

6101448

UNIVERSITY OF UTAH
RESEARCH INSTITUTE
EARTH SCIENCE LAB.

Aquifer chemistry of four high-temperature geothermal systems in Iceland

STEFÁN ARNÓRSSON, KARL GRÖNVOLD* and SVEN SIGURDSSON
National Energy Authority, Laugavegur 116, Reykjavík, Iceland

(Received 29 April 1977; accepted in revised form 13 January 1978)

Abstract—The deep water feeding wet-steam wells in four high-temperature geothermal areas in Iceland have highly variable salinity as reflected in the chlorine concentrations which vary from 20 to 19000 ppm. Using available values for equilibrium constants, the activities of 26 chemical species involving the major components of the reservoir water have been calculated and quantitative evaluations of solute/solute, mineral/solute chemical equilibria in these geothermal systems have been made.

The unflushed reservoir water is just saturated with calcite. The saline geothermal waters, which represent heated sea-water, are just saturated with anhydrite, but the dilute waters, which are of meteoric origin, are somewhat undersaturated with this mineral. The fluoride mobility is thought to be limited by an ionic exchange reaction where F^- replaces some of the OH^- in the layered silicates. The pH of the unflushed reservoir water is governed by ionic exchange equilibrium in which all the major cations participate. At a given temperature it seems likely that the activity of one cation fixes the activities of all the other major cations and hydrogen ion. If this is so, and we take all the other chemical equilibria which have been demonstrated to exist for granted, it turns out that the major element composition of the unflushed high-temperature geothermal waters is controlled by two independent variables only. These variables are the temperature and the supply to the water of the incompatible element chlorine, incompatible indicating that this element is not incorporated in the geothermal minerals.

INTRODUCTION

This article is based on a geochemical study of fluids discharged from 14 wet-steam wells in 4 of the 18 high-temperature areas in Iceland (Fig. 1). These four areas are of the hot-water type (see WHITE *et al.*, 1971). Of the 14 wells whose chemistry was studied, 12 have been drilled since 1968 both for exploration and exploitation. Between 1 and 15 samples have been collected from individual wells.

Selected analysis of water and steam samples from the 14 wells are presented in Table 1. The chemistry of all the well discharges at Svartsengi and Námafjall are similar but the wells in these two fields are relatively closely spaced (Figs. 2B and 2D). Homogeneous reservoir chemistry at Reykjanes (Fig. 2A) is also indicated by the discharge composition of several wells in that area (BJÖRNSSON *et al.* 1972). Within the Hengill high-temperature area considerable difference in well discharge compositions is observed between Hveragerdi and Nesjavellir. Hveragerdi is located on the southeast boundary of the area but Nesjavellir on the northeast boundary, some 10 km away (Fig. 2C).

The present study was initiated in 1972. At the beginning it involved the adaption and development of suitable routine methods for collection of representative samples of water and steam, and the development of computer programs for the calculation of the composition and chemical speciation of the

aquifer water. The calculations refer to the temperature of equilibrium with quartz and assume one step adiabatic flashing. The well discharge enthalpy is derived from this reference temperature assuming only water to be present. Since this study was initiated a similar computer program has been presented (TRUESDELL and SINGERS, 1974).

The chemical characteristics of geothermal fluids in Iceland have been reviewed recently by ARNÓRSSON (1974). He concluded that with respect to the high-temperature geothermal waters, that three major variables governed their chemical composition. They are temperature, rock type (basalt or acid volcanics), and influx of sea-water into the geothermal system. Juvenile sources of sulphur and carbon may also contribute to the bulk composition in some of the areas.

Influx of sea-water into high-temperature geothermal systems occurs in the Reykjanes Peninsula in southwest Iceland where highly permeable late Quaternary and Recent volcanics reach the coast and where the elevation of the land is low. A gradation from insignificant sea-water influx to 'pure' geothermal sea-water is observed from the more elevated eastern part of the Reykjanes Peninsula to the low lying southwest tip (ARNÓRSSON, 1978a).

The low content of dissolved solids (700–1400 ppm) in the reservoir water of the other high-temperature fields, located in basaltic rocks, is thought to be due to limited supply for leaching of 'soluble anions' such as Cl^- . The limited supply may be partly due to low concentrations of chlorine in the rock (see SIGVALDASON and ÓSKARSSON, 1976), but it may also be due to other parameters such as the internal structure of

* Now with the Nordic Volcanological Institute, Reykjavík, Iceland.

UNIVERSITY OF UTAH LIBRARIES

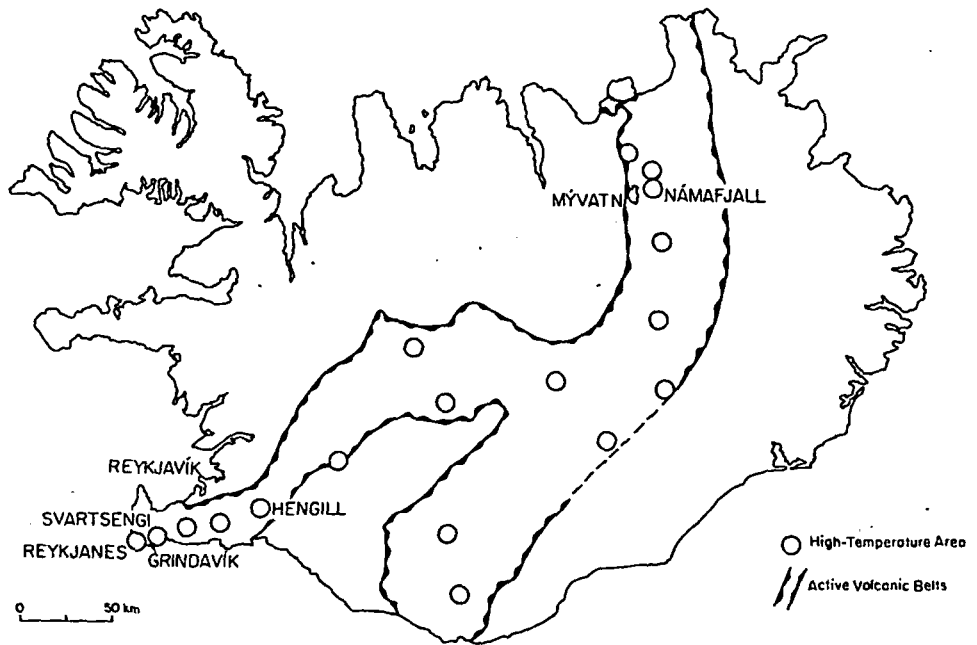


Fig. 1. The distribution of the high-temperature geothermal fields in Iceland.

the rock that determines the size of the contact area between rock and through flowing water (ARNÓRSSON, 1970a). Where geothermal waters of high temperature flow through acid volcanics, the dissolved solids content is higher, particularly as a result of higher chlorine concentrations.

Although the concentrations of some dissolved components (Cl, F, SO₄) not limited by mineral solubilities are observed to increase with temperature in

Iceland low-temperature geothermal areas (ARNÓRSSON, 1974, 1975), such relationship cannot be deduced from available data of high-temperature geothermal fluids. This relationship is thought to reflect increased leaching from the rock as water temperatures increase. The main effect of temperature on the composition of the high-temperature fluids lies in the temperature dependence of mineral solubilities and ion-exchange equilibria that govern the mobility of ma-

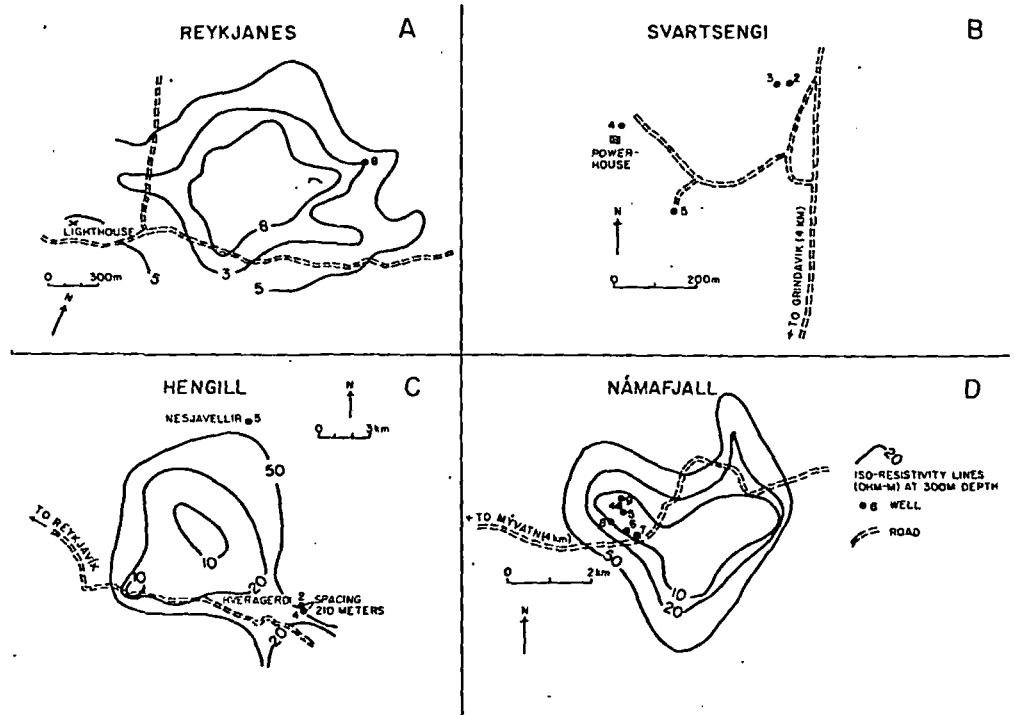


Fig. 2. Location of geothermal wells at (A) Reykjanes (B) Svartsengi, (C) Hengill, and (D) Námafjall.

of the
positio
is trea

The
BONVA
Quater
been c
identif
tures l
are al
92°C

Table
vario
wells
The c

Table 1. Analytical data for the 14 wet-steam wells included in this study

	Reykjanes		Svartsengi				Mánafljell			Nesjavellir				
	well 0	well 2	well 3	well 4	well 5	well 7	well 4	well 5	well 6	well 5	well 6	well 7	well 8	well 9
sample no.	0079	0031	0064	0063	0058	0137	0067	0193	0090	0011	0013	0096	0158	0014
Date of sampling	71.08.06	71.04.27	74.07.23	74.07.22	74.07.16	71.10.31	73.04.25	72.11.23	71.07.19	74.03.08	74.03.09	73.07.19	73.11.17	74.03.09
Sampling pressure bars abs.	13.0	2.9	5.7	8.0	6.5	7.6	5.0	16.3	10.4	8.6	12.6	12.7	10.1	9.0
water sample type														
ml/C	6.58/20	7.55/20	7.22/24	7.40/24	7.03/20	9.21/24	9.24/21	9.15/20	9.20/15	9.05/25	9.06/23	8.84/20	9.14/22	9.10/25
SiO ₂	741	568	563	511	526	297	299	436	659	387	584	597	343	640
Ca	17540	8400	8129	7660	7212	187.7	164.7	152.0	181.0	142.4	153.2	142.4	175.0	146.6
Mg	1883	1300	1309	1150	1190	13.0	12.2	27.6	28.2	21.7	24.9	26.4	25.3	27.8
Co	1868	1236	1113	1174	1100	2.6	1.7	1.3	1.6	2.5	0.8	0.9	1.5	1.1
Na	0.42	1.00	10.9	6.15	8.77	0.04	0.18	0.05	0.13	0.03	0.05	0.14	0.04	0.04
Cl ^{total} **	37.9	34.0	36.2	36.8	48.2	53.2	56.3	29.3	24.7	47.0	36.5	23.8	24.8	33.4
SO ₄	78.4	54.7	37.8	40.5	39.0	82.2	69.9	36.4	122.1	66.3	64.6	86.7	65.6	76.9
Fe ^{total} **	0.5	0.0	0.0	0.0	0.0	21.8	16.6	119.0	94.6	81.6	117.3	137.6	95.3	83.6
Li	23500	18270	13318	13049	11725	117.5	123.8	15.4	18.9	26.1	28.8	23.6	25.2	22.6
F	0.10	-	0.12	0.14	0.16	2.0	2.0	2.0	1.9	0.9	1.0	1.0	1.2	1.2
3 mm. solids	12376	28419	29139	24243	13627	786	754	1089	1201	802	1084	1128	1005	1142
Dissolved ppm														
Cl ⁻	190.0	652.0	495.6	688.4	395.0	645.0	525.0	682.0	184.8	324.7	207.6	218.0	181.0	173.2
SO ₄	40.1	8.0	12.3	6.4	6.8	119.0	92.1	229.0	366.4	200.9	425.7	397.0	388.0	404.6
Ca ppm accompanying carbonate wt. %														
Cl ⁻	97.0	81.3	97.4	96.5	95.3	82.6	84.2	70.0	78.7	38.9	32.4	29.5	37.5	37.3
SO ₄	3.0	9.0	0.7	0.8	0.5	3.2	4.0	12.1	16.3	8.7	19.1	28.0	14.9	19.1
Fe	0.2	0.4	0.0	0.0	0.0	3.2	2.6	12.8	41.8	21.0	37.9	42.2	32.0	34.9
Li ppm wt/wt														
temperature/°C	1.44/36*	0.12/20*	0.38/20*	1.15/30*	1.18/24*	1.09/14*	0.46/25*	0.98/44*	0.63/20*	0.46/11*	1.18/25*	2.67/21*	0.86/14*	0.91/23*

*total carbonate.

** total sulphide.

of the dissolved components. This effect on fluid composition is the main object of the present article and is treated in the last chapter.

GEOLOGICAL FEATURES OF THE HIGH-TEMPERATURE FIELDS

The high-temperature areas in Iceland as defined by BÖDVARSSON (1960) are all located within the zones of late Quaternary and Recent volcanism (Fig. 1). Drilling has been carried out in six of these areas, but 18 have been identified in the country. In all of the drilled areas temperatures higher than 200°C have been found at depths of less than 1000 m. The highest recorded drillhole temperatures are about 350°C at some 2000 m depth in Krafla and 322°C at 1750 m depth at Reykjanes.

Table 2. The calculated concentrations (in mmoles/kg) of various chemical species in the water feeding wet-steam wells in the four geothermal fields included in this study. The calculations refer to the reported quartz equilibrium temperature (t_{q12})

Species	Reykjanes well 0	Svartsengi well 4	Mánafljell well 4	Nesjavellir well 5	Hveragerdi well 4
H ₂ O	5.86	5.47	7.48	7.43	6.99
SiO ₂	355.6	251.8	3.46	5.64	6.38
Ca	34.9	23.6	0.564	0.608	0.298
Mg	37.8	24.5	0.011	0.037	0.024
CO ₂	0.013	0.185	5.42·10 ⁻⁵	7.24·10 ⁻⁵	5.81·10 ⁻⁴
Na	10.00	7.41	8.89	8.97	4.42
Cl ⁻	0.011	0.005	0.272	0.238	0.072
SO ₄	15.6	9.71	1.43	4.06	1.90
Fe	0.479	0.187	0.946	2.24	1.92
Li	2.49·10 ⁻⁶	2.27·10 ⁻⁶	0.0001	0.0002	0.0007
F	0.875	0.044	1.99	2.17	0.337
CO ₃	0.037	0.002	2.79	2.60	0.441
HCO ₃	6.15·10 ⁻⁸	5.00·10 ⁻¹⁰	3.48·10 ⁻⁵	2.88·10 ⁻⁵	1.06·10 ⁻⁶
CO ₃	0.002	0.003	0.003	0.001	0.001
SO ₄	0.027	0.047	0.603	0.180	0.474
CO ₃	0.003	0.002	0.001	0.002	0.0008
CO ₃	0.003	0.004	0.070	0.090	0.094
Ca	446.7	327.3	0.443	0.376	3.14
SO ₄	87.1	27.9	0.0035	0.0032	0.011
Li	4.15	1.31	0.0002	0.0002	0.0001
Fe	0.141	0.172	0.392	0.124	0.156
CO ₂	0.012	0.015	0.040	0.013	0.007
SO ₄	0.057	0.090	0.022	0.011	0.014
CO ₂	0.001	0.028	0.004	0.002	0.006
CO ₃	0.0003	0.0002	0.0003	0.0008	0.0008
Li	1.87·10 ⁻⁷	2.48·10 ⁻⁶	1.36·10 ⁻⁶	3.66·10 ⁻⁶	2.19·10 ⁻⁵
Fe	271.6	237.0	253.3	254.7	198.8

The high-temperature geothermal activity is typically associated with the so-called central volcanoes or volcanic complexes (PÁLMASSON and SÆMUNDSSON, 1974). These volcanic complexes, which are generally 10-20 km in diameter present the foci of greatest magmatic activity within the volcanic belts. They are situated near the centers of elongated swarms of faults and fissures. These swarms often tend to be at an angle (up to 30°) to the axes of the active volcanic zones and form an en-echelon pattern when the volcanic belts are viewed as a whole (PÁLMASSON and SÆMUNDSSON, 1974). All central volcanoes except on the Reykjanes peninsula are associated with acid and intermediate volcanics.

