

ORIGIN OF ^{14}C IN ICELANDIC GROUNDWATER

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ABSTRACT. We report the first attempt to date Icelandic groundwater by the radiocarbon dating technique. We propose that boron concentrations of the water samples can be taken as a measure of the amount of dead CO_2 in the groundwater leached from rock. By assuming that the ratio of boron to CO_2 is the same in the rock and groundwater it is possible to correct the ^{14}C concentration for the contribution of rock-derived carbon in the groundwater and thus calculate the initial (undiluted) ^{14}C concentration. When this correction is applied, the values for the cold and warm waters lie in the range 60 to 110 pMC, which is in accordance with the estimated residence time for the groundwater. We have also calculated the fractions of atmospheric and organic carbon in the water, based on the $\delta^{13}\text{C}$ measurements, and the results agree well with the general hydrology and vegetational cover of the areas. Results from geothermal systems indicate that it is possible to use ^{14}C to estimate relative age differences of the water in a particular geothermal area.

INTRODUCTION

The deuterium content of the mean annual precipitation in Iceland has been used extensively as a tracer to delineate regional movement of groundwater, including geothermal water (Árnason 1976, 1977; Tómasson, Fridleifsson and Stefánsson 1975). From stable isotope measurements and general hydrological considerations, Árnason (1976) concluded that the water in cold groundwater systems is relatively young (an average of a few years to a few decades old). Hot water is of varying ages, and, in most cases, is much older than the cold water. The youngest hot water is thought to be only a few decades old, while the oldest is considered to be from the last glaciation (≥ 10 ka BP) (Árnason 1976).

Carbon in groundwater may be derived from several sources with different ^{14}C concentrations and $\delta^{13}\text{C}$. Thus, age determination of groundwater is complex from a geochemical point of view, and the interpretation of a ^{14}C determination is often unclear. Under certain conditions, absolute groundwater ages can be obtained within certain limits by applying correction procedures using the chemical and stable carbon isotopic composition of the sample (e.g., Dörr, Sonntag and Regenber 1987; Aravena and Suzuki 1990; Aravena and Wassenaar 1993; Taylor 1994). Relative ages can be determined with more certainty. In Iceland, we expect at least three different sources of carbon supply in the water: atmospheric CO_2 , soil CO_2 of organic origin and CO_2 leached from the rock through which the water seeps. Moreover, there may be a supply of CO_2 from a magmatic source in some geothermal systems. Addition of carbon from sources other than the atmosphere and organic soil dilutes the ^{14}C concentration of the water and in this way yields a high apparent ^{14}C age. Because of the multiple character of the carbon supply in the water, a simple two-component isotopic dilution model (Mook 1980) is inadequate to correct ^{14}C measurements for the Icelandic samples.

The first measurements of ^{14}C in Icelandic groundwater were made in a study on aquatic moss samples collected in the active geothermal area at Hveragerdi, some 40 km east of Reykjavík (Sveinbjörnsdóttir *et al.* 1992). The apparent age of the water samples from Hveragerdi ranged from 20 ka BP at the source of a hot spring, to 6 ka BP, as the distance from the source increased. The decrease was explained by exchange with atmospheric CO_2 and dilution with non-geothermal surface water. For the present study, we collected water samples, expected to be modern or only a few decades old, from different geological areas and with different types of vegetational cover, to define a correction procedure based on the chemical and stable carbon isotopic composition of the samples. We sam-

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pled also from low-temperature geothermal systems, but geothermal waters are expected to have considerably higher absolute ages.

Geological and Hydrological Settings

In Iceland, most of the igneous rocks are basaltic (~90%); the rest are of rhyolitic and intermediate composition. *Ca.* 90% of Iceland above sea level consists of volcanic rock, only *ca.* 10% being consolidated sediments, which are mainly interbedded tuffaceous layers of short transport, and tillite. Icelandic bedrock contains no calcareous rock. Geothermal activity is widespread in Iceland, and the thermal areas are conventionally divided into two groups referred to as the high ($\geq 150^{\circ}\text{C}$) and low temperature areas ($\leq 150^{\circ}\text{C}$) (Böðvarsson 1961). It is commonly held that magmatic heat source contribute to the gas and boron content of high-temperature fluids (Ármannsson *et al.* 1982; Arnórsson and Andrésdóttir 1995). On the other hand, the low-temperature activity is non-volcanic, and sources of the dissolved constituents are the atmosphere, the rock with which the water has interacted, and sometimes marine groundwater. For the present study we collected waters only from non-thermal and low-temperature areas.

We report here the results of ^{14}C analyses of groundwater sampled from three localities: 1) the Southern Lowlands; 2) Kjalarnes, South Iceland; and 3) the southwestern part of the Northwest Peninsula (Fig. 1). In addition, we collected some water samples from the Laugarnes low-temperature geothermal field, Reykjavík and also from the Mosfellssveit low-temperature field, just outside of Reykjavík (Fig. 1), together with associated calcite crystals precipitated from geothermal water.

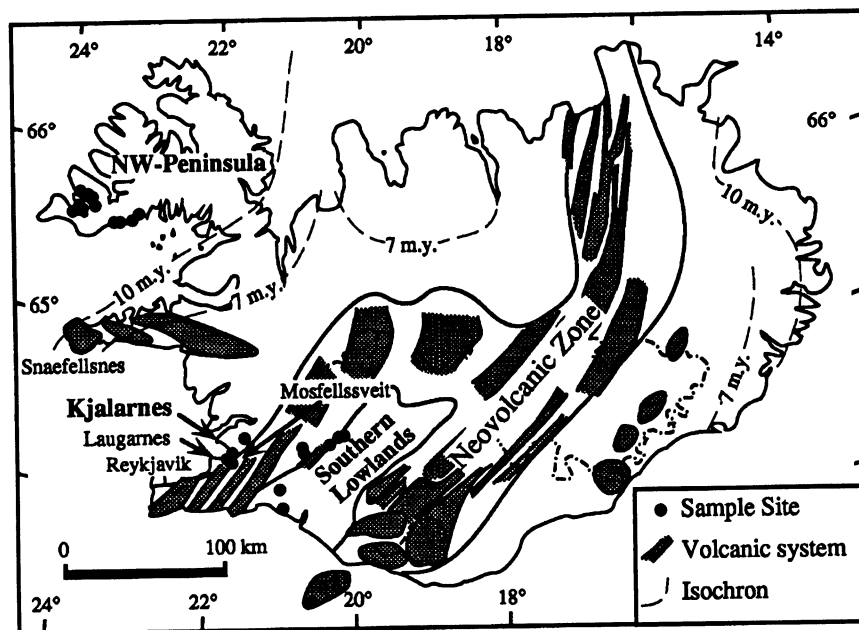


Fig. 1. Map of Iceland showing sample locations

The Southern Lowlands are located in Quaternary rock between the two active volcanic belts in South Iceland. The area is flat and almost completely covered with relatively thick humus and peat soil. Volcanic ash and aeolian material, most of which is volcanic glass, is abundant in the soil. The

