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Saturation state of natural waters in Iceland relative to primary and secondary minerals in basalts

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Abstract—Weathering and hydrothermal alteration of basaltic rocks in Iceland by natural waters include dissolution of the primary rock minerals and glass and precipitation of secondary minerals. The alteration process involves hydrogen ion metasomatism. The proton donors driving the alteration process include carbonic acid, derived from the atmosphere and the decay of organic matter (cold waters), silica (H_4SiO_4) dissolved from the rock (cold groundwaters and waters from low-temperature fields) and carbonic acid and hydrogen sulphide, which are either derived from the rock being altered or from a degassing magma (high-temperature fields). Cold groundwaters in Iceland are undersaturated with olivine, and presumably even more with basaltic glass. They are generally undersaturated with pyroxene but close to equilibrium with plagioclase. These waters seem to be heavily supersaturated with common weathering minerals like smectites, gibbsite, kaolinite and chalcedony. This may be an artifact caused by the small crystal size of the weathering products which increases their solubility. Geothermal waters are invariably undersaturated with plagioclase. They may be close to equilibrium, or somewhat undersaturated, with olivine depending on its composition. These waters tend to be pyroxene supersaturated when below about 150°C but undersaturated at higher temperatures. Heavy supersaturation with respect to the magnetite and hematite components in magnetite-ulvöspinel and ilmenite-hematite, respectively, is observed for thermal waters below about 150°C. Supersaturation decreases with increasing temperature and above about 200°C the waters seem to be characteristically magnetite undersaturated. The geothermal waters closely approach equilibrium with secondary minerals found in the altered rock such as chalcedony/quartz, calcite, K-feldspar, albite, marcasite/pyrite, pyrrhotite and sometimes with laumontite. The close approach to equilibrium is favoured by the relatively "similar" saturation state of both primary and secondary minerals. Thus, the flux of constitutents into the water by dissolution processes can easily be coped with by precipitation reactions without maintaining the solution much supersaturated with the precipitating minerals.

INTRODUCTION

THE STUDY OF hydrothermal alteration in active and fossil geothermal systems in Iceland has clearly revealed that the alteration process involves dissolution of the primary rock minerals and glass and deposition of secondary, or alteration, minerals (*e.g.*, KRISTMANNSDÓTTIR, 1978; ARNÓRSSON, 1987a). Studies of water compositions in active systems with temperatures as low as 50°C indicate that chemical equilibrium is closely approached between all aqueous major elements, except chlorine, and alteration minerals (ARNÓRSSON, 1983; ARNÓRSSON *et al.*, 1983a). Comparable conclusions have been drawn from studies of geothermal systems in many other parts of the world (*e.g.*, ELLIS, 1970; SEWARD, 1974; GIGGENBACH, 1980, 1981).

Unlike thermal waters, reaction rates involving dissolution of the primary rock constituents control the composition of cold, and warm (<35°C) groundwaters (GÍSLASON and EUGSTER, 1987a,b), although some elements like aluminium, iron and magnesium may be incorporated into weathering minerals during the earliest stages of rock dissolution. Similar conclusions have been drawn from the studies of groundwater chemistry elsewhere (REYNOLDS and JOHNSON, 1972; MILLER and DREVER, 1977; WHITE *et al.*, 1980; DEUTSCH *et al.*, 1982). Yet, there still exists an uncertainty in the kinetic process of dissolution because of discrepancies between experimentally derived rate constants and rate constants derived from field data (PACES, 1983; VEBEL, 1986).

Iceland is largely built up of basaltic volcanics (80–85%). Groundwater, cold and thermal, is among the most valuable natural resources in the country. As a result, many drillholes have been sunk into the basaltic volcanics in many areas tapping water with temperatures in the range of about 5–350°C. Large cold springs occur in places in the volcanic belts tapping extremely large groundwater bodies. These springs and, in particular, the drillholes, provide a unique opportunity to study the chemical characteristics of natural waters of widely varying temperatures that are associated with different weathering and hydrothermal mineral assemblages in a homogeneous petrological environment.

In the present contribution an attempt is made to map the characteristics of natural water compositions in Iceland with respect to dissolution and precipitation reactions. The following questions are specifically addressed:

(1) Are the primary minerals of the basaltic rock in contact with natural waters stable or unstable?

(2) If they are unstable, how can the dissolution kinetics be described?

(3) How closely is chemical equilibrium approached between the water and specific weathering and alteration minerals found in the associated basaltic rock?

The data base on water compositions selected to answer the above questions are basically those presented by ARNÓRSSON *et al.* (1983a), GÍSLASON and RETTING (1986) and GÍSLASON and EUGSTER (1987b). In all we use 50 analyses of which 22 are from cold springs, 1 from a spring at 34°C, and 27 from geothermal wells with aquifer temperatures in the range 59–248°C. Sample locations are shown in Fig. 1. The wells selected have one dominant feed zone where downhole measurements have been used to obtain the aquifer temperature. Wells with multiple feeds were avoided as their discharge is necessarily a mixture of water from more than one source.

GEOLOGICAL FEATURES

Iceland is a volcanic island (103,000 km^2) of Tertiary to Recent age. The exposed volcanic pile is predominantly basaltic in composition (80–85%), silicic and intermediate rocks constitute about 10%, the rest being volcaniclastics, fluvial sediments and tillites. In the Tertiary lava pile they are typically 5–10% but are much more abundant in the Quaternary rocks (SAEMUNDSSON, 1979).

As much as 50% of the lava pile erupted from major volcanic centers (WALKER, 1966). In Tertiary formations where these centers are deeply eroded intrusions of dolerite, gabbro and granophyre may constitute as much or more than 50% of the rock by volume. Above the intrusions, geothermal systems developed as indicated by the alteration of the rock, frequently into greenschist mineral assemblages (SIGURDSSON, 1966; ANNELS, 1967; FRIDLEIFSSON, 1983, 1984). Outside the volcanic centers, zeolite facies alteration is typical of the Tertiary lava pile, the extent of alteration being generally rather limited (*e.g.*, WALKER, 1960; KRISTMANNSDÓTTIR, 1978).

Quaternary formations differ from those of the Tertiary, both with respect to structure and morphology. Pillow lavas and hyaloclastites are abundant due to eruptions under the icesheet. As a result

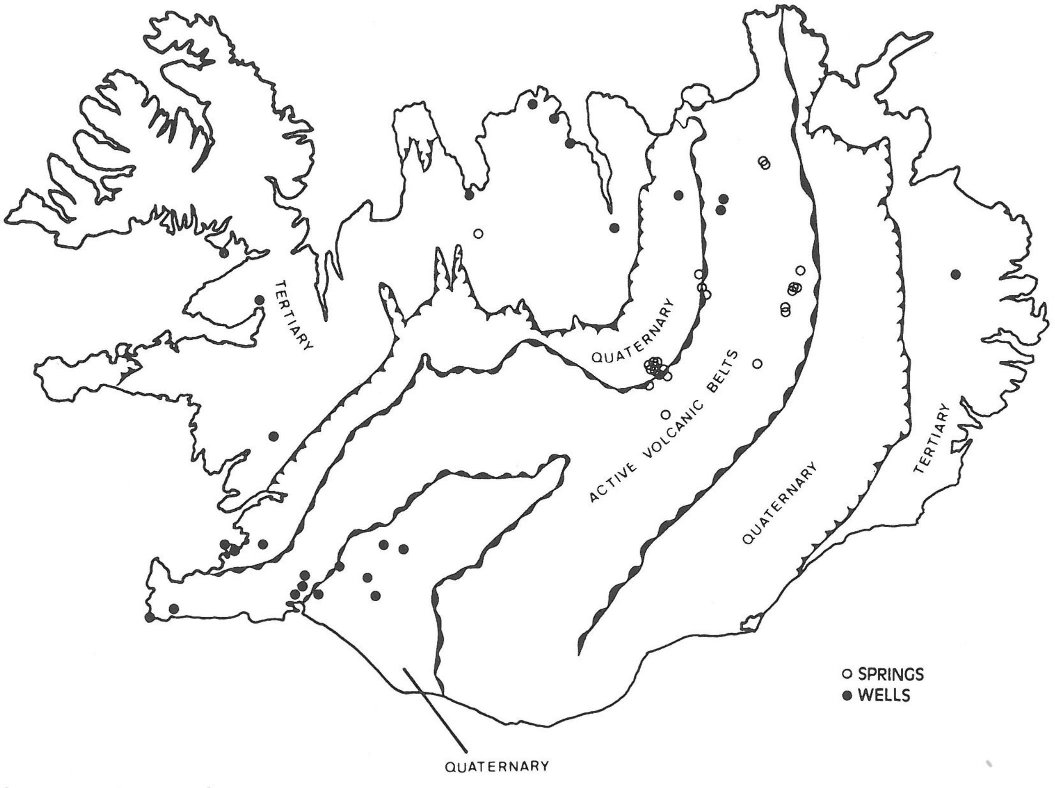

FIG. 1. Map of Iceland showing the distribution of sample sites for the cold and thermal waters considered in the present study.

Table 1. Composition of solid solution groundmass minerals and the mean activity of the pure end-member minerals in the solid solution

Mineral	Crystalline solution	Composition	Mean activity
Forsterite	olivine	Fo_{23}-Fo_{55}	0.19
Fayalite	olivine	Fa_{45}-Fa_{68}	0.33
Enstatite	orthopyroxene	En_{36}	0.3
Ferrosilite	orthopyroxene	Fs_{58}	0.58
Diopside (Ca-rich)	clinopyroxene	$En_{46}Fs_{16}Wo_{38}$-$En_{38}Fs_{29}Wo_{33}$	0.42
Diopside (Ca-poor)	clinopyroxene	$En_{53}Fs_{37}Wo_{10}$	0.11
Hedenbergite (Ca-rich)	clinopyroxene	$En_{46}Fs_{16}Wo_{38}$-$En_{38}Fs_{29}Wo_{33}$	0.22
Hedenbergite (Ca-poor)	clinopyroxene	$En_{53}Fs_{37}Wo_{10}$	0.072
Anortite	plagioclase	An_{29}	0.29
Albite	plagioclase	Ab_{71}	0.71
Magnetite	magnetite-ulvöspinel	Mt_{15}-Mt_{68}	0.35
Hematite	hematite-ilmenite	$Hem_{4.2}$-$Hem_{9.5}$	0.0054

The mole fractions are calculated from the chemical compositions of groundmass minerals in tholeiites and olivine tholeiites (sample 1 to 5, CARMICHAEL, 1967) except the one for orthopyroxene which is from a phenocryst in icelandite (sample 14, CARMICHAEL, 1967) and plagioclase which is from FISK (1978). The activities of the end member mineral compositions are calculated from the mole fractions as described in the text. The mean activity is the mean of the maximum and minimum activities.

glassy, or partially glassy volcanics are much more abundant in the Quaternary than in the Tertiary.

Post-glacial lava flows cover about 12,000 km^2, or more than 10% of the country (JAKOBSSON, 1972; SAEMUNDSSON, 1979). About 90% of these are basaltic, the remainder being either intermediate or silicic.

Geothermal activity is widespread in Iceland (*e.g.*, PÁLMASON and SAEMUNDSSON, 1974; ARNÓRSSON, 1975). Geothermal areas have been classified as high- and low-temperature areas (BÖDVARSSON, 1961). The former have a magmatic heat source, occur within the zones of active volcanism and are most often associated with major volcanic centers. Drillhole data indicate temperatures in excess of 200°C in the uppermost 1000 m. Low-temperature areas are found in Quaternary and Tertiary formations and temperatures are below 150°C in the uppermost 1000 m.

