PROCESSES INFLUENCING THE pH OF GEOTHERMAL WATERS

Stefán Arnórsson, Sigurdur R. Gislason and Audur Andrésdóttir

Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavik, Iceland

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ABSTRACT

The present study is based on geochemical studies of about 400 samples of natural waters in Iceland. They include surface waters and groundwaters ranging in temperature from 5°C (ambient) to over 350°C. The pH of these waters most often lies in the range of about 6 to 10. Surface waters most often have a pH between 6.5 and 8. Cold and warm waters (<50°C) have higher pH, 9-10, but with increasing temperature the pH falls and is generally in the range 6-7 at temperatures above 200°C. There are essentially three processes that affect the water pH. They are: 1) The supply of acids to the water from various sources, 2) rock dissolution and 3) precipitation of various minerals. The second process causes water pH to increase whereas the two other processes cause it to decrease. Cation/hydrogen ion activity ratios in >50°C waters appear to be controlled by close approach to chemical equilibrium between solution and hydrothermal silicate minerals. This equilibrium fixes water pH in these geothermal waters in conjunction with the aqueous cation activity.

1. INTRODUCTION

The hydrogen ion activity of natural waters is of great significance in all chemical reactions associated with rock alteration, i.e. dissolution of the primary rock minerals and precipitation of secondary minerals. The pH of most natural waters lie in the range of 6-9. Much lower pH-values are, however, encountered in acid mine waters and surface waters heated by geothermal steam (Nordstrom et al, 1979; Ellis and Mahon, 1977). Higher values are enountered in evaporative lakes and in some geothermal waters of low dissolved solids content and of relatively low temperature (Eugster and Hardie, 1978; Michard and Roekens, 1983; Arnórsson *et al.,* 1983, 1993).

Hydrogen ion regulation in geothermal and other natural waters is provided by various homogeneous and heterogeneous buffer systems. Boiling and cooling of geothermal water, and mixing with cold shallow groundwater can cause the hydrogen ion activity to change by several orders of magnitude. Such changes affect the chemical quality of geothermal waters and can turn them corrosive or cause precipitation of various minerals and in this way lead to difficulties in exploiting the geothermal fluids including the operation of geothermal wells.

The present contribution is largely based on data from Iceland. It gives an account of the various processes and buffers that affect the pH of natural waters. The sources of supply of the acids providing protons to the water are also discussed.

2. MEASUREMENT AND CALCULATION OF pH

The published literature contains a very large number of data on the pH of natural waters. Generally, however, it is not reported at which temperature the pH was measured although its value is temperature dependent as dictated by the temperature dependence of the dissociation constants of the weak acids in solution, their concentrations and buffer capacity. For a given acid its buffer capacity is largest when the pH and the negative logarithm of the dissociation constant are equal. When the temperature at which the pH is measured is not reported, it is generally assumed to be room temperature (20° or 25°C).

The pH of water samples may change upon storage due to various types of chemical reactions such as precipitation of hydroxides, C02 and H_2S degassing, gain of CO_2 from the atmosphere or oxidation of H_2S. For this reason it is important to collect samples into air-tight bottles and measure the pH soon after collection as e.g. described by Arnórsson (1991). Some researchers have measured the pH on the sampling site. This may cause unnecessary imprecision compared with measurement in a field laboaratory or a hotel at the end of each sampling day due to errors caused by temperature and weather fluctuations outdoors. Unfortunately, the sampling procedure and method of pH measurement is usually not reported with data presented in the literature leaving an unknown margin of error to the measurement of this very important variable.

The accuracy in calculating the pH of natural waters at a temperature other than that at which the pH is measured is dependent on the analytical precision of the acid concentrations that influence the pH, the accuracy of the pH measurement 'and how accurately the dissociation constants of the respective acids are known at different temperatures. Various aqueous speciation programmes, such as WATEQ (Truesdell and Jones, 1974; Ball *et al.*, 1987) SOLMNEQ (Kharaka *et al.,* 1987), SOLVEQ (Reed and Spycher, 1984) and WATCH (Arnbrsson *et al.*, 1982) may be used to cany out such calculations.

3. pH OF NATURAL WATERS

The pH of pure rain water at 25°C in equilibrium with the C02 of the atmosphere is close to 5.6. In Iceland most surface waters in lakes, streams and rivers have considerably higher pH, most waters falling in the range of 6.5-8 (Fig. 1). Cold groundwaters and slightly thermal waters (≤50°C) possess higher pH, mostly in the range of 9 to 10. With increasing temperature above about 50°C the pH of the Icelandic geothermal waters decreases progressively. Most waters above 200°C have a pH in the range 6-7.

Most of the waters plotted in Fig. 1 are dilute. The dissolved solids content of the non-thermal waters is <100 ppm and <1000 ppm for most of the geothermal waters. At any particular temperature saline geothermal waters tend to have lower pH than the dilute waters. Thus, for example, the pH of the 240-270°C geothermal seawater at Svartsengi and Reykjanes on the Reykjanes Peninsula in SW-Iceland is a little above 5 whereas dilute waters in the same temperature range from Námafjall and Krafla in N-Iceland possess pH between about 6.5 and 7.