Eroded central volcanoes are widely distributed within the Tertiary basalt formations in Iceland (WALKER, 1963, 1966; SIGURDSSON, 1970). The hydrothermal alteration, which is typically found in the collapsed centers of these complexes bears witness of ancient geothermal activity.

The typical pattern of alteration minerals found in the high-temperature geothermal drillholes in Iceland has been reviewed recently by KRISTMANNSDÓTTIR (1975). The mineralogy and mineral zoning of the geothermally altered Tertiary central volcanoes is strikingly similar to that of presently active areas as deduced from the drillhole data (SIGVALDASON, 1963; TÓMASSON and KRISTMANNSDÓTTIR, 1972; KRISTMANNSDÓTTIR and TÓMASSON, 1974, 1975; WALKER, 1966; SIGURDSSON, 1966).

Intrusions are very abundant within the Tertiary central volcanoes (WALKER, 1966). The intrusions are mostly sills and dykes, which are few meters thick. WALKER (1966) estimates that the intrusions amount to at least 50% of the rock in some of the Tertiary volcanic complexes in eastern Iceland. Drilling at Nesjavellir, which is included in this study and recent drilling into the Krafla geothermal field (not included here) shows that minor intrusions predominate below about 1200-1400 m depth (KRISTMANNSDÓTTIR, pers. comm.) It appears that one of the characteristics of central volcanoes is abundance of shallow intrusions (WALKER, 1974). This is now known to be the case at Krafla and is suggested by gravity highs in several other high-temperature areas. The intrusions are considered to be the source of heat for the geothermal activity.

The distribution of the geothermal alteration in the eroded Tertiary central volcanoes indicates that the geothermal activity is fairly evenly spread throughout the whole period of the magmatic activity in the volcano. It appears that the life span of these volcanoes is of the order

UNIVERSITY OF UTAH LIBRARIES

of 0.5 to 1.5 million years (PIPER, 1971; GRÖNVOLD, 1972; FRIDLEIFSSON, 1973; SEMUNDSSON and NOLL, 1974).

SAMPLING PROCEDURES

From production wells samples were collected from separators on the wellhead that separate the whole discharge and yield over 99.8% dry steam. Samples of water and steam from exploratory wells were collected with the aid of a small thermally isolated, chromium-steel Webre separator. The separator was fitted to a half inch socket welded on the by-pass pipe in accord with the experimental results of MAHON (1960). Sampling pressures ranged from 3 to 22 bar.

A cold water jacketed pipe of chromium-steel, which is attached to the separator, is used to cool the water samples to 10–30°C and condense and cool the steam samples to about the same temperature. Water samples were collected into two 1 liter plastic bottles for determination of non-volatile constituents and into a 300 ml gas sampling tube for measurement of pH and analysis of dissolved volatile constituents (CO₂ and H₂S). The condensate was collected into a 300 ml gas sampling tube, also for analysis of dissolved volatile constituents. Any gas phase that accompanies the condensate was collected into two 300 ml gas sampling tubes by first filling them with condensate and then turning them upside down to allow the gas to cumulate from the top of the tube as it ejects the condensate. The volume of gas per 1 liter of condensate was recorded. The temperature of the condensate was measured and it is assumed that the temperature of the gas was the same.

Usually the pH and the volatiles in the water and condensate were analysed immediately after collection and always on the same day they were collected. Storage in a container not completely air-tight leads to rapid depletion of the volatile content of the condensate and fairly rapid decline in the H₂S content of the water sample. For determination of non-volatile constituents the water samples were taken to the laboratory as were the gas samples.

Evacuated flasks containing concentrated NaOH solution have also been used to collect non-condensable gases accompanying the steam fraction. In this case CO₂ and H₂S dissolve in the alkaline solution, but the non-soluble gases, mainly H₂ and N₂, form a separate gas phase. The condensate accompanying the gas phase can be measured as an addition to the NaOH solution. This sampling procedure is more accurate, particularly at high gas concentrations, but it is less convenient and more laborious than the one described above.

Since some water may always be carried over with the steam during sampling, the condensate was always analysed for a non-volatile component present in relatively high concentrations in the water phase, usually Na or Cl. If significant concentration of the non-volatile component was found in the condensate a correction is required to evaluate the quantity of volatiles that accompanied the steam.

The pressure drop in the small Webre separator was kept at minimum in order to reduce flashing in it as much as possible. This results in rather low flow rate of water and especially steam from the separator so it may take 5–10 min to collect 1 liter of the aqueous fraction and as much as 20–30 min for collection of 1 liter of condensate.

COMPUTER CALCULATIONS

Calculation of total discharge composition

In the four high-temperature areas under study, reservoir temperature/pressure relationships were such that only a hot-water phase, here termed reservoir water, existed in the aquifers penetrated by the wells before they were put into production. At Námafjall, Nesjavellir and Reykjanes

the pressure drop caused by the discharging wells was sufficient to initiate boiling in the feeding aquifers. On the other hand temperature/pressure measurements in discharging wells at Svartsengi and Hveragerdi, show that flashing starts in the wells in these two localities.

In the computer calculations the flashing of the reservoir water to the point of sample collection on the wellhead is assumed to be adiabatic, without any separation of the two phases, and at thermodynamic equilibrium. Under these conditions the enthalpy of the reservoir water equals that of the steam-water mixture at any sampling pressure. It is split between the two phases as shown by the following equation:

$$h_0 = X_1 G_1 + (1 - X_1) h_1 \quad (1)$$

and

$$h_0 = h_1 + X_1 L_1 \quad (1a)$$

In these equations h_0 represents the enthalpy of the reservoir water, G_1 and h_1 the enthalpies of the steam and water phases respectively at a given pressure, P_1 . L_1 is the latent heat of vaporisation at P_1 and X_1 the fraction of reservoir water that has evaporated.

The relationship expressed in equation (1) is not valid if the well discharge enthalpy deviates from h_0 , a situation that will arise when flashing occurs in the aquifer and separation of the two phases causes the well discharge to become enriched or depleted in steam. Enthalpy data for individual well discharges are not available to reveal this. Yet it is considered that it is a fair assumption to take individual well discharge enthalpies to be equal to that of the unflashed reservoir water. The analytical data were largely collected during the early periods of production and drastic changes in the composition of individual well discharges have not been observed.

The concentrations of the various chemical components dissolved in the unflashed hot-water have been evaluated from analyses of the water and steam phases collected separately on the wellhead at a known pressure. The concentrations of any non-volatile and volatile constituent in the reservoir water are related to their analysed concentrations in the collected water and steam phases respectively as shown by the following equation:

$$m_0 = m_w(1 - X) \quad (2)$$

and

$$v_0 = v_w(1 - X) + v_g X \quad (2a)$$

The subscripts 0, w and g denote reservoir water, flashed water, and steam; m and v represent a non-volatile and a volatile constituent respectively, and X the fraction of steam flashed from the reservoir water. Combined analysis of the condensate and the gas samples yields a value for v_g .

Calculation of activity coefficients and the concentration of individual chemical species

Individual ion activity coefficients were calculated from the extended Debye-Hückel equation:

$$-\log \gamma_i = \frac{Az_i^2 \sqrt{I}}{1 + \lambda B \sqrt{I}} \quad (3)$$

The values of A (the Debye-Hückel limiting law parameter), B (the molal Debye-Hückel coefficient) have been obtained from HELGESON (1969) and the values of λ (the ion size parameter) from GARRELS and CHANG (1965).

As a first approximation the ionic strength was taken as the analysed total concentration of major cations in the water sample:

$$I_{\text{approx.}} = \frac{1}{2} (2m_{\text{Na}} + m_{\text{K}} + 4m_{\text{Ca}} + 4m_{\text{Mg}}) \quad (4)$$

Table
comp

React
H ₂ O(l)
H ₂ CO ₃ (aq)
HCO ₃ ⁻ (aq)
H ₂ S(aq)
HS ⁻ (aq)
CaCO ₃ (s)
MgCO ₃ (s)
MgO(s)
K ₂ SO ₄ (s)
CaSO ₄ (s)
MgSO ₄ (aq)
MgSO ₄ (s)
MgCl ₂ (aq)
MgCl ₂ (s)
H ₂ O(vap)
CO ₂ (vap)
H ₂ O ₂ (aq)

(1)
(2)
(3)

permitting the first and subsequent dissolved ionic species listed gives a new set of correct values corresponding to the chemical speciation.

Activity coefficients and gases were taken

The method of individual chemical speciation will be calculated using the data of CHRIST, 1965; TRUE species and reactions have been listed in Table 1. The solution of the activity dissociation equilibrium temperature.

Specifically for the conservation of charge included. The value of pH and activity of acids and their anions (total sulphide) in the reservoir water and the flashed water fraction.

ESTIMATION OF ENTHALPY

In the present temperature is, if that calculated from silica in solution. The enthalpy is determined only water to data that have been used MOREY *et al.* It has been shown (1970b, 1975) measured temperatures in wells and fluids in New Zealand.

Table 3. Equilibrium constants (-log K) for the chemical reactions considered for the present computer program. The reported values represent a printout from the relevant computer subroutine

Reaction	20°C	50°C	100°C	150°C	200°C	250°C	300°C	350°C	Remarks	Source of data
$H_4SiO_4 \rightleftharpoons H_3SiO_4^-$	10.00	9.53	9.07	8.85	8.85	9.05	9.45	10.07		FITZER (1937) <120°C>; SEWARD (1974) >20°C
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	6.34	6.29	6.47	6.73	7.06	7.67	8.82	10.75		HELGESON (1969)
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	10.31	10.13	10.17	10.30	10.62	11.49	13.31	16.51		HELGESON (1969)
$H_2S \rightleftharpoons H^+ + HS^-$	6.99	6.76	6.64	6.71	6.94	7.37	8.02	8.94		HELGESON (1969)
$HS^- \rightleftharpoons H^+ + S^{2-}$	15.30	14.57	13.62	13.07	12.78	12.60	12.40	12.02		DICKSON (1966)
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$	3.04	3.40	4.00	4.60	5.20	5.80	6.40	7.00	(1)	HELGESON (1969)
$HgCO_3 \rightleftharpoons Hg^{2+} + CO_3^{2-}$	3.04	3.40	4.00	4.60	5.20	5.80	6.40	7.00	(2)	
$KAlSO_4 \rightleftharpoons K^+ + Al^{3+} + SO_4^{2-}$	0.80	0.97	1.28	1.61	1.96	2.32	2.71	3.11	(3)	
$KSO_4 \rightleftharpoons K^+ + SO_4^{2-}$	0.80	0.97	1.28	1.61	1.96	2.32	2.71	3.11		TRUESDELL and SINGERS (1974), Table 5
$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$	2.29	2.39	2.72	3.13	3.57	4.03	4.52	5.01	(1)	HELGESON (1969)
$HgSO_4 \rightleftharpoons Hg^{2+} + SO_4^{2-}$	2.10	2.56	3.31	4.07	4.82	5.57	6.33	7.08	(1)	HELGESON (1969)
$KCl \rightleftharpoons K^+ + Cl^-$	-1.59	-1.40	-1.03	-0.72	-0.40	0.00	0.64	1.63		TRUESDELL and SINGERS (1974), Table 5
$HgCl_2 \rightleftharpoons Hg^{2+} + 2Cl^-$	-1.57	-1.16	-0.70	-0.40	-0.12	0.26	0.92	1.98		TRUESDELL and SINGERS (1974), Table 5
$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	1.92	2.30	2.98	3.72	4.50	5.30	6.13	6.97		LIETZKE et al. (1961)
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	3.11	3.39	3.83	4.36	4.98	5.73	6.59	7.57		ELLIS (1963)
$H_2S(vap) \rightleftharpoons H_2S(aq)$			3.16	2.44	1.95	1.53	1.14	0.76		HELGESON (1969)
$CO_2(vap) \rightleftharpoons CO_2(aq)$			3.52	3.01	2.50	1.99	1.48	0.97		ELLIS and GOLDING (1963)
$SiO_2(qtz) \rightleftharpoons SiO_2(aq)$	4.00	3.65	3.09	2.68	2.35	2.08	1.94			MOREY et al. (1962) <240°C>; KENNEDY (1950) >240°C.

- (1) extrapolated over 200C.
- (2) assumed to be identical with K(CaCO₃).
- (3) assumed to be identical with K(KSO₄), cf. TRUESDELL and SINGERS (1974).

permitting the first calculation of all activity coefficients and subsequent derivation of the concentration of all dissolved ionic species. The total ion concentration so calculated gives a new value for the ionic strength. Iteration gives the correct values for the activity coefficients that correspond to the ionic strength of the solution after chemical speciation has been taken into consideration.

Activity coefficients for non-charged dissolved species and gases were taken to be unity.

The method of calculating the concentration of individual chemical species in reservoir water with a known composition will not be described here, since comparable calculations have been described before (GARRELS and CHRIST, 1965; TRUESDELL and SINGERS, 1974). The chemical species and reactions considered for these calculations have been listed in Table 3. The computer calculations involve solution of the appropriate mass balance equations and dissociation equilibria for these reactions at a given reference temperature.

Specifically for the pH calculations, equations expressing conservation of charge of anions of weak acids must be included. The value for this sum is obtained from measurement of pH and analysis of the total concentration of weak acids and their anions (total silica, total carbonate and total sulphide) in the sample of the water fraction. In the reservoir water this sum is (1 - X) lower than in the flashed water fraction.

ESTIMATION OF RESERVOIR TEMPERATURE AND ENTHALPY OF WELL DISCHARGES

In the present computer program the reservoir temperature is, if not otherwise specified, taken to be that calculated from the content of undissociated silica in solution assuming equilibrium with quartz. The enthalpy is derived from this temperature assuming only water to be present. The quartz solubility data that have been used are those of KENNEDY (1950) and MOREY et al. (1962).

It has been shown (MAHON, 1966, 1970; ARNÓRSSON, 1970b, 1975) that there is a good fit between measured temperatures and quartz equilibrium temperatures in wells in high-temperature geothermal fields in New Zealand and Iceland respectively. In

his demonstration of equilibrium between quartz and dissolved silica ARNÓRSSON (1975) used analyses from wells fed by one aquifer and samples that were collected shortly after the well produced for the first time.

Pressure drop in high-temperature water reservoirs caused by discharging wells may cause increased flashing in the reservoir, especially where the original underground temperatures are near the boiling point curve. Flashing in the reservoir so produced will lower the temperature of the water in the formation and thus cause some precipitation of quartz. Quartz equilibrium temperatures derived from the silica content of discharges of wells that have produced such pressure drop will be intermediate between the original reservoir water temperature and the temperature of inflow into the well.

An example of the fall in quartz equilibrium temperature of well discharges with time is demonstrated in Fig. 3. Well 5 at Námafjall shows the greatest drop observed in this study, or some 45-50°C. If the enthalpy of the discharge of this well corresponds to the quartz equilibrium temperature as it was at the initiation of the discharge period, but not to a value 45-50°C lower, the computer program yields 11% too high values for the concentrations of the non-volatile constituents in the reservoir water and for the volatile constituents, H₂S (total) and CO₂ (total), values which are low by some 40% and 20% respectively.

In evaluating the chemistry of the water feeding the 14 wet-steam wells under study, the limitation of the quartz geothermometer must be kept constantly in mind. It is a further limitation that the solubility and other mineral-solute calculations refer to one temperature, whereas the total well discharge, which is analysed, may be composed of water fractions of different temperatures. In order to get an impression of this effect and the validity of the quartz equilibrium

UNIVERSITY OF UTAH LIBRARIES

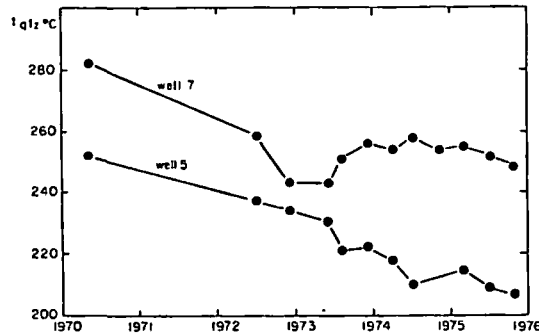


Fig. 3. Variation with time in the quartz equilibrium temperature (t_{qtz}) of the discharges from wells 5 and 7 at Námafjall.

temperature, measured downhole temperatures and aquifer locations have been presented for all the 14 wells in question in Fig. 4.

EVALUATION OF RESULTS

General comments on the chemical speciation in the reservoir water

Examples of the computed chemical speciation in the reservoir water from the four geothermal fields studied are given in Table 2. The analytical data for these computations are given in Table 1.

The calculated pH of the saline reservoir waters is near neutral, being on average about 5.8 for Reykjanes and about 5.5 for Svartsengi. Neutral pH at the quartz equilibrium temperature for Reykjanes and Svartsengi is 5.6. The dilute waters are distinctly alkaline, the pH being in the range of 7.2–7.5 for Námafjall and Nesjavellir (neutral pH 5.6) and on average about 6.9 for Hveragerdi (neutral pH 5.7). A further discussion on factors controlling the pH-level is given in a later section.

