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MAJOR ELEMENT CHEMISTRY OF THE GEOTHERMAL SEA-WATER AT REYKJANES AND SVARTSENGI, ICELAND

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Des. 1977

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OS-JHD-7734

Des. 1977

ABSTRACT

High-temperature geothermal fields in Iceland represent localized anomalies of hot, altered rock in the uppermost part of the crust, which coincide with points of maximum tectonic/magmatic activity. These points correspond to the intersection of oblique fault swarms to the plate boundaries Geothermal activity under mid-ocean ridges follows probably similar tectonic/magmatic anomalies.

Due to high permeability sea-water invades the bedrock of the Reykjanes Peninsula, Iceland, and is overlain by variably thick lense of dilute ground water of meteoric origin. The variable degree of salinity of geothermal waters in the Reykjanes Peninsula has resulted from different degree of mixing of fresh ground water with the underlying seawater-groundwater in the downflow zones around the geothermal fields. At Reykjanes the geothermal water represents heated sea-water without any fresh water mixing. The difference in the composition of seawater or seawater-freshwater mixtures and the geothermal waters is due to basalt/water interaction at elevated temperatures. The major element chemistry of the geothermal water represents an equilibrium composition at the relevant aquifer temperatures. The activities of silica, calcium, sulphate, carbonate are thus limited by the solubilities of quartz, anhydrite and calcite. Fluoride activity is thought to be controlled by an ionic exchange reaction where it substitutes for hydroxyl groups in phyllosilicates. The ratios of individual cations and hydrogen ion are governed by ionic exchange equlibria with hydrothermal minerals, probably smectite and chlorite. The equilibrium pH for the Reykjanes and Svartsengi geothermal waters is $5.^5$ and 5.1 respectively. Sea-water will become somewhat acid upon heating to more than about $300^{\circ}C$ and equilibration with basalt, the acidity increasing with temperature.

INTRODUCTION

Four major geothermal fields occur in the Reykjanes Peninsula (fig. 1). Geothermal manifestions have also been observed at Eldvörp (fig. 2), but it is not known to what extent they reflect the existence of a geothermal reservoir. The Krísuvík area has often been considered to represent two geothermal fields (fig. 2). It seems likely that these two fields are represented by different hot-water convection cells. Three of the geothermal fields on the Reykjanes Peninsula (Reykjanes, Svatsengi, Krísuvík) have been explored by drilling during the last decade by the National Energy Authority, Reykjavík. Maximum recorded downhole temperatures in these three areas are between 240°C and 290°, being highest for Reykjanes and lowest for Svartsengi (Björnsson et al. 1972, Arnórsson et al. 1975a, 1975b). The fluids discharged from the wells or recovered by downhole sampling show a large variation in salinity. Thus, in the Reykjanes geothermal field, which is located on the extreme southwest tip of the Peninsula, the geothermal fluid has the same salinity, expressed as Cl, as sea-water. Moving east the water salinity decreases, being only in the range of 100-1000 ppm Cl in the Krísuvík area, which is farthest east of the three drilled fields.

Figs. 1 and 2

All the geothermal fields in the Reykjanes Peninsula are of the hot-water type (see White et al., 1971). In the upflow zones, which tap the geothermal reservoirs, and in drillholes, the hot water flashes. As a result the reservoir water is degassed, its pH increases somewhat, and its content of non-volatile components increases to an extent determined by the amount of steam formation. Changes of this kind will not take place in the upflow zones of sub-marine geothermal fields as long as the hydrostatic pressure of the overlying body of sea-water is sufficient to prevent flashing.

This presentation is confined to the more saline waters at Reykjanes and Svartsengi, its main aim being to demonstrate how solute/mineral reactions in the hot geothermal reservoir have modified the original sea-water composition or that of the sea-water/fresh-water mixture.

Four wells have been drilled into the Svartsengi geothermal reservoir and another four into the Reykjanes geothermal reservoir. Within each of the two fields the composition of the total discharge from all the wells is very similar indicating a homogeneous reservoir water chemistry. Computed reservoir water chemistry is available for all four wells at Svartsengi, but only for well 8 at Reykjanes. The discussion that follows is based on chemical data from these five wells.

CALCULATION OF RESERVOIR WATER CHEMISTRY

The chemical composition of the unflashed reservoir water has been calculated from chemical analyses of samples of water and steam collected separately at a known pressure on the wellhead. The enthalpy of the well discharge determines the relative amounts of steam and water at the sampling pressure. In the present study the enthalpy was estimated from the silica content of the water assuming equilibrium with quartz in the reservoir, but it has been well established that equilibrium with quartz is attained in high-temperature geothermal reservoirs below the zone of flashing (Mahon, 1966, Fournier and Rowe, 1966, Ellis, 1970, Arnórsson, 1970, 1975). If flashing occurs in the aquifer, before the fluid enters the well, some silica may precipitate from solution and the calculated quartz equilibrium temperature will be low. (Arnórsson et al., 1977). Some separation of water and steam in the aquifer may also cause the well discharge enthalpy to be different from that of the unflashed reservoir water.