Warm waters rich in carbonate occur in several localities in Iceland. They tend to have lower pH than waters of similar temperature and with low content of dissolved total carbonate (Fig. 1).

4. CHEMICAL PROCESSES AFFECTING THE pH OF NATURAL WATERS

Three chemical processes affect the pH of natural waters. They include rock dissolution, the supply of acids to the water and precipitation of some secondary minerals from the water. The fist process tends to increase the water pH whereas the other two processes tend to decrease it. Each of these three processes will be discussed in some detail below.

4.1 Rock Dissolution

Weathering and hydrothermal alteration of rocks may be referred to as hydrogen ion metasomatism. The interaction between water and many common primary rock forming minerals that produces this alteration is appropriately described as a titration process where the aqueous solution plays the role of the acid and the minerals the role of the base. Almost all rocks consist of oxide and silicate minerals. Silicate minerals can be written in terms of a sum of oxides. If their dissolution, i.e. the titration process, releases cations only, or cations

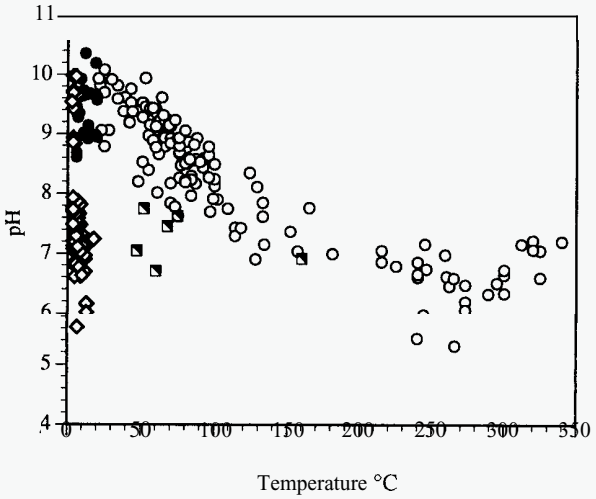

Fig. 1. The pH of natural waters in Iceland. Diamonds represent surface waters, dots non-thermal groundwaters and circles geothermal waters. Waters rich in carbonate are shown by half-filled squares. The pH-values were calculated with the aid of the WATCH chemical speciation programme (Arndrsson *et al.*, 1982) at the temperature shown in the figure.

in excess of anions, it can be exemlified by dissolution of an oxide component, such as MgO:

$$MgO = Mg^{+2} + O^{-2} \quad (1)$$

The O^{-2} ion will react immediately with protons to produce water:

$$O^{-2} + 2H^{+} = H_2O \quad (2)$$

The overall reaction is:

$$MgO + 2H^{+} = Mg^{+2} + H20 \quad (3)$$

The source of the protons is an acid dissolved in the water. Therefore, the rock dissolution process produces an aqueous salt solution in which the cation is derived from the rock and the anion comes from the proton donating acid.

Rock dissolution has sometimes been described as an ion exchange reaction where cations are released into solution as protons are being taken up by the rock (e.g. Gislason and Eugster, 1987). It may well be that this process is operative during non-stoichiometric dissolution of rock forming minerals. However, in hydrothermally altered rocks some, if not all grains of primary minerals, may be completely replaced by hydrothermal minerals. When this is the case, a reaction of the type given by equation (3) truly describes the overall reaction involved in the rock dissolution process.

4.2 Acids and their sources of supply

Acids present in Icelandic geothermal waters as potential proton donators include carbonic acid ($H_2CO_3^o$), silica ($H_4SiO_4^o$), hydrogen sulphide (H_2S) and bicarbonate (HCO_3^-). In geothermal waters in other countries boric acid ($H_3BO_3^o$) and bisulphate (HSO_4^-) may additionally constitute potential proton donators. In most waters the most important acid is $H_2CO_3^o$. However, in some waters of high temperature (>250°C), at least, if associated with basaltic rocks, H_2S may be equally important. In some dilute, high pH, waters of relatively low temperature the main proton donators include $H_4SiO_4^o$ and HCOj. In some geothermal systems associated with andesitic volcanism HSO_4^- together with $H_2CO_3^o$ constitute the acidic constituents. Boron tends to occur in highest concentrations in geothermal waters associated with marine sediments (Ellis and Sewell, 1963).

In surface waters the main proton donating acid is carbonic acid. Its source may either be atmospheric CO_2 or C02 formed by decay of organic matter. As the hydrogen ions formed by dissociation of carbonic acid are consumed by rock dissolution, more carbonic acid dissociates leading to a decrease in its concentration and partial pressure within the solution. Consequently, atmospheric CO_2 tends to dissolve in the water constantly rejuveniating the proton supply. According to Gislason and Eugster (1987) the rate of supply of protons by dissolution of atmospheric CO_2 equals the rate of consumption of protons by dissolution of basaltic rock when the pH is some 7.

