On the Role of Equilibrium Reactions in Bore-Hole Waters in the Skellefte-Field, Northern Sweden

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In a series of bore holes in an acid-intermediate volcanite rock type measurements of pH and pe (in situ), main ionic constituents, silicic acid and aluminium were made. The bore holes covered the pH interval 6.5-8.6, each with a time invariant solution composition. Field data were used as an experimental test of computerized simulation of weathering reactions by means of equilibrium models. The results suggest that a criterion for an undisturbed groundwater system is a high pH and a low pe where the dissolved main components reach a saturation concentration close to that experimentally found. For lower pH values, however, only the subsystem $H^+ - Si(OH)_4 - Al^{3+}$ corresponded to an equilibrium behaviour.

Introduction

The evolution of natural waters is generally described as a result of the irreversible dissolution of primary silicate minerals under the attack of dissolved CO_2. Although a weathering process must be regarded as a nonequilibrium process, a common approach to obtain information on the regulation of natural water composition is through equilibrium calculations. In principle this approach is valid since an irreversible pathway as a whole may be seen as a series of consecutive reactions each of which is in equilibrium with the next. Also, it is possible in an equilibrium model to include metastable stages with reversible and fast kinetics compared to the irreversible steps that control the concentration of solute species. Besides their relative simplicity, the equilibrium models always show the direction towards which the system is striving. Further, in systems where they cannot

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explain observed conditions, these models may still be used as a guide for new experimental or theoretical work.

One of the most common applications of equilibrium models is to relate analysed concentrations of different species to stability diagrams of some selected minerals. If the analysed species are approximately located along the boundary of two different phases, these phases are interpreted as concentration controlling. However, such models may be misleading since they do not fully show how the concentration of cations ought to follow a change in the master variable pH. In addition, diagrammatic representations cannot tell the absolute amounts of various phases formed or the amounts of a reactant required to transform one phase into another. The latter feature is of great value because it emphasizes the important buffer concept.

This paper discusses the applications and limitations of complex multiphase equilibrium calculations on ground-water systems. The discussion is based on experimental data from bore holes and calculations using the computer program SOLGASWATER (Eriksson 1979).

Experimental

The sampling work was performed in bore holes at three different locations in the Skellefte-field in northern Sweden. All three locations represent acid and intermediate volcanite rocks impregnated by varying degrees of FeS_2. The age of the bore holes were 9-25 years. Two of the locations, Svansele and Rengård, are situated below the highest marine shore line.

The water samples were collected by 0.4 l Ruttner-type sampler made of PVC-plastics and stainless steel. The samples were subsequently transferred to polypropylene bottles without filtering or other pretreatment.

The pH-pe measurements were performed *in situ* using a probe (Lidén et al. 1980). All pH measurements refer to the NBS buffer scale. The concentrations of the dissolved main components were determined by the following methods: Ca^{2+} + Mg^{2+} = EDTA-titration; Mg^{2+} – atomic absorption spectroscopy; Na^+ and K^+ – atomic emission spectroscopy; dissolved silica – the silica molybdo blue method (Koch 1964); Cl^- – ion selective electrode using the standard addition method; SO_4^{2-} – colorimetrically by the Thorin-method (Persson 1966); alkalinity – potentiometric titration. Aluminium was determined by a spectrofluorometric method using the reagent Lumogallion (Hydes and Liss 1976). The samples for Al analyses were filtered through a 0.10 μm Millipore filter in field and transferred directly into preweighed polypropylene bottles containing the acetate- Lumogallion buffer solution. The sampler and acetate buffer together yielded a blank concentration of ≈ 6 nM.

The sampled water from all bore holes contained varying degrees of finely

suspended matter originating from the walls of the holes. The mineralogy of some of this suspended matter were investigated by X-ray diffraction (XRD) on a Philips OW 050/80 instrument. Special attention was paid to the presence of clay minerals.