Downhole temperature measurements at Svartsengi show that flashing does not set in until in the wells and the measured temperatures at aquifer inflows fit well with the quartz equilibrium temperature (fig. 3). Therefore, the assumptions used to derive the downhole water composition are valid. At Reykjanes, well 8, there exists evidence that flashing occurs in the aquifers feeding that well, which may cause the discharge to be relatively enriched or deplated in steam. Measurements of the discharge enthalpy are not available but they could verify this. Despite this uncertainty it is considered that the calculated downhole composition for the Reykjanes water, based on the assumptions stated above, closely approaches the real composition. This is supported by the fact that the composition of the discharge of well 8 has not changed to any extent from the time when the well was first put into production in 1970 until 1974 when it was closed down.

Fig. 3

Having obtained the compostion of the downhole water the chemical speciation is computed by simultaneous solution of various dissociation equilibria and mass balance equations. The computer programme used in the present study considers 17 dissociation equilibria given by Arnórsson et al. (1977) who also outline the methods of computation. Specifically the downhole pH is computed by simultaneous solution of the various weak acid dissociation equilibria listed by Arnórsson et al. (1977), the relevant mass balance equations for these weak acids, and assuming the equivalent sum of the anions of the weak acids in the water phase to be conserved during flashing. This sum is found from the measured pH of the water sample and an analysis of the respective weak acid components (total silica, total carbonate, total hydrogen sulphide).

The computed pH of the reservoir water at Reykjanes and Svartsengi mostly depends on the value obtained for bicarbonate (HCO_3^-) in the water sample. The bicarbonate concentration is in turn derived from the total carbonate (H_2CO_3 + HCO_3^- + CO_3^{--}) and the pH of the water sample. There is some doubt regarding the accuracy of the total carbonate analyses in the water samples as discussed by Arnórsson et al. (1977). Total carbonate values in the water phase computed from the analysed carbon dioxide in the steam and assuming equilibrium between the two phases were considered preferrential. Values so obtained have been used in the present study.

GEOLOGY OF THE GEOTHERMAL FIELDS

The geothermal fields on the Reykjanes Peninsula are of the high-temperature type (see Bödvarsson, 1960), but 18 such fields are known in Iceland. All these geothermal fields are confined to the active volcanic belts and are characteristically associated with the so-called central volcanic complexes (Pálmason and Sæmundsson, 1974). These volcanic complexes lie in the middle of en-echelon shaped fault swarms that run at an angle of 5-30^{o} to the axes of the volcanic belts, the plate boundary. The tensional forces diverging the crustal plates are at right angles to the fault swarms (Björnsson and Einarsson, 1974). Within the active volcanic belts the volcanic complexes present foci of maximum volcanic activity and apparently also intrusive activity. Here differentiated rocks tent to be located. Walker (1966) has estimated that intrusives account for more than 50% of the rocks in some of the eroded Tertiary central volcanic complexes in eastern Iceland. It is believed that these intrusives constitute the major source of heat for the geothermal systems.

All the geothermal fields on the Reykjanes Peninsula lie on the plate boundary as defined by earthquakes (Björnsson and Einarsson, 1974). They possess all the major tectonic structures characterizing the central volcanic complexes but other features such as differentiated volcanics and caldera structures have not been identified. In this respect the geothermal fields on the Reykjanes Peninsula might resemble more those on the sub-marine extension of the volcanic belts, the Mid-Atlantic Ridge, than other high-temperature geothermal fields in Iceland.

The lack of differentiated rocks on the Reykjanes Peninsula might be related with temperatures deep in the crust in turn related to the Kverkfjöll hot spot (Sigvaldason, 1974) but most authors favor generation of these rocks by partial melting of basalt deep in the crust.

In Iceland the distance between individual high-temperature geothermal fields is approximately in the range of 20-100km. The distance is apparently less and the geothermal fields smaller the larger the angle between the fault swarms and the plate boundary. For this reason one might not expect sub-marine geothermal systems to be equally closely spaced on the Reykjanes Ridge as they are on its land extension, the Reykjanes Peninsula (see Klein et al., 1973).

Two hypothesis have been suggested for the distribution of geothermally altered rocks in the oceanic crust. The first favours uniform alteration at depth in the crust but only around faults, which act as flow channels, nearer the sea bottom (Barett and Aumento, 1970; Hart, 1973). The second hypothesis assumes alteration along faults only, and that during the faulting geothermal fluids were admitted through, altering the wall rock at the time (Melson et al., 1968; Cann and Vine, 1966). It is the opinion of the present author that these hypotheses have not taken into account the strong relationship between geothermal activity (of the high-temperature type) and structural-magmatic anomalies in the volcanic belts of Iceland. Such anomalies are likely to occur also in the sub-marine parts of ocean ridges. They lead to the development of geothermal systems because they favour water convection. Geothermal anomalies on the sea floor should be correlated with local tectonic-magmatic anomalies rather than the tectonic features of the mid ocean ridges as a whole. The Reykjanes and Svartsengi geothermal systems represent anomalies of this kind. They are limited in space (<50 km^3), as judged from their areal extent (5 km^2) and the distribution of fossil Tertiary systems in Iceland exposed by erosion (Walker, 1966).

