

Meteoric water-basalt interactions. II: A field study in N.E. Iceland

SIGURDUR R. GISLASON* and HANS P. EUGSTER

Department of Earth and Planetary Sciences, Olin Hall, The Johns Hopkins University, Baltimore, MD 21218, U.S.A.

(Received October 7, 1986; accepted in revised form July 27, 1987)

Abstract—The compositions of rain, snow, melt, spring and geothermal waters from the rift zone of N.E. Iceland can be explained by seaspray addition, chemical fractionation at the seawater-air interface, burning of fossil fuel, farming activities, purification by partial melting of snow and ice, dissolution of basalts and buffering by alteration minerals. The dissolution of the rocks appears to be incongruent. During solute acquisition, spring compositions move through the stability fields of kaolinite and smectite to the laumontite and illite fields. All but four of the springs are undersaturated with respect to calcite. Silica concentrations are compatible with the solubility of basaltic glass. The reactions reflected in the spring waters appear to have taken place sealed off from atmospheric CO₂ after initial saturation.

The geothermal waters which are recharged by the spring waters are depleted in Mg and Ca but enriched in carbon and sulfur with respect to dissolution of primary rocks. Expressions are derived relating dissolution rates of rocks, age of groundwaters, physical properties of groundwaters and mass transfer. The characteristic rock particle radii in the cold water aquifers range from 0.2 to 2 cm and the characteristic crack openings are of the order 0.04 to 0.4 cm. Using laboratory studies on the Icelandic lavas as a guide, the residence times of the cold waters in the aquifers can be estimated at 60 days to 4 years. The average active surface area of the aquifers enclosing 1000 g of spring water is of the order of 0.6 to 6 m² and these 1000 g of water have reacted with 0.1 to 1 g of basaltic rocks. The same mass of thermal water has interacted with 100 to 300 g of unaltered rocks.

INTRODUCTION

THE INTERPRETATION OF the compositions of the Sierra Nevada springs by GARRELS and MACKENZIE (1967) inspired a variety of studies of solute acquisition and weathering reactions by meteoric waters. Most of these contributions, such as those of PAČES (1969, 1973), TARDY (1971), REEDER *et al.* (1972), REYNOLDS and JOHNSON (1972), DREVER (1971), MILLER and DREVER (1977), WHITE *et al.* (1980), CRERAR *et al.* (1981), ANTWEILER and DREVER (1983), FRAPE *et al.* (1984) have dealt with granitic, rhyolitic, metamorphic and mixed terranes.

Ultrabasic waters were investigated by BARNES and O'NEIL (1971), BARNES *et al.* (1978) and NESBITT and BRICKER (1978). In contrast, the interaction of basalts with meteoric waters has received far less attention. HAY and JONES (1972) defined weathering reactions of basaltic tephra in Hawaii and CHESWORTH *et al.* (1981) analyzed a basalt weathering profile in France. Geothermal waters of meteoric origin associated with basaltic rocks have been studied by ELLIS and MAHON (1964, 1977), ARNASON (1977), ARMANNSSON *et al.* (1982) and ARNÓRSSON *et al.* (1983a,b).

The alteration of basalt by seawater has received much attention during the last decade. Discovery and study of submarine hydrothermal systems (*e.g.* CORLISS *et al.*, 1979; EDMOND *et al.*, 1979; EDMOND, 1980; EDMOND and VON DAMM, 1983; VON DAMM *et al.*, 1985) in conjunction with laboratory experiments on seawater-basalt systems (BISCHOFF and DICKSON, 1975;

HAJASH, 1975; BISCHOFF and SEYFRIED, 1978; MOTTLE and HOLLAND, 1978; SEYFRIED and MOTTLE, 1982; MOTTLE, 1983) have radically changed our understanding in at least three important areas: The significance of seawater circulation to the alteration of the oceanic crust, the importance of basalt alteration for the abundance of major and minor seawater solutes and the significance of seawater dominated hydrothermal systems for ore deposition.

These studies, however, deal largely with bulk chemical changes. Dilute meteoric waters respond more readily than does seawater to dissolution and precipitation reactions and thus they can be used as geochemical probes to define the nature of such reactions. N.E. Iceland provides a unique opportunity to study solute acquisition by meteoric waters in a basaltic terrane which is unpolluted, and sparsely vegetated. Such a study involves sampling and analysis of rain, snow, melt water, cold springs, hot springs and geothermal fluids, which have been derived from meteoric inflow. These data allow us to define processes of solute acquisition, saturation states of the waters with respect to primary and alteration minerals, reaction paths, reaction progress and mass transfer. Equations can then be derived which relate residence time to active surface area, characteristic rock particle radii, characteristic crack widths and hydraulic conductivities of aquifers. In a parallel study, recent basalt flows from the Krafla caldera were subjected to dissolution experiments under a variety of laboratory conditions and dissolution rates were determined (GISLASON and EUGSTER, 1985, 1987). These rates can be used to link chemical and hydraulic information on the N.E. Iceland groundwater system, the system responsible for recharge of the Krafla geothermal field.

* Present address: Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavik, Iceland.

GEOLOGY AND CLIMATE OF THE N.E. ICELAND RIFT ZONE

The neovolcanic or rift zone of N.E. Iceland (SAEMUNDSSON, 1974; BJÖRNSSON *et al.*, 1977, 1979) represents the boundary between the American and European plates. It is characterized by several fault and fissure swarms, each passing through a central volcano (Fig. 1). Geothermal systems are associated with the central volcanoes and sometimes the nearby fissure swarm. The rift zone borders on rocks older than 0.7 m.y. to the E and W, the Arctic Ocean in the N and the Vatnajökull glacier in the S. The predominant rock type is basaltic in composition—olivine tholeiite—with some minor acid and intermediate rocks associated with the central volcanoes (SIGVALDASON, 1967; JAKOBSSON, 1972; SIGURDSSON and SPARKS, 1981; GRONVOLD and MAAKIPAA, 1978). The Upper-Pleistocene–Holocene volcanic rocks fall into three types with regard to structure and morphology. Extensive subareal lava flows erupted during interglacial periods and glacial erosion has removed their surface features and exposed their coarser-grained interiors. To the second type belong subglacial pillow lavas and hyaloclastite rocks. These rocks generally dip gently towards the center of the rift zone. The third group are the post-glacial lava flows which cover a considerable part of the rift zone. These lava flows have rugged and permeable surfaces which trap precipitation, allowing no surface run-off (see Fig. 2). Hence surface run-off is confined to areas free of post-glacial lavas. Some sedimentary rocks of volcanic origin, mainly basaltic in composition, are present in the form of tillites and wind-blown sand from the glacial outwash planes in the south.

Precipitation ranges from 400 to 1200 mm per year in the zone north of the glacier, but reaches 4000 mm per year on

the middle part of the glacier. The average temperature in the rift zone is -4 to -8°C in January and 4 to 10°C in July (EYTHÓRSSON and SIGTRYGGSSON, 1971).

Groundwater paths in the rift zone have been traced by deuterium analyses (ARNASON, 1976, 1977). Arnason concluded that the source of groundwater flow into the geothermal systems of Krafla and Namafjall could extend as far south as the Vatnajökull glacier. According to TOMASSON *et al.* (1975), large aquifers are far more likely to exist at lava-hyaloclastite contacts than within lavas or hyaloclastites.

The cold springs are usually confined to the base of the post-glacial lava fronts at 300 to 900 meters above sea level, with their major source areas at elevations of 1500 to 2000 m (ARNASON, 1976). Average hydraulic gradient is 0.07 to 0.01 where springs closest to the glacier are located in the steepest gradient. Hydraulic conductivity k of post-glacial lava was found to be in the range of 1 to 10 cm/sec (TOMASSON, 1971).

The geology, rock compositions, alteration mineralogy and hydrology of the Krafla area have been described in detail (THORARINSSON, 1979; BJÖRNSSON *et al.*, 1977, 1979; EINARSSON, 1978; STEFANSSON, 1981; KRISTMANNSDÓTTIR, 1978; STEINTHORSSON and SVEINBJÖRNSDÓTTIR, 1981; GRONVOLD and MAAKIPAA, 1978; among others). The Krafla volcano is a resurgent caldera located on a fissure swarm (Fig. 1). An elongated high temperature field exists within the caldera and surface activity is associated with a series of explosion craters. The area has been drilled for steam. The rocks at depth consist of hyaloclastites, olivine tholeiite lavas and some intrusive rocks of tholeiitic and rhyolitic composition. The abundance of intrusions increases with depth. Characteristic alteration minerals change from smectite-zeolite near the surface to chlorite-actinolite at depth (1 km). The chemistry of the thermal fluids has been analyzed and interpreted by

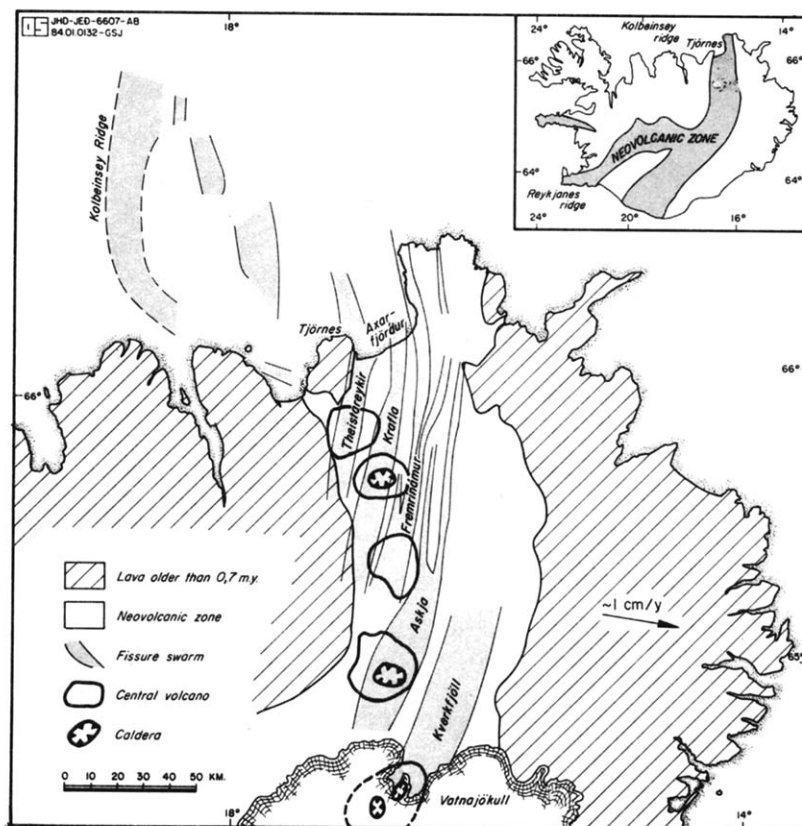


FIG. 1. Rift zone, central volcanoes and associated fissure swarms in northern Iceland (from BJÖRNSSON, 1985).