When waters are cut off the supply of CO_2 from the atmosphere, as is the case with waters seeping into the ground, continued rock dissolution tends to raise the pH above the steady state value attained by surface waters. When basaltic rock is being dissolved the pH tends to stabilize in the range of 9 to 10. At this pH the rate of consumption of protons by rock dissolution equals their rate of production by dissolution of silica from the rock and subsequent dissociation to form $H_3SiO_4^-$ (Gislason and Eugster, 1987).

Common igneous rocks contain significant amounts of carbon and sulphur. The concentrations of carbon as CO_2 in undegassed tholeiitic basaltic magma has been estimated as about 1800 ppm (Hoefs, 1969). Intermediate and silicic igneous rocks contain somewhat higher carbon concentrations (Hoefs, 1969). Lavas, as well as intrusive bodies, contain less carbon due to degassing of the magma as it rises through the upper part of the crust and subsequently consolidates. Undegassed basalt magma contains about 800 ppm S (Moore, 1965; Gunnlaugsson, 1977) but, as a result of degassing, lavas and high level intrusions of basaltic composition most often contain 200-400 ppm S (Gunnlaugsson, 1977).

The amount of carbonate and sulphur (both sulphide sulphur and sulphate sulphur) dissolved from basaltic rocks increases with increasing temperatures as witnessed by the positive relation between their aqueous concentrations and water temperature (Arnórsson *et al.*, 1983; Arndrsson and Gunnlaugsson, 1985). Increased supply of carbonate and sulphide from the rock to the water is considered to be partly responsible for the progressive decrease in water pH with rising temperature (Fig. 1), but enhanced precipitation of secondary silicate minerals also contributes.

Many geothermal systems, particularly those of high temperature (>200°C) and associated with relatively recent volcanism seem to have a magmatic heat source. Degassing of the magma may supply various acids to the water in the overlying geothermal system. They include CO_2, H_2S, SO_2 and HCl. When new batches of magma are being intruded into magma chambers in the roots of geothermal systems degassing may be particularly pronounced as was e.g. observed in Krafla following the eruptive episode that started at the end of 1975 (Ármannsson *et al.*, 1982). Magma degassing of this kind may render the geothermal reservoir water strongly acid (Arnórsson, 1981; Ármannsson *et al.*, 1982).

4.3 Precipitation of secondary silicates

Many weathering and hydrothermal minerals have pH dependent solubility. Their formation, i.e. precipitation from solution, causes a decrease in water pH. Examples of such minerals include smectite, chlorite, epidote and prehnite. The first three silicates are among the most important hydrothermal minerals in most geothermal systems. Smectite is the most abundant alteration mineral below about 200°C being replaced by chlorite at higher temperatures. Epidote is a major alteration mineral in many geothermal systems with temperatures above about 250°C. Prehnite, although widespread, tends to be present in smaller amounts in altered rocks than the first three mentioned minerals.

Major cation/proton ratios in Icelandic geothermal waters attain approximately a fixed value at any particular temperature (Fig. 2). This is attributed to an approach to equilibrium between the solution and hydrothermal minerals. In most cases two aluminium silicates seem to be involved containing aluminium and another cation in different proportions. Precipitation of such minerals, including approach to solution equilibrum with them, is, as already mentioned, only one of the three processes that affect the pH of geothermal waters in Iceland. Since the precipitation process appears to be the controlling factor for water pH, it must constitute the rate determining step in the overall hydrothermal alteration process. This may be due to relatively large surface area between solution and the precipitating alteration minerals that form many small crystals protruding into vugs and cracks but also relatively slow dissolution rate of the primary rock constituents at the stabilized pH-value.

Examples of reactions involving two Al-silicates and solution are given below. For heulandite, Ca-montmorillonite and solution we have:

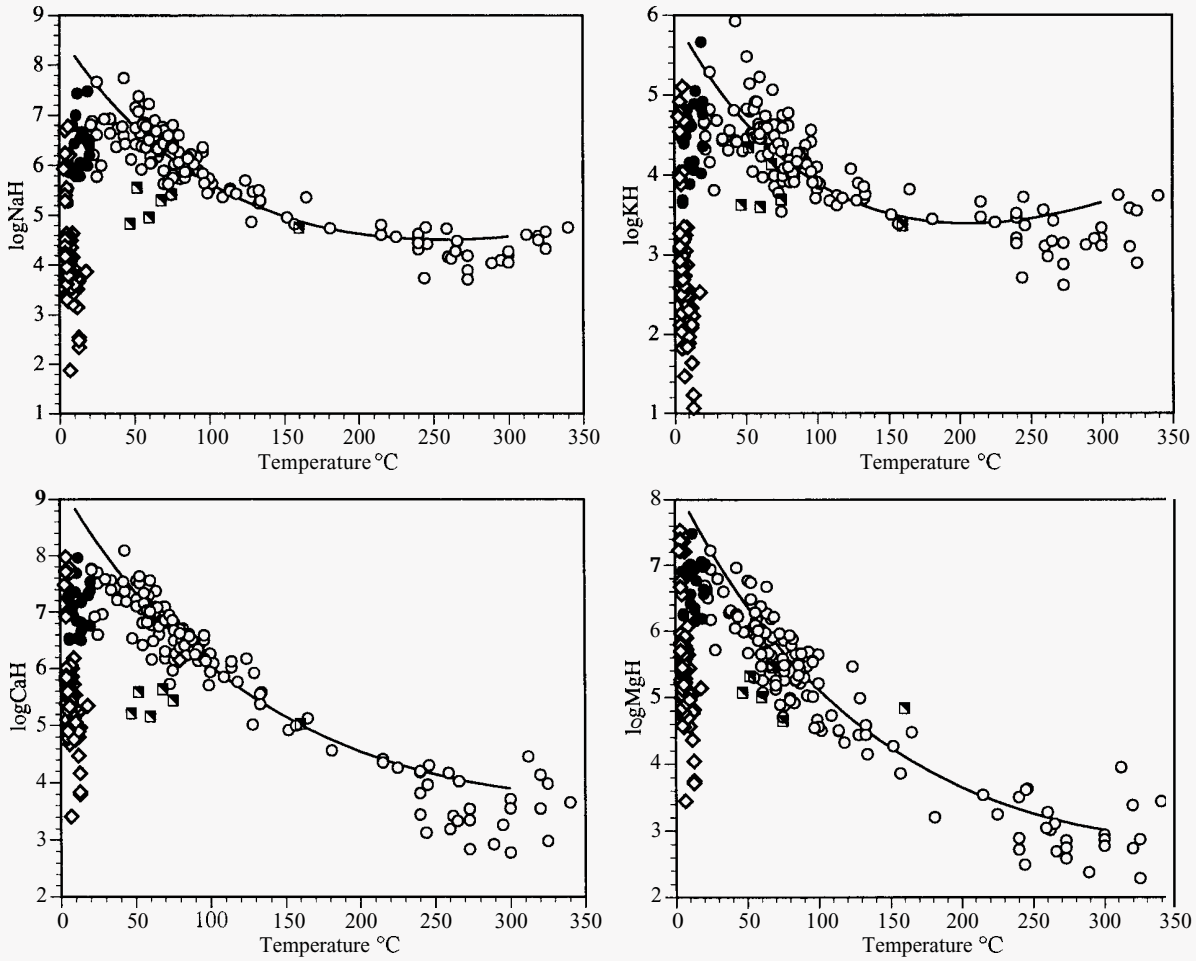

Fig. 2. Major cation/proton activity ratios in thermal and non-thermal waters in Iceland. Diamonds indicate surface waters, dots, non-thermal groundwaters and circles geothermal waters. Half-filled squares represent waters rich in carbonate. NaH = a_{Na^+}/a_{H^+}, CaH = $a^{0.5}_{Ca^{+2}}/a_{H^+}$ and similarly for KH and MgH.

$$7\underset{\text{heulandite}}{CaAl_2Si_7O_{18}\cdot 6H_2O} + 12H^+ = \underset{\text{Ca-montmorillonite}}{CaAl_{14}Si_{22}O_{60}(OH)_{12}} + 27\underset{\text{chalcedony}}{SiO_2} + 42H_2O + 6Ca^{+2} \quad (4)$$

where the equilibrium constant, K, is

$$K = \frac{a^6_{Ca^{+2}}}{a^{12}_{H^+}} \quad (5)$$

Similarly, equilibrium between clinozoisite (iron-free epidote), prehnite and solution is given by

$$3\underset{\text{Prehnite}}{Ca_2Al_2Si_3O_{10}(OH)_2} + 4H^+ = \underset{\text{Clinozoisite}}{2Ca_2Al_3Si_3O_{12}(OH)} + 3\underset{\text{Quartz}}{SiO_2} + 4H_2O + 2Ca^{+2} \quad (6)$$

where

$$K = \frac{a^2_{Ca^{+2}}}{a^4_{H^+}} \quad (7)$$

Reactions involving aqueous solution and two Al-silicates can always be expressed in such a way that the aluminium only enters these minerals and is, thus, eliminated as an aqueous species. Silica that does not enter the Al-silicates can be taken to form quartz or chalcedony, as shown in equations **(4)** and (6) above. When reactions are written in this way and, if the two Al-silicates contain the aluminium and another cation in different proportions, the equilibrium constant is always equal to a cation/proton activity ratio. Thus, for a specific cation, like e.g. Ca^{+2}, involved in an equilibrium between solution and two such AI-silicates and quartz or chalcedony, we may write

$$CaO + 2H^+ = Ca^{+2} + H20 \quad (8)$$

In general for a cation with a charge equal to 2X we have

$$Z_YO_X + 2XH^+ = YZ^{(+2X/Y)} + XH_2O \quad (8a)$$

where Z represents the respective cation and **X** and Y are stoichiometric constants. The solubility of silicates which do not contain Al is always pH dependent. Equation (8a) is also valid for them.