Results from Field Measurements

The analytical results of 9 different bore holes from the three investigated areas are summarized in Table 1. Except for the bore hole SV 32, no significant depth gradient in pH could be observed down in the bedrock. Therefore only one depth level per hole was sampled for further ionic analysis since the intention was to follow the dependence of the ionic constituents on pH over as broad an interval as possible. All samples were taken at minimum 15 m below the soil-bedrock interface, which proved to be sufficient to prevent the contamination from the iron-tubing that penetrated the soil cover.

Notable for the holes from Svansele is the significant concentration variation in solution composition despite that all bore holes are located only some hundred metres apart from each other in a non-variant terrain-type. This observation is also relevant to the Kankberg area although not all these holes were completely sampled. Common for all holes, but less conspicuous for KA 54 and 96, are the time constancy of the quantities pH, alkalinity and $[Si(OH)_4]$. Regularly the repeatability in pH was within 0.05 units, 15-40 µM in the alkalinity and about 20 µM in the $[Si(OH)_4]$ over the period August 1978 to November 1979. The higher content of Na^+ and Cl^- in the bore holes from Svansele and Rengård compared to the bore holes from Kankberg is most likely due to contributions from relict sea water.

Fe^{2+} was not included in the analysis, but only in one bore hole (SV 39) any precipitation of FeOOH could be observed by visual inspection after exposing the sample to air. Hence the systematic overrepresentation of negative charges cannot be explained by the lack of Fe^{2+}-data.

According to the examination of core samples by the Boliden Metal Company, the rock type in all bore holes are characterized as keratophyre, quartzite and sericite. This means a mineral assembly dominated by sodium rich plagioclases, quartz, potash-feldspar and clays.

The presence of these minerals could be verified by the XRD analysis on suspended matter from the bore holes SV 24, SV 32 and RE 18. In addition illite and chlorite type clays were also present in all three samples. As will be shown later, experimental data indicated the presence of an Al-controlling solid phase. Therefore, special attention was paid to identify kaolinite in the XRD analysis. However, interference from the chlorite and illite peaks made it impossible to unequivocally prove the presence of kaolinite.

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Table 1 – Concentrations (in μmoles/1) of the analysed components from bore holes in Svansele, Rengård and Kankberg. The water temperature was 3-4°C in all holes. Sampling depth within parentheses.

Constituent	RE 8 (33 m)	RE 14 (33 m)	RE 17 (40 m)	KA 54 (40 m)*	KA 96 (40 m)*	SV 24 (45 m)*	SV 32 (45 m)	SV 32 (60 m)	SV 36 (50 m)	SV 39 (60 m)
pH	7.85	8.05	8.0	6.5	6.8	7.05	8.6	8.45	7.7	7.3
pe	-1	-3	-1	7	8	5	-9	-9	-9	-1
Na^+	170	260	190	110	90	130	420	410	180	140
K^+	60	60	70	10	10	60	110	110	70	100
Ca^{2+}	560	590	580	290	220	620	730	740	700	960
Mg^{2+}	140	190	170	30	20	140	140	140	120	140
Al_{TOT}	52×10^{-3}	35×10^{-3}	55×10^{-3}	36×10^{-3}	220×10^{-3}	<DL	130×10^{-3}	73×10^{-3}	10×10^{-3}	<DL
$Si(OH)_4$	290	250	290	230	180	210	260	200	190	250
Alkalinity	1500	1590	1570	280	450	1310	1600	1630	1470	2070
Cl^-	100	110	60	70	<DL	60	480	550	170	110
SO_4^{2-}	60	110	100	240	100	210	120	100	180	150
$\Sigma C_i^+ Z_i - \Sigma C_i^- Z_i$	-90	-40	-70	-70	-70	-80	-50	-100	-110	-40

* Suspendate brown from iron oxides.
<DL Lower than the detection limit.

