

Dissolution of primary minerals in natural waters II. Mineral saturation state

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Abstract

The saturation state of olivine, plagioclase, clinopyroxene, orthopyroxene, Fe–Ti oxides and apatite of variable composition has been assessed in natural waters in Iceland, with temperature ranging from 0°C to 300°C and in situ pH from below 5 to above 10. Cold waters are undersaturated with respect to olivine, orthopyroxene, clinopyroxene and plagioclases indicating that all these minerals tend to dissolve under weathering conditions. With increasing pH and temperature, the waters approach saturation with pyroxene, olivine, and plagioclases. Also, the degree of undersaturation of olivine and orthopyroxene decreases with increasing Fe content of the minerals and Fe-rich olivine and orthopyroxene are stable between 50°C and 150°C, whereas Mg-rich ones tend to dissolve. Natural waters in Iceland are saturated with respect to pure albite when above 50°C. They are, on the other hand, undersaturated with Ca-rich plagioclase up to 250°C where the waters reach saturation. Pure magnetite and hematite are stable at all temperatures. With increasing titanium content, the minerals become unstable, and the waters are undersaturated with respect to pure ulvöspinel at temperatures up to 300°C. Pure ilmenite is, however, close to saturation under weathering conditions but undersaturated above 200°C. F-apatite is close to saturation at all temperatures. On the other hand, undersaturation with respect to OH-apatite is observed at all temperatures. The weathering susceptibilities of primary minerals of basalt in Icelandic waters in increasing order are Mg-olivine > Fe-olivine, Ti-rich magnetite > Ca-plagioclase, Mg-orthopyroxene > Fe-orthopyroxene, clinopyroxene > Na-plagioclase, F-apatite > Ti-rich ilmenite ≫ Ti-poor magnetite, Ti-poor hematite. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Basalt; Mineral stability; Cold water; Geothermal water; Weathering

1. Introduction

Dissolution of primary minerals is one of the main source of dissolved aqueous species in natural

waters. Knowledge of their potential of dissolution and dissolution rates is essential for quantitative interpretation of natural water compositions and for the study of the cycling of elements in the environment. Information about the saturation state of natural waters with respect to primary minerals is important as it indicates whether a particular mineral tends to dissolve or not, and within a critical range the mineral dissolution rate depends on mineral saturation.

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Table 1

Chemical composition of selected cold and thermal waters from Iceland. Concentrations are in $\mu\text{mol}/\text{kg}$

Sample no.	Sample location	Type ^a	T (°C) ^b	pH/°C ^c	pH _T ^d	Si	B	Na	K	Ca	Mg
97-JA001	Peat near Móholt	p	16	7.40/24	7.44	265	n.a.	653	15.6	139	133.8
97-JA002	River in Lágustadargil	r	12	7.31/24	7.39	145	n.a.	394	9.6	57	47.9
97-JA003	Kúludalsá	r	9	7.00/24	7.09	159	n.a.	418	13.1	72	62.7
97-JA004	Brunná	r	10	7.46/24	7.56	145	n.a.	366	7.9	66	51.3
97-JA005	Thverá at Geitaberg	r	13	7.35/24	7.42	128	n.a.	238	7.0	77	56.3
97-JA006	Laxá í Leirársveit at Hurdarbak	r	13	7.24/24	7.31	106	n.a.	231	5.1	81	49.7
97-JA007	Skardsá	r	11	7.43/24	7.51	119	n.a.	206	3.2	101	40.0
97-JA008	Geldingaá	r	17	7.65/24	7.70	225	n.a.	616	23.8	258	133.4
97-JA009	Laxá í Leirársveit at Vogatungu	r	16	7.25/25	7.30	106	n.a.	228	5.5	81	46.0
97-JA010	Fellsendi	r	15	7.32/24	7.38	154	n.a.	460	9.7	63	54.1
97-JA011	Djúpá	r	15	7.45/24	7.51	144	n.a.	336	9.1	60	52.8
97-JA012	Djúpilaekur	r	11	7.20/23	7.27	120	n.a.	277	8.2	53	44.9
97-JA013	Berjadalsá	r	13	7.43/24	7.50	162	n.a.	379	11.2	70	57.4
97-JA014	Mörkin	so	10	6.59/23	6.67	223	n.a.	504	14.5	85	104.6
97-JA016	Burstarás	r	13	7.32/24	7.39	214	n.a.	550	13.8	100	93.5
97-JA017	Kalmansá	r	13	7.34/24	7.40	21	n.a.	1165	26.4	412	328.5
97-JA018	Katanes	so	10 ^j	5.96/24	6.04	537	n.a.	895	10.2	306	265.5
97-JA019	Peat, Katanes	p	12	7.71/25	7.80	443	n.a.	937	22.9	387	369.5
97-JA020	Urridaá	r	12	7.31/24	7.38	81	n.a.	848	27.6	286	268.7
97-JA021	Brandslaekur	r	11	7.35/24	7.43	208	n.a.	351	7.5	106	76.6
97-JA022	Fossá	r	12	7.31/24	7.39	212	n.a.	344	7.7	103	61.4
97-JA033	Mörkin	so	10 ^j	6.33/24	6.41	261	n.a.	532	16.5	88	99.6
97-JA034	Mörkin	so	10 ^j	6.64/24	6.72	242	n.a.	529	13.2	72	89.2
97-JA038	Katanes	so	10 ^j	4.87/24	4.95	913	n.a.	727	12.3	425	228.2
97-JA042	Klafastadi	so	10 ^j	5.95/25	6.04	495	n.a.	1060	12.1	188	234.0
97-JA043	Katanes	so	10 ^j	5.92/25	6.01	553	n.a.	775	5.5	296	233.2
97-JA045	Galtarholt	so	10 ^j	5.93/20	5.99	541	n.a.	674	2.5	255	196.2
96-3707	Medalfellsvatn	csp	4	7.39/21	7.51	208	0.75	439	7.8	153	99.8
96-3716	Peat, Taglalaekur	p	15	6.11/24	6.16	248	0.46	174	4.8	84	77.9
96-3722	Svínadalsá	r	8	7.26/25	7.37	183	0.55	219	5.0	88	43.2
96-3724	Skálafell	csp	3	8.94/25	9.37	159	0.45	217	3.3	128	7.5
96-3733	Spring, Móskaardshnúkar	csp	2	8.41/19	8.70	240	0.35	217	6.9	272	66.3
96-3734	Írafell	p	5	6.45/25	6.58	279	0.63	285	9.6	164	86.4
96-3740	Írafell	p	4	6.30/20	6.44	288	0.98	299	10.4	159	84.1
97-3701	Laxá í Kjós at Brynjudalsvogur	r	0	7.43/20	7.58	204	0.87	306	6.8	134	93.5
97-3709	Kjálká	r	2	7.21/20	7.34	172	0.49	269	11.1	96	81.0
97-3710	Mjóavatnslaekur	r	0	7.00/25	7.17	140	0.74	233	13.8	111	127.4
97-3711	Thverá	r	2	7.33/24	7.48	153	0.36	246	6.2	79	44.7
97-3712	Trönudalsá	r	3	7.48/24	7.69	193	0.50	276	3.9	124	42.3
97-3714	Thverlaekur	r	0	6.99/24	7.15	189	0.58	264	13.6	149	148.3
97-3715	Sandá	r	3	7.40/24	7.55	168	0.42	240	6.2	95	46.3
97-3716	Flekkudalsá	r	3	7.28/24	7.42	143	0.51	222	6.4	62	40.2
97-3717	Bugða	r	4	7.37/24	7.51	149	0.56	264	6.6	102	64.6
97-3718	Daelisá	r	4	7.22/24	7.35	144	0.58	205	7.3	74	43.5
97-3719	Laxá í Kjós at Brynjudalsvogur	r	4	7.28/22	7.40	148	0.34	226	7.4	88	67.3
88-3037	Brúará	csp	3	9.02/4	9.03	198	n.d.	247	8.1	50	17.3
88-3040	Brúará	r	4	8.57/4	8.57	206	n.d.	263	7.9	53	17.5
88-3045	Brúará	r	4	8.77/3	8.76	158	1.94	182	6.9	42	18.9
88-3046	Brúarárskörd	csp	2	9.74/3	9.75	175	n.d.	199	7.1	46	25.1
90-3002	Hvítá south of Hvítárvatn	r	0	8.81/0	8.81	194	n.a.	295	5.9	93	30.7

DIC ^c	SO ₄	H ₂ S	Cl	F	PO ₄ ^f	Al	Fe _{total}	Fe ^{II}	Ti ^g	IB % ^h	References
572	59	n.a.	633	2.7	0.54	0.31	4.62		0.0045	−4.67	This study
311	30	n.a.	303	1.8	0.65	0.32	0.03		0.0027	−5.10	This study
351	36	n.a.	364	1.8	0.59	0.42	0.11		0.0044	−3.30	This study
257	33	n.a.	327	1.4	0.94	0.15	0.03		0.7143	−3.92	This study
300	20	n.a.	201	1.7	0.48	0.28	0.48 ⁱ	0.23 ⁱ	0.0359	−0.60	This study
316	19	n.a.	191	1.4	0.33	0.27	0.19		0.0054	−2.62	This study
325	17	n.a.	172	1.4	0.40	0.14	0.36		0.0039	−3.39	This study
813	74	n.a.	546	4.0	0.24	0.53	4.20		0.0043	−3.39	This study
302	19	n.a.	193	1.5	0.18	0.17	0.81 ⁱ	0.38 ⁱ	0.0016	−2.53	This study
257	37	n.a.	415	1.8	0.25	0.35	0.05		0.0018	−3.00	This study
217	26	n.a.	280	1.5	0.36	0.15	0.03		0.0019	5.93	This study
244	23	n.a.	232	1.4	0.27	0.20	0.05		0.0027	−2.75	This study
300	31	n.a.	328	1.5	0.24	0.20	0.01		0.0029	−3.75	This study
336	44	n.a.	583	1.7	0.14	0.09	0.01		0.0013	1.43	This study
371	54	n.a.	528	1.8	0.28	0.25	0.11		0.0019	−2.89	This study
1404	154	n.a.	1084	5.5	0.21	2.70	6 ⁱ	3.68 ⁱ	0.0172	−0.12	This study
2407	251	n.a.	816	5.8	0.17	2.68	170.47		0.0104	15.17	This study
1572	46	n.a.	819	4.0	0.32	0.47	31.13		0.0112	3.83	This study
1229	89	n.a.	694	4.2	0.25	0.54	3.01		0.0086	−0.11	This study
476	34	n.a.	240	2.1	0.27	0.27	3.07		0.0039	−2.23	This study
415	26	n.a.	278	2.0	0.22	0.27	0.11		0.0016	−3.66	This study
696	47	n.a.	568	1.6	< 0.05	0.07	0.00		0.0070	−8.52	This study
433	57	n.a.	571	2.6	< 0.05	0.03	0.01		0.0039	−11.90	This study
11 641	836	n.a.	805	23.2	n.a.	63.69	160.65		0.0082	−13.75	This study
2254	64	n.a.	1202	5.3	n.a.	0.83	15.42		0.0098	−2.96	This study
2975	200	n.a.	710	5.3	n.a.	2.12	200.53		0.0132	13.23	This study
4895	16	n.a.	565	5.3	n.a.	2.82	299.86		0.0242	10.90	This study
587	34	n.a.	439	3.1	< 0.05	0.15	0.04		0.0020	−9.22	Stefánsson and Gíslason (2000)
1052	10	n.a.	175	1.3	< 0.05	0.45	49.95		0.0045	6.95	Stefánsson and Gíslason (2000)
375	22	n.a.	120	1.8	< 0.05	0.19	0.04		0.0016	−6.84	Stefánsson and Gíslason (2000)
300	19	n.a.	165	1.5	0.56	0.66	0.04		0.0039	−10.18	Stefánsson and Gíslason (2000)
433	136	n.a.	197	13.9	0.31	0.19	0.03		0.0065	−2.86	Stefánsson and Gíslason (2000)
890	54	n.a.	272	2.0	0.08	0.85	0.56	0.42 ⁱ	0.0075	−9.81	Stefánsson and Gíslason (2000)
1126	25	n.a.	217	1.9	0.14	0.64	1.47		0.0520	3.11	Stefánsson and Gíslason (2000)
416	22	n.a.	319	1.9	0.08	0.25	1.04		0.0418	−0.15	Stefánsson and Gíslason (2000)
309	24	n.a.	338	1.1	0.07	0.77	2.39		0.0074	−4.48	Stefánsson and Gíslason (2000)
564	16	n.a.	246	0.8	0.08	0.23	3.80		0.0034	−2.35	Stefánsson and Gíslason (2000)
245	19	n.a.	261	1.1	0.09	0.27	0.08		0.0016	−5.51	Stefánsson and Gíslason (2000)
366	22	n.a.	201	2.3	0.26	0.16	0.05		0.0030	−5.80	Stefánsson and Gíslason (2000)
680	21	n.a.	287	1.3	0.08	0.32	7.41		0.0044	1.80	Stefánsson and Gíslason (2000)
267	26	n.a.	249	2.3	0.80	0.37	0.15		0.0067	−4.72	Stefánsson and Gíslason (2000)
203	19	n.a.	235	1.3	0.06	0.33	0.25		0.0109	−6.75	Stefánsson and Gíslason (2000)
298	25	n.a.	313	1.6	0.06	0.18	0.56		0.0083	−6.12	Stefánsson and Gíslason (2000)
238	18	n.a.	220	1.0	0.06	0.23	0.52		0.0055	−5.30	Stefánsson and Gíslason (2000)
320	22	n.a.	256	1.4	0.68	1.08	2.01 ⁱ	0.32 ⁱ	0.0042	−6.70	Stefánsson and Gíslason (2000)
207	13	n.a.	110	0.3	1.01	3.62	0.34		0.0433	7.58	Gíslason (1989)
261	15	n.a.	108	3.2	0.62	4.96	0.78		0.0692	0.38	Gíslason (1989)
174	13	n.a.	103	2.7	0.59	3.01	0.04		0.0043	−1.12	Gíslason (1989)
120	13	n.a.	107	0.3	0.04	0.56	0.31		0.0343	11.47	Gíslason (1989)
407	29	n.a.	91	4.1	0.68 ^k	1.68	0.79		0.0244 ^k	−3.63	Gíslason and Arnórsson (1993)

