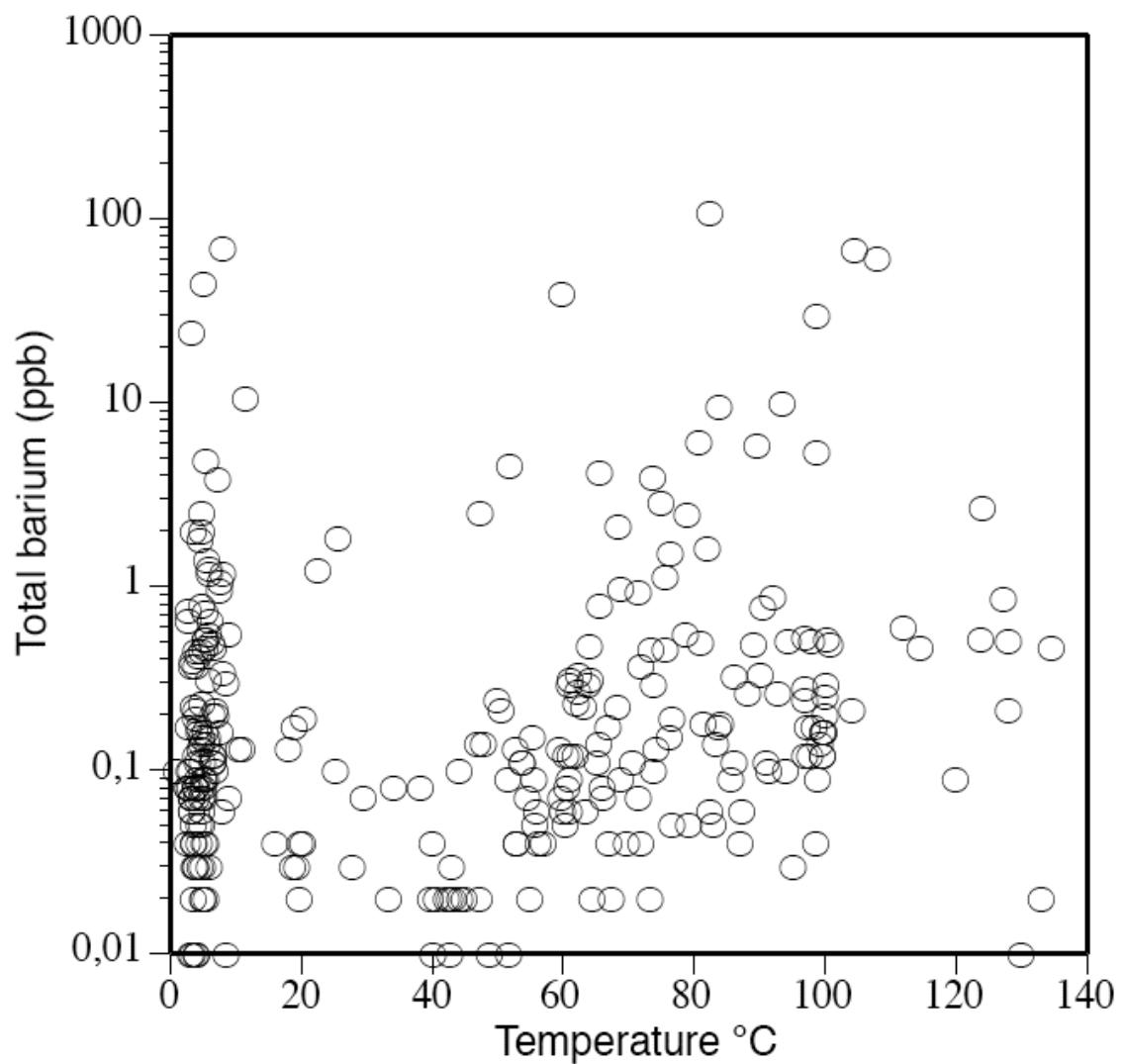


Figure 1a. Barium concentrations versus temperature in Icelandic ground and geothermal waters.