Equilibrium Model Calculations

Considering the time that had been allowed for the water-rock system in the bore holes to interact and the time invariant concentrations of several of the measured quantities, these waters were found suitable for a test of the validity of an equilibrium approach. This approach was based on a series of equilibrium model calculations performed with thermodynamic data selected from the literature and treated with the computer program SOLGASWATER.

In order to define the different equilibrium model systems a certain number of chemical species, i.e. components, were chosen (see Ingri 1977). These components, H^+-$Si(OH)_4$-Al^{3+}-Na^+-K^+-Mg^{2+}-Ca^{2+}-H_2CO_3, are the minimum number of chemical species required to describe the composition of all phases and solute species. H_2O is not considered in Table 2 since its activity is set to unity in the calculations. The anions Cl^- and SO_4^{2-} were not considered in the model experiments since they are not included in the silicate minerals.

The application of equilibrium constants of silicate minerals to natural water model systems is associated with some difficult problems. First, the equilibrium constants are usually not experimentally obtained but extrapolated using data (e.g. heat capacities, entropies) from elevated temperatures. In some cases even the thermodynamic data at elevated temperatures are estimated. Secondly, the silicate phases occurring in nature are not idealized pure phases, but instead solid solutions are ubiquitous. In Table 2 the formation constants for the solid phases are extrapolated to 0°C and an ionic strength of 0.1 M (Sjöberg 1983). Considering the uncertainties mentioned above, it was not found worthy to pursue the extrapolations to still lower ionic strengths. The equilibrium constants for the solid phases are with only few exceptions selected from one source (Helgeson 1969) in order to make the data consistent.

In a first set of model calculations the answer to the following question was sought for: what is the resulting pH and ionic composition when pure water with a p_{CO2} correspondong to atmospheric air is equilibrated with either of the four minerals albite, anorthite, microcline or chlorite? Note that it was not assumed that an equilibrium between atmospheric air and a ground water in the deep rock was attained by setting p_{CO2} fix. The reason was rather to allow sufficient formation of HCO_3^- to balance dissolved cations to satisfy the electro-neutrality condition.

The results of the model experiments are shown in Table 3. From the table it may be concluded that all four minerals will tend to increase the pH of a H_2O-CO_2(aq) system to slightly alkaline pH values. Further it is evident that the resulting total concentrations of the different components in solution with few exceptions will be in reasonable good agreement with the experimental results. It is only the $[Na^+]$ and the $[Si(OH)_4]$ in the albite calculation that exceed the observed concentrations by approximately one order of magnitude. The resulting

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pH for the two end members of the plagioclase series will be around 8.5. According to the calculations anorthite was soluble enough to be completely transformed into the secondary minerals calcite and kaolinite. The less soluble microline gave a lower pH (= 7.48). The trace constituent in solution, Al, was sensitive for the choice of the hydrolysis constants and this element will therefore be treated separately in later paragraphs.

The conclusion of the set of equilibrium calculations above is that although the included components are not controlled by these four minerals in the sense of a reversible reaction, the concentration of the dissolved main components as well as the pH of the more alkaline bore holes of Table 1 will be governed by the mineral solubility.

In order to illustrate how much the equilibrium constants of the solids in Table 2 must be adjusted in order to completely explain the experimentally found concentrations, Table 4 is given. In this table log a (where a stands for activity) of some minerals that are relevant in the investigated bore holes have been calculated over the experimentally covered pH-range. The activities are calculated for a solution composition that representts a mean of the data from the bore holes. A negative value of log a indicates that the solid tends to dissolve and a log a larger than zero indicates that the solid is supersaturated and hence will not be a source of cations under the selected conditions. Provided that the thermodynamic data used to obtain the results in Table 4 were reasonably correct an adjustment of only some units in log K (1 unit in log K corresponds to 5.23 kJ mol^{-1} in $\triangle G_f^o$) would yield unit activity of all solids in Table 4 at a pH between 8 and 8.5.

Considering the uncertainties of the Gibbs free energies of formation of many silicates (Tardy and Garrels 1974) such an adjustment is within the estimated errors of the selected constants.