glass has been partly altered into allophane and ferrihydrate, but sheet-structured clay minerals are rare or absent (Wada *et al.* 1992). The water samples were taken from springs or flowing boreholes with temperatures ranging from 3°C to 22°C. Kjalarnes is also located in Quaternary rock, just west of the western volcanic belt. The Kjalarnes water samples were taken from springs with temperatures *ca.* 6°C. The springs emerge at the foot of mountain slopes and humus soil cover upstream is limited. The third area (Northwest Peninsula) is located in Miocene flood basalts 10–13 Ma old and dissected by deep, glacially eroded valleys and fjords separated by a 500–600-m high plateau. Humus and peat soil cover is sparse except along the coast and in low valleys. Our water samples from the Northwest Peninsula are all from flowing boreholes and range in temperature from 3°C to 43°C.

Most of the boreholes sampled for this study are <100 m deep and cased only down to bedrock. All of them have natural discharge. For this reason, we expect the borehole water had no chance to interact with the atmosphere during ascent and sampling. This is, of course, not the case for surface waters and springs, particularly those which emerge from the bottom of the talus slopes (*i.e.*, Mógilsá, Ingólfsfjall, Medalfellsvatn).

We expect that a component of the carbon in the water samples derives from the rock and that the relative amount of this component increases with the extent of the water-rock interaction. We have used the aqueous boron concentration to estimate the fraction of rock-derived carbon in the water samples. This estimate assumes that boron acts as a mobile element in the Icelandic basalt-water environment (Arnórsson and Andréðóttir 1995). It is well known that boron is removed from an aqueous solution into sheet-structured clay minerals, in particular illite (Harder 1970), but as previously noted, these minerals are rare or absent in Icelandic soils. The dissolved solids content of non-thermal and warm waters in Iceland is, according to Gíslason and Arnórsson (1993), controlled to a large extent by dissolution of basaltic glass, which is abundant in both the soil and bedrock. We assume carbon and boron in the rock is concentrated in the glass, which is logical since both elements are fugitive. Therefore, glass dissolution should release carbon and boron into the water in stoichiometric proportion.

Data on carbon in basalts from Iceland are very limited. Flower *et al.* (1982) report CO_2 in the range 0.05 to 0.3% by weight (wt) for lavas in the IRDP drill hole in Eastern Iceland, which penetrated Tertiary formations. The average for 250 analyses is 0.13% wt CO_2 ; the average for 78 dike samples is 0.14% wt CO_2 . Most values lie in the range 0.03% to 0.07% wt. Therefore, the median value of 0.05% wt CO_2 has been selected as the average CO_2 content of Icelandic basalts. The average value based on the results of Flower *et al.* (1982) is affected by high values in hydrothermally altered basalts. The basalts in our study area have not been significantly hydrothermally altered.

Arnórsson and Andréðóttir (1995) present data on boron in Icelandic basalts. The range is considerable (0.05 to 3.3 ppm) but the average boron content of tholeiites is 1.2 ppm. We have chosen this value, together with the average CO_2 content of 0.05% wt, to represent the ratio in which boron and carbon are dissolved from the rock. In this respect it is important to realize that the water has contacted many eruptive units. For this reason, we expect that the relative content of boron and carbon gained through rock dissolution will be close to the average boron-carbon ratio of the volcanic rock. Some of the aquatic boron, particularly in the surface waters, is of marine origin (sea spray and aerosols). Following Arnórsson and Andréðóttir (1995), we have estimated the marine boron component (B_M) from the known Cl/B molal ratios in seawater, $\text{Cl}_M/B_M=1330$, and Icelandic basalt, $\text{Cl}_R/B_R=30$ (Arnórsson and Andréðóttir 1995)

$$B_M = [\text{Cl}_W - (\text{Cl}_R/B_R)B_W]/[(\text{Cl}_M/B_M) - (\text{Cl}_R/B_R)]$$

where Cl_W and B_W represent the Cl and B concentration in the water sample. Rock-derived boron (B_R) is represented by the difference in analyzed boron (B_W) and the calculated value of B_M . (Measured values for B_W , Cl_W and calculated values of B_R are given in Table 2.)

METHODS

We collected one liter of each water sample and precipitated carbon from the samples as $BaCO_3$ by adding a solution of 10 ml 1M $BaCl_2$ and 10 ml 1M NaOH. The two reagents were mixed and filtrated beforehand to remove atmospheric CO_2 contamination of the NaOH. The precipitate from the sample was transformed to CO_2 by reaction with 86% phosphoric acid in an evacuated vial placed in a water bath at 20°C. The released CO_2 was then partly used for $\delta^{13}C$ measurements at the Science Institute, Reykjavík, and partly converted to graphite for AMS ^{14}C measurements at the University of Aarhus. We followed the same CO_2 procedure for the hydrothermal calcite crystals ($CaCO_3$). Further information on sample preparation, the graphitization system in Reykjavík and the AMS system in Aarhus is given in Sveinbjörnsdóttir *et al.* (1993). ^{14}C results were normalized to a $\delta^{13}C$ of -25‰ PDB and expressed in "percent modern carbon" (pMC) relative to 0.95 times the ^{14}C concentration of NBS oxalic acid (HOxI).