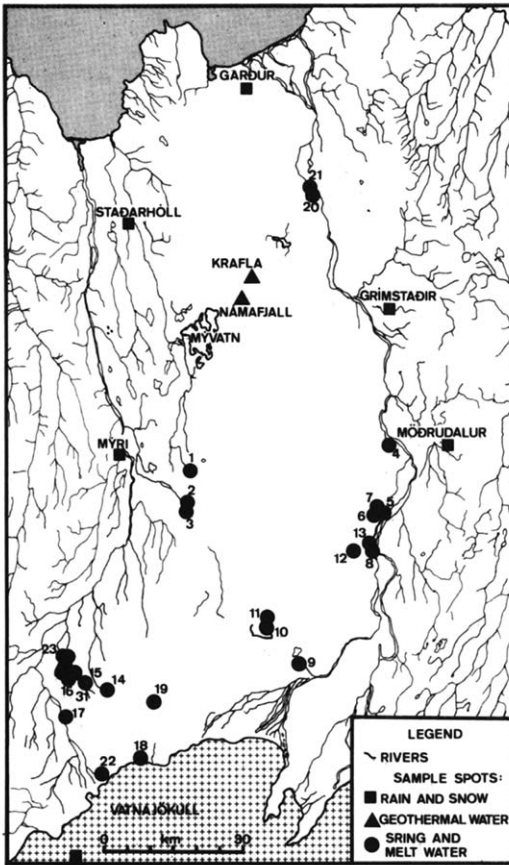


FIG. 2. Sampling localities and surface drainage in and outside the rift zone in northern Iceland.

ARNORSSON (1978), ARNORSSON *et al.* (1983a,b), ARMANNSSON *et al.* (1982) and GISLASON and EUGSTER (1984).

COMPOSITIONS OF RAIN AND SNOW

In order to define the solute input into surface waters from atmospheric precipitation, five sampling stations were operated during 1982 and 1983 (see Fig. 2). Samples were collected once a month during the summer months. Sampling procedures and analytical techniques (Table 1) have been discussed by GISLASON (1985) and GISLASON and RETTIG (1986). Average values of eight samples for the five stations are listed in Table 2. In addition, a 4 m thick layer of snow representing precipitation from the winter of 1982 was collected on the Vatnajökull glacier (see Fig. 2). The average composition of the melted snow is also listed in Table 2.

Solute concentrations decrease with increasing distance from the Arctic Ocean, indicating seaspray as the principal source. The snow sample represents winter precipitation and has a higher aerosol content. This can be accounted for by higher winter winds and by the fact that aerosol removal by snow is much more efficient than by rain (GRAEDEL and FRANEY, 1975). Rain and snow solutes can be accounted for by mixing pure water with seawater in the ratio of about 1 to

10,000. Amounts in excess of those expected from a seawater source are present for silica, calcium, potassium and sulfate. These could be due to dissolution of basaltic dust caught in the collector, fractionation of seaspray (CHESSELET *et al.*, 1972), burning of fossil fuel, magmatic gases, biogenic input or farming activities.

COMPOSITIONS OF SPRING WATERS

The compositions of four meltwaters and 27 springs collected in July, 1982 and August 1983 are listed in Table 3 and their locations are plotted in Fig. 2. Except for 10 and 17, all springs are dilute and cold. Sample 10 is from the Askja caldera lake and has been affected by geothermal fluids. Similar processes must have modified spring 17, which has a temperature of 34.2°C. Springs 20 and 21 are only 30 km from the Arctic Ocean and their somewhat unusual compositions can be accounted for by higher aerosol contents.

In Fig. 3, solutes are plotted against chloride. Also shown is the seawater mixing line and two lines labelled basalt, which start from the average chloride values for rain and snow precipitation. The basalts of the N.E. Iceland rift have an average chloride content of 193 ± 68 ppm (SIGVALDASON and OSKARSSON, 1976). Congruent dissolution would produce a water with the following weight ratios: $\text{Na}/\text{Cl} = 95$, $\text{K}/\text{Cl} = 24$, $\text{Ca}/\text{Cl} = 340$, $\text{Mg}/\text{Cl} = 175$, $\text{SO}_4/\text{Cl} = 6$ and $\text{CO}_2/\text{Cl} = 11$ (CARMICHAEL, 1964; HEIER *et al.*, 1966; JAKOBSSON, 1972; SIGVALDASON and OSKARSSON, 1976; GUNNLAUGSSON, 1977). These are the ratios shown as dashed lines in Fig. 3. The spread of the lines indicates an uncertainty of one standard deviation.

Figure 3 shows that the major cations are acquired largely from dissolution of basaltic material by runoff which already contains 1–2 ppm Cl^- . The melt waters sampled in July and August are purified precipitation. This is due to the partial melting of snow and ice in early spring, which causes an enrichment of solutes in melt waters, leaving behind purified snow and ice (JOHANNESSEN and HENRIKSEN, 1978; COLBECK, 1981). During their passage through the groundwater system, these waters pick up chloride more rapidly than they would be congruent dissolution of basaltic glass. This chloride selectivity is especially noticeable with reference to Mg, Ca, K and, although not shown on Fig. 3, SiO_2 . This could be caused by selective leaching of Cl from glassy rocks and interstitial glass in crystalline basalts, since crystallization of silicates and oxides will increase the chloride content in the residual glass. Alternately, it could be caused by precipitation of alteration minerals containing Si, Al, Fe, Mg, Ca and K. The latter mechanism can account for the composition of warm spring 17 with smectites, zeolites and calcite the likely alteration minerals.

In order to define the nature of the dissolution reactions, P_{CO_2} has been calculated from field measurements of pH and alkalinity and the results are plotted against pH in Fig. 4. Initially, waters are close to saturation with respect to atmospheric CO_2 , but many

Table 1. Analytical Methods

	Analytical Method	Reference
pH	Measurements were done in the field at the temperature of the springs, using a portable pH meter, a combination glass electrode and three pH buffer solutions.	Gislason (1985) Gislason and Rettig (1986)
Si	Spectrophotometric, yellow silico-molibdic acid.	Gunnlaugsson and Arnorsson (1980)
Na	Atomic absorption spectrophotometry	Skougstad et al. (1979)
K	"	"
Ca	"	"
Mg	"	"
C	Alkalinity titration done in the field at the temperature of the springs using a portable pH meter, a combination glass electrode and 0.1 N HCl solution.	Gunnlaugsson and Arnorsson (1980)
SO ₄	Spectrophotometric, turbidimetrically.	Tabatabai (1974)
H ₂ S	Titration with 0.1 N (CH ₃ COO) ₂ Hg using dithizone as an indicator.	Archer (1955)
F	Ion sensitive electrode	Skougstad et al. (1979)
Cl	"	"

springs have a high pH and very low P_{CO_2} values. This indicates that water-rock interactions proceeded out of contact with the atmosphere and that there was no noticeable input of soil CO_2 as there is in more temperate climates. During the interaction essentially all available CO_2 is converted to HCO_3^- , balancing the cations released from the basaltic material. Further dissolution without mineral precipitation requires that H_4SiO_4 dissociates to $H_3SiO_4^-$ and H^+ and bicarbonate be converted to carbonate, increasing the pH. The only CO_2 -rich sample comes from the Askja caldera lake, where geothermal gases are discharged into the lake.

Some carbonate could be removed from the spring waters by calcite precipitation. Shown in Fig. 5 is the IAP, $a_{Ca^{2+}} \times a_{CO_3^{2-}}$, in the spring and melt waters and the equilibrium constant for the dissolution of calcite

as given by PLUMMER and BUSENBERG (1982). All but four of the waters are undersaturated with respect to calcite. Similar calculations, using WATEQF (PLUMMER *et al.*, 1984), indicate that with the exception of magnetite, the waters are also undersaturated with respect to the primary minerals olivine, plagioclase and Cpx.

The state of saturation of the spring waters with respect to silica phases indicates that all waters are supersaturated with respect to chalcedony, but undersaturated with respect to amorphous silica (Fig. 6). Both of these phases commonly occur in Icelandic geothermal systems. It is plausible that the silica contents of the cold springs are controlled by the silica activity of the basaltic glass. Assuming ideal solutions in the glass and the water, we can write

$$\begin{aligned} &(\mu_{SiO_2}^0)_{glass} + RT \ln (X_{SiO_2})_{glass} \\ &= (\mu_{SiO_2}^0)_{aq} + RT \ln (m_{SiO_2})_{aq} \end{aligned} \tag{1}$$

where X is the mol fraction of silica. Using pure silica glass and a hypothetical ideal one molal solution of aqueous silica at 25°C and 1 atm as standard states and data from ROBIE *et al.* (1978) and WALTHER and HELGESON (1977) yields

$$\log (m_{SiO_2})_{aq} - \log (X_{SiO_2})_{glass} = -3.00. \tag{2}$$

The chemical compositions of 12 basalts from the Askja-Krafla area give an average X of 0.54, hence

$$\log (m_{SiO_2})_{aq} = -3.27 \tag{3}$$

In order to extrapolate from 25°C to the actual spring temperatures the enthalpy of dissolution was assumed to be constant. Results are plotted in Fig. 6. The ob-

Table 2. Composition of Snow and Rain Waters in N.E. Iceland in ppm.

Station	pH	SiO ₂	Na	Ca	K	Mg	SO ₄	Cl
Saov	6.7	0.9	2.04	0.81	0.78	0.21	2.68	2.64
MYRI	5.5	0.5	0.74	0.20	0.19	0.08	1.03	0.91
Mördalur	5.1	0.7	0.66	0.40	0.24	0.10	1.63	1.01
Grimstadir	5.6	1.2	1.02	0.40	0.51	0.24	1.48	1.14
Staðarhóll	5.5	1.2	1.67	0.43	1.12	0.24	3.42	2.33
Gardur	5.7	0.5	2.55	0.38	0.41	0.32	2.32	3.15

4 mm long snow core collected by Helgi Bjornsson at 1620 m.a.s.l., 16°50' west and 65°30' north, Vatnajökull glacier.

pH measured in the laboratory.

Table 3. Composition of Melt* and Spring Waters in N.E. Iceland in ppm.