5. EFFECT OF TEMPERATURE CHANGES, BOILING AND MIXING ON pH

The pH of geothermal reservoir waters, which have closely approached chemical equilibrium with hydrothermal minerals, can change drastically in upflow zones where the water may cool conductively, boil and/or mix with shallower water of lower temperature. pH changes associated with conductive cooling are dictated by the temperature changes in the dissociation constants of those acids which buffer the pH. Since $H_2CO_3^o$ tends to be the main pH buffer in most geothermal waters lowering of water temperature to 50-100°C is accompanied by a decrease in pH. This is exemplified in Fig. 3 for the fluids from wells 11, 13 and 8 at Námafjall, Krafla and Reykjanes in Iceland. Below about 50°C the pH tends rise somewhat with falling temperature. The overall pH change is in harmony with the change in the dissociation constant of carbonic acid (see Fig. 5).

Boiling causes pH to rise drastically because the acids $H_2CO_3^o$ and H_2S^o are transferred from the water and into the steam that forms (Fig. 4). When dissociation of the bisulphate ion exerts a buffering effect on pH cooling by boiling from high temperatures to atmospheric pressure may cause a drastic decrease in the pH. This

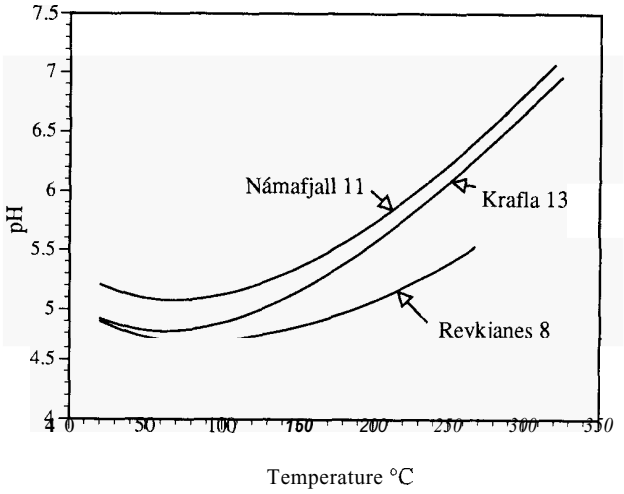

Fig. 3. pH changes associated with conductive cooling of geothermal reservoir water from the following wells in Iceland Námafjall 11, Krafla 13 and Reykjanes 8. The water in the first two wells is very dilute (1000 ppm dissolved solids) but in the Reykjanes reservoir the water has saewater salinity.

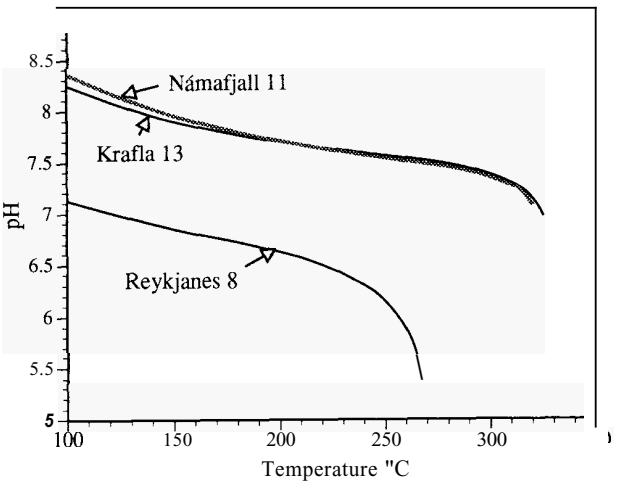

Fig. 4. pH changes associated with adiabatic boiling and equilibrium degassing of water from the three wells plotted in Fig. 3.

produces a strongly acid solution at the surface although the reservoir water may have a near neutral pH. The cause of this pH decrease is the strong increase in the dissociation constant for the bisulphate ion with falling temperature (Fig. *5)*.

Mixing of geothermal water with cold water in upflow zones tends to have a similar effect as conductive cooling, at least, if the mixing process prevents boiling. The acid concentrations tend to be higher in geothermal waters than in cold waters and for this reason the buffering effect of the hot water component in the mixture tends to dominate.

Decrease in water pH in upflow zones of geothermal systems tends to increase the degree of undersaturation with the primary minerals of most common igneous rock. This enhances their dissolution and causes the water composition *to* change significantly. Increase in water pH will, on the other hand, together with cooling retard even inhibit such dissolution but cause precipitation of some hydrothermal minerals from the water. However, precipitation of Mg and **Al**-bearing minerals, which are the most important hydrothermal minerals, tends to be limited because of the low concentrations of these elements in geothermal waters **As** a result changes in geothermal water compositions in upflow zones tend to be limited if the water pH increases in the upflow.