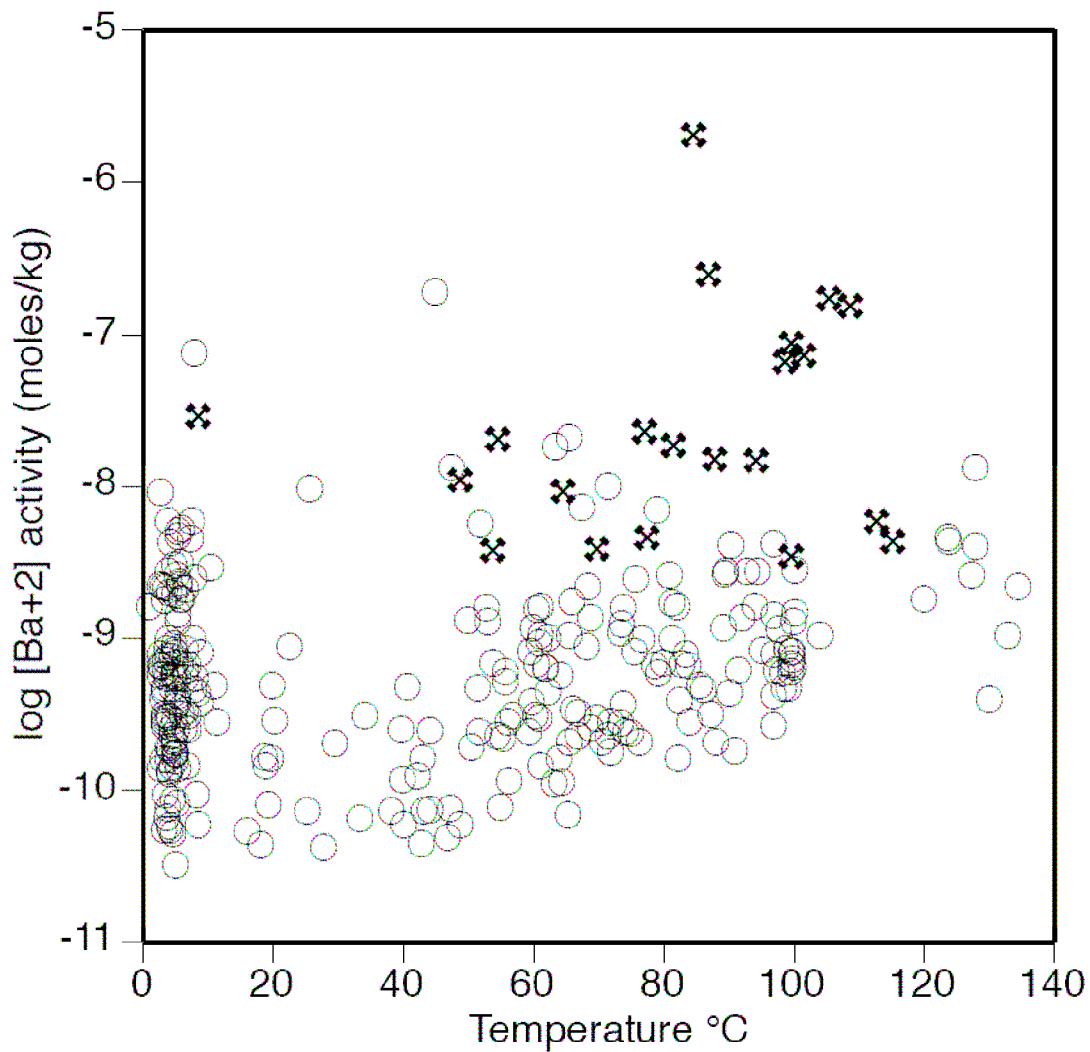


Figure 1b. $\log [B^{+2}]$ activity in moles/kg versus temperature in Icelandic ground and geothermal waters. The samples with chlorine concentrations >300 ppm are marked separately (X).

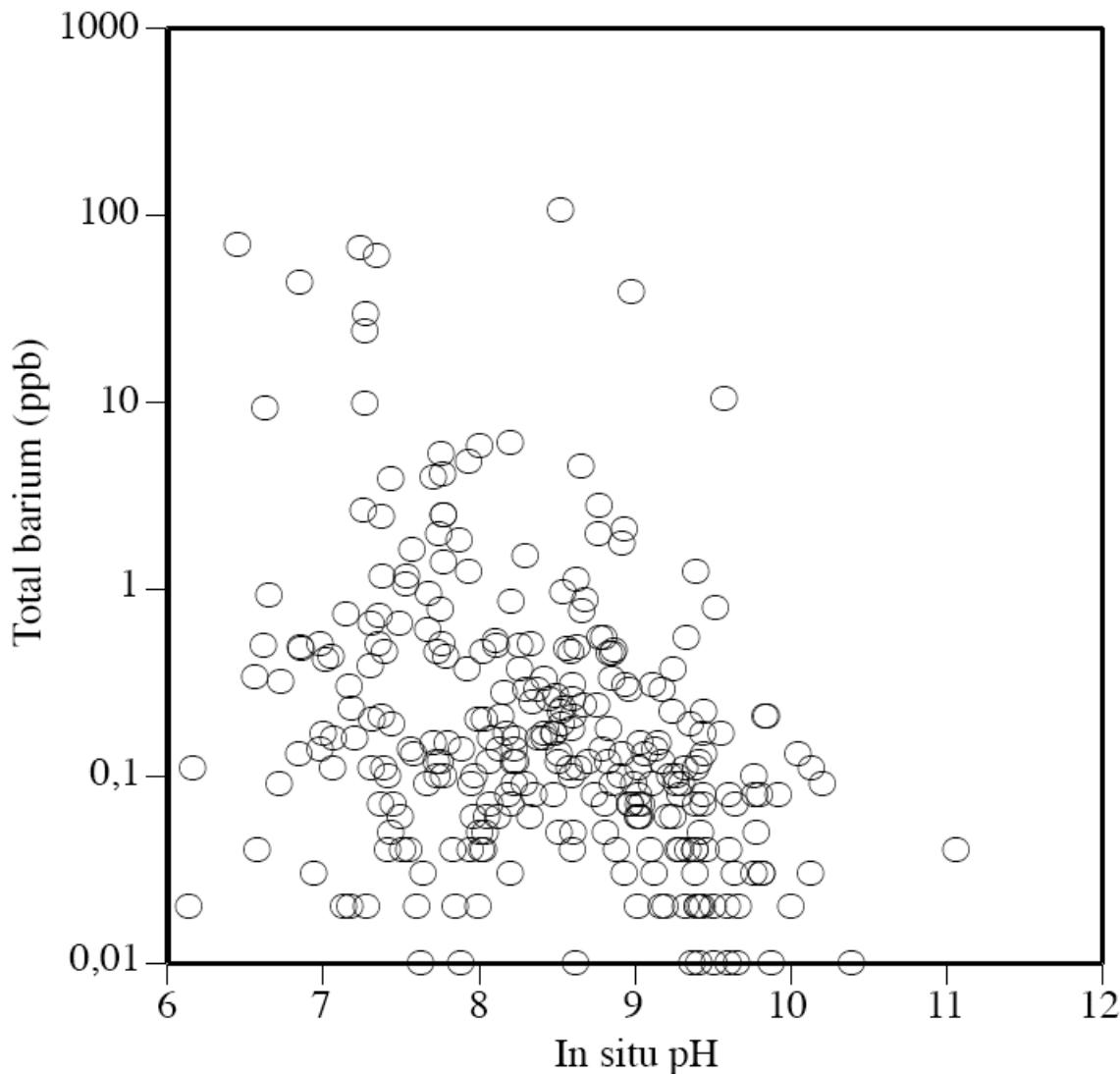


Figure 2. In situ pH versus total barium concentrations in Icelandic ground and geothermal waters.

In contrast to lack of correlation between Ba on one hand and temperature and pH on the other, there is an observable correlation between the Cl content of the waters and their Ba concentrations, Ba concentrations increasing with increasing Cl content (Fig. 3).

The source of Cl to ground and geothermal waters is seawater spray and aerosols, the rocks with which the water interacts and seawater which infiltrates the bedrock in coastal areas (Giggenbach, 1991) but also in lowland area in Iceland that were transgressed by the ocean around the end of the last glaciation (Arnórsson and Andrésdóttir, 1995). The Icelandic basalts contain low Cl. As a consequence of this and the oceanic climate of Iceland, far the larger part of Cl in Icelandic ground water is of marine origin.

Geothermal waters from low-temperature fields in Iceland, which are considered for the present study, in general do not contain more than a few tens of ppm of Cl derived from basalt dissolution. Waters with over 100 ppm Cl are likely to contain a relative large marine Cl component. The average Ba concentration of seawater is 15 ppb (Krauskopf and Bird, 2003). The Cl/Ba ratio of river water is considerably lower than that of seawater. Marine sediments contain relatively high concentrations of Ba, precipitated as barite, largely in estuaries and elsewhere near land. Barium may also be removed from seawater by adsorption onto clay.