Virtually all the silicic acid is undissociated in the saline waters and far the larger part of the carbonic

acid and the hydrogen sulphide. In the dilute waters silicic acid is insignificantly dissociated (1–3%) but some half of the carbonic acid and hydrogen sulphide is. Therefore, the pH of the dilute reservoir waters is strongly buffered by the two latter mentioned weak acids. Of total fluoride, HF^0 amounts to 20–40% in the saline waters, but its concentration is insignificant in the dilute waters, being less than 2%. HSO_4^- is virtually all dissociated in both types of water.

Of the major anions sulphate is largely complexed as $NaSO_4^-$ and $CaSO_4^0$ in both saline and dilute reservoir waters. In the dilute waters these complexes include a significant fraction of the total sodium and calcium. Only $\frac{1}{3}$ of the total sulphate forms free SO_4^{2-} ions in the saline waters and $\frac{1}{2}$ to $\frac{3}{4}$ in the dilute waters. Chloride is considerably complexed as $NaCl^0$ and KCl^0 in the saline waters.

Carbonate ions (CO_3^{2-}) are present in considerably lower concentrations than the corresponding $CaCO_3$ and $MgCO_3^0$ ion pairs in both types of water. It is evident that sulphide ions (S^{2-}) occur in higher concentrations in the dilute waters than in the saline waters although the reported values in Table 2 are uncertain due to the uncertainty in the value of K_{HS^-} . The values of DICKSON (1966) used here are probably too high (see ELLIS and GIGGENBACH, 1971). The higher S^{2-} concentrations in the dilute waters are expected to maintain the mobility of the free ions of the base metals at a lower level than in the saline waters. This is supported by the available data for iron. Its concentration is in the range of 5–10 ppb for the dilute waters but some 500 ppb for the saline waters (ARNÓRSSON, 1970c).

The distribution of CO_2 and H_2S between steam and flashed water

The computed activity of carbon dioxide and hydrogen sulphide in the samples of water and steam from the separator suggests that equilibrium distribu-

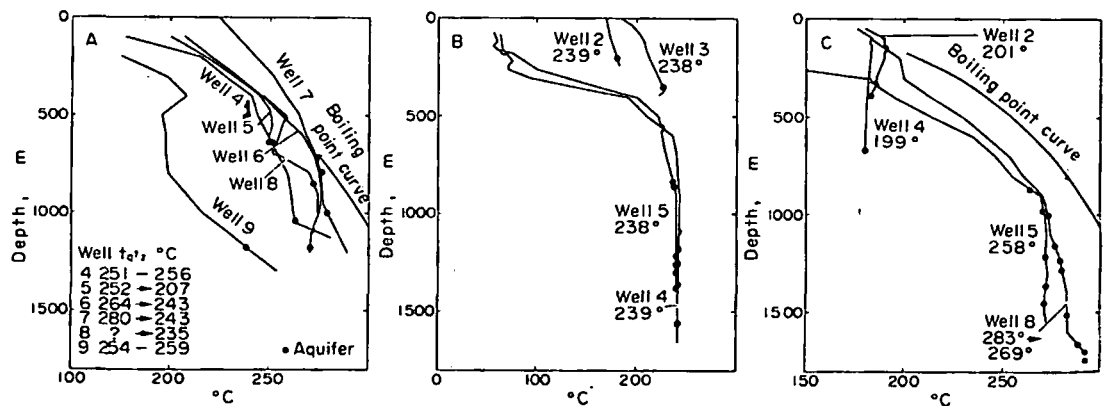


Fig. 4. Measured downhole temperatures and location of aquifers in (A) wells 4–9 at Námafjall, (B) wells 2–5 in Svartsengi, and (C) well 8, Reykjanes, wells 2 and 4 in Hveragerdi, and well 5 at Nesjavellir. The temperature profile for well 9, Námafjall, was taken shortly after completion of drilling and is considered to represent much too low temperatures. The figures with each temperature profile (in the bottom left corner of Figure A) represent the temperature of equilibrium with quartz (t_{qtz}). An arrow between a set of figures indicates trend towards lowering of the quartz equilibrium temperature with time.

is attained for these volatile compounds between the two phases. The activities of carbon dioxide and hydrogen sulphide in the water fraction were calculated from the analysed total carbonate and total sulphide and the measured pH and refer to the temperature of separation. The activities of carbon dioxide and hydrogen sulphide in the steam phase were derived from analysis of the condensed steam and accompanying gas phase.

In the dilute waters, the total carbonate ($H_2CO_3 + HCO_3^- + CO_3^{2-}$) determination is semi-quantitative, explaining to some extent the great scatter of points for the computed values of CO_{2w}/CO_{2g} (Fig. 5). The average for each well discharging the dilute waters is reasonably close to the equilibrium value. Total carbonate in the water fraction is determined by titration with dilute hydrochloric acid solution and subtracting on a theoretical basis the interference from silica, hydrogen sulphide and water. Total sulphide was determined by titration with mercuric acetate or iodine solutions, which are accurate methods. This is reflected in the better fit of the hydrogen sulphide data to the equilibrium distribution (Fig. 5).

The saline waters at Reykjanes and Svartsengi

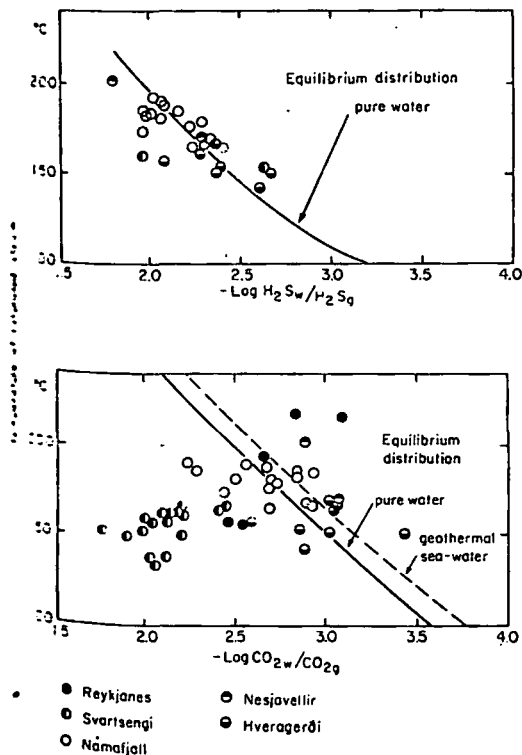


Fig. 5. The calculated distribution of CO_2 and H_2S between the water and steam phases in the separators from which samples were collected. The calculations are based on the analysed concentrations of total carbonate and total sulphide in the respective samples of water and steam. The temperature of separation has been derived from the pressure in the separator assuming this pressure to be determined by saturated steam.

present a special problem in this respect. The calculated activity of carbon dioxide in the water sample is determined by the analysed total carbonate and the measured pH. The saline waters are sulphide deficient, so one might expect a rather good precision for the total carbonate determination in the water sample. This appears, however, not to be the case as is reflected in the large variation of these values for well 8 at Reykjanes (15–65 ppm). The measured pH and the analysed content of total carbonate determine the calculated value of bicarbonate in the water sample. For the saline waters it is this value for bicarbonate that has the greatest effect on the computed reservoir water pH. The measured pH of the water fraction in Svartsengi is 7.2–7.5 at 20°C. Relatively large error in the pH measurement does not affect much the calculated bicarbonate concentration because the major part of the total carbonate is as bicarbonate at this pH level. The error in the bicarbonate values is approximately proportional to the error in the total carbonate analysis.

The reservoir water pH at Svartsengi has been calculated from a total carbonate value in the water sample in turn derived from the analysed carbon dioxide in the steam phase and the measured pH of the water sample assuming equilibrium distribution of carbon dioxide between the two phases. The pH so calculated fits well with calcite saturation and 'expected' metal/H ratios, as is discussed in a later section. By contrast the analytical total carbonate value yields a strong calcite supersaturation and a relatively high pH. Application of the same procedure to obtain the pH for the Reykjanes reservoir water yields rather consistent results and $CaCO_3$ activity product that fits with some calcite supersaturation. The analytical CO_2 -data for the water samples give on the other hand widely varying pH values for different samples and a large range in the computed $CaCO_3$ activity product from strong calcite undersaturation to strong supersaturation.

There is no reason to believe on grounds of discharge enthalpy and separation conditions that equilibrium distribution of volatiles is attained in the dilute fluids but not in the saline fluids and for H_2S but not for CO_2 . Therefore, by virtue of the good fit with calculated pH and calcite saturation, when equilibrium distribution is assumed for the calculations, it is thought that the low analytical values for the ratio of CO_2 between steam and water at Svartsengi and the random values for Reykjanes are due to poor precision in the analyses of total carbonate in the water samples of the well discharges.

GLOVER (1970) reported values for the distribution of CO_2 and H_2S between water and steam discharged from separators at Wairakei to be 2–7 times lower than the equilibrium distribution values. It is believed that his calculated figures may be somewhat low, because, as he pointed out, conversion of HCO_3^- into CO_2 as flashing proceeds at lower pressure, was not taken into account.

UNIVERSITY OF OXFORD LIBRARY

Major cation ratios

The temperature dependence of the relative concentrations of the major cations (Na, K, Ca) in geothermal waters has been discussed repeatedly in the literature (see e.g. FOURNIER and TRUESDELL 1973). For this reason a detailed discussion will not be given here for the Icelandic geothermal waters.

The cationic ratios of the dilute and saline Icelandic geothermal waters are such that empirical NaK- and NaKCa-geothermometers (see TRUESDELL, 1975) yield temperature values that fit well with quartz equilibrium temperatures and measured downhole temperatures (Table 2, Fig. 4). Yet the potassium content of the Reykjanes geothermal sea-water is somewhat low. This is thought to be due to insufficient amount of potassium in the rock available for leaching to maintain equilibrium with the sodium and calcium concentrations (ARNÓRSSON, 1978a).

Cold ground waters in Iceland are normally much lower in sodium and potassium than the dilute geothermal waters, but higher in calcium and magnesium. The relative concentrations of these major cations in the dilute geothermal waters are therefore attained by leaching of sodium and potassium from the rock and by loss of calcium and magnesium from solution. By contrast, the saline geothermal waters, which have derived their salinity from sea-water, obtain their major cation ratios by leaching of calcium and potassium from the rock and by strong depletion of magnesium and slight depletion of sodium from solution. The attainment of fixed cationic ratios at a given temperature by different reaction trends between water and rock, suggest that these distributions represent an equilibrium distribution. Individual cation ratios can be derived from their relation to hydrogen ions presented in Fig. 6.

The pH of the reservoir water

The calculated pH of the saline reservoir waters at Reykjanes and Svartsengi is about 5.8 and 5.5 respectively, but it lies in the range 6.7–7.7 for individual samples of the dilute waters of the Hengill and Námafjall areas. In calculating the pH of the saline waters, the total carbonate in the water sample was obtained from the measured CO₂ in the steam, the measured water sample pH and assuming equilibrium distribution of carbon dioxide between the two phases, but not from the analytical values of total carbonate in the water sample. The analytical values are considered unreliable as discussed previously and yield widely varying pH values for the Reykjanes reservoir water (5.3–6.1; average of 6 samples 5.7) and systematically higher values (0.6–1.0 pH units) for the Svartsengi waters.

Of the dilute waters, Hveragerdi has the lowest pH, or 6.87 (average of 7 analyses from 2 wells; range 6.73–7.03). The reservoir water feeding the Hveragerdi wells has not flashed in the aquifer. Flashing occurs in the aquifers in Námafjall and Nesjavellir (northeast Hengill), where the average pH is 7.33 (22 analyses from 6 wells; range 6.98–7.69) and 7.27 (3 analyses

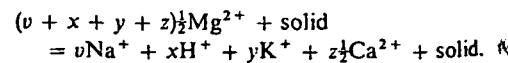
from 1 well; range 7.12–7.41) respectively. The lowest pH values at Námafjall correspond to the well fed by the hottest aquifer and containing the highest concentrations. The highest pH values correspond on the other hand to the shallowest well, which is fed by the coldest aquifer.

At Námafjall the underground temperature follows approximately the boiling point curve (Fig. 4), at least to the level of the deepest wells. At Nesjavellir a temperature maximum of 284°C is observed at 1000 m depth. Nesjavellir is on the boundary of the Hengill area. It seems likely that some separation of steam has occurred in the aquifer feeding the wells in these areas, so the total well discharges are somewhat depleted relative to the unflashed reservoir water. This will cause the calculated pH to be higher than the actual pH of the unflashed reservoir water. Decreasing quartz equilibrium temperatures for wells at Reykjanes indicates flashing in the aquifer, explaining, it is believed, why the calculated pH of the Reykjanes water is somewhat higher than that at Svartsengi.

Reactions influencing reservoir water pH

During alteration of the basaltic rock in the Icelandic high-temperature systems various hydrated silicates form, which may participate in ionic exchange equilibria governing the relative activities of the cations and protons in solution. Such minerals would include zeolites and the layered silicates, smectite and chlorite. The chemical composition of these minerals and their potential role is not known, so it cannot be concluded at this stage what their role is in determining the pH of the associated geothermal water. According to MAHON (1970) the pH of the New Zealand geothermal waters is mainly controlled by K-mica and K-feldspar. Neither of these minerals have been observed in the Icelandic geothermal fields.

In quantitative terms smectite and chlorite are the most important alteration minerals in the Icelandic geothermal fields. Because of their wide distribution and abundance, and the possibility that chlorite always forms via smectite, it seems likely that adsorption of cations and protonated water molecules between the layers of smectites are important in determining the pH of the geothermal waters. Ion exchange reaction of this kind is expressed by the following equation:



The values of v , x , y and z depend on the stoichiometry of the reaction, which in turn is determined by the composition of the minerals involved. An equilibrium constant for equation (6) can be expressed as

$$\log K = v \log \frac{\text{Na}}{\text{H}} + y \log \frac{\text{K}}{\text{H}} + z \log \frac{\sqrt{\text{Ca}}}{\text{H}} - (v + x + y + z) \log \frac{\sqrt{\text{Mg}}}{\text{H}}$$

The value of K is temperature dependent and varies insignificantly with temperature by vir

For interpretation of high-temperature data from the Reykjanes area it is seen that the data can be expressed by the equation (6) and that the Mg ratios have a particularly important influence on the results. The results indicate that the log of the activity of these v cations is

The high-temperature data are not based on ion activity ratios of the cations and protons at the low-temperature end and refers to a temperature of the water as indicated by ARNÓRSSON and SIGURDSSON (1978) and conductive conductivity measurements

Reykjanes / Svartsengi

A

Fig. 6. Water (<180°C) MOREY parabolic major cation ratios

Fig. 6. Water (<180°C) MOREY parabolic major cation ratios

The value of K , the equilibrium constant, is temperature dependent. If the standard heat of the reaction varies insignificantly with temperature, $\log K$ will simply vary with the reciprocal of the absolute temperature by virtue of the van't Hoff equation

$$\frac{d \log K}{d(1/T)} = \frac{H_{(r)}^0}{4.5758} \quad (8)$$

For interpretation of the metal/proton ratios of the high-temperature waters, the data from the wet-steam wells have been supported with additional unpublished data from the low-temperature areas in Iceland. It is seen that a temperature relationship of the kind expressed by the van't Hoff equation (for $H_{(r)}^0 = \text{constant}$) is obtained for Na/H, K/H, and $\sqrt{\text{Ca}/\text{H}}$ (Fig. 6). Mg ratios have not been studied. The relationship is particularly good for $\sqrt{\text{Ca}/\text{H}}$, but it is poorest for K/H. The results presented in Fig. 6, which demonstrate the log metal/H relationships with $1/T$ for the low-temperature waters are taken to indicate that the pH of these waters is governed by ionic exchange equilibria.

The high- and low-temperature data as plotted in Fig. 6 are not exactly comparable. The former are based on ion activities but the latter on total concentrations of the cations, because computed activity values are not yet available for these data. The pH of the low-temperature data is, however, computed and refers to conductive cooling for springs and wells and a temperature derived from the silica content of the water assuming equilibrium with chalcedony (ARNÓRSSON unpublished work). The assumption of conductive cooling seems to be sound when measured temperatures in hot-springs are below about 95°C.

It appears, however, that high pH values are obtained for boiling springs as is reflected in relatively high metal/proton ratios of some points in the temperature interval of 100–150°C. Since underground temperatures are below about 150°C in the low-temperature areas flashing is confined to the uppermost 40 m or so. For the chemistry of the low-temperature waters, preliminary calculations show that the deep water pH would not be lowered by more than 0.5 units if maximum degassing was assumed instead of conductive cooling.

