

CHEMISTRY OF SOME GROUND WATERS IN IGNEOUS ROCKS

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Chemical changes in water circulating deep in the fissures of the solid rock are studied. The ultimate chemical composition is determined by the conditions of percolation through the soil zone. For each liter of water 1 g of mineral will be destroyed. An alkaline environment favors an early formation of Na-montmorillonite. The turnover time varies from some years to thousands of years.

This paper deals mainly with the chemical changes in water circulating deep in the fissures of the solid rock. Much of the ultimate chemical composition is determined by the conditions of percolation through the soil zone, where the water is acidified when dissolving carbon dioxide. Cation to H^+ ratios are used as indicators of the progress of weathering. A set of clay minerals is formed as the result of weathering. For each liter of water about 1 g of minerals will be destroyed. The bulk of these are plagioclases. The weathering course depends on the environment. An alkaline environment favors an early formation of Na-montmorillonite. The turn-over time of these ground waters is highly variable, from some years to thousands of years, which can be demonstrated by studying their chemistry.

Sampling, analysis and treatment of data

Sampling has been made in the following areas in Sweden: Stockholm, Gothenburg, Bergslagen, Blekinge, Småland, and Piteå. The rock in these areas consists

of archean granites and gneisses. In Bergslagen the rock is leptonite, a crystalline rhyolitic rock. The sampling was made in wells drilled to depths between 60 and 100 m. Some samples were taken in tunnels and in mines. pH generally was measured in the field. On some samples the redox potential (E_h) also was measured. In non-producing wells, water was extracted from different depths by means of a special sampler.

The samples have been analyzed in the laboratory at the Department of Land Improvement and Drainage, Royal Institute of Technology, Stockholm. The laboratory is one of those intercalibrated within the IHD program in Scandinavia.

For the equilibrium calculations, activities instead of concentrations were used because using concentrations would give systematic errors due to the fact that the activity coefficient is less than 1 for all charged species. Uncharged species such as H_4SiO_4 can have an activity coefficient larger than 1, but this was judged to be negligible here.

The equilibrium considerations are based on ionic ratios in logarithmic form. If cations in solution are complexed to a considerable degree, this will affect the equilibrium computations. According to Pačes (1969) $CaHCO_3^+$ and $CaSO_4(aq)$ would be expected to be the most abundant complexes in water from granitic-gneissic rocks. In order to check the effect of complexing a water rich in Ca^{++} , HCO_3^- and SO_4^{--} was chosen. Equilibrium constants were those of Garrels & Thompson (1962). The calculations comprise a couple of iterative procedures.

Sample: Kopparmora, Värmdö by Stockholm

| No complexing | | | Complexing | | | | |
|-------------------------------|------|--------|-------------------------------|------|---------------------------------|-------|--------|
| K ⁺ | 0.12 | mmol/l | K ⁺ | 0.12 | CaHCO ₃ ⁺ | 0.071 | mmol/l |
| Na ⁺ | 2.98 | | Na ⁺ | 2.97 | CaSO ₄ | 0.042 | |
| Ca ⁺⁺ | 1.39 | | Ca ⁺⁺ | 1.26 | CaCO ₃ | 0.018 | |
| Mg ⁺⁺ | 0.52 | | Mg ⁺⁺ | 0.47 | MgHCO ₃ ⁺ | 0.021 | |
| Cl ⁻ | 0.70 | | Cl ⁻ | 0.70 | MgSO ₄ | 0.018 | |
| SO ₄ ⁻⁻ | 0.43 | | SO ₄ ⁻⁻ | 0.37 | MgCO ₃ | 0.011 | |
| HCO ₃ ⁻ | 5.20 | | HCO ₃ ⁻ | 5.08 | Na-comp. | 0.01 | |

No more than 10 % of the total concentrations of Ca^{++} and Mg^{++} are tied up in complexes. Hence it has not been considered necessary to account for complex formation.

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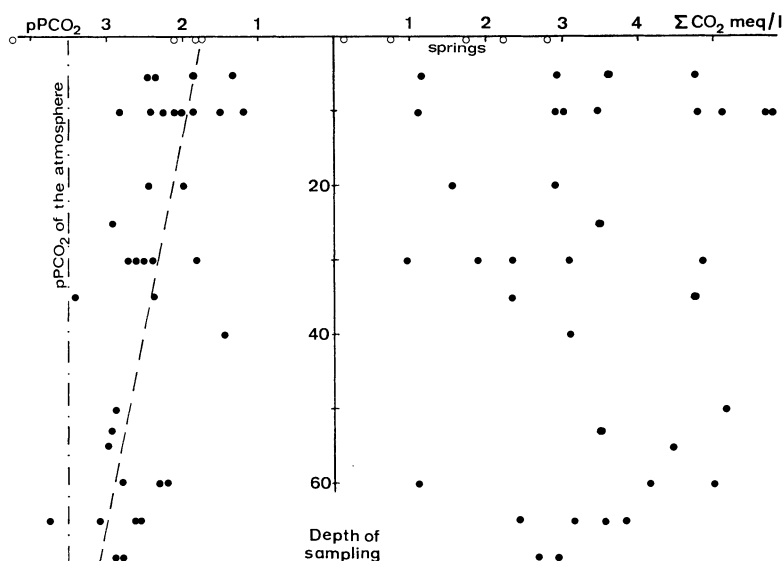


Fig. 1.

pPCO₂ (-log PCO₂) and total carbonate against depth of sampling for a number of waters from Gnesta and Skokloster, Stockholm area.

Infiltration conditions

There are mainly three ways by which ground water gets its dissolved salts. First, atmospheric deposition which is responsible for 0.3–1.1 meq/l of cations depending on the situation of the area. Second, by weathering of minerals in the soils and rocks. Third, by mixing in of sea water from glacial times, left over in the soil or in the rock. In addition to this there are also biologic processes. Root respiration gives off CO₂ to the soil atmosphere which is dissolved in the water. Breakdown of organic matter produces even more CO₂ and releases NH₄⁺, NO₃⁻ and SO₄⁻.

The acidity of percolating water is due mainly to the presence of dissolved CO₂ even if humic acids and chelating substances (e. g. salicylates, citrate, tartrate) also are active in destroying minerals (Stumm & Morgan 1970, Huang & Keller 1972). The atmosphere contains 0.03 % CO₂, while the soil atmosphere generally contains at least ten times more and even up to 10 % (Russel 1961). The composition of the soil atmosphere and the rate of percolation determine the initial acidity of the water and thus the ultimate quantity of cations in the water.

If infiltration is rapid, saturation with CO_2 occurs first and then when the water reaches the ground water table, weathering takes place. If infiltration is slow, weathering may take place already in the soil zone to a large degree and the water is continuously fed with CO_2 replacing what is consumed. It is obvious that the latter type of infiltration will give water more total carbonates ($\text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{--}$) and ultimately more cations.

Fig. 1 shows pPCO_2 ($-\log \text{PCO}_2$) and total carbonate in a number of wells in Gnesta and Skokloster near Stockholm. pPCO_2 varies from about 1.6 to near 3.5, i.e., the value in the atmosphere, at greater depth. Weathering consumes CO_2 as the water penetrates deeper. pPCO_2 is equivalent to 2.5 % CO_2 in the soil atmosphere. This partial pressure (0.025 atm) of CO_2 gives 1.6 meq/l CO_2 at equilibrium. In Fig. 1 it is seen that the waters contain about 3 meq/l as a rough mean. This means that weathering equivalent to about 1.4 meq/l CO_2 occurs during the passage though the soil zone. Fig. 1 shows that CO_2 is added only in the soil zone since total carbonate remains constant towards the depth. The variations in values therefore must be due to variations in infiltration conditions.

The partial pressure of CO_2 and the rate of infiltration of water in the soil are more or less soil characteristics and should be different in different kinds of soils and types of terrain. Troedsson (1955) stated that margins of bare rocks are important infiltration routes. In areas with much bare rock, biologic activity is slow due to lack of water. In such areas infiltrating water is expected to contain low total carbonate. This was also frequently observed in this investigation.

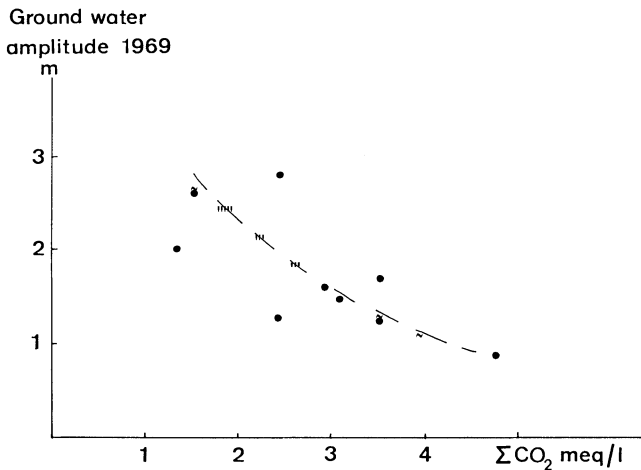


Fig. 2.

