

# Evolution of groundwater chemical composition by plagioclase hydrolysis in Norwegian anorthosites

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## Abstract

The Precambrian Egersund anorthosites exhibit a wide range of groundwater chemical composition (pH 5.40–9.93,  $\text{Ca}^{2+}$  1.5–41 mg/L,  $\text{Na}^+$  12.3–103 mg/L). They also exhibit an evolutionary trend, culminating in high pH, Na-rich, low-Ca groundwaters, that is broadly representative of Norwegian crystalline bedrock aquifers in general. Simple PHREEQC modelling of monomineralic plagioclase– $\text{CO}_2$ – $\text{H}_2\text{O}$  systems demonstrates that the evolution of such waters can be explained solely by plagioclase weathering, coupled with calcite precipitation, without invoking cation exchange. Some degree of reaction in open  $\text{CO}_2$  systems seems necessary to generate the observed maximum solute concentrations, while subsequent system closure can be invoked to explain high observed pH values. Empirical data provide observations required or predicted by such a model: (i) the presence of secondary calcite in silicate aquifer systems, (ii) the buffering of pH at around 8.0–8.3 by calcite precipitation, (iii) significant soil gas  $\text{CO}_2$  concentrations ( $\text{PCO}_2 > 10^{-2}$  atm) even in poorly vegetated sub-arctic catchments, and (iv) the eventual re-accumulation of calcium in highly evolved, high pH waters.

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## 1. Introduction

Our understanding of the evolution of the hydrochemical composition of groundwater in silicate-dominated crystalline rock aquifers is still founded in the pioneering work of researchers such as Garrels (1967) and Garrels and Mackenzie (1967), who considered the composition of spring waters emerging from the Sierra Nevada and elsewhere in the USA. Their model (with additions by later researchers) for the hydrochemical evolution of groundwaters of low-to-moderate total dissolved solids (TDS) in igneous and high-grade metamorphic crystalline rocks can be summarised in the following statements:

- Groundwaters tend to be of  $\text{Na-Ca-HCO}_3^-$  composition in feldspar-rich rocks, with the Na/Ca ratio in the groundwater reflecting that in the rock's plagioclase mineralogy. The presence of trace amounts of rapidly reacting calcite in unweathered rock (White et al., 2005) or in superficial materials can, however, result in an apparent excess of Ca (White et al., 1999).
- Plagioclase and mafic minerals (biotite, amphibole, and pyroxene) react significantly faster than quartz and K-feldspar (White et al., 1998). Thus, if (as is often the case) plagioclase has a larger modal abundance than these mafics, the groundwater chemical composition can largely be explained in terms of plagioclase weathering. Garrels and Mackenzie (1967) suggested that around 80% of the hydrochemical composition of their spring waters can be explained by plagioclase hydrolysis. In geologically recent Icelandic basaltic rocks, Gislason and Eugster (1987) suggested, however, that any glass phase present will be the fastest reacting element and will dominate the water composition.

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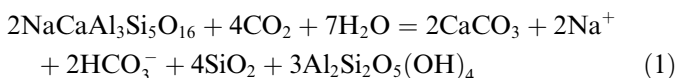
- Mafic minerals such as biotite, amphiboles and pyroxenes will be the dominant sources of potassium and magnesium to the groundwater.
- Groundwater evolution pathways tend to suggest an initial  $PCO_2$  of around  $10^{-1.5}$  atm, characteristic of the soil gas environment (rather than the atmosphere, with a  $PCO_2$  of ca.  $10^{-3.5}$  atm), with the groundwater system becoming closed with respect to  $CO_2$ .
- Kaolinite is typically the initial alteration product of many crystalline rocks, although in more hydrochemically evolved waters (typically where the molar ratio of  $HCO_3^-/Si$  exceeds three), a “calcium montmorillonite” (calcium smectite in current terminology) was suggested to be a more likely alteration product.

Indeed, Garrels (1967) boldly proposed that major ion groundwater chemical composition in many silicate rocks is determined largely by two factors:

1. The initial  $PCO_2$  of the recharge water.
2. The extent to which the  $CO_2$  has been converted to  $HCO_3^-$  by hydrolysis of plagioclase.

This has been substantiated in practice by large scale empirical studies of groundwaters from various crystalline bedrock lithologies, such as that of Banks et al. (1998), who concluded that groundwater pH and major ion composition in such aquifers was not strongly governed by aquifer lithology, but largely by hydrodynamic factors (residence time, fracture geometry) and a limited set of common thermodynamic equilibria (e.g., calcite saturation).

One potential limitation of the “classical” studies of crystalline rock groundwater and more recent syntheses (e.g., Bowser and Jones, 2002) is that the groundwaters considered have been relatively hydrochemically “immature.” Thus, their further hydrochemical evolution (e.g., past the point of calcite saturation) is poorly documented in mainstream literature. Garrels (1967) hinted that saturation with and precipitation of calcite might be expected to result in depletion of calcium from solution and evolution of sodium-rich, alkaline waters [e.g., Eq. (1)].



High pH, Na-rich, Ca-depleted groundwaters are commonly observed in Norwegian igneous and metamorphic rock types (Banks et al., 1998). Nordstrom et al. (1989) invoked this mechanism to explain calcium-depleted groundwaters in the Swedish Stripa granite, while Wood and Low (1988) also suggested its role in the evolution of groundwaters in the Snake River aquifer system. In at least one of the studies (Vekol Valley, Arizona) reviewed by Bowser and Jones (2002), there are indications that calcite precipitation, Ca depletion, preferential Na accumulation, and closure with respect to  $CO_2$  are occurring.

In this study, which was summarised previously by Frengstad and Banks (2000), we shall assess, via empirical data and the use of simple thermodynamic modelling, whether the “classic” model of Garrels (1967), invoking plagioclase hydrolysis by  $CO_2$ , can adequately explain the early evolution of anorthosite groundwater hydrochemical composition. We shall then evaluate the calcite precipitation mechanism as an explanation for the later-stage hydrochemical evolution of such waters, resulting in depletion in Ca and enrichment in Na, and will also briefly consider the alternative mechanism of cation exchange. Furthermore, the importance of initial  $CO_2$  concentrations in recharge water will be assessed, as will the degree of openness or closure of the system. Finally, the significance of the secondary alteration product (kaolinite vs. smectite) will be considered.

We shall evaluate theoretical considerations and modelling work against real data sets derived from groundwaters sampled from wells in crystalline Norwegian bedrock, largely of Caledonian and Precambrian age. In particular, we consider groundwater in Precambrian anorthosite bodies, especially the Egersund anorthosite complex in south-western Norway. It is believed that the hydrochemistry of the anorthosite groundwaters is of particular interest because the lithology is relatively simple, being dominated by plagioclase feldspar, with subsidiary pyroxene. This allows the hydrochemist to study plagioclase water–rock interaction in the field, with minimal interference from other mineral assemblages. If Garrels (1967) hypothesis that plagioclase hydrolysis dominates water–rock interaction processes in many other types of crystalline rock is correct, it should be possible to recognise the anorthosite evolutionary trends in other lithologies. The sampled wells in the Egersund Complex span a wide range of pH values and include a number of highly evolved high-pH, Ca-poor, Na- $HCO_3^-$  waters that appear to violate Garrels (1967) hypothesis that the groundwater’s Na/Ca ratio reflects plagioclase composition (see above).

## 2. The Egersund anorthosite aquifer system

Egersund is situated in the county of Rogaland, south-east of Stavanger on the southwestern coast of Norway (Fig. 1). The Egersund-Ogna anorthosite massif is part of the Rogaland igneous complex, comprising three large anorthosite massifs, two smaller leuconorite bodies, a layered leuconorite lopolith and three granitoid plutons. The Egersund-Ogna massif has a rock composition of coarse-grained, homogeneous, 1–3 cm plagioclase crystals ( $An_{40-50}$ ), with sub-ophitic aggregates and megacrysts of plagioclase and high-Al orthopyroxene megacrysts (Ashwal, 1993). Very pure, approximately monomineralic anorthosite occurs within the complex and is worked industrially at Hellvik and Rekefjorden. The age of the complex is not well constrained, but Rb–Sr and U–Pb zircon studies of granitoids obtain a clustering of ages in the range 900–950 Ma (Ashwal, 1993). There is very little Quaternary cov-

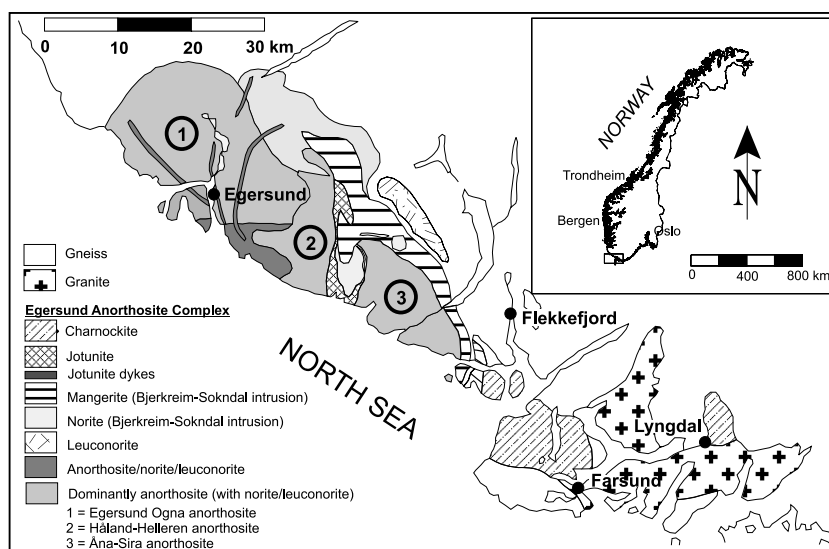


Fig. 1. Map of the Egersund anorthosite complex with inset-map of Norway showing the location of Egersund. Partially redrawn from Schiellerup (2001).

er, and the bedrock appears relatively fresh at outcrop, having been recently glacially scoured. No calcite mineralization can be observed with the naked eye in fractures at outcrop or in tunnels (Frengstad, 2002). Samples of anorthosite have been subject to X-ray diffraction analysis and results are reported in Table 1. It will be noted that, although the major mineralogy is dominated by plagioclase and pyroxene, other minerals do exist in small, but detectable, quantities. Determinations of cation exchange capacity (CEC) in various southern Norwegian hard rock lithologies are compared with other standard geological materials in Table 2.

### 3. Methods: sampling and analysis of groundwater and soil gas

#### 3.1. Sampling of Norwegian crystalline bedrock groundwaters

During 1996 and 1997, the Norwegian Radiation Protection Authority (NRPA) and the Geological Survey of Norway (NGU) analysed groundwater samples from

1604 relatively shallow (typically <100 m) boreholes in Norwegian Precambrian and Palaeozoic crystalline bedrocks (Banks et al., 1998; Frengstad et al., 2000, 2001). Samples were typically collected by staff of Local Public Health Laboratories from domestic boreholes in regular use. Samples had not been subject to water treatment and were relatively particle-free. For practical reasons (i.e., collection of samples by non-specialist staff) described by Banks et al. (1998), samples were not field-filtered. pH and alkalinity were measured in the laboratory.