The grain size and the amount of glass in basaltic rocks in Iceland are, of course, very variable. In the case of Post-glacial lavas from the Reykjanes Peninsula the average diameter for groundmass minerals at 2 m below the surface range between 5 and 200 μm (JAKOBSSON, pers. comm.). The largest phenocrysts may be as much as 1 cm across. Plagioclase is the most abundant phenocrysts and olivine is second. The amount of phenocrysts is very variable, occasionally it is as much as 50% but generally they constitute only a small portion of the basalts. In Post-glacial lava flows from the western Reykjanes Peninsula phenocrysts amount to about 4% by volume on average (JAKOBSSON *et al.*, 1978). Phenocrysts are not, therefore, important for water-rock interactions.

In quenched rocks the composition of the glass corresponds closely to that of the bulk rock. Interstitial glass is, on the other hand, differentiated and commonly of rhyolitic composition (MAYER and SIGURDSSON, 1978). The primary minerals of basaltic rock, olivine, pyroxene, plagioclase and Fe-Ti oxides, occur both as phenocrysts and in the groundmass.

The chemistry of phenocrysts in the basaltic rocks of Iceland has been extensively studied (CARMICHAEL, 1964, 1967; JAKOBSSON *et al.*, 1978; GRÖNVOLD and MÄKIPÄÄ, 1978; FISK, 1978; THY, 1983), but analytical data for groundmass minerals is relatively scarce. CARMICHAEL (1964, 1967) made a detailed study of groundmass minerals in rocks (basaltic to silicic) of the Tertiary Thingmúli central volcano in eastern Iceland. FISK (1978) studied some groundmass olivine and plagioclase in Post-glacial lavas from the Reykjanes Peninsula in SW-Iceland. Table 1 shows the average composition of groundmass minerals for basalts from Thingmúli and the Reykjanes Peninsula. As would be expected, individual grains show considerable zoning and are less basic than coexisting phenocrysts.

Hydrothermal alteration of basaltic rocks in active and fossil geothermal systems has been studied extensively (WALKER, 1963; SIGVALDASON, 1963; TÓMASSON and KRISTMANNSDÓTTIR, 1972; KRISTMANNSDÓTTIR, 1982; STEINTHÓRSSON and SVEINBJÖRNSDÓTTIR, 1981; EXLEY, 1982; MEHEGAN *et al.*, 1982; RAGNARSDÓTTIR *et al.*, 1984). It is evident from studies of eroded Tertiary and Quaternary formations that a very minor part of the volcanic pile has suffered extensive alteration. The alteration is concentrated in the blocky tops and bottoms of lava flows, along fault planes and around vesicles. The alteration mineralogy is extremely varied, with calcite, quartz, chalcedony and various zeolites being particularly abundant as amygdale minerals along with celadonite, smectite and chlorite. The alteration minerals occur, however, not only in vugs but also permeate the whole rock, occupying angular spaces between the igneous mineral grains or replacing them. A regular distribution of zeolites has been observed in the Tertiary formations (WALKER, 1960) with certain mineral assemblages occupying flat lying zones which cut across the stratigraphy. Most of the regional hydrothermal alteration appears to have occurred within active volcanic zones before the rock drifted outside these belts in response to continued crustal accretion (STEINTHÓRSSON *et al.,* 1986).

Hydrothermal alteration in low-temperature geothermal fields is similar to the regional alteration just described. Much more intense alteration is observed in the cores of eroded central volcanoes and at depth in active high-temperature geothermal systems. The alteration typically belongs to the greenschist metamorphic facies with chlorite, albite, epidote, and quartz as the most prominent minerals but calcite, various sulphides, prehnite and actinolite are also quite common. Complete reconstitution of the rock is not uncommon when the alteration grade belongs to the greenschist facies.

Very limited information is available on the surface weathering products of the Icelandic basalts. ROALDSET (1983) studied sediment horizons interbedded with Tertiary basalts. The observed alteration mineralogy was the result of several processes, such as palagonitization, weathering and burial metamorphism/diagenesis. The alteration product included minerals such as kaolinite, halloysite, smectite, amorphous Al-Fe-oxides, and some zeolites. DOUGLAS (1987) observed that manganese-rich rock coatings are widespread in basalt lavas in Iceland. These coatings are associated with hydrothermal clay-filled fracture systems.

HYDROLOGICAL FEATURES

Precipitation in Iceland is abundant, ranges from less than 400 to more than 4000 mm a year and averages about 2000 mm and the average relative humidity is rather high, about 80% (EYTHÓRSSON and SIGTRYGGSSON, 1971). Some of the precipitation is stored temporarily in the ice-sheets, some of it evaporates directly, some of it runs off on the surface, and some infiltrates and enters groundwater bodies. In Tertiary and early Quaternary formations run-off dominates. The global permeability of the rock is low, $5*10^{-5}$–10^{-7} cm^3/cm^2 sec (INGIMARSSON and SIGURDSSON, 1987), due to sealing by secondary mineralization. Permeable anomalies are found in these formations in association with young tectonic fractures where low-temperature geothermal systems tend to develop (ARNÓRSSON, 1987b). Late Quaternary formations have higher permeability, 10^{-2}–10^{-4} cm^3/cm^2 sec (INGIMARSSON and SIGURDSSON, 1987). Post-glacial lavas have no surface run-off due to extremely high permeability, 1–10^{-2} cm^3/cm^2 sec (INGIMARSSON and SIGURDSSON, 1987). Evapotranspiration may be high from such lavas due to abundant moss trapping the precipitation. Otherwise the precipitation infiltrates. In the Late Quaternary and Post-glacial rocks permeability comprises both primary and secondary fissures, scoriaceous tops and bottoms of lavas, contraction cracks in lavas and matrix permeability in sedimentary horizons.

The water in the high-temperature geothermal fields is most often local precipitation (ÁRNASON, 1977; ARNÓRSSON, 1985) but sometimes seawater or a mixture of seawater and local precipitation. The high-temperature fields are often in areas which rise topographically over the surrounding land. In the low-temperature fields the water is in most cases precipitation that has fallen in the highlands of the central part of the country (ÁRNASON, 1977). Thus, a regional groundwater flow has been envisaged from the central highlands towards the coast (ÁRNASON, 1977; EINARSSON, 1966). Opinion is divided whether the regional groundwater flow for the low-temperature systems occurs at deep or shallow levels from the recharge areas in the highlands (EINARSSON, 1966; BÖDVARSSON, 1982; ARNÓRSSON and ÓLAFSSON, 1986). Flow from the highlands at shallow levels is likely for some systems. The shallow flowing water decends to deep levels close to the boundary of the low-temperature fields forming the downflow limb of a convection cell (BJÖRNSSON, 1980; ARNÓRSSON and ÓLAFSSON, 1986).

Little is known about the residence time of water in the groundwater and geothermal systems. In extreme cases it may exceed 8000 years (ÁRNASON, 1976). The average surface area of a Post-glacial lava flow aquifer in contact with one liter of water ranges from about 600 to about 6000 cm^2 and the effective water/rock mass ratio for cold groundwater systems in NE-Iceland is of the order of 10^3 GÍSLASON and EUGSTER, 1987b). Corresponding figures for low- (30–60°C) and high-temperature (200–350°C) geothermal systems, also in NE-Iceland, are 100 and less than 10, respectively (GÍSLASON and EUGSTER, 1987b).

THE CHEMICAL COMPOSITION OF NATURAL WATERS IN ICELAND

Geothermal waters in Iceland are generally low in dissolved solids (200–2000 ppm) compared with such waters from geothermal fields in other countries. However, in some fields near the coast chloride contribution from seawater may cause the water salinity to become higher (ARNÓRSSON *et al.*, 1989). At Reykjanes in SW-Iceland the geothermal water represents heated seawater which has modified its original composition by reactions with the basaltic rock (BJÖRNSSON *et al.*, 1972). Cold groundwaters are lower in dissolved solids (50–100 ppm) than are thermal waters. Surface waters are comparable to cold groundwaters. However, total carbonate concentrations tend to be higher in the former, but most dissolved solids lower. Representative analyses of surface-, ground- and geothermal waters are given in Table 2.

GÍSLASON and EUGSTER (1987a,b) have elucidated the process governing the pH of cold waters in Iceland, through both, experimental work and field studies. We consider that the same process governs the pH of thermal waters. Because of the importance of pH for the dissolution/precipitation reactions considered in this contribution a brief summary will be given of the pH evolution of commonly occurring natural waters in Iceland.

The pH of pure rain water is about 5.6. Surface waters attain a higher pH (about 7) through proton uptake by the soil and rock and simultaneous dissolution of cations (GÍSLASON and EUGSTER, 1987b). Cold groundwaters develop higher pH, 9–10, and low temperature geothermal waters (less than about 100°C) even higher pH, up to 10.5. Carbonic acid derived from atmospheric CO_2 and the decay of organic matter constitutes the proton donor for surface waters. Steady state conditions are attained when proton generation by dissociation of carbonic acid into bicarbonate equals the rate of rock dissolution which dictates the rate of proton uptake. The proton donor of groundwaters isolated from the atmosphere is silica which is dissolved from the rock. Here steady state conditions are attained when proton donation rate by aqueous silica ionization equals the rate of proton uptake by the rock being dissolved (GÍSLASON and EUGSTER, 1987a,b). With increasing temperatures above about 100°C pH begins to drop. This is due to increasing mobility of both carbonic acid and hydrogen sulphide which generate protons through ionization into bicarbonate and bisulphide, respectively. The gases forming these acids may originate from the rock being dissolved or a degassing magma intrusion. It is generally agreed that shallow level intrusions constitute the heat source to high-temperature geothermal

Table 2. Chemical composition (ppm) of some natural waters in Iceland

No.	T°C	pH/T°	SiO_2	B	Na	K	Ca	Mg	Fe	Al	ΣCO_2	SO_4	ΣH_2S	Cl	F
1	—	7.00/10	3.6	—	1.48	0.09	1.02	0.18	0.025	0.07	3.3	0.2	<.01	0.47	.02
2	—	—	12.0	—	9.12	0.53	4.03	1.57	—	—	26	4.81	—	5.18	—
3	2.6	9.13/4	15.4	—	9.13	0.68	3.39	2.17	0.046	0.09	24	2.9	<.01	1.60	0.15
4	19.5	9.55/21	27.6	.016	16.2	0.63	1.88	0.18	—	0.042	7.1	3.8	<.01	14.3	0.10
5	43	9.93/22	39.0	.016	28.3	0.33	2.51	.009	—	0.12	19.2	4.31	<.01	17.4	0.07
6	75	8.46/12	68.7	.128	159	3.66	31.1	.061	—	0.043	21.0	59.1	0.02	235	0.24
7	92	9.54/22	154	.078	79.5	2.14	2.53	.023	—	0.086	22.2	54.1	1.03	34.4	0.71
8	152	7.31/152	249	.639	100	6.10	1.26	.047	0.0069	0.413	97.4	69.5	4.75	40.9	1.83
9	246	6.66/246	379	1.41	131	20.4	3.83	.072	0.016	0.085	741	41.3	383	14.1	0.36
10	240	5.31/240	425	6.87	6382	989	1066	1.29	0.156	0.056	421	32.2	5.56	13506	0.13

Sample no. 1 is a snow melt from Herdubreid, NE-Iceland that has interacted for a short time with basalt in contact with the atmosphere (Sp 12, GÍSLASON and EUGSTER, 1987). Sample no. 2 is a weighed average composition of Icelandic rivers (GÍSLASON and ARNÓRSSON, 1989). Sample no. 3 is from spring by Hrauná, NE-Iceland (Sp 15, GÍSLASON and EUGSTER, 1987). Sample no. 4 is from a well at Sveinseyri, NW-Peninsula. Sample no. 5 is from a well at Krossholt NW-Peninsula. Sample no. 6 is from well 13 at Selfoss, Southern Lowlands. Sample no. 7 is from a well at Reykjarhóll, Bökkum, North Iceland. Sample 8 is from well 1 at Reykjaból, Southern Lowlands (ARNÓRSSON *et al.*, 1983a), the deep water concentration and pH is shown for sample 8, 9 and 10 as calculated by the WATCH programme (ARNÓRSSON *et al.*, 1982). Sample 9 is from well 8 at Námafjall, NE-Iceland (ARNÓRSSON *et al.*, 1983a). Sample 10 is from well 4 in the Svartsengi geothermal field which is located on the Reykjanes peninsula (ARNÓRSSON *et al.*, 1983a).

systems in Iceland, located within the belts of active volcanism but low-temperature systems, located in Quaternary and Tertiary formations are for the most part non-volcanic (ARNÓRSSON and ÓLAFSSON, 1986).