To define a background level for the groundwater samples, we collected CO_2 -rich waters on the Snæfellsnes Peninsula, West Iceland. No rigorous definition is available for " CO_2 -rich" waters, but those collected for this study contain 1400 and 4000 ppm of total carbonate (calculated as CO_2) as opposed to some 10–100 ppm total carbonate in cold and thermal waters of the low-temperature geothermal fields. We prepared three kinds of samples from the CO_2 -rich waters, *i.e.*, from full concentration and dilution to 50 ppm and 10 ppm, respectively.

The concentration of total inorganic carbon ΣCO_2 was measured by titration with 0.1M HCl. Boron was measured by a modification of the curcumin method (Wikner 1981). For a 50-ml sample, aliquot sensitivity is *ca.* 0.001 ppm B.

RESULTS

Table 1 gives the results of ^{14}C measurements, stable isotopes and the most important chemical parameters. The concentration of total CO_2 is variable—it is lowest in the samples from the Northwest Peninsula (8–16 ppm), but considerably higher in samples from Southern Iceland (12–93 ppm). The water samples from the geothermal areas in Mosfellssveit and Laugarnes (70–130°C) have ΣCO_2 concentrations between 17 and 26 ppm.

The $\delta^{13}C$ in the cold ($<10^\circ C$) groundwater samples from Southern Iceland ranges from -7.2 to -21‰ , whereas the range is much smaller for the cold groundwater samples from the Northwest Peninsula, *i.e.*, -12 to -14‰ . The $\delta^{13}C$ in the warm water samples ($10 < T < 40^\circ C$) ranges from -12 to -17‰ and -10 to -15‰ for the Southern Lowlands and the Northwest Peninsula, respectively. The geothermal water in Mosfellssveit and Reykjavík give $\delta^{13}C$ values between -6 and -13‰ .

For the cold and up to $40^\circ C$ groundwater samples, the ^{14}C concentration ranges from 45 to 117 pMC, corresponding to apparent ^{14}C ages from *ca.* 5500 BP to modern, bomb-influenced values of present atmospheric ^{14}C excess. The water samples from the geothermal areas in Mosfellssveit and Laugarnes (70–130°C) range from *ca.* 11 to 63 pMC, corresponding to apparent ^{14}C ages from *ca.* 17,600 to 3700 BP. Where stable isotopes of oxygen and hydrogen suggest that the cold groundwater is of local meteoric origin, the ^{14}C concentration varies from 101 to 117 pMC in samples from South Iceland, and from 88 to 98 pMC in the Northwest Peninsula. This difference could stem from the

TABLE 1. Primary Data for Groundwater and Geothermal Water Samples

Sample no.	Location	AAR no.	Temp (°C)	Σ CO ₂ (ppm)	pH	¹⁴ C concentration (pMC)	Conv. ¹⁴ C age (yr BP)	δ ¹³ C ‰ PDB	δ ¹⁸ O ‰ SMOW	δD ‰ SMOW	Boron (ppm)
<i>Kjalarnes (Springs)</i>											
190701	Hrísbú	1337	6.9	21.3	8.9	103.12 ± 0.94	-247 ± 73	-14.36	-8.82	-61.2	--
190702	Mógilásá	1338	5.6	19.7	7.6	107.63 ± 0.98	-591 ± 73	-8.73	-9.15	-63.5	--
190703	Steypustöð	1339	6.2	26.8	7.2	108.36 ± 0.88	-645 ± 65	-7.21	-8.70	-63.3	--
190705	Medalfellsvatn	1340	5.8	24.1	6.9	115.28 ± 0.90	-1142 ± 63	-14.61	-9.04	-64.6	--
<i>Southern Lowlands</i>											
<i>Springs</i>											
200701	Gaulverjabær	1341	4.9	93.1	6.7	116.76 ± 0.99	-1245 ± 68	-21.01	-8.32	-56.9	--
200702	Ingólfsfjall	1342	3.6	21.8	8.9	101.44 ± 0.80	-115 ± 63	-10.05	-8.30	-56.6	--
200704	Ljósuár (04)	1343	3.0	12.0	9.8	--	--	-8.83	-10.50	-73.1	0.0030
200705	Ljósuár (05)	1344	5.7	18.5	9.2	82.71 ± 0.77	1525 ± 75	-12.78	-10.54	-74.1	0.0030
200706	Hrúta	1345	4.3	17.3	8.9	100.22 ± 0.92	-18 ± 74	-11.04	-9.74	-70.6	0.0036
<i>Drill Holes</i>											
200707	Gýgiarhólskot	1346	22.4	48.4	9.4	80.04 ± 0.68	1788 ± 68	-17.42	-8.92	-62.5	0.0075
200708	Einholt	1347	19.8	70.1	9.2	51.43 ± 0.57	5341 ± 89	-12.28	-8.72	-60.1	--
200709	Tungufell	1348	13.7	35.6	8.8	87.30 ± 0.76	1091 ± 70	-16.61	-9.19	-63.5	0.0039
<i>Northwest Peninsula (Drill Holes)</i>											
220707	Thverá I	1361	21.7	12.7	9.8	59.28 ± 0.70	4200 ± 95	-15.29	-9.29	-63.4	0.0077
230701	Thverá II	1446	20.9	11.3	9.9	57.00 ± 1.37	4516 ± 114	-14.73	-9.35	-65.3	0.0095
220708	Flókalundur	1362	36.9	13.0	10.0	45.10 ± 0.75	6396 ± 134	-13.91	-9.61	-62.9	0.0151
230702	Krossholt	1364	43.0	15.5	9.8	47.25 ± 0.76	6022 ± 129	-14.06	-9.20	-63.1	0.0201
230703	Tungumúli	1365	24.8	13.7	9.7	51.23 ± 1.36	5373 ± 213	-14.87	-9.04	-61.1	0.0085
230704	Norðurbotn I	1366	17.5	9.7	10.0	79.61 ± 1.31	1832 ± 132	-14.58	-9.65	-65.4	0.0075
230705	Norðurbotn II	1367	20.1	10.4	9.9	50.21 ± 2.24	5535 ± 358	-13.24	-9.61	-64.1	0.0094
230706	Sveinseyri	1368	20.1	10.4	9.5	62.09 ± 2.30	3829 ± 298	-12.64	-9.77	-66.0	0.0107
230707	Litli Laugardalur	1369	40.2	12.9	9.8	48.98 ± 0.93	5734 ± 153	-10.14	-9.92	-67.2	--
230708	Undir Hlíðinni	1370	12.5	10.9	9.5	63.39 ± 0.74	3662 ± 94	-13.45	-9.62	-64.8	0.0079
230709	Patreksfjörður	1371	3.8	8.1	9.2	87.55 ± 3.07	1068 ± 282	-12.16	-10.10	-69.6	--
230710	Mikldalur	1447	2.9	9.0	7.9	98.47 ± 1.68	124 ± 137	-13.28	-9.56	-65.6	0.0042
230711	Hnjótur	1372	6.0	8.1	9.2	88.20 ± 2.65	1009 ± 241	-13.94	-8.46	-57.8	0.0071