Total carbonate against groundwater amplitude for the year 1969 for the nine wells in Gnesta.

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Table 1.

| Area | Mean of ΣCO_2 | Stand. dev. | Samples | Terrain |
|-----------------------|-----------------------------|-------------|---------|-------------------------------|
| Gnesta, Stockholm | 2.6 | 1.1 | 27 | bare rocks, forest pasture |
| Skokloster, Stockholm | 4.4 | 1.3 | 14 | forest, pasture |
| Verka, Stockholm | 4.2 | 1.2 | 28 | arable land |
| Angered, Gothenburg | 1.5 | 0.5 | 12 | bare rocks, forest |
| Angered, Gothenburg | 2.9 | 2.1 | 13 | arable land |
| Bergslagen | 1.8 | 0.7 | 32 | forest |
| Blekinge & Småland | 2.4 | 0.9 | 15 | forest, pasture |
| Piteå | 2.4 | 1.2 | 13 | arable land |

If the rate of infiltration is high, this results in raising the ground water level after heavy rains or at snowmelt. Such wells are supposed to have large amplitude in ground water levels during the year. In Fig. 2, amplitude and total carbonate are plotted against each other for the nine wells in Gnesta. This shows some relationship.

Water having high total carbonate is observed to have a slightly raised Cl^- content. Water passing slowly through the soil is subjected to more intense evapotranspiration, raising Cl^- content.

The mean of total carbonate for different sampled areas has been calculated. This is interesting because the areas as well as the local climates are different. Climate is probably important, since in some parts of the country infiltration occurs throughout the year while in others infiltration is not possible because of frost or insufficient rain.

The most striking point in this is the two values from Gothenburg, with the two-fold difference between wells on the higher elevations (bare rocks, forest) and wells in the valleys (arable land). The value for the areas with bare rocks and forest in Angered is the lowest in the Table. This may be due to very good infiltration conditions, and also to the fact that a considerable infiltration occurs during winter when biologic activity, and hence partial pressure of CO_2 , is low. Skokloster has an anomalously high value, and Verka also has a high value. This may be due to the presence of calcite in the soil. On weathering, calcite also adds carbonate to the water. According to Lindström (1898) and Gillberg (1967), calcite is common in clays and fine fractions of moraine north of Stock-

holm (Skokloster and Verka). Calcite in soil is much less abundant south of Stockholm (Gnesta).

As a contrast to the given figures, and to illustrate the importance of biologic activity, it may be mentioned that the total carbonates in some ground waters collected by Danell & Wahlberg (1970) in the Kebnekaise mountains were 0.2–0.3 meq/l.

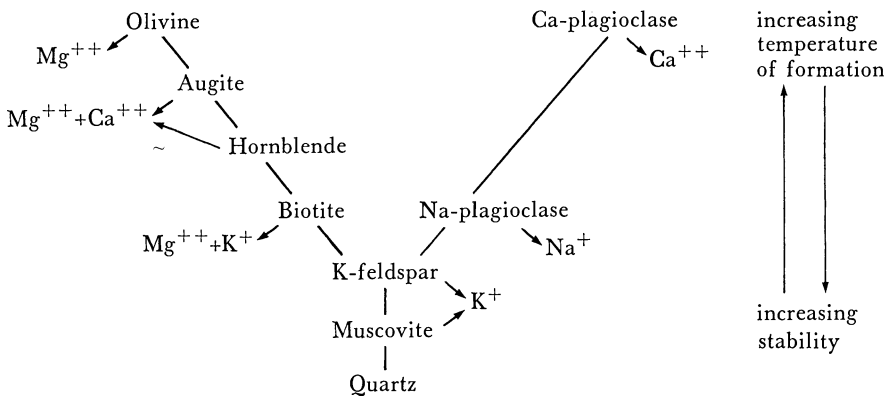
Weatherability of minerals and rocks

Some components in rocks are more easily dissolved than others. Lukashev (1958) gave the following relative mobilities of rock constituents in relation to chloride:

| | | | | | |
|-----------------|-----|----|------|--------------------------------|------|
| Cl | 100 | Ca | 3.00 | SiO ₂ | 0.20 |
| SO ₄ | 60 | Na | 2.40 | Fe ₂ O ₃ | 0.04 |
| | | Mg | 1.31 | Al ₂ O ₃ | 0.02 |
| | | K | 1.25 | | |

Weathering means that soluble minerals are partly dissolved and partly transformed into more insoluble secondary minerals. The type of weathering and minerals formed depends mainly on the nature of the solution in contact with the rock. When a rock weathers it becomes richer in components with low mobilities. Extremes in this evolution are laterites and bauxites.

The sensitivity of minerals to weathering is mainly a function of the temperature of formation. One of the earliest workers in this field, Goldich (1938), found that weathering follows the crystallization order according to Bowen (1928):



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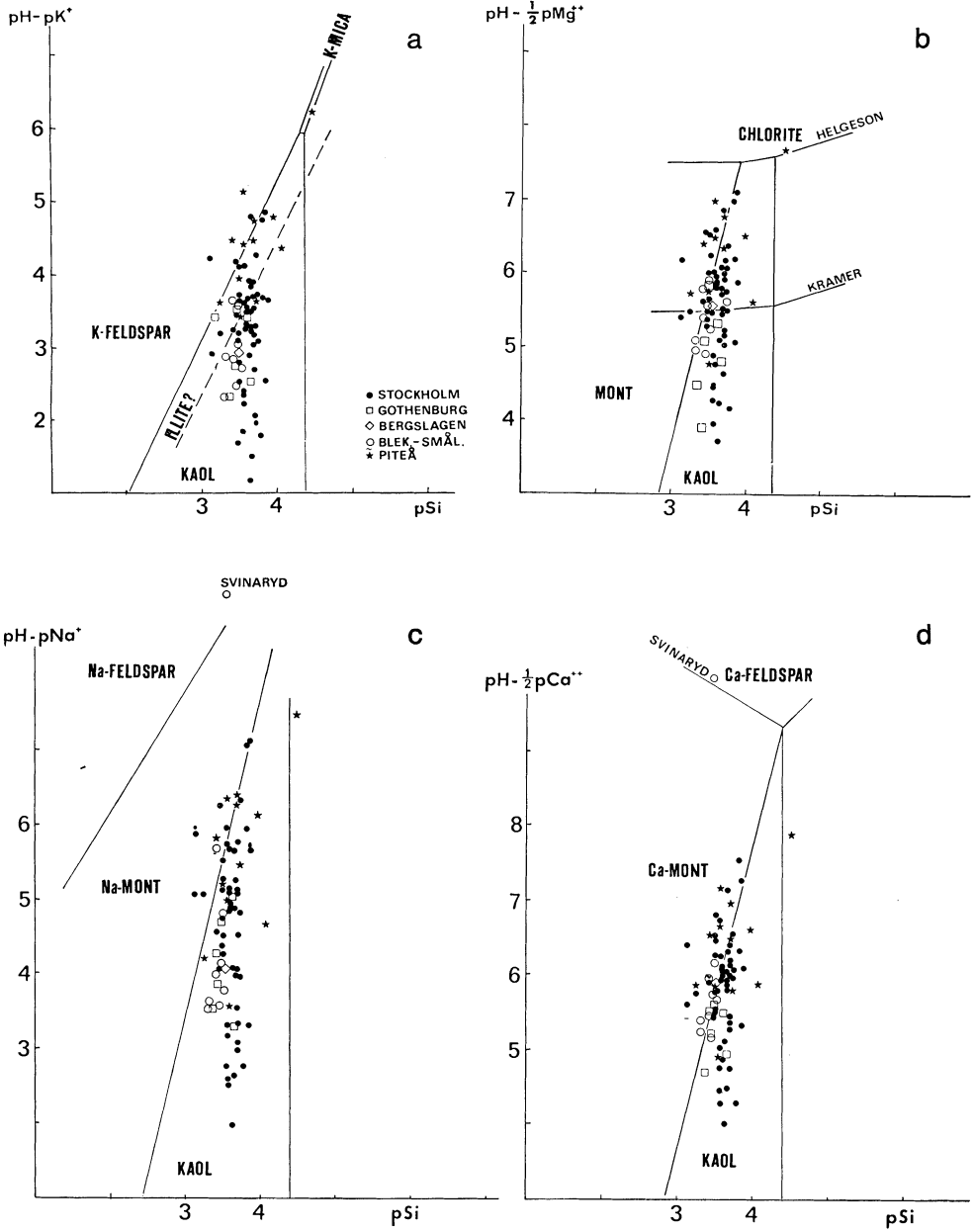


Fig. 3.