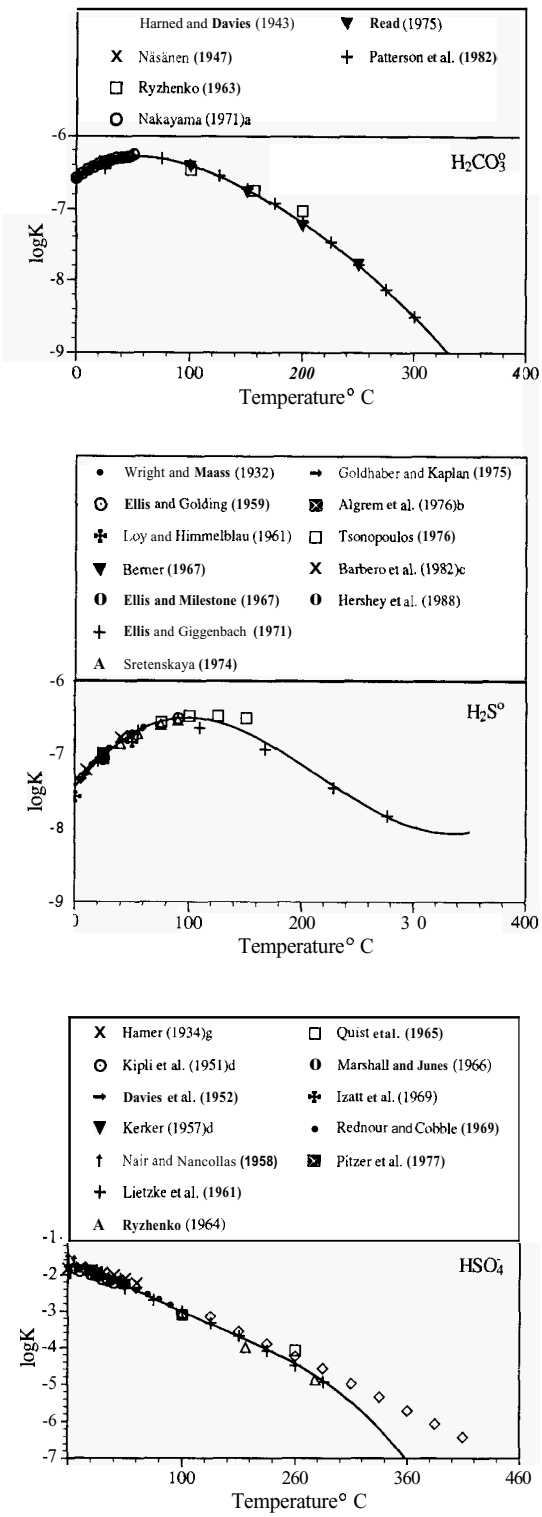

Fig. 5. Experimental data on the dissociation constants (K) of some acids influencing the pH of natural waters. The sources of the data are given on each diagram. [a]Recalculated from the data of Harned and Davies (1943). [b]Recalculated by Millero (1986). Calculated for this study assuming constant heat capacity. [d]As reported by Sillén and Martell (1964). The curves in each figure were obtained by multiply linear regression through the data points. They describe well the temperature dependence of the respective dissociation constants. Their logK values for $H_2CO_3^o$, H_2S^o and HSO_4^-, respectively, are given by:
$467.22 - 13331.76/T + 0.18650T - 8.42 \cdot 10^{-5} \cdot T^2 - 192.765 \cdot \log T$
$-1415.98 + 28752.62/T - 0.73065T + 30.82 \cdot 10^{-5} \cdot T^2 + 607.404 \cdot \log T$
$2788.57 - 63640.67/T + 1.35758T - 60.51 \cdot 10^{-5} \cdot T^2 - 1183.322 \cdot \log T$

REFERENCES

Almgren, T., Dryssen, D., Elgquist, B. and Johannsson, J. (1976). Dissociation of hydrogen sulphide in seawater and comparison of pH scales. *Mar. Chem.*. Vol.4, pp. 289-297.

Armannsson, H., Gislason, G. and Hauksson, T. (1982). Magmatic gases in well fluids aid the mapping of flow pattern in a geothermal system. *Geochim. Cosmochim. Acta,* Vol.46, pp. 167-177.

Arnórsson, S. (1981). Mineral deposition from Icelandic geothermal waters: Environmental and utilization problems. *J. Petrol. Tech.* V01.33, pp. 181-187.

Arnórsson, S. (1991). Geochemistry and geothermal resources in Iceland. In: *Application of Geochemistry in Geothermal Reservoir Development,* F. D'Amore (Co-ordinator). UNITAR/UNDP Publ., Rome, pp. 145-196.

Arnórsson, S., Sigurdsson, S., and Svavarsson, H. (1982). The chemistry of geothemial waters in Iceland. I. Calculation of aqueous speciation from 0° to 370°C. *Geochim. Cosmochim. Acta,* Vol.46, pp. 1513-1532.

Arnbrsson, S., Gunnlaugsson, E. and Svavarsson, H. (1983). The chemistry of geothermal waters in Iceland. II. Mineral equilibria and independent variables controlling water compositions. *Geochim. Cosmochim. Acta,* Vol.47, pp. 547-566.