TABLE 1. (Continued)

Sample no.	Location	AAR no.	Temp (°C)	Σ CO ₂ (ppm)	pH	¹⁴ C concentration (pMC)	Conv. ¹⁴ C age (yr BP)	δ ¹³ C ‰ PDB	δ ¹⁸ O ‰ SMOW	δD ‰ SMOW	Boron (ppm)
<i>Geothermal Areas</i>											
140701	Laugarnes-19	1373	128.0	19.2	9.5	28.30 ± 0.94	10,140 ± 266	-9.02 (-5.86)	-9.65	-62.5	-
140702	Laugarnes-5	1374	127.5	17.1	9.4	--	--	-9.48	-9.91	-64.8	-
140703	Mosfellssveit-25	1375	93.4	22.5	9.6	35.53 ± 0.89	8312 ± 202	-13.45	-9.25	-62.7	-
140704	Mosfellssveit-11	1376	84.5	25.9	9.6	63.33 ± 1.25	3669 ± 158	-11.13	-9.16	-63.4	-
140705	Mosfellssveit-22	1377	85.7	25.7	9.6	41.33 ± 1.73	7098 ± 337	-10.65	-9.17	-63.8	-
901010f11	Mosfellssveit-23	177	75.6	--	--	52.38 ± 0.65	5195 ± 100	-12.97	-8.73	-61.9	-
140706	Mosfellssveit-31	1378	72.4	23.6	9.6	59.30 ± 1.22	4198 ± 165	-5.81	-8.78	-57.6	-
901010f10	Mosfellssveit-35	176	92.6	--	--	11.17 ± 0.28	17,610 ± 200	-7.37	-9.40	-64.5	-
T-9	Tap water, Rvík.	167	70.0	--	--	42.05 ± 0.63	6960 ± 120		-9.33	-63.3	-
<i>Calcite from Geothermal Drillings</i>											
608m	Mosfellssveit-23	1054				<0.9	>39,000	-4.07			
546m	Mosfellssveit-23	1055				<0.7	>40,000	-4.12			
1390m	Mosfellssveit-35	1052				<2.6	>30,000	-3.12			
1532m	Mosfellssveit-35	1053				<2.5	>30,000	-2.66			
948m	RV-30	167				<0.4	>45,000	-3.90			
<i>Blanks: Carbon Dioxide Waters from Snæfellsnes</i>											
220701	Lýsuhóll-1	1382	--	10.0	--	3.22 ± 0.22	27,600 ± 540	-3.10	--	-60.1	--
220701	Lýsuhóll-1	1381	--	50.0	--	2.25 ± 0.14	30,470 ± 500	-2.82	-8.79		--
220701	Lýsuhóll-1	1380	--	1400.0	--	2.15 ± 0.19	30,840 ± 700	-2.80	--		--
220702	Lýsuhóll-7	1385	--	10.0	--	7.01 ± 0.30	21,350 ± 340	-2.80	--	-58.7	--
220702	Lýsuhóll-7	1384	--	50.0	--	1.84 ± 0.15	32,100 ± 660	-2.49	-8.78		--
220702	Lýsuhóll-7	1383	--	1400.0	--	2.22 ± 0.17	30,600 ± 620	-2.70	--		--
220703	Ölkelda	1387	--	10.0	--	6.23 ± 0.31	22,300 ± 400	-3.50	--		--
220703	Ölkelda	1386	--	50.0	--	2.34 ± 0.19	30,150 ± 660	-3.00	-9.74	-64.1	--

fact that, in South Iceland, the water is sampled from springs, whereas water from the Northwest Peninsula is collected from shallow drill holes. Where it is possible to locate the recharge areas to the springs some 50 km away from the sampling point, the concentration drops to *ca.* 83 pMC. For warm water, the ^{14}C concentration varies from 45 to 80 pMC and from 51 to 87 pMC for the Northwest Peninsula and the Southern Lowlands, respectively.

Calcite (CaCO_3) formed by precipitation from the thermal water is a very common alteration mineral in Icelandic thermal systems. Four calcite crystals were analyzed from two boreholes in the Mosfellssveit thermal area and one crystal from a borehole in Reykjavík. The results, shown in Table 1, suggest that the calcite crystals have ^{14}C concentrations too low for ^{14}C dating (>30 ka BP), even though the geothermal water collected from the three boreholes have very different, but measurable ^{14}C apparent ages, ranging from 5200 to 17,600 BP.

Figure 2 shows that the ^{14}C concentration generally drops with increasing groundwater temperature. This correlation can be explained by dilution of atmospherically derived younger carbon with dead carbon dissolved from the basaltic rock as the water seeps into the ground and gains heat. The extent of dilution is expected to be governed by the initial carbon content of the surface water infiltrating the bedrock and the amount of rock dissolution, which increases with temperature.