The correlation between Ba and Cl, depicted in Fig. 3, and the conclusion that the Cl in high Cl ground and geothermal water is of marine origin, implies that increased Cl content of the water enhances dissolution of Ba from the basalt. Bearing in mind electric neutrality of aqueous solution, increased content of dissolved Cl in any aqueous solution means that there must be an equal increase in the equivalent sum of cations. In view of this, increased Cl content may lead to redistribution of cations in solution in favour of increased mobility of Ba.

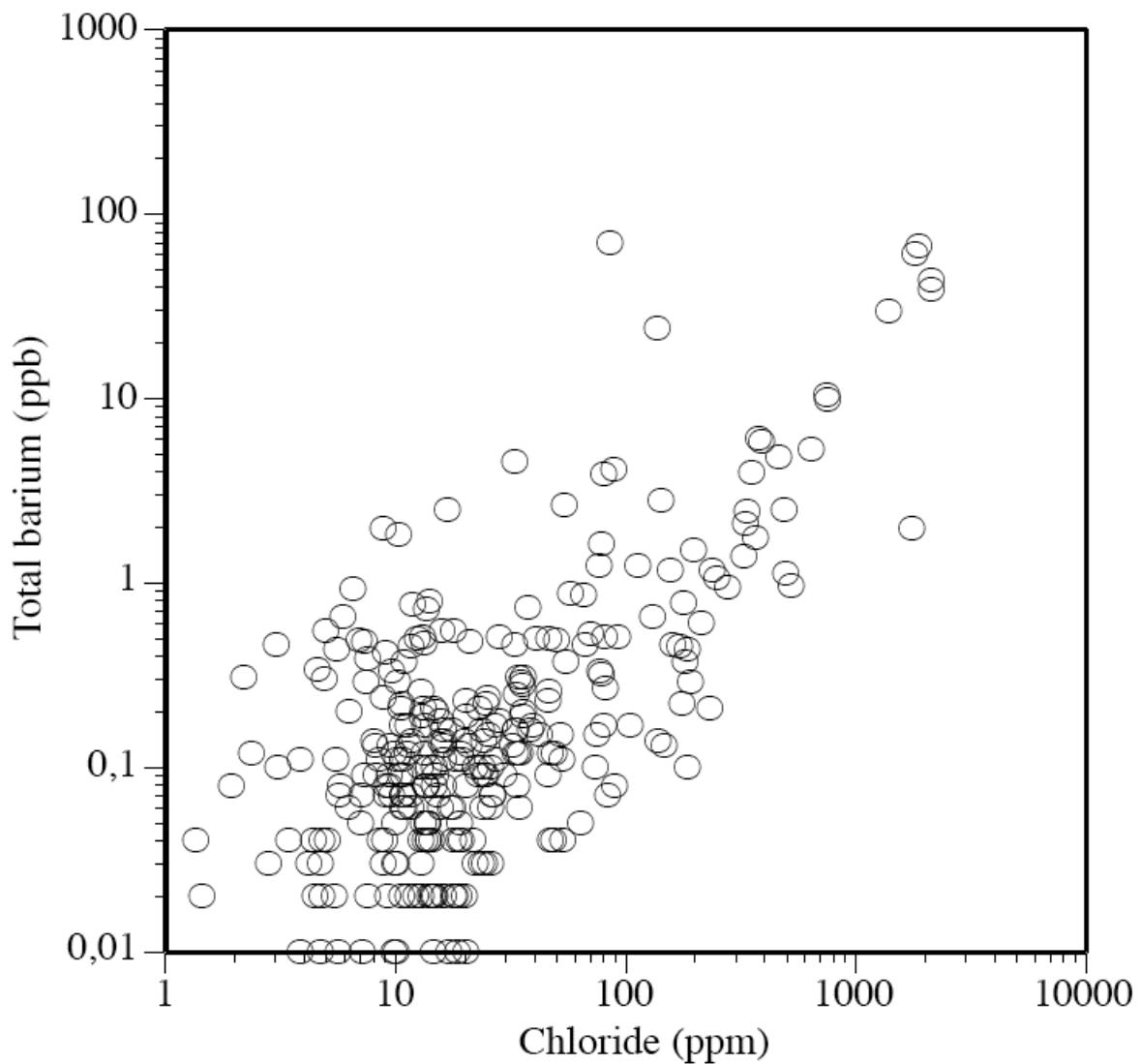


Figure 3. Total barium versus total chloride concentrations in Icelandic ground and geothermal waters.

7. Distribution of Ba species and Ba⁺²-cation relationship

The activities of the barium species listed in Table 2 were calculated by a special supplement to the WATCH speciation program. Activities of OH⁻, Cl⁻, F⁻, SO₄⁻² and CO₃⁻², which form ion pairs with Ba⁺², were taken from WATCH. For these calculations, the effective ionic radius of Ba⁺², BaOH⁺ BaCl⁺ and BaF⁺ were selected as 4.5, dd, ee and xx, respectively for calculation of the activities of these species. The activity of the neutral species of BaCO₃[°] and BaSO₄[°] were taken to be equal to unity.

The free Ba⁺² ion dominates over all other barium species, Most often (%) it constitutes over 95% of the total Ba and in 200 of the 308 samples considered for the present study it is over 98%.

Figures 4 to 6 show how the activity of Ba⁺² relates to the activities of Ca⁺², K⁺ and H⁺. These plots are based on the assumption that exchange reactions between silicate minerals govern the relative distribution of the elements in the waters. Since silicate minerals may be expressed as sum of hydroxides we can write

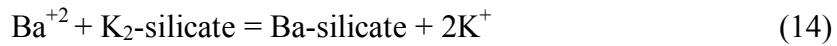


Or specifically for the cations considered



The relationships in Figures 4 to 6 indicate that the activities of the four cations for which data are plotted in Figures 4 to 6 are internally related. In view of the similarities of the geochemical behavior of Ba⁺² and K⁺, the relationship observed between the two ions (Fig. 5) is considered to reflect a geochemical process whereas the relations between Ca⁺² and H⁺, on the other hand is considered to be a consequence of the internal relationship

between K^+ , Ca^{+2} and H^+ . In accordance with this, it is considered that the relative activities of K^+ and Ba^{+2} is the consequence of the exchange equilibrium or adsorption reaction described by



The equilibrium constant being

$$K = \frac{Ba^{+2} [K_2\text{-silicate}]}{[Ba\text{-silicate}] K^{+2}} = \frac{Ba^{+2}}{K^{+2}} \quad (15)$$