In the next set of theoretical experiments the resulting set of solid phases and solution composition after a stepwise variation of the pH from the original p_{CO2}-mineral value down to pH = 5.0 was calculated (cf. Figs. 1-3). These calculations illustrate how the selected mineral-water systems change when additional protons, emanating from e.g. pyrite oxidation are added. For all three figures is a trend towards increasing solubility as pH decreases, accompanied by phase transformations. Albite is successively converted into Na-montmorillonite and amorphous SiO_2. Microline is stable over the complete pH interval and secondary minerals

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1) Sjöberg (1983), Danielsson and Sjöberg (to be published)
2) Stumm and Morgan (1970)
3) Baes and Mesmer (1978)
4) Dyrssen and Wedborg (1980)
5) Helgeson (1969)
6) Estimated mean of the $\triangle G_f^o$-values of Helgeson and Zen (cf. Tardy and Garrels 1974)
* Valid at 25°C

Table 2 – Composition matrix (computer output) containing 22 aqueous species and 17 solid phases. Equilibrium constants $\beta_{pqr...}$ defined according to the general equilibria $\qquad pA + qB + rC + ... \Leftrightarrow A_pB_qC_r...; \beta_{pqr...}$

where $A \equiv H^+$, $B \equiv Si(OH)_4$, $C \equiv Al^{3+}$, $D \equiv Na^+$, $E \equiv K^+$, $F \equiv Mg^{2+}$, $G \equiv Ca^{2+}$, $H \equiv CO_2(aq)$. Most equilibirum constants in the solute phase are valid at infinite dilution whereas the β-values of the solids are valid at $I \equiv 0.1$ M. Unless otherwise stated the equilibrium constants have been extrapolated to $0°C$.

| Species/solids	$lg\beta_{pqr...}$	H^+ p	$Si(OH)_4$ q	Al^{3+} r	Na^+ s	K^+ t	Mg^{2+} u	Ca^{2+} v	$CO_2(aq)$ x
H^+	0.00	1	0	0	0	0	0	0	0
$OH-$	−14.90	−1	0	0	0	0	0	0	0 1)
H_2CO_3	0.00	0	0	0	0	0	0	0	1
HCO_3^-	−6.57	−1	0	0	0	0	0	0	1 2)
CO_3^{2-}	−17.17	−2	0	0	0	0	0	0	1 2)
$Si(OH)_4$	0.00	0	1	0	0	0	0	0	0
$SiO(OH)_3^-$	−10.30	−1	1	0	0	0	0	0	0 1)
$SiO_2(OH)_2^{2-}$	−24.94	−2	1	0	0	0	0	0	0 1)
Al^{3+}	0.00	0	0	1	0	0	0	0	0
$AlOH^{2+}$	−4.97	−1	0	1	0	0	0	0	0 3)*
$Al(OH)_2^+$	−9.30	−2	0	1	0	0	0	0	0 3)*
$Al(OH)_3$	−15.00	−3	0	1	0	0	0	0	0 3)*
$Al(OH)_4^-$	−23.00	−4	0	1	0	0	0	0	0 3)*
Na^+	0.00	0	0	0	1	0	0	0	0
K^+	0.00	0	0	0	0	1	0	0	0
Mg^{2+}	0.00	0	0	0	0	0	1	0	0
$MgOH^+$	−11.68	−1	0	0	0	0	1	0	0 4)
$MgHCO_3^+$	−5.84	−1	0	0	0	0	1	0	1 4)*
$MgCO_3$	−14.53	−2	0	0	0	0	1	0	1 4)*
Ca^{2+}	0.00	0	0	0	0	0	0	1	0
$CaHCO_3^+$	−5.79	−1	0	0	0	0	0	1	1 4)*
$CaCO_3$	−14.26	−2	0	0	0	0	0	1	1 4)*
am. SiO_2	2.74	0	1	0	0	0	0	0	0
Mikroklin	−2.13	−4	3	1	0	1	0	0	0 5)
Albit	−5.18	−4	3	1	1	0	0	0	0 5)
Illit	−13.54	−8	3.5	2.3	0	0.6	0.25	0	0 5)
Kaolinit	−10.25	−6	2	2	0	0	0	0	0 5)
Klorit	−69.00	−16	3	2	0	0	5	0	0 6)
Na-mont.	−27.87	−22	11	7	1	0	0	0	0 5)
Muskovit	−21.46	−10	3	3	0	1	0	0	0 5)
K-mont.	−26.90	−22	11	7	0	1	0	0	0 5)
Tremolit	−63.07	−14	8	0	0	0	5	2	0 5)
Mg-mont.	−54.99	−44	22	14	0	0	1	0	0 5)
Levcit	−10.02	−4	2	1	0	1	0	0	0 5)
Ca-mont.	−55.24	−44	22	14	0	0	0	1	0 5)
Anortit	−29.51	−8	2	2	0	0	0	1	0 5)
Analcim	−11.14	−4	2	1	1	0	0	0	0 5)
Kalcit	−8.85	−2	0	0	0	0	0	1	1 6)
Gibbsit	−9.60	−3	0	1.0	.0	0	0	0	0 5)