Arnbrsson, S. and Gunnlaugsson, E. (1985). New gas geothermometers for geothermal exploration - calibration and application. *Geochim. Cosmochini. Acra,* Vol.49, pp. 1307-1325.

Arnbrsson, S., Andrésdóttir, A. and Sveinbjomsdbttir, A.E. (1993). The distribution of Cl, B, FD and $\delta^{18}O$ in natural waters in the Southern Lowlands in Iceland. In: *Geofluids* '93. *Contributiom to an International Conference on fluid evolution, migration and interaction in rocks,* J. Pernell, A. H. Ruffell and N. R. Moles (Eds.). British Gas, pp. 313-318.

Ball, J. W., Nordstrom, D. K. and Zachmann, D. W. (1987). WATEQ4F - A personal computer fortran translation of the geochemical model WATEQ2 with revised data base. *U.S. Geological Survey Open-File Report 87-50,* 108 pp.

Barbero, J.A., McCurdy, K.G., and Tremaine, P.R. (1982). Apparent molal heat capacities and volumes of aqueous hydrogen sulfide and sodium hydrogen sulfide near 25°C: The temperature dependence of H_2S ionization. *Can. J. Chem.,* Vol.60, pp. 1872-1880.

Berner. R.A. (1967). Thermodynamic stability of sedimentary iron sulphides. *Amer. J. Sci.*, Vol.265, pp. 773-785.

Davies, C. W., Jones, H. W. and Monk, C. B. (1952). E.M.F. studies of electrolytic solutions. Part I. - Sulphuric acid in water. *Trans. Faraday Soc.*, Vol.48, pp. 921-928.

Ellis, A.J. and Giggenbach, W. (1971). Hydrogen sulfide ionization and sulphur hydrolysis in high temperature solution. *Geochim. Cosmochim. Acta,* Vol.35, pp. 247-260.

Ellis, A.J. and Golding, R.M. (1959). Spectrophotometric determination of the acid dissociation constants of hydrogen sulphide. *J. Chem. Soc.*, Vol.111, pp. 127-130.

Ellis, A. J. and Mahon, W. A. J. (1977). *Chemistry and geothermal systems.* Academic Press, New York, 392pp.

Ellis, A.J and Milestone, N.B. (1967). The ionization constants of hydrogen sulphide from 20 to 90°C. *Geochim. Cosmochim. Acta,* Vol.31, pp. 615-620.

Ellis A. J. and Sewell J. R. (1963). Boron in rocks and waters of New Zealand hydrothermal areas. *N. Z. J. Sci.*, Vol.6, pp. 589-606.

Eugster, H. P. and Hardie, L. A. (1978). Saline lakes. In: *Physics, Chemistry and Geology of Lakes,* A. Lerman (Ed.) Springer-Verlag. New York, pp. 237-293

Gislason, S.R. and Eugster, H.P. (1987). Meteoric water-basalt interactions. II. A field study in northeastern Iceland. *Geochini. Cosmochim. Acta*, Vol.51, pp. 2841-2855.

Goldhaber, M.B. and Kaplan. I.R. (1975) Apparent dissociation constant of hydrogen sulfide in chloride solutions. *Mar. Chem.,* Vol.3, pp. 83-104.

Gunnlaugsson, E. (1977). The origin and distribution of sulphur in fresh and geothermally altered rocks in Iceland. *Unpubl. Ph.D. thesis,* Univ. Leeds, 192 pp.

Harned, H.S. and Davies, R.Jr. (1943). The ionization constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salts solutions from 0 to 50°C. *J. Amer. Chem. Soc.*, Vol.65, pp. 2030-2037.

Hershey, J.P., Plese, T., and Millero, F.J. (1988). The pK_1^* for the dissociation of H_2S in various ionic media. *Geochim. Cosmochim. Acta,* Vol.52, pp. 2047-2051.

Hoefs, J. (1969) In: *Handbook of Geochemistry,* K. H. Wedepohl (Ed.), Springer-Verlag, New York, pp. 6-E-1-6.

Izatt, R.M., Eatough, D., Christensen, J.J., and Bartholomew, C.H. (1969). Calorimetrically determined LogK, ΔH^o, and ΔS° values for the interaction of sulphate ion with H^+, Na^+, and K^+ in the presence of tetra-n-alkyl-ammonium ions. *J. Chem. Soc., (A),* Vol.45, pp. 45-47.

Kharaka, Y. K., Gunter, W. D., Aggarwal, P. K., Perkins, E. H. and DeBraal, J. D. (1988). SOLMINEQ.88: A computer program for geochemical modeling of water-rock interactions. *U.S. Geological Survey. Water-Resources Investigations Report 88-4227*, 420 pp.

Lietzke, M.H., Stoughton, R.W., and Young, T.F. (1961). The bisulfate acid constant from 25 to 225°C as computed from solubility data. *J. Phys. Chem.,* Vol.65, pp. 2247-2249.