(continued on next page)

Table 1 (continued)

Sample no.	Sample location	Type ^a	T (°C) ^b	pH/°C ^c	pH _r ^d	Si	B	Na	K	Ca	Mg
90-3003	Seydisá	r	0	7.90/0	7.90	236	n.a.	311	11.1	82	48.5
90-3004	Blanda, Langadal	r	0	7.92/0	7.92	292	n.a.	448	20.1	151	140.9
90-3005	Blanda, Blöndudal	r	0	7.87/1	7.88	279	n.a.	453	16.6	130	104.4
90-3006	Svartá west	r	0	8.15/0	8.15	351	n.a.	418	33.0	160	267.8
90-3007	Eystri Jökulsá	r	0	7.77/1	7.78	258	n.a.	276	8.4	72	26.9
90-3008	Svartá east	r	1	8.12/1	8.13	426	n.a.	491	31.0	156	256.0
90-3009	Vestari Jökulsá	r	0	8.15/1	8.16	366	n.a.	346	24.0	141	335.7
90-3010	Midhlutará	r	1	8.86/0	8.85	366	n.a.	389	29.0	124	229.2
90-3011	Eystri Jökulsá	r	0	9.80/1	9.82	241	n.a.	365	8.7	80	25.0
90-3014	Skjálfafljót	r	0	8.53/1	8.54	287	n.a.	531	10.3	115	76.9
90-3016	Sog near Ljósafoss	r	11	8.32/11	8.32	181	n.a.	364	11.9	104	56.9
90-3017	Brúara near Dynjanda	r	8	8.82/9	8.83	227	n.a.	372	7.3	90	37.6
90-3019	Tungufljót	r	7	8.17/8	8.18	275	n.a.	307	9.6	69	33.0
90-3020	Hvítá near Ferjukot	r	7	8.14/9	8.15	194	n.a.	317	7.6	87	53.1
90-3021	Nordurá near Stekkur	r	11	8.17/13	8.19	168	n.a.	324	7.0	109	72.2
90-3022	Hvítá by Kljáfoss	r	6	8.74/7	8.75	212	n.a.	297	7.4	77	37.2
90-3024	Fossá near Jadar	r	11	8.00/12	8.01	384	n.a.	391	19.9	161	117.3
90-3025	Hvítá near Fremmstaver	r	8	7.75/12	7.78	170	n.a.	253	7.6	96	44.6
90-3026	Hvítá south of Hvítárvatn	r	9	7.83/11	7.84	141	n.a.	240	4.8	94	30.5
	Hrísbrú	csp	7	8.80/22	9.07	271	0.00	535	19.4	135	79.8
	Ingólfssjall	csp	4	9.04/22	9.38	242	0.00	536	10.0	165	38.7
96-3006	Vindheimar, 2	td	59	10.32/20	9.59	1219	23.34	2024	7.4	36	0.06
96-3015	Svartá	r	10	7.78/24	7.89	348	0.70	343	30.3	145	203.3
96-3016	Reykjafoss II	td	69	9.92/25	9.20	1488	26.50	2918	17.6	50	0.20
96-3022	Ytri-Maelifellsá, 1	td	31	10.20/20	9.98	1032	17.59	1959	4.9	46	0.28
96-3028	Hvammskotslaug	ts	47	10.17/19	9.64	1311	16.73	2077	9.1	41	0.13
96-3049	Vídivellir 1	td	18	10.02/25	10.15	1047	15.59	1780	26.7	1.9	0.19
97-3046	Víkurkot II	td	14	10.12/19	10.22	607	0.00	1189	5.1	31	0.39
97-3053	Nordurá	r	5	7.61/19	7.72	167	0.00	93	12.0	56	33.7
97-3075	N-Fossárdalur	csp	2	8.89/23	9.33	217	0.00	110	16.2	62	14.1
7904	Geysir	tsp	72	9.23/16	8.41	8089	87.87	10787	670.1	19	0.08
7910	Árbaer 1	td	86	9.51/20	8.56	1393	12.95	2723	41.4	38	1.73
7919	Reykjavík 11	td	129	9.44/20	8.11	2460	4.62	2484	66.5	64	0.99
7920	Seltjarnarnes 4	td	114	8.62/20	7.44	1866	22.20	15463	255.8	3468	4.11
7929	Vadmálahver	tsp	100	9.23/16	8.12	2546	35.15	3454	69.6	49	2.88
7930	Reykjaból 1 ¹	td	152	9.28/20	7.38	4137	59.20	4371	156.3	31	1.93
7932	Hveragerdi 4 ¹	td	181	8.82/20	7.00	4507	55.50	6426	330.2	42	0.08
7933	Öxnalaekur 1	td	157	6.86/20	7.04	3860	55.50	6916	258.3	209	1.23
7934	Bakki 1	td8wó	134	8.36/20	7.17	2224	30.52	16855	501.3	1674	2.96
7942	Dalvík, 10	td	64	10.11/20	9.32	1589	7.40	2018	17.1	49	1.15
8106	Hjaltadalur 1	td	58	10.12/13	9.29	1694	46.25	2331	16.4	56	0.25
8111	Glerárgil 7	td	55	10.08/25	9.28	1381	17.57	2027	18.7	47	0.49
8113	Grytubakki 1	td	22	10.02/16	9.89	647	0.92	1031	2.8	60	0.66
8116	Hveragerdi 6 ¹	td	215	9.05/20	6.87	6780	81.40	6582	488.5	49	0.66
8117	Hveragerdi 7 ¹	td	225	8.86/20	6.79	6812	84.17	7038	498.2	38	0.53
8125	Ljósuár	csp	4	9.70/21	10.08	248	0.00	478	2.3	45	2.47
8555	Árbaer 1	td	81	9.65/22	8.77	1229	11.47	2549	28.4	40	1.69
8707	Reykjarhóll, Fljót 1	td	60	10.01/23	9.36	1956	4.20	2410	18.9	47	0.37
8709	Reykjarhóll, Bökkum 1	td	92	9.54/22	8.55	2769	6.29	3454	62.7	70	1.28
8711	Flókalundur 1	td	38	9.77/20	9.38	543	1.40	1163	12.2	67	0.99
8716	Tungumúli 1	td	28	9.24/18	9.06	438	0.79	913	5.9	76	0.53
8723	Tunga	cd	6	9.19/13	9.35	356	0.34	474	15.9	74	14.7

DIC ^c	SO ₄	H ₂ S	Cl	F	PO ₄ ^f	Al	Fe _{total}	Fe ^{II}	Ti ^g	IB % ^h	References
457	30	n.a.	100	4.4	1.11 ^k	1.01	0.50		0.0096 ^k	-3.21	Gíslason and Arnórsson (1993)
879	34	n.a.	131	7.1	0.76 ^k	0.26	0.30		0.0175 ^k	-0.20	Gíslason and Arnórsson (1993)
786	38	n.a.	136	7.5	1.41 ^k	2.39	1.84		0.0475 ^k	-3.23	Gíslason and Arnórsson (1993)
1166	24	n.a.	41	6.7	2.06 ^k	0.17	0.09		0.0427 ^k	5.30	Gíslason and Arnórsson (1993)
441	15	n.a.	48	4.7	0.47 ^k	0.91	0.03		0.0195 ^k	-3.69	Gíslason and Arnórsson (1993)
1202	42	n.a.	119	10.2	1.81 ^k	0.10	0.36		0.0208 ^k	-3.59	Gíslason and Arnórsson (1993)
1177	44	n.a.	67	11.1	2.79 ^k	0.16	0.11		0.0234 ^k	0.50	Gíslason and Arnórsson (1993)
988	24	n.a.	74	8.9	1.87 ^k	0.27	0.03		0.0174 ^k	-1.92	Gíslason and Arnórsson (1993)
370	18	n.a.	154	5.6	0.93 ^k	3.11	0.40		0.0661 ^k	15.00	Gíslason and Arnórsson (1993)
704	73	n.a.	76	7.6	1.30 ^k	0.77	0.22		0.0400 ^k	-1.34	Gíslason and Arnórsson (1993)
539	25	n.a.	184	4.1	0.49 ^k	0.56	0.08		n.d. ^k	-10.88	Gíslason and Arnórsson (1993)
436	22	n.a.	141	4.5	0.14 ^k	1.67	0.96		0.0433 ^k	-1.35	Gíslason and Arnórsson (1993)
403	15	n.a.	115	4.1	0.55 ^k	0.88	0.89		0.0301 ^k	-5.26	Gíslason and Arnórsson (1993)
417	21	n.a.	167	4.1	0.41 ^k	1.48	0.28		0.0339 ^k	-3.67	Gíslason and Arnórsson (1993)
404	25	n.a.	254	2.3	0.24 ^k	0.08	0.16		0.0101 ^k	-1.95	Gíslason and Arnórsson (1993)
366	18	n.a.	127	4.5	0.70 ^k	2.29	0.08		0.02684 ^k	-2.97	Gíslason and Arnórsson (1993)
752	23	n.a.	217	6.5	0.27 ^k	0.14	0.40		0.0166 ^k	-3.89	Gíslason and Arnórsson (1993)
450	37	n.a.	71	4.7	0.32 ^k	0.62	0.08		0.0022 ^k	-6.68	Gíslason and Arnórsson (1993)
402	19	n.a.	74	3.3	0.15 ^k	0.56	0.03		0.0159 ^k	-1.93	Gíslason and Arnórsson (1993)
514	2.1	n.a.	386	2.8	n.a.	1.59	0.17 ⁱ	0.16 ⁱ	n.a.	-4.86	Data file, University of Iceland
516	1.4	n.a.	373	3.7	n.a.	1.11	0.05 ⁱ	0.04 ⁱ	n.a.	-6.68	Data file, University of Iceland
559	119	1.1	228	36.2	0.04	6.83	0.11		0.0043	-13.22	Data file, University of Iceland
1003	23	< 0.2	120	7.4	1.53	0.85	1.21		0.0418	-5.09	Data file, University of Iceland
544	350	2.6	814	89.2	0.09	5.10	0.21		0.0032	-5.72	Data file, University of Iceland
535	116	0.6	278	36.8	0.08	1.40	0.23		0.0197	-1.96	Data file, University of Iceland
490	146	1.0	296	28.5	0.06	2.86	0.74		0.0100	-2.68	Data file, University of Iceland
686	67	< 0.2	152	38.0	6.97	3.22	0.49		0.1617	-9.00	Data file, University of Iceland
506	24	0.7	76	11.9	0.16	1.23	0.32		0.0167	-1.49	Data file, University of Iceland
197	10	< 0.2	74	1.6	0.40	0.26	0.19		0.0110	0.09	Data file, University of Iceland
213	10	< 0.2	38	2.1	0.79	0.82	n.d.		0.0028	-10.31	Data file, University of Iceland
3108	1218	25	3735	455.8	n.a.	0.00	0.54 ⁱ	0.39 ⁱ	n.a.	2.29	Data file, University of Iceland
832	294	8.8	745	26.8	n.a.	7.04	0.08		n.a.	4.79	Arnórsson et al. (1983)
398	202	12	1027	43.2	n.a.	6.67	0.32		n.a.	6.16	Arnórsson et al. (1983)
148	2132	7.9	18921	45.8	n.a.	n.d.	0.93		n.a.	-3.80	Arnórsson et al. (1983)
1009	611	39	705	79.0	n.a.	10.01	0.47 ⁱ	0.32 ⁱ	n.a.	3.66	Data file, University of Iceland
2181	34	139	1154	96.3	n.a.	15.31	0.13		n.a.	-6.85	Arnórsson et al. (1983)
3497	21	681	2976	92.3	n.a.	5.00	0.14		n.a.	5.21	Arnórsson et al. (1983)
2722	606	90	4293	68.4	n.a.	7.41	0.16		n.a.	-1.06	Arnórsson et al. (1983)
152	1275	16	18574	29.0	n.a.	2.59	0.38		n.a.	-3.36	Arnórsson et al. (1983)
318	147	1.8	288	27.4	n.a.	4.45	0.35		n.a.	1.83	Arnórsson et al. (1983)
325	206	2.1	668	63.2	n.a.	1.41	0.75		n.a.	-3.31	Data file, University of Iceland
386	322	1.8	305	26.3	n.a.	2.04	0.27		n.a.	-2.65	Data file, University of Iceland
359	115	0.9	259	11.6	n.a.	2.37	0.57		n.a.	-15.05	Data file, University of Iceland
5018	17	843	4450	46.6	n.a.	33.13	0.61		n.a.	-2.10	Arnórsson and Gunnlaugsson (1985)
6821	16	1140	4809	29.8	n.a.	34.90	0.13		n.a.	-0.56	Arnórsson and Gunnlaugsson (1985)
223	0.6	n.a.	155	2.6	n.a.	0.00	0.07 ⁱ	0.06 ⁱ	n.a.	0.59	Data file, University of Iceland
752	277	56	560	21.6	n.a.	8.38	0.82 ⁱ	0.70 ⁱ	n.a.	3.68	Data file, University of Iceland
359	221	0.4	275	25.8	n.a.	2.74	0.30		n.a.	3.22	Data file, University of Iceland
504	573	30.2	970	37.4	n.a.	4.93	2.78		n.a.	1.03	Data file, University of Iceland
343	79	0.3	379	4.2	n.a.	10.63	0.61		n.a.	8.81	Data file, University of Iceland
589	34	< 0.2	359	2.1	n.a.	2.56	2.15		n.a.	-4.51	Data file, University of Iceland
114	40	< 0.2	318	2.1	n.a.	2.66	2.75		n.a.	17.16	Data file, University of Iceland

(continued on next page)

Tabel 1 (continued)