#### 3.2. Sampling of groundwaters from the Egersund Anorthosites

Nine of the wells in the Egersund Anorthosites that were sampled in the National Survey of 1996/97 (see above) were revisited in May 1997 by NGU hydrochemists and sampled more rigorously (Frengstad, 2002). These additional water samples were typically taken from domestic taps in regular use, after the water had been run for at least 5 min and until its temperature was stable, to ensure that fresh groundwater was sampled. pH, Eh (where appropri-

Table 1  
Minerals present in samples of the Egersund anorthosite according to non-quantitative X-ray diffraction (XRD) analyses, reported by Frengstad (2002)

Sample	Sample description	Mineralogy by XRD
11	Grey/violet coarse-grained anorthosite	Andesine, albite, enstatite, anorthite, and lanarkite
12	Grey/violet medium-grained anorthosite with iron oxide	Andesine, albite, muscovite, orthoclase, diopside, phlogopite, quartz, and tremolite
13	Grey/pink medium-grained anorthosite	Albite, enstatite, biotite, fayalite, and diopside
15	Brownish/pink medium-grained anorthosite (weathered), with iron-oxide/epidote?	Andesine, albite, cristobalite, enstatite, augite, petalite, and pargasite
16	Dark grey/violet medium to coarse-grained magmatic rock	Albite, andesine, cristobalite, enstatite, willemite, and petalite
17	Dark greenish coarse-grained anorthosite	Andesine, albite, cristobalite, annite, pargasite, enstatite, anapaite, and muscovite
18	Bluish coarse-grained anorthosite (weathered)	Andesine, albite, cristobalite, augite, petalite, and yeelimite
19	Light bluish coarse-grained anorthosite with accessory biotite (weathered)	Andesine, albite, cristobalite, enstatite, augite, fayalite, diopside, biotite, and neptunite

Table 2  
Determinations of cation exchange capacity (CEC) in crystalline rocks and fracture fillings from Southern Norway, compared with CEC in other geological materials

Material	CEC (mEq/100 g)
Precambrian anorthosites, granites and gneisses, Southern Norway ( $n=30$ ), crushed rock samples (unpublished studies by B. Frengstad)	Minimum = 0.04 Median = 2.46 Maximum = 5.38
Smectite fracture fillings in Precambrian Iddefjord Granite (Kocheise, 1994)	Minimum = 15 Median = 85 Maximum = 100
Kaolinite (Appelo and Postma, 1996)	3–15
Montmorillonite (Smectite)	80–120
Illite	20–50
Chlorite	10–40
Organic matter	150–400 (at pH 8)

ate), and groundwater temperature were measured in the field using a Palintest Micro 900 m. Alkalinity was determined in the field by titration against dilute HCl with both phenolphthalein (*p*-alkalinity at end-point pH = 8.2) and mixed indicators (*t*-alkalinity at end-point pH = 4.3), using an Aquamerck 11109 alkalinity test kit. The alkalinity is cited as the average of typically three determinations, with an estimated accuracy of 0.1 mEq/L. A 500-mL polyethylene flask (rinsed, prior to sampling, with well water) was filled with unfiltered water. Water was additionally syringe-filtered at 0.45  $\mu\text{m}$  into 100-mL polyethylene flasks (which had been washed with filtered well-water). The appearance of the sample and the used filters, any smell or other characteristics of the water were noted. The water samples were transported to NGU's laboratory, where the filtered samples that were destined for ICP analysis were acidified with concentrated Ultrapur  $\text{HNO}_3$  (to re-dissolve any absorbed/precipitated element content). Samples were stored in a dark room at 4 °C prior to analysis. The 500 mL unfiltered sample was brought to NGU's laboratories and used for laboratory determination of pH, alkalinity, EC, turbidity and colour. The 0.45  $\mu\text{m}$ -filtered 100-mL water samples were analysed at NGU's laboratories by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to determine 30 elements and by ion chromatography for seven anions (NGU-Lab, 1997). One filtered quantum of each sample was also analysed by inductively coupled plasma mass spectrometry (ICP-MS) at the Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany. Field and analytical procedures are documented by Frengstad (2002).

### 3.3. Soil gas sampling

As part of this study, in situ measurements of  $\text{PCO}_2$  in the soil gas were performed in September 1999 in the vicinity of two boreholes in the Egersund area yielding high-pH groundwaters (Frengstad, 2002): (i) Eigerøya and (ii) Nål-augviga. At each site an iron tube with one opening in each end (i.e., a rock drill rod) was placed into the ground with the use of a sledghammer. The mouth of the tube was pro-

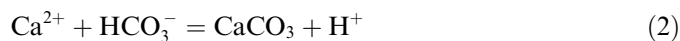
tected from ingress of soils by plastic foil. Before measuring the tube was lifted around 5 cm to allow soil gas to enter the tube. The annulus around the tube was sealed at the surface. A Teflon hose from the  $\text{CO}_2$  detector was inserted into the iron tube and fixed tightly by tape. A BINOS(R)100 NDIR-gas-analyser from Leybold AG was used for measurements of  $\text{CO}_2$  concentration in the soil gas by infrared absorption. During measurements, the atmospheric pressure at Obrestad Lighthouse (30–40 km from the study area) varied from 998 to 1007 hPa.

## 4. Results: groundwater chemistry and soil gas $\text{CO}_2$

### 4.1. Norwegian crystalline bedrock groundwaters: National study

Following the National Groundwater Sampling Study of 1996/97, there was an initial expectation that hydrochemical composition would exhibit a clear correlation with lithology. In fact, only a relatively small number of parameters, such as radon, uranium, and fluoride, exhibited such a lithological dependence. The pH, the major ions and many other parameters, appeared to be controlled largely by hydrodynamic and kinetic factors and more universal thermodynamic equilibria (Banks et al., 1998). A significant number of waters, in a range of lithologies, were found to be dominated by sodium and alkalinity, with low Ca and high pH. Indeed, such waters were also documented in calcium-rich mafic rocks and anorthosites, such as those of the Egersund complex (Fig. 1, Duchesne and Michot, 1987) in southern Norway.

Cumulative frequency distribution curves for pH in all 1604 analysed crystalline bedrock groundwaters, together with a similar curve for those waters from Precambrian anorthosites (lithological group 93 of Banks et al., 1998), from the national study of 1996/97 are shown in Fig. 2. Although there may be other plausible explanations, Banks et al. (1998) interpreted the sharp kink at pH = 8.0–8.3 as indicative of calcite precipitation, which provides a mechanism for pH buffering.



Several major compositional parameters (alkalinity, calcium, chloride [indicative of marine salt input], lithogenic sodium [sodium corrected for marine input on the basis of chloride concentrations] and silicon) have been plotted against pH to reveal possible pH-related trends (Fig. 3). In particular, the low calcium and high non-marine sodium concentrations of the highest pH waters should be noted. This observation is confirmed in the plot of the Na/Ca ratio versus pH. The Na/Ca ratio undergoes a sharp increase at around pH 8.3–8.5, suggesting removal of calcium from the dissolved phase.

pH-related trends can also be identified with the following hydrochemical ratios (Fig. 4): (i) Na/alkalinity (increases around pH 8.3–8.5), (ii) Ca/alkalinity (decreases with increasing pH), and (iii) (Na+Ca)/alkalinity (centred



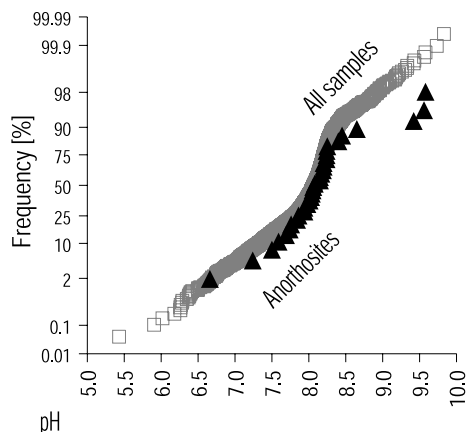


Fig. 2. Cumulative frequency diagram showing the distribution of pH values for all 1604 analysed crystalline bedrock groundwaters from the Norwegian 1996–97 national survey (grey squares), and solely the Precambrian anorthosite groundwaters sampled during the same national survey (solid triangles—lithological group 93 of Banks et al., 1998). Note the probability scale on the y axis.

around an equivalent ratio of 1:1, although with a significant degree of variation). The relationships of Mg, B, and Li to pH in samples from the 1996/97 study are also plotted in Fig. 4. Magnesium exhibits a weak tendency to low concentrations at very high pH, and boron to elevated concentrations. Lithium exhibits no clear trend.

#### 4.2. Groundwaters from Egersund anorthosites

Selected analytical results from the groundwater samples collected from the Egersund anorthosites in May 1997, and saturation indices calculated using the USGS code PHREEQCI, are shown in Table 3. The analyses are also plotted as large solid circles on Figs. 3 and 4, confirming that the same trends may be identified as from the 1996/97 studies. From Fig. 3 to 4, and Table 3, the anorthosite groundwaters may be characterised by the following:

- (i) A wide range of pH values, from 5.4 to around 10.
- (ii) A bias towards pH values of around 8.0–8.2, possibly suggesting a pH buffering system.
- (iii) Low  $\text{Ca}^{2+}$  and high lithogenic  $\text{Na}^+$  concentrations in waters above  $\text{pH} = \text{ca. } 8.3\text{--}8.5$ .
- (iv) Alkalinity concentrations of up to around 5 mEq/L in the highest pH waters.
- (v) Calcium concentrations of <50 mg/L, with maximum concentrations at  $\text{pH} = \text{ca. } 8$ .
- (vi) Lithogenic sodium concentrations below 50 mg/L up to  $\text{pH} = \text{ca. } 8.5$ , with maximum concentrations of some 100 mg/L at the highest pH values.
- (vii) Silicon concentrations typically between 2 and 8 mg/L, with a slight tendency to higher concentrations at elevated pH.
- (viii) High-pH anorthosite waters exhibit elevated B and  $\text{F}^-$ .

- (ix) As one might expect, from the solubility of the amphoteric Al hydroxide, aluminium concentrations are elevated in the low and high pH waters.
- (x) Strontium and magnesium exhibit low concentrations in the high-pH, calcium-poor waters. These are found to be saturated with respect to both dolomite (not shown in Table 3) and calcite.

In the field, low Eh measurements and the presence of an  $\text{H}_2\text{S}$  odour were not typically observed, suggesting that reducing conditions are not common in these shallow groundwaters.

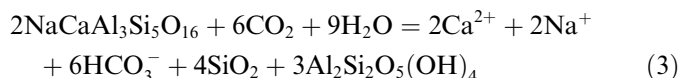
#### 4.3. Soil gas determinations

Results of soil gas determinations are shown in Table 4. These, admittedly sparse, results demonstrate that soil gas partial  $\text{CO}_2$  pressures in excess of  $10^{-2}$  atmospheres are realistic for Southern Norway.

### 5. Hydrochemical evolution of groundwater in anorthosite aquifers

#### 5.1. Early hydrochemical evolution

Garrels (1967) suggested that the early stages of hydrochemical evolution in igneous rocks are dominated by the hydrolysis of plagioclase feldspar by  $\text{CO}_2$  to produce kaolinite. For example, for a labradorite of  $\text{An}_{50}$  composition:



In this model, the molar ratio of dissolved Na/Ca should be approximately equal to that in the plagioclase (in this case  $\text{Na}/\text{Ca}_{(\text{molar})} = 1$ ). If, however, traces of calcite are present in soils, superficial sediments or as accessory minerals in the rock itself (White et al., 1999, 2005), excess calcium may be derived from this source, depressing the Na/Ca ratio. The presence of marine salts in recharge waters may, conversely, tend to elevate the ratio. From Eq. (3), one would also predict that the sum of calcium and sodium (as equivalents) will equal the bicarbonate alkalinity of the water. In passing, it should be noted that several researchers, including Stober and Bucher (1999) and Bowser and Jones (2002), have cast doubt on the assumption of congruent dissolution and have suggested that there may be a tendency to preferential calcium release (and thus albitisation of remnant feldspar) during early weathering stages. In this context, it is furthermore noted that feldspar composition may be zoned and thus certain An-rich zones may be subject to preferential weathering (Clayton, 1988).