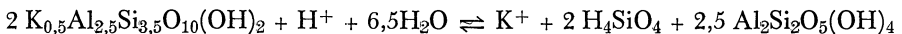
Stability diagrams for K-, Mg-, Na- and Ca-silicates. Data after Kramer (1968) and Helgeson (1969) extrapolated to 7°C, 1 atm.

The real course of events when a mineral is subjected to weathering is a question that has caused much debate in the literature. The hydrogen ion is responsible for the initial attack because of its unique charge-to-radius ratio (Loughnan 1969). In recent literature most investigators are agreed that this leads to complete collapse of the mineral into sub-units (Correns 1961, Loughnan 1969). Some of these sub-units are dissolved and ions are removed, while some are used up in assembling secondary minerals.

MINERAL-WATER EQUILIBRIA

If individual cations are plotted against total salinity or alkalinity (Figs. 6, 7, 8) it will be seen that some of the cations reach saturation as weathering proceeds. Alkalinity is a good parameter as HCO_3^- is the only anion produced in water with CO_2 -acidity. The saturation with respect to some cations is due to the formation of a set of stable secondary minerals. From thermodynamic data it is possible to construct stability diagrams for mineral associations (Garrels & Christ 1965, Eriksson & Khunakasem 1968). (Fig. 3).

K^+ appears to be the first ion to reach saturation. From Fig. 3 it seems obvious that the primary minerals K-feldspar and muscovite are not far from being stable in water from the beginning of the weathering process. Kramer (1968) placed the boundary kaolinite-muscovite even lower, at $\text{pH}-\text{pK}^+ \cong 4$. K^+ added to the water probably comes from the sensitive biotite. K^+ from biotite can be fixed in secondarily formed illite. Thermodynamic data are not abundant in the literature (Kramer 1968, Karpov et al. 1968, Helgeson 1969, Routson & Kittrick 1971) nor do they fit very nicely into the stability diagram. Illite is a common mineral, however, and it seems likely that the equilibrium kaolinite-illite is reached. In order to check this hypothesis it is necessary to calculate the equilibrium constant and observe whether the expression gives a constant value.



$$\frac{a_{\text{K}^+} \cdot a_{\text{H}_4\text{SiO}_4}^2}{a_{\text{H}^+}} = K \quad (\text{a} = \text{activity})$$

If this is treated logarithmically, then

$$\text{pH} - \text{pK}^+ - 2\text{pH}_4\text{SiO}_4 = -\text{pK}$$

and if this is plotted against alkalinity as in Fig. 4 it is seen that an equilibrium is attained at an alkalinity of about 2 meq/l. The alkalinity is not in the formula, but is produced by the reactions:

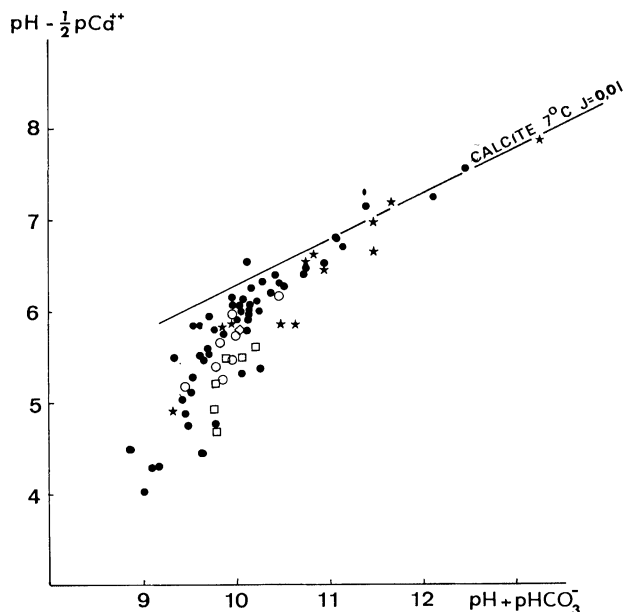
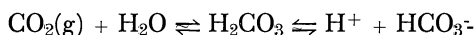
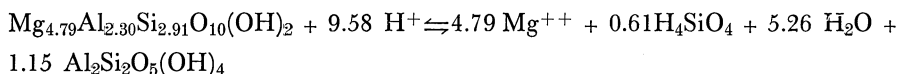


Fig. 4.

Stability diagram for calcite at 7°C and ionic strength of solution = 0.01.



Mg^{++} behaves as K^+ . Its origin is generally biotite, which can be transformed to vermiculite or chlorite (Barshad 1948, Loughnan 1969). A possible equilibrium is that of kaolinite-chlorite.



$$\frac{a_{\text{Mg}^{++}}^{4.79} \cdot a_{\text{H}_4\text{SiO}_4}^{0.61}}{a_{\text{H}^+}^{9.58}} = K$$

This gives in logarithmic terms:

$$\text{pH} - \frac{1}{2}\text{pMg}^{++} - 0.06\text{pH}_4\text{SiO}_4 = -\text{pK}/9.58$$

This expression also goes to equilibrium, and has the theoretical value given by Kramer (1968).

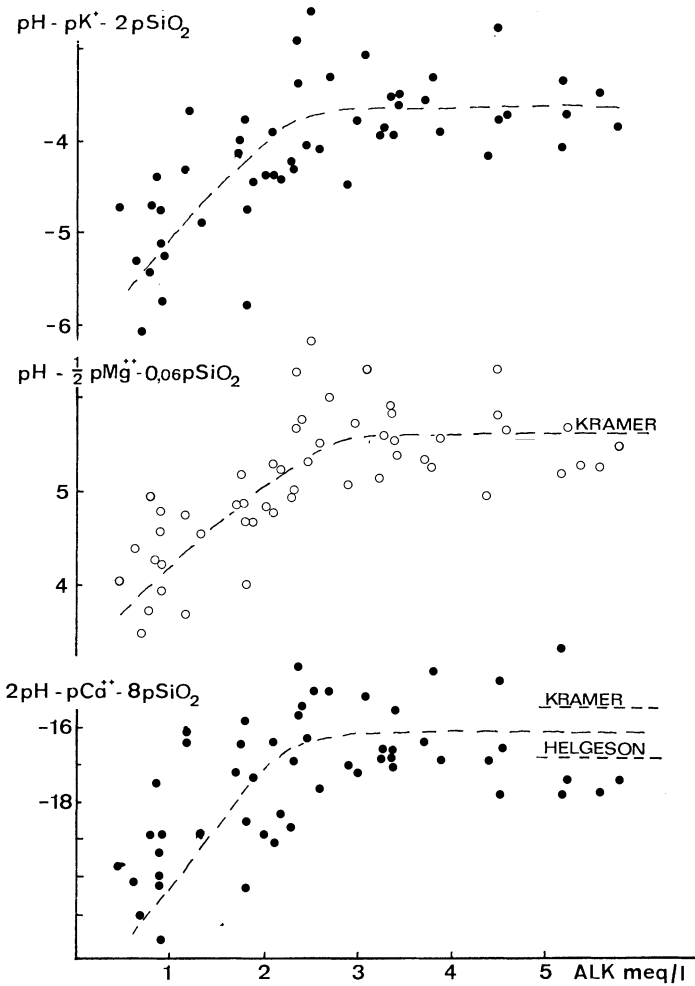
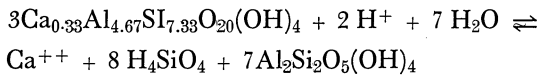


Fig. 5.
Mineral-water equilibrium expressions plotted against alkalinity.

The third ion to show saturation (Figs. 6,7) is Ca^{++} . From the stability diagram it could be concluded that this depends on the formation of Ca-montmorillonite in addition to kaolinite.



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$$\frac{a_{Ca^{++}} \cdot a_{H_4SiO_4}^8}{a_{H^+}^2} = K$$

$$\text{or } 2pH - pCa^{++} - 8pH_4SiO_4 = -pK$$

This expression is also plotted against alkalinity (Fig. 4) and it shows that the equilibrium is attained at about 2.5 meq/l alkalinity, slightly later than the above equilibria. The equilibrium suggested by the plot lies close to the values calculated from thermodynamic data by Kramer (1968) and Helgeson (1969).