Sample #	C*	pH	SiO ₂	Na	Ca	K	Mg	SO ₄	Cl	F	CO ₂ ⁽¹⁾
SP 11*	0.5	6.15	0.6	.93	.22	.03	.07	2.2	.57	.02	1.2
SP 12*	8.5	7.00	3.6	1.48	1.02	.09	.18	0.2	.47	.02	3.3
SP 18*	0.3*	6.88	1.4	1.77	1.03	.11	.20	.20	.42	.02	6.7
SP 19*	0.0*	5.22	.4	.95	0.12	.02	.08	.96	.81	.02	3.0
SP 01	4.4	9.00	18.1	15.8	4.35	1.11	2.44	8.6	2.30	.28	35.6
SP 02	4.6	9.15	16.3	14.4	4.93	1.01	2.15	7.3	1.59	.26	30.0
SP 03	4.4	9.17	16.9	14.6	5.07	1.00	2.15	7.2	1.62	.25	31.0
SP 04	2.6	9.22	14.4	14.9	5.57	1.00	1.13	6.9	2.83	.20	29.6
SP 05	4.4	9.18	16.5	17.0	5.40	.86	2.17	8.8	2.70	.24	35.3
SP 06	5.4	9.26	18.2	17.4	5.58	.92	2.11	10.4	2.83	.24	32.7
SP 07	4.9	9.17	17.4	17.0	6.48	.85	2.78	14.6	2.87	.21	33.0
SP 08	6.2	8.82	17.4	22.6	5.06	1.01	2.39	10.9	3.15	.28	44.0
SP 09	6.9	8.88	22.2	20.2	5.54	1.67	2.71	16.2	3.23	.27	38.2
SP 10	5.2	7.73	93.2	127.5	74.1	9.5	21.8	400	20.18	.88	85.4
SP 13	4.4	9.10	17.8	19.2	5.38	.91	2.55	10.0	2.93	.26	39.6
SP 14	2.0	9.28	14.8	9.48	3.30	.72	1.98	2.7	1.53	.15	23.3
SP 15	2.6	9.13	15.4	9.31	3.39	.68	2.17	2.9	1.60	.15	24.2
SP 16	1.7	8.51	12.4	7.21	3.36	.45	1.95	2.5	2.10	.12	21.6
SP 17	34.2*	10.23/17*	45.5	37.3	1.27	.95	.04	11.2	3.41	.46	23.6
SP 20	6.1*	8.74	16.7	16.1	10.1	2.03	7.83	9.9	6.60	.16	66.0
SP 21	8.7*	8.66	20.7	20.2	9.68	2.38	8.95	9.7	6.18	.21	75.1
SP 22	7.2*	8.40	35	21.6	8.20	.94	10.4	21.0	2.2	.31	76.3
SP 23	4.2*	8.93	15	8.23	3.61	.45	1.72	2.6	1.8	.12	18.9
SP 24	3.1*	9.15	15	7.63	3.52	.42	1.70	2.5	1.7	.11	18.6
SP 25	3.9*	9.18	15	8.00	3.51	.41	1.66	2.4	1.7	.11	19.8
SP 26	3.9*	9.45	16	9.23	3.46	.44	1.50	2.3	1.8	.12	19.1
SP 27	2.8*	8.54	13	6.63	3.50	.34	1.70	1.7	1.8	.09	19.4
SP 28	2.0*	8.16	14	6.70	3.48	.43	1.96	2.3	1.7	.11	21.8
SP 29	2.3*	8.11	16	8.30	3.82	.58	2.36	3.1	1.6	.14	27.5
SP 30	2.8*	9.20	16	8.48	3.41	.54	2.10	2.7	1.5	.14	23.9
SP 31	2.3*	8.60	15	7.00	3.57	.43	1.96	2.5	1.7	.11	21.2

(1) Total dissolved carbon as ppm CO₂

served silica values fit this simple model well, indicating that SiO₂ may be determined by the silica activity of the basaltic glass. Perhaps silica is saturated with respect to an amorphous aluminum silicate precursor gel such as that described by EUGSTER and JONES (1968).

Activity diagrams can be used to interpret the chemistry of the spring waters with respect to alteration minerals. The most common low-temperature alteration minerals found in Iceland are Ca-rich zeolites (chabazite, scolecite, stilbite), smectites, celadonite, chalcedony and calcite (WALKER, 1960; KRISTMANNSDÓTTIR, 1982). The smectites are dominantly trioctahedral Fe and Mg types, but interstratification of smectites and illite also exist (KRISTMANNSDÓTTIR, 1978, 1982). The celadonite is commonly a potassium-rich illite but some of it appears to be mixed layer mineral of mica and smectite or chlorite (MEHEGAN *et al.*, 1982; KRISTMANNSDÓTTIR, 1982). With increasing temperature (>100°C), low temperature Ca-rich zeolites are replaced by laumontite and smectites become interlayered (KRISTMANNSDÓTTIR, 1982).

Activity diagrams are shown in Fig. 7 and 8. Locations of the stability field boundaries are dictated by the thermodynamic data and the idealized stoichiometry assigned to minerals, whose compositions in natural systems are variable. No thermodynamic data are available for the low temperature Ca-rich zeolites, so laumontite is used to represent these zeolites. The smectites used are idealized endmembers. Thermodynamic data were taken from HELGESON (1969), HELGESON *et al.* (1978), PARKER *et al.* (1971), HEMINGWAY and ROBIE (1977), WALTHER and HELGESON (1977), and CODATA (1976). All diagrams are drawn

at 25°C, a permissible simplification considering the many other uncertainties. Because of the idealized stoichiometry, stability field boundaries appear as single straight lines on the diagrams, whereas in reality these boundaries should be thought of as transition bands from one mineral to another due to the highly variable composition of the minerals (SPOSITO, 1985).

Figure 7 shows spring and melt waters superimposed on the mineral stability fields. Waters derived from melting snow fall within the gibbsite field, but all spring waters lie within the Ca-Smectite and laumontite fields. The two waters with the highest silica activity have been affected by geothermal activity (22 and 10). The log silica activity of all other spring waters is confined to a value close to -3.6. Hence, constant silica activity sections are shown in Fig. 8. The diagrams indicate that the spring waters evolve through the kaolinite and Mg-smectite fields towards the laumontite and illite fields in agreement with the observed alteration products.

In summary the reactions of the basalts with the spring waters take place sealed off from the atmosphere after initial atmospheric saturation. All primary minerals except magnetite have the capacity to dissolve. Mg smectites, laumontite and illite could precipitate from the more evolved waters. Silica concentration is controlled by the basaltic glass, or by a precursor gel. The most evolved waters are reaching saturation with respect to calcite. The order of saturation is chalcedony and Mg-smectite, then illite and laumontite and finally calcite. Sodium and chloride are the most likely major solutes to behave conservatively in the cold spring waters (0 to 10°C).

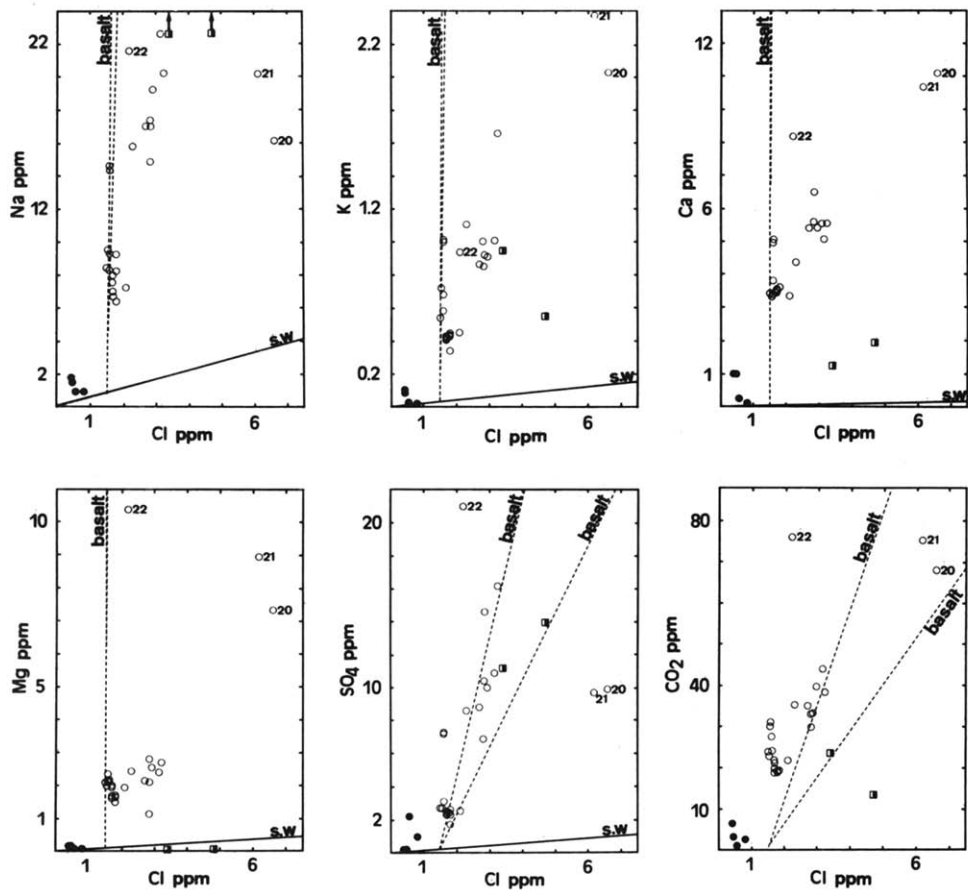


FIG. 3. Concentrations of major elements in melt waters (dots), cold springs (circles) and hot springs (half filled squares) plotted against the concentration of chloride. The dashed lines represent stoichiometric dissolution of basalts from N.E. Iceland, solid lines are sea water ratios. CO₂ stands for dissolved carbon species.

The spring compositions listed in Table 3 can be combined with the dissolution rates for the basalts of the N.E. Iceland rift zone as measured in the laboratory under conditions designed to mimic the natural meteoric water-basalt interaction (GISLASON and EUGSTER, 1987). This will permit estimates of the ages of the groundwaters and some of the aquifer properties, such as the active surface area in contact with one unit

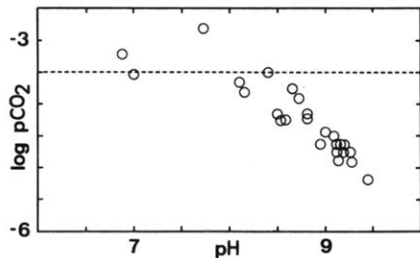


FIG. 4. P_{CO_2} versus pH of spring and melt waters. The pH and the partial pressure of CO₂ are measured and calculated respectively at the temperature of the springs. The reference line is atmospheric P_{CO_2} .