In all the anorthosite waters at  $\text{pH} < 8$ , the molar ratio  $\text{Na}_{\text{corr}}/\text{Ca}$  is approximately or less than unity (Fig. 3), where  $\text{Na}_{\text{corr}}$  is the sodium concentration corrected for marine sources using the chloride concentration of the

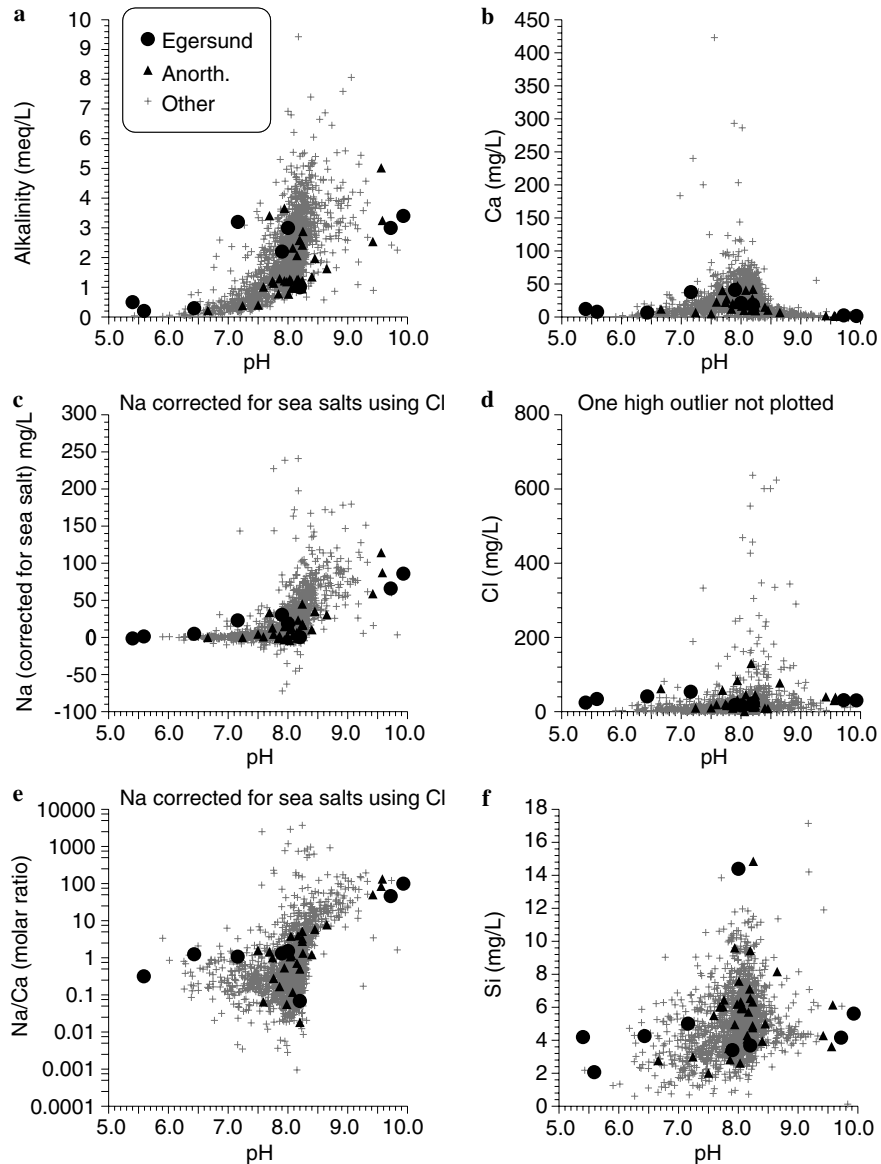


Fig. 3.  $x$ - $y$  diagrams showing the relationship of (a) alkalinity, (b) calcium, (c) lithogenic sodium, (d) chloride, (e) lithogenic sodium:calcium molar ratio and (f) silicon to pH for the nine new groundwater samples from the Egersund Anorthosites (“Egersund,” solid circles, Table 3), the Precambrian anorthosite groundwaters sampled during the 1996–97 Norwegian national survey (“Anorth.,” solid triangles—lithological group 93 of Banks et al., 1998) and groundwaters from other crystalline bedrock lithologies sampled during the Norwegian 1996–97 national survey (“Other,” grey crosses). “Lithogenic” sodium is corrected for input of marine salts and is calculated by the formula  $\text{Na} - (\text{Cl} \times 10600/19000)$ .

groundwater. This is thus entirely consistent with congruent dissolution according to Eq. (3) and the  $\text{An}_{40-50}$  composition of the anorthosite plagioclase. Furthermore, although there is a significant degree of variation, the milliequivalent ratio of  $(\text{Na}_{\text{corr}} + \text{Ca})/\text{alkalinity}$  exceeds unity in the low pH groundwaters (Fig. 4). This is likely to be due to the fact that, in immature groundwaters, there may be a degree of silicate hydrolysis by protons from strong acids (nitric, sulphuric) in “acid rain” as well as by carbon dioxide. This will result in generation of sodium and calcium without accompanying bicarbonate alkalinity. At higher pH values, the value of  $(\text{Na}_{\text{corr}} + \text{Ca})/\text{alkalinity}$  clusters more nearly around unity (although still with significant variation), as predicted by Eq. (3).

Thus far, it appears that the empirical data broadly support Garrels (1967) model. The significant variation in the values of these ratios can be ascribed to (i) uncertainties in the method of correction of Na on the basis of  $\text{Cl}^-$  for marine salt input (there may be anthropogenic sources for  $\text{Cl}^-$ , leading to overcorrection), (ii) alternative mineral sources of alkalinity than plagioclase weathering by  $\text{CO}_2$ , or (iii) sinks for either Ca or Na in non-kaolinite alteration products or ion exchange.

## 5.2. Mature hydrochemical evolution

Above pH 8–8.5 it can be seen that a significant hydrochemical transition is reached, with sodium accumulating

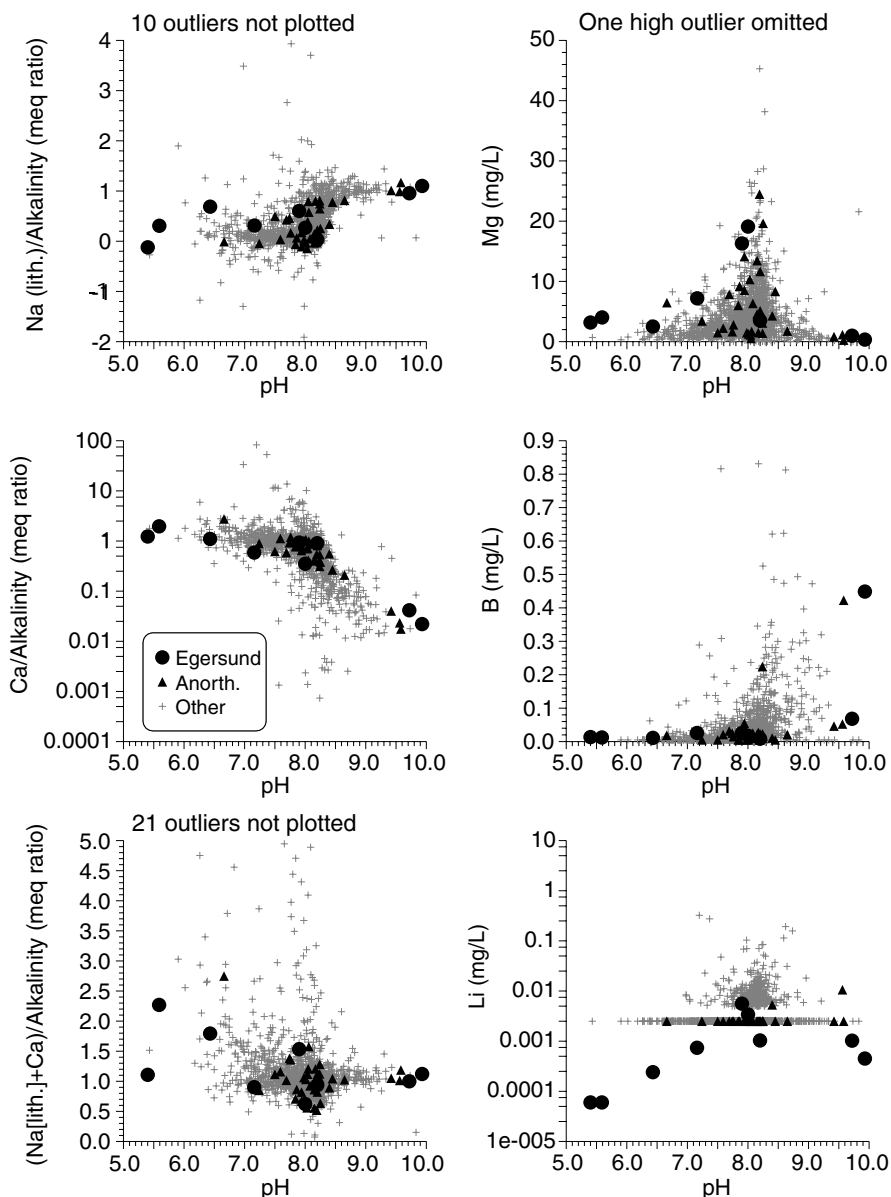


Fig. 4.  $x$ - $y$  diagrams showing the dependence on pH of concentrations of Mg, B, and Li and the milli-equivalent ratios Na/alkalinity, Ca/alkalinity and (Na + Ca)/alkalinity, for the sampled Norwegian groundwaters. Na corrected for marine salts. For key, see Fig. 3. Samples below detection limit plotted at a value of half the detection limit. Note many samples for lithium fall below a rather high detection limit for the 1996–97 survey.

in the groundwaters and calcium being depleted. We can infer from the calculated calcite saturation indices (Table 3), which approach zero at  $\text{pH} = 8$  and exceed zero in the highest pH waters, that the most likely explanation for this is calcite saturation and precipitation in a system which is closed with respect to  $\text{CO}_2$  (note the progressively declining calculated  $P\text{CO}_2$  with increasing pH in Table 3). The chemical equations demonstrating the various stages of evolution according to this model are shown in Table 5. The stages of evolution can be described as follows:

- I. A slightly acidic or circumneutral Na–Ca– $\text{HCO}_3^-$  groundwater, where the Na/Ca ratio reflects that in the plagioclase feldspar.
- II. Progressive loss of calcium during calcite saturation and precipitation, resulting in a circum-neutral sodium bicarbonate water.
- III. Following the consumption of  $\text{CO}_2$  in a closed system, the evolution of an alkaline sodium (bi)carbonate water.
- IV–VI. Theoretically, provided saturation with respect to the feldspar phases does not limit continued reaction, the closed system could then further develop (Stages IV and V), following the depletion of carbonate species in the water, to the re-accumulation of calcium, and to a highly alkaline calcium-dominated water (Stage VI).