It is, of course, possible that the solubility of calcite is reached and that this brings about the retention of Ca^{++} . From Fig. 4, however, it is evident that cal-

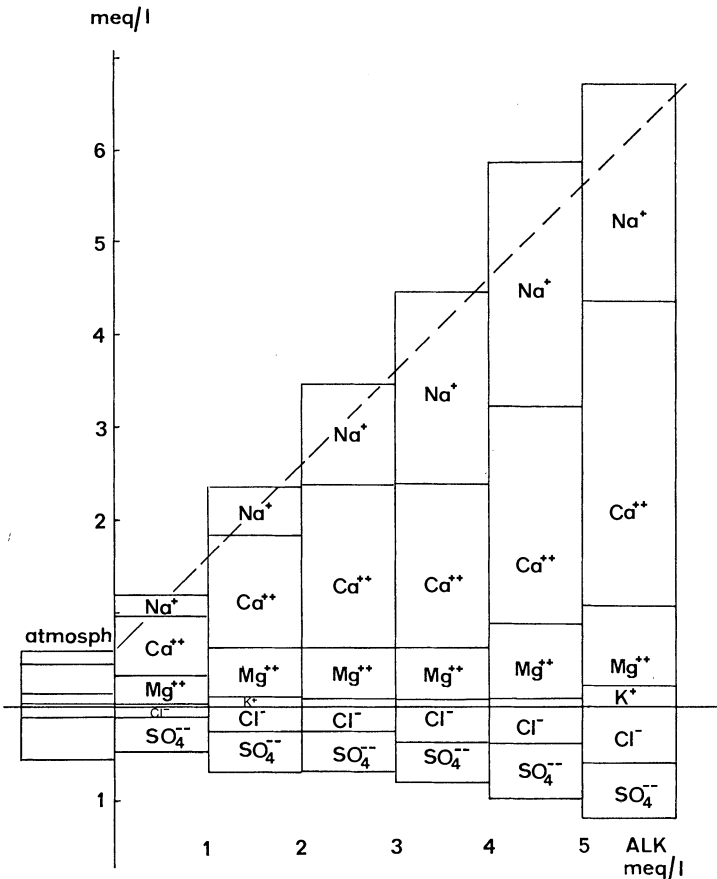


Fig. 6.
Stockholm area, staple diagram for anions and cations with alkalinity as parameter.
80 waters are included.

cite solubility is reached fairly seldom, and definitely later than Ca-montmorillonite stability.

In the last staples of the Stockholm diagram (Fig. 6) and the Gothenburg diagram (Fig. 7), Na^+ shows some tendency to be retained. From the stability diagrams it is evident that Na-montmorillonite is formed after Ca-montmorillonite, and generally under saline conditions. This will be discussed later.

In the stability diagrams, the Svinaryd well water is found to be in equilibrium with the primary minerals (Fig. 3). The well was drilled in a very solid rock and yielded no water. It was sampled two years after drilling. The water had obviously equilibrated with the fresh mineral surfaces on the walls and in the drilling mud.

The presence of the solid phases of the equilibria, the clay minerals, is documented in geological literature. Kaolinite and illite are common (Grönwall 1915, Lundqvist et al. 1931, Åhman 1961, Roosaar 1965) although montmorillonites are mentioned more often in later literature due to the technical importance of the swelling varieties when tunneling. A classic description of montmorillonite in a gneiss-granite was made by Eckermann (1954). Roosaar (1965) and Pusch (1970) mentioned several occurrences of montmorillonite and chlorite. Apart from this, chlorite is a very common mineral in metamorphic rocks.

Even under quite different climatological conditions, as in southern India, the same mineral association appears to form in the reaction between the water and the minerals in igneous rocks. In addition to the minerals mentioned above, amorphous silica appears to form as a result of intense evapotranspiration (Jacks 1973a).

It is not only the macro-constituents in ground water which are controlled by mineral-water equilibria. Jenne (1968) proposed that hydrous oxides of Mn and Fe furnish the principal control on the fixation of Co, Ni, Cu and Zn.

The solubility of fluoride in ground waters from igneous rocks appears to be restricted by the solubility of fluorite (Jacks 1973a).

Origin of chemical composition under weathering conditions

When the weathering reactions are known, it is possible to ponder the whole of the weathering process and progress. A good starting point is to construct staple diagrams for cations and anions using alkalinity as parameter. In water which has a CO_2 -acidity, alkalinity is a good measure of the progress of neutralization. Staple diagrams have been constructed for the Stockholm area, the Angered area in Gothenburg, and the Bergslagen area. In order to illustrate weathering conditions, only those analyses having Cl- contents below, and just above, 1 meq/l are included.

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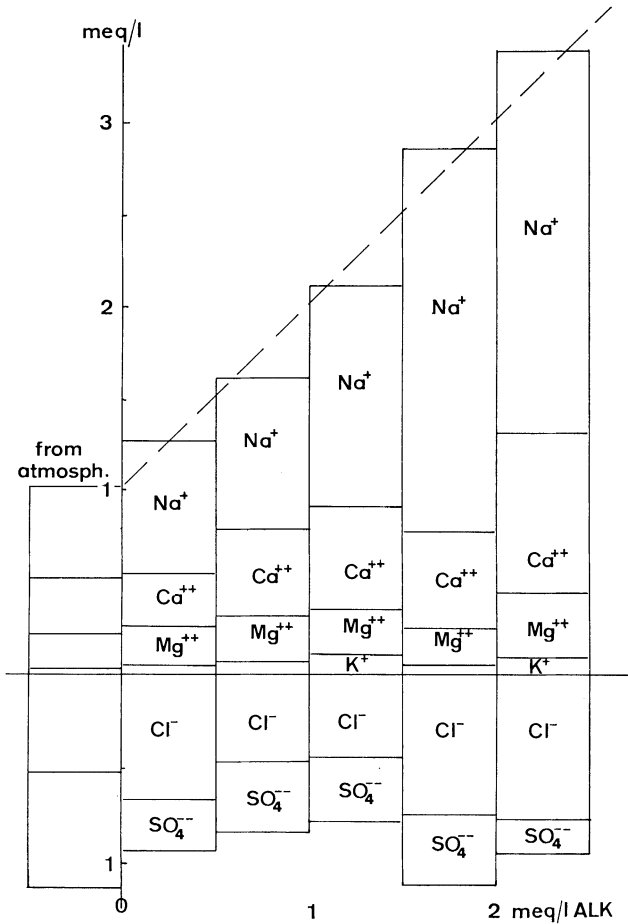


Fig. 7.

Gothenburg area, staple diagram for anions and cations with alkalinity as parameter. 22 waters are included.

Stockholm area (Fig. 6). The analyses, 80 altogether, have been divided into six classes extending to 6 meq/l alkalinity.

The atmospheric fallout via precipitation is measured by the Meteorological Institute of the University of Stockholm. From data for Ultuna-Uppsala Näs (1955-66), Erken (1955-63) and Strängnäs (1955-60), a mean has been calculated. The deposition with precipitation would be:

| K ⁺ | Na ⁺ | Ca ⁺⁺ | Mg ⁺⁺ | Cl ⁻ | SO ₄ ⁻⁻ | |
|----------------|-----------------|------------------|------------------|-----------------|-------------------------------|-----|
| 0.27 | 0.42 | 0.90 | 0.17 | 0.57 | 3.18 | ppm |

In well drained areas with no sea water influence, Cl⁻ in ground water is almost entirely of atmospheric origin (Eriksson 1960, Feth et al. 1964). This affords the possibility of calculating the atmospheric contribution of salts to ground water. The higher concentration in ground water compared to precipitation is caused by evapotranspiration and dry fallout. For these ground waters 0.11 meq/l Cl⁻ appears to be of atmospheric origin. This is the mean for the group 0–1 meq/l alkalinity. 0.11 meq/l equals 3.9 ppm. This means a seven-fold concentration in comparison to precipitation. If all the other ions are concentrated in the same way, atmospheric salts in ground water should be:

| K ⁺ | Na ⁺⁺ | Ca ⁺⁺ | Mg ⁺⁺ | Cl ⁻ | SO ₄ ⁻⁻ | |
|----------------|------------------|------------------|------------------|-----------------|-------------------------------|-------|
| 0.048 | 0.13 | 0.32 | 0.10 | 0.11 | 0.46 | meq/l |

The calculation appears to be fairly correct, as a line drawn at 45° from 0.6 meq/l, the sum of the atmospheric cations, passes through the middle of at least the first staples.