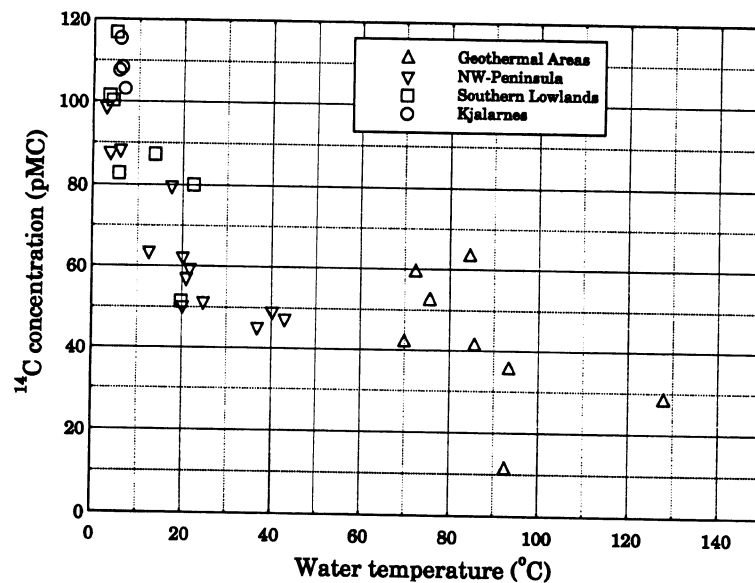


Fig. 2. Relation between temperature of groundwater and ^{14}C concentration

Since we found no clear correlation between ^{14}C concentration and $\delta^{13}\text{C}$ in the young groundwaters, it was no surprise to find that a simple, two-component (*i.e.*, rock and organic derived carbon) $\delta^{13}\text{C}$ model, to correct for dissolution of old carbon, resulted in strongly varying ^{14}C concentrations (100–700 pMC). Therefore, we tried to use the boron analysis, available for some of the water samples (Table 2), as according to Arnórsson, Andréðóttir and Sveinbjörnsdóttir (1993), it is possible to use the amount of the mobile element boron in geothermal waters as a leaching indicator, *i.e.*, its aqueous concentration is a measure of the amount of rock with which the water has reacted. We observe a negative correlation between the boron concentration and the ^{14}C concentration of the water samples (Fig. 3). The fit is hyperbolic, as expected if the boron concentration is a measure of dilution with ^{14}C -dead CO_2 .

TABLE 2. Boron Concentration in Groundwater as an Indicator of CO₂ Leached from Rock

Sample no.	Location	Boron, B _w (ppm) water	Cl _w (ppm) water	Boron, B _r (ppm) rock	Rock CO ₂ fraction X _R	¹⁴ C pMC meas.	¹⁴ C pMC corr.	δ ¹³ C ‰ PDB	Atm. CO ₂ fraction X _A	Org. CO ₂ fraction X _O	Atm. CO ₂ (ppm)	Org. CO ₂ (ppm)
<i>Kjalarnes (Springs)</i>												
190701	Hrisbrú	0*			0	103	103	-14.36	0.59	0.41	12.6	8.7
190702	Mógilsá	0*			0	108	108	-8.73	0.90	0.10	17.8	1.9
190703	Steypustöð	0*			0	108	108	-7.21	0.99	0.01	26.5	0.3
190705	Medalfellsvatn	0*			0	115	115	-14.61	0.58	0.42	13.9	10.2
<i>Southern Lowlands</i>												
<i>Springs</i>												
200701	Gaulverjabær	0*			0	117	117	-21.01	0.22	0.78	20.6	72.5
200702	Ingólfsfjall	0*			0	101	101	-10.05	0.83	0.17	18.1	3.7
200704	Ljósuár (04)	0.0030	5.5	0.0018	0.06	--	--	-8.83	0.78	0.12	9.9	1.3
200705	Ljósuár (05)	0.0030	5.5	0.0018	0.04	83	86	-12.78	0.63	0.33	11.7	6.1
200706	Hrúta	0.0036	5.5	0.0024	0.06	100	106	-11.04	0.71	0.23	12.2	4.0
<i>Drill Holes</i>												
200707	Gýgjarhólskot	0.0075	10.5	0.0052	0.04	80	84	-17.42	0.37	0.59	17.9	28.4
200709	Tungufell	0.0039	8.4	0.0020	0.02	87	89	-16.61	0.44	0.54	15.6	19.1
<i>Northwest Peninsula (Drill Holes)</i>												
220707	Thverá I	0.0077	12.8	0.0049	0.16	59	71	-15.29	0.35	0.49	4.5	6.2
230701	Thverá II	0.0095	12.6	0.0068	0.25	57	76	-14.73	0.28	0.47	3.1	5.3
220708	Flókalundur	0.0151	13.4	0.0123	0.39	45	74	-13.91	0.16	0.45	2.0	5.9
230702	Krossholt	0.0201	17.4	0.0165	0.44	47	85	-14.06	0.09	0.47	1.4	7.2
230703	Tungumúli	0.0085	12.7	0.0057	0.17	51	62	-14.87	0.36	0.47	5.0	6.4
230704	Norðurbotn I	0.0075	14.2	0.0043	0.19	80	98	-14.58	0.36	0.45	3.5	4.4
230705	Norðurbotn II	0.0094	13.7	0.0064	0.26	50	68	-13.24	0.35	0.39	3.7	4.0
230706	Sveinseyri	0.0107	14.3	0.0076	0.30	62	89	-12.64	0.33	0.36	3.4	3.8
230708	Undir Hlíðinni	0.0079	11.0	0.0055	0.21	63	80	-13.45	0.40	0.39	4.3	4.3
230710	Miklidalur	0.0042	15.6	0.0006	0.03	98	101	-13.28	0.62	0.35	5.6	3.2
230711	Hnjótur	0.0071	22.1	0.0021	0.11	88	99	-13.94	0.49	0.40	4.0	3.3

*Boron values assumed

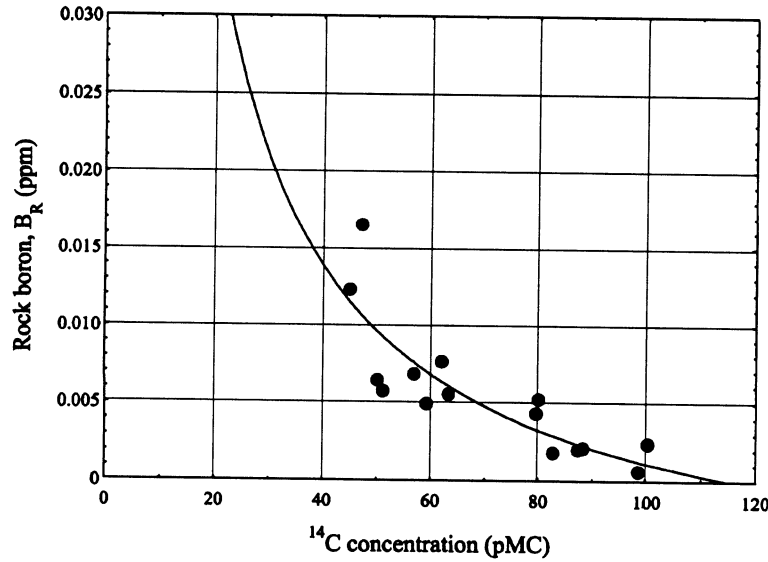


Fig. 3. Relation between boron concentration of groundwater and ^{14}C concentration. The fit is hyperbolic as expected if the boron concentration is a measure of dilution with ^{14}C -dead CO_2 .