HYDROLOGICAL FEATURES OF THE REYKJANES PENINSULA

The extremely high rock permeability in the low lying western half of the Reykjanes Peninsula is reflected in the low level of the groundwater table. In the center of this part of the peninsula, about 10 km from the coasts, the watertable is only 1.5 m above mean sea level (unpublished data of the National Energy Authority). This high permeability is to be related with the post-glacial lava flows which cover most of the western half of the peninsula. At depth they are replaced by sub-glacial hyaloclastites and pillow lavas and interglacial lava flows of lower permeability. The eastern part of the Reykjanes peninsula is more elevated (200-400 m). Here the Quaternary rocks are much more abundant on the surface and the groundwater table is higher.

Drilling outside the geothermal fields has revealed the existence of sea-water in the rock underlying a lense of fresh gorund water of limited thickness. Around the Reykjanes field, which is on the southwest tip of the peninsula, this fresh water lense has practically vanished. The thickness of the fresh water lense is determined by the elevation of the groundwater table and the density differences or fresh water and sea water, being approximately 35 meters for 1 meter elevation of the watertable.

The variation in salinity of the geothermal drillhole fluids in the Reykjanes Peninsula (see table 1) are explained by mixing of fresh ground-water with the underlying sea-water in the downflowing part of the convection cells of the systems. At Reykjanes, the fresh water component is negligible because the fresh water lense is lacking in the downflow zone, but in the eastern part of the Krísuvík geothermal field (well 5, table 1) sea- water mixing is negligible due to the great thickness of the fresh water lense in this locality. A schematic sketch of this hydrological model is presented in fig. 4, showing the convection cells for Svartsengi.

Fig. 4

ROCK ALTERATION

The pattern of alteration and the distribution of geothermal minerals in the Reykjanes geothermal field have been described by Tómasson and Kristmannsdóttir (1972). A detailed study of rock alteration in Svartsengi has not been carried out. It seems, however, clear that it follows the same general pattern as that of Reykjanes.

The similarity of the alteration at Reykjanes with that of other studied high-temperature fields in Iceland (Sigvaldason, 1963, Gíslason, 1973, Kristmannsdóttir, 1975) suggests that temperature primarily determines the type of alteration and not so much the composition of the water entering the system.

The dominant geothermal minerals at Reykjanes include smectite and chlorite. Smectite dominates in the upflow zone where temperatures are below about 200^{o}C, being replaced by chlorite at greater depths (Tómasson and Kristmannsdóttir, 1972). A random mixed layer mineral of smectite and chlorite occurs at the interface of these two major mineral zones. Quartz, calcite, and pyrite are widely distributed, and are particularly abundant in the flashing zone. A variety of zeolites have also been reported in this zone, but at temperatures above some 230°C they disappear. Sporadic amounts of anhydrite occur througout the altered rock. Other geothermal minerals that are reported by Tómasson and Kristmannsdóttir (1972) include prehnite, epidote, and hematite. They also observed some albitization of the plagioclase, which may explain the slight lowering of sodium in the geothermal sea-water, discussed later.

The extent of the alteration depends very much on the texture of the rock, tuffs being most susceptible to alteration but the massive middle parts of lava flows are most resistent. Total replacement of the primary rock constituents by geothermal minerals is hardly ever observed. Therefore, sufficient material seems to be available in the rock to react with the sea-water and modify its composition so it will correspond to chemical equilibrium with the geothermal minerals.

THE CHEMICAL CHARACTERISTICS OF GEOTHERMAL SEA-WATER

Chemically the Reykjanes geothermal water differs significantly from sea-water as originally pointed out by Björnsson et al. (1972). Compared to sea-water the concentrations of calcium and potassium have increased roughly 4 times, but sulphate and magnesium have been largely removed from solution. Silica has increased strongly to a level of about 600 ppm. Sodium has decreased slightly but chlorine remained constant. Fluorine has decreased about 10 times. These chemical changes compare very well with those obtained experimentally by reacting basalt with sea-water at elevated temperatures (Mottl et al., 1974, Bischoff and Dickson, 1975, Wolery and Sleep, 1976).