Sample no.	Sample location	Type ^a	T (°C) ^b	pH _T /°C ^c	pH _T ^d	Si	B	Na	K	Ca	Mg
8725	Tálknafjörður 1	td	14	9.14/16	9.18	673	1.38	957	15.1	19	4.55
8742	Selfoss 13	td	75	8.46/12	7.63	1143	11.84	6899	93.6	777	3.25
8754	Laugaland 5	td	96	9.75/29	8.78	1771	23.22	4241	47.6	69	0.99
8773	Einholt 1	td	20	9.69/19	8.94	722	1.14	1970	99.2	54	26.5
8812	Kópsvatn 1	td	99	8.84/22	7.90	2878	22.75	3968	78.1	100	1.87
8813	Reykjadalur 1	td	100	9.24/22	8.24	3141	29.32	4986	85.5	87	1.34
8814	Midfell 1	td	62	9.27/23	8.66	1671	12.95	2911	26.7	89	0.31
8815	Sydra-Langholt 1	td	66	9.63/23	8.94	1336	16.65	2745	23.1	79	0.20
8817	Hjallanes 1	td	53	10.56/25	9.95	1484	14.15	3053	12.9	51	0.47
8820	Blesastadir	td	76	9.54/24	8.70	1244	29.60	15798	107.3	939	0.74
8822	Hlemmiskeid 2	td	56	9.70/24	9.15	1288	12.02	5647	67.7	198	1.65
8823	Brautarholt 1	td	70	9.70/24	8.92	1292	16.46	7200	66.7	385	0.33
8825	Reykir 2	td	70	9.62/23	8.84	1322	14.06	4660	43.8	205	0.35
8833	Eyvík 1	td	75	8.01/21	7.62	2942	12.58	6892	135.7	113	3.20
8835	Thóróddstadir 1	td	118	8.52/21	7.45	2127	25.44	12139	252.3	947	1.88
8839	Audsholt 1	td	83	9.54/20	8.57	1815	17.67	3245	39.6	92	0.15
8910	Gygjarhólskot 2	td	23	9.11/20	9.06	672	1.42	1462	47.3	96	10.9
8920	Hagaós 1	td	90	9.50/22	8.53	1877	16.00	3484	58.3	86	2.84
8941	Reykir, Fnjóskad. 2	td	88	10.07/16	8.93	2007	6.13	2140	22.5	44	0.33
8944	Reykhús 1	td	76	9.88/18	8.94	1694	21.83	2872	27.1	101	0.63
8945	Hrafnagil 10	td	86	9.92/18	8.82	1468	13.32	2183	29.7	98	0.47
8951	Otradalur 1	td	12	10.12/22	10.35	479	1.40	1319	4.2	34	2.84
8954	Sveinseyri B	cd	8	9.05/22	9.35	370	0.35	446	17.0	38	13.8
8956	Gileyri 4	td	14	9.50/22	9.67	562	0.89	798	19.4	22	4.98
8961	Thverá C	td	21	9.91/22	9.93	296	1.02	791	11.4	89	1.50
9049	Krókur 1	td	11	9.55/22	9.74	364	1.78	1836	5.9	113	5.14
8843	Krafla 20 ¹	td	283 ^m	7.45/15	6.29	11520	111	6573	810.8	11	0.37
8844	Krafla 14 ¹	td	271 ^m	9.23/16	6.55	11982	441	6410	668.6	23	3.33
8845	Krafla 12 ¹	td	281 ^m	9.28/16	6.60	12431	285	6864	832.5	23	2.51
8846	Krafla 13 ¹	td	261 ^m	9.16/17	6.62	10236	169	9173	750.2	78	2.14
8848	Krafla 21 ¹	td	258 ^m	6.37/17	6.44	8625	63.8	5502	475.0	27	1.81
8850	Krafla 15 ¹	td	280 ^m	7.10/17	6.08	9370	308	4979	496.2	32	4.03
8851	Námafjall 11 ¹	td	238 ⁿ	9.03/24	6.57	6855	290	4241	316.4	15	0.08
8852	Námafjall 12 ¹	td	265	9.35/25	6.60	8948	459	5533	495.7	11	0.29
8853	Námafjall 4 ¹	td	259	9.77/23	6.97	8074	81	6264	471.9	85	0.53
94-5084	Nesjavellir NJ-11 ¹	td	305	8.88/21	7.22	10634	0.00	4169	505.1	5.0	0.62
94-5085	Nesjavellir NJ-16 ¹ 8wó	td	285	8.87/21	7.80	10207	0.00	4588	535.6	17	0.16
94-5087	Nesjavellir NG-6 ¹	td	300	8.14/21	7.24	10131	0.00	4316	545.6	3.0	0.08
94-5088	Nesjavellir NJ-13 ¹	td	300	8.42/21	7.47	11248	0.00	4213	566.0	1.7	0.08

Various studies have aimed at identifying the stability of primary minerals of basalt and the loss of chemical constituents under weathering conditions by comparing the chemistry and mineralogy of fresh and weathered basalt (Craig and Loughnan, 1964; Colman, 1982; Eggelton et al., 1987; Banfield et al., 1991; Nesbitt and Wilson, 1992). Studies have also been carried out on the stability of primary basaltic minerals under hydrothermal conditions from a mineralogical standpoint (e.g. Steinhórrsson and Svein-

björnsdóttir, 1981). Further, Gíslason and Arnórsson (1990, 1993) assessed the stability of olivine, orthopyroxene, and plagioclase of various compositions in selected natural waters in Iceland.

The aim of this study is to assess the saturation state of olivine, orthopyroxene, clinopyroxene, plagioclase, Fe–Ti oxides and apatite of variable composition with respect to natural waters in basaltic terrain. The solubility of these minerals, both end-members and solid solutions of fixed composition,

DIC ^c	SO ₄	H ₂ S	Cl	F	PO ₄ ^f	Al	Fe _{total}	Fe ^{II}	Ti ^g	IB % ^h	References
291	46	< 0.2	397	7.4	n.a.	1.81	2.55		n.a.	14.86	Data file, University of Iceland
477	615	0.6	6634	12.6	n.a.	4.26	0.16 ⁱ	0.14 ⁱ	n.a.	2.08	Data file, University of Iceland
457	702	1.2	1376	48.4	n.a.	9.15	0.91 ⁱ	0.38 ⁱ	n.a.	0.91	Data file, University of Iceland
1622	45	n.d.	283	32.1	n.a.	7.12	3.92		n.a.	3.17	Data file, University of Iceland
1257	654	22	1052	85.8	n.a.	6.12	1.97		n.a.	6.00	Data file, University of Iceland
1091	842	50	700	65.8	n.a.	8.21	1.61		n.a.	20.75	Data file, University of Iceland
702	502	22	609	53.7	n.a.	1.22	0.18 ⁱ	0.13 ⁱ	n.a.	−11.02	Data file, University of Iceland
545	492	18	663	62.1	n.a.	2.77	0.10		n.a.	1.07	Data file, University of Iceland
386	294	< 0.2	496	72.1	n.a.	7.73	0.29 ⁱ	0.25 ⁱ	n.a.	−11.93	Data file, University of Iceland
136	1260	0.9	14 227	66.8	n.a.	5.72	0.25 ⁱ	0.02 ⁱ	n.a.	1.68	Data file, University of Iceland
429	586	< 0.2	3486	115.3	n.a.	2.11	1.13 ⁱ	0.47 ⁱ	n.a.	3.59	Data file, University of Iceland
216	737	1.2	4950	139.0	n.a.	3.28	0.24		n.a.	7.72	Data file, University of Iceland
282	592	7.3	4386	150.5	n.a.	2.85	0.23		n.a.	−25.49	Data file, University of Iceland
2843	680	4.1	3137	99.0	n.a.	5.44	1.36		n.a.	−2.44	Data file, University of Iceland
364	950	4.1	11 632	35.3	n.a.	7.10	1.27		n.a.	1.78	Data file, University of Iceland
325	529	13	948	91.6	n.a.	5.38	0.25		n.a.	13.83	Data file, University of Iceland
1029	66	< 0.2	293	30.5	n.a.	2.89	0.13 ⁱ	0.02 ⁱ	n.a.	5.13	Data file, University of Iceland
618	426	122	1357	87.9	n.a.	7.71	4.82		n.a.	0.90	Data file, University of Iceland
464	187	4.1	148	21.1	n.a.	9.04	0.27		n.a.	−1.61	Data file, University of Iceland
407	650	1.8	313	29.0	n.a.	4.30	0.17		n.a.	4.54	Data file, University of Iceland
293	494	1.5	195	28.4	n.a.	6.72	0.17		n.a.	3.63	Data file, University of Iceland
325	42	< 0.2	432	9.9	n.a.	2.96	0.55		n.a.	0.45	Data file, University of Iceland
220	25	< 0.2	239	2.6	n.a.	1.28	0.60		n.a.	−1.05	Data file, University of Iceland
277	30	< 0.2	327	5.8	n.a.	1.56	0.44		n.a.	−1.01	Data file, University of Iceland
279	35	< 0.2	291	2.1	n.a.	3.51	0.18		n.a.	4.77	Data file, University of Iceland
954	75	< 0.2	372	17.8	n.a.	2.15	0.56		n.a.	15.40	Data file, University of Iceland
195 272	8	9658	2882	48.5	0.04 ^g	34.59	0.56		0.1340	−5.47	Data file, University of Iceland
77 487	8	6550	1864	194.4	< 0.03 ^g	27.13	7.38		0.1290	1.69	Data file, University of Iceland
114 997	28	8446	2176	88.6	< 0.03 ^g	25.11	3.39		0.2530	−19.48	Data file, University of Iceland
55 152	118	6540	823	47.3	< 0.03 ^g	47.95	1.46		0.1650	−11.76	Data file, University of Iceland
32349	24	5011	2443	38.0	< 0.03 ^g	49.05	10.13		0.2470	3.12	Data file, University of Iceland
228 753	34	12 102	692	43.5	< 0.03 ^g	25.15	4.20		0.5850	0.07	Data file, University of Iceland
17 863	20	8784	706	31.8	0.03 ^g	38.66	1.92		0.1980	−16.69	Data file, University of Iceland
47 926	5	17 939	1871	27.5	0.05 ^g	29.51	1.82		0.1730	−18.54	Data file, University of Iceland
22 099	16	8067	868	31.4	< 0.03 ^g	22.23	1.24		0.0836	−7.98	Data file, University of Iceland
53 879	4.6	24 109	1646	41.3	n.a.	75.88	0.86		n.a.	−8.37	Arnórsson and Geirsson (1995)
32 097	10	5805	1311	49.4	n.a.	64.86	0.21		n.a.	−13.17	Arnórsson and Geirsson (1995)
56 583	1.4	18 180	2482	33.1	n.a.	52.70	0.19		n.a.	5.95	Arnórsson and Geirsson (1995)
39 617	0.9	10 107	2331	40.0	n.a.	58.54	0.25		n.a.	4.91	Arnórsson and Geirsson (1995)

has recently been reviewed and assessed (Arnórsson and Stefánsson, 1999; Stefánsson, 2000) indicating somewhat different solubility than previously reported. Of primary importance are much higher solubilities below 100°C, due to new thermodynamic data on aqueous H₄SiO₄^o, based on quartz and amorphous silica solubilities (Rimstidt, 1997; Gunnarsson and Arnórsson, 2000). Analyses of 141 natural water samples have been selected for the calculation of saturation indices for the primary basaltic minerals.

They range in temperature from 0°C to 300°C and have in situ pH values from 5 to over 10.

2. Database for waters

For the present study, we selected 141 analyses of natural waters from Iceland from a database of over 700 samples. They include samples of cold water from springs and drillholes, peat water sampled at

the surface, soil waters, which were sucked out of the soil, at approximately 50-cm depth, river water, and samples of thermal springs and geothermal wells. The chemical composition, type of water, and the source of the data are given in Table 1.

Of the samples, 27 were specially collected and analyzed for the present study, including river-, peat-, and soil waters. The water was filtered on site through 0.2- μm millipore membrane (cellulose acetate) with a polypropylene filter holder into low-density polyethylene bottles. Before sampling, 0.5–1 l of water was pumped through the filtration unit. Samples for the determination of major cations were acidified with Suprapur[®] concentrated nitric acid, 0.5–100 ml. Two amber glass bottles with specially designed taps that prevented entrapment of air-bubble under the tap were used to collect samples for the determination of pH and alkalinity. To prevent any organic development, samples for the determination of PO_4 were refrigerated (-18°C) within hours after collection and kept frozen until analyzed. Samples for the determination of Cl, F, B and K were not treated.

Eight soil water samples were collected for the present study. These waters were sucked from a soil profile at approximately 50-cm depth with Prenat leekicups at constant underpressure of 600 mbars for 24–48 h. After collection, the waters were filtered and preserved in the manner described above.

Alkalinity and pH were determined within 2 days after sampling using a Metrohm titrator and an Orion pH Triod[™] electrode, respectively. For the pH measurements, the pH electrode was placed directly into

the glass amber bottle, which had a top of almost equal diameter as the electrode. This was done to prevent any diffusion of CO_2 from the bottle during measurement that could cause a change in the pH. Chlorine and F concentrations were determined by ion-sensitive electrodes. Magnesium Ca, Na, Si and SO_4 and Al and Fe in most cases were analyzed on a Thermo Jarrel Ash ICP–AES and K on a Wescan HPLC. The concentrations of PO_4 were determined colorimetrically with an Alkem autoanalyzer.

Most of the Ti analyses given in Table 1 were measured on high resolution ICP–MS at Svensk Grundamnesanalys, Sweden, and are considered to be precise within $\pm 10\%$. Some of the Ti analyses of river waters were measured on ICP–AES and considerable imprecision is considered to be associated with these analyses. However, these errors are not thought to significantly change the results of the saturation state of waters relative to Ti-bearing minerals discussed in this paper.

Eighteen cold and thermal water samples were collected for the determination of total and divalent iron, the concentrations of which were measured spectrophotometrically after complexing with TPTZ with and without addition of ascorbic acid, respectively (Dougan and Wilson, 1973). These samples were filtered on site through 0.1- μm millipore membranes (cellulose nitrate) with a polysulfone filter holder into two opaque low-density polyethylene bottles. One sample was acidified with 1 ml of 6N HCl in a 100-ml sample for the determination of total Fe. Reagents for the determination of total Fe^{II}

Notes to Table 1:

^a r = river water, p = surface peat water, csp = cold spring water, cd = cold groundwater, tsp = thermal springs, td = thermal water from drillhole.