If cation concentrations for the low-temperature data were replaced by free cation activities the relevant points in Fig. 6 would be shifted down, particularly for calcium. At a temperature of $1000/T = 2$ (227°C) this would amount to some 0.1 units for $\log \text{Na}/\text{H}$ and $\log \text{K}/\text{H}$ for the ionic strength of the low-temperature waters, but of the order of 0.6 units for $\log \sqrt{\text{Ca}/\text{H}}$. The dashed lines in Fig. 6 indicate the approximate position of the best fit line through the low-temperature data, if cation concentrations were replaced by cation activities. Extrapolation of the dashed line shows that the Hveragerdi and Svartsengi waters have metal/H ratios comparable with the low-temperature waters, if the effect of temperature is eliminated. Other high-temperature waters (Reykjanes, Námafjall, Nesjavellir), including one analysis from Wairakei, obtained from TRUEDEL and SINGERS (1974), show higher metal/H ratios. As was mentioned earlier the temperature/depth relationships are such in Hveragerdi and Svartsengi that the water feeding the wells has not flashed in the aquifer. The calculated pH for the reservoir waters in these areas is believed to present equilibrium values for the

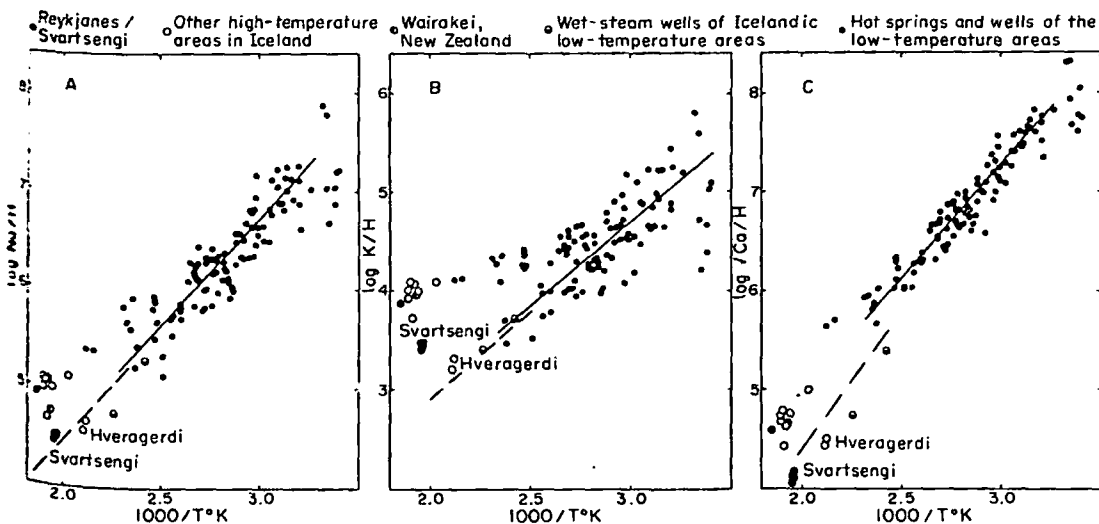


Fig. 6. The relation between the activities of H^+ , Na^+ , K^+ and Ca^{2+} in geothermal waters in Iceland. Water temperatures have been derived from those of equilibrium with quartz ($> 180^\circ$) and chalcedony ($< 180^\circ$). The quartz and chalcedony solubility data have been derived from KENNEDY (1950) and MOREY *et al.* (1962) and FOURNIER (1973) respectively. The low-temperature data are not exactly comparable with the high-temperature data. The former are based on the total concentrations of the major cations and H^+ activity, whereas the latter are based solely on activities. The dashed lines indicate the approximate position of the best fit line through the low-temperature data, if cation concentrations were replaced by free cation activities.

UNIVERSITY OF UTAH LIBRARY

hydrogen ion activity relative to the activities of other cations in solution. The higher metal/H ratios for the Reykjanes, Námafjall and Nesjavellir waters are explained by the influence of flashing in the aquifer and simultaneous loss of some steam (and gas) from the fluid entering the wells. Depletion of gas has such an effect on the computer calculations that a high pH is obtained relative to that of the unflashed reservoir water.

The difference of the plotted metal/H values for the flashed high-temperature waters and the extrapolated line from the low-temperature data varies with the cation. It is largest for potassium but smallest for calcium. Removal of calcium from solution by calcite precipitation, which accompanies the flashing process, could not account for the low $\sqrt{\text{Ca}/\text{H}}$ values compared with those of K/H. It is believed that this may reflect different rate of re-equilibration for the different cations to satisfy the new pH conditions. Calcium re-equilibrates fastest but potassium slowest. In this respect it may be mentioned that reactions caused by flashing could yield too high temperature values from the NaK- and NaKCa-geothermometers, because of removal of sodium and calcium from solution in excess of potassium.

Calcite saturation

Calcite is an abundant geothermal mineral in the upflow zones of the high-temperature geothermal fields where flashing occurs (BJÖRNSSON *et al.*, 1972; GÍSLASON, 1973; KRISTMANNSDÓTTIR, pers. comm.). It may amount to 10–20% of the rock by volume. Below the flashing zone calcite is much less abundant (1–2%) (BJÖRNSSON *et al.*, 1972). During flashing the activity of CO_3^{2-} in the water increases sharply, des-

pite a decrease in its total carbonate content. This is due to the increase in the pH of the water caused by the transfer of carbon dioxide and hydrogen sulphide into the steam. The increase in the activity of CO_3^{2-} is always sufficient to bring about supersaturation in an originally saturated solution, at least during the early stages of flashing (ARNÓRSSON, 1977). Therefore, flashed reservoir waters may be calcite-supersaturated, at least if precipitation rates are not sufficient to restore equilibrium.

The Hveragerdi and Svartsengi waters fall just on the calcite solubility curve, but flashing, and therefore degassing, does not occur in the aquifers feeding the wells in these areas. On the other hand the computed CaCO_3 activity product for the wells at Námafjall, Nesjavellir, and Reykjanes plots on the supersaturation side of the calcite solubility curve (Fig. 7A). As was pointed out earlier, flashing occurs in the aquifers feeding the wells in these areas. Some separation of steam (and gas) in the aquifers is believed to occur from the fluid entering these wells as has indeed been demonstrated for Námafjall (ARNÓRSSON, 1978b). Such loss of steam will cause the total water discharges to become lower in gas than the unflashed reservoir water. The outcome is that the calculation will yield some supersaturation, if the unflashed water was just saturated. At Námafjall the degassing is strongest for the coolest and shallowest aquifers. Hence the calculated calcite supersaturation is also large.

The calculated calcite supersaturation has not resulted from the use of an erroneous reference temperature, as might be suspected, but it was pointed out earlier that quartz equilibrium temperatures are expected to be lower than the temperatures of the unflashed reservoir water, if flashing occurs in the

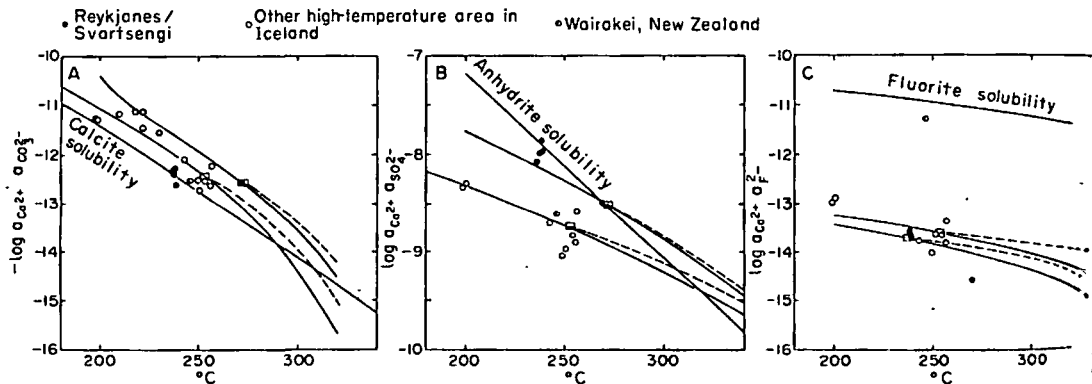


Fig. 7. A graphic illustration of the state of (A) calcite-, (B) anhydrite-, and (C) fluorite-saturation in high-temperature geothermal waters in Iceland. The reference temperature is that of equilibrium with quartz (t_{qu}). The plotted points represent averages of 1–8 samples displaying a narrow range of t_{qu} . Due to uncertainty in the validity of the quartz equilibrium temperature, the respective ion activity products have been calculated for selected samples at higher and lower temperatures, represented by the solid and dashed lines. The dashed lines correspond to conductive cooling above the quartz equilibrium temperature. The solid lines correspond to one step adiabatic flashing. The reservoir water compositions, which the latter set of calculations are based on, are variable. These compositions for each given reference temperature are derived from equations (2) and (3). The value of X (the steam fraction in the discharge) in these equations is determined by the respective reference temperature. The solubility data for calcite, anhydrite and fluorite have been obtained from HELGESON (1969), BLOUNT and DICKSON (1969), and NORDSTROM and JENNE (1977) respectively. The Wairakei data are from TRUESDELL and SINGERS (1974).

aquifer due to the increase in the pH of the water caused by the transfer of carbon dioxide and hydrogen sulphide into the steam. The increase in the activity of CO_3^{2-} is always sufficient to bring about supersaturation in an originally saturated solution, at least during the early stages of flashing (ARNÓRSSON, 1977). Therefore, flashed reservoir waters may be calcite-supersaturated, at least if precipitation rates are not sufficient to restore equilibrium.

The interplay between the unflashed and flashed calcite saturation under the CaCO_3 corresponds

anhydrite saturation. The saline water is saturated with respect to anhydrite. The saline water is saturated with respect to anhydrite. However, sufficient anhydrite is contained in the saline geothermal water compared with the unflashed water, as is in the case of the unflashed water.

Anhydrite is a common mineral in the upflow zone of the geothermal fields (BJÖRNSSON, 1972). It is thought to be derived from the precipitation of this water. Upon subsequent heating, the impermeable caprock is being the upflow zone of the geothermal field, anhydrite is precipitated. Anhydrite has been found in the dilute water of the geothermal field.

It is possible that a deeper than peridotite saturation is present and insufficient leaching is required to maintain saturation at the present temperature and as a geothermal field.

The solid and dashed lines for CaSO_4 activity product for two selected samples and conductive cooling of these lines

aquifer due to silica precipitation. The solid and dashed lines in Fig. 7A show how the computed CaCO_3 activity product of two selected samples varies with an arbitrarily selected reference temperature for one step adiabatic flashing and conductive cooling respectively. For both dilute and saline waters, a relatively large variation in the reference temperature does not significantly affect the fit of the computed CaCO_3 activity product with the calcite solubility curve.

The interpretation which is favoured here, is that the unflashed geothermal reservoir waters are always just calcite saturated. Loss of gas by some steam separation underground at Námafjall, Nesjavellir and Reykjanes is responsible for the calculated value of the CaCO_3 activity product of these waters which corresponds to supersaturation.

Anhydrite saturation

The saline waters at Reykjanes and Svartsengi are just saturated with anhydrite at the quartz equilibrium temperature but the dilute waters are somewhat undersaturated (Fig. 7B). Sea-water, the parent fluid of the saline geothermal waters, is somewhat undersaturated with respect to anhydrite. Slight heating is, however, sufficient to produce saturation. Sea-water contains much higher concentrations of sulphate than the saline geothermal waters, or about 2500 ppm as compared with some 20 ppm. Saturation is maintained upon further heating by anhydrite precipitation, as is indicated by the lowering of the sulphate contents from that of the original sea-water.

Anhydrite is abundant locally in the rocks of the upflow zone of the Reykjanes area (BJÖRNSSON *et al.*, 1972). It is thought that this anhydrite has precipitated from cold sea-water-groundwater, which surrounds the upflow zone, during intermittent invasion of this water into the geothermal system and subsequent heating. Tectonic movements, which open the impermeable cap of altered vesicle-filled rock enveloping the upflow zone, give passage of the sea-water-groundwater into the geothermal system. Dissolution of anhydrite thus formed is believed to maintain anhydrite saturation of the cooling, ascending saline geothermal water.

Anhydrite has not been reported in the altered rock of the dilute water geothermal systems. It is, however, possible that anhydrite saturation exists at levels deeper than penetrated by the drillholes and that undersaturation is produced by cooling in the upflow zone and insufficient oxidation of sulphide and insufficient leaching of calcium and sulphate from the rock to maintain saturation. If this were the case, the computed temperature of anhydrite saturation could be used as a geothermometer.

The solid and dashed lines in Fig. 7B show how the CaSO_4 activity product varies with temperature for two selected samples for one step adiabatic flashing and conductive cooling respectively. The intersection of these lines with the anhydrite solubility curve

gives an indication of the temperature of anhydrite saturation. It is 320–340°C for Námafjall and some 300°C for Nesjavellir and Hveragerdi. Only solute-solute reactions were considered in calculating the CaSO_4 activity product 'lines'. If the ionic exchange reactions, discussed previously, had also been considered, a lower water pH would have been obtained and therefore lower SO_4^{2-} activities, because higher portion of the sulphate would be as bisulphate (HSO_4^-). Therefore the CaSO_4 activity product 'lines' in Fig. 7B represent maximum values, i.e. minimum temperature values for anhydrite saturation. It is of particular interest to reveal, if the temperature of anhydrite saturation could be used as a geothermometer.

It is certainly possible that the mobility of sulphate in the dilute geothermal waters is not limited by anhydrite solubility below the upflow zone but by the following redox equilibrium with sulphide:



The mobility of H_2S , H^+ and H_2 are not expected to vary independently since they are involved in other mineral/solute equilibria. Further study is needed on the possible effect of this reaction on sulphate mobility.

Factors affecting the mobility of fluoride

All the high-temperature waters are considerably fluorite undersaturated according to the fluorite solubility values of NORDSTROM and JENNE (1977) and other fluorite solubility data (Fig. 7C). The CaF_2 activity products of the Icelandic waters are much lower than that of the only sample from Wairakei, New Zealand, which is plotted in Fig. 7C. The Wairakei sample yields a CaF_2 activity product that fits rather well with fluorite saturation according to the solubility data of NORDSTROM and JENNE (1977).

As can be seen from Fig. 7C, the plotted points for the CaF_2 activity product fall roughly on a line running parallel with the fluorite solubility curve. The saline geothermal waters contain roughly ten times less fluorine than sea-water so this element has evidently been lost from solution upon heating of the sea-water and its development into a geothermal brine. On the other hand the fluorine in the dilute geothermal waters is much higher than in their parent fluid, cold groundwater of meteoric origin. Cold groundwaters in Iceland contain generally less than 0.05 ppm of fluorine. This increase in fluorine has presumably resulted from leaching of this element from the rock by the hot water. Increase in fluorine in one type of water and decrease in the other type, which leads to the same CaF_2 activity product at a given temperature might suggest that the calcium and fluoride activities are limited by mineral solubility. This is, however, by no means certain. As discussed previously (Fig. 6C), the ratio of $\sqrt{\text{Ca}/\text{H}}$ is approximately constant at a given temperature. By virtue of this relationship and since $(\text{H}^+)(\text{OH}^-) = \text{dK}_w$, it can

UNIVERSITY OF OTTAWA LIBRARY

be shown that a constant CaF_2 activity product at a given temperature, could simply be a consequence of constant F^-/OH^- for a given temperature. Hence the explanation is favoured that the fluoride activity of the Icelandic geothermal waters, included in this study, is governed by an ionic exchange equilibrium with hydroxide ions. The fluoride would replace some of the hydroxyl groups of the layered geothermal silicates such as smectite and chlorite. These waters are all associated with basaltic rocks.

It is well known that acid volcanic rocks contain much more fluorine than basaltic rocks. Upon alteration of the rock the fluorine is transferred into solution. It seems possible that the quantity released from acid rocks is sufficient to saturate the respective layered silicates, so that the fluoride concentrations in solution will build up until fluorite saturation is reached. This explanation is compatible with the fact that the CaF_2 activity product of the Wairakei sample plotted in Fig. 7C fits rather well with fluorite saturation, but the geothermal reservoir at Wairakei is situated in acid volcanic rock formations. This explanation also conforms with the conclusions of NORDSTROM and JENNE (1977) that the fluoride mobility of unmixed geothermal waters in the western United States is controlled by fluorite solubility, and the fact that thermal waters in Iceland located in acid rocks possess much higher CaF_2 activity product than water of comparable temperatures issuing from basaltic rocks.

DISCUSSION

In the foregoing discussion it has been demonstrated how the distribution of the major cations, Na, K, Ca and hydrogen ion is controlled by ionic exchange equilibria, how silica mobility is governed by quartz solubility, carbonate (CO_3^{2-}) by calcite solubility, and fluoride (F^-) apparently by an ionic exchange reaction. According to ARNÓRSSON (1978a) it also seems likely that Mg^{2+} activities are controlled by ionic exchange equilibria. Some uncertainty exists regarding factors limiting the sulphate mobility. The nature of the analytical data indicates, however, that chemical equilibria with minerals and/or other solutes exert a limiting mobility on this constituent in the water. Accordingly chemical equilibria involving interaction of the water with geothermal minerals, determine the mobility of nine (SiO_2 , pH, Na, K, Ca, Mg, CO_2 total, SO_4 , F) of the eleven major components in the geothermal waters. The remaining major components are H_2S (total) and Cl.