Table 3  
Selected parameters for the nine samples collected from boreholes in the Egersund anorthosites in 1997, sorted according to increasing pH

Sample	1	2	3	4	5	6	7	8	9
Eh	+267	+260			+171	+186	+203	+70	+103
pH	5.40	5.59	6.43	7.16	7.90	8.00	8.20	9.72	9.93
Alkalinity	0.5	0.2	0.3	3.2	2.2	3.0	1.0	3.0	3.4
Na	12.3	20.5	27.9	52.9	40.7	28.0	13.1	83.2	103
Ca	12.3	7.86	6.64	37.7	40.9	21.2	18.1	2.49	1.50
Mg	3.16	4.02	2.49	7.18	16.3	19.1	3.52	0.97	0.33
K	0.97	2.16	<0.5	7.53	3.11	3.55	0.57	0.63	<0.5
Cl	24.5	34.2	41.5	53.5	18.1	16.9	22.2	30.9	30.5
SO <sub>4</sub>	9.55	13.9	11.8	15.8	33.9	27.1	7.02	12.1	18.4
NO <sub>3</sub>	8.96	12.5	<0.05	7.05	127	9.32	1.64	<0.05	11.7
F	<0.05	<0.05	<0.05	0.06	0.06	0.05	0.05	0.07	0.13
Si	4.19	2.06	4.26	5.01	3.41	14.4	3.68	4.16	5.61
Sr <sup>a</sup>	63.2	57.1	42.6	84.7	287	179	78	23.5	12.9
Al <sup>a</sup>	49.4	64.8	18.6	9.1	24.8	5.49	5.83	12.1	23.3
B <sup>a</sup>	13.8	12.3	11.0	25.5	25.7	17.0	8.48	68.3	449
Li <sup>a</sup>	0.06	0.06	0.24	0.74	5.58	3.40	1.03	1.02	0.45
IBE %	-3.16	+0.69	+1.06	-1.86	-2.16	-3.16	-0.62	-3.64	-2.72
Saturation index (SI)									
Kaolinite	+2.60	+3.10	+5.36	+4.64	+3.79	+3.54	+2.03	-0.57	-0.31
Gibbsite	+0.82	+1.38	+2.20	+1.76	+1.51	+0.76	+0.60	-0.61	-0.54
Ca-Mont.	-0.46	-0.26	+3.06	+2.67	+1.70	+2.24	-0.26	-3.07	-2.67
Chalcedony	-0.38	-0.69	-0.38	-0.30	-0.47	+0.15	-0.44	-0.53	-0.48
Calcite	-3.65	-4.06	-3.12	-0.68	-0.09	-0.12	-0.40	+0.43	+0.34
log(PCO <sub>2</sub> ) atm.	-1.00	-1.59	-2.26	-1.98	-2.89	-2.85	-3.51	-4.71	-4.95

pH and Eh were measured in the field. Alkalinity was titrated in the field to pH 4.3 and is cited as mEq/L. Element concentrations are given as mg/L, except for Sr, Al, B, and Li, given as µg/L. Eh is cited as mV. Sulphate/nitrate cited as mg/L SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>. Saturation indices are calculated using the program PHREEQCI, assuming a temperature of 7 °C. The ion balance error (IBE) in % is also calculated by PHREEQCI.

<sup>a</sup> Values in µg/L.

Table 4  
Results of soil gas measurements in hollow iron spikes inserted into Drift materials overlying the Egersund anorthosite aquifer (data from Frengstad, 2002)

	Eigerøya	Nålaugviga
Drift material	Till	Talus and soil
Depth of pipe = 0.6 m	3.4 vol.% = 10 <sup>-1.47</sup> atm	
Depth of pipe = 0.7 m		1.0% = 10 <sup>-2</sup> atm
Depth of pipe = 0.8 m	3.3 vol.% = 10 <sup>-1.48</sup> atm	

CO<sub>2</sub> cited as volume % and partial pressure (atmospheres).

It would appear, from the field data, that Stages I–III are being observed in the anorthosite groundwaters from Egersund. Furthermore, Stage II provides a mechanism for the apparent pH buffering effect observed in Fig. 2

(Eq. (2)). It will be noted that the ratio Na/Ca in the groundwater will depend on the initial plagioclase composition, the amount of reaction that has taken place under conditions of calcite saturation and precipitation and the amount of hydrolysis which has taken place in the effective absence of CO<sub>2</sub>.

Alternatively, one might hypothesise that Ca-removal might be taking place via cation exchange. Indeed, hydrochemical evolution pathways culminating in soft, sodium bicarbonate waters of high pH and low calcium concentration are observed in a remarkably wide range of aquifers throughout the world, such as the British Lincolnshire Limestone (Edmunds, 1981), a gabbro-anorthosite pluton in Ontario (Bottomley et al., 1990), Dutch Quaternary coastal sediments (Appelo and Postma, 1996), the Coal

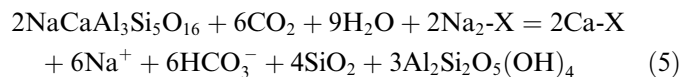
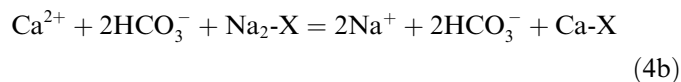
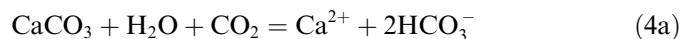
Table 5  
Reactions characterising the various stages of hydrochemical evolution of groundwater in plagioclase-dominated rocks, coupled with calcite saturation and precipitation as a mechanism for limiting calcium concentrations

Stage	Reaction
I	2NaCaAl <sub>3</sub> Si <sub>5</sub> O <sub>16</sub> + 8CO <sub>2</sub> + 9H <sub>2</sub> O = 2Ca <sup>2+</sup> + 2Na <sup>+</sup> + 6HCO <sub>3</sub> <sup>-</sup> + 4SiO <sub>2</sub> + 3Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> + 2CO <sub>2</sub>
II	4NaCaAl <sub>3</sub> Si <sub>5</sub> O <sub>16</sub> + 8CO <sub>2</sub> + 14H <sub>2</sub> O = 4CaCO <sub>3</sub> + 4Na <sup>+</sup> + 4HCO <sub>3</sub> <sup>-</sup> + 8SiO <sub>2</sub> + 6Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
III	6NaCaAl <sub>3</sub> Si <sub>5</sub> O <sub>16</sub> + 8CO <sub>2</sub> + 19H <sub>2</sub> O = 6CaCO <sub>3</sub> + 6Na <sup>+</sup> + 2CO <sub>3</sub> <sup>2-</sup> + 2OH <sup>-</sup> + 12SiO <sub>2</sub> + 9Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
IV	8NaCaAl <sub>3</sub> Si <sub>5</sub> O <sub>16</sub> + 8CO <sub>2</sub> + 28H <sub>2</sub> O = 8CaCO <sub>3</sub> + 8Na <sup>+</sup> + 8OH <sup>-</sup> + 16SiO <sub>2</sub> + 12Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
V	12NaCaAl <sub>3</sub> Si <sub>5</sub> O <sub>16</sub> + 8CO <sub>2</sub> + 46H <sub>2</sub> O = 8CaCO <sub>3</sub> + 4Ca <sup>2+</sup> + 12Na <sup>+</sup> + 20OH <sup>-</sup> + 24SiO <sub>2</sub> + 18Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
VI	20NaCaAl <sub>3</sub> Si <sub>5</sub> O <sub>16</sub> + 8CO <sub>2</sub> + 82H <sub>2</sub> O = 8CaCO <sub>3</sub> + 12Ca <sup>2+</sup> + 20Na <sup>+</sup> + 44OH <sup>-</sup> + 40SiO <sub>2</sub> + 30Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>

Although the equations represent subsequent stages in feldspar weathering, they are written for the total reaction from initial starting reactants (fixed CO<sub>2</sub>, feldspar and water) to the stage in question. Equations have been written for a labradorite/andesine plagioclase, and all reactions are written assuming a system closed with respect to CO<sub>2</sub> and a standardised fixed initial quantity of 8 mol CO<sub>2</sub> available.

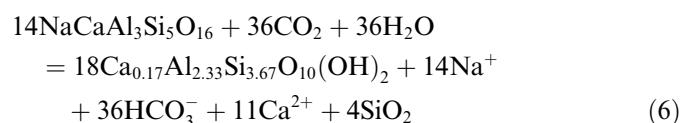


Measures of the English East Midlands (Banks, 1997). The low calcium concentrations typically permit the solution of high concentrations of fluoride (if present in the aquifer matrix), which can have adverse health impacts when consumed in excess. Many authors prefer to explain the origin of these waters in terms of a model where calcite or plagioclase dissolution is followed by cation exchange:



Calcium is continuously removed from the system and the water thus remains undersaturated with respect to calcite. Calcite or silicate dissolution may continue until dissolved  $\text{CO}_2$  has been consumed and the pH increases still further. For cation exchange to be a plausible mechanism for our anorthosite aquifer, there would need to exist sodium charged cation exchange media within the rock unit. Certainly, the occurrence of smectite-dominated fracture fillings with high CEC is well documented within Norway (Table 2), and the recent emergence of coastal terrains from the ocean due to post-glacial isostatic rebound could provide a mechanism for sodium charging of exchange media. However, it is unclear why any cation exchange process should suddenly be “activated” at  $\text{pH} = 8.2$  (as would seem the case from Fig. 3).

Finally, one might postulate that calcium is being removed by a secondary alteration product, such as a zeolite or a calcic smectite (Ca-beidellite is shown in Eq. (6), below), rather than kaolinite.



From the stoichiometry of this equation [compare with Eq. (3)], it will be seen that this reaction merely slows the rate (with respect to plagioclase consumption) of accumulation of  $\text{Ca}^{2+}$  in the solution (by a factor of 11/14) and does not result in calcium depletion. It also results in somewhat lower rates of alkalinity production and significantly lower rates of silica release than the kaolinite reaction. Even if we postulate the smectitisation of existing kaolinite Eq. (7), this would require 7 mol kaolinite to remove 1 mol calcium ions from solution (Garrels, 1967). Thus, while smectitisation may play some role in regulating calcium concentrations in solution, it is stoichiometrically inadequate as a mechanism for calcium depletion.

## 6. Hydrochemical modelling with PHREEQC

The code PHREEQC (Parkhurst, 1995) has been employed to simulate the weathering of a monomineralic sili-

cate system, namely an anorthosite comprising only plagioclase feldspar. In this study, the input file essentially specified that a given amount of plagioclase was dissolved in  $\text{CO}_2$ -charged pure water in 30 equal steps. Initially, for simplicity, alteration to kaolinite was assumed to be the dominant process and the phases calcite, chalcedony, kaolinite, and gibbsite were permitted to precipitate when they became oversaturated. Saturation with respect to feldspar phases was not considered to be a limiting factor, due to kinetic factors and the uncertainty around equilibrium conditions for feldspar dissolution/precipitation (Strömberg and Banwart, 1999; Bowser and Jones, 2002). The initial concentration of  $\text{CO}_2$  was specified, as was the type of system (open or closed with respect to  $\text{CO}_2$ ) and the temperature ( $7^\circ\text{C}$ , typical for southern Norway). Table 6 shows an example of a PHREEQC input file, corresponding to the weathering of labradorite in a closed system see Eq. (5).

Five idealised plagioclase minerals were modelled for a closed system with an initial  $\text{PCO}_2 = 10^{-1.5}$  atm, namely:

- Albite,  $\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16}$ , simulated by adding Na, Ca, Al, and  $\text{SiO}_2$  in the ratios 2:0:2:6,
- Oligoclase,  $\text{Na}_{1.5}\text{Ca}_{0.5}\text{Al}_{2.5}\text{Si}_{5.5}\text{O}_{16}$ ,
- Labradorite,  $\text{NaCaAl}_3\text{Si}_5\text{O}_{16}$ ,
- Bytownite,  $\text{Na}_{0.5}\text{Ca}_{1.5}\text{Al}_{3.5}\text{Si}_{4.5}\text{O}_{16}$ ,
- Anorthite,  $\text{Ca}_2\text{Al}_4\text{Si}_4\text{O}_{16}$ .

Above, the formulae of the feldspars have been normalised such that the stoichiometry of the defined reactions is analogous for all five model runs. In each case  $1.5 \times 10^{-3}$  mol feldspar (as defined by these formulae) have been dissolved in 30 steps. The results of the modelling runs are shown graphically in Figs. 5a–e. Additionally, the weathering of labradorite was simulated in

- open systems of  $\text{PCO}_2 = 10^{-3.5}$  (atmospheric pressure),  $10^{-2.5}$  and  $10^{-1.5}$  atm (soil gas in soils with high biological respiration activity).
- closed systems of initial  $\text{PCO}_2 = 10^{-3.5}$  and  $10^{-2.5}$  atm.