^b If not otherwise indicated, the reported temperature is the measured one of the discharge.

^c Measured pH at temperature $^\circ\text{C}$. Note that this is not in situ pH as calculated by the WATCH program at the selected reference temperature.

^d In situ pH at the selected reference temperature as calculated by the WATCH program.

^e Total dissolved inorganic carbon.

^f Measured spectrophotometrically.

^g Measured by ICP–MS.

^h Ionic balance as calculated by the WATCH program.

ⁱ This study.

^j Soil temperature.

^k Measured by ICP–AES.

^l The reported concentrations are those of the aquifer water as calculated by the WATCH program.

^m Average geothermometry (quartz, Na–K, Na–K–Ca) temperature (Gudmundsson and Arnórsson, 2000).

ⁿ Temperature calculated from the quartz geothermometer given by Fournier and Potter (1982).

were added immediately after collection to the other sample. All analyses were carried out within 10 h of sampling.

Most of the PO_4 data given in Table 1 are based on spectrophotometric analyses as discussed above. However, for some river waters, the PO_4 concentrations were determined by ICP–AES, which is considered to be less precise than the spectrophotometric measurements. For high-temperature thermal waters, the PO_4 concentrations were measured on high resolution ICP–MS at Svensk Grundamnesanalys, Sweden.

3. Aqueous speciation

3.1. Speciation calculations

The WATCH program (Arnórsson et al., 1982), version 2.1A (Bjarnason, 1994), was used to calculate the aqueous speciation for the waters selected for the present study. The thermodynamic database is that given in Table 5 of Arnórsson et al. (1982), except for Al-hydroxy complex dissociations and gas solubility constants which are from Arnórsson and Andréðdóttir (1999) and Arnórsson et al. (2000), respectively. For the present study, the dissociation constants for Fe^{III} -hydroxy complexes were revised according to the data given by Diakonov et al. (1999) and Diakonov and Tagirov (2000). Also, a supplement was added to the program to include phosphor-oxy anions (Shock and Helgeson, 1988; Shock et al., 1989), iron-, magnesium-, and calcium phosphate complexes (Kharaka and Barnes, 1973) and Ti-hydroxy and Ti-phosphate species (Ziemniak et al., 1993). In the WATCH program, Al hydroxy, fluoride, and sulphate species are considered but not Al–Na and Al–K ion pairs. These species may constitute a significant fraction of the dissolved aluminium in waters of both high temperature and relative high salinity (Pokrovskii and Helgeson, 1995, 1997; Diakonov et al., 1996). Therefore, these complexes have been incorporated in the speciation calculations for the present study using data on their stability as given by Arnórsson and Andréðdóttir (1999) which are based on the results of Pokrovskii and Helgeson (1995, 1997) and Diakonov et al. (1996).

In all cases in the present study, the pH at the reference temperature, referred as the *in situ* pH, was calculated from the measured pH at around room temperature and chemical analyses of the fluid samples. These calculations were carried out with the aid of the WATCH speciation program. In the 2.1A version of the program, the pH is calculated while taking into account all species of major components which H^+ can combine, whereas only carbonate, sulphide, silica, borate and sulphate species were considered in the original 1982 version.

The primary advantage of the WATCH program, compared to most other aqueous speciation programs, has to do with speciation calculations of geothermal waters. The chemical composition of samples of nonthermal and nonboiled thermal water samples represents the composition of the waters in nature. However, water samples collected from the wellhead of wet-steam wells are not representative of the parent aquifer water where steam formation due to boiling and associated degassing have modified its chemical composition. The WATCH program calculates the aquifer water composition and aqueous speciation of the aquifer water from the data on water and steam samples collected at the wellhead. For these calculations, adiabatic boiling is assumed. However, such conditions are not always met, at least when extensive boiling starts in the producing aquifers of wells, resulting in excess discharge enthalpy (Arnórsson et al., 1990). When this is the case, the model used to calculate aquifer fluid compositions, aqueous speciation and mineral saturation indices assumes that the excess enthalpy was due to the phase segregation in the aquifer (Arnórsson et al., 1990).

The WATCH program calculates the activities of aqueous Fe^{II} and Fe^{III} species from the analysis of total Fe using the calculated redox potentials between aqueous H_2S° and SO_4^{2-} . When sulphide is not detected as is the case for almost all cold waters and many low-temperature geothermal waters, the WATCH program assumes total aqueous Fe to be equal to Fe^{II} , which has been considered to be a good approximation (Gunnlaugsson and Arnórsson, 1982; Gíslason and Arnórsson, 1990, 1993). Chemical equilibrium between redox couples in nonthermal waters is rarely attained (e.g. Morris and Stumm, 1967; Lindberg and Runneles, 1984; Steinmann and

Shotyk, 1997) and the lack of agreement between the redox potentials calculated from the activity ratios of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{SO}_4^{2-}/\text{H}_2\text{S}^\circ$ is well documented for such waters. The calculated difference in redox potential ranges from 6 to 8 pe units for cold groundwater (Lindberg and Runneles, 1984) and can be as large as 12 pe units for peat bog waters (Steinmann and Shotyk, 1997). The $\text{SO}_4^{2-}/\text{H}_2\text{S}^\circ$ redox equilibrium and probably most redox equilibria are probably not closely approached in geothermal water unless possibly at temperatures in excess of 200°C. In view of this, it is considered that $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ distribution as calculated by the WATCH program is not reliable, at least at low temperatures.

Cold spring water samples and low-temperature thermal water samples selected for the present study generally have in situ pH between 8 and 10. Under these conditions, Fe^{II} and Fe^{III} speciation distribution is extremely sensitive to small changes in the Eh values selected for the speciation calculations. The only way to obtain reliable values for the activities of the Fe^{II} and Fe^{III} species in these waters is to measure separately total Fe concentration and the Fe^{II} and/or Fe^{III} concentrations. However, Fe^{II} , Fe^{III} , and Fe_{total} concentrations are usually not analyzed separately during routine analyses and, as a result, there is a general lack of information of distribution of aqueous iron species in natural waters in Iceland.

For the present study, the concentrations of total iron (Fe_{total}) and divalent iron (Fe^{II}) were measured in 8 cold water samples with in situ pH ranging from 6.5 to over 10 as well as in 10 geothermal water samples ranging from 20°C to 100°C. These measurements made it possible to predict, with reasonable confidence, the redox potentials based on $\text{Fe}^{3+}/\text{Fe}^{2+}$ activity ratios of these water samples. This was done by first calculating separately the speciation of Fe^{II} and Fe^{III} in the 18 samples. Subsequently, the $\text{Eh}_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ was calculated using the expression:

$$\text{Eh}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = \text{Eh}^\circ + \log \frac{RT}{F} \left(\frac{m_{\text{Fe}^{3+}} \gamma_{\text{Fe}^{3+}}}{m_{\text{Fe}^{2+}} \gamma_{\text{Fe}^{2+}}} \right) \quad (1)$$

where Eh° is the standard redox potential for the half cell reaction $\text{Fe}^{2+} = \text{Fe}^{3+} - e^-$ (Arnórsson et al., 1982), R , T , and F are the gas constant, temperature in K, and the Faraday constant, respectively, and m_i

and γ_i are the concentration and activity coefficients of the i -th aqueous species. The redox potentials calculated with the aid of Eq. (1) correlate well with the pH for cold waters and with temperature of low-temperature geothermal waters. The best fit, using a linear least square method, through the data for the cold water samples is:

$$\text{Eh}_{\text{Fe}^{3+}/\text{Fe}^{2+}} \equiv -188\text{pH} + 1635 \quad (2)$$

where pH is the in situ pH. For thermal waters, the relationship is given by:

$$\text{Eh}_{\text{Fe}^{3+}/\text{Fe}^{2+}} \equiv -3.8T + 996 \quad (3)$$

where T is in K. With one exception, the deviation of the measured redox state from the regressed line is 33 and 75 mV for cold- and thermal waters, respectively (Fig. 1).

The correlations given by Eqs. (2) and (3) permit empirical estimation of aqueous $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ ratios

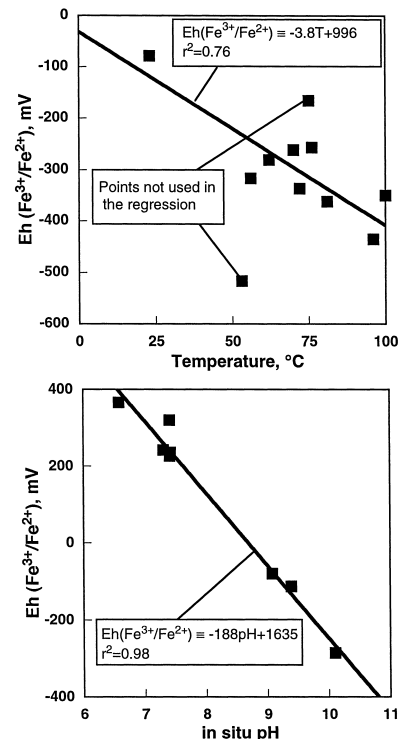


Fig. 1. Correlation of pH and temperature with redox potential calculated from $\text{Fe}^{3+}/\text{Fe}^{2+}$ activity ratios as based on measured divalent- and total iron concentrations in cold- and low-temperature geothermal waters, respectively.

where data on total Fe are only available. These correlations are only considered to be valid for cold surface waters and low temperature thermal waters of the basaltic terrain of Iceland.

Eqs. (2) and (3) were used to calculate the activity $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios for water samples where analysis of total Fe were only available, except for soil waters, where all Fe was assumed to be divalent (Fe^{II}). This, of course, incorporates uncertainty for the estimated saturation state of Fe-bearing minerals. However, as seen in Figs. 3–16, the distribution of data points based on measured Fe^{II} and total Fe, on one hand, and that calculated using Eqs. (2) and (3) and analyzed total Fe, on the other, show complete overlap suggesting that the calculation of aqueous iron speciation using the correlations given by Eqs. (2) and (3) is reasonable.

With increasing temperature, redox potentials calculated from $\text{Fe}^{3+}/\text{Fe}^{2+}$ approach those calculated from $\text{SO}_4^{2-}/\text{H}_2\text{S}^{\circ}$ and for waters with temperature greater than 100°C , these redox potentials are similar. Therefore, the distribution of Fe^{II} and Fe^{III} of the thermal waters with temperature greater than 100°C has been predicted from the $\text{SO}_4^{2-}/\text{H}_2\text{S}^{\circ}$ redox state as calculated by the WATCH speciation program.

The reaction quotients (activity products) for olivine, pyroxene, plagioclase, apatite and Fe–Ti oxides of various compositions, according to dissolution reactions given in Table 1 of Stefánsson (2000) have been retrieved from the speciation calculations. These reaction quotients are compared below with the corresponding mineral solubilities as given by Stefánsson (2000).

3.2. Distribution of aqueous species in natural waters in Iceland

The relationship between temperature and the in situ pH of the waters used for the present study is shown in Fig. 2. In surface waters, the pH reaches a steady-state value of about 6.5–8 when the rate of consumption of protons by rock dissolution equals the rate of proton generation by precipitation of OH-bearing minerals and transfer of CO_2 to the water, either from the atmosphere or from the decaying organic matter in the soil (Gíslason and Eugster, 1987b; Arnórsson et al., 1995). In peat waters, the pH may reach values below 5 due to organic acids

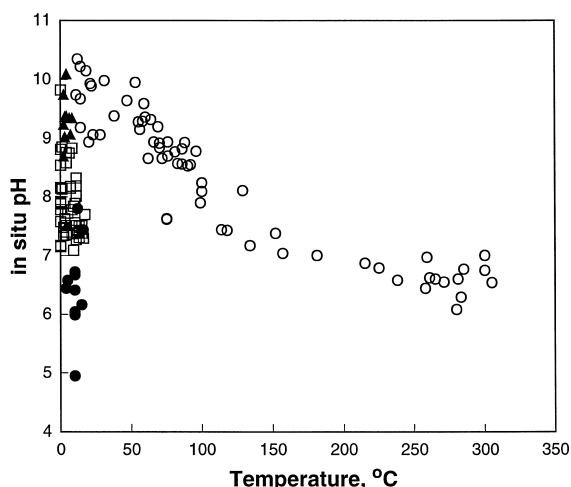


Fig. 2. Temperature vs. in situ pH in natural waters in Iceland. Dots represent surface peat water (p) and soil water (so), squares represent river water (r), triangles represent cold spring (csp) and ground water (cd), and circles represent thermal water (tsp, td). The pH, referred to as the in situ pH, is that calculated at the respective temperature with the aid of the WATCH program (Arnórsson et al., 1982) version 2.1A (Bjarnason, 1994).

and CO_2 from decaying organic matter. In cold and slightly thermal groundwaters, the pH reaches a steady state value of around 10 when proton production by dissociation of aqueous silica and precipitation of OH minerals equals its consumption by rock dissolution. In thermal waters at temperatures in excess of 40°C , the pH is controlled by a close approach to equilibrium with silicates (Arnórsson et al., 1995). In equilibrated geothermal waters, the pH is fixed at any particular salinity by temperature alone (Arnórsson et al., 1983). Since most Icelandic waters display limited variation in salinity, their pH displays limited variation at any particular temperature.

The dominant aqueous Si, Ca, Mg, Na and K species in almost all the water samples of the present study are $\text{H}_4\text{SiO}_4^{\circ}$, Ca^{2+} , Mg^{2+} , Na^+ and K^+ , usually accounting for more than 90% of the total measured concentrations of these elements. This is in good agreement with previous results of Arnórsson et al. (1983). It is only in the high pH (> 9.5) low-temperature geothermal waters that a significant proportion of $\text{H}_4\text{SiO}_4^{\circ}$ dissociates to form H_3SiO_4^- .