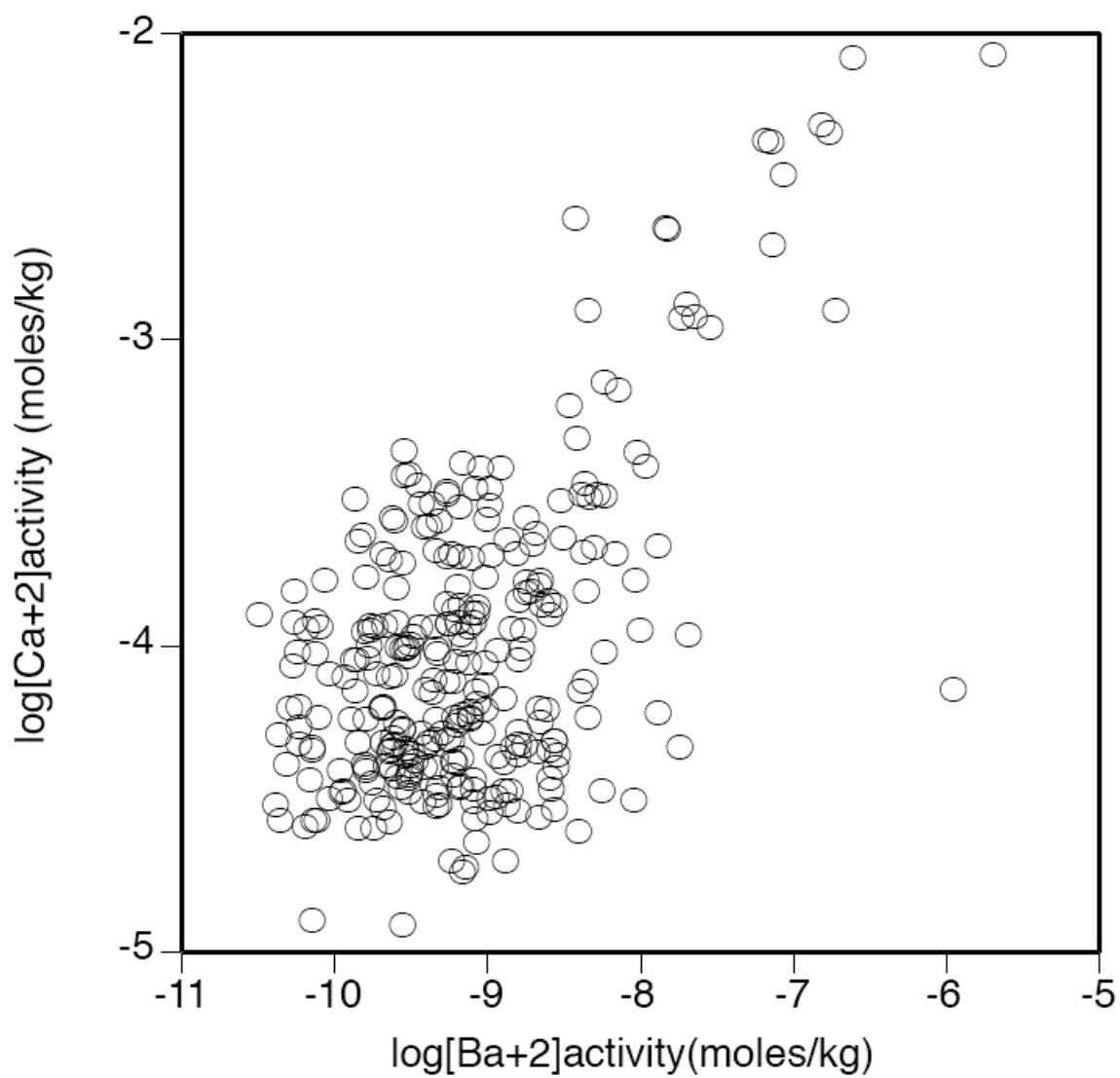


Figure 4. $\log [Ca^{+2}]$ activity versus $\log [Ba^{+2}]$ activity in moles/kg.