We propose, therefore, that the boron concentration may be taken as a measure of the amount of dead CO_2 in the groundwater leached from the rock. Accordingly, we have calculated the ^{14}C dilution, assuming the typical concentrations of 1.2 ppm boron and 500 ppm CO_2 for the basaltic bed-rock in the Northwest Peninsula (Arnórrsson and Andréðdóttir 1995). The concentration of leached CO_2 in the water sample is calculated as

$$\text{ppm}(\text{CO}_2, \text{leached})_{\text{WATER}} = \text{ppm}(\text{B}, \text{leached})_{\text{WATER}} \times \text{ppm}(\text{CO}_2)_{\text{ROCK}} / \text{ppm}(\text{B})_{\text{ROCK}} . \quad (1)$$

We calculate the CO_2 fraction derived from the rock as

$$X_R = \text{ppm}(\text{CO}_2, \text{leached})_{\text{WATER}} / \text{ppm}(\text{CO}_2, \text{total})_{\text{WATER}} . \quad (2)$$

Accordingly, corrected pMC values are calculated from the measured pMC values as

$$\text{pMC}_{\text{corr}} = \text{pMC}_{\text{meas}} (1/(1-X_R)) . \quad (3)$$

Here we assume that the rock-derived CO_2 component contains no measurable ^{14}C . Dilution-corrected ^{14}C concentrations (pMC_{corr}) are given in Table 2, representing the atmospheric and organic soil carbon components of the groundwater, where influence of rock-derived CO_2 (no ^{14}C) has been eliminated. Figure 4 illustrates the relative success of this boron-based correction, as the ^{14}C results are more uniform and closer to the expected modern level after the correction is applied. We can then use these values to estimate the absolute ^{14}C ages of the groundwater.

We can use the calculated values of the rock-derived carbon X_R to determine the CO_2 fractions derived from the atmosphere (X_A) and organic material (X_O):

$$X_A + X_O = 1 - X_R \quad (4)$$

or

$$X_O = (1 - X_R) - X_A . \quad (5)$$

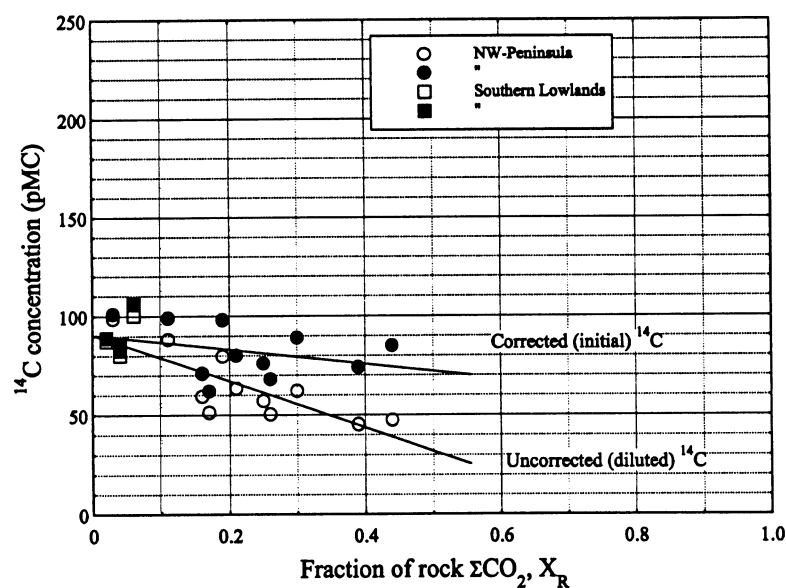


Fig. 4. Relation between boron-based corrected pMC values and the calculated fraction (X_R) of carbon dissolved from the rock

If a substantial fraction of the carbon entering the water has precipitated as calcite, the X_R value in equation (2) is overestimated and X_A and X_O correspondingly underestimated. We now use the measured $\delta^{13}\text{C}$ values (δ_m). By assuming the standard atmospheric $\delta^{13}\text{C}$ value as -7‰ (δ_A), organic $\delta^{13}\text{C}$ value as -25‰ (δ_O) and $\delta^{13}\text{C}$ values for basaltic rock as -4‰ (δ_R), which is the typical value for calcite in basaltic rock in Iceland, we can express the measured δ_m as

$$\delta_m = X_A \delta_A + X_R \delta_R + X_O \delta_O \quad (6)$$

Inserting the right side of equation (5) and rearranging, we obtain

$$X_A = (\delta_m - \delta_O + X_R(\delta_O - \delta_R)) / (\delta_A - \delta_O) \quad (7)$$

The atmosphere-derived CO_2 (X_A) and organics-derived CO_2 (X_O) are given in Table 2, both as fractions and absolute concentrations (ppm). Figure 5 shows the calculated concentrations of atmospheric and organics-derived carbon *versus* calculated fraction (X_R) of carbon dissolved from the rock. The results serve to explain why a two-component (*e.g.*, rock/organic) model is not adequate, as there are significant fractions of three components: rock, organics- and atmosphere-derived carbon. We note that the organic and atmospheric concentrations of carbon in the Northwest Peninsula samples are uniform despite the considerable range (20–70%) in X_R . For the spring samples, the atmospheric carbon concentration is somewhat higher than the organic concentration, whereas the organic-carbon concentration of the drill hole samples from the Southern Lowlands is very high, as expected, because this is an agricultural area.