Unpublished work by the first author indicates that the high-temperature geothermal waters are pyrrhotite saturated. It seems, however, unlikely that the solubility of this mineral will determine the iron concentration in the water. An ionic exchange equilibrium seems more likely. If this is so, the pyrrhotite solubility and an ionic exchange reaction fix together the S^{2-} activity in the water and the H_2S (total) activity in conjunction with the ionic exchange equilibria

governing the water pH. The concentrations of Cl in the water is only determined by its supply to the geothermal system whether it is leaching or seawater, since this element is not expected to be incorporated in the geothermal minerals, which precipitate from the water (see ELLIS and MAHON, 1964; 1967).

If we take all these mineral-solute chemical equilibria for granted, it turns out that the major element composition of the unflushed, deep, high-temperature geothermal waters is controlled by two independent variables only. They are temperature and the supply to the water of the incompatible element chlorine, incompatible indicating that this element is not incorporated in the geothermal minerals. The effect of temperature is complicated. It lies mostly in its influence on the value of the various equilibrium constants describing the relevant solute-solute and mineral-solute chemical equilibria, but it may also affect leaching of chlorine from the rock. A large supply of chlorine leads to high concentrations of this element in the water, whether it is sea-water, chlorine-rich rock, or magmatic source. Apart from the various chemical equilibria, it is the amount of chlorine that goes into solution that mostly governs the absolute concentrations of the major cations in solution, although the ionic exchange equilibria determine their relative distribution.

The low chlorine content of the Icelandic basaltic (SIGVALDASON and ÓSKARSSON, 1976) may explain the low concentrations of this element in the dilute geothermal waters. Insufficient supply of the major cations are not believed to be a limiting factor in determining the salinity of the geothermal waters except possibly for potassium for some of the geothermal sea-waters as is indicated by the Reykjanes data. Otherwise, these cations are present in plentiful amounts in the silicates of the original rock and are released upon their disintegration and will go into solution to an extent determined by the supply of anions with which they form relatively soluble salts.

The chemical equilibria in the high-temperature geothermal systems are upset in the upflow zone where degassing occurs and the water cools either by flashing or conduction. Mixing with cold water on the boundaries of the upflow zones may also upset these chemical equilibria, but it is thought that mixing is generally of less importance in upsetting these equilibria than degassing and cooling.

Acknowledgements—This article was prepared by the first author while he was working at the Department of Geology of Oslo University but it is based on data from the National Energy Authority, Reykjavik, Iceland, which has accumulated during the last 5 yr. Financial support, which was given by the Royal Norwegian Council for Scientific and Industrial Research, while the first author was staying at the University of Oslo, is sincerely acknowledged.

REFERENCES

- ARNÓRSSON S. (1970a) Geochemical studies of thermal waters in the southern lowlands of Iceland. *Geothermics Special Issue 2*, 2, 547-552.

ARNÓ
rotl
con
2, 2
ARNÓ
men
Issu
ARNÓ
in Ic
activ
tic A
L. K
ARNÓ
omet
land.
ARNÓ
geoth
Seco
tion,
ARNÓ
therm
Mine
ARNÓ
and s
therm
ull. 10
BÖRNSS
Econc
area,
2380-
BÖUNT
of an
and 1
227-24
BÖVARS
heat r
Source
DICKSON
quartz
29. 605
ELLIS A.
ation
4300-4
ELLIS A.
charact
Special
ELLIS A. J
ionizati
solution
ELLIS A.
carbon
chloride
ELLIS A. J.
mal sys
tions, G
ELLIS A. J.
mal sys
tions—1.
FÖRNER
Faja qua
Phil. the
FÖRNER I
and field
national
chemistry
122-139.
FÖRNER I
Na-K-Ca
Cosmoch
FÖRNER R.
and Equil
FÖRNER C
mal alter
U.S.C. thes

- ARNÓRSSON S. (1970b) Underground temperatures in hydrothermal areas in Iceland as deduced from the silica content of the thermal water. *Geothermics, Special Issue 2*, 2, 536-541.
- ARNÓRSSON S. (1970c) The distribution of some trace elements in thermal waters in Iceland. *Geothermics, Special Issue 2*, 2, 542-546.
- ARNÓRSSON S. (1974) The composition of thermal fluids in Iceland and geological features related to the thermal activity. In *Geodynamics of Iceland and the North Atlantic Area*. Proc. NATO Advanced Study Institute (editor L. Kristjánsson), pp. 307-323. Reidel.
- ARNÓRSSON S. (1975) Application of the silica geothermometer in low temperature hydrothermal areas in Iceland. *Am. J. Sci.* 275, 763-784.
- ARNÓRSSON S. (1977) Precipitation of calcite from flashed geothermal waters in Iceland. In *Proceedings of the Second International Symposium on Water-Rock Interaction, Strasbourg, 17-20 August, 1977*, p. III 152-169.
- ARNÓRSSON S. (1978a) Major element chemistry of the geothermal sea-water at Reykjanes and Svartsengi, Iceland. *Mineral. Mag.*, to be published.
- ARNÓRSSON S. (1978b) Changes in the chemistry of water and steam discharged from wells in the Námafjall geothermal field, Iceland, during the period 1970-1976. *Jökull*, to be published.
- BJÖRNSSON S., ARNÓRSSON S. and TÓMASSON J. (1972) Economic evaluation of the Reykjanes thermal brine area, Iceland. *Bull. Am. Assoc. Petrol. Geologists* 56, 2380-2391.
- BLOUNT C. W. and DICKSON F. W. (1969) The solubility of anhydrite (CaSO_4) in $\text{NaCl-H}_2\text{O}$ from 100 to 450°C and 1 to 1000 bar. *Geochim. Cosmochim. Acta* 33, 227-245.
- BJÖRVARSSON G. (1960) Physical characteristics of natural heat resources in Iceland. U.N. Conference on New Sources of Energy, Rome, 1960, paper G/6.
- DICKSON F. C. (1966) Solubilities of metallic sulfides and quartz in hydrothermal sulfide solutions. *Bull. Volcanol.* 29, 605-627.
- ELLIS A. J. (1963) The effect of temperature on the ionization of hydrofluoric acid. *Chim. Soc. (Lond.) J.* 4300-4304.
- ELLIS A. J. (1970) Quantitative interpretation of chemical characteristics of hydrothermal systems. *Geothermics, Special Issue 2*, 2, 516-528.
- ELLIS A. J. and GIGGENBACH W. (1971) Hydrogen sulphide ionization and sulphur hydrolysis in high temperature solutions. *Geochim. Cosmochim. Acta* 35, 247-260.
- ELLIS A. J. and GOLDING R. M. (1963) The solubility of carbon dioxide above 100°C in water and in sodium chloride solutions. *Am. J. Sci.* 261, 47-60.
- ELLIS A. J. and MAHON W. A. J. (1964) Natural hydrothermal systems and experimental hot-water-rock interactions. *Geochim. Cosmochim. Acta* 28, 1323-1357.
- ELLIS A. J. and MAHON W. A. J. (1967) Natural hydrothermal systems and experimental hot-water-rock interactions—II. *Geochim. Cosmochim. Acta* 31, 519-531.
- FARLEIFSSON I. B. (1973) Petrology and structure of the Esja quaternary volcanic region, southwest Iceland. D. Phil. thesis, 208 p., Oxford University (England).
- FOURNIER R. O. (1973) Silica in thermal waters: laboratory and field investigations. In *Proceedings of the International Symposium on Hydrogeochemistry and Biochemistry, Japan 1970*, 1 (Hydrogeochemistry), pp. 122-139. Clark.
- FOURNIER R. O. and TRUESDELL A. H. (1973) An empirical Na-K-Ca-geothermometer for natural waters. *Geochim. Cosmochim. Acta* 37, 1255-1275.
- GARRELS R. M. and CHRIST C. L. (1965) *Solutions, Minerals and Equilibria*. Harper and Row.
- GELASON G. (1973) Study of high-temperature hydrothermal alteration in Krisuvik and Námafjall. Unpublished B.Sc. thesis, University of Iceland (In Icelandic).
- GLOVER R. B. (1970) Interpretation of gas compositions from the Wairakei field over 10 years. *Geothermics, Special Issue 2*, 2, 1355-1366.
- GRÖVOLD K. (1972) Structural and petrochemical studies in the Kerlingarfjöll region, Iceland. D. Phil. thesis, 280 p., Oxford University (England).
- HELGESON H. C. (1969) Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Am. J. Sci.* 267, 729-804.
- KENNEDY G. C. (1950) A portion of the system silica-water. *Econ. Geol.* 45, 629-653.
- KRISTMANNSDÓTTIR H. (1975) Hydrothermal alteration of basaltic rocks in Icelandic geothermal areas. In *Proc. Second United Nations Symposium on the Development and Use of Geothermal Resources 1*, 441-445.
- KRISTMANNSDÓTTIR H. and TÓMASSON J. (1974) Nesjavellir. Hydrothermal alteration in a high-temperature area. In *Proc. International Symposium on Water-Rock Interaction, Praha, 1974*, pp. 170-177.
- KRISTMANNSDÓTTIR H. and TÓMASSON J. (1975) Hydrothermal alteration in Icelandic geothermal fields. *Soc. Sci. Islandica, Greinar VI*, 167-176.
- LIETZKE M. H., STOUGHTON R. W. and YOUNG T. F. (1961) The bisulfate acid constant from 25 to 225°C as computed from solubility data. *J. Phys. Chem.* 65, 2247-2249.
- MAHON W. A. J. (1960) Sampling of geothermal drillhole discharges. U.N. Conference on New Sources of Energy, Rome, 1960, paper E/35/9/46.
- MAHON W. A. J. (1966) Silica in hot water discharged from drillholes at Wairakei, New Zealand. *New Zealand J. Sci.* 9, 135-144.
- MAHON W. A. J. (1970) Geochemistry in the exploration and exploitation of hydrothermal systems. *Geothermics, Special Issue 2*, 2, 1310-1322.
- MOREY G. W., FOURNIER R. O. and ROWE J. J. (1962) The solubility of quartz in water in the temperature interval from 25 to 300°C. *Geochim. Cosmochim. Acta* 26, 1029-1043.
- NORSTROM D. K. and JENNE E. A. (1977) Fluorite solubility equilibria in selected geothermal waters. *Geochim. Cosmochim. Acta* 41, 175-188.
- PIPER J. D. A. (1971) Ground magnetic studies of crustal growth in Iceland. *Earth Planet. Sci. Lett.* 12, 199-207.
- PÁLMASSON G. and SÆMUNDSSON K. (1974) Iceland in relation to the Mid-Atlantic Ridge. *Ann. Rev. Earth Planet. Sci.* 2, 25-63.
- PITZER K. S. (1937) The heats of ionization of water, ammonium hydroxide, carbonic, phosphoric and sulphuric acids. The variation of ionization constants with temperature and enthalpy change with ionization. *J. Am. Chem. Soc.* 59, 2365-2371.
- SÆMUNDSSON K. and NOLL H. (1974) K/Ar ages of rocks from Húsafell, western Iceland and the development of the Húsafell central volcano. *Jökull* 24, 40-59.
- SEWARD T. M. (1974) Determination of the first ionization constant of silicic acid from quartz solubility and borate buffer solutions to 350°C. *Geochim. Cosmochim. Acta* 38, 1651-1664.
- SIGURDSSON H. (1966) Geology of the Setberg area, Snæfellsnes, Western Iceland. *Soc. Sci. Islandica, Greinar IV*, No. 2.
- SIGURDSSON H. (1970) The petrology and chemistry of the Setberg volcanic region and of intermediate and acid rocks in Iceland. Ph.D. thesis, University of Durham (England).
- SIGVALDASON G. E. (1963) Epidote and related minerals in two deep drill holes, Reykjavik and Hveragerdi, Iceland. U.S. Geol. Survey Prof. Paper 450E, E77-79.
- SIGVALDASON G. E. and ÓSKARSSON N. (1976) Chlorine in basalts from Iceland. *Geochim. Cosmochim. Acta* 40, 777-789.
- TÓMASSON J. and KRISTMANNSDÓTTIR H. (1972) High tem-

UNIVERSITY OF DURHAM

- perature alteration minerals and thermal brines, Reykjanes, Iceland. *Contrib. Mineral. Petrol.* 36, 123-137.
- TRUESDELL A. H. (1975) Geochemical techniques in exploration. In *Proc. Second United Nations Symposium on the Development and Use of Geothermal Resources*, 1, 53-86.
- TRUESDELL A. H. and SINGERS W. (1974) The calculation of aquifer chemistry in hot-water geothermal systems. *J. Res. U.S. Geol. Surv.* 2, 271-278.
- WALKER G. P. L. (1963) The Breiddalur central volcano, eastern Iceland. *Quart. J. Geol. Soc. Lond.* 119, 29-63.
- WALKER G. P. L. (1966) Acid volcanic rocks in eastern Iceland. *Bull. Volcanol.* 29, 375-406.
- WALKER G. P. L. (1974) Eruptive mechanisms in Iceland. In *Geodynamics of Iceland and the North Atlantic Area*. Proc. NATO Advanced Study Institute (editor L. Kristjánsson), pp. 189-202. Reidel.
- WHITE D. E., MUFFLER L. P. J. and TRUESDELL A. H. (1971) Vapordominated hydrothermal systems compared with hot-water systems. *Econ. Geol.* 66, 75-97.

~~D. Strahsacker 8/9~~
RK Edqvist 9/7

Aug 10
~~Strahsacker~~

UNIVERSITY OF UTAH
RESEARCH INSTITUTE
EARTH SCIENCE LAB.

Natural concentrations of mercury in Iceland

JEFFREY A. CODERRE* and SIGURDUR STEINTHÓRSSON

Science Institute, University of Iceland, Jarðfræðahús Haskólan, Reykjavík, Iceland

(Received 25 May 1976; accepted in revised form 24 September 1976)

Abstract—The results are presented of a survey of mercury concentrations in various parts of the Icelandic environment. Values for air and gas samples include: $<0.03 \mu\text{g}/\text{m}^3$ for Reykjavík, 15–20 km away from a hydrothermal area; $1\text{--}3 \mu\text{g}/\text{m}^3$ for air in a hydrothermal area near Lake Mývatn; $12\text{--}30 \mu\text{g}/\text{m}^3$ for air in Heimaey during the 1973 eruption; and $16 \mu\text{g}/\text{m}^3$ for a sample of fumarole gas. Values for fresh igneous rocks, of various compositions, extrusive (subaerial), subaqueous (up to 3000 m depth), and intrusive, range between 2 and 9 ppb. Highest values obtained for uncontaminated samples are 37 ppb for a pyrite-bearing zone in a hydrothermal drill hole, and 125 ppb for a volcanic sublimate. The sources of the mercury levels observed are briefly discussed.

INTRODUCTION

THIS PAPER reports the results of a survey of the distribution and geochemical behaviour of mercury in Iceland. The data may be grouped into four main classes: (1) atmospheric and natural water samples, to indicate the baseline mercury concentration in Iceland; (2) atmospheric samples taken during a volcanic eruption and samples of thermal gases, to study, in a qualitative way, the actual mercury emission from a volcanic and a hydrothermal system; (3) mercury contents of subaerial lavas, to obtain an idea of the average crustal mercury content in an area built up entirely by volcanic rocks; (4) mercury contents of volcanic rocks which, due to special environmental conditions, may have retained some or all of their initial mercury.

The range of mercury values reported in the literature for various parts of the world ranges from fractions of a ppb in natural waters to hundreds of ppm in rocks from some areas. The baseline values for mercury have been set at $0.001\text{--}0.01 \mu\text{g}/\text{m}^3$ for unpolluted air (McCARTHY *et al.*, 1970), and 0.1 ppb, or less, in natural waters (WERSHAW, 1970). RANKAMA and SAHAMA (1950) stated that the average mercury concentration of igneous rocks at the Earth's surface is 77 ppb. EHMAN and LOVERING (1967) felt that this value was too high and placed the average below 40 ppb.

Much of the work done on mercury has been associated with economic mineral deposits or with environmental pollution. ESHLEMAN *et al.* (1971) showed that Hawaiian volcanism is a natural source of mercury pollution. Time variable mercury anomalies have been discovered in the bottom waters of the Mid-

Atlantic Ridge rift valley (CARR *et al.*, 1974, 1975). High atmospheric mercury concentrations have also been reported during active Icelandic volcanism (ÓLAFSSON, 1975). WHITE *et al.* (1970) have shown mercury to exist in higher than normal concentrations in and around geothermal areas. SIEGEL *et al.* (1973) have found high atmospheric mercury concentrations all over Iceland, especially at geothermal areas. The reported data on mercury values for Icelandic natural waters and igneous rocks is sparse.