Loy, H.L. and Himmelblau, D.M. (1961). The first ionization constant of hydrogen sulphide in water. *J. Phys. Chem.,* Vol.65, pp. 264-267.

Marshall, W.L. and Jones, E.V. (1966). Second dissociation constant of sulphuric acid from 25 to 350°C evaluated from solubilities of calcium sulphate in sulphuric acid solutions. *J. Phys. Chem.,* Vol.40, pp. 4028-4040.

Michard, G. and Roekens, E. (1983). Modelling of the chemical composition of alkaline hot waters. *Geothermics,* Vol.12, pp. 161-169.

Millero, F.J. (1986). The thermodynamics and kinetics of the hydrogen sulfide system in natural waters. *Mar. Chem.,* Vol.18, pp. 121-147.

Moore, J.G. (1965). Petrology of deep-sea basalts near Hawaii. *Amer. J. Sci.*, Vol.263, pp. 40-52.

Nair, V.S.K., and Nancollas. G.H. (1958). Thermodynzmics of ion association. Part V. Dissociation of bisulphate ion. *J. Chem. Soc.* (19581, pp. 4144-4147.

Nakayama, F.S. (1971). Thermodynamic functions for the dissociation of $NaHCO_3^o$, $NaCO_3^-$, $H_2CO_3^o$ and HCOj. *J. Inorg. Nucl. Chem.,* Vol.33, pp. 1287-1291.

Näsänen, R. (1947). Potentiometric study of the first ionization of carbonic acid in aqueous solution of sodium chloride. *Acta Chem. Scand*, Vol.1, pp. 204-209.

Nordstrom, D. K., Jenne, E. A. and Ball, J. W. (1979). Redox equilibria of iron in acid mine waters. In: *Chemical Modeling in Aqueous System*. E. A. Jenne (Ed.), ACS, Washington, pp. 51-79.

Patterson, C.S., Slocum, G.H., Busey, R.H. and Mesmer, R.E. (1982). Carbonate equilibria in hydrothermal systems: first ionization constant of carbonic acid in NaCl media to 250°C. *J. Soln. Chem.,* Vol.46, pp. 1653-1663.

Pitzer, K.S., Roy, R.N., and Silvester, L.F. (1977). Thermodynamics of electrolytes. 7. Sulphuric acid. *J. Amer. Chem. Soc.*, Vol.99, pp. 15-21.

Quist. A.S.. Marshall, W. L. and Jolley, H. R. (1965). Electrical conductances of aqueous solutions at high temperature and pressure. II. The conductances and ionization constants of sulphuric acid-water solutions from 0 to 800°C and pressures up to 4000 bars. *J. Phys. Chem.,* Vol 69, pp. 2726-2735.

Read, **A.J.** (1975). The first ionization constant of carbonic acid from 25 to 250°C and to 2000 bar: ***J.*** *Soln. Chem.,* Vol.4, pp. 53-70.

Reed, M. H. and Spycher, N. (1984). Calculation of pH and mineral equilibria in hydrothermal waters with application to geothermometry and studies of boiling and dilution. *Geochim. Cosmochim. Acta,* Vol.48, pp. 1479-1492.

Readnour, J.M., and Cobble, J.W. (1968). Thermodynamic properties for the dissociation of bisulfate ion and the partial molal heat capacities of bisulfuric acid and sodium bisulfate over an extended temperature range. *lnorg. Chem.,* Vol.8, pp. 2174-2182.

Ryzhenko, B.N. (1963). Determination **of** the dissociation constants of carbonic acid and the degree of hydrolysis of the CO_3^{-2} and HCO_j anions in solutions of alkali carbonates and bicarbonates at elevated temperatures. *Geochemistry (1963),* pp.151-164.

Ryzhenko, B.N. (1964). Determination of the second dissociation constant **of** sulfuric acid, and precipitation of salts in the reciprocal system Ca^{+2}, Ba^{+2}/SO_4^{-2}, CO_3^{-2}, under hydrothermal conditions. *Geochem. Intl.,* Vol.1, pp. 8-13.

Sillén, L. G. and Martell, **A.** E. (1964). *Stability constants.* Spec. Publ. No. 17, The Chemical Society, London, 754 pp.

Sretenskaya, N.G. (1974). Electrical conductivity of aqueous solutions of hydrogen sulphide and the first dissociation constant of hydrogen sulphide at different temperatures. *Geochem. Intl.* Vol.11, pp. 681-687.

Truesdell, **A.H.** and Jones. B. F. (1974). WATEQ - a computer program for calculating chemical equilibria of natural waters. ***J.*** *Res. U. S. Geol. Survey,* Vol.2, pp. 233-248.

Tsonopoulos, C., Coulson, D.M., and Inman, L.B. (1976). Ionization constants of water pollutants. ***J.*** *Chem.* ***Eng.*** *Data,* Vol.21, pp. 190-193.

Wright, R.H. and Maass, **O.** (1932). The electrical conductivity of aqueous solutions of hydrogen sulphide and the state of dissolved gas. *Can. J.* ***Res.,*** Vol.6, pp. 588-595.