At all temperatures, the Al-hydroxy complexes are found to be the dominant aqueous Al spe-

cies. Aqueous Al-fluoride, Al-sulphate species, NaAl(OH)_4° and KAl(OH)_4° were never observed to be of importance. The dominant aqueous Al species in thermal waters was found to be Al(OH)_4^- , generally accounting for more than 90% of the total dissolved Al. For cold surface waters, Al(OH)_3° becomes important and in low pH peat waters, the Al(OH)_2^+ was found to dominate.

The distribution of aqueous Fe species is affected by the pH and the redox state of the waters. The calculated Eh value from the activity ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in peat and surface waters are generally in the range 0–200 mV. For such waters, Fe^{II} is the predominant form of Fe, ranging from 5% to 100% with an average value of 76%. Aqueous Fe^{2+} is the dominant form of Fe^{II} in these waters accounting on average for 73% of total Fe. The dominant aqueous Fe^{III} species is Fe(OH)_3° accounting for up to 58% of total Fe with an average value of 10%. With increasing temperature, the Fe^{III} aqueous species become more important accounting on average for 60% of the total Fe in low-temperature waters (< 150°C). In such waters, the Fe^{2+} and Fe(OH)_4^- are the most important Fe^{II} and Fe^{III} aqueous species, respectively. For high-temperature geothermal waters (> 150°C) almost all Fe is presented as Fe^{III} accounting on average for 95% of total Fe. The dominant Fe^{III} species are Fe(OH)_4^- and Fe(OH)_3° , the importance of the latter increasing with increasing temperature. For the highest temperatures the Fe(OH)_3° dominates. The dominant aqueous Fe^{II} species in the high-temperature geothermal waters are FeOH^+ , but Fe^{2+} and Fe(OH)_2° are also important. Thus, it is clear that no single Fe species is dominant over the whole range of pH and temperature for the samples considered in the present study. Therefore, some uncertainties are related to the calculation of saturation indices for Fe^{II} -bearing minerals at high temperatures where aqueous Fe^{III} -hydroxy species predominate and for Fe^{III} -bearing minerals at low temperatures where Fe^{2+} is the dominant Fe aqueous species. Other Fe species considered in the speciation calculations (Fe-chloride and sulphate complexes) were never found to be significant.

At all temperatures, the dominant aqueous Ti species is Ti(OH)_4° . In cold and low-temperature geothermal water, more than 98% of total Ti is presented as Ti(OH)_4° . In high-temperature geother-

mal waters, Ti(OH)_5^- becomes important accounting for 15% to 44% of total dissolved aqueous Ti. Titanium–P complexes were not observed to be of importance in any of the waters considered.

The relative abundance of aqueous P species is very variable, depending on pH, temperature and aqueous Ca and Mg concentrations. In cold waters, phosphor-oxy anions dominates with H_2PO_4^- and $\text{H}_2\text{PO}_4^{2-}$ accounting on average for 32% and 60% of the total dissolved P, respectively. With increasing temperature, Mg- and Ca–P complexes become the dominant aqueous P species. In low-temperature geothermal waters (< 150°C), aqueous P is mostly presented as CaPO_4^- and MgPO_4^- accounting on average for 50% and 36% of total P. In the high-temperature geothermal waters (> 150°C), $\text{CaH}_2\text{PO}_4^+$ and $\text{MgH}_2\text{PO}_4^+$ dominate accounting generally for over 85% of the total P. Phosphor-oxy anions were not observed to be of importance in geothermal waters and P–Ti complexes did not account for a significant proportion of the aqueous P concentrations.

4. Mineral saturation

4.1. The temperature dependence of mineral saturation state

4.1.1. Olivine

Cold waters are undersaturated with respect to olivine regardless of composition except for few spring waters with in situ pH of around 10 where supersaturation is observed for pure fayalite (Fig. 3). The waters approach saturation as the temperature increases. For pure forsterite and olivine phenocrysts ($\text{Fo}_{80}\text{Fa}_{20}$) almost constant undersaturation of around 5 log units is observed between 50°C and 250°C. Above 250°C, the data points are scattered around the solubility curve. The stability of olivine is clearly very sensitive to its composition, in general making the Mg-rich olivine less stable at temperatures up to 250°C compared to Fe-rich olivine, whereas Fe-rich olivine becomes progressively less stable with increasing temperature.

4.1.2. Pyroxene

Similar trends are indicated for the saturation state of pyroxene in natural waters as for olivine (Figs. 4

and 5). Cold waters are undersaturated with respect to all types of pyroxenes except cold spring waters having in situ pH greater than 9.5 where supersaturation is observed for relatively Fe-rich ortho- and clinopyroxene. All types of pyroxenes approach satu-

ration with increasing temperature. For pure enstatite, constant undersaturation is observed in the range 50–250°C but above 250°C, the waters are close to saturation. As for fayalite, saturation or slight supersaturation is observed for pure ferrosilite between 50°C and 150°C. In the range 150–250°C, the waters are on average close to saturation but above 250°C, they are undersaturated. For groundmass orthopyroxene (En₃₈Fs₆₂), the trend is similar to that for ferrosilite except that the degree of undersaturation above 250°C is less than that for ferrosilite. For diopside, hedenbergite, and augite, supersaturation is indicated between 50°C and 150°C, suggesting that these minerals are stable in these temperature ranges. At higher temperatures, the water samples are saturated or undersaturated with respect to clinopyroxene. Therefore, the stability of clinopyroxene is less sensitive to its composition than is the case for orthopyroxene.

4.1.3. Plagioclase

Cold waters are undersaturated with respect to all types of plagioclases except high pH waters, which are close to saturation with respect to pure high-albite (Fig. 6). The degree of undersaturation increases with increasing Ca content of the plagioclase indicating that Na-rich plagioclases are more stable than Ca-rich ones. However, the greatest degree of undersaturation is observed for plagioclase of phenocryst composition (An₇₀Ab₃₀) but not pure anorthite. This is related to the solid solution model used to estimate the thermodynamic properties of plagioclases and hence their solubilities, which incorporates the transformation of highly disordered high-albite with respect to Si and Al to ordered anorthite, resulting in highest solubility of plagioclases with composition around An₇₀Ab₃₀ (Arnórsson and Stefánsson, 1999). Geothermal waters are close to saturation with high-

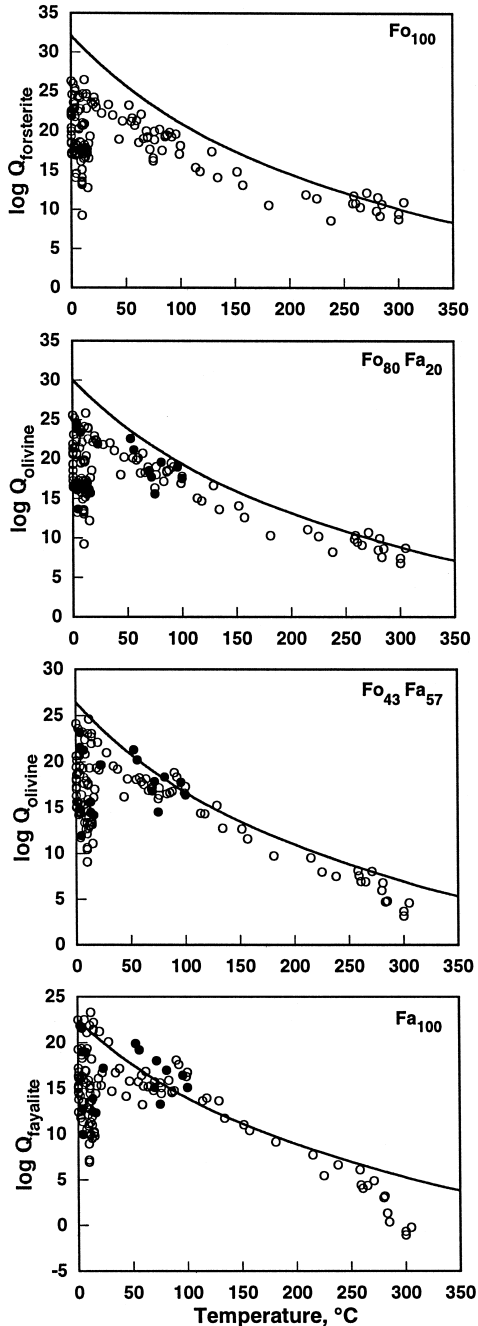


Fig. 3. The temperature dependence of the saturation state of olivine in cold- and thermal waters in Iceland. The olivine composition is shown in the upper right-hand corner and represents pure forsterite (Fo₁₀₀), pure fayalite (Fa₁₀₀), average olivine phenocryst (Fo₈₀Fa₂₀) and groundmass olivine (Fo₄₃Fa₅₇). The filled circles are samples where divalent and total iron concentrations were measured. Open circles represent samples where only total iron concentrations were measured. The solid curves represent the solubilities of the minerals (Stefánsson, 2000).

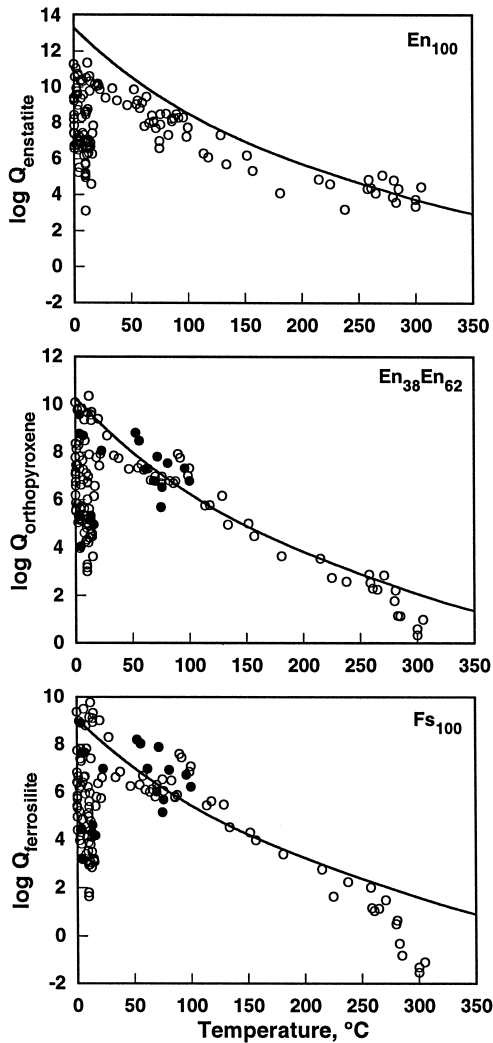


Fig. 4. The temperature dependence of the saturation state of orthopyroxene in cold- and thermal waters in Iceland. The orthopyroxene composition is shown in the upper right-hand corner and represents pure enstatite (En_{100}), pure ferrosilite (Fs_{100}) and average orthopyroxene phenocryst in icelandite ($\text{En}_{38}\text{Fs}_{62}$). Symbols and curves have the same notion as in Fig. 3.

albite over the whole temperature range. For all other plagioclase compositions, the waters are undersaturated below 200°C but close to saturation at higher temperatures.

4.1.4. Fe–Ti oxides

All type of waters are supersaturated with respect to pure hematite and magnetite at all temperatures,

except for four samples of high-temperature geothermal waters which are slightly undersaturated relative to pure magnetite (Figs. 7 and 8). With increasing Ti content of the minerals, their stability decreases and for pure ulvöspinel, undersaturation is observed at all temperatures (Fig. 8). Cold waters are generally undersaturated with pure ilmenite, but waters above

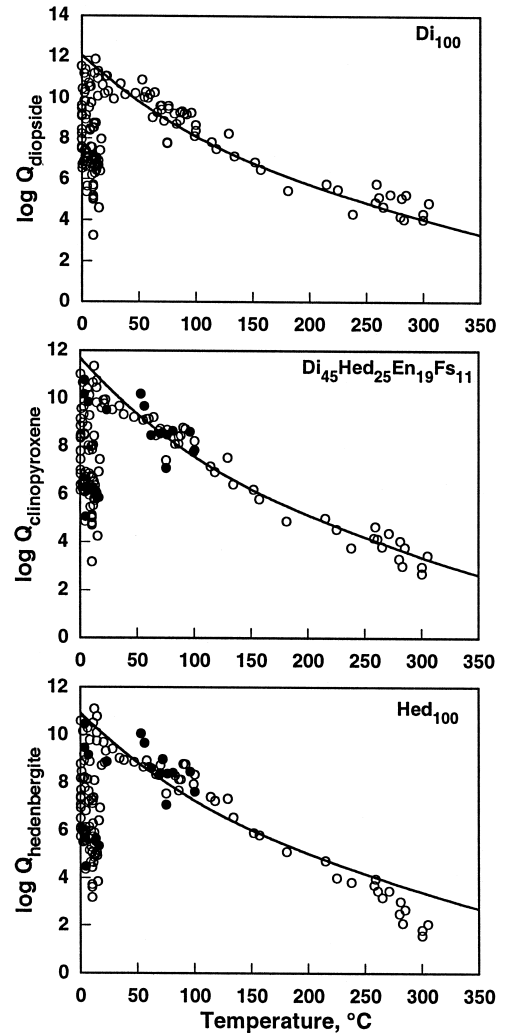


Fig. 5. The temperature dependence of the saturation state of clinopyroxene in cold- and thermal waters in Iceland. The clinopyroxene composition is shown in the upper right-hand corner and represents pure diopside (Di_{100}), pure hedenbergite (Hed_{100}) and average groundmass clinopyroxene ($\text{Di}_{45}\text{Hed}_{25}\text{En}_{19}\text{Fs}_{11}$). Symbols and curves have the same notion as in Fig. 3.