ANALYTICAL PROCEDURE†

All analyses were carried out on a Coleman Instruments MAS 50 mercury analysis system based on the method developed by HATCH and OTT (1968). The system is designed to read directly in $\mu\text{g Hg}$ if a 100 ml liquid sample is used and the analysis is carried out in a 300 ml Biological Oxygen Demand (BOD) bottle. Modifications of this method were used for the analysis of gas and solid samples where it was found convenient to employ directly 200 ml bottles of polyethylene instead of the standard BOD bottles. The lower limit of detection for the MAS 50 was found to be 1–2 ppb Hg (or $0.1 \mu\text{g}/\text{l}$ for 100 ml liquid samples), and the response of the instrument linear within the concentration range observed in this study (cf. GATEHOUSE and WILLIS, 1961; VOGEL, 1961; BUTLER and KOKOT, 1971).

Gaseous samples were collected by drawing them through a trap of concentrated HNO_3 . For analysis 10 ml aliquots were removed and diluted to 100 ml with distilled water.

Water-soluble volcanic sublimates from lava surfaces were weighed out and dissolved directly in 100 ml distilled water in the BOD bottle.

For the rock samples a 'cold' solution process was devised: The sample was crushed to a powder ≤ 100 mesh and dissolved in acids under oxidizing conditions: 2.000 g portions were weighed out and transferred directly to 200 ml polyethylene bottles and the following solutions added: (1) 8 ml of 5% KMnO_4 , (2) 20 ml of 1:1, 5.6 N HNO_3 :18 N H_2SO_4 , (3) 20 ml of 40% HF. The bottles were quickly sealed and placed in a water bath to minimize heating caused by an exothermic reaction at this stage. Then they were placed on a shaking machine for 2–3 hr and allowed to stand overnight. On the following day, 50 ml of saturated boric acid solution was added to complex any excess fluoride, and the bottles cooled again. The

* Present address: Department of Chemistry, Yale University, New Haven, Mass., U.S.A.

† A detailed description of analytical procedure, and a discussion of sensitivity, accuracy and precision of the measurements, is available from the second author upon request.

excess KMnO_4 was reduced with 5 ml of 1.5% hydroxylamine hydrochloride, and the mercury (present in solution as Hg^{2+}) was reduced to metallic Hg^0 by the addition of 5 ml of 10% stannous chloride. The bubbler apparatus was inserted immediately after the addition of SnCl_2 .

Reagent blanks were carried through during all analyses. In the case of rock samples reagent blanks and reference standard rock powder were carried through the solution process (in triplicate) along with the samples. For a reference standard a rock was selected containing a relatively high level of mercury, the concentration of which was accurately determined by the method of standard addition.

SAMPLE CONTAMINATION

Analyses carried out on rock powders that had been stored in the laboratory in sealed plastic jars, some for periods in excess of 10 yr, gave inconsistent results, for example: twelve samples from the Askja 1961 lava flow (THORARINSSON and SIGVALDASON, 1962) ranged from 9 to 116 ppb; twelve analyses of samples from the 1973 Heimaey lava (THORARINSSON *et al.*, 1973) gave values from 1 to 72 ppb. The USGS standards G-1 and GSP-1 both gave values about 1000 ppb; according to FLEISCHER (1970) the average of seven values for G-1 is 155 ppb (range 70–340), and of five values for GSP-1 20 ppb (range 15–41). MCNEAL *et al.* (1972) have demonstrated inhomogeneity of the USGS standards with respect to mercury, and both FLEISCHER (1970) and MCNEAL *et al.*

(1972) have suggested contamination during storage as a possible cause for such inhomogeneity. This suggestion was substantiated by the analysis of freshly crushed rocks compared with the *same rock* stored as a powder; almost invariably the freshly crushed sample had a lower mercury content than the stored counterpart.

The contamination of at least some of the samples may be traced to surficial absorption of mercury from the atmosphere at the site of eruption, or in the proximity of geothermal activity. High levels of atmospheric mercury were measured during the 1973 Heimaey eruption (ÓLAFSSON, 1975; CARR and WILKNISS, personal communication to S. Steintthórsson; data in this work—see Table 1), and also during the recent Hawaiian volcanism (ESHLEMAN *et al.*, 1971). Different portions of such a sample would contain different amounts of mercury. This is almost certainly the case with a tephra collected at Búrfell, as it fell, during the initial phase of the 1970 Hekla eruption (THORARINSSON and SIGVALDASON, 1972). The Búrfell tephra was used as the reference rock standard during these experiments. SIEGEL *et al.* (1973) reported 375 ppb of readily water-soluble mercury from this tephra sample. Two separate portions of this tephra, freshly crushed and homogenized at different times, showed values of 91 and 160 ppb Hg. Thus, the mercury seems to be heterogeneously distributed throughout

Table 1. Data

Sample	[Hg] ($\mu\text{g}/\text{m}^3$)	Remarks	
<i>Air samples</i>			
Heimaey	26.8	Collected in Heimaey town downwind from the volcano during eruption, on Feb. 3–5 1973. Duplicate samples taken at three different sites. Each value is the average of three determinations	
	27.4		
	12.3		
	12.1		
	19.7		
	19.1		
Leirhnúkur		Krafla area (all are air samples except no. 4). Active geothermal area—site of recent eruption, Dec. 20, 1975	
	1.		Hverarönd fumarole area
	2.		Bjarnarflag geothermal area, well no. 4.
	3.		Bjarnarflag, steam explosion crater near well no. 4
	4.		Fumarole gas—fumarole ca. 500 m north of Krafla power plant
	5.		Air sample, same location as no. 4 above
	6.		Air sample at Reynihlid
7.	Air sample at Reynihild		
Reykjavik air	N.D. ($<0.03 \mu\text{g}/\text{m}^3$)	3 samples taken in lab.	
<i>Natural Waters</i>			
Rivers	N.D. ($<0.1 \mu\text{g}/\text{l}$)	10 samples	
Lakes	N.D. ($<0.1 \mu\text{g}/\text{l}$)	6 samples	
<i>Igneous rocks</i>			
Dykes	[Hg] (ppb)	Dense, fine-grained, feldspathic basalts, collected in S.E. Iceland	
	HOF 40		2
	HOF 40		4
	KAL 62	2	
Basaltic pillow		Erupted subglacially, collected at Kálfstindar, S. Iceland	
			3
			3
			5
			2

Table 1.—continued

Sample	[Hg] (ppb)	Remarks
Abyssal basalts		Mid-Atlantic (MAR) and Kolbeinsey (KR) Ridges
432-D-II-1*	7	olivine tholeiite, depth 2500–2782 m, MAR, small vesicles (≤ 1 mm), 40°24'N 29°33'W
432-D V-2*	5	olivine tholeiite, depth 2800–2940 m, MAR, small vesicles, 40°28'N 29°82'W
L-72-9 A*		Kolbeinsey Ridge, olivine tholeiite pillow, depth 575–620 m, 67°58.5'N 18°23.6'W
	6	crystalline center
	4	glassy rim
L-72-10 A*		KR, sample may have been pillow fragment. Both glassy and crystalline areas present, depth 875–1100 m, 68°30.0'N 17°19.4'W
	2	glassy area
	1	crystalline area
L-71-18-1†		MAR, quartz tholeiite, § 15 cm core taken through pillow. Very vesicular, depth 200 m, 63°32.5'N 23°39.9'W (see BROOKS <i>et al.</i> , 1974, for complete analysis)
	3	top 5 cm of core
	6	middle 5 cm of core
	6	bottom 5 cm of core
L-71-19-1†		MAR, olivine tholeiite, very vesicular. Depth 68 m 63.252°N 23°52.3'W (see JAKOBSSON, 1974, for complete analysis)
B13-74-54‡	4	KR, tholeiite, 15 cm core taken. Very vesicular, altered by sea water. Colour reddish brown. Depth 200 m, 67°04'N 18°43'W
	9	top 5 cm of core
	8	middle 5 cm of core
	5	bottom 5 cm of core
<i>Miscellaneous Samples</i>		
Basalts	5	Average of 14 Icelandic basalts (Range 1–13)
Obsidian (A-TH)	4	Hrafninnuhryggur
Granite	5	From Sweden
Gneiss	10	From Greenland (erratic)
Gabbro (B-GA)	6	Hoffell
Minerals:		
anorthosite (B-PL)	3	Hrappsey
pyroxene	9	Jan Mayen (phenocrysts separated from ankaramite)
olivine	5	Budahraun (separated from alkali olivine basalt)
Krafla drill hole samples:		Samples taken during drilling June–July 1975. Sample from 98 m very reducing. Visible amounts of pyrite
78 m	7	
98 m	37	
104 m	10	
448 m	9	
1440 m	9	
Pyrite analysis:		Altered sample from Hvannagil, S.E. Iceland; pure pyrite picked from crushed sample
pyrite	20	
surrounding matrix	10	
Volcanic sublimates:		
Askja 1961	125	Water-soluble salts (average of 3 trials) (Range 124–126)
Heimaey 1973	100	(Range 86–121)
Hekla 1970	65	(Range 60–69)
Jan Mayen Rock suite:		
Jan. 149 rhyolite	13	Stored powders—contamination possible
Jan. 35 trachyte	10	
Jan. 82 tristanite	17	
Jan. 71 basaltic tristanite	9	
Jan. 46 alkali basalt	14	
Jan. 166 ankaramite	11	

* Collected during cruise of R.V. *Akademik Kurchatov*.† Collected during cruises of R.V. *Lynch* 1971 and 1972.

‡ Sample brought up by trawl net.

§ The difference between the quartz tholeiite and the olivine tholeiites is very slight; both are very close to the zero line between quartz and olivine normative.

|| Symbols denote rock standards used in the Science Institute laboratory.

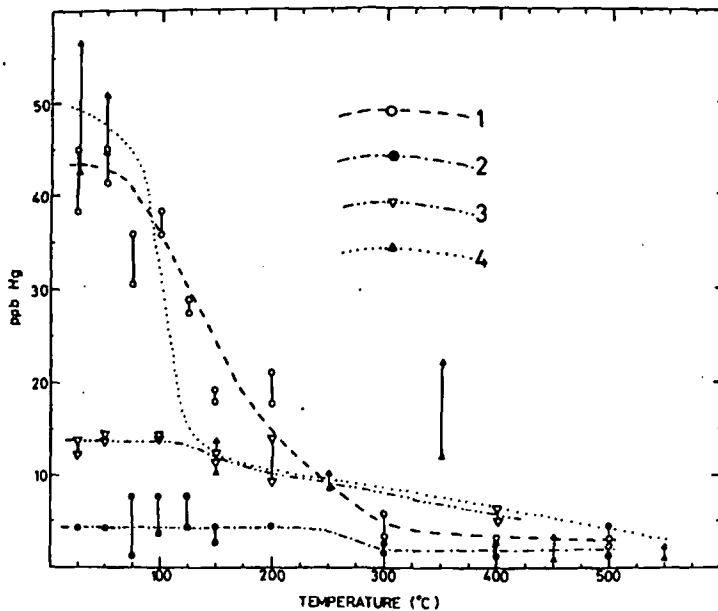


Fig. 1. Volatilization of mercury as a function of temperature. The samples were held at each temperature for 1 hr. 1. Lava from the 1973 Heimaey eruption (VMG 9, cf. THORARINSSON *et al.*, 1973). The sample was stored in the laboratory in powder form since 1973. 2. Freshly crushed portion of same sample (VMG 9). 3. Freshly crushed lava from Námafjall, North Iceland. 4. Lava from the Askja 1961 eruption (cf. THORARINSSON and SIGVALDASON, 1962). The sample (A-6) was stored as powder in the laboratory since 1962.

this single tephra sample primarily as a surface phenomenon. Volcanic sublimates, from the surface of cooling lava and collected from the lavas of three different eruptions, contained amounts of mercury ranging from 65 to 125 ppb (see Table 1). This could be explained as the incorporation of mercury present in the atmosphere at the time of accretion and cooling.

Heating experiments were performed on both stored powders of relatively high mercury contents and freshly crushed powders. Distinct differences are evident in the manner in which mercury is volatilized as a function of temperature. In Fig. 1, powders 1 and 2 are from the same rock sample. Despite the large initial difference between the two samples, after most of the surface mercury is volatilized from the stored sample, the two lines converge reasonably well. The freshly crushed sample shows consistently low mercury values throughout the temperature range indicating little, if any, readily volatilized surficial mercury. Powders 3 and 4 show a similar situation but here the two powders are from different rock samples. Again, the two lines converge as the surficial mercury is volatilized. The freshly crushed powder also lost some mercury between 50 and 150°C, although not nearly as much as the stored powder (15% as opposed to 75%). It seems that the freshly crushed sample also has some readily volatilized surficial mercury present.

These heating experiments show that when contamination of stored powders is suspected, a better (but obviously qualitative) estimate of the original mercury content of the sample may be obtained by first preheating the sample to 150–200°C for 1 hr. Exactly how much contamination occurs in the labor-

atory and how much occurs *in situ* is unknown and varies with each sample and the individual storage history. All the analyses reported here were carried out using freshly crushed samples.

ATMOSPHERIC MERCURY

'Unpolluted air' has been stated to contain from 0.001 to 0.010 $\mu\text{g}/\text{m}^3$ of mercury (McCARTHY *et al.*, 1970). Mercury values reported for Reykjavik air vary from 0.007 $\mu\text{g}/\text{m}^3$ (ÓLAFSSON, 1975) to 0.6 $\mu\text{g}/\text{m}^3$ (SIEGEL *et al.*, 1973). Attempts made to measure the mercury content of the air in the laboratory failed because the sensitivity of the MAS 50 was not great enough. It can be stated confidently, however, that the mercury level was below 0.03 $\mu\text{g}/\text{m}^3$. All of these samplings are widely separated in time and many factors could affect the atmospheric mercury levels. Rain, for example, could wash the air free of mercury (McCARTHY *et al.*, 1970).

SIEGEL *et al.* (1973) have reported atmospheric mercury concentrations for various sites around Iceland, all of which are well above the value accepted for unpolluted air. Air samples taken at Leirhnjúkur in the north of Iceland during the last week of January 1976 show mercury values ranging from 1.0 to 2.7 $\mu\text{g}/\text{m}^3$ (see Table 1). This area is the site of recent, shortlived volcanic activity (December 20, 1975) and of continuing geothermal activity.

MERCURY ASSOCIATED WITH GEOTHERMAL AREAS

As stated previously, high levels of mercury have been demonstrated during Icelandic and Hawaiian

phase. If not, we are led to the conclusion that the magma may have never contained mercury in excess of 10 ppb.

Acknowledgements—We are greatly indebted to Mr. NIELS OSKARSSON for providing a number of samples, for suggestions as to analytical techniques, and for discussion. Dr. S. P. JAKOBSSON supplied most of the dredge samples, from the collection of the Museum of Natural History. Dr. PETER RICKWOOD improved the first draft greatly by constructive criticism. This research was done during the tenure of Jeffrey Coderre as a Fulbright student at the University of Iceland.