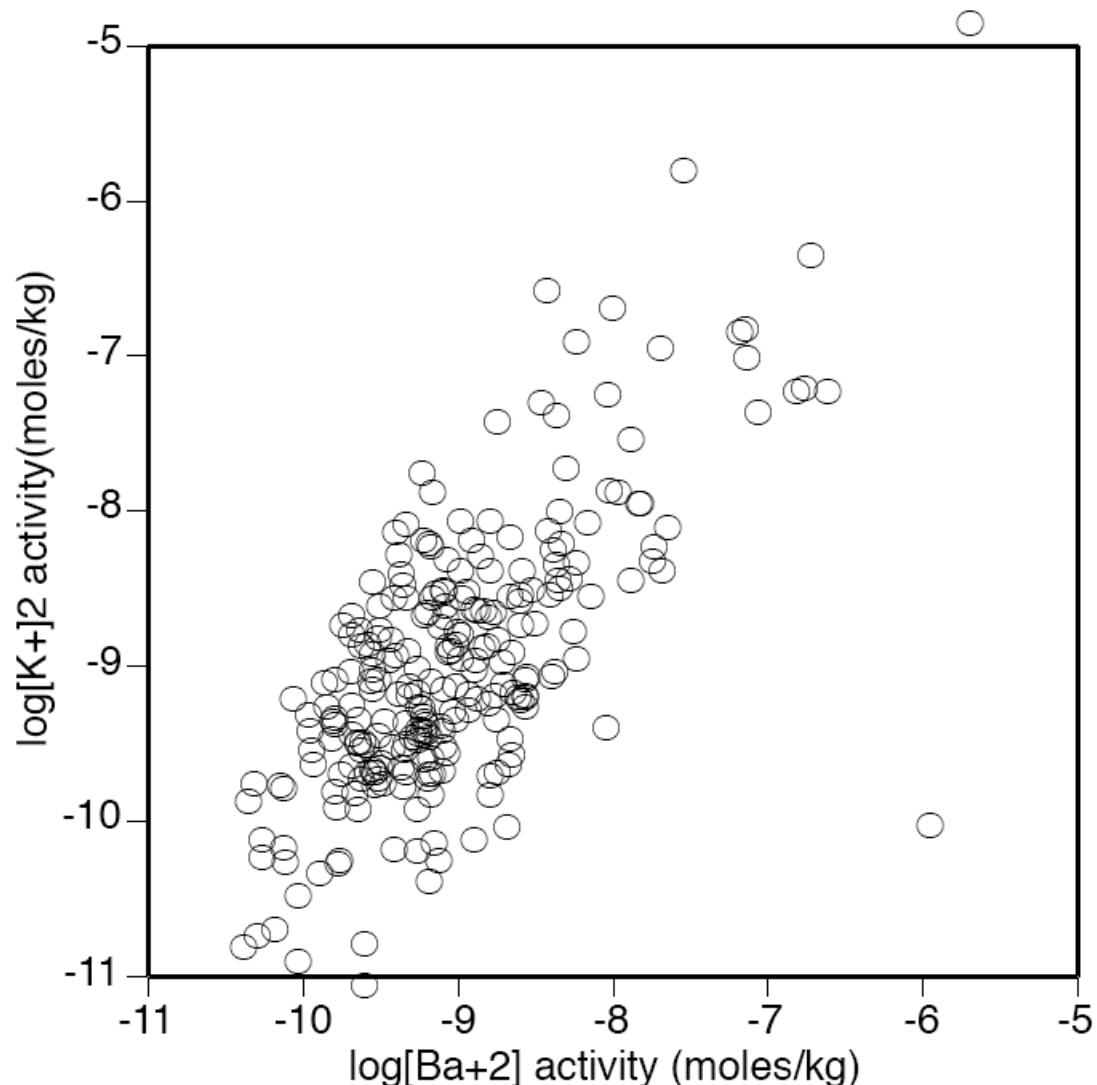


Figure 5. $\log [\text{K}^+]^2$ activity versus $\log [\text{Ba}^{+2}]$ activity in moles/kg.

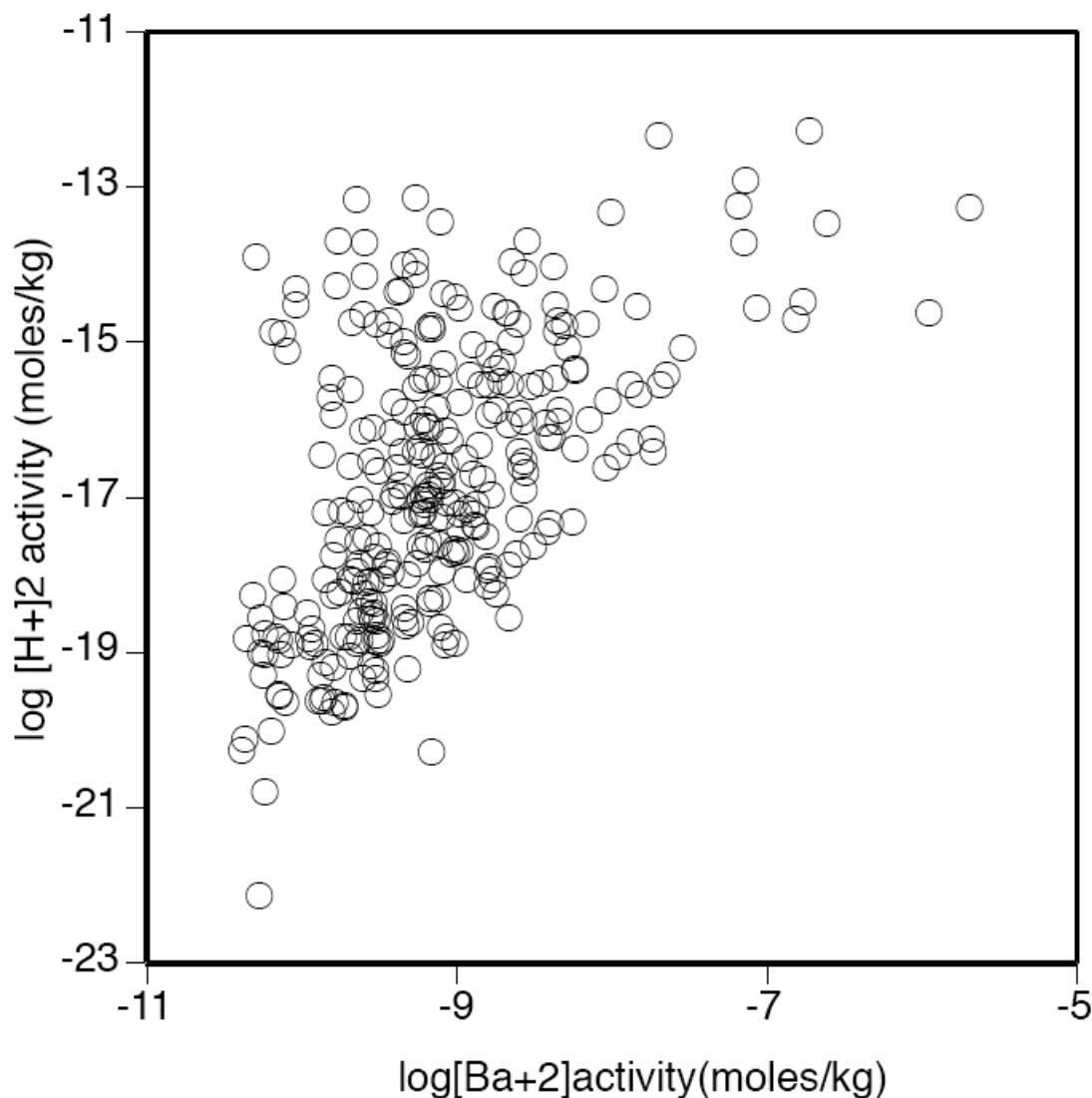


Figure 6. $\log [\text{H}^+]^2$ activity versus $\log [\text{Ba}^{+2}]$ activity in moles/kg

8. Barium mineral saturation

All water samples are strongly under-saturated with respect to witherite (Fig. 7). Most samples are also barite under-saturated (Fig. 8). Yet, some are close to saturation. These samples are relatively high in Ba and contain relatively high Cl due to the presence of a marine ground water component in these waters. Several waters with low chloride are also close to barite saturation. They represent warm waters formed by mixing of boiled high-temperature water from the Námafjall field in Northeast Iceland and ground water.

These waters are relatively high in Ba as well as in sulphate. The high sulphate is the consequence of H₂S oxidation and the high Ba is likely due to enhanced basalt dissolution by the mixed water. The mixing of the two water types produces a relatively low water pH leading to increased under-saturation of the primary basalt minerals, thus enhancing their dissolution (Arnórrsson, 1985).