Tables 1 and 2

The calculated concentration of chlorine in the unflashed reservoir water at Reykjanes compares well with that of sea-water (table 1). An uncertainty in the true chlorine concentration of the unflashed geothermal water lies in the estimation of the enthalpy of the well discharge. Due to flashing in the reservior around well 8 at Reykjanes and simultaneous precipitation of silica from solution, the calculated quartz equilibrium temperature has become lower with time. Initially it was 283°C, a figure comparing well with the measured downhole temperature between 1000 and 1700 meters where aquifers enter the well (fig. 3). The six samples, for which average is presented in table 1, were collected during 1973 and 1974 after which the quartz equilibrium temperature had reached a stable value of about 269°C corresponding to the new pressure conditions imposed after an initial pressure drop produced by the discharging well. It is bleieved that the enthalpy corresponding to the initial quartz equilibrium temperature of 283°C fits better with the enthalpy of the discharge of well 8 than that corresponding to 269°C. Therefore, the latter column for Reykjanes in table 1 gives the better picture of the composition of the unflashed reservoir water.

The analytical precision for the chlorine determination is ± 3%, so the difference in the concentration of the element in sea-water and the Reykjanes geothermal water is well within the limit of analytical precision. This implies that the Reykjanes geothermal water has not leached significant chlorine out of the basalt, and that the geothermal system is an open one, i.e. does not involve recirculation of flashed hot water. It is difficult to believe that precisely sea-water concentration of chlorine would be obtained for the geothermal water by leaching from marine sediments as has been proposed to explain the deuterium content of the geothermal water (Árnason, 1975).

The concentration of total carbonate (expressed as CO_2 in table 1) is much higher in the Reykjanes water than in sea-water and considerably higher in Svartsengi. The source of carbon dioxide in the geothermal fluids is believed to be in part derived directly from intrusives yielding the heat to the system, and partly leached from the rock being altered. Carbon dioxide can be expected to be trapped in rapidly cooled volcanics, especially the glassy fraction, which will be released upon. mineralogical transformation of the rock. The difference in the concentration of total carbonate in Svartsengi and Reykjanes results from the temperature difference of the water in the two systems and mineral/ solute equilibria discussed later.

The concentrations of total sulphide (expressed as H_2S, in table 1) are considerably higher in the geothermal fluids, especially Reykjanes although they are much lower than in the dilute geothermal waters of other high-temperature fields in Iceland (Arnórsson, 1974). High sulphide is characteristic of high-temperature dilute waters flowing through basaltic rocks. The lower sulphide concentrations in the saline geothermal waters can be related to their higher oxidation potential and the combined effect of several mineral/ solute chemical equilibria. Reduction of sulphate to sulphide is not considered necessary to account for the sulphide in the water nor the pyrite in the hydrothermally altered rock.

The geothermal sea-water at Svartsengi and Reykjanes has a near neutral pH of about 5.5 and 5.9 respectively (table 2) whereas sea-water is distinctly alkaline, both at room-temperature (Garrels and Thompson, 1962) and at the temperature of the geothermal waters. The pH value for Reykjanes compares rather well with that calculated at 200°C by Bischoff and Dickson (1975) for experimentally reacted sea-water with basalt. The increased hydrogen ion activity in the geothermal water results from uptake of OH in hydrous silicates such as smectite and chlorite and simultanous dissociation of water.

The calculated distribution of chemical species in sea-water and the geothermal water is presented in table 2. The difference, which is considerable, is mostly due to the elevated temperature of the latter but also water/rock interaction. Increased temperature leads to an overall increase in complexing as is apparent from the decrease in ionic strength. Thus, 88% of the sulphate is complexed in the geothermal water as compared with 54% in sea-water. Comparable figures for chlorine are 8-16% and 0.6%. The lower value of 8% refers to Svartsengi. Calcium and magnesium form practically only free ions in the geothermal water due to the low concentrations of the anions with which they tend to complex, SO_4^{--} and CO_3^{--}. As a result of the low pH, carbonic acid and hydrogen sulphide are mostly undissociated.

MINERAL/SOLUTE EQULIBRIA

The difference in the major element composition of sea- water and the geothermal sea-water at Reykjanes can be explained by mineral/solute chemical equilibria that have been established at the high temperatures in the geothermal reservoir. The same holds for Svartsengi, if mixing of sea-water with fresh water in the ratio of 2/1 is taken into account.

Anhydrite Saturation

The calculated $CaSO_4$ activity product for the Svartsengi and Reykjanes waters indicates that these waters are just saturated with anhydrite, but other high-temperature waters in Iceland are, on the other hand, somewhat undersaturated (fig. 5). The activity product for individual wells plotted in fig. 5 refers to the quartz equilibrium temperature. Because there is some uncertainty in the validity of this temperature for the Reykjanes water, the $CaSO_4$ activity product was calculated for higher temperatures also. It is evident from these calculations that about equally good fit with the anhydrite solubility curve is obtained, if the

Fig. 5

original quartz equilibrium temperature for well 8 of 283° was used instead of 269°C. This is mostly due to the rapid decrease of the activity coefficients of Ca^{++} and SO_4^{--} with increasing temperatures in the respective temperature range. This effect helps to maintain anhydrite saturation in a cooling geothermal water. Decreased complexing of SO_4^{--} at lower temperatures has the same effect. Despite these two effects leaching of calcium and/or sulphate from the rock (or oxidation of sulphide) is necessary in the upflow zones to maintain saturation where the water cools by flashing, but the chemistry of hot springs at Reykjanes, which contain 100-200 ppm of sulphate (Björnsson et al., 1972)indicates that anhydrite saturation is maintained throughout the upflow zone where the hot-water cools.