## 7. Results of modelling

### 7.1. General characteristics

In closed systems (Figs. 5a–e), one can, as predicted by Table 5, identify the following stages of groundwater evolution:

- Stage I. Accumulation of Na, Ca, bicarbonate alkalinity in solution; rapid increase of pH.
- Stage II. Removal of Ca and alkalinity from solution due to calcite precipitation; continued accumulation of Na, buffering effect on pH between pH 8 and 8.5.

Table 6

Specimen input file for PHREEQC for the weathering of  $1.5 \times 10^{-3}$  mol labradorite (defined as  $\text{NaCaAl}_3\text{Si}_5\text{O}_{16}$ ) or  $3 \times 10^{-3}$  mol (defined as  $\text{Na}_{0.5}\text{Ca}_{0.5}\text{Al}_{1.5}\text{Si}_{2.5}\text{O}_8$ ) by water in a closed system of initial  $\text{PCO}_2 = 10^{-1.5}$  atm and temperature  $7^\circ\text{C}$

```

Title Dissolution of labradorite
SOLUTION 1
  units mol/l
  pH      4.6  charge
  pe      8
  temp    7
  C(4)    1.914e-3
REACTION 1
  Na      1
  Ca      1
  Al      3
  SiO2    5
  1.5e-3  moles  in      30      steps
Equilibrium_phases 1
O2(g)    -0.7
#Anorthite -3 0
#Albite  -1 0
Calcite  0 0
Gibbsite 0 0
Kaolinite 0 0
Chalcedony 0 0
SELECTED_OUTPUT
-file Output
-totals Ca      Na      Si  Alkalinity
-molalities HCO3- CO3-2  OH-  CO2(g)
-equilibrium_phases Calcite Chalcedony Gibbsite
-saturation_indices Calcite Chalcedony Ca-Montmorillonite Gibbsite CO2(g)
-gases CO2(g) O2(g)
END

```

Precipitation of gibbsite, chalcedony, kaolinite, and calcite are permitted when oversaturated. Note: the mineral designated Ca-montmorillonite by PHREEQC would today be more accurately known as Ca-beidellite.

- Stages III–VI. Continued increase in pH in range 8.5–11, increase in carbonate (Stage III) and then hydroxide alkalinity (Stages IV and V), with eventual re-accumulation of Ca in system (Stage VI).

Interestingly, modelling indicates that Ca-beidellite does not reach saturation during these reactions.

### 7.2. Influence of feldspar composition

From Fig. 5 it will be noted that the composition of feldspar is important for determining the evolution of water composition in a closed system; in particular, at which stage calcium is removed by calcite precipitation and the quantities of sodium and calcium released during Stages I and II. In the case of labradorite, <30 mg/L Na are released during Stages I and II, with only 24 mg/L  $\text{Ca}^{2+}$  being released during Stage I. The weathering of oligoclase results in more sodium and less calcium being released, while the weathering of bytownite has the reverse effect. In the case of bytownite, although  $\text{Ca}^{2+}$  accumulates more “steeply” in the water in Stage I, it is also removed efficiently during Stage II, and the commencement of Stages III and VI (re-accumulation of calcium) may be observed in the final stages of the modelling run. In all cases, the Stage II pH buffer is observed at between 8.0 and 8.5.

### 7.3. $\text{CO}_2$ conditions: closed systems

The simulations in Fig. 5 were run assuming closed systems with an initial  $\text{PCO}_2$  of  $10^{-1.5}$  atm. Simulations were also run for labradorite in closed systems with lower initial  $\text{PCO}_2$  values of  $10^{-2.5}$  and  $10^{-3.5}$  atm (Fig. 6). It will be seen that the low initial content of  $\text{PCO}_2$  (for example,  $10^{-2.5}$  atm) allows very little calcium (around 0.1 mmol = 4 mg/L) to dissolve from the plagioclase before the system becomes saturated with respect to calcite at a high pH of around 10. Alkalinity is also very low at this point, at a little over 0.2 mEq/L. This water chemistry, evolving under closed  $\text{CO}_2$  conditions with a low initial  $\text{PCO}_2$  (characteristic of vegetation- and soil-poor Iceland) provides an explanation for some of the high pH, low TDS basalt groundwaters described by Gislason and Eugster (1987) from Iceland. In the PHREEQC simulation, calcium can continue to accumulate in highly alkaline waters, beyond the point of calcite saturation, when all  $\text{CO}_2$  is consumed and carbonate species are depleted from solution. Silicon also accumulates in such high pH waters. It is dubious whether the simple PHREEQC model can adequately simulate such conditions, however, as other components and saturation with respect to other mineral phases may become important at such high pH. In summary, closed systems seem to require a relatively high initial  $\text{PCO}_2$  of around  $10^{-1.5}$  to generate quantities of calcium

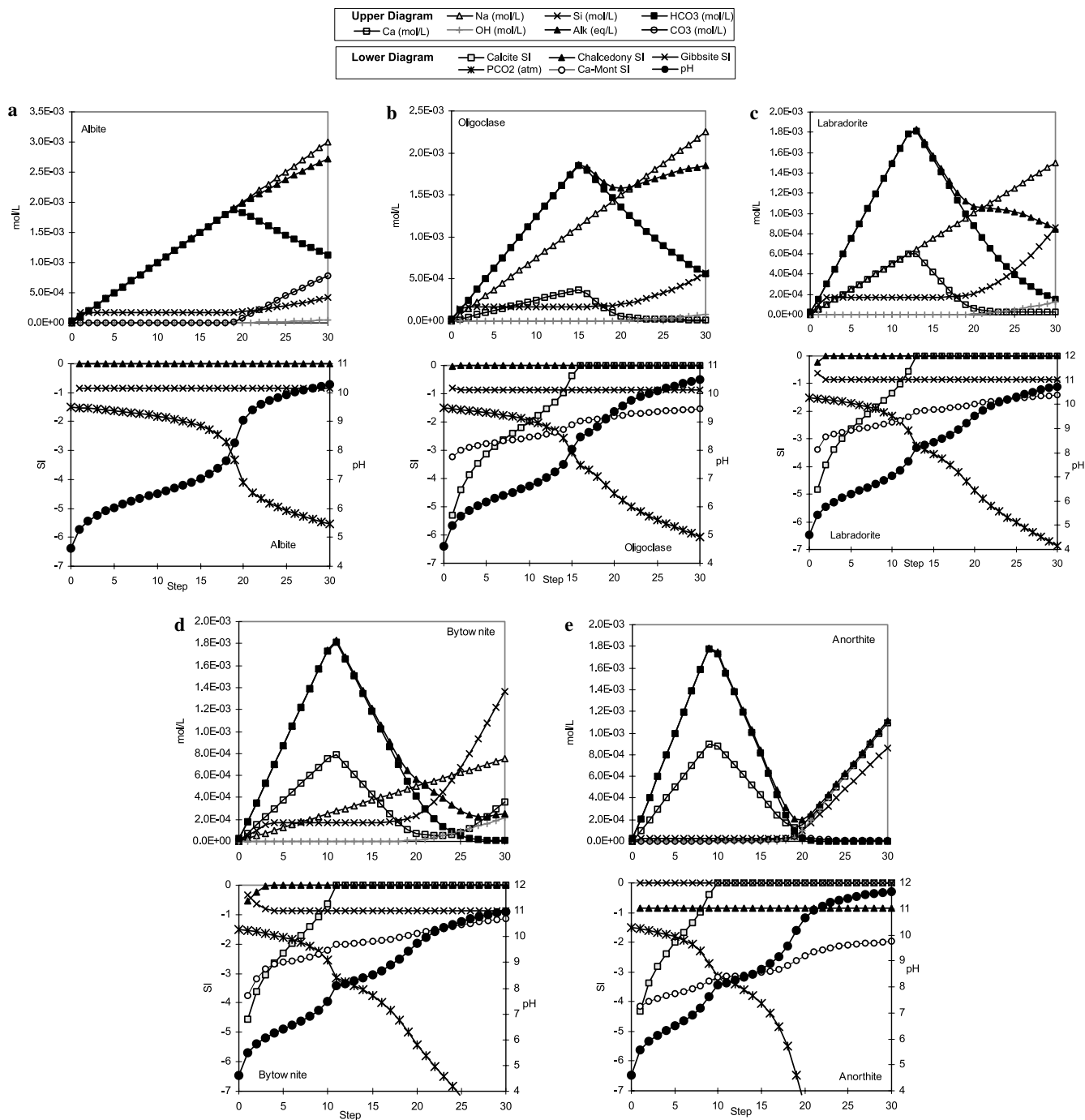


Fig. 5. Modelled evolution of groundwater chemical composition, using PHREEQC, by dissolving  $1.5 \times 10^{-3}$  mol (using molar formulae described in text) of five different plagioclase feldspars [(a) albite, (b) oligoclase, (c) labradorite, (d) bytownite, and (e) anorthite] in water of temperature  $7^\circ\text{C}$  and initial  $PCO_2 = 10^{-1.5}$  atm (closed  $CO_2$  system) in 30 steps. Precipitation of calcite, kaolinite, gibbsite, and chalcodony is permitted if oversaturated. The diagrams on the top show the evolution of total element concentrations, those on the bottom show saturation indices (SI).  $\log_{10}(PCO_2)$  is also plotted on the SI axis. Note that alkalinity is defined as the equivalent per litre (eq/L) sum of  $HCO_3^-$ ,  $CO_3^{2-}$  and  $OH^-$  and does not include other alkaline species formed at high pH such as Si-anions. Note that the ratio Na/alkalinity increases as the Na/Ca ratio in the feldspar increases.

and alkalinity to the dissolved phase which are compatible with field observations.

#### 7.4. $CO_2$ conditions: open systems

Simulations have also been carried out assuming ranges of initial  $PCO_2$  conditions for open systems

(Fig. 7). Simulated open systems do not typically achieve the highest pH values observed in real waters from Norwegian anorthosites (and indeed, the calculated  $PCO_2$  values for these waters in Table 3 demonstrate that they are evolving in closed systems). Rather low partial  $CO_2$  pressures of around  $10^{-3}$  atm are required to attain a pH value of around 8.2 (characteristic of