During the initial stages of rock dissolution by surface waters the aqueous concentrations of major components increase. This is reflected in the approximately constant aqueous ratio of the elements (GÍSLASON and EUGSTER, 1987a,b). However, some surface waters and groundwaters may show relative depletion in some elements, like aluminium, iron, magnesium and potassium, due to their uptake into weathering minerals. It is considered that all major components in geothermal waters, except chloride, closely approach chemical equilibrium with alteration minerals at temperatures as low as 50°C (ARNÓRSSON *et al.*, 1983a).

THE CHEMICAL THERMODYNAMIC DATA BASE AND DATA TREATMENT

The WATCH programme of ARNÓRSSON *et al.* (1982) was used to calculate the aqueous speciation for the waters selected for the present study. The data base is that given in their Table 5 except for aqueous aluminium hydroxy complexes where the data of KUYUNKO *et al.* (1983) were used.

The WATCH programme calculates the ratio of ferrous to ferric ion from analyses of total iron in solution and a redox potential calculated on the assumption that equilibrium between aqueous sulphide and sulphate is attained. When sulphide is not detectable, as is the case for cold and slightly thermal waters, analysed aqueous iron is taken to be equal to ferrous iron. This is considered to be a good approximation. However, sulphide/sulphate redox equilibrium may not be closely approached, even at high temperatures, (ARNÓRSSON and GUNNLAUGSSON, 1985) causing an uncertainty in the calculated distribution of the iron-bearing aqueous species and in the calculated state of water saturation for iron bearing minerals. At low temperatures Fe^{+2} tends to be the dominant iron species but $Fe(OH)_4^-$ dominates at temperatures above 200°C.

For minerals we selected the data base of HELGESON *et al.* (1978) and, for the clay minerals, HELGESON (1969). We consider that the data on quartz solubility recommended by FOURNIER and POTTER (1982) are better than those of (WALTHER and HELGESON, 1977) which were used by HELGESON *et al.* (1978), at least in the temperature range of interest for this study (0–250°C). To use the quartz solubility data of FOURNIER and POTTER (1982) would have required correction of practically the whole data base of HELGESON *et al.* (1978). This we have not done. The discrepancy so produced is quite small and does not affect our conclusions, being 0.06 Log K units at 25°C and 0.08 units at 250°C. A comparison of quartz solubility is given later using the data of FOURNIER and POTTER (1982) and WALTHER and HELGESON (1977). The calcite solubility curve used is that given by ARNÓRSSON *et al.* (1982). Below 100°C it is almost identical to that of PLUMMER and BUSENBERG (1982) who carried out calcite solubility experiments in the range 0–90°C.

There is considerable disagreement in the literature on the thermodynamic data base for Al-silicates. HELGESON *et al.* (1978) used data for gibbsite reported by HEMINGWAY and ROBIE (1977) together with the composition of mineral assemblages and interstitial water in Jamaican bauxite deposits and weathered Hawaiian basalts to obtain free energy data for kaolinite. Free energy values for all Al-silicates rest on the value for kaolinite so obtained which according to HEMINGWAY *et al.* (1982) may be too high, by 6.5 kJ per mole of aluminium. There is considerable and variable difference between the thermodynamic parameters for the Al-silicates given by HELGESON *et al.* (1978) and HEMINGWAY *et al.* (1982). The reason is not only disagreement on kaolinite. The data recommended by the different authors are based on different experiments. It is important to note that the conclusions of the present study on the state of mineral saturation are equally valid using either of the two data bases.

In the present study two types of dissolution reactions were considered. One involves the pure end-member composition of solid solutions of the igneous rock minerals (olivine, pyroxenes, plagioclase and iron-titanium oxides). The other involves congruent dissolution of the igneous mineral solid solution. The solid solution compositions selected for detailed discussion are those presented in Table 1 (see the discussion in the second section of this contribution). Only end-member compositions were considered for the alteration minerals. The reactions used to describe dissolution/precipitation for minerals are summarized in Table 3.

Equilibrium constants for the dissolution of pure end-member igneous and alteration minerals were calculated at one bar pressure up to 100°C and along the liquid-vapour curve at higher temperatures. The apparent standard partial molal Gibbs free energy of formation of the minerals at T and P was calculated according to the thermodynamic data and formulation given by HELGESON *et al.* (1978). The apparent standard partial molal Gibbs free energy of formation of the aqueous species was calculated using the revised equation of state for the standard molal properties of ions and electrolytes (TANGER and HELGESON, 1986) using equation of state parameters from HELGESON and KIRKHAM (1974), TANGER and HELGESON (1986) and SHOCK and HELGESON (1988, 1989) with the exception of the standard partial molal Gibbs free energy of formation of Al^{+3} which we take to be −489,578 J/mole. This value is consistent with the value reported for $Al(OH)_4^-$ by SHOCK and HELGESON (1988) and is based on KITTRICK (1966) and the thermodynamic values for aqueous aluminum hydroxy complexes given by KUYUNKO *et al.* (1983). SHOCK and HELGESON (1988) used data on the equilibrium between Al^{+3} and $Al(OH)_4^-$ reported by COUTURIER *et al.* (1984) to obtain a value for the apparent standard partial molal Gibbs free energy of formation for Al^{+3}. Our value for Al^{+3} is almost the same as that reported by ROBIE *et al.* (1979), −489,400 J/mole.

The igneous minerals in the basalts dissolved by water represent solid solutions requiring the application of solid solution models for calculation of the activity of the end-members in these crystalline solutions. The temperature regime under consideration in the present study (0–250°C) is far below the temperature range (600–1400°C) where the experiments have been carried out that constrain empirical and theoretical solid solution models. For this reason simple ideal solid solution models have been adapted. For such models we have:

$$a_i = (X_i)^n \quad (1)$$

where a_i represents the activity of end-member i in a solid solution, X_i is its mole fraction and the exponent n refers to the number of exchange sites. The activities of forsterite and fayalite in olivine and of ferrosilite and enstatite in orthopyroxene have been obtained from Equation (1).

Clinopyroxene is taken to represent an ideal solid solution with multi-side mixing on the M_1, M_2 and the tetrahedral sites assuming that Fe and Mg are distributed between the M_1 and M_2 sites in equal proportions. It is further assumed that there is equal number of both positions in the formula unit (WOOD and FRASER, 1977). Thus, the activity of diopside ($CaMgSi_2O_6$) in a clinopyroxene solid solution is taken to be equal to the mole fraction of $MgSiO_3$ in this solution (X_{Mg}), which is assigned to the M_1 sites, times the mole fraction of $CaSiO_3$ (X_{Ca}), assigned to the M_2 sites, times the square of the mole fraction of Si (X_{Si}), assigned to the tetrahedral sites.

For the feldspars, the local charge balance model has been employed (KERRICK and DARKEN, 1975; NORDSTROM and MUNOZ, 1985). Thus, the activities of the end-member components in the solution equal the mole fraction of that component. For example, the activity of the albite component in feldspar solid solution equals the mole fraction of $(NaSi)AlSi_2O_8$.

Mixing in the magnetite-ulvöspinel solid solution is assumed to be confined to the octahedral sites. Thus, the activity of magnetite in the solid solution is equal to the square of the mole fraction of Fe(III) occupying the octahedral sites. The hematite-ilmenite solid solution is treated in the same way; the activity of hematite in this solution equals the square of the mole fraction of Fe(III). The calculated mean activities of the various end member components in groundmass minerals in some Icelandic basalts are shown in Table 1.

Equilibrium constants for the stoichiometric (congruent) dissolution (THORSTENSON and PLUMMER, 1977) of the actual igneous minerals were obtained by assuming that they represented ideal solid solutions and choosing the standard state to be a solid solution of a fixed composition at the temperature and pressure of interest. This implies that the entalhpy of mixing equals zero and since

$$\Delta S_{\text{ideal mix}} = -nR \sum_i X_i \ln X_i \quad (2)$$

we have that the free energy of mixing is equal to:

$$\Delta G_{\text{ideal mix}} = nRT \sum_i X_i \ln X_i \quad (3)$$

and for an ideal binary solution of a given composition at T and P the apparent standard state Gibbs free energy of formation, $\Delta G^0_{f,ss}(T, P)$ is

$$\Delta G^0_{f,ss}(T, P) = X_i \Delta G^0_{f,i}(T, P) + X_j \Delta G^0_{f,j}(T, P) + nRT(X_i \ln X_i + X_j \ln X_j) \quad (4)$$

$\Delta G^0_{f,i}(T, P)$ and $\Delta G^0_{f,j}(T, P)$ refer to the apparent standard state Gibbs free energy of formation of the pure end-members i and j of the solid solution at the temperature and pressure of interest; X_i and X_j are the corresponding mole fractions and $X_j = 1 - X_i$; and n is the number of exchange sites per mineral formula. R is the gas constant and T is absolute temperature. The apparent standard partial molal Gibbs free energy of formation for the pure end-members in the solid solution is obtained by the method described above and once values for X_i and X_j have been selected the stochiometry for the dissolution reactions can be written (Table 3).