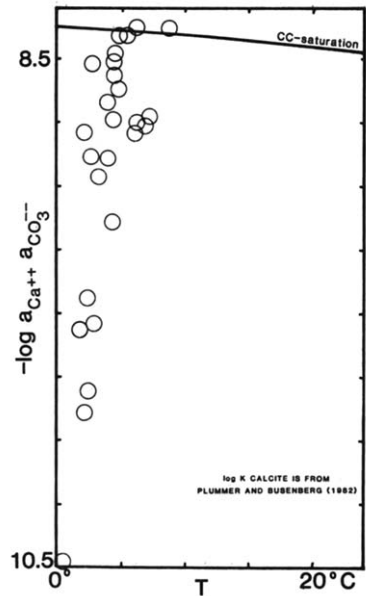


FIG. 5. The IAP for Ca²⁺ and CO₃²⁻ of the melt and spring waters vs. temperature. Calcite saturation curve is from PLUMMER and BUSENBERG (1982).

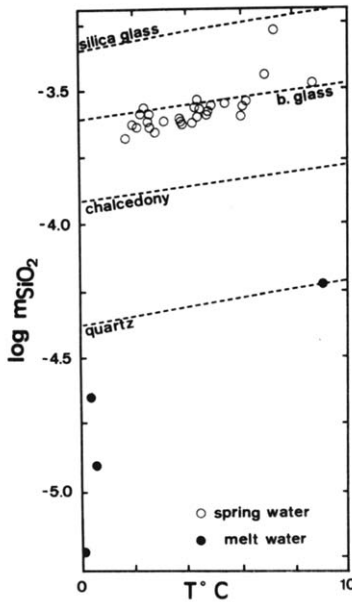


FIG. 6. Molality of the monomeric, undissociated, aqueous silica as a function of temperature for the spring and melt waters of N.E. Iceland. The curves show the solubility of pure silica glass, a glass with 0.54 mole fraction of silica (see text), chalcedony as given by ARNORSSON *et al.* (1983) and quartz as given by WALTHER and HELGESON (1977).

volume of water, active grain size of the rocks and diameters of the rock fractures.

AGE OF GROUNDWATERS AND PHYSICAL PROPERTIES OF THEIR AQUIFERS

The ages of groundwaters can be estimated by several methods, such as combining Darcy's law with an expression of continuity, decay of atmosphere-derived radionuclides, dissolution rates of rocks, the presence of man-made material in groundwater and the correlation of paleoclimatic indicators in waters with a known chronology of past climates (PAČES, 1973; ARNASON, 1976; CLAASSEN and WHITE, 1979; DAVIS and BENTLEY, 1982). The use of laboratory dissolution rates poses special problems. BERNER (1978), PAČES (1983), VELBEL (1985, 1986) have indicated that laboratory rate data are not directly applicable to natural settings because rates in synthetic systems may be several orders of magnitude faster. Reasons cited are differences in the properties of the mineral surfaces. In our case basaltic glass is the main solid which is dissolving and it is reasonable to assume that rate differences will be less severe not only because glass is easier to disaggregate but also because hyaloclastite aquifers are very porous, little soil is present and dissolution is faster than with more siliceous materials. Furthermore, aquifer properties extracted by combining hydrologic with chemical data have an uncertainty of at least one order of magnitude and probably more. Nevertheless, the approach is valuable and can be refined in future studies. In the meantime the assumption that the laboratory and field

dissolution rates are the same must be clearly kept in mind.

The equation for the conservation of mass in one dimension in distributed geochemical models can be written in terms of solute concentrations for a representative volume of homogeneous porous media (FREEZE and CHERRY, 1979).

$$\frac{\partial C_i}{\partial t} + \frac{\partial(C_i v)}{\partial x} - \frac{D \partial^2 C_i}{\partial x^2} = B \quad (4)$$

where C_i is the solute concentration in the pore fluid, v the fluid velocity (Darcy velocity divided by active porosity), D is the coefficient of hydrodynamic dispersion, t is time. The first term in Eqn. (4) represents the rate of change of the mass of solute in a fixed unit volume (cm^3) of porous media. The active porosity can be cancelled by assuming a homogeneous porous media. The second and third terms describe the net mass flux of solute into the unit volume by advection and dispersion, respectively. B stands for all sources and sinks for the solute under consideration including reactions between the fluid and rock surfaces. For a lumped geochemical reactor model we do not distinguish the spatial effects of advection and dispersion, and the mass conservation equation simplifies to

$$\frac{\partial C_i}{\partial t} = B \quad (5)$$

which in integrated form is

$$C = C_0 + Bt. \quad (6)$$

Dividing Eqn. (6) by the surface area of rocks (S) that encloses the unit volume (1 cm^3) of groundwater (cm^2/cm^3) gives,

$$Q = Q_0 + K_l t \quad (7)$$

where Q is the solute flux per unit surface area and K_l is the linear dissolution rate coefficient. Equation (7) is the classic linear dissolution rate expression (*e.g.* BERNER, 1981) and, Eqn. (6) can now be written in terms of the linear dissolution rate coefficient K_l , the surface area S , the concentration before encounter with

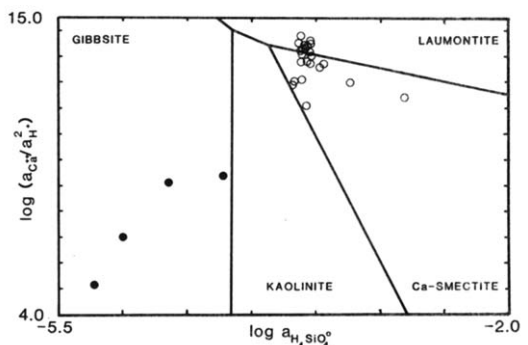


FIG. 7. Activity-activity diagram for the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at 25°C . Shown are melt waters (dots) and spring waters (circles) from N.E. Iceland (0 to 10°C).

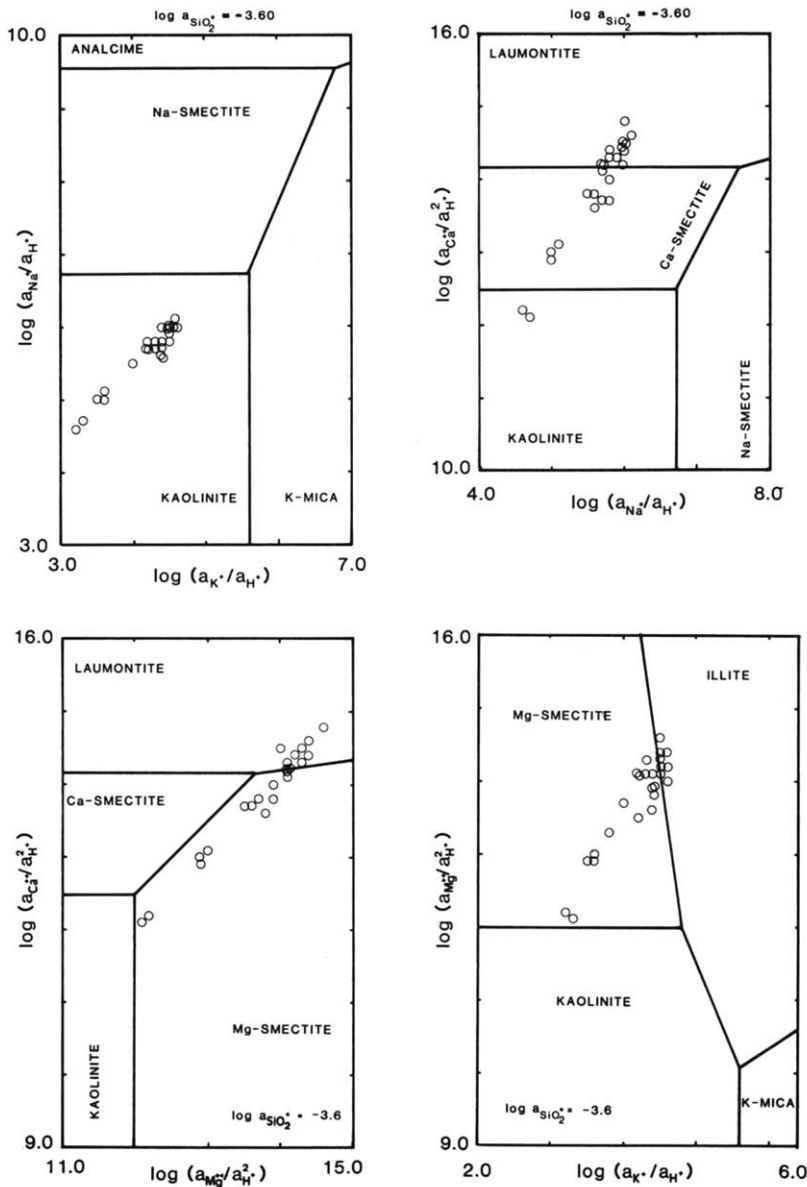


FIG. 8. Activity-activity sections through the system $\text{CaO-MgO-Na}_2\text{O-K}_2\text{O-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ at 25°C and a constant $\log \text{SiO}_{2(\text{aq})}$ molality of -3.60 . Spring water activities shown as circles. For thermodynamic data see text.

the rocks C_0 , and the concentration after interactions with the aquifer rocks. Solving for t yields,

$$t = \frac{C - C_0}{K_1 S} \tag{8}$$

The dissolution rate coefficient K_1 , can be dependent on temperature, pH, ionic strength and the velocity of the fluid. Above, it was assumed that there is no solute sink (precipitation), that after the water enters the aquifer there is no solute source other than dissolution of the aquifer and dispersion is minimal.

The surface area of rocks in contact with a unit volume of water is difficult to measure. One can write S in terms of variables which are easier to measure, for

example the distance between two smooth planes, representing the width of open fractures, or the average active porosity of an aquifer and the average radius of the grains in the same aquifer, assuming that the grains have the shape of spheres.