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Table 3 – The resulting equilibrium concentrations in solution and stable solid phases after equilibrating 1 mol of a mineral with 1 l H_2O and a p_{CO_2} corresponding to atmospheric air.

Mineral	pH	log[Si(OH)$_4$]	log[Me]	log[Al$_{TOT}$]	log[alkalinity]	Stable phases
NaAlSi$_3$O$_8$	8.56	–2.73	–2.60	–6.89	–2.60	albite, Na-montmorillonite, am. SiO$_2$
CaAl$_2$Si$_2$O$_8$	8.31	–4.47	–3.16	–4.91	–2.85	calcite, kaolinite
KAlSi$_3$O$_8$	7.48	–3.39	–3.69	–6.36	–3.69	microline, kaolinite
Mg$_5$Al$_2$Si$_3$O$_{10}$(OH)$_8$	8.02	–4.13	–3.46	–5.43	–3.15	chlorite, kaolinite

Table 4 – The logarithm of the activity of some solids in contact with a solution of the following composition log[Si(OH)$_4$] = –3.63, log[Na$^+$] = –3.68, log[K$^+$] = –4.18, log[Mg^{2+}] = –3.91, log[Ca^{2+}] = –3.22, log[CO$_2$(aq)] = –4.61. Log[Al^{3+}] corresponds to an equilibrium with kaolinite. All equilibrium constants as in Table 2.