Little K⁺ is added to the waters, suggesting that illites are formed fixing K⁺ at early stages of the weathering process. Mg⁺⁺ parallels the behavior of K⁺. Mg⁺⁺, like K⁺, originates from biotite and can be retained in illite and chlorite. Ca⁺⁺ is added largely at the beginning of the weathering process. After 2 meq/l alkalinity, dissolution of Ca⁺⁺ almost stops as a result of retention of Ca⁺⁺ in Ca-montmorillonite. In the last staples there is very little increase in Na⁺. This may be due to the effect of retention of Na⁺ in Na-montmorillonite.

SO₄⁻⁻ is seen to be of atmospheric origin, except for a slight increase at the end of the diagram which parallels an increase of Cl⁻. This means that pyrite oxidation on the whole is of no importance.

An attempt has been made to determine from which minerals the ions originate. First the kaolinization stage is handled. As a representative for the end of this stage, the mean of groups 1–2 and 2–3 meq/l alkalinity has been taken. This mean has an alkalinity of 2 meq/l which is the breakpoint of the plots in Fig. 5. The model for the determinations is taken from Garrels & Mackenzie (1967). The minerals are taken in order of weatherability except for calcite, which is responsible for the rest of Ca⁺⁺. The most common plagioclase in the Stockholm region is an oligoclase (Stålhös 1969). The oligoclase used in the calculations is Ab₇₅An₂₅, which has a molar ratio of Na: Ca of 75:25.

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Table 2.
Kaolinization stage to an alkalinity of 2 meq/l

| K ⁺ | Na ⁺ | Ca ⁺⁺ | Mg ⁺⁺ | |
|----------------|-----------------|------------------|------------------|--|
| 0.096 | 0.84 | 1.53 | 0.53 | meq/l |
| -0.048 | -0.13 | -0.32 | -0.10 | atmospheric fallout |
| 0.048 | 0.71 | 1.21 | 0.43 | from 0.048 mmol biotite |
| -0.048 | | | -0.10 | (KMgFe ₂ (OH) ₂ AlSi ₃ O ₁₀) |
| 0.000 | | | 0.33 | from 0.55 mmol hornblende |
| | | -0.22 | -0.33 | (Ca ₂ Mg ₃ Fe ₂ (OH) ₂ Si ₆ O ₂₂) |
| | | 0.99 | 0.00 | from 0.95 mmol plagioclase |
| | -0.71 | -0.47 | | (Na _{0,75} Ca _{0,25} Al _{1,25} Si _{2,75} O ₈) |
| | 0.00 | 0.52 | | from 0.26 mmol calcite |
| | | -0.52 | | (CaCO ₃) |
| | | 0.00 | | |

0.4 g of minerals is affected, but only 0.08 g is dissolved in the water. The latter figure includes 15 ppm SiO₂. It is surprising that so much calcite appears to be involved. It is of course possible to use a more calcic plagioclase to consume more Ca⁺⁺. In order to consume all Ca⁺⁺, leaving none for calcite, an andesine, Ab₅₉An₄₁, is necessary. Such a plagioclase is found only in basic rocks. As mentioned above, the calcite is probably found in the soil.

After the kaolinization, Ca-montmorillonite becomes stable along with chlorite and illite. A mean of groups 3-4 and 4-5 meq/l alkalinity is used in the calculations.

Table 3.
Montmorillonization stage, 2-4 meq/l alkalinity.

| K ⁺ | Na ⁺ | Ca ⁺⁺ | Mg ⁺⁺ | |
|----------------|-----------------|------------------|------------------|----------------------------|
| 0.079 | 2.25 | 1.97 | 0.66 | meq/l |
| -0.096 | -0.84 | -1.53 | -0.53 | kaolinite weathering |
| -0.017 | 1.41 | 0.44 | 0.13 | from 1.88 mmol plagioclase |
| | -1.41 | -0.30 | | making montmorillonite |
| | 0.00 | 0.14 | 0.13 | |

0.5 g plagioclase is affected, giving off 0.04 g of Na^+ and Ca^{++} . Most of the changes could thus be accounted for by the Ca-montmorillonite formation from plagioclase.

The calculations seem to fit the progressive weathering of the minerals in igneous rocks, mainly the plagioclases. There is, however, one problem that has not yet been considered. This is the low mobilization of silica. The SiO_2 -concentration generally does not exceed 20 ppm. It remains constant throughout the alkalinity range. Kaolinization of a plagioclase should release SiO_2 and HCO_3^- in a ratio of 1:1. Montmorillonitization releases less SiO_2 .

There are a number of possible explanations for the low SiO_2 -concentration. First, the method of analysis which uses the molybdate method. Some investigators claim that only part of the silica reacts with molybdate. However, for ground water there appears to be no objection (Kramer 1968). Spectrographic determinations of SiO_2 in ground water give results similar to those obtained here (Bergström 1972).

Another possibility is the precipitation of SiO_2 as quartz. The solubility of quartz is about 6 ppm at 25°C (Krauskopf 1956 van Lier et al. 1960). Siever (1962) states that precipitation of quartz is very slow. Millot (1970) is of the opinion that precipitation of quartz from supersaturated solutions is common in nature.

A third possibility is that silica is never mobilized but remains polymerized at the place of the dissolved mineral. Loughnan (1969) says that this happens initially when a silicate mineral is broken down. Amorphous silica, however, has a solubility of about 60 ppm at 5°C (Krauskopf 1956, Polzer 1967).

A fourth way of explaining the SiO_2 retention is that it is used up in forming secondary clay minerals. The formation of Ca-montmorillonite from kaolinite requires large amounts of SiO_2 , and relatively small amounts of Ca^{++} . Montmorillonites formed probably from kaolinite have been observed in tunnels in Gothenburg (Lundgren 1971). The pre-existence of kaolinite could be due to a more leaching weathering effect in the geological past. Precambrian kaolinite is found in several places, such as at Ivö (Grönwall 1915) and Lugnås (Lundqvist et al. 1931). Very old clay zones in the archaic rocks can thus be subjected to a kind of diagenesis in which kaolinite is changed to montmorillonite.

Angered area, Gothenburg (Fig. 7). The 22 analyses lie within a narrower alkalinity range than the Stockholm analyses. This made it feasible to use the staple width 0.5 meq/l alkalinity. Data on deposition with precipitation has been taken from the harbor of Gothenburg for the period 1957–66:

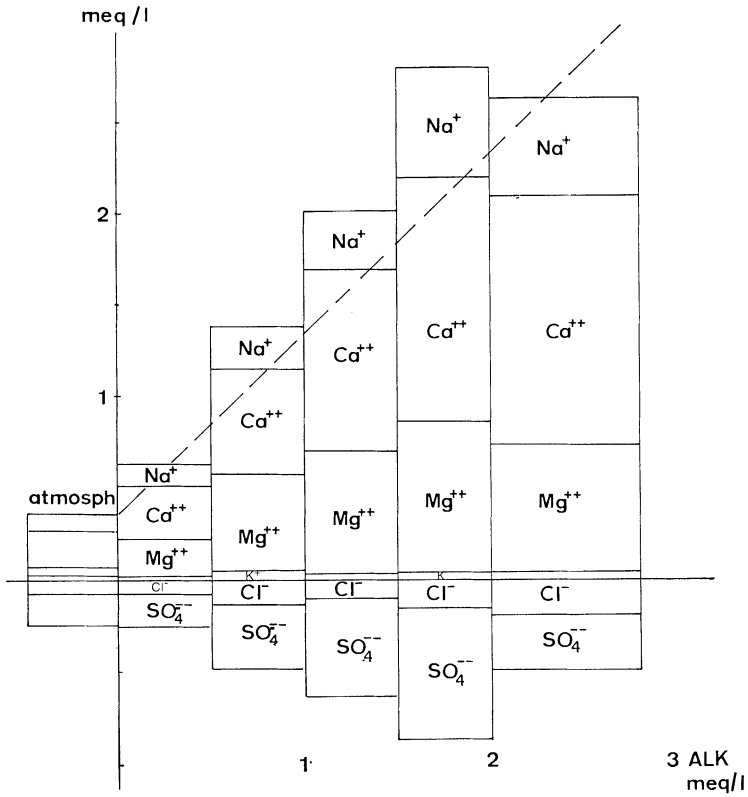


Fig. 8.