The surface area of two parallel planes in contact with a unit volume of water, written in terms of their distance, d , is,

$$S = \frac{2}{d} \tag{9}$$

Substituting in Eqn. (8) gives,

$$t = \frac{(C - C_0)d}{2K_1} \tag{10}$$

Alternatively, the surface area of rocks in contact with a unit volume of water can be written in terms of the average active porosity, n_0 and the average radius, r , of spherical grains in the aquifer:

$$S = \frac{V_r S_s}{V_s} \quad (11)$$

where V_r is the rock volume, without the pores, which contains one cm^3 of water. V_s and S_s are, respectively, the volume and surface of a sphere

$$V_r = \frac{1}{n_0} - 1 \quad (12)$$

and

$$n_0 = \frac{V_p}{V_r + V_p} \quad (13)$$

where V_p is the pore volume of a rock volume containing one cm^3 of water. Substituting Eqns. (12) and (13) into (11) gives

$$S = \frac{3}{n_0 r} - \frac{3}{r} \quad (14)$$

Substitution of Eqn. (14) into (10) yields,

$$t = \frac{(C - C_0)r}{3K_f(1/n_0 - 1)} \quad (15)$$

HYDRAULIC PARAMETERS AND CHEMICAL DATA

Equations (10) and (15) provide the link necessary for combining hydraulic with chemical data, the former in terms of open fractures with an average width d and the latter with respect to porosity formed by spherical mineral particles. The active porosity n_0 can be eliminated by solving Eqn. (15) together with the expression for the age of groundwaters given by DAVIS and BENTLEY (1982).

$$t = \frac{n_0 \Delta L^2}{k \Delta h} \quad (16)$$

where ΔL and Δh are the length and head drop of the flow path and k is the hydraulic conductivity. Assuming steady state flow, minimal dispersion and uniform hydraulic properties of the aquifer, Eqns. (15) and (16) yield,

$$t = \frac{\Delta L^2}{k \Delta h} \frac{(C - C_0)r}{K_f 3000} \quad (17)$$

The time-dependent Eqns. (8), (10), (15) and (16) can be interpreted by introducing the chemical data. To illustrate the approach, springs 23–31 in the SW of the Rift zone are used (see Fig. 2). Their recharge area has been defined by ARNASON (1976), and a possible flow path from the recharge area to the springs can be constructed. Assuming that the rocks are water saturated to the surface at the base of the glacier and at the elevation of the springs, estimates can be made for Δh and ΔL of the flow path. The chemistry of the springs is well defined (see Table 3). In order to define C_0 and C , an element must be chosen that is not lost

along the flow path by mineral precipitation or exchange on active surfaces and for which good dissolution rate constants are available for the aquifer rocks. Sodium is the obvious choice, although some loss is possible by sorption, adding a further uncertainty to these order-of-magnitude calculations. K_f for sodium at the average temperature of the springs (3°C) can be calculated from the dissolution rate constants at 25°C and the activation energy for basaltic glass given by GISLASSON and EUGSTER (1987). The linear dissolution rate coefficient for sodium ion in basaltic glass was shown to be independent of ionic strength at a pH from 7 to 9. The average hydraulic conductivity of postglacial lavas in Iceland ranges from 1 to $10 \text{ cm}^3/\text{cm}^2 \text{ sec}$ (TOMASSON, 1971), within the range for gravel (see FREEZE and CHERRY, 1979), and about five times higher than the value suggested for unweathered primitive Hawaiian basalts by MINK and LAU (1980). The hydraulic gradient calculated for the flow path is 0.015 and the average linear velocity, v , assuming 0.2 active porosity (PALSSON *et al.*, 1984), is 0.08 to 0.8 cm/sec . The Peclet number can be used as a criterion for the distance over which advective transport and molecular diffusion are equally important (BERNER, 1980). The migration distance where advective and diffusive transports are of similar importance is 0.01 to 1 microns. In other words, no significant diffusive zone is present close to the surfaces of the rocks. Hence the experimental dissolution rate coefficients measured by GISLASSON and EUGSTER (1987) under highly advective conditions can be applied to the groundwater system of N.E. Iceland. The residence time t of the waters in the subsurface can be calculated from Eqn. (16) using the maximum and minimum values for the hydraulic conductivity (1 to 10 cm/sec) and assuming an active porosity of 0.2, the average of the dense, vesicular and scoriaceous parts of basaltic lava flows (PALSSON *et al.*, 1984). The calculated residence time ranges from 40 to 402 days. These times can be used in Eqn. (10) to calculate average fracture width or in Eqn. (15) to obtain the characteristic radii of spherical aquifer grains, and the active surface area enclosing a unit volume of water (Eqn. 8). The results are as follows:

t: 402 to 40 days ($10^{7.54}$ to $10^{6.54}$ sec). Calculated from Eqn. (16). k is set at 1 to $10 \text{ cm}^3/\text{cm}^2 \text{ sec}$ (TOMASSON, 1971), n_0 as 0.2 (PALSSON *et al.*, 1984) and ΔL as $2.57 \cdot 10^6 \text{ cm}$. ΔL is measured along the flowpath of the waters as predicted by deuterium data (ARNASON, 1976). Δh is equal to $0.038 \cdot 10^6 \text{ cm}$, assuming that the rocks are water saturated to the surface, at the base of the glacier and at the elevation of the springs.

r: 2.1 to 0.21 cm. Calculated from Eqn. (15). K_f for Na dissolution from basaltic glass at 3°C is $10^{-14.82} \text{ mole/cm}^2 \text{ sec}$ (GISLASSON and EUGSTER, 1987). $(C - C_0)$ is $2.97 \cdot 10^{-7} \text{ mole/cm}^3$. n_0 is 0.2 (PALSSON *et al.*, 1984) and t is 402 to 40 days as calculated above.

d: 0.36 to 0.036 cm. Calculated from Eqn. (10). K_f for Na dissolution from basaltic glass, $(C - C_0)$ and t are the same as above.

S : 56 to 5.6 cm^2 per one cm^3 of water. Calculated from Eqn. (8). K_1 for Na dissolution from basaltic glass, ($C - C_0$) and t are the same as above.

The characteristic radius of the grains in the aquifer obtained in this manner is in the pebble size, in agreement with the hydraulic conductivity obtained by TOMASSON (1971) and lending credence to this attempt of calculating hydraulic parameters from chemical data.

COMPOSITIONS OF GEOTHERMAL FLUIDS

The groundwaters discussed in the previous section provide the recharge for the fluids of the Krafla and Namafjall geothermal fields. Compositions of these fluids after boiling down to the sampling pressure under isolated conditions are listed in Table 4.

Calculations of total concentrations in a mixture of steam and water at T and P in the aquifers is difficult. Except for wells 8 and 9 in Table 4, all wells have aquifers with boiling waters; that is, the measured discharge enthalpy at the well head is higher than the enthalpy of water at the aquifer temperature. The methods of ARNORSSON *et al.* (1987) have been employed for concentration calculations, assuming no enhanced boiling. The total concentrations of the volatile components have the greatest uncertainties. The results for total concentrations of solutes in a mixture of steam and water at T and P are shown on Fig. 9. Information on wells from the Namafjall area, except for wells 11 and 12, are taken from ARNORSSON (1977). The total concentration of CO_2 at T and P , in a mixture of steam and water, is, for example:

$$m_{\text{CO}_2, \text{total}(T,P)} = m_{\text{CO}_2(T,P)_{\text{steam}}} X + m_{\text{CO}_2(T,P)_{\text{water}}} (1 - X)$$

where X is the mass fraction of steam at T and P , $m_{\text{CO}_2(T,P)_{\text{steam}}}$ is the calculated concentration of CO_2 in steam at T and P (ppm) and $m_{\text{CO}_2(T,P)_{\text{water}}}$ is the calculated concentration of CO_2 (ppm) in water at T and P . The fluids are silica-rich Na- HCO_3 - SO_4 waters with varying amounts of K, Cl and H_2S and they are essentially devoid of Ca and Mg. The chemistry of geothermal waters of Iceland have been discussed in detail by ARNORSSON *et al.* (1983a,b). Silica contents and Na/K ratios are controlled largely by temperature (FOURNIER, 1977; FOURNIER and POTTER, 1982; FOURNIER and TRUESDELL, 1973; HENLEY *et al.*, 1984) and the respective mineral reactions. Using the spring compo-

sitions of Table 3 as a guide, we can evaluate the effect of continued reaction of the groundwaters with the volcanic rocks in the geothermal areas. Figure 9 shows that Na, K and Cl total concentrations at T and P have increased substantially over those of the cold waters. Although there is considerable scatter, K and Cl are acquired at about the same rate as in the cold springs, whereas Na contents are distinctly lower. Additional chloride could have been provided by magmatic degassing, but it is much more plausible that Na was removed by mineral precipitation, including zeolites and feldspars. Ca and Mg are removed even earlier, as shown by spring 17, a warm spring (see Table 3, Fig. 3). In the geothermal waters Mg is removed quantitatively and Ca levels are very low. The minerals responsible probably are Ca-rich zeolites, calcite and Mg-Fe-smectites. The mixtures of geothermal water and steam at P and T in Krafla and Namafjall are enriched in carbon and sulfur above what can be accounted for by dissolution of the primary rocks (Fig. 9). The Krafla system is rich in carbon, whereas Namafjall is rich in sulfur. These additional sources for carbon and sulfur are probably of magmatic origin (ARMANSSON *et al.*, 1982).

The IAP values for calcite for the geothermal waters, calculated by WATCH1 (ARNORSSON *et al.*, 1982) as well as for warm and cold springs are shown in Fig. 10. They indicate saturation with respect to calcite in the most evolved springs and saturation for all geothermal waters (ARNORSSON *et al.*, 1983a).

MASS TRANSFER AND WATER/ROCK RATIOS

Any conservative solute can be used to scale mass transfer, provided that its concentration and distribution in the rocks are known. We need to determine the mass of rock that one kg of water has to react with in order to account for the observed water compositions. Thus the calculated mass transfer is intergrated over the flow path from the recharge area to the point of sampling. However, the rate of mass transfer can change with time and the calculations represent only that time interval when water is actually flowing through the system. From the conservation of mass for a homogeneous rock, such as basaltic glass, we have

$$C_w^a = C_w^b + 1/X(C_r^b - C_r^a) \quad (18)$$

where C_w^b is the solute concentration in water before

Table 4. Concentration (ppm) of elements and gases in geothermal water and steam as collected at the wellhead.

Sample	Date	pH/T°C	T°C	SiO ₂	Na	K	Ca	Mg	CO ₂	SO ₄	H ₂ S	Cl	CO ₂ **	H ₂ S**	Sampling Pressure (bars abs)	Measured Enthalpy (MJ/kg)	Latent gas per kg of condensate/°C
Krafla Well 6	7/02/81	6.62/23*	300*	799.90	165.80	33.04	1.68	0.017	291.30	106.50	27.50	30.00	11171.00	131.00	2.8	1.940	1.73/20*
Krafla Well 11	7/01/81	7.80/23*	253*	468.80	192.90	32.87	1.07	0.024	193.00	123.00	21.50	26.30	36912.00	498.00	8.2	2.075	3.45/20*
Krafla Well 8	8/18/81	9.75/27*	215*	410.10	193.00	25.46	1.60	0.000	46.40	202.40	37.10	53.20	1977.00	193.30	2.5	0.919	0.05/20*
Krafla Well 9	7/02/81	7.55/20*	240*	557.40	171.50	25.40	1.42	0.000	180.80	182.40	35.40	50.70	6955.00	353.00	7.8	1.036	0.09/20*
Krafla Well 7	8/19/81	6.75/20*	256*	734.70	190.40	34.30	1.24	0.006	277.40	159.80	36.90	56.60	15678.00	14.00	8.3	1.762	2.73/20*
Krafla Well 13	8/20/81	9.15/20*	325*	902.50	223.60	46.16	1.72	0.006	129.20	182.60	29.60	40.90	9363.00	402.30	4.1	1.877	0.88/20*
Krafla Well 14	8/21/81	7.55/20*	295*	775.20	144.20	32.40	0.32	0.000	193.70	13.50	44.90	91.00	26814.00	95.90	13.7	2.663	3.75/20*
Krafla Well 16	8/21/81	8.70/20*	300*	633.30	142.40	30.47	0.51	0.004	158.30	39.40	53.70	70.00	13683.00	839.50	7.3	1.607	0.74/20*
Namafjall 11	7/03/81	8.15/24*	320*	486.80	89.20	16.96	0.39	0.021	10.90	22.00	97.80	40.50	2489.00	1307.00	21.1	2.355	4.80/20*
Namafjall 12	7/03/81	8.48/24*	253*	509.30	113.60	18.40	0.09	0.010	18.10	28.50	136.10	23.00	2615.00	1408.00	22.0	2.380	3.66/20*

*Temperature calculated from the Na-K chemical geothermometer (Arnorsson *et al.*, 1983).