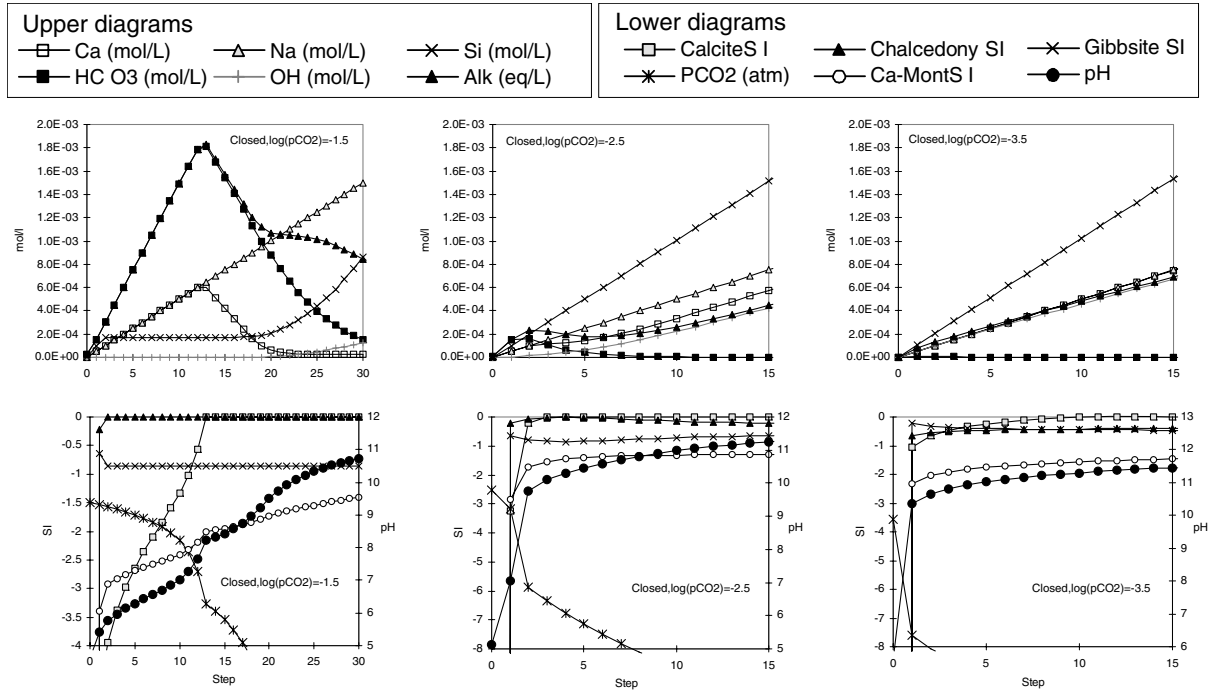


Fig. 6. Modelled evolution of groundwater chemical composition, using PHREEQC, by dissolving  $1.5 \times 10^{-3}$  mol (using molar formulae described in text) of labradorite in water of temperature  $7^\circ\text{C}$  and initial  $\text{PCO}_2$  values (from left to right)  $10^{-1.5}$ ,  $10^{-2.5}$ , and  $10^{-3.5}$  atm (closed  $\text{CO}_2$  system) in 30 steps (only 15 steps shown for  $10^{-2.5}$  and  $10^{-3.5}$  atm). Precipitation of calcite, kaolinite, gibbsite, and chalcedony is permitted if oversaturated. See Fig. 5 for explanation.

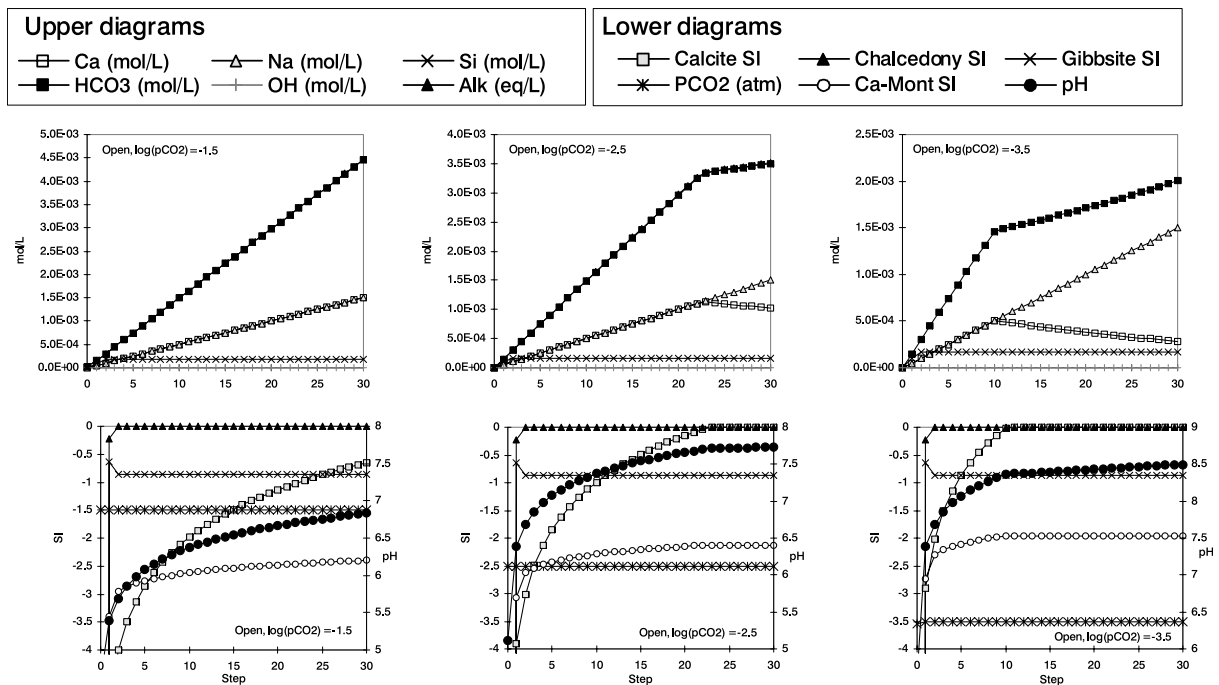


Fig. 7. Modelled evolution of groundwater chemical composition, using PHREEQC, by dissolving  $1.5 \times 10^{-3}$  mol (using molar formulae described in text) of labradorite in water of temperature  $7^\circ\text{C}$  and  $\text{PCO}_2$  values of (from left to right)  $10^{-1.5}$ ,  $10^{-2.5}$ , and  $10^{-3.5}$  atm (open  $\text{CO}_2$  system) in 30 steps. Precipitation of calcite, kaolinite, gibbsite, and chalcedony is permitted if oversaturated. See Fig. 5 for explanation.

the bulk of the Norwegian crystalline bedrock groundwaters). Under open  $\text{CO}_2$  conditions, silicate weathering systems can, however, result in calcium removal by calcite precipitation (Fig. 7) and thus in the formation of

sodium bicarbonate waters. Note that the modelled open system with  $\text{PCO}_2 = 10^{-1.5}$  atm attains pH values of around 7, but is capable of accumulating greater amounts of dissolved calcium (around 104 mg/L), sodi-

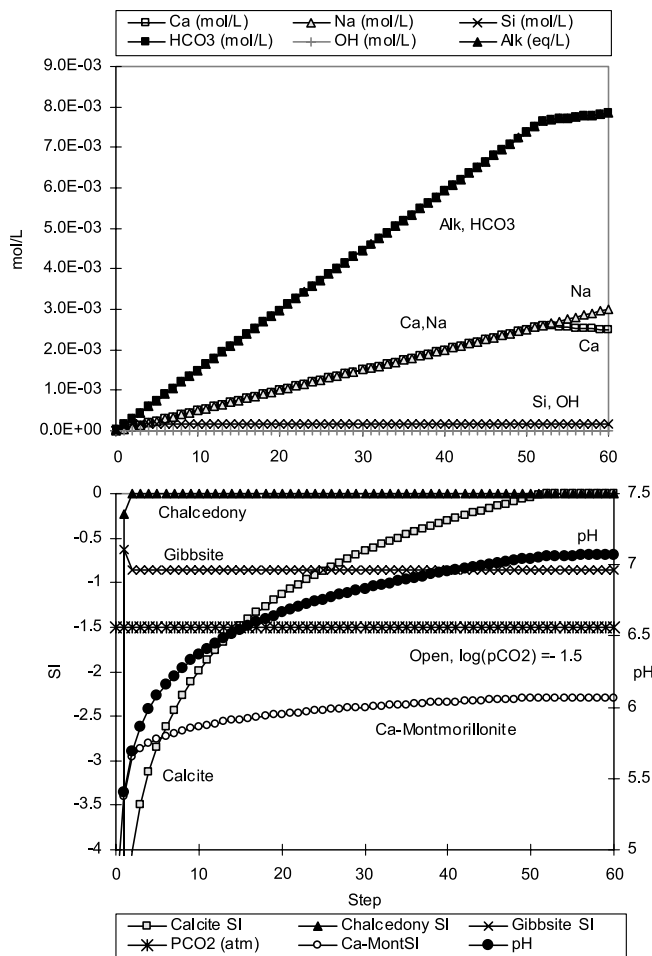


Fig. 8. Extended version of Fig. 7 for  $PCO_2 = 10^{-1.5}$  atm, by dissolving  $3 \times 10^{-3}$  mol of labradorite in water of temperature  $7^\circ\text{C}$  in 60 steps. Precipitation of calcite, kaolinite, gibbsite, and chalcidony is permitted if oversaturated.  $\log_{10}(PCO_2)$  is also plotted on the SI axis.

um (around 60 mg/L) and alkalinity (around 7.7 mEq/L) before calcite saturation is achieved (not shown in Fig. 7, but occurring at around step 52 in an extended version of the model, as shown in Fig. 8).

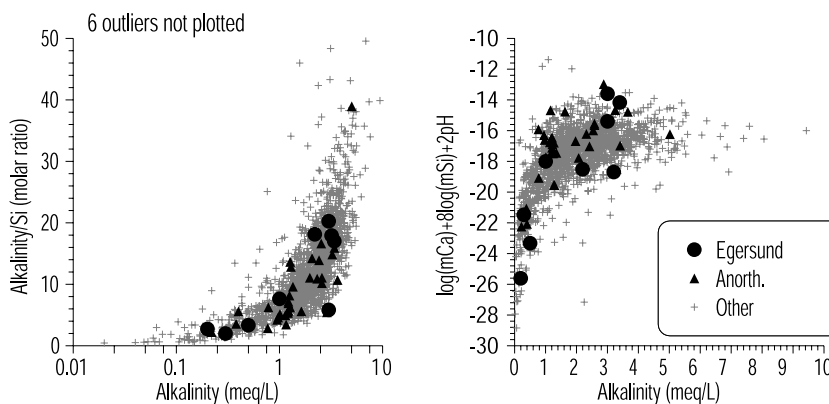
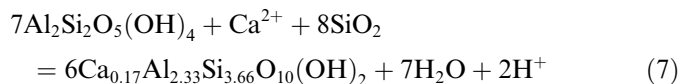


Fig. 9. Plot of (left) the molar ratio alkalinity/Si plotted against alkalinity and (right) the expression  $\log_{10}(mCa) + 8\log_{10}(mSi) + 2pH$ , plotted against alkalinity, where  $mCa$  and  $mSi$  are molar concentrations of calcium and silicon, for the sampled Norwegian groundwaters. For key, see Fig. 3.

### 7.5. Influence of choice of alteration product

Garrels (1967) and subsequent authors (Gislason and Eugster, 1987; Bowser and Jones, 2002) have suggested that, while kaolinite might be the initial alteration product in the context of plagioclase weathering, calcic smectite might be a more likely alteration product during later stages of evolution. Note that clay terminology has changed since Garrels' time and that his "Ca-montmorillonite" would now be termed a calcic smectite or, more specifically, Ca-beidellite. By comparing Eqs. (3) and (6), it will be seen that alteration of labradorite to kaolinite results in a molar  $HCO_3^-/SiO_2$  ratio of 1.5, while smectite (Ca-beidellite) alteration results in a ratio of 9. Garrels (1967) regarded a ratio in excess of 3 as diagnostic of smectite alteration. However, Garrels (1967) also assumed that silica saturation was not a control on dissolved silica concentrations. In the PHREEQC simulations of this study, chalcidony becomes saturated before Ca-beidellite and (kinetic factors permitting) constrains silicon concentrations at modest levels. Fig. 9 shows Garrels (1967) "diagnostic" plot of molar  $HCO_3^-/Si$  ratio versus alkalinity for the Norwegian data. The trend described by the data certainly reflects that in Garrels' data, but do the high molar ratios reflect smectite formation or merely silica saturation controlling Si concentrations? If the latter hypothesis is true, it may even cast some doubt on thermodynamic data for smectite/beidellite used in models such as PHREEQC, as these data may ultimately be derived from assumptions made concerning the Sierra Nevada spring studies.

Garrels (1967) pointed out that at equilibrium between kaolinite and Ca-beidellite:



Thus, neglecting activity in favour of molality, and designating  $mCa^{2+}$  the molal concentration of calcium, etc.

$$\log_{10}mCa^{2+} + 8\log_{10}mSi + 2pH \approx \text{constant}$$



If the above expression is plotted against alkalinity for the Norwegian groundwaters (Fig. 9), we do indeed find that it tends towards a constant value of around  $-16$  at high values of alkalinity, indicating equilibrium with calcium smectite in the more hydrochemically mature waters.