From the previous discussion it is evident that anhydrite is not expected to precipitate from the cooling ascending geothermal water. This conclusion may not seem to fit with the reported local abundance of anhydrite in the altered rock of the upflow zone. As pointed out by Tómasson and Kristmannsdóttir (1972), however, the presense of this anhydrite is considered to be due to its precipitation from cold seawater-groundwater that heats up when it invades the geothermal reservoir during intermittent tectonic movements. These movements fracture the otherwise impermable cap of vesicle filled rock enveloping the upflow zone, allowing inflow of the surrounding cold seawater-groundwater into the geothermal reservoir. Dissolution of anhydrite so formed by the cooling, ascending geothermal water is considered to be responsible for maintaining anhydrite saturation in the upflow zone.

Factors affecting the mobility of fluoride

The calculated CaF_2 activity product for the Reykjanes and Svartsengi waters and the available fluorite solubility data, which Nordstróm and Jenne (1977) have evaluated recently, indicate that these waters are strongly undersaturated with fluorite. Yet, the fluorine in the geothermal sea-water has decreased about 10 times relative to its concentration in the parental fluid, ordinary sea-water, and at a given temperature, the calculated CaF_2 activity product fits well with that of other high-temperature geothermalfluids in Iceland. It is considered that this relation of fluorine with calcium may be a coincidence in the sense that it results from the combined effect of several mineral/solute reactions. As is discussed in the following section, the ratio $\sqrt{Ca}/H$ is approximately constant at a given temperature. By virtue of this relation, and since $(H^+)(OH^-) = K_w$, it can be shown that constant CaF_2 activity product at a given temperature is obtained, if the ratio F^-/OH^- is constant at a given temperature. Here, the interpretation is favoured that the fluorine mobility is limited by an inonic exchange reaction with hydrated silicates where F^- replaces some of the hydroxyl groups. When the fluorine content of rocks of geothermal systems is high, as is the case with acid volcanics, fluoride concentrations in the associated waters may be limited by fluorite solubility as is indicated by the Wairakei analysis plotted in fig. 5 and the results of Nordstróm and Jenne (1977).

Major cations and hydrogen ion

Relative to sea-water the eqivalent sum of the major cations in the Reykjanes water has decreased slightly, or to the extent that corresponds to the removal of sulphate from the original sea-water. The ratios of individual cations and hydrogen ion have, however, changed drastically. This is considered to be due to ionic exchange reactions occuring during formation of minerals such as smectite and chlorite from the original constituents of the rock.

A chemical reaction of the following type describes the changes in the cation and hydrogen content of sea-water as it reacts with basalt

$$\text{"solid"} + H_2O + aNa^+ + \frac{b}{2}Mg^{++} = \text{"solid"} + cK^+ + dH^+ + \frac{e}{2}Ca^{++} \qquad (1)$$

Since the stoichiometry of the reaction is not known the values of the coefficients a, b, c, d, and e are not known. An equilibrium constant for reaction (1) can be expressed in a number of ways. For example by relating the activities of all ions to that of hydrogen, we have

$$\log K^* = c \cdot \log\frac{K}{H} + (a+b-c-d)\log\frac{Ca}{H} - a \cdot \log\frac{Na}{H} - b \cdot \log\frac{Mg}{H} \qquad (2)$$

The value of K^*, and therefore the ratio of individual cations, is temperature dependent as described by the van't Hoff equation

$$\frac{d\ \log K^*}{d\ (1/T)} = \frac{-\ \Delta H_r^o}{4.5758} \qquad (3)$$

where T is the absolute temperature and ΔH^o the standard heat of reaction at given temperature. If ΔH^o varies insignificantly with temperature a plot of $\log K^*$ against 1/T would fall on a straight line. In the same way would individual cation/hydrogen ratios vary with temperature but the spread of points should decrease, if individual ratios were added up after multiplying them with the appropriate stochiometric constant. Plot of logNa/H, logK/H, log Ca/H and log Mg/H against 1/T for unmixed geothermal waters of widely varying temperatures from over 100 localities in Iceland yields a straight line in all cases (Arnórsson, unpublished work) with the exception of metal/hydrogen ratios for some high-temperature fluids, including Reykjanes, but not Svartsengi, which have flashed in the ground before entering the wells.(fig. 7).