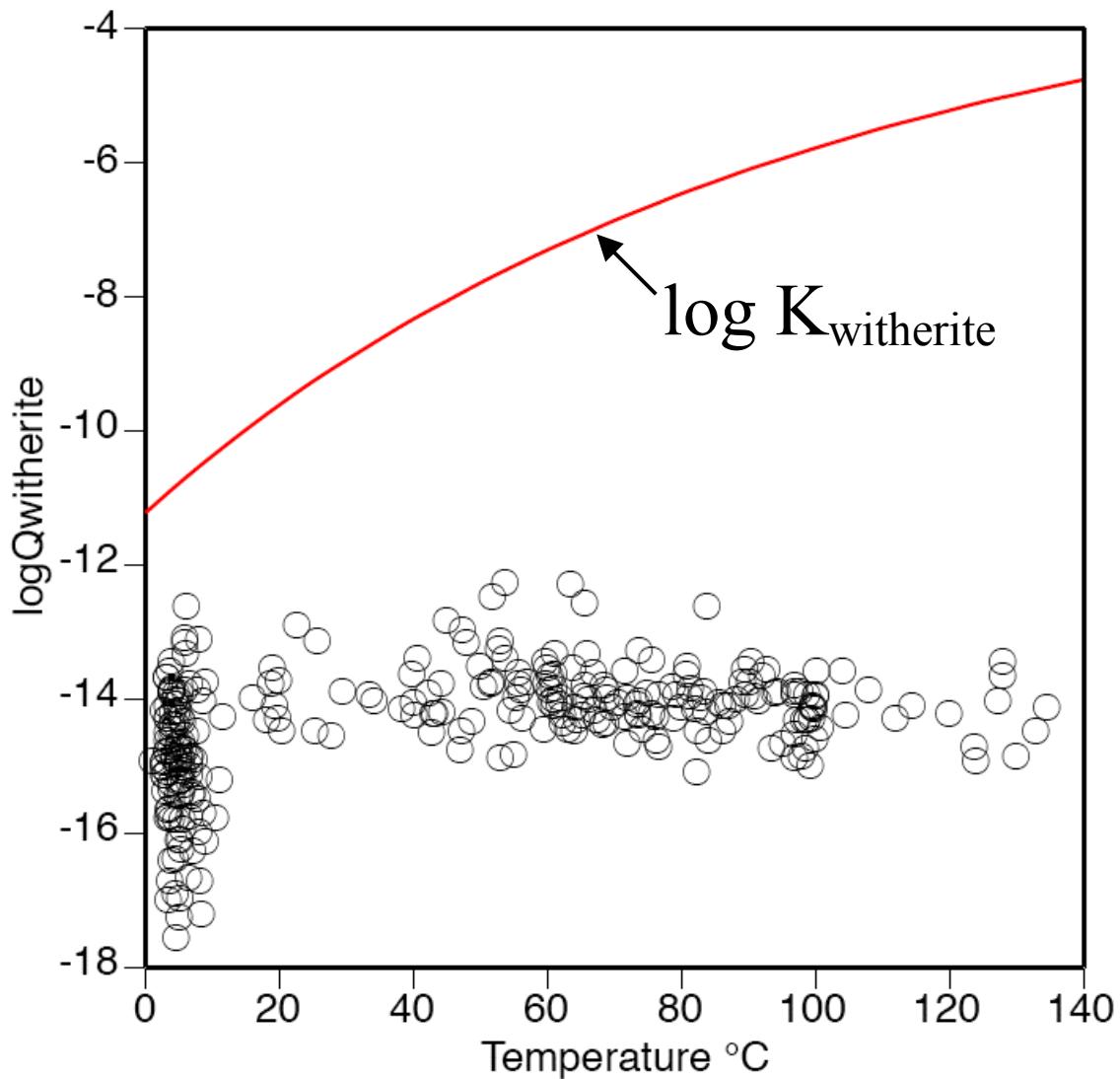


Figure 7. $\log Q_{\text{witherite}}$ versus temperature in Icelandic ground and geothermal waters. The $\log K_{\text{witherite}}$ is shown by the line.