Calculated saturation indices (Table 3) suggest that kaolinite and gibbsite are plausible alteration products in all but the most alkaline waters, and that Ca-beidellite is oversaturated in the circum-neutral waters. Calculated saturation indices for these phases must be treated with caution, however, as dissolved aluminium analyses will be subject to inaccuracy due to the possible presence of colloidal particles, and also because concentrations of  $Al^{3+}$  will be sensitive to complexation with other dissolved species. The chalcedony saturation index tends to be only slightly below zero in most samples and this may be suggestive of a microcrystalline silica phase being a controlling factor for Si in the waters. Clearly, an assessment of the likely alteration products from silicate hydrolysis is not straightforward; substantial oversaturation with respect to kaolinite, gibbsite, and smectite in some samples suggests either that there are kinetic constraints on the formation of these minerals (that are not considered in the PHREEQC modelling) or that other phases (not included in the PHREEQC database) may be actively forming.

Two approaches were used to assess the influence of the selected alteration product on the water chemistry that evolves during the weathering of labradorite/bytownite under closed conditions with an initial  $PCO_2$  of  $10^{-1.5}$  atm. First, precipitation of gibbsite and chalcedony were suppressed in the PHREEQC model runs. This had the effect of moving the Ca-beidellite saturation index (SI) upwards, but saturation was still not achieved within the designated run.

Second, the labradorite and bytownite simulations were re-run, but this time “forcing” the precipitation of Ca-beidellite when the molar ratio  $HCO_3^-/Si$  exceeded three. This was achieved by suppressing the precipitation of gibbsite and kaolinite, and allowing the formation of Ca-beidellite when oversaturated. Fig. 10 illustrates the result. For labradorite, the effect is minimal: calcium accumulates in solution at a slightly lower rate (relative to the consumption of plagioclase), calcium saturation occurs a little later and final pH is slightly lower (compare with Fig. 5c). For bytownite, the effect is more pronounced. While the thermodynamic data for Ca-beidellite employed in the PHREEQC modelling are acknowledged to be uncertain (and based on a very limited number of studies), it is possible to conclude that the main effect of Ca-beidellite as opposed to kaolinite as a secondary alteration product is to have a

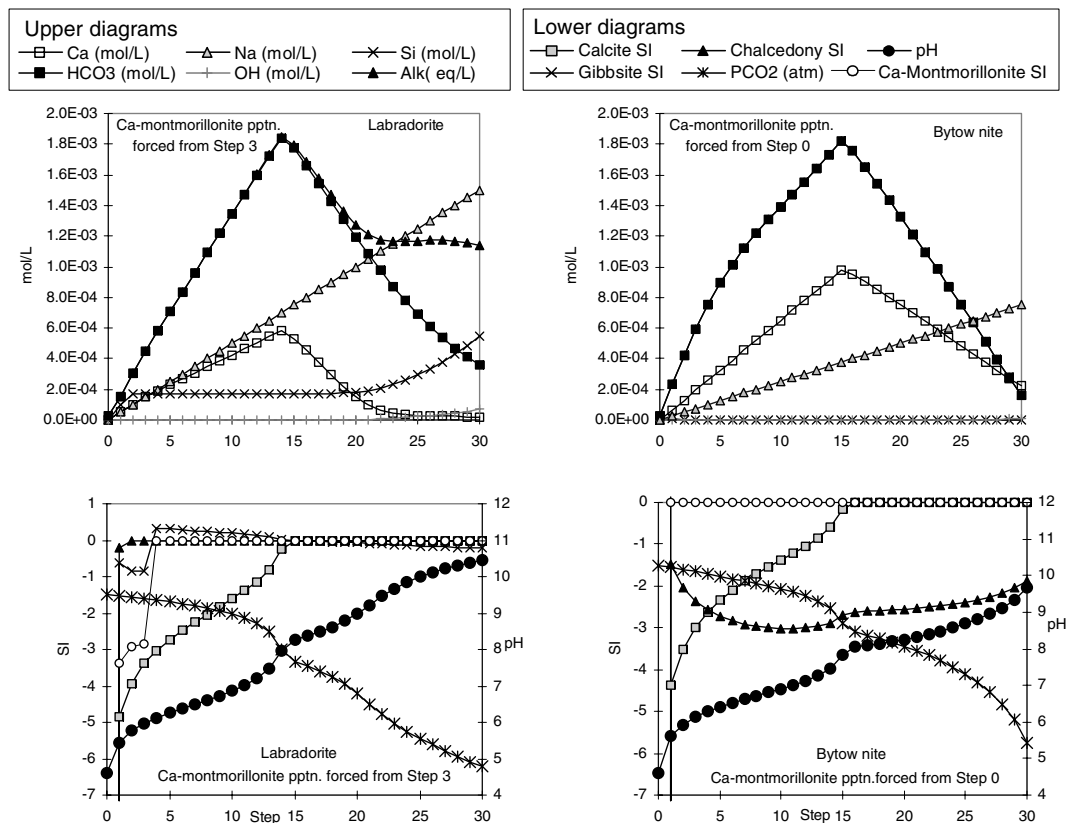


Fig. 10. Modelled evolution of groundwater chemical composition, using PHREEQC, by dissolving  $1.5 \times 10^{-3}$  mol (using molar formulae described in text) of labradorite and bytownite in water of temperature  $7^\circ C$  and initial  $PCO_2$   $10^{-1.5}$  atm (closed  $CO_2$  system) in 30 steps. Precipitation of calcite, kaolinite, gibbsite, and chalcedony is initially permitted if oversaturated. When the molar ratio  $HCO_3^-/Si$  exceeds three, precipitation of kaolinite and gibbsite is suppressed (from Step 3 in the case of labradorite and Step 1 in the case of bytownite) and calcium beidellite is permitted to precipitate. See Fig. 5 for further explanation.

minor effect on the rate (relative to plagioclase dissolution) at which solutes such as Ca, Si, and alkalinity accumulate in the system [compare Eq. (6) with Eq. (3)].

Clearly, other alteration products, such as zeolites or sodic smectites (which might be favoured in waters with a high Na/Ca ratio), might be conceivable in the context of feldspar weathering, but a detailed consideration of these is beyond the scope of this paper. Future research might focus on the empirical identification of secondary plagioclase alteration products at different stages of groundwater evolution.

### 7.6. Summary of modelling

Modelling of a simple system comprising monomineralic plagioclase feldspar suggests that plagioclase weathering alone can broadly result in the main hydrochemical evolutionary features of anorthositic groundwaters, culminating in high-pH, high-Na, low-Ca compositions, without the need to invoke cation exchange. The modelling has tended to assume alteration of plagioclase to a kaolinite alteration product, although forcing Ca-beidellite as the alteration product does not alter the broad evolutionary trends of the water's chemical composition: attainment of calcite saturation is still the main factor controlling calcium and alkalinity concentrations, resulting in a pH buffering effect around 8–8.5.

CO<sub>2</sub> conditions are important for the evolution of such systems:

- (i) Open systems with respect to CO<sub>2</sub> are capable of generating sodium bicarbonate waters of pH around 8.2 by weathering of plagioclase, although low PCO<sub>2</sub> values (ca. 10<sup>-3</sup> atm) are required to achieve such high pH values, and quantities of calcium released to the dissolved phase are rather modest (around 15 mg/L for PCO<sub>2</sub> = 10<sup>-3.5</sup> atm—Fig. 7).
- (ii) Higher PCO<sub>2</sub> values in open systems result in lower pH waters, later stage removal of Ca from solution and accumulation of greater amounts of calcium and alkalinity in the dissolved phase.
- (iii) To achieve sodium bicarbonate water types of pH above ca. 8.5 by plagioclase weathering, it appears that closed systems are necessary. However, the quantities of dissolved cations released are still rather low compared with empirical data.

Finally, it has already been noted that the thermodynamic data for Ca-beidellite employed by hydrochemical models such as PHREEQC are subject to significant uncertainty. If silica saturation (rather than smectite formation) is the correct explanation for elevated HCO<sub>3</sub><sup>-</sup>/Si ratios in our waters, it may even cast further doubt on thermodynamic data for smectite/beidellite used in models such as PHREEQC, as these data may ultimately be derived from assumptions made concerning Garrels' Sierra Nevada spring studies.

## 8. Comparison with empirical data

### 8.1. Concentration of CO<sub>2</sub> in soil gas

If an evolutionary model based solely on silicate weathering is adequate to explain the evolution of high-pH, sodium bicarbonate waters, then it seems that the system must be partially closed with respect to CO<sub>2</sub> to generate a high enough pH. However, closed systems would also require a rather high initial PCO<sub>2</sub> > 10<sup>-2</sup> atm to release sufficient Na from feldspar weathering. In a poorly vegetated, northern area such as Egersund one might not intuitively expect such high PCO<sub>2</sub> values in soil gas. Indeed Brook et al. (1983) produced a world map of soil CO<sub>2</sub> pressure based on an empirical relationship with actual evapotranspiration (as an indirect measure of biological productivity), on which a mean soil CO<sub>2</sub> pressures of between 10<sup>-2.2</sup> and 10<sup>-2.6</sup> atm were indicated during the growing season for South Norway.

However, higher values have been found in similar climatic situations in Canada and Fennoscandia. Nesbitt and Cramer (1993) calculated from pH and alkalinity groundwater CO<sub>2</sub> partial pressures ranging between 10<sup>-1.2</sup> and 10<sup>-2.5</sup> bars with an average of 10<sup>-1.75</sup> bars in Quaternary sands and clays at Pinawa, Manitoba, Canada (1 bar = 0.987 atm). Jacks (1973) found PCO<sub>2</sub> values between 10<sup>-1.6</sup> and 10<sup>-3.5</sup> atm in a number of bedrock boreholes in Gnesta and Skokloster, near Stockholm, Sweden, where the terrain includes bare rock, pasture and forest. He found that total inorganic carbon remained constant with increasing depth, concluding that CO<sub>2</sub> was only added in the soil zone. The varying CO<sub>2</sub> concentrations were thus ascribed to different infiltration conditions, where the kind of soil and type of terrain were the main variables. According to Jacks (1973), areas with much bare rock were likely to have low CO<sub>2</sub> concentrations in the groundwater.

Bottomley et al. (1990) cast doubt on whether silicate weathering is an adequate mechanism to explain the evolution of sodium bicarbonate waters in the Canadian Shield, and consequently favoured an ion exchange mechanism. They argued that, in the transition from Ca-HCO<sub>3</sub> to Na-HCO<sub>3</sub> waters, around 2 mmol/L (46 mg/L) Na is acquired. To achieve this would require an initial partial pressure of around 10<sup>-1</sup> atm, which they regard as unrealistic. However, they themselves recorded PCO<sub>2</sub> of up to 10<sup>-1.3</sup> atm in groundwaters from their shallower wells.

Finally, the results of soil gas analysis from this study (Table 4) confirm that, despite the cool climate and poor vegetation cover, soil gas PCO<sub>2</sub> concentrations of 10<sup>-2</sup> atm or above are not unrealistic for the Egersund area. Indeed, thermodynamic modelling of the anorthosite groundwaters in Table 3 suggests that the least evolved waters are in equilibrium with PCO<sub>2</sub> concentrations of around or above 10<sup>-1.5</sup> atm. Future research could focus on further direct empirical measurements of PCO<sub>2</sub> in soil gas, recharge water and groundwater, and an assessment of whether additional CO<sub>2</sub> may be generated by the decom-

position of complex organic solutes and colloids, such as the humic and fulvic acids often observed in Norwegian bedrock groundwaters.