METHOD OF INTERPRETATION

The degree of unstability of a mineral dissolving in aqueous solution is assessed by evaluating the Gibbs free energy for the dissolution reaction (ΔG_r):

$$\Delta G_r = \Delta G^0_r + RT2.303 \text{ Log } Q \quad (5)$$

where ΔG^0_r is the standard state Gibbs free energy

Table 3. Dissolution reactions for minerals

Minerals	Reactions
Forsterite	$Mg_2SiO_4 + 4H^+ = 2\ Mg^{++} + H_4SiO_4^0$
Fayalite	$Fe_2SiO_4 + 4H^+ = 2\ Fe^{++} + H_4SiO_4^0$
Olivine $(Fo_{0.43}Fa_{0.57})$	$(Mg_{.43}Fe_{.57})SiO_4 + 4\ H^+$ $= 0.86\ Mg^{++} + 1.14\ Fe^{++} + H_4SiO_4^0$
Enstatite	$MgSiO_3 + 2H^+ + H_2O = Mg^{++} + H_4SiO_4^0$
Ferrosilite	$FeSiO_3 + 2H^+ + H_2O = Fe^{++} + H_4SiO_4^0$
Orthopyroxene $(En_{0.38}\ Fs_{0.62})$	$Mg_{.38}Fe_{.62}SiO_3 + 2\ H^+ + H_2O$ $= 0.38\ Mg^{++} + 0.62\ Fe^{++} + H_4SiO_4^0$
Diopside	$MgCaSi_2O_6 + 4\ H^+ + 2\ H_2O$ $= Mg^{++} + Ca^{++} + 2\ H_4SiO_4^0$
Hedenbergite	$FeCaSi_2O_6 + 4\ H^+ + 2\ H_2O$ $= Fe^{++} + Ca^{++} + 2\ H_4SiO_4^0$
Anorthite	$CaAl_2Si_2O_8 + 8\ H_2O$ $= Ca^{++} + 2\ Al(OH)_4^- + 2\ H_4SiO_4^0$
Albite	$NaAlSi_3O_8 + 8\ H_2O$ $= Na^+ + Al(OH)_4^- + 3\ H_4SiO_4^0$
High-plagioclase $(An_{0.29}\ Ab_{0.71})$	$(CaAl)_{.29}(NaSi)_{.71}AlSi_2O_8 + 8H_2O$ $= 0.29Ca^{++} + 0.71Na^+ + 1.29Al(OH)_4^-$ $+ 2.71H_4SiO_4^0$
Magnetite	$FeFe_2O_4 + 4\ H_2O = Fe^{++} + 2\ Fe(OH)_4^-$
Hematite	$Fe_2O_3 + 5\ H_2O = 2\ H^+ + 2\ Fe(OH)_4^-$
Calcite	$CaCO_3 = Ca^{++} + CO_3^{--}$
Chalcedony, quartz	$SiO_2 + 2\ H_2O = H_4SiO_4^0$
Gibbsite	$Al(OH)_3 + H_2O = Al(OH)_4^- + H^+$
Kaolinite	$Al_2Si_2O_5(OH)_4 + 7\ H_2O$ $= 2\ Al(OH)_4^- + 2\ H_4SiO_4^0 + 2\ H^+$
Laumontite	$Ca(Al_2Si_4O_{12})4H_2O + 8\ H_2O$ $= Ca^{++} + 2\ Al(OH)_4^- + 4\ H_4SiO_4^0$
Microcline	$KAlSi_3O_8 + 8\ H_2O$ $= K^+ + Al(OH)_4^- + 3\ H_4SiO_4^0$
Mg-montmorill.	$Mg_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 12\ H_2O$ $= 0.167\ Mg^{++} + 2\ H^+$ $+ 2.33\ Al(OH)_4^- + 3.67\ H_4SiO_4^0$
Ca-montmorill.	$Ca_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 12\ H_2O$ $= 0.167\ Ca^{++} + 2\ H^+ + 2.33\ Al(OH)_4^-$ $+ 3.67\ H_4SiO_4^0$
Na-montmorill.	$Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 12\ H_2O$ $= 0.33\ Na^+ + 2\ H^+ + 2.33\ Al(OH)_4^-$ $+ 3.67\ H_4SiO_4^0$
K-montmorill.	$K_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 12\ H_2O$ $= 0.33\ K^+ + 2\ H^+ + 2.33\ Al(OH)_4^-$ $+ 3.67\ H_4SiO_4^0$
Pyrite	$FeS_2 + 4.5\ H_2O = Fe(OH)_4^- + 1.25\ H^+$ $+ 0.125\ SO_4^{--} + 1.87\ H_2S$
Pyrrhotite	$FeS + 0.125\ SO_4^{--} + 3.5\ H_2O$ $= Fe(OH)_4^- + 0.75\ H^+ + 1.125\ H_2S$

The Ca and Mn present in the orthopyroxene is disregarded for the calculations of its stoichiometric dissolution (Ca is equal to 0.036 and 0.018 mole per mineral formula). The mole fraction for the enstatite and ferrosilite in the solid solution as given in Table 2 is, therefore, raised to make their sum equal to 1. The mole fractions of olivine and plagioclase solid solutions are as given in Table 1.

for the reaction, R is the gas constant, T is temperature in Kelvin and Q the reaction quotient (activity product). Two kinds of standard states for minerals have been chosen as discussed in the previous section. One is the pure end member composition in the solid solution at T and P. The other represents the actual mineral composition at T and P. An assumption inherent to the choice of this second type of standard state is that the respective solid solution mineral dissolves congruently.

Since $\Delta G_r^0 = -RT2.303\ \text{Log}\ K$, where K is the equilibrium constant, it follows that

$$\Delta G_r = RT2.303(\text{Log}\ Q - \text{Log}\ K) \qquad (6)$$

At equilibrium, the Gibbs free energy of reaction is equal to zero so $K = Q$. The difference between K and Q is a measure of the degree of undersaturation/supersaturation of a mineral in a particular aqueous solution. It is also a measure of the Gibbs free energy driving the respective reaction. If a given mineral is unstable or dissolving, ΔG_r is less than zero but positive if the mineral is stable or precipitating for the reactions as written in Table 3.

Numerous experimental studies have been carried out in the past on dissolution rates for rock forming minerals and glasses far from equilibrium (*e.g.*, LAGACHE, 1976; BUSENBERG and CLEMENCY, 1976; GRANDSTAFF, 1980; SCHOTT *et al.*, 1981; WHITE 1983; CHOU and WOLLAST, 1984; GÍSLASON and EUGSTER, 1987a). At 25°C the reaction rate becomes in most cases steady and linear after a few tens of days, even less:

$$dQ^*/dt = k^* \qquad (7)$$

where Q^* is the flux of elements entering the solution per unit area of the solid that is dissolving, t is time and k^* is the linear rate constant (mole $cm^{-2}\ sec^{-1}$).

In general dissolution rates can be described by the following equation (WALTHER and WOOD, 1986; LASAGA, 1981):

$$dQ^*/dt = k^*(1 - e^{\Delta G_r/RT}) \qquad (8)$$

WALTHER and WOOD (1986) pointed out that the dissolution rate can simply be described by the linear rate constant, k^* (equation (7)), if $\Delta G_r/RT$ is smaller (greater negative number) than -6. The value of -6 corresponds to a Log (Q/K) value of -2.6 and a ΔG_r value of 15 kJ at 25°C and 26 kJ at 250°C. If Log (Q/K) lies in the range from -2.6 to -0.17 dissolution rates are best described by equation (8), but if the difference is greater than about -0.17 (smaller negative number) the dissolution rate is satisfactorily formulated as follows:

$$dQ^*/dt = -k^*e^{\Delta G_r/RT} \qquad (9)$$

This is because the first factor within the parenthesis in equation (8) contributes little to the reaction rate when Log Q/K (and ΔG_r) take such low numbers.

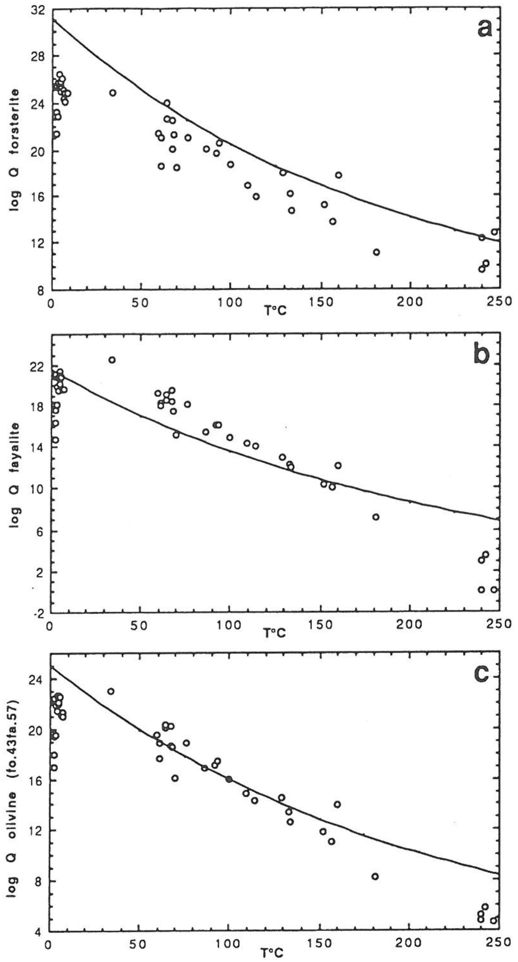

FIG. 2. The state of olivine saturation in natural waters in Iceland. Parts a and b show the state of saturation for the forsterite and fayalite components in olivine of the composition $fo_{.43}fa_{.57}$. Part c shows the state of saturation for stoichiometric dissolution of olivine of the composition indicated.

By assessing the value of ΔG_r or the Log (Q/K) for specific igneous and alteration minerals, and natural water compositions, the kinetic relationship best describing the rates of igneous mineral dissolution and secondary mineral deposition under natural conditions may be determined.

RESULTS AND DISCUSSION

Igneous minerals

The WATCH programme (ARNÓRSSON *et al.*, 1982) has been used to evaluate the state of saturation of selected cold spring and geothermal well waters relative to igneous minerals of basalt (icelandite in the case of orthopyroxene). The evaluation was made for end member compositions as well as solid solutions of fixed composition (Table 1). The results are shown in Figs. 2 to 6. The solid solution compositions selected are based on groundmass plagioclase data from the Reykjanes Peninsula (FISK, 1978) and the average for groundmass minerals presented by CARMICHAEL (1964, 1967) for basalts from the Thingmúli central volcano in eastern Iceland (Table 3). The activities of the end member components in the solid solutions are incorporated in the reaction quotient and were evaluated as described previously. Equations for the reaction quotient corresponding to the dissolution reactions in Table 3 are shown in Table 4. The curves in Figs. 2 to 6 depict the equilibrium con-

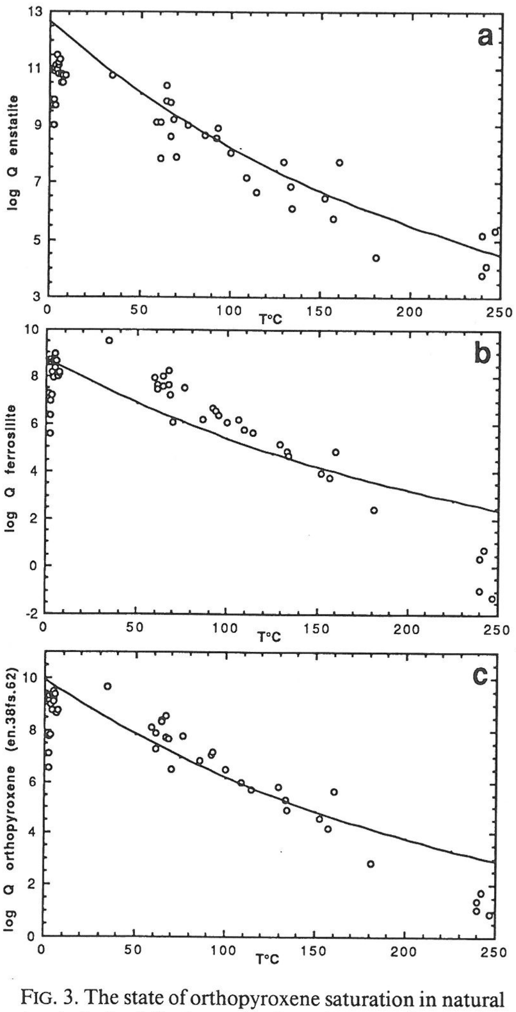

FIG. 3. The state of orthopyroxene saturation in natural waters in Iceland. Parts a and b show the state of saturation for the enstatite and ferrosilite components in pyroxene of the composition $en_{.38}fs_{.62}$. Part c shows the state of saturation for stoichiometric dissolution of orthopyroxene of the composition indicated.