pH	log[Al^{3+}]	Microcline	Albite	Illite	Chlorite	Calcite
8.5	–15.90	0.90	–1.65	1.70	4.76	0.32
8.0	–14.40	0.40	–2.15	1.15	–0.24	–0.68
7.5	–12.90	–0.10	–2.65	0.60	–5.24	–1.68
7.0	–11.40	–0.60	–3.15	0.05	–10.24	–2.68
6.5	–9.90	–1.10	–3.65	–0.50	–15.24	–3.68
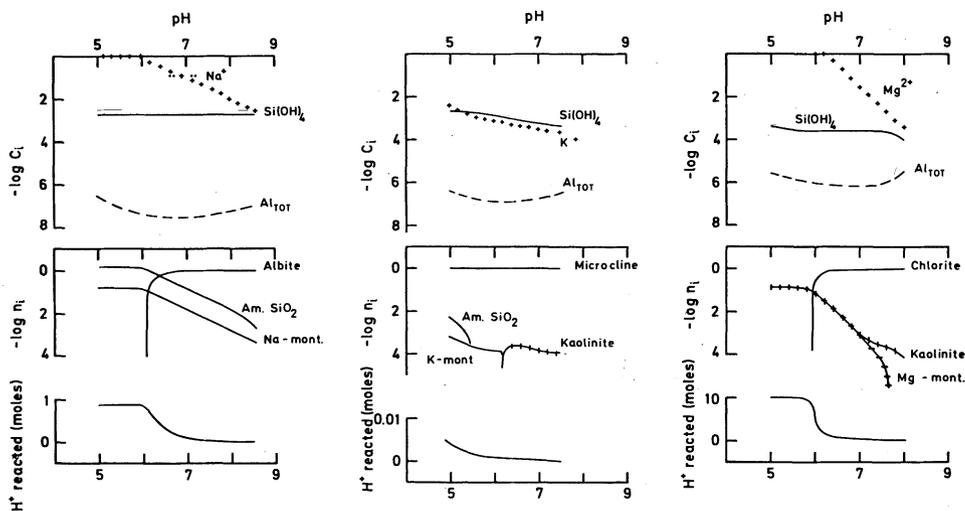
Figs. 1-3. The solution composition and absolute amounts (moles) of solids formed calculated at each pH corresponding values given in Table 3 and pH $\equiv$ 5 for albite, microcline and chlorite respectively. At the bottom of each figure the number of moles H^+ neutralized by the mineral dissolution are given. All calculations assume 1 mole of mineral in contact with 1 l of solution.

are formed only in small amounts, and chlorite is completely converted into kaolinite and Mg-montmorillonite at a pH < 6. Since anorthite showed to be unstable with respect to kaolinite and calcite even at pH of 8.5 this mineral was excluded here.

To illustrate the pH-buffer characteristics of the model systems, a 'titration curve' was included in each of the figures 1-3. Clearly, an addition of protons to albite and chlorite must be done in large amounts in order to get a pH below the value where the buffer intensity (= $\delta H^+_{reacted}/\delta$ pH) starts to raise. From an equilibrium standpoint the pH of ground water in contact with albite or chlorite should therefore not be expected to be below neutrality. However, the 'titration curves' indicate that the high pH obtained in the previous pure water-mineral equilibirum calculations is poorly buffered. Contradictory to albite and chlorite, microcline buffers poorly over the complete pH-interval 8-5. Similar to the results of Table 3 the discussion above concerning Figs. 1-3 is of a qualitative nature. A quantitative interpretation of the figures suggests that the concentrations of the main species in solution (except Al) would increase as a function of pH in a way that is not observed in nature (Paces 1971, Lahermo 1971). It is also evident that Table 1 does not show any systematic trend in alkali ion concentrations with pH. This means that if an equilibrium control were to prevail the pH value in the bore holes would either always be slightly alkaline or very salty. Clearly, lower pH

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values indicate that the aqueous phase and the solid phases interact so slowly that the measured pH-value will be ruled by the solution composition alone. That is, in a natural environment where an addition of 'foreign' protons is frequent the ground-water chemistry will be kinetically controlled. If equilibrium reactions were to control the large amounts of cations released from primary silicates some types of reverse weathering had to be effective. However, experimental evidence for the formation of secondary silicates containing alkali ions is lacking. According to laboratory experiments (Busenberg 1976, 1978, Petrovic 1976) the cryptocrystalline phases formed after artificial weathering contain only Al and Si. After direct study of the surfaces of feldspar grains sampled in various soils using XPS and SEM (X-ray Photo electron Spectroscopy; Scanning Electron Microscopy) analysis, Berner and Holdren (1979) were unable to find any weathering products other than some of kaolinite type phase.

The influence of pH on the cation concentrations according to an equilibrium model is likewise relevant for clay minerals that, if present in sufficient amounts, may act reversible as cation exchangers. Notable is that this pattern is independent of the value of log K and hence cannot be dismissed as an effect of poor thermodynamical data.