The plots for Na/k, Na/ Ca, and Na/ Mg are shown in fig.6 for the geothermal fluids at Reykjanes and Svartsengi including also data of dilute waters from the Hengill and

Námafjall fields (Arnórsson et al., 1977) and Wairakei, New Zealand (Truesdell and Singers 1974). The rather good relation of log $Na/\sqrt{Ca}$ with 1/T is taken to indicate that the calcium and sodium activities in the Svartsengi and

Fig. 6

Reykjanes waters are determined by ionic exchange chemical equilibria with geothermal minerals explaining in quantitative terms the increase in calcium of geothermal seawater relative to ordinary sea-water. The relatively low potassium of the Reykjanes water for its temperature, which is illustrated by its anomalous log Na/K value (fig. 6), may be due to insufficient availability of this cation in the rock. According to Björnsson et al. (1972) fresh basalt in the Reykjanes area contains only 0.1-0.25% K_2O, which is comparable to its concentration in the geothermal seawater. This interpretation is in accordance with the experimental work of Mottl et al. (1974) who found potassium to be practically totally removed from basalt when heated with sea-water.

The drastic lowering of the magnesium concentrations is thought to be due to its effective uptake by geothermal smectite and chlorite. As magnesium is incorporated in these newly formed minerals, potassium and calcium go into solution from the disintegrating primary constituents of the rock.

On the assumptions stated previously the calculated pH of the water feeding the four discharging wells at Svartsengi is between 5.4 and 5.5. Similarly, a pH of 5.9 and 6.0 is obtained for the water feeding well 8 at Reykjanes, referring to a quartz equilibrium equilibrium temperature of 169°C and 283°C respectively.

The metal/proton ratio for the Svartsengi waters falls on the extrapolated plot of these ratios against 1/T of unmixed low-temperature waters in Iceland. This is demonstrated in fig. 7 for Na/H, but an equally good fit is obtained, for the other ratios. On the other hand, the Reykjanes geothermal sea-water yields a considerably higher value for these ratios and the plots form a cluster with waters from some other high-temperature fluids in Iceland and from Wairakei, New Zealand. By virtue of the strong relation between the metal/hydrogen ratios in unmixed geothermal waters in Iceland, it is thought that the calculated pH for the Svartsengi water of 5.4-5.5 represents an equilibrium value at 240°C, which is determined by some ionic exchange reaction, as yet of unknown stochiometry. The higher pH of the Reykjanes water is thought to have resulted from degassing in the aquifer outside the well. Underground temperature conditions are such at Reykjanes, as well as in the other high-temperature fields having similar metal/proton ratios that the present drillholes have not penetrated below the deepest point of flashing in the upflow zone. This is, however, not the case at Svartsengi and in another field, Hveragerdi, the latter having metal/proton ratios comparable with the former.

Fig. 7

Extrapolation of the proposed "equilibrium" Na/H line (see fig. 7) suggests that an equilibrium pH at 270-280°C for the Reykjanes geothermal sea-water would be about 5.1 and that the pH would become progressively lower with increasing temperature. Thus, at 300° and 330°C the equilibrium pH would be roughly 4.8 and 4.4 respectively, at least if the stoichiometry of the reaction remained the same at these high temperatures. The neutral pH of water at 300° and 330° is 5.7 and 5.9 respectively. Thus, geothermal sea-water, if sufficiently heated, will become considerably acid through reaction with basalt. The pH of 5.6 calculated by Bischoff and Dickson (1975) for sea-water experimentally reacted with basalt at 200°C, corresponds well with my proposed equilibrium value of 5.4-5.5.

Calcite saturation.

Calcite is very abundant in the upflow zones of the Svartsengi and Reykjanes fields where flashing occurs (see Tómasson and Kristmannsdóttir, 1972), but it is also relatively abundant below the flashing zone. When the water flashes (and cools adiabatically) its pH increases because carbon dioxide is lost from the water and transferred into the steam phase. As a result of the pH increase, the concentration of CO_3^{--} increases strongly (fig 8b) and leads to calcite supersaturation for an originally saturated solution despite the increase in the calcite solubility at lower temperatures. The calculated variation in the $CaCO_3$ activity product of the Reykjanes water, as it flashes, is shown in fig. 8a. Since calcite equilibrates easily with aqueous solutions at high temperatures one would expect the unflashed reservoir water to be just saturated, although flashed water in the upflow zones and in wells may be supersatured.

Fig. 8

The calculated reservoir water pH of 5.4 - 5.5 for the 4 wells in Svartsengi yields a value for the $CaCO_3$ activity product that just fits calcite saturation (fig. 8a). On the other hand, it is seen that the reservoir water at Reykjanes is somewhat supersaturated with respect to calcite.