**Concentration of gases (ppm) in NaOH condensation.

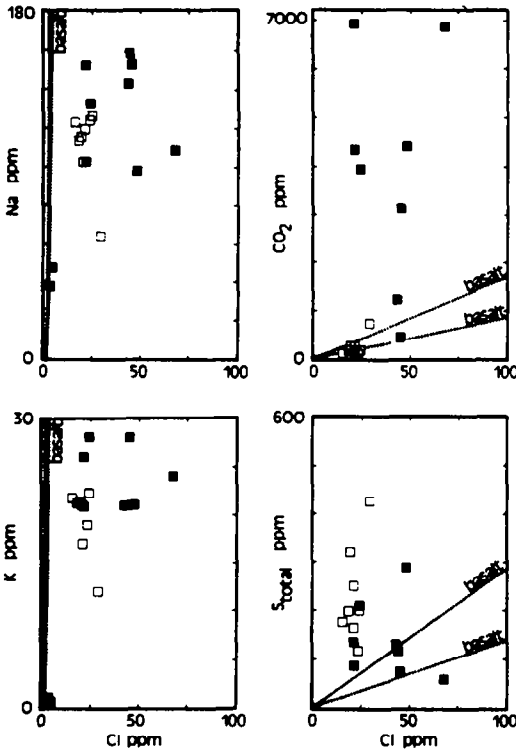


FIG. 9. Sodium, potassium, carbon and sulfate concentrations in hot springs (half filled squares), mixtures of geothermal steam and water at T and P from Namafjall (open squares) and Krafla (solid squares), plotted against chloride. The dashed lines represent the ratio of components in the rocks. The spread of the lines indicates uncertainties in the calculated ratios assuming one standard deviation for the average Cl value for the rocks.

and C_r^b after reaction, whereas C_r^b is the solute concentration in the rock before and C_r^a after reaction. X is the water-rock ratio, that is the mass fraction of 1 kg water that reacts with 1 kg rock. Provided dissolution of the element of interest is complete, eqn. (18) can be simplified to

$$X = C_r^b / \Delta C_w \quad (19)$$

where ΔC_w is the concentration increase in the water after it has reacted with the rocks. In these calculations, the concentration effect due to water taken up by alteration minerals is neglected, as are external sources for the element of interest other than precipitation, as well as incomplete dissolution of the primary rocks.

If the rocks are microscopically heterogeneous, selective leaching of the elements needs to be taken into account. In a crystallizing magma elements that are rejected by the crystals are fractionated into the residual melt, or if crystallization goes to near completion, into crystal boundaries. These incompatible elements will be present in increased concentrations in the interstitial glass. Along with olivine the interstitial glass is often found to be the first phase to become altered (SWATESON and KRISTMANNSDOTTIR, 1978). Interstitial glass, located on crystal boundaries, dissolves more than an

order of magnitude faster than the crystals (GISLASON and EUGSTER, 1987) and thus provides a readily available source of incompatible elements. During early alteration of the dense interior of a lava flow, incompatible elements such as Cl, S, B, Li, Ba, Sr, P and Rb, can be leached selectively, a fact clearly recognized by ELLIS and MAHON (1964). This uneven distribution of elements must be taken into account in the mass transfer calculations. The conservation of mass for one kg of rock is

$$C_r^b = X_c C_c + (1 - X_c) C_g \quad (20)$$

where X_c is the mass fraction of crystals in the primary rocks, $(1 - X_c)$ is the mass fraction of glass in the rocks, C_g is the concentration of the element in question in the glass and C_c in the crystals. In the case of an incompatible element which is fractionated completely into the residual melt, C_c is zero, and Eqn. (20) simplifies to

$$C_r^b = (1 - X_c) C_g \quad (21)$$

For this case, the water-rock ratio X can be written as

$$X = \frac{C_r^b / (1 - X_c)}{\Delta C_w} \quad (22)$$

We have identified three types of alteration that can be quantified by an incompatible element such as chlorine: Water reacts with basaltic glass, with crystalline basalt that is totally altered, or with crystalline basalt containing interstitial glass. Equation (19) refers to the first two cases and Eqn. (22) to the third case. Using these equations, we can calculate the ratio of water to altered rock mass for the groundwater system of N.E. Iceland and the Namafjall and the Krafla

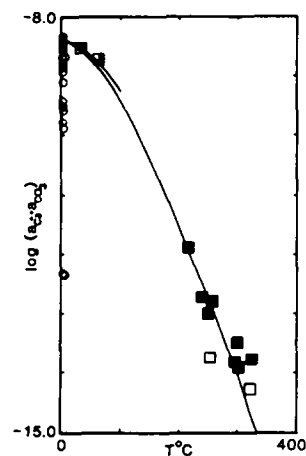


FIG. 10. The IAP for Ca^{2+} and CO_3^{2-} as calculated by WATEQF (PLUMMER *et al.*, 1984) for melt and spring waters from N.E. Iceland (circles), by WATCH1 (ARNORSSON *et al.*, 1982) for hot springs (half filled squares) and high temperature geothermal waters from Krafla (solid squares) and Namafjall (open squares) as a function of temperature. Solubility of calcite as given by ARNORSSON *et al.* (1982) and PLUMMER and BUSENBERG (1982), lower and upper curves, respectively.

geothermal systems. When ΔC_w in Eqn. (19) and (22) approaches zero, X becomes extremely sensitive to a small change in water composition. On the other hand, when ΔC_w is close to the concentration in the rocks, X is insensitive to changes in water composition. Judging from the values listed in Table 2, ΔC_w for chloride in the cold springs ranges from .2 to 2 ppm and ΔC_w for sodium from 5 to 20 ppm. This makes sodium more suitable for water-rock ratio calculations for the cold waters, whereas chlorine is the only possible element for the geothermal waters. The water-rock ratio in the Krafla area calculated from Cl by Eqn. (19) is in the range of 3 to 10. This means that 1000 g of geothermal water has reacted with 100 to 300 g of the rock, assuming that the rock altered is glassy, or if it is crystalline, it is totally altered. The mass of altered glassy rocks and strongly altered crystalline rocks is much larger than that of relatively unaltered crystalline rocks (SWANTESSON and KRISTMANNSDOTTIR, 1978). Hence, the values calculated from Eqn. (19) are probably closer to reality than values obtained from Eqn. (22). The results from Eqn. (19) are in good agreement with water-rock ratios of 5 for the Krafla system based on oxygen isotopes (HATTORI and MUEHLENBACHS, 1982). We conclude that 1000 g of the cold springs have altered 0.3 to 1 g of rocks, waters at 30° and 60°C have altered 2 to 16 g and 1000 g of the high temperature geothermal waters of Krafla and Namafjall have reacted with 100 to 300 g of pristine rocks.

SUMMARY

Atmospheric precipitation in N.E. Iceland ranges from 40 to 120 cm/year, and seawater is an important source of solutes. However, amounts in excess of the seawater mixing line are present for silica, calcium, potassium and sulfate. This could be due to the dissolution of basaltic dust in the collectors, fractionation of seaspray, burning of fossil fuel, addition of magmatic gases or farming activities. Aerosol concentrations are greatest close to the coast and in snow.

After initial saturation with atmospheric CO_2 , dissolution and precipitation reactions in the spring waters take place sealed off from the atmosphere and without significant CO_2 contributions from soils. Consequently, the pH increases from 6 to 10, with protons consumed during the dissolution of the basalt rocks provided by conversion of bicarbonate to carbonate and dissociation of aqueous silica.

Cold groundwaters not affected by geothermal fluids acquire their major solutes, SiO_2 , Na, K, Ca, Mg, SO_4 , CO_2 , and Cl by basalt dissolution. However, cations are released to the waters more slowly than Cl is, indicating that dissolution of the basalts is not congruent. In addition, the two springs closest to the ocean are enriched in Cl. All but four of the springs are undersaturated with respect to calcite. Silica concentrations in the waters are compatible with silica activity of the basaltic glass. During solute acquisition, spring compositions move through the calculated kaolinite,

smectite, laumontite and illite fields. In the hot springs and geothermal fluids, Ca and Mg are strongly depleted, presumably due to precipitation of calcite, smectites, zeolites and feldspars. Through input of magmatic gases, the geothermal waters of Krafla and Namafjall are enriched in carbon and sulfur above what can be expected by dissolution of basaltic rocks.

Compositional data of the groundwaters combined with dissolution rates measured in the laboratory on the same rocks, makes it possible to characterize hydraulic parameters of the aquifers in a quantitative fashion. The assumption that laboratory dissolution rates can be transferred to the field situation allows us to estimate the residence time of cold water in the aquifers from two months to four years. The average active surface area of the aquifers enclosing 1000 g of water ranges from 0.6 m² to 6 m². The characteristic grain radii of the cold spring aquifers are in the range 0.2 to 2 cm and characteristic crack widths are 0.4 to 0.04 cm. 1000 g of cold spring water have interacted with 0.1 to 1 g of rock, affecting a surface layer of rocks 10 to 2000 Å thick. Waters of intermediate temperatures (30–60°C) have altered 2 to 16 g of rocks and 1000 g of the high temperature geothermal waters at Krafla and Namafjall have reacted with 100 to 300 g of unaltered rocks.

Acknowledgements—We are grateful to Blair Jones, Stefan Arnorsson, Shirley Rettig, Eugene Ilton, Glenn Wilson, Katherine Cashman, Andres Gudmundsson, Gisli Sigurdsson, Grant Garven, Niel Plummer, Einar Gunnlaugsson, Hreinn Hjartarson, Freysteinn Sigurdsson, Karl Gronvold, Ron Spencer, Helgi Björnsson for contributing ideas, comments and assistance with calculations and fieldwork. Perceptive and very helpful reviews of an earlier version by R. F. Stallard, A. Velbel and A. White are deeply appreciated.