REFERENCES

- ASTON S. R., BRUTY D., CHESTER R. and RILEY J. P. (1972) The distribution of mercury in North-Atlantic deep-sea sediments. *Nature Phys. Sci.* 237, 125.
- BOSTRÖM K. and FISHER D. E. (1969) Distribution of mercury in East Pacific sediments. *Geochim. Cosmochim. Acta* 33, 743-745.
- BRESSAN D. J., CARR R. A., HANNAN P. J. and WILKNISS P. E. (1974) The determination of trace metals and fluoride in mineralogical and biological samples from the marine environment. *J. Radioanal. Chem.* 19, 373-381.
- BROOKS C. K., JAKOBSSON S. P. and CAMPSIE J. (1974): Dredged basaltic rocks from the seaward extensions of the Reykjanes and Snaefellsnes volcanic zones, Iceland. *Earth Planet. Sci. Lett.* 22, 320-327.
- BUTLER L. R. P. and KOKOT M. L. (1971) Atomic absorption. In *Modern Methods of Geochemical Analysis*, (editors R. E. Wainardi and E. A. Uken), Chapter 8, pp. 205-243. Plenum Press.
- CARR R. A., JONES M. M. and RUSS E. R. (1974) Anomalous mercury in near-bottom water of a Mid-Atlantic Rift valley. *Nature* 251, 489-490.
- CARR R. A., JONES M. M., WARNER T. B., CHEEK C. H. and RUSS E. R. (1975) Variation in time of mercury anomalies at the Mid-Atlantic Ridge. *Nature* 258, 588-589.
- EHMAN W. D. and LOVERING J. F. (1967) The abundance of mercury in meteorites and rocks by neutron activation analysis. *Geochim. Cosmochim. Acta* 31, 357-376.
- ESHLEMAN A., SIEGEL S. M. and SIGEL B. Z. (1971) Is mercury from Hawaiian volcanoes a natural source of pollution? *Nature* 233, 471-472.
- FLEISHER M. (1970) Summary of the literature on the inorganic geochemistry of mercury. *U.S. Geol. Surv. Prof. Paper* 713, 6-13.
- GATEHOUSE B. M. and WILLIS J. R. (1961) Performance of a single atomic absorption spectrophotometer. *Spectrochim. Acta* 17, 710-718.
- HARRISS R. C. (1968) Mercury content of deep-sea manganese nodules. *Nature* 219, 54-55.
- HATCH W. R. and OTT W. L. (1968) Determination of sub-microgram quantities of mercury by atomic absorption spectrophotometry. *Anal. Chem.* 40, 2085-2087.
- JAKOBSSON S. (1974) Volcanic eruptions at Eldeyjarbodi the Reykjanes Ridge. *Náttúrufræðingurinn* 44, 22-40.
- MCCARTHY J. H., JR., MEUSCHKE J. L., FICKLIN W. H. and LEARNED R. E. (1970) Mercury in the atmosphere. *U.S. Geol. Surv. Prof. Paper* 713, 37-39.
- MCNEAL J. M., SUHR N. H. and ROSE A. W. (1972) Inhomogeneity of mercury in the U.S.G.S. rock standards. *Chem. Geol.* 10, 307-311.
- MOORE J. G. (1965) Petrology of deep-sea basalts near Hawaii. *Amer. J. Sci.* 263, 40-52.
- ÓLAFSSON J. (1975) Volcanic influence on seawater at Heimaey. *Nature* 255, 138-141.
- OZEROVA N. A., GOLOVNYA S. V. and SHIKINA N. D. (1974) The distribution of mercury in eclogites. *Geochem. Int.* 1974, 861-865; trans. from *Geokhimiya* No. 8, 1247-1251, 1974.
- RANKAMA K. and SAHAMA T. G. (1950) *Geochemistry*, 912 pp. University of Chicago Press.
- SIEGEL B. Z., SIEGEL S. M. and THORARINSSON F. (1973) Icelandic geothermal activity and the mercury of the Greenland icecap. *Nature* 241, 526.
- THORARINSSON S. and SIGVALDASON G. E. (1962) The eruption of Askja, 1961, a preliminary report. *Amer. J. Sci.* 260, 641-651.
- THORARINSSON S. and SIGVALDASON G. E. (1972) The Hekla eruption of 1970. *Bull. Volcanol.* 36, 269-288.
- THORARINSSON S., STEINTHÓRSSON S., EINARSSON TH., KRISTMANNSDÓTTIR H. and ÓSKARSSON N. (1973) The eruption of Heimaey, Iceland. *Nature* 241, 372-375.
- VOGEL A. I. (1961) Colorimetric and spectrophotometric analysis. In *A Textbook of Quantitative Inorganic Analysis*, 3rd edition, Chapter X, pp. 738-837. Longmans, Green.
- WERSHAW R. L. (1970) Sources and behavior of mercury in surface waters. *U.S. Geol. Surv. Prof. Paper* 713, 29-31.
- WHITE D. E., HINKLE M. E. and BARNES I. (1970) Mercury contents of natural thermal and mineral fluids. *U.S. Geol. Surv. Prof. Paper* 713, 25-28.

-25° S). Rev. Géogr. phys. Géol. dyn.
(1967), p. 259-268.
TAYLOR, A., 1967, Pyroxene and Magnetite
Inclusions in the Taupo Quaternary
Volcanic Pumice Deposits, New Zealand
Mineral. Mag., 36 (278), p. 180-194.
TAYLOR, P. W., ROOBOL, M. J., WALKER, G. A.,
ROOBOL, P. R. and COWARD, M., 1977, The
Lago de San Pablo Volcanoes of Northern
Chile and Their Hot Aqueous
Deposits. Geol. Rundsch., 63 (1), p. 57-67.
TOKOV, G. S., 1959, Gigantic Eruption of the
Volcano Bezymianny. Bull. Volcanol., 23,
p. 77-112.
TÖRVALD, P., 1963, On the Energy and Duration
of Volcanic Eruptions. Bull. Volcanol.,
25, p. 373-385.
TÖRVALD, P., 1904, La Montagne Pelée et ses
Éruptions. Masson & Cie, Paris, 662 pp.
TÖRVALD, P., 1950, On Explosive Activity of
Andesitic Volcanoes and Their Associated
Eruptive Phenomena. Bull. Volcanol., 14,
p. 87.
TÖRVALD, P., I. A. and SELF, S., 1978, Explosive
Eruptions and Pyroclastic Avalanches from
Mount St. Helens in February 1975. J. Volcanol.
& Geothermal Res., 3 (1-2), p. 39-60.
TÖRVALD, P., R. L., 1960, Ash Flows. Geol. Mag.,
77, p. 795-842.
TÖRVALD, P., S. R., 1969, Trace Element Chemistry of
Andesites and Associated Calc-alkaline
Rocks. In: A. R. McBirney (Ed.),
Proceedings Andesite Conference, 1969,
p. 10. Geol. Miner. Ind., Bull., 65, p. 10.

Manuscript received March, 1978; revised
manuscript received April 1978

Final manuscript received and accepted October 1978

S-wave Shadows in the Krafla Caldera in NE-Iceland, Evidence for a Magma Chamber in the Crust

P. EINARSSON *Science Institute, University of Iceland, Reykjavik*

ABSTRACT

During the present tectonic activity in the volcanic rift zone in NE-Iceland it has become apparent that the attenuation of seismic waves is highly variable in the central region of the Krafla volcano. Earthquakes associated with the inflation of the volcano have been used to delineate two regions of high attenuation of S-waves within the caldera. These areas are located near the center of inflation, have horizontal dimensions of 1-2 km and are interpreted as the expression of a magma chamber. The top of the chamber is constrained by hypocentral locations and ray paths to be at about 3 km depth. Small pockets of magma may exist at shallower levels. The bottom of the chamber is not well constrained, but appears to be above 7 km depth. Generally S-waves propagate without any anomalous attenuation through layer 3 ($v_p = 6.5 \text{ km sec}^{-1}$) across the volcanic rift zone in NE-Iceland. The rift zone therefore does not appear to be underlain by an extensive magma chamber at crustal levels. The Krafla magma chamber is a localized feature of the Krafla central volcano.

INTRODUCTION

The Krafla central volcano in NE-Iceland has been going through a series of inflation-deflation cycles since 1975 (Björnsson *et al.*, 1977). Magma is apparently accumulating at a fairly constant rate at the depth of approximately 3 km beneath the volcano causing a slow inflation. The inflation is interrupted by short periods of rapid deflation when magma is injected horizontally into the

rift zone that transects the volcano from south to north.

The structure of the volcanic rift zone in NE-Iceland is dominated by NNE-trending fault swarms that are arranged *en échelon* within the N-S trending zone (Fig. 1). Several of these swarms pass through central volcano complexes where acidic rocks and geothermal activity are common and volcanic activity is high (Saemundsson, 1974). A few of these central volcanoes such as the Krafla volcano have developed calderas. The Krafla caldera was formed in the last interglacial period and has since been filled with volcanic products.

The present activity of the Krafla volcano and the associated fault swarm has been accompanied by considerable seismic activity, both earthquakes and continuous volcanic tremor. Soon after the increase in seismic activity in 1975 it became apparent that the attenuation of seismic waves, especially S-waves, was very variable in the Krafla area. Periods of high seismic activity in the caldera and a recently installed network of short period seismographs have offered a rare opportunity to study the S-wave attenuation in the central region of inflation. This paper describes the first results of such a study in the Krafla region.

S-Wave attenuation has been studied before in other volcanic regions. Gorshkov (1958) used the disappearance of S-waves to infer the presence of a magma chamber at the depth of 60-80 km under the Klyuchevskaya volcano in Kamchatka. Similar results have been obtained by

FEDOTOV and FARBEROV (1966) in Kamchatka, KUBOTA and BERG (1967) and MATUMOTO (1971) in the Katmai volcanic range in Alaska and ASPINALL *et al.* (1976) in St. Lucia in the West Indies. Recently evidence has accumulated that indicates the presence of crustal magma bodies in the Socorro area of the Rio Grande Rift in New Mexico (SANFORD *et al.*, 1977a, b). This conclusion is partly based on the screening of SV-waves from local earthquakes.

Abnormal attenuation of S-waves is also reported from the mid-ocean ridge system. MOLNAR and OLIVER (1969) found that Sn-waves propagate inefficiently across the mid-ocean ridge system and the concave side of most island arcs. SOLOMON (1973) found that long period shear waves from an earthquake in the Charlie-Gibbs Fracture Zone that passed under the southern end of the Reykjanes Ridge were strongly attenuated. REID *et al.* (1977) found a zone of high S-wave attenuation that coincides with the crest of the East Pacific Rise near 21°N.

INSTRUMENTATION

The locations of the seismograph stations used for this study are shown in Fig. 1. Six of these stations are permanent and are a part of a larger network that covers most of the volcanic and seismic zones of Iceland. The stations SD and SN were temporary stations, operated in snow huts in March and April 1977. All the instruments were made at the Science Institute of the University of Iceland and are of similar design. The instrument consists of a vertical geophone with 2.3 Hz natural frequency, an amplifier with variable gain and filter settings, and a drum recorder. A continuous radio time signal is recorded with the seismic signal, thus time corrections are eliminated.

The pass-band of the instrument is between 3 and 30 Hz, limited by the natural frequency of the geophone at the low frequency end and the pen motor of the recorder at the high frequency end.

The peak of the displacement response is between 10 and 15 Hz. Peak magnification depends on noise conditions, but is frequently used. These instruments are ideally suited to record small local earthquakes in the presence of large seismic disturbances.

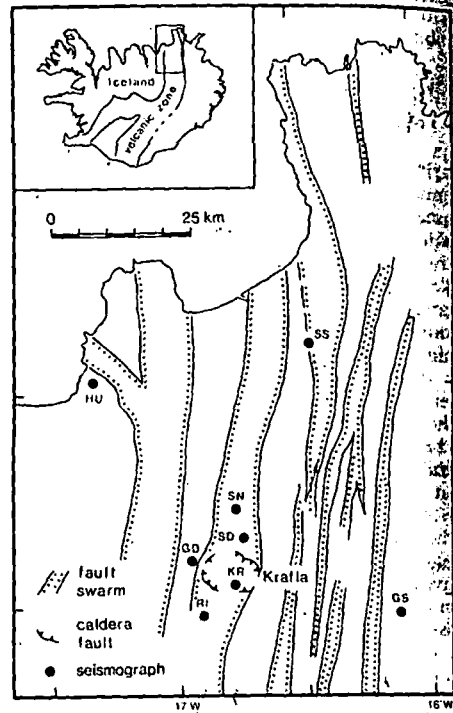


FIG. 1 - Index map showing the structure of the volcanic zone of NE-Iceland and the location of the seismograph stations used in this study. The fault swarms and the Krafla caldera fault are drawn after BJÖRNSSON *et al.* (1977).

THE DATA AND DATA ANALYSIS

During the period February-September 1976 the caldera region at Krafla was in a state of inflation. The elevation of the central part of the caldera increased by

SEISMICITY IN THE

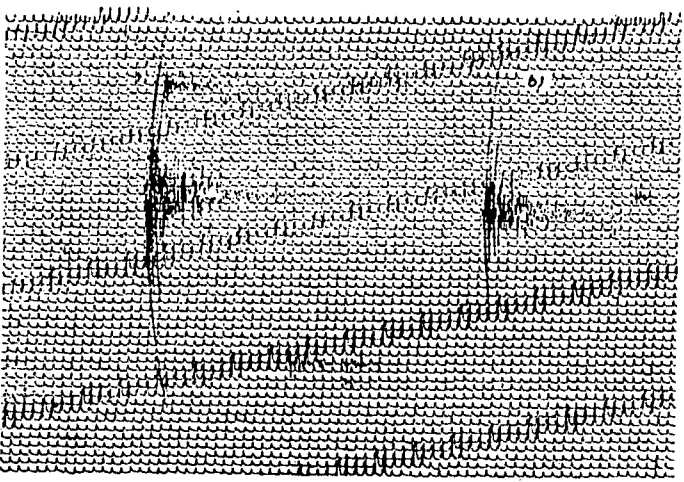
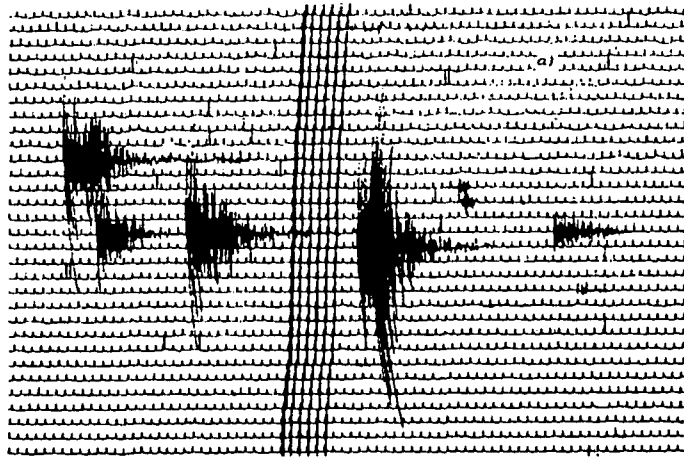


Fig. 2 - Seismogram sections from the stations RI (a) and SN (b and c). The small tick marks are second marks. Typical earthquakes with clear S-waves (a and c) and without S-waves (a and b) can be seen.

F
Epic
with
blac.
with
of 11
X. A
are
after

In
the
basi
Furt
reco
with
Fc
side
the
prop
wav
regu
is h
regio
mec.
abse
but
As
is ca
path
regio
ly a
large
for
seisr
in t
two

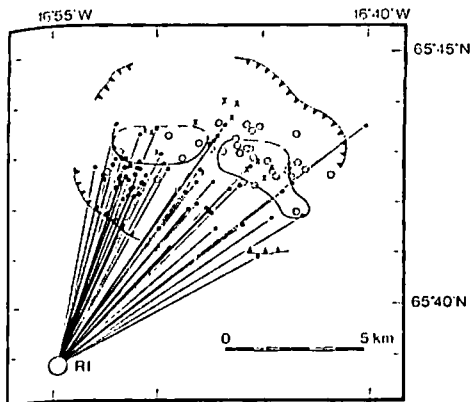


FIG. 3 - S-wave paths to the station RI. Epicenters of earthquakes that are recorded with a clear S-wave are marked with a black dot, open circles denote earthquakes with no recorded S-wave at RI. Earthquakes of intermediate character are marked with X. Areas of maximum attenuation of S-waves are delineated. The caldera fault is drawn after Björsson *et al.* (1977).

In the case of the Krafla earthquakes the first reason can be excluded on the basis of P-wave first motion data. Furthermore, many earthquakes are recorded with S-waves at one station but without S-waves at another station.

Focal mechanism effects are not considered to be a likely explanation for the absence of the S-waves. The large proportion of earthquakes without S-waves would require extremely high regularity in the focal mechanisms which is hardly to be expected in the central region of an inflating volcano. The focal mechanism may be responsible for the absence of the S-wave in a few cases, but not all.

Assuming that the absence of S-waves is caused by attenuation along the wave paths one can attempt to map the regions of maximum attenuation. Relatively accurate earthquake locations and a large number of ray paths are needed for a meaningful study of this sort. The seismic stations RI, GS and SN are used in this study since the separation between the different types of wave trains

is most clearly seen at these stations. In Figs. 3, 4 and 5 the wave paths are marked along which clear S-waves have been transmitted. No abnormal attenuation seems to take place in regions crossed by such paths. In particular, attenuation appears to be normal in most of the SW-part of the caldera (Fig. 3) and in areas adjacent to the caldera. S-waves propagate across the rift zone to the station GS without much attenuation.

Epicenters of earthquakes that are recorded without S-waves at the respective station are marked with open circles in Figs. 3, 4 and 5. By combining the data from all three stations one can find the approximate boundaries of the attenuating regions. Two separate areas appear to be largely responsible for the disappearance of the S-waves. One area is located in the eastern and south-eastern part of the caldera. This area is delineated mostly by waves recorded at RI and GS (Figs. 3 and 4). The other area is located in the western part of the caldera and is delineated by waves recorded at RI and SN (Figs. 3 and 5). This area is displaced slightly to the north with respect to the epicentral area. Most earthquakes in the western part of the caldera are thus recorded with a clear S-wave at RI, but at SN the S-wave is missing on a large majority of the earth-

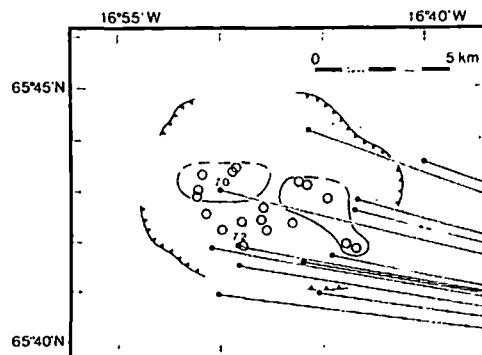


FIG. 4 - S-wave paths to the station GS. Symbols as in Fig. 3. Numbers show the depth of earthquakes that are deeper than 5 km.

Fig. 2 - Seismogram sections from the stations RI (a) and SN (b and c). The small tick marks are second marks. Typical earthquakes with clear S-waves (a and c) and without S-waves (a and b) can be seen.

quakes. The southern boundary of the attenuative area is better defined than the northern boundary. The conclusion that there are two areas is mostly based on the recording of S-wave at RI (Fig. 3). Several rays pass between the two areas. These rays are shallow and the attenuating body may be undivided at greater depth.