One might expect that the apparent supersaturation of the Reykjanes water was due to an erroneous value of the reference temperature (the quartz equilibrium temperature) applied, but as was mentioned before, flashing in the reservoir leads to silica precipitation and thus yields low quartz equilibrium temperatures. This is, however, not the case. The two dotted lines in fig. 8a show how the calculated $CaCO_3$ activity product varies with an arbitrarily selected reference temperature for one step adiabatic flashing (1) and conductive cooling above the quartz equilibrium temperature (2).

It is believed that the unflashed reservoir water at Reykjanes is just calcite saturated. Flashing, which occurs in the aquifers feeding the well, is considered to be accompanied with some steam (and gas) loss with the effect that the total well discharge is somewhat gas deficient relative to the unflashed reservoir water. The outcome of this effect for the calculations of the $CaCO_3$ activity product is that one obtains some supersaturation, if the unflashed reservoir water was just calcite saturated. Such steam and gas loss in the aquifer also explains the relatively high calculated pH value for the Reykjanes water.

SUMMARY AND CONCLUSIONS

In the preceeding discussion it was demonstrated that the activities of most of the chemical species, and thus the chemical components in the geothermal waters were controlled by mineral solubilities or ionic exchange equilibria. Thus the distribution of Na^+, K^+, Ca^{++}, Mg^{++}, and H^+ was attributed to ionic exchange equilibria. The respective reaction involves probably smectite and/or chlorite and alkalifeldspar. Carbonate and sulphate activities are controlled by calcite and anhydrite solubilities respectively. The mobility of fluoride is thought to be limited by an ionic exchange reaction where it replaces some of the OH^- groups in phyllosilicates. Silica concentrations are governed by quartz solubility. The only remaining dissolved major constituents are chlorine and hydrogen sulphide. Factors affecting the mobility of the latter have not been studied, but it is thought that sulphide (S^{--}) activity may be limited by pyrite and/or pyrrhotite solubility. Chloride is not incorporated in the geothermal minerals and because of the low concentrations of this element in basaltic rocks (see Sigvaldason and Óskarsson, 1976) that could be leached out by the hot water, the chlorine content of the geothermal seawateris for all practical purposes determined by its concentration in the parental fluid. It is therefore concluded that the major component compostion of geothermal sea-water is is only governed by two sets of independent variables. Firstly the compostion of the parent fluid, sea-water, and secondly by an interplay of several mineral/solute equilibria. These equilibria, which have been demonstrated to control the chemistry of the Reykjanes and Svartsengi geothermal fluids, hold at higher and lower temperatures, the composition of geothermal sea-water can be calculated at any specifie temperature on the basis of the present results. Such calculations might be of interest to those involved in predicting the influence of sub-marine geothermal activity on the chemical balance of the oceans in geologic time.

ACKNOWLEDGEMENTS

This article was prepared while the author was working with Professor I.Th. Rowenqvist´s research group at the Geology Department of Oslo University, but it is based on data from the National Energy Authoriy, Reykjavík. The author expresses his sincere appreciation to Dr. J. Jónsson for preparing the simplified geological map of the Reykjanes Peninsula presented in fig. 2. Financial support from the Royal Norwegian Council for Scientific and Industrial Research is acknowledged.

This article was orginally presented at the triennal melting of the Mineralogical Society, held in Leeds, April 1977.

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CAPTION TO FIGURES:

1. The distribution of high-temperature geothermal activity in Iceland in relation to the major tectonic features. Compiled by K. Sæmundsson.

2. Location of geothermal fields in the Reykjanes Peninsula. From unpublished data of J. Jónsson.

3. Downhole temperatures for well 4, Svartsengi, and well 8, Reykjanes. Figures at the bottom indicate the quartz equilibrium temperature (t_{qtz}). For well 8, Reykjanes, the value of 283°C corresponds to the initial t_{qtz} but 269°C to the stabilized t_{qtz} of continously discharging well. See text.

4. Schematic west-east hydrological section through the Reykjanes peninsula demonstrating how the variable salinity of the geothermal waters depends on the thickness of the fresh water lense overlying the seawater-groundwater.

5. Computed activity product of $CaSO_4$(A) and CaF_2 (B) for the Svartsengi and Reykjanes geothermal waters. The solubility data for anhydrite were obtained from Blount and Dickson (1969) and that for florite from Nordstróm and Jenne (1977).

6. The ratios of major cations in relation to temperature in high-temperature geothermal waters in Iceland. Computed activities of free cations were used.

7. Relation between Na/H and temperature for geothermal waters in Iceland. The solid line repersents the best fit for the low-temperature data. The low-temperature data (1000/T 2.3, T 160°C) are not entirely comparable with the high-temperature ones, since the former is based on sodium concentration but the latter on activity of free Na^+ ions. The dashed line shows approximately how this best fit line would shift, if Na concentrations were replaced by Na activities.