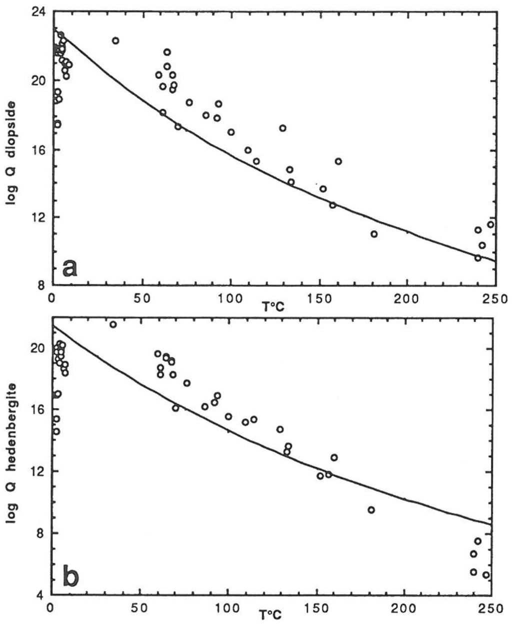

FIG. 4. The saturation state of diopside and hedenbergite components in calcium-rich clinopyroxene in natural waters in Iceland. The activities selected for diopside and hedenbergite were 0.377 and 0.658, respectively (Table 4).

stant. These curves probably represent minimum solubility of the respective minerals and end members since the minerals may be considerably disordered crystallographically and of such small crystals that their resulting surface free energy could increase their solubility.

Olivine

The saturation state (reaction quotient) for the selected natural waters with respect to the forsterite component in olivine with the composition $fo_{43}fa_{57}$ (see Table 4) is plotted against water temperature in Fig. 2a. All but four of the waters are undersaturated with respect to the forsterite component. Increasing forsterite content in the olivine will decrease the Log Q value, thus increasing the degree of undersaturation. However, the position of the data points in Fig. 2a are not very sensitive to the composition of the olivine. Changing from fo_{43} to fo_{81} would cause a decrease in Log Q corresponding to the diameter of the data points. Similarily, decreasing the forsterite content from fo_{43} to fo_{23} would shift Log Q up equivalent to the diameter of the data points.

The saturation state with respect to the fayalite component in the olivine is depicted in Fig. 2b. Most of the waters are somewhat supersaturated. The only undersaturated waters are from cold springs with "relatively low" pH (8–9) and thermal waters with temperatures above about 180°C.

It is not known whether olivine dissolves congruently (stoichiometrically) in natural waters or if ion exchange reactions are involved although the former seems more probable since olivine solid solution (fo_{82}) dissolves congruently in experiments carried out in the temperature range 1 to 50°C (GRANDSTAFF, 1980, 1986) and the same is true for other solid solutions (*i.e.*, BUSENBERG and PLUMMER, 1989). If ion exchange was associated with olivine dissolution over the temperature range considered here (0–250°C), the forsterite component alone would dissolve in cold waters with pH above about 9 and in thermal waters up to about 150°C making the remaining olivine more fayalite-rich. In cold waters with pH of less than about 9,

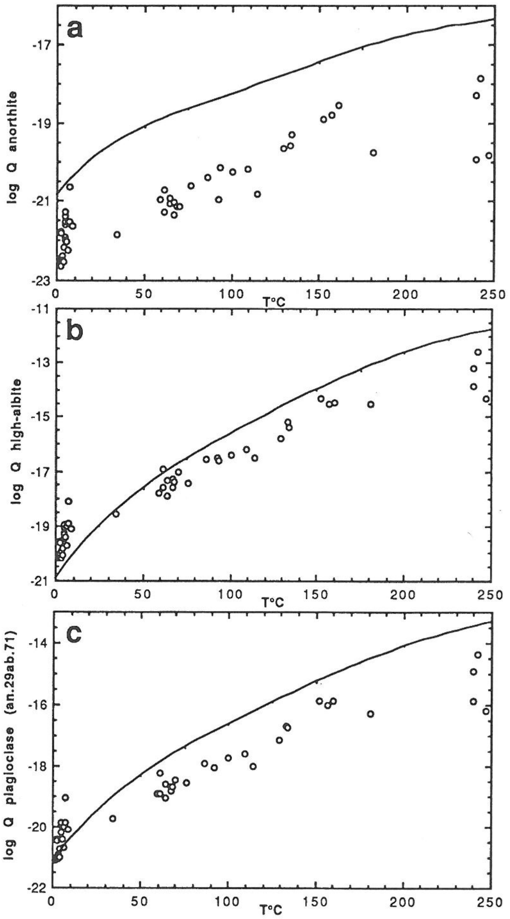

FIG. 5. The state of saturation of plagioclase in natural waters in Iceland. Parts a and b show the saturation state for the anortite and high-albite components in plagioclase of the composition $an_{.29}ab_{.71}$. Part c shows the state of saturation for stoichiometric plagioclase dissolution with the composition indicated.

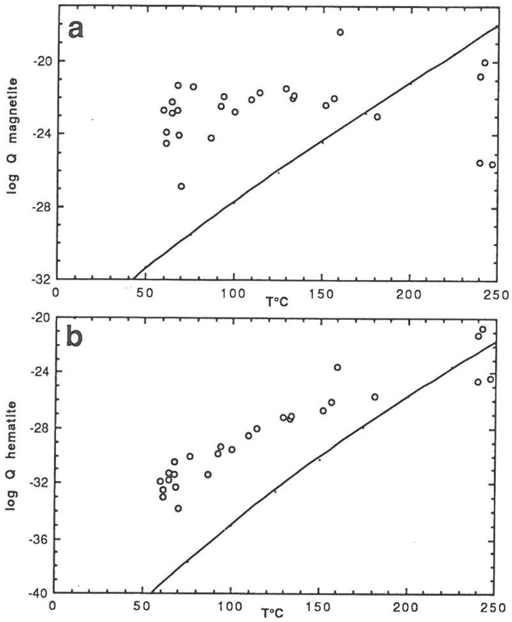

FIG. 6. The saturation state of magnetite and hematite components in ulvö-spinel and ilmenite in natural waters in Iceland.

both components would dissolve, but forsterite preferentially. The data points at 240–250°C (Fig. 2a and b) indicate that the forsterite component is somewhat unstable but the fayalite component is highly unstable. Accordingly, dissolution involving ion exchange would lead to increasing magnesium content of the olivine.

If olivine dissolves stoichiometrically, as seems likely, it can be deduced from Fig. 2c that this mineral is highly unstable in cold groundwaters and in waters above about 150°C. In the range 30–150°C most waters are relatively close to equilibrium with the olivine solid solution. What is important to note here is that the stability of olivine is very sensitive to its composition assuming that it dissolves stoichiometrically. Increasing forsterite content decreases the stability of olivine. Thus, for example, all but six of the waters plotted in Fig. 2c would be undersaturated with olivine containing fo_{70}.

The results presented in Fig. 2a to c are based on the average composition ($fo_{43}fa_{57}$) of groundmass olivine in basalts from Thingmúli (Table 1). As can be seen from Table 1, the composition of the groundmass olivine of the Thingmúli basalts varies between fo_{23} and fo_{55}. Olivine phenocrysts are much more forsterite rich, up to fo_{90} (GRÖNVOLD and MÄKIPÄÄ, 1978). Thus, it can be concluded that, if olivine dissolves stoichiometrically, phenocrysts of this mineral are unstable in contact with natural Icelandic waters at all temperatures. Groundmass olivine may, on the other hand, be stable in the temperature range of about 30–150°C but unstable at lower and higher temperatures.

Cold waters and waters above about 180°C are

Table 4. Expressions for the logarithm of the reaction quotient (Log Q) for primary and some secondary minerals in basalts

Log Q	Expression
Log $Q_{\text{forsterite}}$	$= 2 \text{ Log } a_{Mg^{++}} + \text{Log } a_{H_4SiO_4^0} - 4 \text{ Log } a_{H^+}$ $+ 0.721$
Log Q_{fayalite}	$= 2 \text{ log } a_{Fe^{++}} + \text{Log } a_{H_4SiO_4^0} - 4 \text{ Log } a_{H^+}$ $+ 0.481$
Log Q_{olivine}	$= 0.86 \text{ Log } a_{Mg^{++}} + 1.14 \text{ Log } a_{Fe^{++}}$ $+ \text{Log } a_{H_4SiO_4^0} - 4 \text{ Log } a_{H^+}$
Log $Q_{\text{enstatite}}$	$= \text{Log } a_{Mg^{++}} + \text{Log } a_{H_4SiO_4^0} - 2 \text{ Log } a_{H^+}$ $+ 0.444$
Log $Q_{\text{ferrosilite}}$	$= \text{Log } a_{Fe^{++}} + \text{Log } a_{H_4SiO_4^0} - 2 \text{ Log } a_{H^+}$ $+ 0.237$
Log $Q_{\text{orthopyroxene}}$	$= 0.38 \text{ Log } a_{Mg^{++}} + 0.62 \text{ Log } a_{Fe^{++}}$ $+ \text{Log } a_{H_4SiO_4^0} - 2 \text{ Log } a_{H^+}$
Log Q_{diopside}*	$= \text{Log } a_{Mg^{++}} + \text{Log } a_{Ca^{++}} + 2 \text{ Log } a_{H_4SiO_4^0}$ $- 4 \text{ Log } a_{H^+} + 0.377_{\text{Ca-rich}}$
Log $Q_{\text{hedenbergite}}$*	$= \text{Log } a_{Fe^{++}} + \text{Log } a_{Ca^{++}} + 2 \text{ Log } a_{H_4SiO_4^0}$ $- 4 \text{ Log } a_{H^+} + 0.658_{\text{Ca-rich}}$
Log $Q_{\text{anorthite}}$	$= \text{Log } a_{Ca^{++}} + 2 \text{ Log } a_{Al(OH)_4^-} + 2 \text{ Log}$ $a_{H_4SiO_4^0} + 0.538$
Log $Q_{\text{high-albite}}$	$= \text{Log } a_{Na^+} + \text{Log } a_{Al(OH)_4^-} + 3 \text{ Log } a_{H_4SiO_4^0}$ $+ 0.149$
Log $Q_{\text{plagioclase}}$	$= 0.29 \text{ Log } a_{Ca^{++}} + 0.71 \text{ Log } a_{Na^+}$ $+ 1.29 \text{ Log } a_{Al(OH)_4^-} + 2.7 \text{ Log } a_{H_4SiO_4^0}$
Log $Q_{\text{magnetite}}$	$= \text{Log } a_{Fe^{++}} + 2 \text{ Log } a_{Fe(OH)_4^-} + 0.456$
Log Q_{hematite}	$= 2 \text{ Log } a_{Fe(OH)_4^-} + 2 \text{ Log } a_{H^+} + 2.268$
Log Q_{calcite}	$= \text{Log } a_{Ca^{++}} + \text{Log } a_{CO_3^{--}}$
Log $Q_{\text{quartz, chalcedony}}$	$= \text{Log } a_{H_4SiO_4^0}$
Log Q_{gibbsite}	$= \text{Log } a_{Al(OH)_4^-} + \text{Log } a_{H^+}$
Log $Q_{\text{kaolinite}}$	$= 2 \text{ Log } a_{Al(OH)_4^-} + 2 \text{ Log } a_{H_4SiO_4^0}$ $+ 2 \text{ Log } a_{H^+}$
Log $Q_{\text{laumontite}}$	$= \text{Log } a_{Ca^{++}} + 2 \text{ Log } a_{Al(OH)_4^-}$ $+ 4 \text{ Log } a_{H_4SiO_4^0}$
Log $Q_{\text{microcline}}$	$= \text{Log } a_{K^+} + \text{Log } a_{Al(OH)_4^-} + 3 \text{ Log } a_{H_4SiO_4^0}$
Log $Q_{\text{Mg-montmorill.}}$	$= 0.167 \text{ Log } a_{Mg^{++}} + 2 \text{ Log } a_{H^+}$ $+ 2.33 \text{ Log } a_{Al(OH)_4^-} + 3.67 \text{ Log } a_{H_4SiO_4^0}$
Log $Q_{\text{Ca-montmorill.}}$	$= 0.167 \text{ Log } a_{Ca^{++}} + 2 \text{ Log } a_{H^+}$ $+ 2.33 \text{ Log } a_{Al(OH)_4^-} + 3.67 \text{ Log } a_{H_4SiO_4^0}$
Log $Q_{\text{Na-montmorill.}}$	$= 0.33 \text{ Log } a_{Na^+} + 2 \text{ Log } a_{H^+}$ $+ 2.33 \text{ Log } a_{Al(OH)_4^-} + 3.67 \text{ Log } a_{H_4SiO_4^0}$
Log $Q_{\text{K-montmorill.}}$	$= 0.33 \text{ Log } a_{K^+} + 2 \text{ Log } a_{H^+}$ $+ 2.33 \text{ Log } a_{Al(OH)_4^-} + 3.67 \text{ Log } a_{H_4SiO_4^0}$
Log Q_{pyrite}	$= \text{Log } a_{Fe(OH)_4^-}$ $+ 1.25 \text{ Log } a_{H^+} + 0.125 \text{ Log } a_{SO_4^{--}}$ $+ 1.87 \text{ Log } a_{H_2S}$
Log $Q_{\text{pyrrhotite}}$	$= \text{Log } a_{Fe(OH)_4^-} + 0.75 \text{ Log } a_{H^+}$ $+ 1.125 \text{ Log } a_{H2_s} - 0.125 \text{ Log } a_{SO_4^{--}}$