Bergslagen area, staple diagram for anions and cations with alkalinity as parameter. 29 waters are included.

| K ⁺ | Na ⁺ | Ca ⁺⁺ | Mg ⁺⁺ | Cl ⁻ | SO ₄ ⁻⁻ | |
|----------------|-----------------|------------------|------------------|-----------------|-------------------------------|-----|
| 0.32 | 3.01 | 1.62 | 0.56 | 4.86 | 7.50 | ppm |

The Cl⁻-concentration in ground water can be set at 0.53 meq/l or 18.8 ppm. This is four times the concentration in precipitation. The atmospheric contributions should thus be:

| K ⁺ | Na ⁺ | Ca ⁺⁺ | Mg ⁺⁺ | Cl ⁻ | SO ₄ ⁻⁻ | |
|----------------|-----------------|------------------|------------------|-----------------|-------------------------------|-------|
| 0.033 | 0.52 | 0.32 | 0.18 | 0.53 | 0.62 | meq/l |

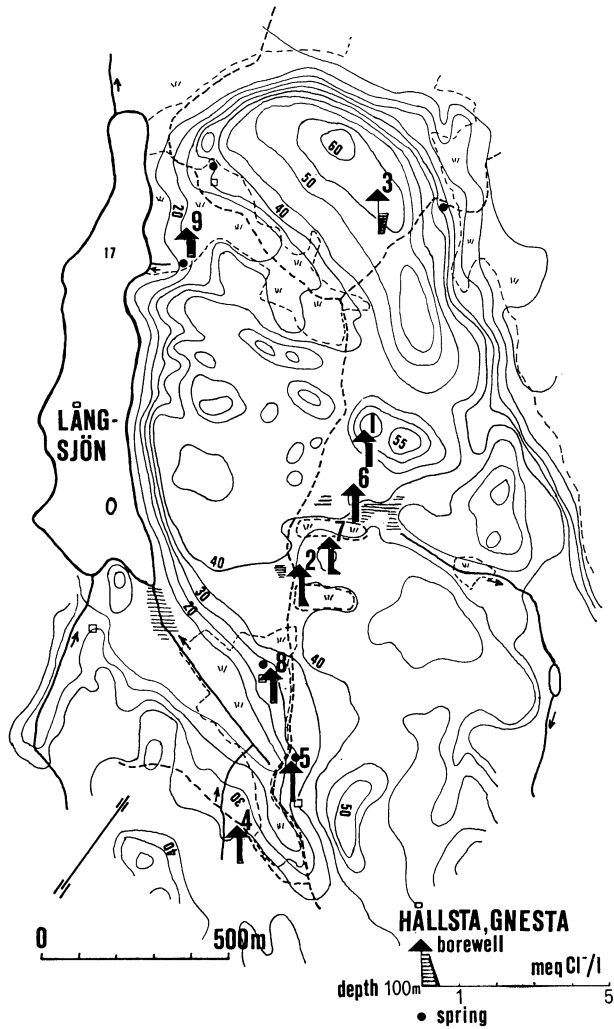


Fig. 9.

Content of Cl⁻ in relation to topography in Gnesta.

The diagram shows much the same as that for Stockholm waters. The atmospheric fallout, however, is about double in Gothenburg and dominated by Na⁺. Then there is the above-mentioned smaller range in alkalinity, indicating a smaller original acidity in the Gothenburg waters. This could be due to infiltration conditions as mentioned above. Because of the smaller original acidity

and the higher concentration of salts in precipitation, the kaolinite-montmorillonite equilibrium is reached earlier in Gothenburg. In Gothenburg, montmorillonites should be found nearer the surface than in Stockholm. The alkalic water (more Na^+ from the atmosphere and absence of calcite in the soil) makes it more likely that Na-montmorillonite will be found. Few analyses have been available from the island of Hisingen in Gothenburg, but they indicate even more alkalic conditions.

Bergslagen (Fig. 8). The diagram is composed of data from 29 analyses. Data on deposition with precipitation has been taken from Forshult in the eastern part of Värmland for the period 1955–66:

| K^+ | Na^+ | Ca^{++} | Mg^{++} | Cl^- | SO_4^{--} | |
|--------------|---------------|------------------|------------------|---------------|--------------------|-----|
| 0.20 | 0.34 | 0.74 | 0.12 | 0.47 | 3.15 | ppm |

Assuming Cl^- in ground water is 0.07 meq/l (a value deduced from sampling of ground water runoff in small streams) gives a multiplication factor of 5.3. The atmospheric contribution is calculated as:

| K^+ | Na^+ | Ca^{++} | Mg^{++} | Cl^- | SO_4^{--} | |
|--------------|---------------|------------------|------------------|---------------|--------------------|-------|
| 0.027 | 0.09 | 0.20 | 0.05 | 0.07 | 0.17 | meq/l |

This diagram is less regular than the two preceding ones. The analyses stem from leptite rocks, a kind of supracrustal rock found in Sweden. One reason for the irregularity is that these waters are affected by pyrite oxidation which has raised the SO_4^{--} -content. Another thing that differs in this diagram, is the large amount of dissolved Mg^{++} . The abundance of Ca^{++} and Mg^{++} is probably due to the mineralogic composition of the leptites. Mg^{++} probably comes from such ferromagnesian minerals as pyroxenes and amphiboles rather than from biotite.

Salt water retention

The sampling areas in Stockholm, Gothenburg and Piteå have been drained out of the sea in postglacial time.

The most obvious sign of sea water retention is Cl^- . If Cl^- is higher than about 0.15 meq/l this indicates a trace of sea salts in the Stockholm region. In Gothenburg the limit is set higher because of the greater quantity of airborne salts.

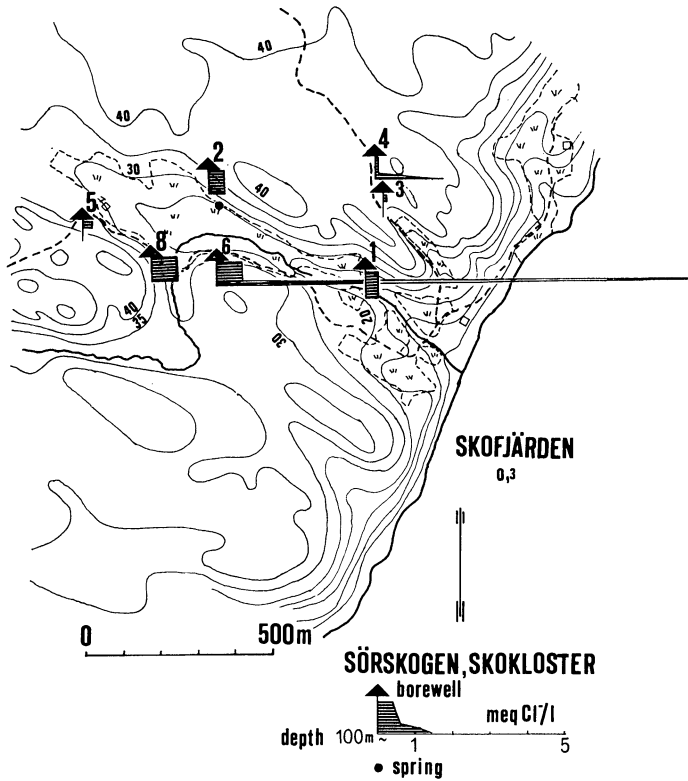


Fig. 10.
Content of Cl⁻ in relation to topography in Skokloster.

Figs. 9, 10 and 11 show the influence of topography on ground water turnover. In Gnesta, where the terrain is quite hilly, there is no tendency towards raised Cl⁻ content. In Skokloster the relief of the terrain is smaller. At depths of wells 4 and 6 the Cl⁻ content is substantially higher. The Markim valley in the Verka area lies lower than the other areas, and in comparison with them it is very flat. The latter fact is probably the main reason for the high Cl⁻ concentrations. The concentration increases with depth in the well, illustrating the exponential decrease in rapidity of ground water flow with depth (Gustafsson 1968).