DISCUSSION

Cold and Warm Groundwater

The pH of pure rainwater in equilibrium with the CO_2 of the atmosphere at 25°C is close to 5.7. Most of the water samples we collected for this study have a pH in the range of 9 to 10, typical values for

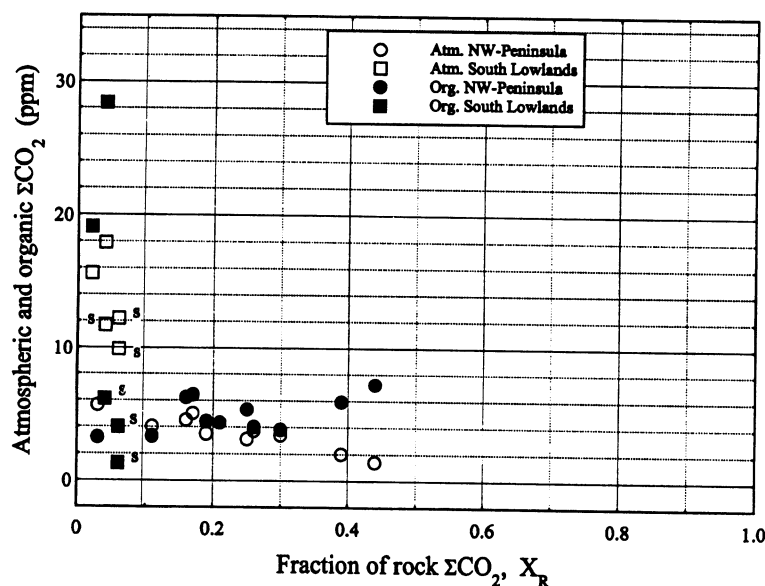


Fig. 5. Relation between the concentration of atmospheric and organic-derived carbon vs. calculated fraction (X_R) of carbon dissolved from the rock. Data points from springs are denoted by S.

groundwaters that have reacted substantially with the basaltic rock. The pH increase is the result of hydrolysis of silicates. On the other hand, all samples from Kjalarnes, one from the Southern Lowlands (Gaulverjabær) and one from the Northwest Peninsula (Miklidalur) have $\text{pH} < 8$, which is typical for shallow and non-equilibrated cold water (Arnórsson 1983). Most of the water samples are saturated with calcite (Fig. 6), in accordance with Ellis (1970) and Arnórsson (1978), who have shown that geothermal reservoir waters are always close to saturation with calcite, whereas cold groundwaters, and especially surface waters, tend to be strongly undersaturated.

For the drill-hole samples, we observed a clear linear relation between the $\delta^{13}\text{C}$ values and the calculated fraction (X_R) of carbon dissolved from the rock, based on boron analyses (Fig. 7). The $\delta^{13}\text{C}$ values increase with increasing X_R , and for $X_R = 1$, the line extrapolates to $\delta^{13}\text{C} = -5\text{‰}$, similar to the typical $\delta^{13}\text{C}$ value of calcite in basaltic rock. Four samples fit the line poorly. Two of them (Flókalundur and Krossholt) are from areas with unusually high vegetational cover, explaining their low $\delta^{13}\text{C}$ values. The third (Miklidalur) has the lowest X_R of the Northwest Peninsula samples. It has a character of a non-equilibrated cold water ($\text{pH} = 7.9$), showing a high atmospheric component and a less negative $\delta^{13}\text{C}$ value. The fourth sample (Hnjótur) is more difficult to explain and needs further study. Samples from springs (Ljósuár and Hrútá) have reacted with the atmosphere and show less negative $\delta^{13}\text{C}$ values.

As mentioned above, the boron-based corrected pMC values (Table 2) are shown in Figure 4 in relation to the calculated fraction (X_R) of carbon dissolved from the rock. The corrected values lie in the range 60 to 110 pMC. In contrast to the original values (45–100 pMC), also shown in the figure, the corrected values exhibit only a weak correlation with X_R . We take this as an indication that boron is indeed a good indicator of the amount of CO_2 leached from the rock. In fact, if, as a fitting parameter, we assume $\text{ppm}(\text{CO}_2)_{\text{ROCK}} = 600$ instead of 500 in Equation 1, the correlation disappears entirely.

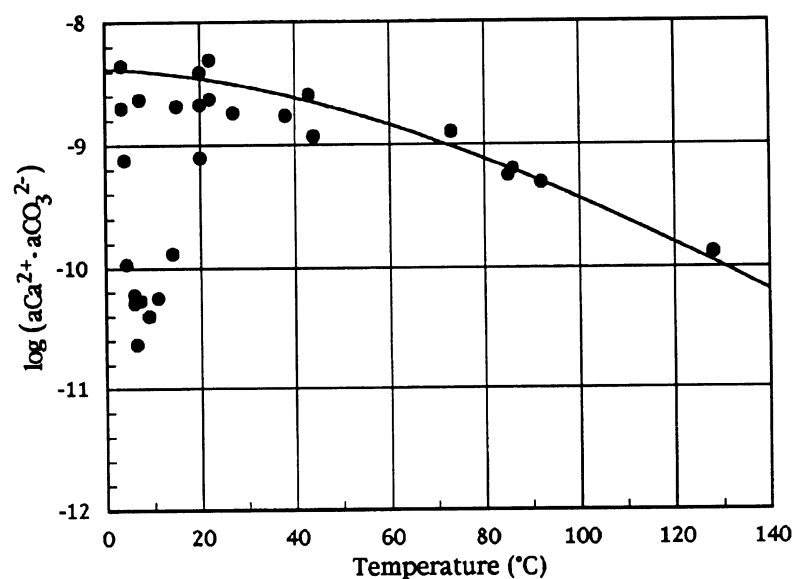


Fig. 6. Relation between temperature and ion activity product of Ca^{2+} and CO_3^{2-} of the water samples. The calcite saturation curve is shown for comparison.