* This is the reaction quotient for aqueous ions and the pure end member minerals (diopside and hedenbergite) in Ca-rich groundmass pyroxene (augite) but the activity of the end member minerals, diopside and hedenbergite, in the Ca-poor groundmass pyroxene is 0.959 and 1.143, respectively.

so strongly undersaturated with olivine that its dissolution is expected to be described by the linear rate law (Equation 7). The same situation would generally hold for olivine phenocrysts at all temperatures. Groundmass olivine may be stable in some instances or slightly undersaturated so that Equation (9) appropriately describes its dissolution rate.

Orthopyroxene

Figure 3a to c shows the saturation state of the selected natural waters relative to orthopyroxene of the composition $en_{38}fs_{62}$, which is the average composition of orthopyroxene phenocrysts in icelandite from Thingmúli (Carmichael, 1967) (Table 1). Orthopyroxenes are not found in the basalts of Thingmúli. Fig. 3a shows that the enstatite component is generally unstable for all cold water samples and the majority of thermal water samples. By contrast, most waters from low-temperature fields (30–150°C) are close to equilibrium or somewhat supersaturated with respect to the ferrosilite component. Cold waters with pH above about 9 are close to ferrosilite saturation. Cold waters with lower pH are undersaturated as are waters from high-temperature fields (>180°C).

If orthopyroxene dissolution is associated with ion exchange, the enstatite component would go into solution preferentially in the case of cold waters and thermal waters below about 150°C. As a result the remaining orthopyroxene would become enriched in the ferrosilite component. Waters of higher temperature would, on the other hand, tend to loose the ferrosilite component preferentially to enstatite causing the residual pyroxene to be magnesium enriched.

If orthopyroxene of the composition $en_{38}fs_{62}$ dissolves stoichiometrically, it is undersaturated in cold waters and in waters above about 180°C (Fig. 3c). Waters of intermediate temperatures are close to saturation, some even significantly supersaturated (Fig. 3c). As for olivine, the stability of orthopyroxene is quite sensitive to its composition. Increasing magnesium content leads to decreasing stability, particularly at low temperatures.

It is only in cold groundwaters with relatively low pH (<8) that orthopyroxene undersaturation is so large that its dissolution would be expected to follow the linear rate law (equation 7). The dissolution rate of orthopyroxene in other waters, if it dissolves, would be in accordance with equation (9).

Clinopyroxene

The saturation state of the cold and thermal waters relative to the diopside and hedenbergite components in Ca-rich pyroxene of the composition given by the mole fractions in Table 1, are shown in Fig. 4a and b. This composition is the average for Ca-rich groundmass clinopyroxenes in Thingmúli basalts (Carmichael, 1967) and the calculated average activities of diopside and hedenbergite are 0.42 and 0.22, respectively (Table 1). Cold waters show varying degree of undersaturation depending on their pH. The highest pH waters are just saturated with the diopside component and slightly undersaturated with the hedenbergite component (Fig. 4a and b). Waters in the range 30–150°C are generally supersaturated with both components, the degree of supersaturation falling with rising temperature. Waters at 240–250°C are saturated and supersaturated with diopside but undersaturated with respect to hedenbergite.

With decreasing Ca content of clinopyroxene the waters would become progressively more supersaturated or less undersaturated with respect to both the diopside and hedenbergite components. Thus, taking the composition of Ca-poor clinopyroxene in the groundmass of Thingmúli basalts (Table 1), the reaction quotient for the diopside end member would increase by 0.58 Log units shifting all data points in Fig. 4a up by this value. Similarily, the reaction quotient for hedenbergite would increase by 0.50 Log units. Our results indicate that all thermal waters are supersaturated with respect to Ca-poor clinopyroxenes, except possibly for the waters at and above 180°C. Cold waters with pH somewhat in excess of about 9 are close to saturation but lower pH cold waters are undersaturated.

In this brief contribution an attempt has not been made to assess the stability of clinopyroxene for its stoichiometric dissolution. The pyroxene grains tend to show exsolution into calcium rich and calcium poor components and it is not certain how reliable it would be to treat such exsolved grains as ideal solid solutions.

Plagioclase

Figure 5a to c shows the saturation state of the cold and thermal waters relative to anorthite, high-albite, and plagioclase of the composition $an_{29}ab_{71}$. This composition is that of groundmass plagioclase in Reykjanes Peninsula basalts (Table 1). All the waters are undersaturated with respect to the anorthite component in plagioclase of this composition. Thermal waters above about 60°C are also undersaturated with respect to high-albite in this plagioclase, although to a lesser extent, but cold waters are supersaturated.

Plagioclase dissolution in cold ground waters involving ionic exchange would lead to increasing albite content of the residual plagioclase. The data plotted in Fig. 5c indicate that the groundmass plagioclase is unstable in all the thermal waters, if it dissolves stoichiometrically. It is, on the other hand, stable in all of the cold waters. Plagioclase phenocrysts are much more anorthite rich than the groundmass plagioclase for which data are presented in Fig. 5c. Increasing anorthite content causes increasing instability for plagioclase dissolving stoichiometrically. Plagioclase containing 70% anorthite would be unstable in contact with many of the cold waters plotted in Fig. 5c.

The degree of groundmass plagioclase undersaturation in thermal waters at 30–180°C generally corresponds to about one Log Q unit. This indicates that the dissolution rate will be in accordance with Equation (8) above. Groundmass plagioclase in high-temperature waters and anorthite-rich plagioclase (phenocryst) may dissolve according to the linear rate law (Equation 7).

Iron oxides

Data on titanium are not available for the cold and thermal waters. Some data are available on the composition of iron-titanium oxides in Icelandic basalts (Table 1). Due to lack of data on titanium in the waters, it is only possible to study the state of saturation of the waters with respect to pure iron components in the iron-titanium oxides. Another difficulty in assessing the saturation state is that it is not possible to evaluate the ratio of ferrous to ferric iron in the waters from total iron analysis unless sulphide and sulphate occur in detectable concentrations in the water. Sulphide is not detectable in any of the cold waters and when this is the case the WATCH aqueous speciation programme assumes that all the analysed iron is on the ferrous form. This is probably a good approximation, but it excludes the possibility of studying water-mineral reactions involving ferric iron in non-sulphide bearing waters.

The results for the state of saturation with respect to the iron components in ilmenite-hematite and magnetite-ulvöspinel are shown in Fig. 6a and b. Mineral compositions are those presented in Table 1. Thermal waters below about 180°C are supersaturated with respect to the magnetite component in the magnetite-ulvöspinel solid solution. At higher temperatures undersaturation is indicated. Supersaturation is particularly strong at low temperatures. Results for hematite are similar except that some waters near 240–250°C seem to be near equilibrium with the hematite component in the ilmenite.

It is of interest to point out here that quite strong negative magnetic anomalies have been observed in some of the high-temperature geothermal fields in Iceland indicating that the magnetite of the rock is destroyed, or partially destroyed, as a result of the geothermal processes (PÁLMASON, 1975).

The results depicted in Fig. 6 should be considered with some reservation. The calculation of the ferrous to ferric ratio in the thermal waters by assuming redox equilibrium between sulphide and sulphate may not be entirely valid, particularly at low temperatures, because this redox equilibrium may not be closely approached in the thermal waters. If the waters were actually less reducing than indicated by the sulphide to sulphate ratio, supersaturation with respect to the hematite component in ilmenite would be even greater than implied by the results in Fig. 6b. The same holds for the magnetite component in the magnetite-ulvöspinel solid solution.

Glass

Thermodynamic data are not available to assess the solubility of basaltic glass in aqueous solution. It is, however, evident that such glass will have higher solubility than any of the basaltic minerals as the glass has retained relatively more energy from its parent magmatic environment than the minerals. This is indeed supported by experimental data (GÍSLASON and EUGSTER, 1987a) which show that basaltic glass dissolves considerably more rapidly in water than any of the basaltic minerals. The relatively high solubility of basaltic glass could cause stabilization of the igneous minerals. For example, release of calcium, magnesium, iron and silica from the glass could reduce the degree of undersaturation with respect to olivine and may even cause the water to become supersaturated with respect to pyroxene. If glass was not present for dissolution, either due to its absence or previous dissolution, the rock dissolution pattern would probably be different. Under these circumstances the water would remain at greater olivine undersaturation and pyroxene would be less supersaturated or more undersaturated. In other words, the dissolution of the constituents of the basaltic rock could follow a specific sequence depending on the relative amount and composition of the igneous minerals and glass present, glass disappearing first, then, in succession, olivine and plagioclase, and finally pyroxene. As the chemical composition of cold water is largely affected by the dissolution process, this would lead to some changes in its chemistry depending on how far the alteration of the rock had proceeded. The composition of the thermal water could also be affected by this evolutionary process, but probably to a lesser extent because thermal water compositions are controlled by close approach to chemical equilibrium with alteration minerals (see discussion below). However, changing dissolution processes could affect the composition and even the type of alteration minerals forming, and in this way affect the chemistry of the thermal water.