Fig. 12 shows a plot of analyses against time from a well in Skånela in the Verka area. The salinity varies with time but is of the same order as the salinity in observation pipe 23 in the quaternary near the well. The well lies in a clay covered terrain. If the salt water is found only in the fissures of the rock, the

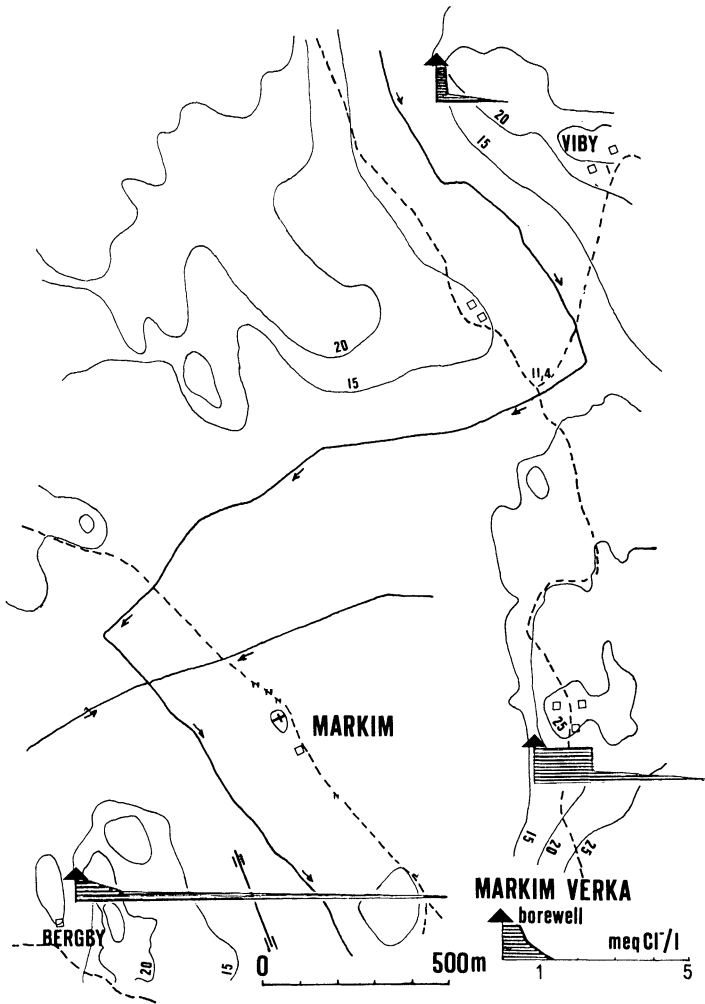


Fig. 11.
Content of Cl⁻ in relation to topography in Markim valley, Verka.

chances of pumping it away are greater. In the infiltration area of the well Skansen not far from Skånela, there are no clays. After the well was brought into use, the Cl⁻ content diminished from 2 to 0.2 meq/l.

The well in Smâris had a very high salinity. As wells in the quaternary in the valleys on both sides of the boring were non-saline (Fig. 13), an attempt was

made to pump away the salt water. The test was partially successful, as salinity decreased during pumping to 2/3 of the initial value. The interpretation is that the water in the crush zones in the valleys is less salty than in the adjacent rock surrounding the well, but still quite saline.

The saltiest waters are found in Värmdö, near Stockholm.

| | K ⁺ | Na ⁺ | Ca ⁺⁺ | Mg ⁺⁺ | Cl ⁻ | SO ₄ ⁻⁻ | HCO ₃ ⁻ | meq/l |
|----------|----------------|-----------------|------------------|------------------|-----------------|-------------------------------|-------------------------------|-------|
| Småris | 0.15 | 30.9 | 28.4 | 1.97 | 59.5 | 0.03 | 0.24 | |
| Fruvik | 0.63 | 73.5 | 51.2 | 18.6 | 135 | 16.5 | 2.02 | |
| Byholmen | 0.53 | 53.0 | 73.3 | 21.9 | 141 | 6.25 | 1.04 | |

The two last waters have salinities of 8.7 and 8.4 ‰, thus substantially higher than is found in the surface layers of the Baltic (5 ‰). The postglacial history of the area is as follows: an ice lake, the Yoldia sea, the Ancylus lake and the Litorina sea about 4000 years B.C. This means two salinity maxima, the higher one during early Litorina time. From the study of clay series, Ståhlberg (1952) and Ekman & Fries (1970) concluded that the salinity during early Litorina time was about 10–15 ‰ with about 170 meq/l Na⁺. The 170 meq/l should be compared with the sum of Na⁺ and Ca⁺⁺ in the ground waters

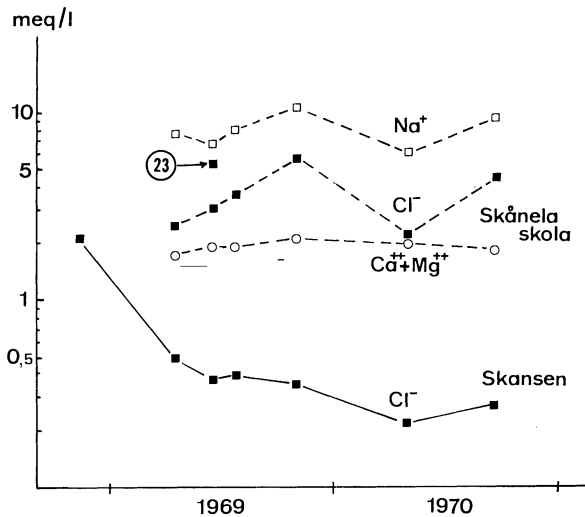


Fig. 12.

Time series of chemical constituents for two wells in Verka, Stockholm area.

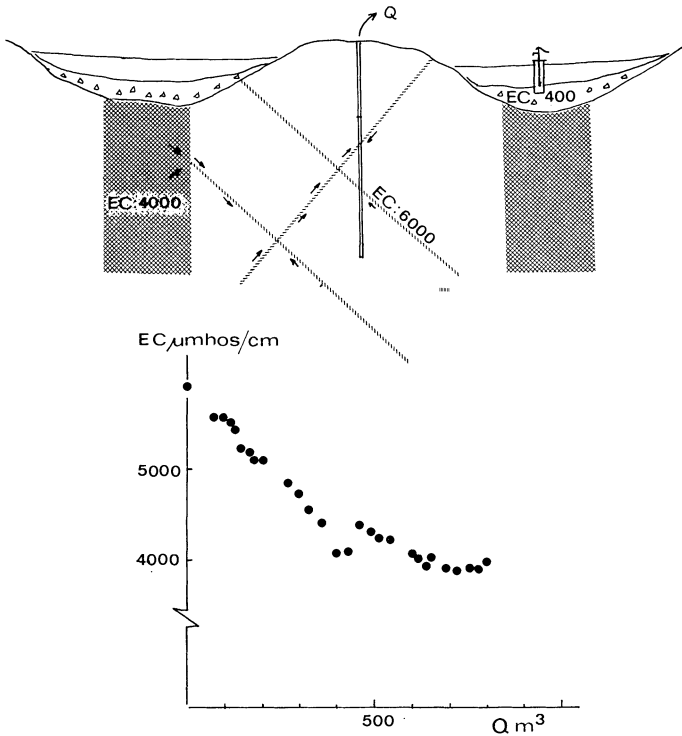


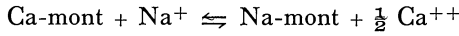
Fig. 13.

Pumping test of the Småris well, Värmdö, Stockholm. Below, electric conductivity of water during pumping; above, geological interpretation of the test.

above, as Ca^{++} comes from the exchange of Na^+ for Ca^{++} on clay minerals in the rock (see next section). In the ground waters from Fruvik and Byholmen the sum is around 125 meq/l, thus not far from the value stated for the early Litorina sea. It would therefore appear that these waters have lain almost intact for 6000 years. The main reasons for this are the higher specific weight because of salinity, the absence of gradients, and little permeability.

Mineral-water equilibria in saltier waters

As mentioned earlier, Na-montmorillonite appears to be a stable weathering product formed very late in the weathering process. The exchange reaction of montmorillonite can be written as:



and the equilibrium constant in logarithmic terms:

$$p\text{Na}^+ - \frac{1}{2} p\text{Ca}^{++} = pK$$

If this expression is plotted against electrical conductivity, as in Fig. 14, some interesting features are revealed. The encircled plots for Stockholm and Gothenburg have more or less a reversed S-shape. The configuration can be interpreted as follows. The first part with constant values represents kaolinization of plagioclases; the ratio should correspond to the ratio of Na to Ca in the plagioclases. The dipping part of the plot represents Ca-montmorillonite formation. Ca^{++} is partially retained. Finally the plot levels out at the exchange constant of Na-Ca-montmorillonite. It emerges clearly from the diagram that the montmorillonite formation begins at lower salinities in Gothenburg. The whole sequence of events can occur within the depth of a single well.

The Na-Ca-montmorillonite equilibrium should lie on 1.4 according to Kramer (1968) and on -0.3 according to Helgeson (1969). Fig. 14 suggests a value in between the two, or 0.4-0.5 for $p\text{Na}^+ - \frac{1}{2}p\text{Ca}^{++}$.

The calcite equilibrium can, of course, affect the expression $p\text{Na}^+ - \frac{1}{2}p\text{Ca}^{++}$, as Ca^{++} can be withdrawn from the solution by means of calcite precipitation.