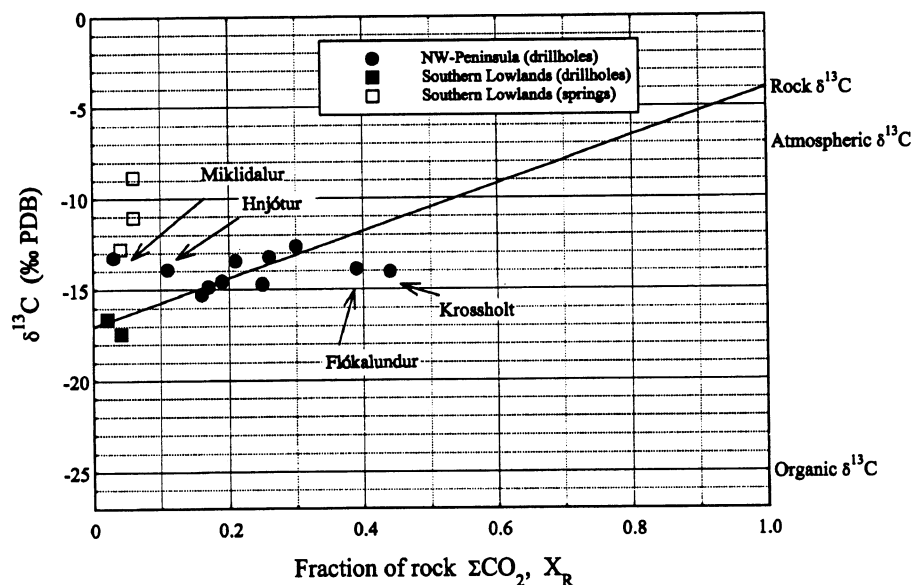


Fig. 7. Relation between $\delta^{13}\text{C}$ and the calculated fraction (X_R) of carbon dissolved from the rock

All of the samples from the Northwest Peninsula were taken from boreholes. Most of the samples were warm (20–40°C) and their corrected pMC values ranged from 60–100, corresponding to a water age from about 4000 BP to modern. For 3 of the 4 cold water samples (3–12°C) results of boron analyses are available (Table 2). One of the samples shows corrected ^{14}C concentration of *ca.* 80 pMC, corresponding to an apparent water age of 2000 BP, whereas the remaining two show mod-

ern levels of *ca.* 100 pMC. Since we expected all four samples to be close to modern, the boron correction seems to be too low in one case.

The samples from the Southern Lowlands show similar results. The local spring sample (Hrúta) gives a modern, bomb-influenced ^{14}C value of 110 pMC after correction, whereas the borehole samples and the spring sample from a distance source show corrected ^{14}C concentration of *ca.* 90 pMC. This corresponds to a water age of *ca.* 1000 BP, which, according to hydrological considerations, could well be the true residence time for the samples.

We have no boron data for the Kjalarnes samples and two of the Southern Lowland samples (Gaulverjabær and Ingólfssjall). All of these samples show modern, bomb-influenced ^{14}C levels, from 101–117, as expected. Assuming no boron in these samples (*i.e.*, $X_R = 0$), we calculated fractions of atmospherically derived and organic carbon in the water (Table 2). The fraction of calculated organic carbon varies from 0.01–0.78, in qualitative agreement with the different plant cover and hydrology of the areas.

Geothermal Water

Geographically, the Mosfellssveit low-temperature geothermal area can be divided into the Helgadalur field and the South Reykir field. It is clear from Table 1 that the geothermal waters fall into three categories: 1) thermal water from well 35, which is in the Helgadalur field, with apparent ages of *ca.* 17,600 BP; 2) thermal water from wells 25 and 22 in the field of South Reykir, with apparent ages of *ca.* 8000 BP; and 3) thermal water from wells 11, 23, 31 in the field of South Reykir with apparent ages of *ca.* 4000 BP. These data suggest a distinct difference in the ^{14}C concentration of the thermal water circulating in the area, and agree with Sveinbjörnsdóttir's (1988) suggestion, based on oxygen and hydrogen isotopic data, that the Mosfellssveit thermal water is oldest within the Helgadalur field and youngest in the southernmost South Reykir field. The present ^{14}C results on thermal water indicate that ^{14}C dating may be useful in estimating relative age differences of thermal water within a particular geothermal area. The results also encourage further measurements on thermal water from numerous boreholes in the Mosfellssveit area (*ca.* 40) to obtain a fuller picture of the carbon isotopes and to estimate their usefulness in mapping groundwater circulation. ^{14}C concentrations of calcite crystals that have precipitated from the thermal water are, on the other hand, too low for ^{14}C dating, indicating that calcite crystals and the associated thermal waters are in disequilibrium with ^{14}C .

CONCLUSION

Our results show that boron concentrations of water samples can be used successfully to indicate leaching, *i.e.*, the aqueous concentration of boron is a measure of the amount of rock with which the water has reacted. By assuming that the ratio of boron to CO_2 is the same in rock and groundwater, one can correct for the contribution of rock-derived carbon in groundwater. When we apply this correction, the ^{14}C values for the cold and warm water samples lie in the range 60–110 pMC, which accords with the estimated residence time of the groundwater. In some instances, our boron based correction may be too low. Future research will aim at further investigation using a fuller data set and performing tritium analyses.

After having calculated the fraction of carbon (X_R) dissolved from the rock, based on the boron analyses, and by using the measured $\delta^{13}\text{C}$ values, we calculated the CO_2 fractions derived from the atmosphere (X_A) and organic material (X_O) by using the standard $\delta^{13}\text{C}$ values for the atmosphere (-7‰), organic material (-25‰) and basaltic rock (-4‰). The results agree well with the general hydrology and plant cover of the areas.

For borehole samples, we observe a clear relation between the $\delta^{13}\text{C}$ values and the calculated fraction (X_R) of carbon dissolved from the rock, based on boron analyses. The $\delta^{13}\text{C}$ values increase with increasing X_R , and when $X_R = 1$, $\delta^{13}\text{C} = -5\text{‰}$, similar to the typical $\delta^{13}\text{C}$ value of calcite in basaltic rock. Water from springs has reacted with the atmosphere and shows less negative $\delta^{13}\text{C}$ values.

The results from geothermal systems indicate that it is possible to use ^{14}C in the geothermal water to estimate relative age differences of thermal water within a particular geothermal area.

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