The subsystem H^+-$Si(OH)_4$-Al^{3+} has been proposed by several workers as controlling the aqueous concentrations of aluminium. Paces (1973, 1978) has interpreted field data in the three component system above as due to the presence of a reversible reaction between solution and a cryptocrystalline aluminosilicate of varied composition. Hem et al. (1973) and Busenberg (1978) explained their experimental results by a halloysite type phase (the same empirical formula as kaolinite). Using the appropriate data of Table 1 it may be concluded that the total dissolved Al follows a pattern which is in agreement with an equilibrium control (cf. Fig. 4) by kaolinite.

The calculated reaction quotients for the tentative phase $Al_2(OH)_4Si_2O_5$ are given in Table 5. Since the data of both Hem and Busenberg represent freshly

Table 5 – The reaction quotient of the equilibrium $2Al^{3+} + 2Si(OH)_4 + H_2O \Leftrightarrow Al_2(OH)_4Si_2O_5(s) + 6H^+$. Concentration data from Table 1 and Al-hydrolysis data from Table 2.

Source	log Q	Phase
This investigation	−8.5	Tentative composition
This investigation	38.1*	Tentative composition
Busenberg (1978)	−11.58	Halloysite
Hem (1973)	−11.28	Halloysite
Kittrick (1966)	−7.19	Kaolinite

* represents the reaction $2Al(OH)_4^- + 2Si(OH)_4 \Leftrightarrow Al_2(OH)_4Si_2O_5(s) + 7H_2O$ assuming $[Al]_{exp} = Al(OH)_4^-$.
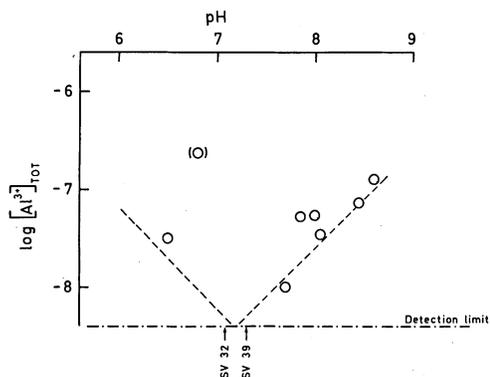
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Fig. 4. The total concentration of dissolved aluminium from water samples filtered through a 0.10 μm filter plotted versus pH measured in situ. The solid lines drawn represent the theoretical slope for the concentrations of $Al(OH)_2^+$ and $Al(OH)_4^-$ respectively in equilibrium with kaolinite. Note that the lines are not fitted to the data by any regression analysis.

precipitated phases their apparent constants have been used to calculate probable Al-concentrations in natural waters where pH and $\log[Si(OH)_4]$ are known. It is therefore worthy to note that the result presented here, valid for a field investigation, predicts a significantly lower solubility than that of halloysite. By approximating the measured Al-concentration to $[Al(OH)_4^-]$ and using only data from Fig. 4 for which pH > 7.5 the calculated reaction quotient will be independent of Al-hydrolysis constants. It may also be observed from Fig. 4 that the solubility minimum is about 0.5 pH units more alkaline than in the model experiments. This may at least in part be explained by the fact that Fig. 4 represents a temperature of 3°C but the hydrolysis constants of Al used are valid for 25°C because no appropriate enthalpy data are available. Generally, the hydrolysis of cations becomes weaker at lower temperatures and therefore the use of data valid at 0°C would shift the model solubility minimum towards a more alkaline pH.