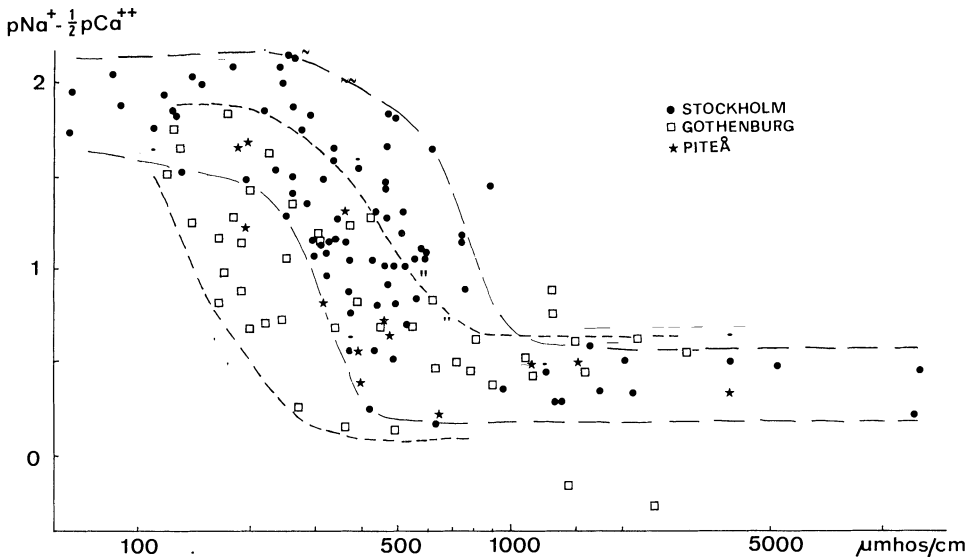


Fig. 14.

$p\text{Na}^+ - \frac{1}{2}p\text{Ca}^{++}$ as function of electric conductivity. Plots for Gothenburg and Stockholm are encircled.

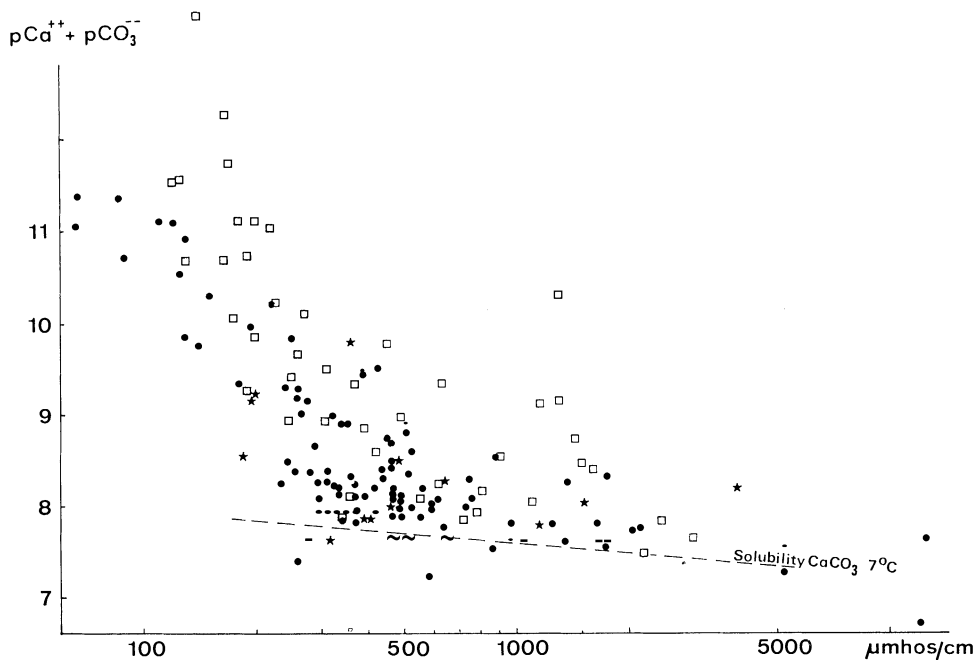


Fig. 15.

$pCa^{++} + pCO_3^{-}$ against electric conductivity. Plots as in Fig. 14. Solubility of calcite at $7^\circ C$ indicated.

From Fig. 15 it is seen that the solubility is reached first around $400 \mu\text{mhos/cm}$, and that some waters never reach it even at high salinity.

Ionic composition of 125 water samples, ranging in salinity from 100 to 4000 $\mu\text{mhos/cm}$, has been illustrated in staple diagrams in Fig. 16. What is interesting in the cation diagram is the increase in Ca^{++} at higher salinities. This must be the effect of ionic exchange on montmorillonite as described above. In the anion diagram Cl^- increases steadily as does SO_4^{--} . The amount of HCO_3^- declines after $1000 \mu\text{mhos/cm}$. This bears witness to the fact that calcite precipitation is operating only in quite saline waters.

Redox conditions

The species involved in redox reactions in these waters are iron, sulfur and nitrogen species.

The solution of iron from the primary minerals (mainly biotite) is a complic-

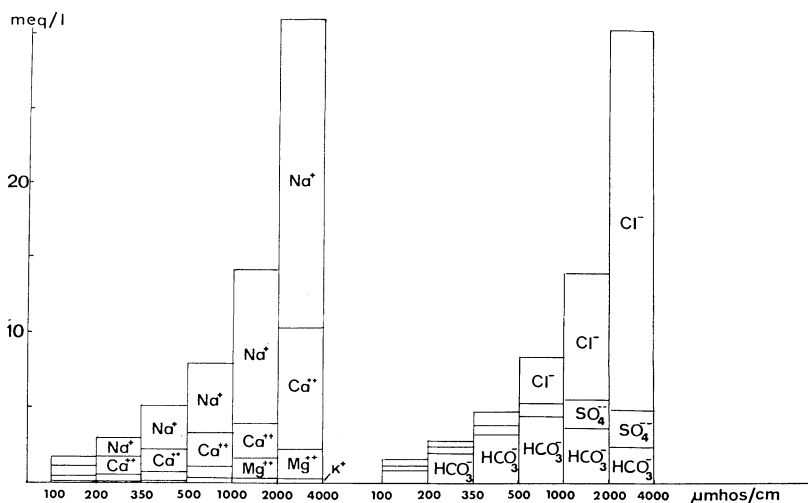


Fig. 16.

Staple diagram for anions and cations in 125 waters ranging in electric conductivity from 100 to 4000 $\mu\text{mhos/cm}$.

ated process in which chelating substances of organic origin play an important role. Most of the dissolved iron is removed from the water in the B-horizon in podsoles in the form of tri-valent hydroxides. If measured pH and E_h (redox pot.) are plotted in a pH- E_h -diagram for iron species (Langmuir 1969) it can be concluded that Fe^{++} content in water is regulated by the solubility of $\text{Fe}(\text{OH})_3$ as freshly precipitated.

The conditions are not reducing enough to convert SO_4^{--} to S^{--} . The reverse reaction should readily take place if pyrite was present. In Bergslagen this is observed quite often.

The conversions between the different nitrogen species are biologically mediated. This means that addition or removal should largely be restricted to the soil zone. The sum of NH_4^+-N and NO_3^--N in forested areas is generally below 1 ppm with a mean around 0.3 ppm. In Verka with mainly arable land the mean of 24 analyses is 1.4 ppm. The molar ratio $\text{NO}_3^-/\text{NH}_4^+$ is 0.6 in forested areas and 15 in the Verka area. In the acid forest soil NH_4^+ is dominating, while in agricultural soil conditions are more neutral and oxidizing.

There are no visible changes towards depth either in total N or in the ratio $\text{NO}_3^-/\text{NH}_4^+$. NO_3^- has very little interaction with minerals. NH_4^+ is similar to K^+ and could be subjected to exchange reactions.

Conclusions and applications

The composition of ground water from igneous rocks is governed by mineral-water equilibria. As these equilibria are established slowly, it is possible to roughly date the waters. It is possible to say whether the water is freshly infiltrated, some years old, or substantially older. Such a judgment is valuable not only on a question about water wells but also in connection with seepage into tunnels. This seepage may drain clays and cause settlement of construction on the ground. In some cases it is important to stop seepage and in others it may be an unnecessary cost.

From the water composition, it is possible to deduce what kind of clay minerals is encountered by the waters. The fact that montmorillonite is more common in Gothenburg than in Stockholm is nicely illustrated by the analyses in this work. This may be of value when planning to build tunnels or underground construction in a new area. By means of some water analyses from borewells, it would be possible to tell whether or not the clays in the fissures would cause trouble when tunneling in the rock.

Salty ground waters retained from glacial time were found during this work. Sometimes this salt water can be pumped away. The situation of the well is important in avoiding salt water. Large local gradients in the ground water table and permeable tectonic zones have favored the washing out of the old sea water. These old sea waters have a very specific character. Due to ion exchange they contain much Ca^{++} in contrast to fresh sea waters. This provides a means to distinguish them from fresh sea water which has invaded an aquifer due to pumping.

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