Hydrogen ion metasomatism

Weathering and hydrothermal alteration of basalt involves uptake of protons and simultaneous release of other cations as the primary constituents of the rock dissolve (Table 3) and secondary minerals precipitate. The extent of H^+ metasomatism is much affected by the supply of protons to the system. In surface waters, the source of protons is carbonic acid derived from atmospheric CO_2 and the decay of organic matter. In groundwaters and thermal waters of relatively low temperature (<150°C) ionization of silica being dissolved from the rock ($H_4SiO_4^0 \rightarrow H_3SiO_4^- + H^+$) is the main source of protons to drive hydrogen ion metasomatism. The mobility of CO_2 and H_2S in thermal waters of high temperature is much higher than that at low temperature and it increases with increasing temperatures (ARNÓRSSON and GUNNLAUGSSON, 1985). These gases form weak acids which constitute the main proton donors in high-temperature waters. Their source could be the rock being dissolved or a degassing magma intrusion.

Natural waters in Iceland, especially those of ambient to low temperatures, tend to have relatively high pH compared to such waters in many other parts of the world. There are basically two reasons for this. One is the high reactivity of basaltic minerals and, especially, basaltic glass. The other is limited supply of organic CO_2. On high ground in Iceland vegetation is sparse and, as a result, organic soil formation is negligible. Thus, surface waters seeping into the ground pick up little organic CO_2 and relatively limited proton uptake through rock dissolution is required to raise the water pH to 9 or more after it has been isolated from the atmosphere.

In some lowland areas in Iceland where the bedrock is covered with a peat soil several meters thick, surface waters tend to have much higher CO_2 contents than surface waters in unvegetated areas. Where mixing of such water and geothermal water has taken place in the upflow of low-temperature fields, the composition of the mixed water indicates extensive reaction with the enclosing rock linked with the conversion of carbonic acid into bicarbonate and the simultaneous increase in pH and major cation concentrations, especially magnesium and potassium (MAGNÚSDÓTTIR, 1989). It is evident that surface waters rich in carbonic acid have a much higher potential to dissolve the minerals and glass of basalt than do waters, poor in carbonic acid.

The effect of increasing proton availability is to enhance the dissolution process, but to a variable extent for individual minerals. To express this in a different way, the lowering of water pH leads to a higher degree of undersaturation with respect to the various igneous minerals. pH lowering has a particularly profound effect on the degree of undersaturation for olivine, but it also decreases the stability of pyroxene as may be deduced from the respective reactions in Table 3 and the Log Q expressions in Table 4. pH in the range occurring in the Icelandic natural waters (about 6–10) has insignificant effect on the stability of plagioclase. This can be inferred from the respective reactions in Table 3 because $Al(OH)_4^-$ is the dominant aluminium-hydroxide species over this pH range. However, pH variation in this range at any particular temperature could affect the value taken by the dissolution rate constants, k^*. In the case of albite, experiments show that its dissolution rate decreases by about a factor of 5 when pH changes from 10 to 8 at 25°C (CHOU and WOLLAST, 1984). The rate of olivine dissolution decreases by a factor of about 6 for the same pH change at 25°C, in water with partial pressure of CO_2 equal to, or less than $10^{-4.5}$ atm. (WOGELIUS and WALTHER, 1989). However, if the partial pressure of CO_2 is equal to the atmospheric one ($10^{-3.5}$ bars), the rate is independent of pH in the range 6–12 and is equal to the minimum dissolution rate for olivine in the low P_{CO_2} waters (WOGELIUS and WALTHER, 1989).

Magmatic gases are known to migrate into overlying groundwater systems, whether thermal or not (ARNÓRSSON, 1986). Such gas emission is most likely linked to relatively short-lived events of magma intrusion. These gases include CO_2, SO_2 and HCl, all of which are acid gases and, therefore, upon dissolution, proton donors. It is known that gas emission of this kind has significantly lowered the pH of geothermal reservoir waters, for example to values as low as 2 in the Krafla geothermal field in northeast Iceland (ARNÓRSSON, 1986). Such pH lowering will enhance dissolution of all the igneous basalt minerals and glass and upset equilibria with alteration minerals.

Hydrothermal and weathering minerals

Quartz and chalcedony

Cold waters are somewhat supersaturated with chalcedony whereas thermal waters when less than about 180°C are very close to equilibrium with this fine crystalline variety of quartz (Fig. 7a). Waters

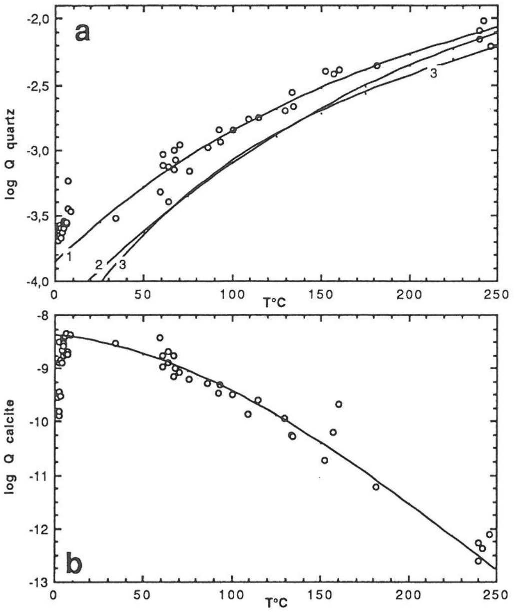

FIG. 7. The state of chalcedony/quartz (a) and calcite (b) saturation in natural waters in Iceland. Curve 1 in part a represents chalcedony solubility according to FOURNIER (1977). Curves 2 and 3 indicate quartz solubility according to FOURNIER and POTTER (1982) and WALTHER and HELGESON (1977), respectively.

at higher temperatures closely approach equilibrium with the more stable phase, quartz (ARNÓRSSON, 1975; ARNÓRSSON *et al.,* 1983a,b) (Fig. 7a). The chalcedony solubility curve used here is that of FOURNIER (1977). It corresponds to the solubility of quartz crystals of 0.04 μm diameter at 0°C to about 0.15 μm diameter at 200°C (GÍSLASON *et al.,* 1989). The supersaturation observed for the cold waters for quartz in this size range could result from formation of even smaller crystals, that would therefore be more soluble. Alternatively "chalcedony crystal size" could still be forming but its precipitation rate would not be sufficient to cope with the silica being dissolved from the rock until the observed degree of supersaturation is attained.

Calcite

Cold waters are generally undersaturated with calcite but all geothermal waters are very close to being saturated (Fig. 7b). As rain water seeps into the ground and reacts with the rock, calcite saturation is approached through dissolution of calcium from the rock and an increase in the carbonate ion concentration with increasing pH. Extensively reacted cold waters (pH greater than about 9) and all slightly thermal waters seem to have closely approached calcite saturation.

Smectite

Montmorillonite group clay minerals (smectites) constitute the most abundant hydrothermal alteration product in low-temperature Icelandic geothermal systems. Practically no data are available on the composition of these minerals and their crystal and thermodynamic properties may be complicated by various types of interlayering with illite, vermiculite and chlorite. Fig. 8 indicates that the cold waters invariably are supersaturated with the calcium, magnesium, sodium and potassium end member components. Supersaturation would be even greater in real montmorillonite mixtures where the activity of the end member components is less than unity. This apparent supersaturation could be due to sluggish precipitation rates causing the water to be maintained in a state of supersaturation. Alternatively the minerals forming at these low temperatures may be of such small crystal size that surface energy contributes significantly to their increased solubility.

Contrary to the cold waters, the geothermal waters are, with few exceptions, undersaturated with the pure end member montmorillonite components. For the calcium and magnesium end members the degree of undersaturation is generally equivalent to 1–1.5 Log Q units. It is slightly greater for the sodium end member, and close to 2 Log Q units for the potassium end member. This apparent but rather constant undersaturation could be due to equilibration of the geothermal waters with montmorillonite having the following end member component activities: $a_{\text{Mg-mont.}} = 10^{-1}$, $a_{\text{Ca-mont.}} = 10^{-1.5}$, $a_{\text{Na-mont.}} = 10^{-1.5}$, $a_{\text{K-mont.}} = 10^{-2}$. Because data on the chemical composition of montmorillonite are lacking the above explanation can only be regarded as tentative.

Low albite and K-feldspar

Cold waters are substantially supersaturated with respect to both low-albite and microcline (the stable K-feldspar at low temperatures). Geothermal waters are close to equilibrium although there appears to be slight supersaturation at the lowest temperatures (below about 75°C) and data at 240–250°C are erratic and inconclusive (Fig. 9a and b).

Albite is an abundant mineral in high-temperature geothermal fields and K-feldspar has also been identified, although it is much less abundant as a result of the low potassium content of the basaltic rock. Igneous plagioclase in hydrothermally altered rock has typically been replaced by albite and calcium bearing minerals such as calcite and epidote. Evidence, thus, favours that albite and K-feldspar

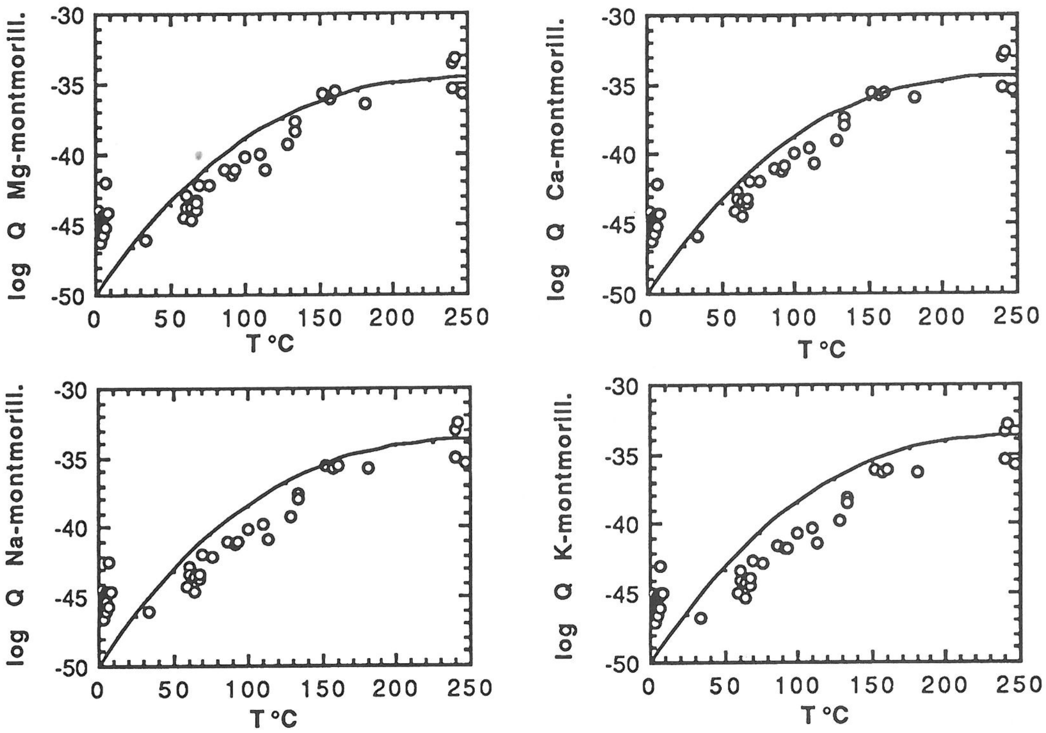

FIG. 8. The saturation state of natural waters in Iceland with respect to pure Mg-, Ca-, Na- and K-smectites.

form as alteration minerals from the Icelandic natural waters, at least, if they are considerably thermal (ARNÓRSSON *et al.*, 1983a).

As for the smectites, the apparent albite and K-feldspar supersaturation in cold waters could be due to sluggish precipitation of these minerals at low temperatures, or it may be an artifact of their small crystal size.