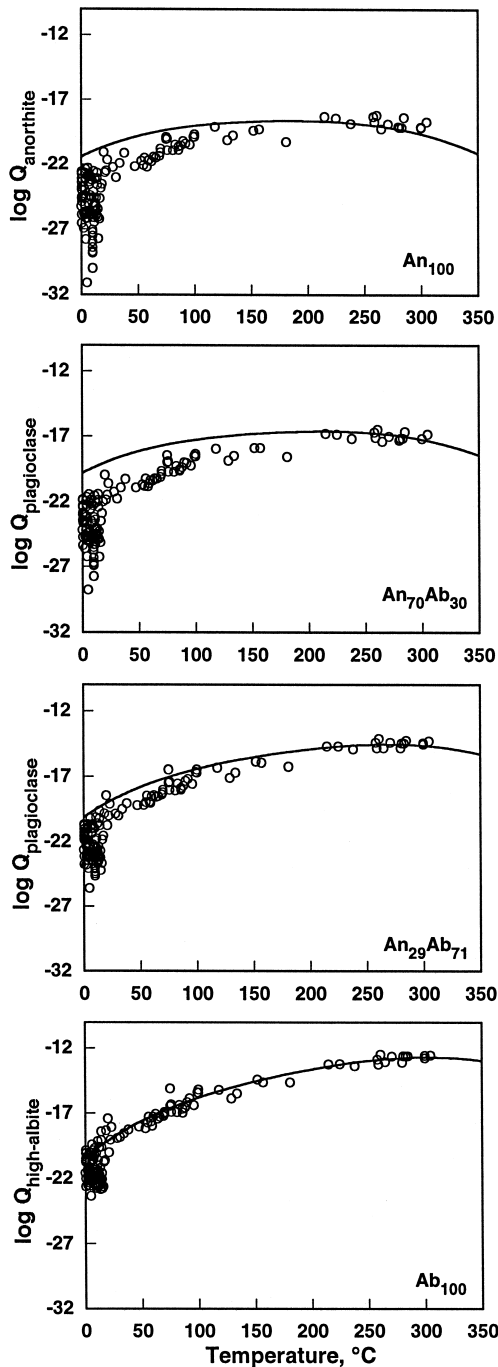


Fig. 6. The temperature dependence of the saturation state of plagioclase in cold- and thermal waters in Iceland. The plagioclase composition is shown in the lower right-hand corner and represent pure anorthite (An_{100}), pure high albite (Ab_{100}), average plagioclase phenocryst ($An_{70}Ab_{30}$) and groundmass ($An_{29}Ab_{71}$). The curves represent the solubilities of the minerals (Arnórsson and Stefánsson, 1999).

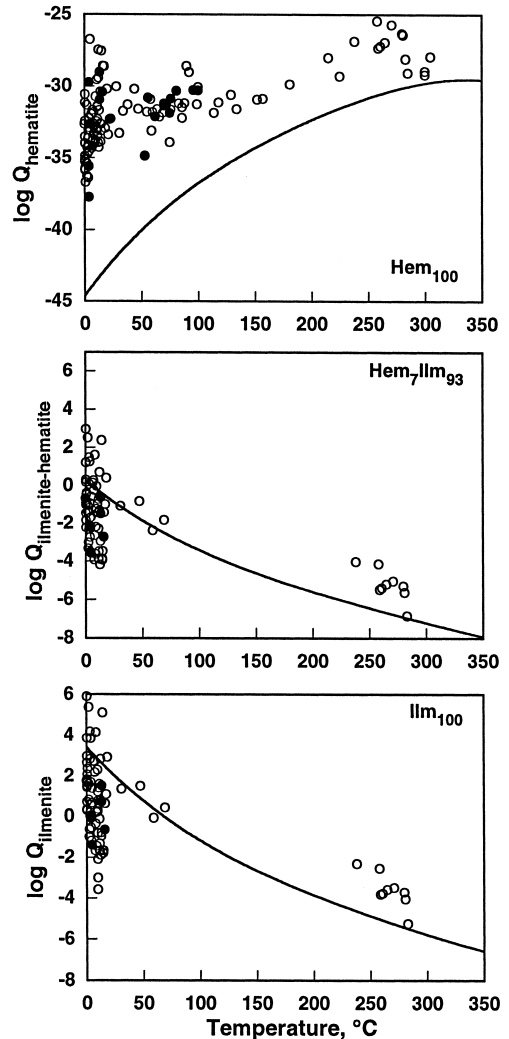
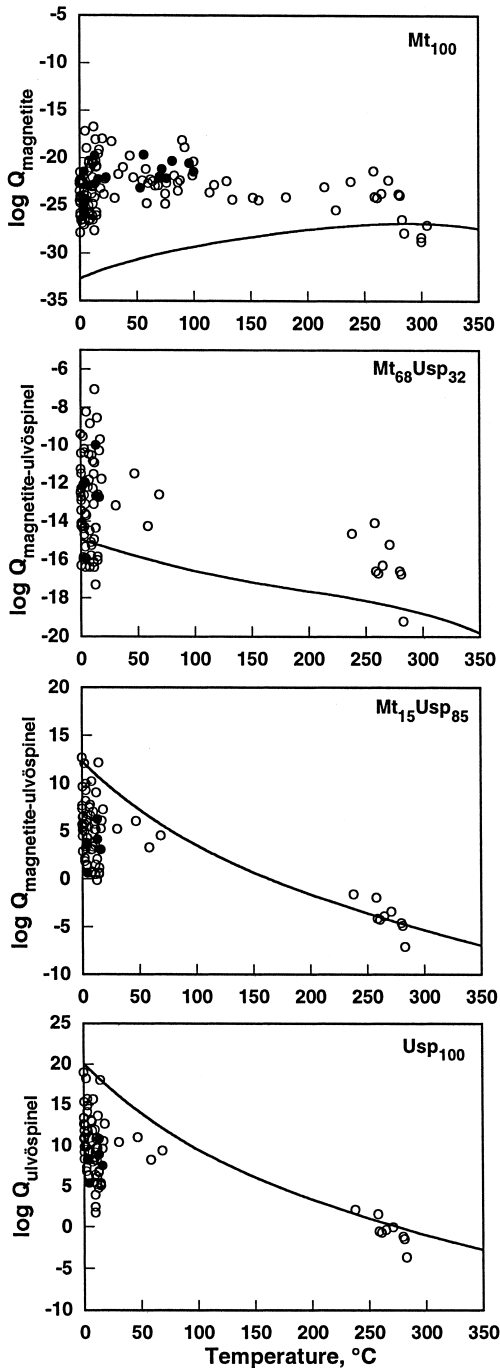


Fig. 7. The temperature dependence of the saturation state of ilmenite–hematite in cold and thermal waters in Iceland. The compositions are shown in the lower/upper right-hand corner and represent pure hematite (Hem_{100}), groundmass ilmenite (Hem_7Ilm_{93}), and pure ilmenite (Ilm_{100}). Symbols and curves have the same notion as in Fig. 3.

250°C are undersaturated. Similar trend is observed for natural groundmass ilmenite (Hem_7Ilm_{93}) as for pure ilmenite (Fig. 7). The state of saturation with respect to groundmass titanomagnetite is very variable. Ti-poor titanomagnetite is generally stable at all temperatures, whereas Ti-rich titanomagnetite is unstable. Therefore, the saturation state of titanomagnetite is very sensitive to its composition.

As can be seen from Figs. 7 and 8, the difference in the solubilities between hematite and ilmenite, on one hand, and magnetite and ulvöspinel, on the



other, is large, making the mineral solubilities of intermediate composition very sensitive to the mineral composition. Also, the thermodynamic properties of ilmenite–hematite solid solution are difficult to predict due to ordering–disordering and extensive immiscibility gaps at low temperatures. In addition, considerable uncertainties are related to the aqueous titanium speciation calculations affecting the calculated stability of all titanium bearing minerals. Therefore, estimation of saturation state of the waters with respect to Fe–Ti oxides is subject to considerable uncertainty that should be borne in mind when evaluating the present results.

4.1.5. Apatite

Cold waters are supersaturated with respect to F-apatite. On the other hand, undersaturation is observed with respect to OH-apatite for some cold waters and low-temperature waters but supersaturation for others (Fig. 9). At high temperatures, the waters are somewhat supersaturated with respect to F-apatite, but close to saturation with OH-apatite. Primary apatites of igneous rocks are considered to be F-rich (Deer et al., 1992). Accordingly, it seems likely that naturally occurring primary apatite is generally stable under weathering conditions.

4.2. The pH dependence of mineral saturation state under weathering conditions

4.2.1. Olivine

For all types of olivine, the nonthermal waters are undersaturated regardless of mineral composition with the exception of alkaline waters in contact with pure fayalite (Fig. 10). The degree of undersaturation decreases as the in situ pH increases. This is not surprising as the reaction quotient for olivine is inversely related to the proton activity to the fourth power. It is also clear from Fig. 10 that the degree of

Fig. 8. The temperature dependence of the saturation state of titanomagnetites in cold and thermal waters in Iceland. The compositions are shown in the upper right-hand corner and represent pure magnetite (Mt_{100}), pure ulvöspinel (Usp_{100}) and the two compositional extremes of groundmass titanomagnetites found in Icelandic rocks ($Mt_{68}Usp_{32}$ and $Mt_{15}Usp_{85}$). Symbols and curves have the same notion as in Fig. 3.

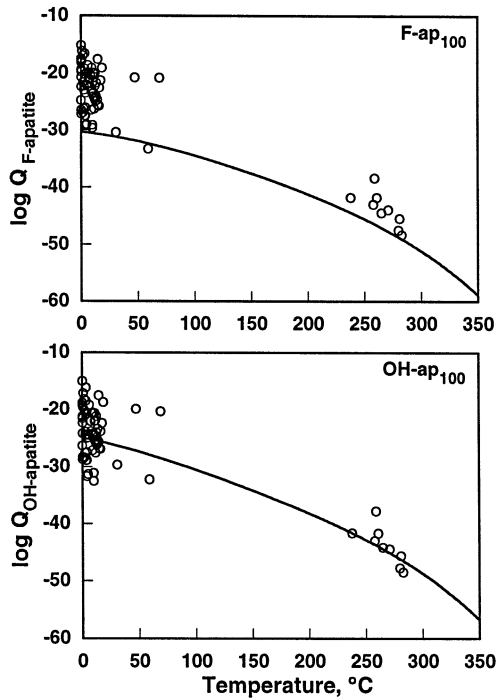


Fig. 9. The temperature dependence of the saturation state of apatite in cold and thermal waters in Iceland. The compositions are shown in the upper right-hand corner and represent pure fluor-apatite (F-ap₁₀₀) and pure hydroxy-apatite (OH-ap₁₀₀). The solid lines represent the solubilities of the minerals (Stefánsson, 2000).

undersaturation of olivine under weathering conditions is reduced as the Fe content of the mineral increases.

4.2.2. Pyroxene

All types of waters are undersaturated with respect to pyroxene regardless of composition except for few spring water samples with in situ pH above 9.5, which are observed to be supersaturated relative to pure ferrosilite (Figs. 11 and 12). Therefore, pyroxenes are unstable under weathering conditions. Their saturation state depends on pH, making low pH waters more undersaturated than high pH waters. As for olivine, the stability of orthopyroxene decreases with increasing Fe content. However, the stability of clinopyroxenes seems to be insensitive to its composition.

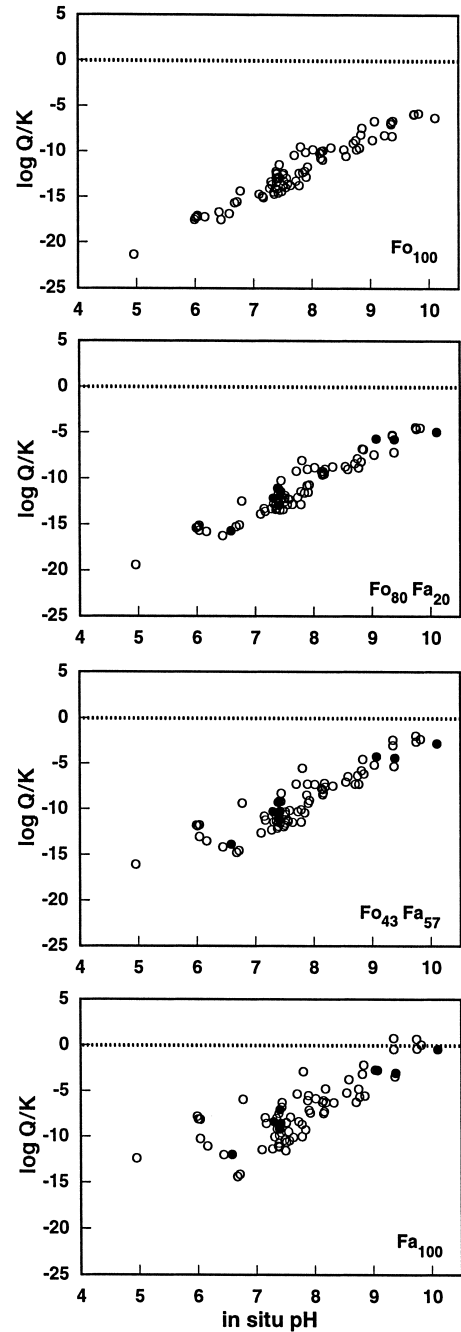


Fig. 10. The pH dependence of the saturation state of olivine in river-, cold spring-, surface peat- and soil waters. The olivine composition is shown in the lower right-hand corner of the figures and represent pure forsterite (FO₁₀₀), typical olivine phenocryst (FO₈₀Fa₂₀), groundmass olivine (FO₄₃Fa₅₇), and pure fayalite (Fa₁₀₀). The dotted lines represent equilibrium. Symbols have the same notion as in Fig. 3.