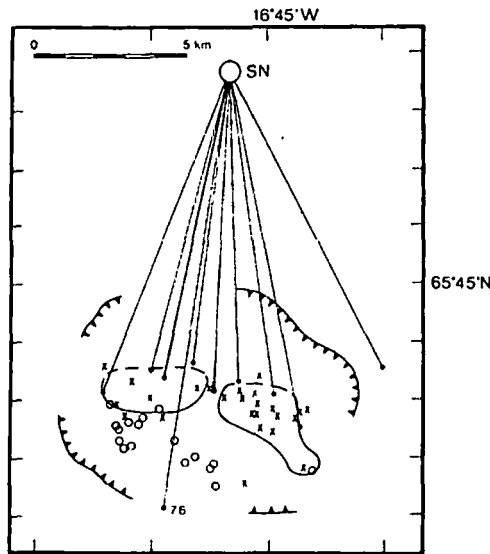


FIG. 5 - S-wave paths to the station SN. Symbols as in Fig. 3.

The horizontal extent of the attenuating zones is given in Figs. 3, 4 and 5. The diameters are of the order of 1-2 km. The vertical extent is more difficult to ascertain. In the vertical dimension the wave path is critically dependent on the depth of the hypocenter and the velocity structure, neither of which is well enough known for a detailed mapping of the attenuating bodies. One can, however, put some constraints on the upper and lower boundaries.

The hypocenters are mostly at depths of 3 km or less. The seismic rays recorded at RI, GS and SN are in most cases critically refracted rays. Because of the limited horizontal extent of the attenuat-

ing bodies and their proximity to the epicentral zones one can conclude that only a small proportion of the rays reaches depths greater than 3 km in the areas of attenuation. The depth to the upper boundary of the attenuating bodies is therefore not likely to be larger than 3 km. On the other hand, the depth to the boundary is not likely to be much less than 3 km. The earthquakes are clearly associated with the inflation process of the Krafla volcano and can be explained by brittle failure of the crust above an inflating magma body. This inflating body may be small and is not necessarily identical with the body that causes the attenuation. Brittle failure is not likely to occur within the attenuating body. The upper limit of the body is therefore likely to coincide with the depth where the frequency of earthquakes begins to decrease, which is about the depth of 3 km. Small, discontinuous bodies may, however, occur at smaller depths. The boundaries of the attenuating zones drawn in Figs. 3, 4 and 5 should be regarded as contours of the attenuating bodies at the depth of approximately 3 km.

The lower boundary of the attenuating bodies is not well constrained. Most of the available seismic rays cross the caldera at shallow levels and only few probe the deeper regions. The deeper rays have to come from relatively deep earthquakes, and only three earthquakes could be found that were usable for this study. All of them occurred at the depth of about 7 km (Figs. 4 and 5). The rays pass through the caldera region without suffering much attenuation, which indicates that the lower boundary of the attenuating bodies is shallower than 7 km.

LIMITATIONS OF THE METHOD

The method of analysis as described in the previous section can only be applied successfully under favorable conditions. The first condition is the availability of a large number of seismic rays crossing the region to be studied. One therefore needs either a large number of seismic

and their proximity to the zones one can conclude that a small proportion of the rays paths greater than 3 km in the attenuation. The depth to the boundary of the attenuating bodies are not likely to be larger than the other hand, the depth to any is not likely to be much more than 3 km. The earthquakes are associated with the inflation of the Krafla volcano and can be caused by brittle failure of the crust of the inflating magma body. This body may be small and is not identical with the body that causes the attenuation. Brittle failure is likely to occur within the attenuating body. The upper limit of the body is likely to coincide with the depth of the frequency of earthquakes decrease, which is about the 3 km. Small, discontinuous earthquakes, however, occur at smaller boundaries of the attenuating body as shown in Figs. 3, 4 and 5 should be considered as contours of the attenuating body. The depth of approximately

the boundary of the attenuating body is not well constrained. Most of the available seismic rays cross the upper shallow levels and only few reach deeper regions. The deeper earthquakes come from relatively deep regions, and only three earthquakes are found that were usable for this study. Two of them occurred at the depth of 3 km (Figs. 4 and 5). The rays from the Krafla region without significant attenuation, which indicate the lower boundary of the attenuating bodies is shallower than 7 km.

CONCLUSIONS OF THE METHOD

The method of analysis as described in this section can only be applied under favorable conditions. The condition is the availability of a number of seismic rays crossing the shadow to be studied. One therefore requires a large number of seismo-

graphs or numerous favorably located earthquakes. The latter condition was partly fulfilled in the case of Krafla.

Several factors limit the resolution of the method. Location errors, the effects of focal mechanism, «false» S-waves, diffraction and lateral refraction blur the picture of the bodies to be delineated.

The location errors in the case of Krafla were of the order of 1 km in the horizontal directions. Fortunately the dimensions of the attenuating areas were somewhat larger. Minor inconsistencies in Figs. 3, 4 and 5 can be accounted for by errors in epicenter locations. Obviously no consistent results can be obtained in areas where the errors are larger than the dimensions of the bodies to be delineated.

In some cases the focal mechanism and the source-station relationship may be such that the station is located on a nodal surface for the SV-wave. The seismogram may therefore give the impression that the ray has passed through attenuating material. This effect is only rarely observed in other seismically active areas in Iceland and is not believed to be important in Krafla, although it may cause inconsistency in a few cases.

Waves other than the S-wave may arrive late in the wave train and be difficult to distinguish from a true S-wave. These may be reflected P-waves, converted waves or surface waves. An attenuated wave train may thus be classified as an unattenuated one and cause an apparent inconsistency.

The presence of an attenuating body implies lateral heterogeneity in the structure, which means that the seismic rays may be refracted horizontally. This effect may cause some uncertainty in the location of the earthquakes and thus in the position of the boundary of the attenuating body, but errors exceeding 1 km are not expected.

Seismic waves will be diffracted around a body that has velocity different from its surroundings. In particular, S-waves will be diffracted around the attenuating bodies delineated in this

study. The bodies do not cast sharp, infinitely long shadows. Some S-wave energy is diffracted into the geometrical shadow region with the result that the bodies appear to be smaller than they really are.

The diffraction of seismic waves has been studied theoretically by many authors. In general the sharpness of the shadow is dependent on the wavelength relative to the dimensions of the diffracting body. The shadow is sharper and deeper for waves of higher frequency. But there are also effects that depend on the shape of the body.

TENG and RICHARDS (1969) studied the diffraction around a cylindrical cavity. In this case the effect on P-, SV-, and SH-waves is not equal. For a horizontal cylinder the half-amplitude point is shifted outward from the geometrical shadow boundary for P- and SV-waves but inward for SH-waves. The effect on the S-waves would be reversed for a vertical cylinder. There may thus be a broad region where the body has a polarizing effect on the S-waves. This effect was used by KUBOTA and BERG (1967) to conclude that magma chambers in the Katmai Volcanic Range were of spheroidal shape with a horizontal major axis.

The effects of diffraction limit the applicability of the S-wave screening method in volcanic areas. Clearly the frequency of the available seismic waves sets a limit to the size of the magma chambers that can be detected. For optimum results high frequency, three-component seismographs should be used. In the Krafla area the energy of the S-waves is mainly within the frequency band 5-10 Hz, i.e. the wavelengths are of the order of 300-600 m. This gives some idea of the resolution.

DISCUSSION

The attenuation effects in the Krafla area are large, or else a study of this sort would not give positive results. One can attempt to give a maximum estimate of the quality factor Q_s in the attenuating

bodies. The attenuated wave trains had no sign of an S-wave, which means that for some of them the S-wave must have been attenuated by a factor of at least 10. The wavelengths are 0.3-0.6 km and the horizontal extent of the bodies is about 1-2 km or 2-7 wavelengths. Attenuation by a factor of 10 in 7 wavelengths gives a Q_s of 10. This is a maximum value, the true value is probably much lower.

The attenuating bodies are located in the central part of the Krafla caldera. In other areas of the world where abnormal attenuation of S-waves has been found, there also seems to be a close association with volcanism, and it is usually assumed that the attenuation is caused by magma. This interpretation also seems to be the most plausible one in the case of Krafla. Here the center of inflation and deflation during the present tectonic and magmatic activity is also near the center of the caldera (BJÖRNSSON *et al.*, 1977; TRYGGVASON, 1978) which further strengthens the interpretation.

The seismic evidence can give little information about the internal structure of the magma chamber at Krafla and only a rough idea about its shape. The «chamber» could be a massive lump of molten magma, but it might also consist of a number of small, more or less interconnected chambers, pockets, sills or dykes. It is probable that the inflation presently taking place in the Krafla caldera is caused by a steady inflow of magma into this magma chamber or some subdivision of it. Deflation events are caused by horizontal injection of magma away from the central region of the Krafla volcano.

The formation of a magma chamber large enough to be detected by seismic waves is a process that requires much time, probably a considerable part of the life time of the volcano. Repeated injection of magma into the roots of a volcano results in elevated temperatures. Depending on the rate of injection and the rate of cooling the magma may stay in a molten state at some critical depth. Some remelting may take place in the surrounding material. The present injection

mechanism in the Krafla volcano is particularly effective. Magma is brought from below to a depth of about 3 km where it stays for a while and delivers heat to the surrounding material. Then the magma is injected horizontally away from the central part of the volcano and is replaced by fresh magma from below. Thus heat is delivered to the central part of the volcano with only limited increase in volume.

The magma chamber of Krafla is located in the upper part of and slightly above crustal layer 3 ($v_p = 6.5$ km/s) which is at the depth of about 3.5 km in this region (PÁLMASSON, 1963). The depth to the bottom of layer 3 is not accurately known in this region, but is probably in the range 10-15 km. S-waves are usually transmitted efficiently through layer 3. In particular we note that S-waves from Krafla earthquakes are well recorded at the station GS which is located east of the volcanic rift zone. This means that S-waves are transmitted across the rift zone at crustal levels without any abnormal attenuation. The attenuating bodies at Krafla appear to be a local phenomenon associated with the central volcano and are not a general feature of the rift zone.

Only a part of the available data have been analyzed in this study and inflation of the Krafla caldera continues at the time of writing. There is therefore no doubt that the picture presented in this paper will be improved and refined in the future.

CONCLUSIONS

The main conclusions of this study can be summarized as follows:

1. Two areas within the Krafla caldera have been delineated where S-waves of local earthquakes are strongly attenuated.
2. The attenuation is interpreted as being caused by magma in some kind of a magma chamber.
3. The extent of the magma chamber can be estimated by seismic ray tracing and the location pattern of earth-

4.
AC
T
Nat
and
Mit
ass
ana
Hal
Ins
heli
und
the
disc
seat
Sve
das
valt
of 1
REJ
ASPI
1
3
S
Björ
P
N
C
Fed
th
W
M
C
L
V
V
Gör
A
I

SUNAMUN 1974 10 11 11:10

anism in the Krafla volcano is very effective. Magma is brought down to a depth of about 3 km, stays for a while and delivers the surrounding material. Then magma is injected horizontally away from the central part of the volcano, and is replaced by fresh magma from below. Magma is delivered to the central part of the volcano with only limited increase

in the magma chamber of Krafla. In the upper part of and slightly below the depth of about 3.5 km in layer 3 ($v_p = 6.5$ km/s) (PALMASON, 1963). The depth of the bottom of layer 3 is not accurately known in this region, but is probably in the 10-15 km. S-waves are usually recorded efficiently through layer 3. As we note that S-waves from earthquakes are well recorded at station GS which is located east of the rift zone. This means that S-waves are transmitted across the rift zone at crustal levels without any significant attenuation. The attenuating effect of Krafla appear to be a local phenomenon associated with the central part of the caldera and are not a general feature of the rift zone.

Part of the available data have been used in this study and inflation of the Krafla caldera continues at the present time. There is therefore no doubt that the picture presented in this paper can be improved and refined in the future.

CONCLUSIONS

The conclusions of this study can be summarized as follows:

1. The magma chamber is located within the Krafla caldera and is delineated where S-waves of earthquakes are strongly attenuated.

2. The attenuation is interpreted as being caused by magma in some kind of a chamber.

3. The location of the magma chamber can be determined by seismic ray tracing and the location pattern of earth-

quakes within the caldera. The upper limit of the magma body is at the depth of about 3 km and the lower limit is probably shallower than 7 km. The body is divided near its top.

4. The volcanic rift zone in Northern Iceland is not underlain by a continuous magma chamber at crustal levels. The Krafla magma chamber is a localized feature of the Krafla central volcano.

ACKNOWLEDGEMENTS

This work was partly supported by the National Energy Authority in Reykjavik and by a special grant from the Icelandic Ministry of Education. Many persons assisted in the data collection and analysis, but special thanks are due to Halldór Ólafsson, Nordic Volcanological Institute, and Sverrir Tryggvason who helped operate the stations SD and SN under difficult circumstances. Many of the ideas presented in this paper were discussed extensively in an informal research group on the Krafla events. Sveinbjörn Björnsson, Guðmundur Sigvaldason and Eysteinn Tryggvason offered valuable suggestions for the improvement of the manuscript.

REFERENCES

- ASPINALL, W. P., MICHAEL, M. O., TOMBLIN, J., 1976, *Evidence for Fluid Bodies beneath the Sulphur Springs Geothermal Region, St. Lucia, West Indies*. Geophys. Res. Lett., 3, p. 87.
- BJÖRNSSON, A., SAEMUNDSSON, K., EINARSSON, P., TRYGGVASON, E., GRÖNVOLD, K., 1977, *Current Rifting Episode in North Iceland*. Nature, 266, p. 318-323.
- FEDOTOV, S. A. and FARBEROV, A. I., 1966, *On the Absorption of Transverse Seismic Waves in the Earth's Crust and Upper Mantle in the Region of the Avachinskii Group of Volcanoes*. In: *Volcanism and Deep Structure of the Earth*, Trudy Vtorogo Vses. VulcanoI. Soveshchaniya, Vol. 3, Izd. Nauka, Moscow.
- GORSHKOV, G. S., 1958, *On Some Theoretical Problems of Volcanology*. Bull. Volcanol., 19, p. 108-113.
- KUBOTA, S. and BERG, E., 1967, *Evidence for Magma in the Katmai Volcanic Range*. Bull. Volcanol., 31, p. 175-214.
- LAHR, J. C. and WARD, P. L., 1976, *Hypoellipse: A Computer Program for Determining Local Hypocentral Parameters, Magnitude and First Motion Pattern*. U.S. Geol. Surv. Open-File Report.
- MATUMOTO, T., 1971, *Seismic Body Waves Observed in the Vicinity of Mount Katmai, Alaska, and Evidence for the Existence of Molten Chambers*. Geol. Soc. Amer. Bull., 82, p. 2905-2920.
- MOLNAR, P. and OLIVER, J., 1969, *Lateral Variations of Attenuation in the Upper Mantle and Discontinuities in the Lithosphere*. J. Geophys. Res., 74, p. 2648-2682.
- PALMASON, G., 1963, *Seismic Refraction Investigation of the Basalt Lavas in Northern and Eastern Iceland*. Jökull, 13, p. 40-60.
- REID, I., ORCUTT, J. A., PROTHERO, W. A., 1977, *Seismic Evidence for a Narrow Zone of Partial Melting Underlying the East Pacific Rise at 21°N*. Geol. Soc. Amer. Bull., 88, p. 678-682.
- SAEMUNDSSON, K., 1974, *Evolution of the Axial Rifting Zone in Northern Iceland and the Tjörnes Fracture Zone*. Geol. Soc. Amer. Bull., 85, p. 495.
- SANFORD, A. R., MOTT, R. P., SHULESKI, P. J., RINEHART, E. J., CARAVELLA, F. J., WARD, R. M., WALLACE, T. C., 1977a, *Geophysical Evidence for a Magma Body in the Crust in the Vicinity of Socorro, New Mexico*. Amer. Geophys. Union Monograph, 20, p. 385-403.
- , RINEHART, E. J., SHULESKI, P. J., JOHNSTON, J. A., 1977b, *Evidence from Microearthquake Studies for Small Magma Bodies in the Upper Crust of the Rio Grande Rift near Socorro, New Mexico* (Abstract). Trans. Amer. Geophys. Union, 58, p. 1188.
- SOLOMON, S. C., 1973, *Shear-wave Attenuation and Melting beneath the Mid-Atlantic Ridge*. J. Geophys. Res., 78, p. 6044.
- TENG, T. and RICHARDS, P. G., 1969, *Diffracted P, SV and SH Waves and Their Shadow Boundary Shifts*. J. Geophys. Res., 74, p. 1537-1555.
- TRYGGVASON, E., 1978, *Tilt Observations in the Krafla-Mývatn Area 1976-1977*. Nordic Volcanological Institute, Reykjavik, Report 78 02, 45 pp.

Manuscript received July 1978; reviewed Aug. 1978

Revised ms. received Nov. 1978