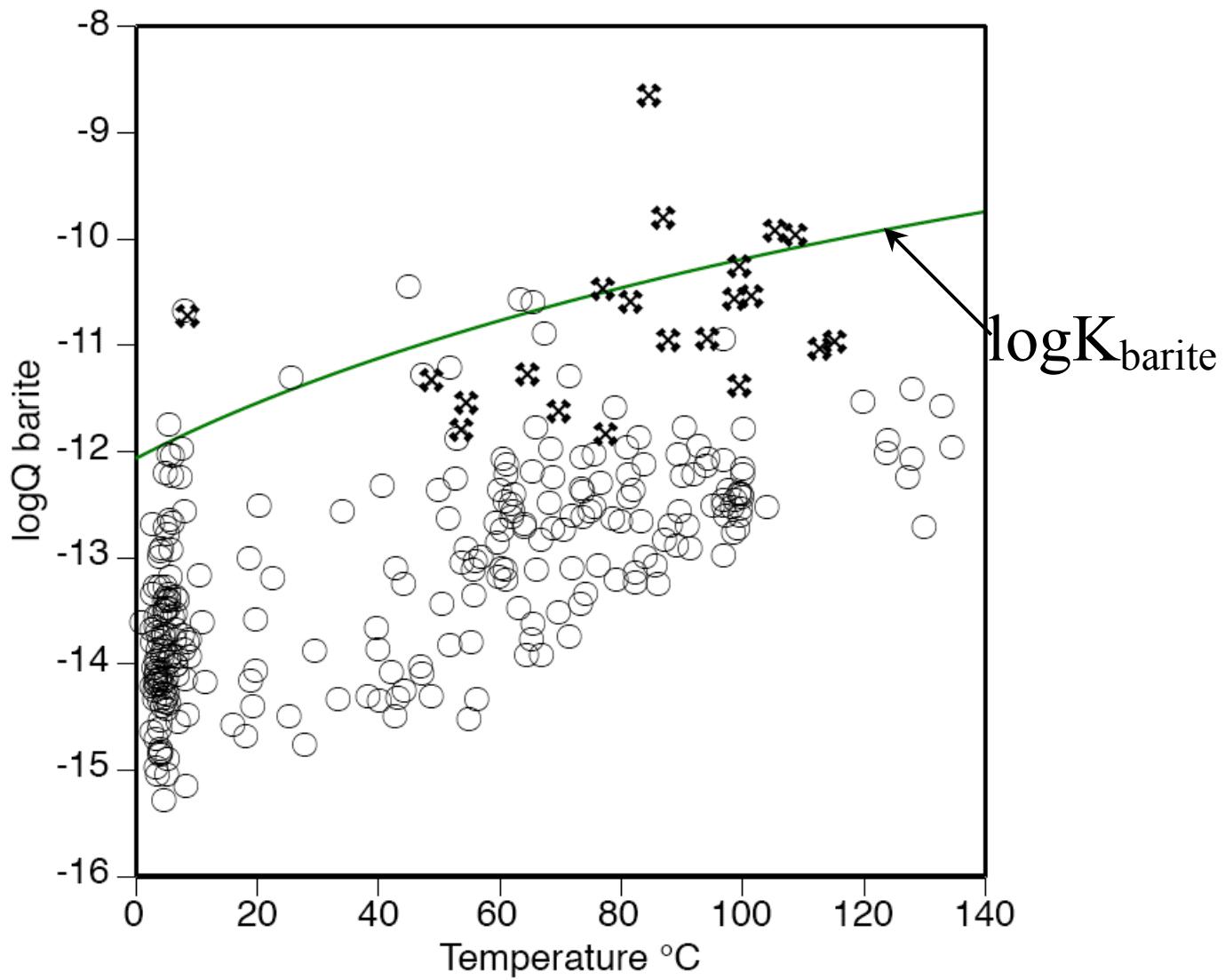


Figure 8. $\log Q_{\text{barite}}$ versus temperature in Icelandic ground and geothermal waters. The samples with chlorine concentrations $>300 \text{ ppm}$ are marked separately (X). The $\log K_{\text{barite}}$ is shown by the line.

9. Relative mobilities of Na, K, Mg, Ca, Sr and Ba

Estimates of the mobility of barium relative to the mobility of the other elements of interest was done by calculating their average concentration ratio in the water samples, and dividing this by the corresponding average concentration ratio in rock:

$$\frac{\text{Ba}_w/\text{Na}_w}{\text{Ba}_r/\text{Na}_r}, \frac{\text{Ba}_w/\text{K}_w}{\text{Ba}_r/\text{K}_r}, \frac{\text{Ba}_w/\text{Ca}_w}{\text{Ba}_r/\text{Ca}_r}, \frac{\text{Ba}_w/\text{Mg}_w}{\text{Ba}_r/\text{Mg}_r} \text{ and } \frac{\text{Ba}_w/\text{Sr}_w}{\text{Ba}_r/\text{Sr}_r}$$

For the concentrations of these elements in rocks we use data on basalts in Skagafjörður in North Iceland. These data give the following average concentrations, shown in table 4:

Table 4. Average concentrations of the elements
of interest in basaltic rock in Iceland

Element	Concentration in basalts (ppm)
Mg	38779
Ca	80474
Na	18546
K	2740
Ba	75
Sr	241

The results of these calculations are shown in figure 9. The calculations show a clear order in the relative mobilities of these elements. The results show that their mobility is in this order: Na > K > Ca > Ba > Mg > Sr.

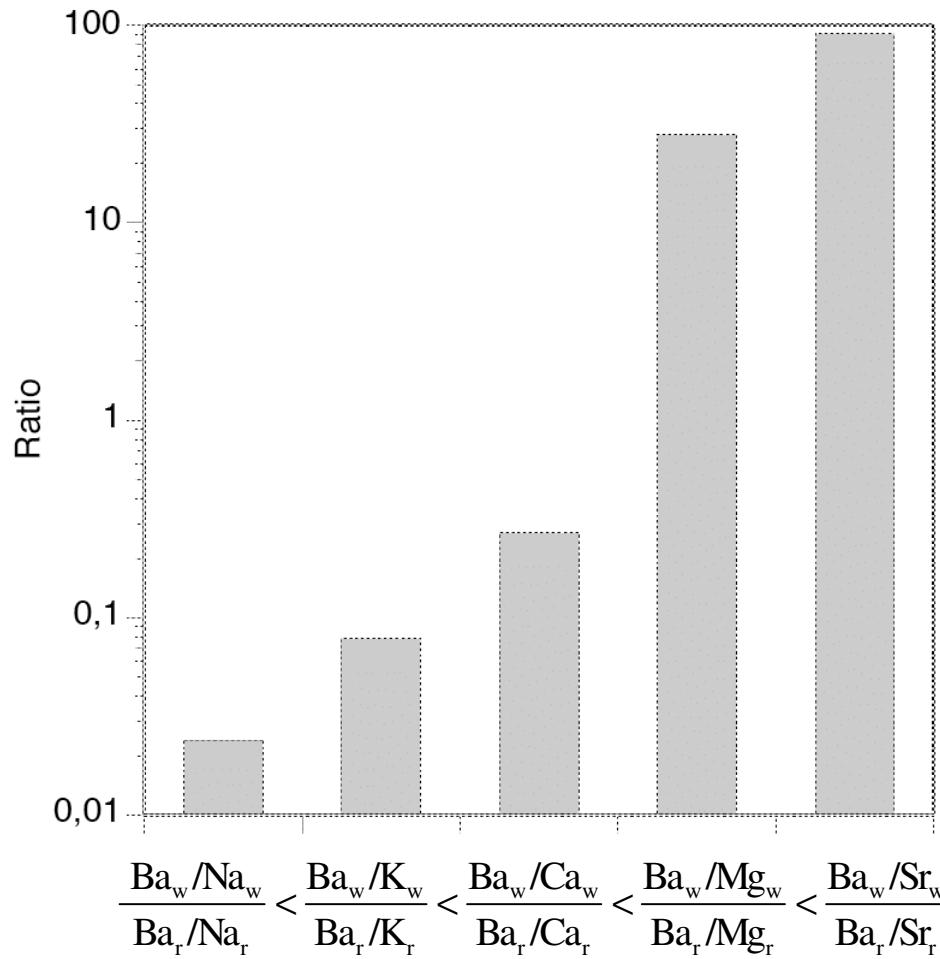


Figure 9. The mobilities of Ba relative to Na, K, Mg, Ca and Sr in the studied waters.

10. Summary and conclusions

The concentrations of Ba in ground waters and <150°C waters from low-temperature geothermal fields in Iceland are highly variable, ranging from <0.01 ppb to about 300 ppb. An average Ba concentration in selected Icelandic basalts is 75 ppm. In basalts Ba is largely present in plagioclase where it replaces potassium.

Aqueous Ba concentrations increase with increasing chloride content of the water, as do other cations, in particular the divalent ones, such as Mg, Ca and Sr. Barium occurs largely as free Ba⁺² ion, being over 98% in two-thirds of the samples analyzed and

always >92%. All waters are strongly witherite under-saturated. Most of the sampled waters are also barite under-saturated. Yet, waters with above some 100 ppm Cl tend to be rather close to saturation as are some waters of mixed origin. In these waters barite solubility controls aqueous Ba concentrations. A correlation is observed between the activities of Ba^{+2} and K^+ . It is known that Ba substitutes for K in K-bearing rock-forming minerals due to the similar size of the Ba^{+2} and K^+ ions. It is considered that aqueous Ba concentrations in barite under-saturated waters are controlled by exchange equilibria between Ba^{+2} and K^+ in secondary K-bearing minerals or possibly by adsorption of Ba^{+2} onto clay mineral surfaces where it competes with K^+ and other ions.