## 8.2. Norwegian bedrock groundwater data

The empirical Norwegian bedrock groundwater data appear to confirm the existence of a pH buffer at 8.2–8.3 (Fig. 2), which can be explained either by closed-system CO<sub>2</sub> plagioclase weathering or by an open system at a low PCO<sub>2</sub> of some 10<sup>-3</sup> atm (Fig. 5–7). Real data (Figs. 3, 4 and Table 3) indicate that during Stages I and II, some 30–50 mg/L lithogenic Na<sup>+</sup> accumulates in the dissolved phase of groundwaters in anorthosite rocks. The quantities of sodium that may be generated by assuming various initial concentrations of carbon dioxide in a closed system are calculated in Table 7, where the groundwater temperature is assumed to be 280 K (ca. 7 °C), which is regarded as typical for southern Norway. The solubility of carbon dioxide in water at this temperature is calculated using the algorithm provided by Appelo and Postma (1996, Appendix B). It would appear that a PCO<sub>2</sub> of around 10<sup>-2</sup> to 10<sup>-1.5</sup> is required to generate 30–50 mg/L Na using a closed system silicate weathering model (Table 7, Figs. 5, 6). Such concentrations could be generated using an open system model, even with a relatively low PCO<sub>2</sub> of 10<sup>-3</sup> atm (Fig. 7).

The observed alkalinities of up to 5 mEq/L and calcium concentrations of up to 50 mg/L in anorthosite groundwaters cannot be explained by the closed CO<sub>2</sub> system models (Figs. 5 and 6) alone. Some component of open system CO<sub>2</sub> weathering is required to generate such concentrations (Fig. 7). The observed silicon concentrations are compatible with a saturation control due to a silica phase at low and intermediate pH values. It thus seems that a single model is inadequate to explain all aspects of major ion chemistry in the water samples. However, a silicate weathering model involving a system initially open to CO<sub>2</sub> (to accumulate sufficient quantities of dissolved ions and alkali-

linity), followed by closure (to generate a high pH in the resultant water) is regarded as plausible. This pathway is reminiscent of the Vekol Valley study of Bowser and Jones (2002).

## 8.3. Further implications: empirical evidence from literature sources

If the simple hydrochemical evolution model for anorthosite groundwater described in this paper is correct, certain predictions can be made that can be compared with field evidence. Furthermore, if Garrels and Mackenzie's (1967) assertion that plagioclase weathering is responsible for 80% of the groundwater chemical composition in other silicate crystalline lithologies, one might expect to observe the same evolutionary trend in many other rock types also.

First, the model predicts that secondary calcite is precipitated during Stages II and III of groundwater evolution (Table 5). The upper portions of a crystalline aquifer would be expected to be depleted of any calcite due to dissolution by hydrochemically immature (Stage I) groundwaters. However, if the model is correct, it should be possible to identify secondary calcite, derived from groundwaters, at deeper levels in an aquifer system. Indeed, White et al. (1998) documented calcite contents of 300–3000 mg/kg in fresh granitoid rocks, as micro-fracture fillings, as replacement for plagioclase and as disseminated matrix crystals. They do not propose a unique genesis for such calcite but suggest a probability that it is partially hydrothermally derived. White et al. (2005) favoured late-stage (subsolvus) magmatic processes for the occurrence of much accessory calcite in granitoid rocks. Fritz and Mohr (1984), however, provided a description of secondary calcite precipitation in a boulder of weathered anorthosite from Oklahoma. The calcite was found in sealed microscopic solution channels. The authors clearly ascribed its origin to the weathering of bytownite feldspar, and its precipitation in a solution channel closed to atmospheric carbon dioxide. Moreover, Iwatsuki et al. (2002) studied the granitic rocks to around 1000 m depth in the Tono area of Central Japan. In addition to hydrothermal and marine calcite, they identified secondary calcite deposited by fresh groundwaters in the relatively recent past (probably during the last 50,000 years). In these groundwaters, the hydrochemical composition became progressively dominated by sodium bicarbonate with depth at the expense of calcium.

In the model proposed in this paper, the dissolved inorganic carbon content of the crystalline rock groundwaters is entirely derived from soil gas carbon dioxide, and would be expected to have a corresponding inorganic carbon δ<sup>13</sup>C isotopic signature. Any deviation from this signature would be indicative of, for example, dissolution of calcite from superficial sediments. In the above-mentioned study by Iwatsuki et al. (2002), the carbon in the secondary freshwater calcite had a negative δ<sup>13</sup>C signature, reaching as low as -29‰, consistent with it being ultimately derived from weathering of plagioclase by soil gas carbon dioxide (i.e.,

Table 7

The quantities of sodium generated during Stages I and II, Stages I–IV, respectively, during plagioclase weathering as described by Eqs. (II) and (IV) in Table 5, assuming a closed CO<sub>2</sub> system with varying initial soil gas partial pressures of CO<sub>2</sub>, a Al<sub>50</sub>An<sub>50</sub> plagioclase silicate composition and a temperature of ca. 7 °C

Initial CO <sub>2</sub>	Stages I and II	Stages I–IV
Ratio Na released: CO <sub>2</sub> consumed (mol)	0.5:1	1:1
PCO <sub>2</sub> = 10 <sup>-1.5</sup> atm = 1.91 mmol/L = 84 mg/L	Na = 0.95 mmol = 22 mg/L	Na = 1.91 mmol = 44 mg/L
PCO <sub>2</sub> = 10 <sup>-2.0</sup> atm = 0.60 mmol/L = 27 mg/L	Na = 0.30 mmol = 6.9 mg/L	Na = 0.60 mmol = 14 mg/L
PCO <sub>2</sub> = 10 <sup>-2.5</sup> atm = 0.19 mmol/L = 8.4 mg/L	Na = 0.095 mmol = 2.2 mg/L	Na = 0.19 mmol = 4.4 mg/L

no carbon input from weathering of, for example, primary marine calcite). Current groundwater in the granites had  $\delta^{13}\text{C}$  signatures of around  $-15\text{‰}$  to  $-18\text{‰}$ , somewhat lower than one might expect if bicarbonate were derived solely from dissolution of marine carbonate by soil gas  $\text{CO}_2$ , and consistent with at least a component of direct plagioclase weathering by soil gas  $\text{CO}_2$ . Carbon isotope ( $^{13}\text{C}$  and  $^{14}\text{C}$ ) analyses of dissolved carbon phases in water and of any aquifer carbonate phases might be a fruitful topic of future research in the Egersund anorthosites. Pure silicate weathering by dissolved  $\text{CO}_2$  would be expected to result in dissolved (bi)carbonate having a  $^{13}\text{C}$  signature similar to soil gas carbon dioxide.

Finally, the silicate hydrolysis model allows the possibility (see Stage VI of Table 5 and Figs. 5d and e) that in extremely evolved, high pH waters, where carbonate species are absent, calcium dominated waters may eventually develop. Intriguingly, Bottomley et al. (1990) and Gascoyne and Kamineni (1993) described the evolution of groundwaters with depth in the Canadian shield. The most typical evolutionary sequence progressed from  $\text{Ca-HCO}_3$ , through  $\text{Na-HCO}_3$  to  $\text{Na-Cl}$  and  $\text{Ca-Cl}$ . In other words, the re-accumulation of calcium (in the absence of bicarbonate) in solutions as the culmination of the evolutionary pathway was observed. A similar pattern is observed in the granites of Stripa, Sweden (Nordstrom et al., 1989). The dominance of chloride in the anionic composition can be explained by the progressive admixture of the evolving water with a deep seated brine (not uncommon in many hard-rock shield areas).

## 9. Conclusions

On the basis of modelling work presented in this paper, it is argued that plagioclase weathering by  $\text{CO}_2$  is an adequate model to explain the evolution of the main hydrochemical features (i.e., Ca, Na, pH, and alkalinity trends) of the groundwaters found in the Egersund anorthosite complex, culminating in a high pH, sodium-dominated, calcium-poor hydrofacies. To derive the observed solute concentrations in anorthositic groundwaters one may invoke silicate weathering under open or closed  $\text{CO}_2$  conditions:

- (i) Under closed  $\text{CO}_2$  conditions a relatively high initial  $PCO_2$  of maybe  $10^{-1.5}$  is required to generate the highest observed quantities of dissolved lithogenic Na. Field studies in Fennoscandia and Canada do appear to suggest that soil gas  $PCO_2$  values in excess of  $10^{-2}$  atm are realistic. This closed  $\text{CO}_2$  model alone, however, fails to generate the quantities of dissolved Ca and alkalinity observed in empirical samples.
- (ii) Under open  $\text{CO}_2$  conditions a lower  $PCO_2$  of some  $10^{-3}$  atm is adequate to generate sodium bicarbonate waters of pH up to ca. 8.2 (where a calcite precipitation buffer controls pH). Such a model also generates quantities of calcium, bicarbonate and sodium more

closely resembling observed concentrations. However, to generate pH values in excess of 8.5, it appears necessary to invoke some form of cation exchange (to remove calcium and thus negate the calcite precipitation buffer) or closure with respect to  $\text{CO}_2$ .

A purely closed model does not quite generate the observed concentrations of solute species, and a purely open model does not attain the observed high pH values. However, a mixed model involving initially open  $\text{CO}_2$  conditions (to generate adequate quantities of dissolved calcium, bicarbonate, and sodium), followed by closure with respect to  $\text{CO}_2$  (to achieve elevated pH values) is probably the most realistic scenario. It should also be remembered that the equations cited and PHREEQC modelling work presented in this paper represent a highly idealised system. Reality will be more complex, providing grounds for some divergence of real from modelled data, for the following reasons:

- The anorthosite groundwater samples are not derived from a single groundwater evolution pathway.
- The anorthosite massif is *geochemically* heterogeneous, ranging from monomineralic plagioclase rocks (of the type simulated using PHREEQC, above) to more complex multiminerale assemblages including mafic and accessory phases. In lithologies comprising silicate minerals other than plagioclase feldspar, weathering of non-calcium silicates is likely to release alkalinity in excess of calcium, facilitating early calcite saturation and removal of calcium from the dissolved phase.
- The sampled boreholes possibly may draw water from more than one fracture system. Such systems are likely to be *hydraulically* and *hydrochemically* heterogeneous.
- The groundwater, during its evolution may have been subject to rock–water interaction under both open (e.g., in superficial Quaternary deposits, possibly with a significant calcite content) or closed (deep fracture) conditions.
- The sampled waters may have been recharged in vegetation-poor (highland anorthosite outcrop), low  $PCO_2$  conditions or lowland, soil-covered areas, with high  $PCO_2$  conditions.

The major ion hydrochemical composition of the anorthosite groundwaters is broadly similar to that in a wide range of other Norwegian crystalline silicate lithologies (Figs. 3 and 4 and 9). The work presented here thus supports Garrels (1967) and Garrels and Mackenzie's (1967) assertions that:

- (i) The groundwater chemical composition in many silicate lithologies is dominated by plagioclase weathering.
- (ii) The composition of any given groundwater in such rocks is largely a function of (a) the initial  $PCO_2$  in the system, (b) the composition of the plagioclase feldspar and (c) the degree to which  $\text{CO}_2$  has been consumed and converted to  $\text{HCO}_3^-$ .



This work has demonstrated that, at least in silicate crystalline rocks with a significant plagioclase content, one need not invoke cation exchange as a mechanism for the generation of sodium-dominated, calcium-poor, and high pH waters. While cation exchange remains the preferred mechanism for generating such waters in quartz, carbonate, and clay-dominated sedimentary environments, it is interesting to speculate whether silicate hydrolysis coupled to calcite precipitation might be an important process in some feldspar-rich sedimentary rock environments, such as the UK Coal Measures (Banks, 1997), where cation exchange has traditionally been invoked.

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