The Redox Level

Because of the lack of redox couples occurring in sufficient amounts and with fast and reversible electrode kinetics enough, pe-values measured in natural waters are, except in some few cases (Boulege 1977) not possible to use quantitatively (Stumm and Morgen 1970, Whitfield 1973). As a qualitative information, however, parallels can be drawn between the experimental pe-values of Table 1 and the theoretical redox titration curve shown in Fig. 5. In ground waters where the inflow of oxidants is negligible with respect to rate of consumption one could expect pe at the negative side of the S_2^{2-}-SO_4^{2-} buffer extension. In other systems where the oxidation of sulfide minerals is more rapid one could expect pe to be
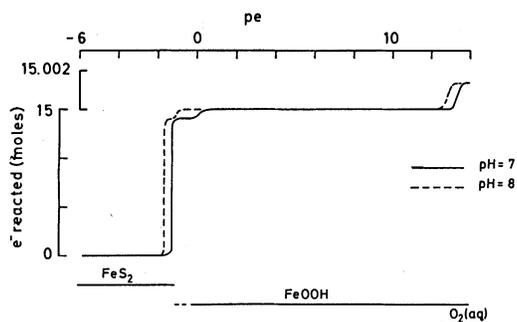
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Fig. 5. The imaginary redox titration curve when an oxidant (e.g. oxygen) is added in portions to 1 mol of pyrite in 1 l of solution. The following equilibria have been considered $FeS_2 + 8H_2O \Leftrightarrow Fe^{2+} + 2SO_4^{2-} + 14e^- + 16H^+$; log K $\equiv$ −85.4
$Fe^{2+} + 2H_2O \Leftrightarrow FeOOH(s) + e^- + 3H^+$; log K = −18.3
$2H_2O \Leftrightarrow O_2(aq) + 4H^+ + 4e^-$; log K $\equiv$ −85.8

The extension of the stability of FeS_2, FeOOH and $O_2(aq)$ (> 10 μM) have been -marked by lines.

buffered by conversion of Fe^{2+} into FeOOH. The oxidation of Fe^{2+} by dissolved oxygen is rapid on the time scale of weathering (Pankowich and Morgan 1981). Therefore it is likely that a situation develops where all introduced oxygen reacts with ferrous iron to form a Fe^{2+}-FeOOH redox couple. In a third case, if the inflow of oxygen is more rapid than the mobilisation of Fe^{2+} from silicate weathering or pyrite oxidation, the measured redox level will be significantly influenced by dissolved oxygen. If the measured pe-values are interpreted according to this discussion the bore holes SV 32, SV 39 and RE 8-17 represent situations of negligible or very small influence from dissolved oxygen. In the bore holes KA 54-96 and SV 24 the turnover rate of oxygenated water is faster than the time required for redox reactions and as a consequence the measured pe is high. As both the oxidation of pyrite and Fe^{2+} by oxygen release protons, it should be noted that the bore holes with the highest pe-values have the most acid pH. Consequently, in the bore holes where the most reducing conditions prevail little foreign protons are added and the pH is high as predicted for the undisturbed silicate mineral-water systems discussed previously.

Conclusions

If the solution composition resulting from an equilibration between representative silicate minerals and pure water of p_{CO2} corresponding to air is calculated, one finds reasonable agreement (log-units) with field data. These theoretical experiments suggest that in an undisturbed ground water (i.e. negligible inflow of excess

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protons) the primary silicate minerals will tend to increase the pH to slightly alkaline values where the dissolved main components reach an irreversible saturation value. Another criterion of an undisturbed system would be a low pe buffered by sulfide in FeS_2 or Fe^{2+} resulting from e.g. pyroxene weathering since no pe raising oxidant as inflowing dissolved oxygen will be present.

However, if the solution composition after an addition of protons is simulated by a stepwise decrease in pH, it is obvious that silicate minerals, including secondary clay minerals, react too slowly to control the ground water by means of any equilibrium reaction. For most silicate solution equilibria one unit change in pH would require a tenfold or larger change in the concentration of main cations. Such a dependency upon pH is not observed in nature.

The only main component of the silicate minerals modeled where reversible equilibrium reactions seem to control the solution composition is aluminium.

Although a silicate mineral-water equilibirum obviously does not prevail in a system where pH has been decreased by the addition of protons, it is important to realize the strong pH-buffer that has to be crossed in order to convevt e.g. a plagioclase to dissolved ions. This means that as long as these primary silicates remain in the system the pH will always strive towards the alkaline side.

Acknowledgements

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