Laumontite

Laumontite is one of many zeolites found in altered rocks of low-temperature geothermal fields (KRISTMANNSDÓTTIR, 1978) and in Tertiary basalts altered by burial metamorphism (WALKER, 1960). Measured temperatures in geothermal wells indicate a lower stability limit for laumontite at about 120°C (KRISTMANNSDÓTTIR, 1978). Other studies indicate that this stability limit may occur at higher temperatures, may be around 200°C (*e.g.*, MIYASHIRO, 1971).

The data plotted in Fig. 9c indicate that geothermal waters at and above about 180°C are significantly laumontite-undersaturated. Waters in the range 100–150°C are close to saturation but as temperatures decrease below 100°C supersaturation progressively increases. Cold water are enormously laumontite-supersaturated. Even if laumontite formed from 50–70°C waters, where supersaturation is highest among the thermal waters, its precipitation rate would be described by Equation (8) above as the degree of supersaturation is at most 2 Log Q units.

Pyrite, marcasite and pyrrhotite

Cold groundwaters do not contain detectable H_2S and for this reason their state of equilibration with respect to the iron sulphide minerals can not be assessed. Waters from the low-temperature geothermal fields are supersaturated with pyrite but close to marcasite saturation (GUNNLAUGSSON and ARNÓRSSON, 1985) (Fig. 10a). Waters above 200°C, however, seem to be close to equilibrium with pyrite. Pyrite is abundant in hydrothermally altered rocks at depth in high-temperature geothermal fields. Marcasite and pyrite have both been identified in low-temperature geothermal fields (GUNNLAUGSSON and ARNÓRSSON, 1985).

Low-temperature waters are close to equilibrium with pyrrhotite, or are slightly supersaturated especially at the lowest temperatures (Fig. 10b). Results for high-temperature waters are conflicting. The data points in Fig. 10b indicate undersatura-

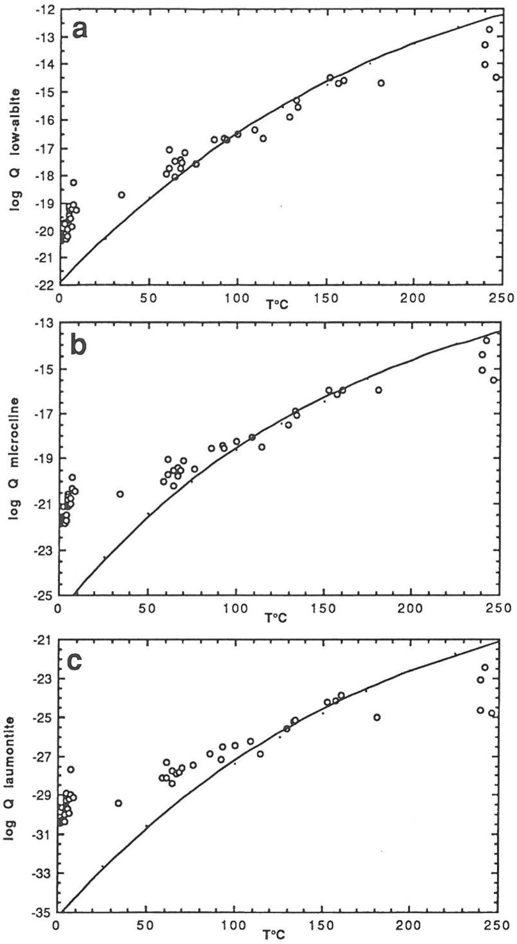

FIG. 9. The saturation state of natural waters in Iceland with respect to pure microcline (the stable K-feldspar at low temperatures), low-albite and laumontite.

tion. However, pyrrhotite is found frequently in altered rocks of high-temperature geothermal systems and data on H_2 and H_2S indicate that the partial pressure of these gases are controlled by equilibrium with a mineral buffer including both pyrite and pyrrhotite (ARNÓRSSON and GUNNLAUGSSON, 1985).

Gibbsite and kaolinite

Cold groundwaters are supersaturated with respect to both gibbsite and kaolinite (Fig. 11) indicating that these minerals, which frequently form weathering products, are stable. The supersaturation may result from sluggish precipitation or be apparent, due to the small crystal size of the minerals.

Geothermal waters above about 50°C are undersaturated with gibbsite, the degree of undersaturation increasing with increasing temperatures,

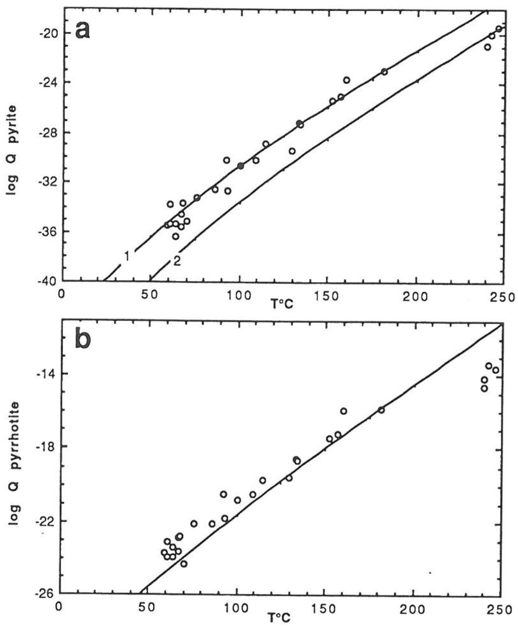

FIG. 10. The state of marcasite (1)/pyrite (2) (a) and pyrrhotite (b) saturation in thermal waters in Iceland.

indicating that gibbsite is unstable in the geothermal waters relative to aluminium silicates.

The geothermal waters are close to saturation with respect to kaolinite or somewhat undersaturated, especially at the highest temperatures. The

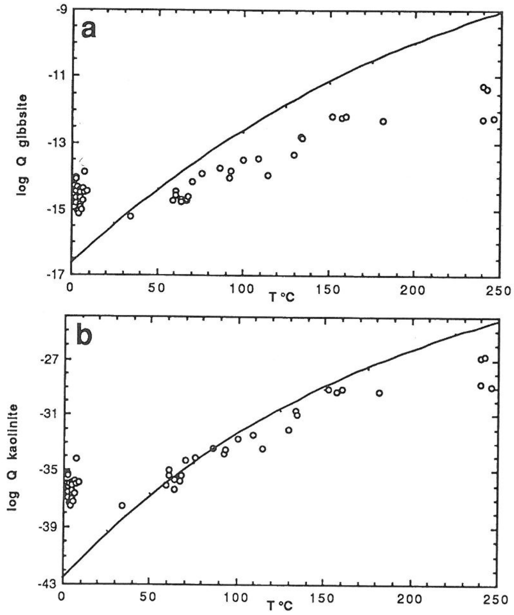

FIG. 11. The state of saturation of pure gibbsite and kaolinite in natural waters in Iceland.

slight supersaturation in waters below about 100°C may not be sufficient to drive kaolinite deposition. This mineral is generally not found at depth in geothermal systems although it has been reported and is then accounted for by acid leaching. The acid waters form most probably by dissolution of magmatic gases in the geothermal water.

SUMMARY

Cold groundwaters are generally highly undersaturated with respect to olivine, and presumably even more so with basaltic glass. The degree of undersaturation increases with increasing forsterite content of the olivine. Waters that have reacted less with the basaltic rock and have, therefore, lower pH than more reacted waters, are more unsaturated.

Cold groundwaters with relatively low pH (<9) are somewhat undersaturated with respect to pyroxene, but higher pH waters are close to equilibrium, even supersaturated. Groundmass plagioclase is close to equilibrium with the cold groundwaters irrespective of pH. Increasing anorthite content leads to progressively greater undersaturation.

Unlike cold waters, geothermal waters of intermediate temperature are close to saturation with groundmass olivine although they are undersaturated with respect to the more magnesian olivine phenocrysts. High-temperature waters are invariably olivine-undersaturated.

Geothermal waters of low-temperature fields tend to be supersaturated with respect to the end members components of both ortho- and clinopyroxenes. The supersaturation and, therefore, stabilization of the pyroxene probably is caused by rapid dissolution of olivine and basaltic glass. High-temperature waters are pyroxene-undersaturated.

Unlike the cold waters, geothermal waters are significantly undersaturated with plagioclase due to the high instability of the anorthite component.

The geothermal waters are generally supersaturated with respect to the magnetite and hematite components in magnetite-ulvöspinel solid solution and ilmenite, respectively. The degree of supersaturation increases with decreasing temperatures. However, high-temperature waters are undersaturated with magnetite, a result which conforms with observed negative magnetic anomalies over many high-temperature fields considered to be caused by destruction of the magnetite in the basaltic rock.

The dissolution kinetics of olivine in cold waters is expected to follow the linear rate law. The same may hold for pyroxene in cold, relatively low pH water (<8–9) and for olivine in thermal waters especially at high temperatures and if the olivine is forsterite rich. Otherwise dissolution rates of the primary basaltic minerals is expected to be described by the general rate law expression (Lasaga, 1981), equation (8), because departure from equilibrium is not so excessive.

Cold waters tend to be strongly supersaturated with common weathering minerals such as smectite, chalcedony, alkali feldspars, gibbsite and kaolinite. This supersaturation may be real and due to sluggish precipitation or be an artifact produced by the inferred small crystal size of the weathering products. These waters are generally calcite-undersaturated unless they have reacted sufficiently with the rock to bring pH to about 9 or more.

Geothermal waters tend to be somewhat undersaturated with both gibbsite and kaolinite but very close to equilibrium with many hydrothermal minerals found in the altered basalts such as calcite, chalcedony (<180°C) or quartz (>180°C), low-albite, microcline, laumontite, pyrrhotite and marcascite (<180°C) or pyrite (>180°C). However, it is noteworthy that waters in the range 50–100°C are somewhat supersaturated with feldspars and laumontite, the degree of supersaturation decreasing with increasing temperatures. The reason for this supersaturation is considered to be the limited precipitation rate at these low temperatures needed to balance the flux of respective chemical components into the water by primary rock mineral dissolution.

With few exceptions equilibrium between water and hydrothermal minerals is so closely approached that the precipitation rate will be described by Equation (9).

The basic chemical reaction involving weathering and hydrothermal alteration of the basaltic rock, and the accompanying changes in the water chemistry, is hydrogen ion metasomatism. The water is "titrated" through the dissolution of the igneous minerals and glass which act as bases, thus causing solution pH to rise (Gíslason and Eugster, 1987a,b). Proton donors accelerate the "titration" process. Sources of protons for surface waters constitute carbonic acid of atmospheric and or organic origin. For cold and low-temperature groundwaters ionization of silica dissolved from the rock is the main proton donor (Gíslason and Eugster, 1987a,b). In the case of high-temperature water dissolved carbonic acid and hydrogen sulphide constitute the dominant source of protons for driving the alteration process. The gases forming these acids through dissolution in water may be of magmatic origin or derived from the rock being dissolved.

There are basically two main reasons for the close approach to chemical equilibrium between thermal waters and alteration minerals, even at temperatures as low as 50°C. One is that the saturation state of the igneous minerals (Fig. 2 through 6), in the thermal waters and presumably also the basaltic glass, is not so much different from that of the hydrothermal minerals (Fig. 7 through 11). Thus, dissolution rates will not differ much from precipitation rates when the solution is close to equilibrium with the precipitating phases. The other reason is that the basaltic rock is low in chloride, *i.e.* soluble salts. Therefore, there is low flux of cations into the water from salt dissolution—cations which participate in secondary mineral deposition.

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