Research supported by NSF Grant AEO-83-18502, the Science Institute of Iceland, the Icelandic Science Foundation, the National Energy Authority of Iceland, the Thor Thors Scholarship, the Waters Fund, the Balk Fund and the Icelandic Student Loan Foundation.

Editorial handling: J. I. Drever

REFERENCES

- ANTWEILER R. C. and DREVER J. I. (1983) The weathering of a late Tertiary volcanic ash: Importance of organic solutes. *Geochim. Cosmochim. Acta* **47**, 623–629.
- ARCHER E. E. (1955) The determination of small amounts of sulphate by reduction to hydrogen sulphide, and titration with mercuric or cadmium salts with dithizone as an indicator. *Analyst* **81**, 181–182.
- ARMANSSON H., GISLASON G. and HAUSSON T. (1982) Magmatic gases in well fluids aid the mapping of the flow pattern in a geothermal system. *Geochim. Cosmochim. Acta* **46**, 167–177.
- ARNASON B. (1976) Groundwater systems in Iceland traced by deuterium. "Rit," *Societas Scientiarum Islandica* **42**, 235p.
- ARNASON B. (1977) Hydrothermal systems in Iceland traced by deuterium. *Geothermics* **5**, 125–151.
- ARNORSSON S. (1977) Changes in the chemistry of water and steam discharged from wells in the Namafjall geothermal field, Iceland, during the period 1970–76. *Jökull* **27**, 47–59.
- ARNORSSON S. (1978) Framvinduskýrsla um efnafræði ut-

- fellaga i borholum vid Kroflu. OS-JHD-7832, National Energy Authority, Reykjavik, Iceland.
- ARNORSSON S., SIGURDSSON S. and SVAVARSSON H. (1982) The chemistry of geothermal waters in Iceland. I. Calculations of aqueous speciation from 0 to 370°C. *Geochim. Cosmochim. Acta* **64**, 1513–1532.
- ARNORSSON S., GUNNLAUGSSON E. and SVAVARSSON H. (1983a) The chemistry of geothermal waters in Iceland. II. Mineral equilibria and independent variables controlling water compositions. *Geochim. Cosmochim. Acta* **47**, 547–566.
- ARNORSSON S., GUNNLAUGSSON E. and SVAVARSSON H. (1983b) The chemistry of geothermal waters in Iceland. III. Chemical geothermometry in geothermal investigations. *Geochim. Cosmochim. Acta* **47**, 567–577.
- ARNORSSON S., BJORNSSON S., MUNA Z. W. and BWIRE-OJAMBO S. (1987) Evaluation of boiling processes, phase separation and the tractioning of equilibrium steam in exploited geothermal reservoirs from the gas content of well discharges with an example from the Olkaria field, Kenya. (in preparation).
- BARNES I. and O'NEIL J. R. (1971) The relationship between fluids in some fresh Alpine-type ultramafics and possible modern serpentinization, Western United States. *Geol. Soc. Amer. Bull.* **80**, 1947–1960.
- BARNES I., O'NEIL J. R. and TRESCASES J. J. (1978) Present-day serpentinization in New Caledonia, Oman and Yugoslavia. *Geochim. Cosmochim. Acta* **42**, 144–145.
- BERNER R. A. (1978) Rate control of mineral dissolution under earth surface conditions. *Amer. J. Sci.* **278**, 1235–1252.
- BERNER R. A. (1980) *Early Diagenesis: A Theoretical Approach*. Princeton Univ. Press, 241p.
- BERNER R. A. (1981) Kinetics of weathering and diagenesis. In *Kinetics of Geochemical Processes* (eds. A. C. LASAGA and R. J. KIRKPATRICK), Vol. 87, Chap. 3. *Reviews in Mineralogy*, pp. 111–134. Mineral Soc. Amer.
- BISCHOFF J. L. and DICKSON F. W. (1975) Seawater-basalt interaction at 200°C and 500 bars: Implications for origin of sea-floor heavy-metal deposits and regulation of seawater chemistry. *Earth Planet. Sci. Lett.* **25**, 385–397.
- BISCHOFF J. L. and SEYFRIED W. E. JR. (1978) Hydrothermal chemistry of seawater from 25°C to 350°C. *Amer. J. Sci.* **278**, 838–860.
- BJORNSSON A. (1985) Dynamics of crustal rifting in N.E. Iceland. *J. Geophys. Res.* **90**, 10151–10162.
- BJORNSSON A., SAEMUNDSSON K., EINARSSON P., TRYGGVASON E. and GRONVOLD K. (1977) Current rifting episode in North Iceland. *Nature* **266**, 318–323.
- BJORNSSON A., JOHNSEN G., SIGURDSSON S., THORBERGSSON G. and TRYGGVASON E. (1979) Rifting of the plate boundary in North Iceland, 1975–1978. *J. Geophys. Res.* **86**, 3029–3038.
- CARMICHAEL I. S. E. (1964) The petrology of Thingmuli, a Tertiary volcano in eastern Iceland. *J. Petrol.* **5**, 435–460.
- CHESSELET R., MORELLI J. and BUAT-MENARD P. (1972) Variations in ionic ratios between reference sea water and marine aerosols. *J. Geophys. Res.* **77**, 5116–5131.
- CHESWORTH W., DEJOU J. and LARROQUE P. (1981) The weathering of basalt and relative mobilities of the major elements at Belbex, France. *Geochim. Cosmochim. Acta* **45**, 1235–1243.
- CLAASSEN H. C. and WHITE A. F. (1979) Application of geochemical kinetic data to groundwater systems: A tuffaceous-rock system in southern Nevada. In *Chemical Modeling in Aqueous Systems* (ed. E. JENNE), pp. 771–793. Amer. Chem. Soc., Washington, D.C.
- CODATA TASK GROUP ON KEY VALUES FOR THERMODYNAMICS (1976) Recommended key values for thermodynamics. *J. Chem. Thermodyn.* **8**, 603–605.
- COLBECK S. C. (1981) A simulation of the enrichment of atmospheric pollutants in snow cover runoff. *Water Resour. Res.* **17**, 1383–1388.
- CORLISS J. G., DYMOND J., GORDON L. I., EDMOND J. M., VON HERZEN R. P., BALLARD R. D., GREEN K., WILLIAMS D., BAINBRIDGE A., CRANE K. and VAN ANDEL Th. H. (1979) Submarine thermal springs on the Galapagos rift. *Science* **203**, 1073–1083.
- CRERAR D., MEANS J., YURETICH R., BORCSIK M., AMSTER J., HASTINGS D., KNOX D., LYON K. and QUIETT R. (1981) Hydrogeochemistry of the New Jersey coastal plain. *Chemical Geol.* **33**, 23–44.
- DAVIS S. and BENTLEY H. (1982) Dating groundwater, a short review. In *Nuclear and Chemical Dating Techniques: Interpreting the Environmental Record* (ed. L. CURRIE). *Amer. Chem. Soc. Symp. Series*, No. 176, pp. 187–222.
- DREVER J. I. (1971) Chemical weathering in subtropical igneous terrain, Rio Ameca Basin, Mexico. *J. Sediment. Petrol.* **41**, 951–961.
- EDMOND J. M. (1980) The chemistry of the 350°C hot springs at 21°N on the East Pacific Rise (abstr.). *Eos* **61**, 992.
- EDMOND J. M. and VON DAMM K. L. (1983) Hot springs on the ocean floor. *Scientific American* **248**, 78–93.
- EDMOND J. R., MEASURES C., MCDUFF R. E., CHAN L. H., COLLIER R., GRANT B., GORDON L. I. and CORLISS J. B. (1979) Ridge crest hydrothermal activity and the balance of major and minor elements in the ocean: The Galapagos data. *Earth Planet. Sci. Lett.* **46**, 1–18.
- EINARSSON P. (1978) S-wave shadows in the Krafla caldera in N.E.-Iceland, evidence for a magma chamber in the crust. *Bull. Volcanol.* **41**, 1–9.
- ELLIS A. J. and MAHON W. A. J. (1964) Natural hydrothermal systems and experimental hot water-rock interactions I. *Geochim. Cosmochim. Acta* **28**, 1323–1357.
- ELLIS A. J. and MAHON W. A. J. (1977) *Geochemistry and Geothermal Systems*. Academic Press, New York, 392p.
- EUGSTER H. P. and JONES B. F. (1968) Gels composed of sodium-aluminum silicate, Lake Magadi, Kenya. *Science* **161**, 160–163.
- EYTHORSSON J. and SIGTRYGGSSON H. (1971) The climate and weather of Iceland. *Zoology of Iceland* **1**, 1–62.
- FOURNIER R. O. (1977) Chemical thermometers and mixing models for geothermal systems. *Geothermics* **5**, 41–50.
- FOURNIER R. O. and TRUEDELL (1973) An empirical Na-K-Ca geothermometer for natural waters. *Geochim. Cosmochim. Acta* **37**, 1255–1275.
- FOURNIER R. O. and POTTER R. W. (1982) A revised and expanded silica (quartz) geothermometer. *Geothermal Res. Council Bull.* **11**, 3–9.
- FRAPPE S., FRITZ P. and MCNUTT R. (1984) Water-rock interaction and chemistry of groundwaters from the Canadian Shield. *Geochim. Cosmochim. Acta* **48**, 1617–1627.
- FREEZE R. A. and CHERRY J. A. (1979) *Groundwater*. Prentice-Hall, 604p.
- GARRELS R. M. and MACKENZIE F. T. (1967) Origin of the chemical composition of some springs and lakes. *Equilibrium Concepts in Natural Water Systems*, pp. 220–242. Amer. Chem. Soc. Adv. Chem. Ser. 67.
- GISLASON S. R. (1985) Meteoric water basalt interactions: a field and laboratory study. Ph.D. dissertation, Johns Hopkins Univ., 238p.
- GISLASON S. R. and EUGSTER H. P. (1984) Oxygen fugacities in a basalt-meteoric water geothermal system: Krafla, N.E.-Iceland (abstr.). *Geol. Soc. Amer. Abstr. Prog.* **16**, 520.
- GISLASON S. R. and EUGSTER H. P. (1985) Interaction of basalt with meteoric water: a field and laboratory study (abstr.). *Eos* **66**, 401.
- GISLASON S. R. and RETTIG S. (1986) Meteoric water-basalt interactions in N.E. Iceland: Methods and analytical results. *U.S. Geol. Survey Open-File Report* 87–49.
- GISLASON S. R. and EUGSTER H. P. (1987) Meteoric water-basalt interactions. I: A laboratory study. *Geochim. Cosmochim. Acta* **51**, 2827–2840 (this issue).
- GRAEDEL T. E. and FRANEY J. P. (1975) Field measurements of submicron aerosol washout by snow. *Geophys. Res. Lett.* **2**, 325–328.
- GRONVOLD K. and MAAKIPAA H. (1978) Chemical compo-