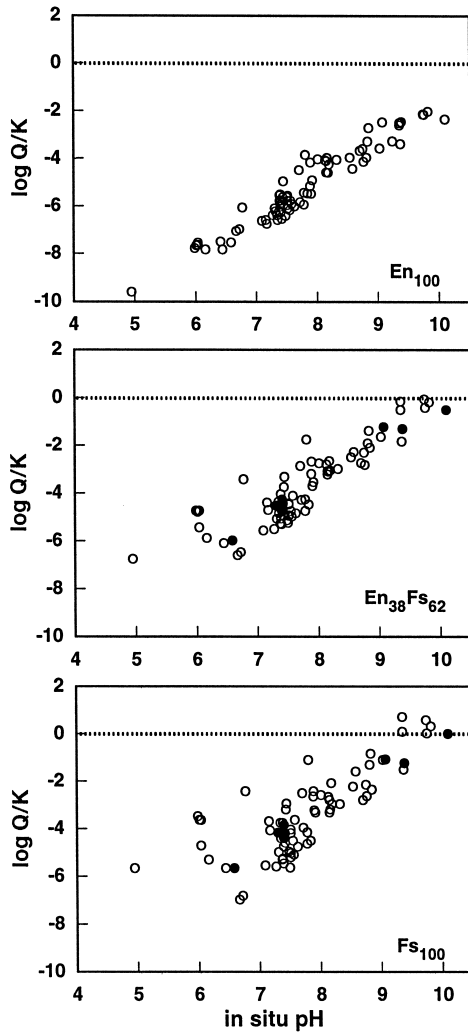


Fig. 11. The pH dependence of the saturation state of orthopyroxene in river-, cold spring-, surface peat- and soil waters. The orthopyroxene composition is shown in the lower right-hand corner of the figures and represent pure enstatite (En_{100}), average orthopyroxene phenocryst in icelandite ($En_{38}Fs_{62}$), and pure ferrosilite (Fs_{100}). The dotted lines represent equilibrium. Symbols have the same notion as in Fig. 3.

4.2.3. Plagioclase

All types of the nonthermal waters are undersaturated with respect to the whole range of plagioclases compositions, except for several spring waters with in situ pH above 9.5, which are supersaturated with respect to high-albite (Fig. 13). The degree of undersaturation increases with increasing Ca content of the plagioclase making Ca-rich plagioclases more unsta-

ble than Na-rich ones. As seen from Fig. 13, the pH dependence of the state of plagioclase saturation decreases with increasing Na content of the mineral.

4.2.4. Fe–Ti oxides

The nonthermal waters are supersaturated with respect to pure hematite suggesting that this mineral

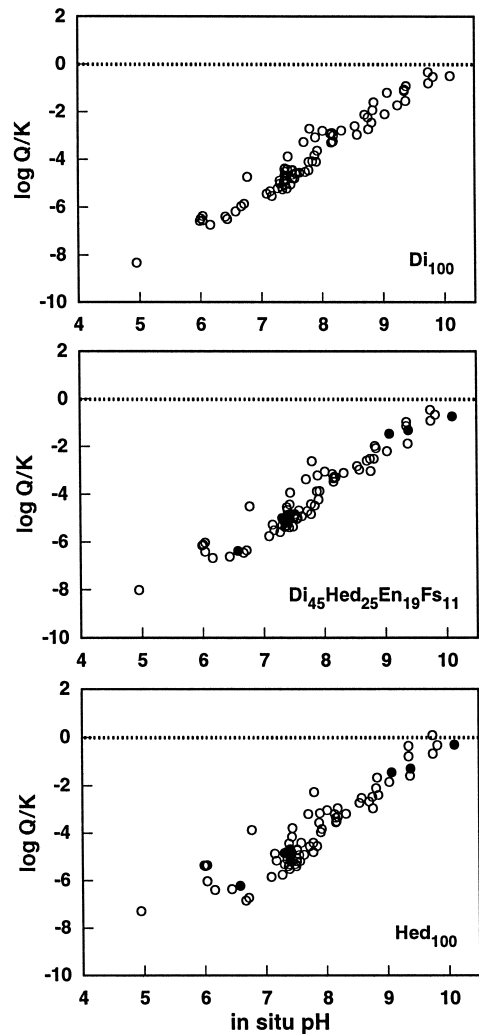


Fig. 12. The pH dependence of the saturation state of clinopyroxene in river-, cold spring-, surface peat- and soil waters. The clinopyroxene composition is shown in the lower right-hand corner of the figures and represent pure diopside (Di_{100}), groundmass clinopyroxene in Icelandic basalts ($Di_{45}Hed_{25}En_{19}Fs_{11}$), and pure hedenbergite (Hed_{100}). The dotted lines represent equilibrium. Symbols have the same notion as in Fig. 3.

is stable under weathering conditions (Fig. 14). On the other hand, low pH waters are undersaturated with both pure ilmenite and groundmass ilmenite in

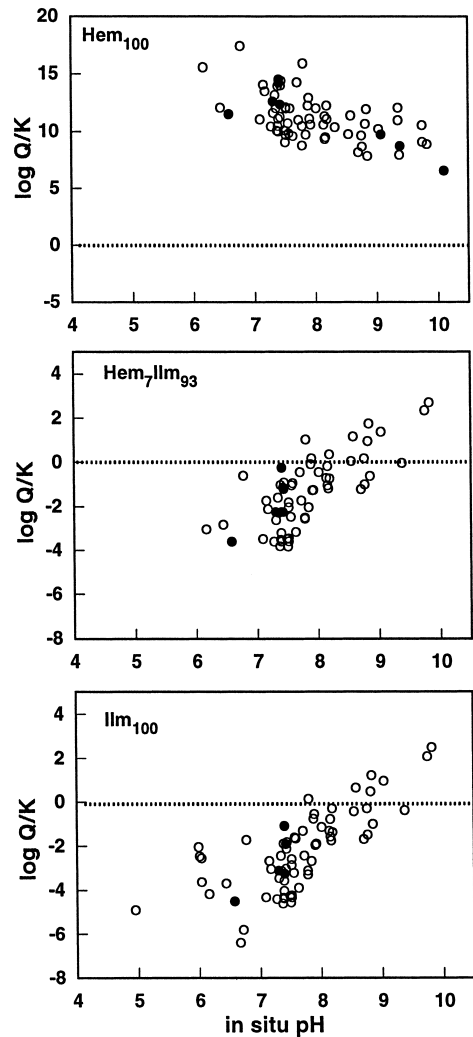
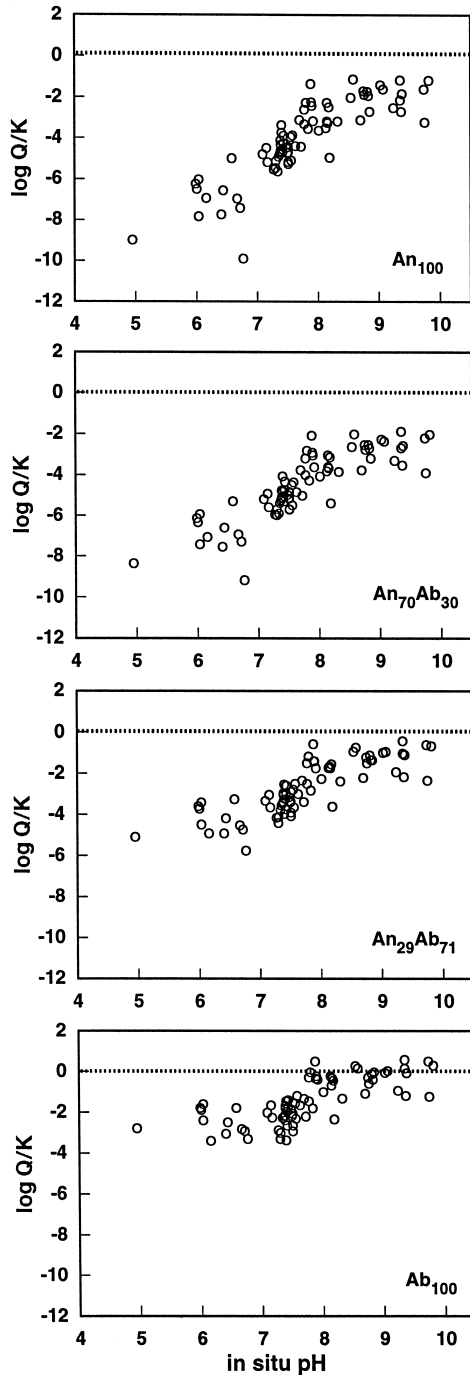


Fig. 14. The pH dependence of the saturation state of ilmenite–hematite in river-, cold spring-, surface peat- and soil waters. The composition is shown in the upper left-hand corner of the figures and represent pure hematite (Hem_{100}), groundmass ilmenite ($\text{Hem}_7\text{Ilm}_{93}$), and pure ilmenite (Ilm_{100}). The dotted lines represent equilibrium. Symbols have the same notion as in Fig. 3.

tholeiites ($\text{Hem}_7\text{Ilm}_{93}$), whereas high pH waters are supersaturated (Fig. 14). The degree of supersatura-

Fig. 13. The pH dependence of the saturation state of plagioclase in river-, cold spring-, surface peat- and soil waters. The plagioclase composition is shown in the lower right-hand corner of the figures and represent pure anorthite (An_{100}), plagioclase phenocryst ($\text{An}_{70}\text{Ab}_{30}$), groundmass plagioclase ($\text{An}_{29}\text{Ab}_{71}$), and pure high-albite (Ab_{100}). The dotted lines represent equilibrium.

tion for hematite increases with decreasing pH, as its solubility is proportional to the proton activity squared. Pure ilmenite shows the opposite trend with pH, which is related to the fact its solubility is inversely related to proton activity raised to the second power (see Stefánsson et al., 2000, Table 1) (Fig. 14).

As can be seen from Fig. 15, pure magnetite is stable under weathering conditions. The degree of supersaturation is independent of pH as proton neither enters the reaction quotient nor does it affect, to a large degree, the aqueous speciation within the observed pH range. However, considerable scatter is observed which can be accounted for by very variable iron concentration in cold waters. All the non-thermal waters are undersaturated with respect to pure ulvöspinel. The degree of undersaturation is highly dependent on pH, being higher at low pH, as the proton activity comes in to the reaction quotient in the fourth power. As can be seen from Fig. 15, the saturation state of naturally occurring titanomagnetite in Iceland depends heavily on its composition, with Ti-poor titanomagnetite being stable but Ti-rich titanomagnetite unstable under weathering conditions, respectively.

4.2.5. Apatite

Fig. 16 shows the saturation state of F-apatite and OH-apatite vs. pH for river-, cold spring-, peat- and soil waters. The lowest pH waters are undersaturated or close to saturation with F-apatite but all other waters are supersaturated. Waters with pH of less than 7.5 are undersaturated with OH-apatite but waters with a higher pH are supersaturated. Accordingly, OH-apatite would generally be unstable in contact with peat waters but stable in groundwaters. As primary apatites of igneous rocks are predominantly F-bearing (Deer et al., 1992), it seems likely

that naturally occurring apatites are stable under weathering conditions, except for the lowest pH waters. This is in good agreement with the findings

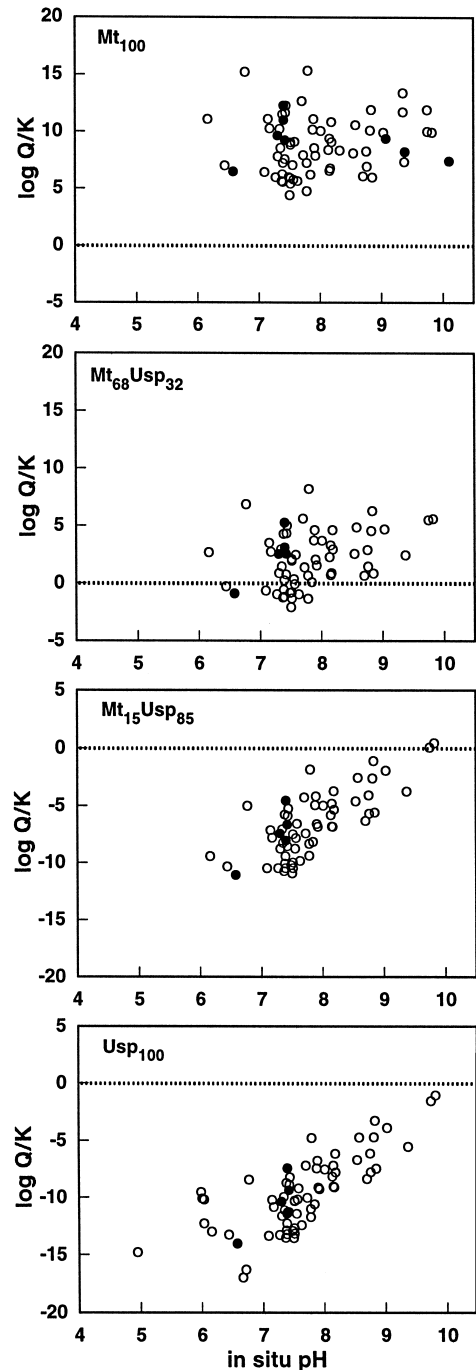


Fig. 15. The pH dependence of the saturation state of titanomagnetite in river-, cold spring-, surface peat- and soil waters. The composition is shown in the upper left-hand corner of the figures and represent pure magnetite (Mt_{100}), the two compositional extremes of groundmass titanomagnetites found in Icelandic rocks ($Mt_{68}Usp_{32}$ and $Mt_{15}Usp_{85}$), and pure ulvöspinel (Usp_{100}). The dotted lines represent equilibrium. Symbols have the same notion as in Fig. 3.

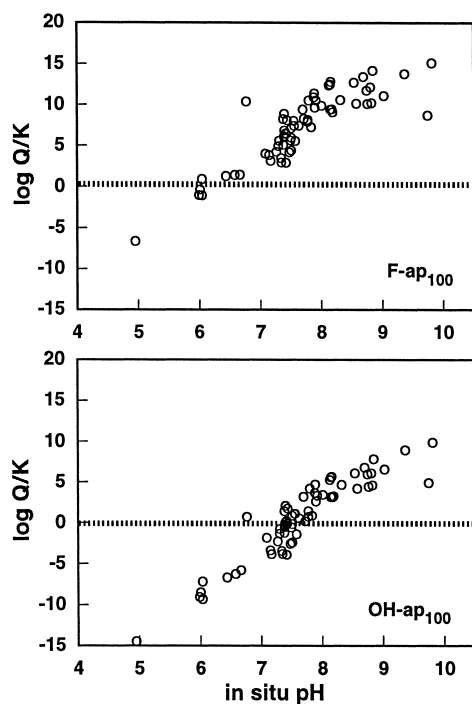


Fig. 16. The pH dependence of the saturation state of F-apatite (F-ap₁₀₀) and OH-apatite (OH-ap₁₀₀) in river-, cold spring-, surface peat- and soil waters. The dotted lines represent equilibrium.

of Banfield et al. (1991) of apatite crystals remaining unaltered in intensively weathered rocks.