8a. Computed activity product of $CaCO_3$ for the Reykjanes and Svartsengi geothermal waters. The dashed line shows how the computed $CaCO_3$ activity product varies during one step adiabatic flashing. The dotted lines show how the calculated $CaCO_3$ activity product varies with an arbitrarily selected reference temperature for one step adiabatic flashing (1) and conductive cooling above the quartz equilibrium temperature (2). The calcite colubility data were obtained from Helgeson (1969).

8b. Variation of pH and $m_{CO_3^{--}}$ with temperature of flashed Reykjanes geothermal water.

TABLE 2. Chemical speciation of sea-water at 25°C and geothermal sea-water. Concentrations in ppm and mmol.

Chemical species	Sea-water[a]		Reykjanes well 8		Svartsengi well 4.	
t_{qtz} °C			271.6		237.0	
pH	8.1[b]		5.86		5.47	
Na^+	10348	470	8188	356	5798	252
K^+	387	9.90	1368	34.9	922	23.6
Ca^{++}	279	9.46	1516	37.8	983	24.5
Mg^{++}	1142	47.0	0.3	0.013	4.5	0.18
H_4SiO_4	-		963	10.00	714	7.41
$H_3SiO_4^-$	-		1.00	0.011	0.43	0.005
H_2CO_3	6.1[c]	0.098	2206	35.6	603	9.71
HCO_3^-	100.2	1.64	29.2	0.48	11.4	0.19
CO_3^{--}	1.4	0.023	0.0001	$0.25 \cdot 10^{-5}$	0.001	$0.23 \cdot 10^{-5}$
H_2S	-		29.8	0.87	1.5	0.044
HS^-	-		1.2	0.037	0.04	0.0015
S^{--}	-		$0.20 \cdot 10^{-5}$	$0.62 \cdot 10^{-7}$	$0.17 \cdot 10^{-7}$	$0.5 \cdot 10^{-9}$
HSO_4^-	-		0.17	0.0018	0.31	0.0033
SO_4^{--}	1473	15.3	2.6	0.027	4.5	0.047
HF	-		0.05	0.0026	0.04	0.0022
F^-	-		0.05	0.0026	0.07	0.0040
Cl^-	18892[d]	533	15868	477	11610	327
$NaCl^o$	180[d]	3.08	5093	87.1	1633	27.9
KCl^o	4.07[d]	0.055	310	4.2	97.9	1.31
$NaSO_4^-$	710	5.96	16.7	0.14	20.4	0.17
KSO_4^-	19.1	0.141	1.6	0.012	2.0	0.015
$CaSO_4^o$	115.9	0.851	7.8	0.057	12.2	0.090
$MgSO_4^o$	735.1	6.11	0.16	0.0014	3.4	0.028
$CaCO_3^o$	11.4[e]	0.113	0.03	0.0003	0.02	0.0002
$MgCO_3^o$	54.8[f]	0.652	$0.15 \cdot 10^{-4}$	$0.18 \cdot 10^{-6}$	$0.6 \cdot 10^{-4}$	$0.25 \cdot 10^{-5}$
I	0.6539		0.4954		0.3513	

[a] From Garrels and Thompson (1962); [b] the pH of sea-water when heated to 240-270°C and no precipitation takes place is of the order of 8.6; [c] caclulated approximately from the reported figure of HCO_3^-; [d] complexing of Na and K with Cl calculated approximately; [e] includes also $CaHCO_3^+$; [f] includes also $MgHCO_3^+$. The calculations refer to the reported quartz equilibrium temperature (tqtz).

TABLE 1

The concentration of analytical components in sea-water and geothermal waters in the Reykjanes Peninsula. Figures in ppm.

Analytical component	Sea-water[a]	Reykjanes[b] well 8		Svartsengi[b] well 4	Krísuvík[e] well 6	Krísuvik[e] well 5
		269°C[c]	283°C[c]			
Na	10556	10135	9629	6279	700	210
K	380	1480	1409	973	119	13.8
Ca	400	1628	1551	950	42.4	10.6
Mg	1272	1.0	1.0	6.0	0.4	0.2
SiO_2	3.0	600	572[d]	444	514	220
CO_2	114	1438	1764	457	62.2[f]	63.0[f]
H_2S	-	26.7	32.7	1.9	6.6[f]	4.4[f]
SO_4	2649	22.2	21.2	34.0	49.6	178.2
F	1.3	0.10	0.10	0.12	0.50	0.45
Cl	18980	19727	18785	12070	1094	118.0

[a] from Mason (1966); [b] average of 6 analyses; [c] the analytical concentrations expressed have been derived from the average quartz equilibrium temperature of 269°C for the 6 samples (range 264.6 - 271.8°) and the initial quartz equilibrium temperature of the well discharge, 283°C.

[d] low silica for the temperature of 283°C due to its removal from solution as the water flashes in the aquifer; [e] downhole samples, from 470 m and 500 m depth respectively; [f] suspected to be low due to degassing of the samples during collection.