- sition of Krafla lavas 1975–1977. *Nordic Volcanol. Inst. Report 16*, Reykjavik, Iceland.
- GUNNLAUGSSON E. (1977) The origin and distribution of sulfur in fresh and geothermally altered rocks in Iceland. Ph.D. dissertation, Univ. of Leeds.
- GUNNLAUGSSON E. and ARNORSSON S. (1980) Sampling and analytical methods for geothermal fluids and gases. U.N. Geothermal Training Program, Iceland.
- HAJASH A. (1975) Hydrothermal processes along mid-ocean ridges: An experimental investigation. *Contrib. Mineral. Petrol.* **53**, 205–226.
- HATTORI K. and MUEHLENBACHS K. (1982) Oxygen isotope ratios of the Icelandic crust. *J. Geophys. Res.* **87**, 6559–6565.
- HAY R. and JONES B. F. (1972) Weathering of basaltic tephra on the island of Hawaii. *Geol. Soc. Amer. Bull.* **83**, 317–332.
- HEIER K. S., CHAPPEL B. W., ARRHENS P. A. and MORGAN J. W. (1966) The chemistry of four Icelandic basalts. *Norsk Geologisk Tidsskrift* **46**, 427–437.
- HELGESON H. C. (1969) Thermodynamics of hydrothermal systems at elevated temperature and pressure. *Amer. J. Sci.* **267**, 729–804.
- HELGESON H. C., DELANY J. M., NESBITT H. W. and BIRD D. K. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. *Amer. J. Sci.* **278A**, 1–229.
- HEMINGWAY B. S. and ROBIE R. A. (1977) The entropy and Gibbs free energy of formation of the aluminum ion. *Geochim. Cosmochim. Acta* **41**, 1402–1404.
- HENLEY R. W., TRUESDELL A. H. and BARTON P. B. (1984) Fluid-mineral equilibria in hydrothermal systems. *Reviews in Econ. Geol.* **1**, 1–267.
- JAKOBSSON S. P. (1972) Chemistry and distribution pattern of recent basaltic rocks in Iceland. *Lithos* **5**, 365–386.
- JOHANNESSEN M. and HENRIKSEN A. (1978) Chemistry of snowmelt: changes in concentration during melting. *Water Resour. Res.*, 615–619.
- KRISTMANNSDOTTIR H. (1978) Alteration of basaltic rocks by hydrothermal activity at 100–300°C. In *International Clay Conference 1978* (eds. M. M. MORTLAND and V. C. FARMER), pp. 358–367. Elsevier, Amsterdam.
- KRISTMANNSDOTTIR H. (1982) Alteration in the IRDP drill hole compared with other drill holes in Iceland. *J. Geophys. Res.* **87**, 6525–6531.
- MEHEGAN J., ROBINSON P. and DELANEY J. R. (1982) Secondary mineralization and hydrothermal alteration in the Reydar-fjörður drill core, eastern Iceland. *J. Geophys. Res.* **87**, 6511–6524.
- MILLER W. R. and DREVER J. I. (1977) Chemical weathering and related controls on surface water chemistry in the Absaroka Mountains, Wyoming. *Geochim. Cosmochim. Acta* **41**, 1693–1702.
- MINK J. F. and LAU S. L. (1980) Hawaiian groundwater geology and hydrology, and early mathematical models. *Technical Memorandum Report No. 62*, Water Resources Research Center, Univ. Hawaii at Manoa.
- MOTTL M. J. (1983) Metabasalts, axial hot springs, and the structure of hydrothermal systems at mid-ocean ridges. *Geol. Soc. Amer. Bull.* **94**, 161–180.
- MOTTL M. J. and HOLLAND H. D. (1978) Chemical exchange during hydrothermal alteration of basalt by seawater—I. Experimental results for major and minor components of seawater. *Geochim. Cosmochim. Acta* **42**, 1103–1117.
- NESBITT H. W. and BRICKER O. P. (1978) Low temperature alteration processes affecting ultramafic bodies. *Geochim. Cosmochim. Acta* **42**, 403–409.
- PACES T. (1969) Chemical equilibria and zoning of subsurface water from Jachymov ore deposit, Czechoslovakia. *Geochim. Cosmochim. Acta* **33**, 591–609.
- PACES T. (1973) Steady-state kinetics and equilibrium between ground water and granitic rock. *Geochim. Cosmochim. Acta* **37**, 2641–2663.
- PACES T. (1983) Rate constants of dissolution derived from the measurements of mass balance in hydrological catchments. *Geochim. Cosmochim. Acta* **47**, 1855–1863.
- PALSSON S., HARALDSSON G. I. and VIGFUSSON G. H. (1984) Edlismassi og poruhluhi bergs. The National Energy Authority, Reykjavik, Iceland. OS-84048/VOD-18 B.
- PARKER V. B., WAGMAN D. D. and EVANS W. H. (1971) Selected values of chemical thermodynamic properties. *U.S. Natl. Bureau of Standards Technical Note* 270-6, 106p.
- PLUMMER L. N. and BUSENBERG E. (1982) The solubilities of calcite, aragonite and vaterite in CO₂-H₂O solutions between 0 and 90°C and an evaluation of the aqueous model for the system CaCO₃-CO₂-H₂O. *Geochim. Cosmochim. Acta* **46**, 1011–1040.
- PLUMMER L. N., JONES B. F. and TRUESDELL A. H. (1984) WATEQF—A Fortran IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters. *U.S. Geol. Surv. Water Resources Investigations*, 76–113.
- REEDER S. W., HITCHON B. and LEVINSON A. A. (1972) Hydrogeochemistry of the surface waters of the Mackenzie river drainage basin, Canada: I. Factors controlling inorganic composition. *Geochim. Cosmochim. Acta* **36**, 825–865.
- REYNOLDS R. C. and JOHNSON N. M. (1972) Chemical weathering in the temperate glacial environment of the Northern Cascade Mountains. *Geochim. Cosmochim. Acta* **36**, 537–544.
- ROBIE R. S., HEMINGWAY B. S. and FISHER I. R. (1978) Thermodynamic properties of minerals and related substances at 289.15 deg.K and 1 bar (10⁵ pascals) pressure and at higher temperature. *U.S. Geol. Surv. Bull.* **1452**, 456p.
- SAEMUNDSSON K. (1974) Evolution of the axial rift zone in northern Iceland and the Tjörnes fracture zone. *Geol. Soc. Amer. Bull.* **85**, 495–504.
- SEYFRIED W. E. and MOTTL M. J. (1982) Hydrothermal alteration of basalt by seawater under seawater dominated conditions. *Geochim. Cosmochim. Acta* **46**, 985–1002.
- SIGURDSSON H. and SPARKS R. (1981) Petrology of rhyolitic and mixed magma ejected from the 1875 eruption of Askja, Iceland. *J. Petrol.* **22**, 41–84.
- SIGVALDASON G. E. (1967) Chemistry of basalts from the Icelandic rift zone. *Contrib. Mineral. Petrol.* **20**, 357–370.
- SIGVALDASON G. E. and OSKARSSON N. (1976) Chlorine in basalts from Iceland. *Geochim. Cosmochim. Acta* **40**, 777–789.
- SKOUGSTAD M., FISHMAN M. V., FRIEDMAN L., ERDMANN D. and DUNCAN S. (1979). Methods for determination of inorganic substances in water and fluvial sediments. *U.S. Geol. Survey, Book 5*, Chap. A-1, 626p.
- SPOSITO G. (1985) Chemical models of weathering in soils. In *The Chemistry of Weathering* (ed. J. I. DREVER), pp. 1–18. NATO ASI Series C: Mathematical and Physical Sciences, vol. 149. D. Reidel.
- STEFANSSON V. (1981). The Krafla geothermal field Northeast Iceland. In *Geothermal Systems: Principles and Case Histories* (eds. L. RYBACH and L. I. P. MUFFLER), pp. 273–294. John Wiley & Sons.
- STEINTHORSSON S. and SVEINBJORNSDOTTIR A. (1981) Opaque minerals in geothermal well no. 7, Krafla, Northeast Iceland. *J. Volc. Geotherm. Rech.* **10**, 245–261.
- SWANTESSON F. and KRISTMANNSDOTTIR H. (1978) Efna-samsetning ummyndads bergs í Kroflu. OS/JHD-7822, National Energy Authority, Reykjavik, Iceland.
- TABATABAI M. A. (1974) Determination of sulphate in water samples. *Sulphate Inst. J.*, 11–33.
- TARDY Y. (1971) Characterization of the principal weathering types by the geochemistry of waters from some European

- and African crystalline massifs. *Chemical Geol.* 7, 253–271.
- THORARINSSON S. (1979) The postglacial history of the Myvatn area. *Oikos* 32, 17–28.
- TOMASSON H. (1971) Hrauneyjafoss, geological report. National Energy Authority, Reykjavik, Iceland.
- TOMASSON J., FRIDLEIFSSON I. B. and STEFANSSON V. (1975) A hydrological model for the flow of thermal water in S.W.-Iceland with special reference to the Reykir and Reykjavik thermal areas. *2nd U.N. Geothermal Symp. Proc., Lawrence Berkeley Lab., Univ. California* 1, 643–648.
- VELBEL M. A. (1985) Geochemical mass balance and weathering rates in forested watersheds of the southern Blue Ridge. *Amer. J. Sci.* 285, 904–930.
- VELBEL M. A. (1986) Influence of surface area, surface characteristics, and solution composition on feldspar weathering rates. In *Chemical Processes at Mineral Surfaces* (eds. J. A. DAVIS and K. F. HAYES), pp. 615–634. Amer. Chem. Soc. Symp. Series No. 323, Washington, D.C.
- VON DAMM K. L., EDMOND J. M., GRANT B., MEASURES O. I., WALDEN B. and WEISS R. F. (1985) Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise. *Geochim. Cosmochim. Acta* 49, 2197–2220.
- WALKER G. (1960) Zeolite zones and dike distribution in relation to the structure of the basalts in Eastern Iceland. *J. Geol.* 68, 515–528.
- WALTHER J. V. and HELGESON H. C. (1977) Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressures and temperatures. *Amer. J. Sci.* 277, 1315–1351.
- WHITE A., CLAASSEN H. and BENSON L. (1980) The effect of dissolution of volcanic glass on the water chemistry in a tuffaceous aquifer, Rainier Mesa, Nevada. *U.S. Geol. Surv. Water-Supply Paper*, 1535-Q.