5. Discussion

5.1. Uncertainties related to mineral saturation state

The conclusions of the present study of the stability of primary minerals of basalt in contact with natural waters in Iceland assume that the errors of the calculated saturation indices are within 1–2 log units. These errors mainly stem from uncertainties in the values of dissociation constants of aqueous species used for the speciation calculations as well as uncertainties in the selected mineral solubility constant. In the case of wet-steam wells, a significant error may also be involved in the calculation of aquifer water composition. On the other hand, analytical uncertainties are generally unimportant.

Various authors (Stumm and Morgan, 1981; Sholkovitz, 1992; Dupré et al., 1996; Viers et al., 1997) demonstrated that the so-called “dissolved form” corresponds in some cases to a mixture of “colloidal” (organic and mineral microparticles) and “true” dissolved species in cold waters. Viers et al. (1997) studied the effect of filtration through different pore size filters (0.22, 0.025 μm or 300 and 5 kDa) on the concentrations of elements in the filtered water, including Al and Fe, both for organic-poor and organic-rich water. As vegetative and soil cover is sparse in many parts of Iceland, most of the waters considered for the present study can be assumed to be low in organic matter. The results of Viers et al. (1997) for organic-poor waters are therefore of particular interest for the present study. They observed that the Fe concentrations in such water samples filtered through 0.22- μm filters and filters of smaller pore size were within analytical errors. On the other hand, Viers et al. (1997) observed that Al concentrations in clear waters are 60% to 75% lower in water filtered through 0.22- μm filter membranes than 5 kDa, demonstrating that the “true” dissolved Al concentration of an organic-poor water is not obtained by standard filtration methods. It is, therefore, possible that Al concentrations reported in the present study are higher than the “true” dissolved concentrations. On the other hand, the Fe concentrations, which were measured in water samples filtered through 0.2- μm filter membranes, are likely to represent the “true” dissolved Fe concentrations.

Stefánsson and Gíslason (2000) demonstrated that Al and Fe are among the least mobile elements under weathering conditions of basaltic rocks in Iceland. They further showed, using the same procedure for speciation calculations and a large proportion of the analytical database used in the present study, that Icelandic cold waters are saturated with amorphous $\text{Fe}(\text{OH})_3$ and saturated or slightly supersaturated (< 1 log unit) with gibbsite depending on crystallinity and imogolite and/or allophane depending on composition, these weathering minerals being the dominant ones for the clay size fraction of the soils (> 700 g/kg of clay) (Arnalds, 1990; Wada et al., 1992; Arnalds et al., 1995). Accordingly, these findings suggest that the Fe and Al concentrations reported in the present study are close to the “true” dissolved concentrations of these elements.

The largest uncertainties in predicting the activities of aqueous species is related to the calculations of pH, selection of temperature, in the case of geothermal waters, and the aqueous species dissociation constants used for the speciation calculations. To minimize these errors, the dissolution reactions were written in terms of the dominant aqueous species as far as possible. Thus, for most activities, aqueous species used to calculate the reaction quotients closely matches the relationship $a_{e,i} \approx m_{i,\text{total}} \gamma_{e,i}$ where $a_{e,i}$ and $\gamma_{e,i}$ are the activities and activity coefficient of the e -th species of i -th element and $m_{i,\text{total}}$ is the total analyzed concentration in the water or calculated for the aquifer water in case of high-temperature geothermal waters (wet-steam wells). However, this relation does not always hold, such as those of Al, Fe, and P, introducing additional uncertainties. They have, however, been minimized in the present study by expressing the dissolution reactions in terms of those aqueous species, which are most frequently most abundant. In this manner, all possible errors have been minimized. However, it is very difficult to quantify them. Such a work would need to incorporate all possible uncertainties related to the analytical data, speciation calculation and mineral solubility. Despite the importance of such work for the interpretation of mineral-equilibria in natural water systems, the problem has never been tackled as far as we know.

5.2. Primary mineral stability in geothermal systems

The bedrock in Iceland is mostly built up of holocrystalline or partly crystalline basalt and basaltic hyaloclastite. However, minor dolerite, icelandite, and rhyolite occur together with their intrusive equivalents. The primary minerals of basalt and the basaltic glass are unstable in contact with geothermal water according to microscopic studies. The glass is most easily altered and then olivine, pyroxene, and plagioclase in that order (Kristmannsdóttir, 1979). These observations are in good agreement with our results. The petrographic studies show that the extent of alteration is very variable from insignificant replacement of the primary constituents by secondary minerals to almost total reconstitution. The age of the geothermal system is considered to be the pri-

mary factor determining the intensity of the alteration, together with the internal structure of the rock that controls the surface between the water and rock. Magnetite appears to be rather easily destroyed in some high-temperature geothermal systems as witnessed by strong negative magnetic anomalies over the geothermal areas (Pálmason, 1975). Our results are consistent with these findings if the titanomagnetite in these geothermal systems are Ti-rich. The observed primary mineral stability in some cases in geothermal systems could be affected by the presence of volcanic glass in the rock. The glass is expected to be more soluble than the primary crystalline phases. Accordingly, dissolution could stabilize these phases by maintaining supersaturation.

Studies of alteration mineralogy and fluid composition in many geothermal systems have demonstrated that equilibrium is closely approached between the solution and, at least, some of the secondary minerals (Browne, 1970, 1978; Ellis and Mahon, 1977; Giggenbach, 1981, 1988; Arnórsson et al., 1983). It is now generally accepted that mineral–fluid equilibrium has been closely approached in geothermal systems for all major components except Cl when temperatures are above 100°C to 150°C (Giggenbach, 1981; Arnórsson et al., 1983) and in some cases to temperatures as low as 50°C (Arnórsson and Andrésdóttir, 1995). Thus, an increase in the solute content of geothermal waters due to primary mineral dissolution leads to precipitation of hydrothermal minerals. As the hydrothermal minerals have lower solubility, their precipitation maintains the solution undersaturated with respect to the primary minerals and as a result they tend to dissolve.

5.3. Primary mineral stability under weathering conditions

The chemistry of major constituents of cold waters in Iceland are governed by (a) dissolution of the primary rocks, (b) formation of weathering minerals, and (c) biomass activity (Gíslason et al., 1996; Moulton and Berner, 1998; Stefánsson and Gíslason, 2000). From the study of elemental mobility, Stefánsson and Gíslason, 2000 concluded that aqueous Na, B, F and S concentrations were determined

by dissolution alone, i.e. these elements are mobile. By contrast, Si, Ca, Mg, K, Al and Fe display lower mobility and because of this, they must be consumed by weathering minerals and/or the biomass. For aqueous Si, Ca, Al and Fe, the former seems to be the case, as cold waters in Iceland are saturated or slightly supersaturated with the most commonly found weathering minerals; amorphous $\text{Fe}(\text{OH})_3$, imogolite, allophane and smectite-like minerals (Douglas, 1987; Arnalds, 1990; Crovisier et al., 1992; Wada et al., 1992; Arnalds et al., 1995; Stefánsson and Gíslason, 2000). For K, and possibly also Mg, the biomass plays an important role (Moulton and Berner, 1998; Stefánsson and Gíslason, 2000).

Basaltic glass is likely to be more soluble than primary basaltic minerals as it has retained more energy from its parent magmatic environment than the minerals. This is supplemented by experiments which show that basaltic glass dissolves up to 10 times faster than fully crystalline basaltic rock (Gíslason and Eugster, 1987a). Therefore, dissolution of basaltic glass may lead to stabilization of the primary minerals of basalt. By contrast, the con-

sumption of solutes by weathering minerals with lower solubility than the primary minerals and the basaltic glass, as well as uptake by the biomass, lowers the concentrations of most of the major components in cold waters maintaining the solution undersaturated with respect to the primary rock constituents and the basaltic glass and, as a result, they continue to dissolve. Therefore, the stability of primary basaltic minerals under weathering conditions is not only determined by dissolution rate but also the formation of weathering minerals and uptake of biomass and by the presence of basaltic glass.

Fig. 17 summarizes the stability of primary basaltic minerals under weathering conditions, not only weathering susceptibility but also the degree of super- and/or undersaturation in terms of Gibbs energy (kJ). Both end-members and minerals with natural composition have been considered. The only minerals that are stable are Ti-poor magnetite and hematite but often also ilmenite and F-apatite. Olivines, pyroxene and plagioclases of all composition are unstable. The relative order of stability compares well with their reactivity originally pro-

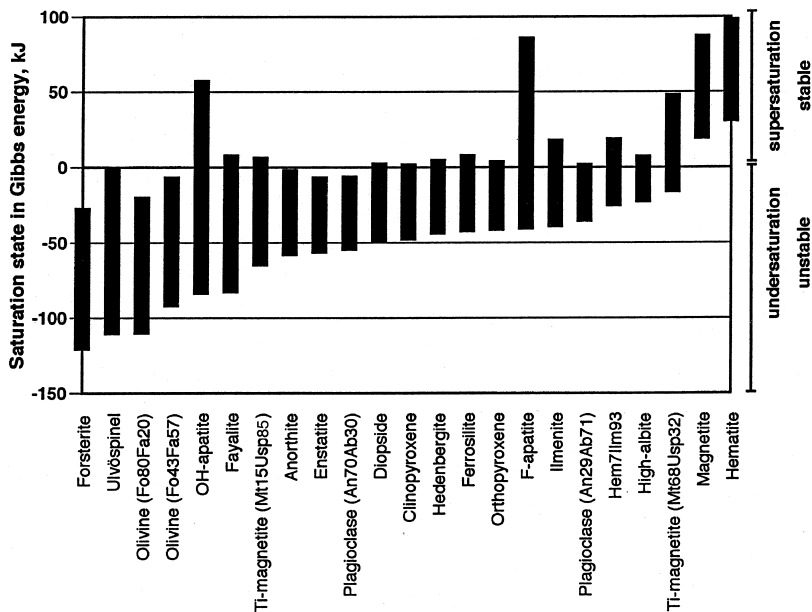


Fig. 17. The stability of primary basaltic minerals under weathering conditions in Iceland as inferred from the composition of surface- and cold groundwaters.

posed by Goldich (1938) which is in decreasing order.

Olivine	Ca plagioclase
Augite	Ca–Na plagioclase
Hornblende	Na–Ca plagioclase
Biotite	Na plagioclase
	Alkali–feldspar
	Muscovite
	Quartz

They are also in accordance with the results of mineralogical studies on the pattern of weathering susceptibility which are olivine > pyroxene > plagioclase > sanidine (Craig and Loughnan, 1964); glass – golvine > pyroxene > amphibole > plagioclase > K-feldspar (Colman, 1982); glass ≈ olivine > plagioclase > pyroxene > opaque minerals (Eggelton et al., 1987); glass, olivine > laihunite > clinopyroxene > orthopyroxene > plagioclase > K-feldspar > magnetite > apatite > rutile, ilmenite > quartz (Banfield et al., 1991) and olivine > glass > plagioclase > clinopyroxene > Fe–Ti oxides (Nesbitt and Wilson, 1992). As seen in the present study, the discrepancies between the relative order of plagioclase and pyroxene may be attributed to mineral composition. For example, the stability sequence of olivine, pyroxene, and plagioclase in weathered Baynton basalts in Australia, as reported by Nesbitt and Wilson (1992), is the same as would be predicted from the results of the present contribution (except for the glass) when taking into account the composition of the minerals. Banfield et al. (1991) studied the weathering of volcanic rocks from Abert Lake in south central Oregon. In these rocks, the primary mineral composition was different from that of the Baynton basalts resulting in a weathering susceptibility different from that of Nesbitt and Wilson (1992), yet consistent with the results of the present contribution.

6. Summary and conclusions

The state of saturation of cold and geothermal waters in the basaltic terrain of Iceland relative to all primary basaltic minerals has been assessed. At low temperatures, the waters are undersaturated with

olivine, pyroxene, and plagioclase. On the other hand, Fe–Ti oxides and apatite are generally close to saturation or even stable under weathering conditions. Undersaturation with respect to olivine, pyroxene, and plagioclase is maintained by the precipitation of less soluble minerals. Their formation affects the mobility of Si, Ca, Al and Fe. With increasing temperature, the waters approach saturation with respect to olivine, pyroxene, and plagioclase. This is explained by increasing dissolution rates with rising temperature, increased retention time of the waters and, as a result, increased reaction with the rock. Also, dissolution of basaltic glass, the solubility of which may be assumed to be greater than for the primary minerals, may lead to the stabilization of the primary minerals. For Mg-rich olivines and pyroxenes, the waters are distinctly undersaturated up to 250°C but at higher temperatures, the data points are scattered around the solubility curves. By contrast, the Fe-rich olivines and pyroxenes are close to saturation or supersaturated below 250°C but undersaturated at higher temperatures. Thermal and non-thermal waters are undersaturated with Ca-rich plagioclase except at the highest temperatures (> 250°C) where they are close to saturation. The degree of undersaturation decreases with increasing Na-content of the plagioclase and pure high-albite is close to saturation at temperatures as low as 20°C. The stability of magnetite–ulvöspinel solid solutions is very sensitive to their composition, pure magnetite being stable at all temperatures but pure ulvöspinel unstable. However, supersaturation with respect to magnetite decreases with rising temperature and the hottest waters are close to saturation. The picture for hematite–ilmenite is the same as for magnetite–ulvöspinel.

On the basis of mineral saturation state, the weathering susceptibility of the primary minerals of basalt in Icelandic waters are in increasing order: Mg-olivine > Fe-olivine, Ti-rich magnetite > Ca-plagioclase, Mg-orthopyroxene > Fe-orthopyroxene, clinopyroxene > Na-plagioclase, F-apatite > Ti-rich ilmenite ≫ Ti-poor magnetite, Ti-poor hematite. These results are in good agreement with observations on mineralogical transformation in weathered basalts (Craig and Loughnan, 1964; Colman, 1982; Eggelton et al., 1987; Banfield et al., 1991; Nesbitt and Wilson, 1992).

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