References

- Allegre, C.J., Dupre, B., Negrel, P., Gaillardet, J., 1996. Sr–Nd–Pb isotope systematics in Amazon and Congo River systems: constraints about erosion processes. *Chem. Geol.* 131, 93–112.
- Arnórsson, S. and Sigurðsson, S., Svavarsson, H., 1982. The chemistry of geothermal waters in Iceland. I. Calculation of aqueous speciation from 0° to 370 °C. *Geochim. Cosmochim. Acta* 46, 1513–1532.
- Arnórsson, S., 1985. The use of mixing models and chemical geothermometers for estimating underground temperatures in geothermal systems. *Journal of Volcanological and Geothermal Research*, 23, 299-335.
- Arnórsson, S., Andrésdóttir, A., 1995. Processes controlling the distribution of B and Cl in natural waters in Iceland. *Geochim. Cosmochim. Acta* 59, 4125–4146.
- Arnórsson, S., Gunnarsson, I., Stefánsson, A., Andrésdóttir, A. & Sveinbjörnsdóttir, Á. E., 2002. Major element chemistry of surface- and ground waters in basaltic terrain, N-Iceland. *Geochimica et Cosmochimica Acta* 66, 4015–4046.

Berner E. K. and Berner R. A., 1996. Global environment: Water, air, and geochemical cycles. Prentice-Hall.

Bishop, J.K.B., 1988. The barite–opal–organic carbon association in oceanic particulate matter. *Nature* 332, 341–343

Bjarnason, J.O., 2004. The speciation program WATCH version 2.3. Icelandic National Energy Authority
[\(http://www.isor.is/Apps/WebObjects/Orkustofnun.woa/wa/dp?id=998\)](http://www.isor.is/Apps/WebObjects/Orkustofnun.woa/wa/dp?id=998)

Blount, C.W., 1977. Barite solubilities and thermodynamic quantities up to 300°C and 1400 bars. *Am. Mineral.* 62, 942–957

Dehairs, F., Baeyens, W. and Goeyens, L., 1992. Accumulation of suspended barite at mesopelagic depths and export production in the Southern Ocean. *Science* 258, 1332–1335

Dymond, J., Suess, E. and Lyle, M., 1992. Barium in deep sea sediments: a geochemical proxy for palaeoproductivity. *Paleo-oceanography* 7, 163–181

Edmond, J.M., Palmer, M.R., Measures, C.L., Grant, B., Stallard, R.F., 1995. The fluvial geochemistry and denudation rate of the Guayana Shield in Venezuela, Columbia and Brazil. *Geochim. Cosmochim. Acta* 59, 3301–3325.

Ellis, A.J., Sewell, J.R., 1963. Boron in rocks and waters of New Zealand hydrothermal areas. *N.Z. J. Sci.* 6, 589–606.

Falkner, K.K., Klinkhammer, G.P., Bowers, T.S., Todd, J.F., Lewis, B.L., Landing, W.M. and Edmond, J.M., 1993. The behaviour of barium in anoxic marine waters. *Geochim. Cosmochim. Acta* 57, 537–554

Gaillardet, J., Dupre, B., Allegre, C.J., Negrel, P., 1997. Chemical and physical denudation in the Amazon River Basin. *Chem. Geol.* 142, 141–173.

Garrels R. M. and Mackenzie F. T. (1971) Evolution of sedimentary rocks. Norton, New York.

Giggenbach, W.F., 1991. Chemical techniques in geothermal exploration. In: D'Amore, F. (Ed.), *Application of Geochemistry in Geothermal Reservoir Development*. UNITAR/UNDP Centre on Small Energy Resources, Rome, 119–144.

Gíslason, S.R., Arnórsson, S., Ármannsson, H., 1996. Chemical weathering of basalt as deduced from the composition of precipitation, rivers, and rocks in Iceland. *Am. J. Sci.* 296, 837–907.

Hall, C., 1995. Scanning probe microscopy: sulphate minerals in scales and cements. International Symposium on Oilfield Chemistry, San Antonio. Society of Petroleum Engineers (USA) Paper 28996.

Helgeson, H. C., 1967. Thermodynamics of complex dissociation and the analysis of precise conductimetric data. *J. Phys. Chem.* 71, 3121–3136

Jóhannesson H. (1991) The mountains west of Eyjafjördur II. Reykjavík, The Icelandic Tourist Association Yearbook. 1991, 246. p. (In Icelandic).

Kojola WH, Brenniman GR, Carnow B., 1978. A review of environmental characteristics and health effects of barium in public water supplies. *Rev Environ Health* 3:79 –95.

Krauskopf, K.B. and Bird. D.K, 2003. Introduction to geochemistry, third edition, McGraw Hill.

Olson, K. R. e. al., 1998. Poisoning & Drug Overdose (Lange Clinical Manual).

Pingitore, N.E., Eastman, M., 1984. The experimental partitioning of Ba^{+2} into calcite. *Chem. Geol.* 45, 113–120.

Tesoriero, A.J., Pankow, J.F., 1996. Solid solution partitioning of Sr^{+2} , Ba^{+2} , and Ca^{+2} to calcite. *Geochim. Cosmochim. Acta* 60 6., 1053–1064.

Torres, M.E., Brumsack, H.J., Bohrmann, G. and Emeis, K.C., 1996. Barite fronts in continental margin sediments: a new look at barium remobilization in the zone of sulfate reduction and formation of heavy barites in diagenetic fronts. *Chem. Geol.* 127, 125–139

Robie R.A., Hemingway B.S., 1995. Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar. (105 Pascals) pressures and at higher temperatures. U. S. G. S. Bull. 2131.

Ryzhenko et al., 1971; in Naumov, G.B., Ryzhenko, B.N. and Khodakovsky, I.L., 1971. Handbook of Thermodynamic Data, Atomizdat.

Shock, E. L. , Sassani, D. C, Willis, M. and Sverjensky, D.A., 1997. Inorganic species in geologic fluids: Correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. *Geochim. Cosmochim. Acta* 61, 907–950

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behavior and distribution of arsenic in natural waters. *Appl. Geochem.* 17, 517– 568.

Sverjensky, D.A., Shock, E. L. and Helgeson, H. C., 1997. Prediction of the thermodynamic properties of aqueous metal complexes to 1000 C and 5 k. *Geochim. Cosmochim. Acta* 61, 1359–1412