

# The hydrochemistry of crystalline bedrock groundwater in Norway

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1604 groundwater samples collected from Precambrian and Palaeozoic crystalline bedrock aquifers and 72 groundwater samples from Quaternary aquifers were analysed for radon, pH, and major and minor elements. A representative subset of 476 samples of bedrock groundwater was further analysed for trace elements.

There appears to be a degree of lithological control on radon, fluoride, uranium and many trace elements, typically manifested as elevated concentrations in granitic groundwaters and depletions in anorthositic groundwaters. However, even within a distinct lithology, the concentration of a particular element in groundwater may span over 4 orders of magnitude, suggesting that other (kinetic and hydrodynamic) factors are equally important. A significant percentage of the analysed hardrock groundwaters do not fulfil the Norwegian standards for drinking water quality (the following as percentages of the n=476 subset), e.g. pH: 7%, Rn: 17%, F: 16%, Na: 1.5%, Fe: 14%, Mn: 26%, Al: 3.8%, Zn: 2.3%, Ba: 8.4%, As: 1.5 %, and U: 12 % (using US norm).

pH values range from 5.4 to 9.8 in the crystalline bedrock groundwater dataset, with a predominance between 8.0 and 8.3, irrespective of rock type, suggesting buffering by the calcium carbonate system. Geochemical modelling indicates that pH values above 8.3 may possibly be due to exhaustion of this buffering system by calcite precipitation, as well as by cation exchange against sodium. pH has also been shown to influence the concentrations of many elements in groundwater. Groundwaters from Quaternary sedimentary aquifers in Norway are generally less mature than their bedrock counterparts, with lower pH values and concentrations of Rn and F well below drinking water norms.

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## Introduction

Crystalline bedrock aquifers represent significant sources of drinking water many places in the world. In Norway, it is estimated that 200,000 people are served by groundwater from bedrock wells. However, the natural chemical quality of this water is not always suitable for drinking and increased knowledge about its composition is required. The studies presented here have mainly tried to address the following four issues:

- what is the distribution of major, minor and trace elements in the crystalline bedrock groundwaters of Norway?
- to what extent is groundwater chemistry dependent on aquifer lithology (bedrock geochemistry)?
- how does groundwater pH influence the concentration of elements in solution?
- why are the great majority of the Norwegian groundwater samples alkaline and why do some exhibit very high pH values of up to 9.8?

## An overview of methodology

In summer 1996, the Norwegian Radiation Protection Authority (NRPA) offered the public radon analyses of water from bedrock wells via the local public health authorities. The Geological Survey of Norway (NGU) joined the project as it represented a unique opportunity to obtain water samples for analysis of other dissolved elements, and 500 ml polyethene bottles were distributed together with the vials for radon sampling. This resulted in a quality-controlled hydrogeochemical dataset (referred to as 'Rock\_corr' in further discussion) comprising pH, major and minor elements in 1604 bedrock groundwater samples (Banks et al. 1998a). UTM coordinates were known for 1337 of the boreholes and they could thus be automatically assigned a bedrock lithological code from NGU's digital bedrock map at scale 1:3,000,000 (Sigmond 1992). As the submission of samples was dependent on the initiative of the well owners themselves, NRPA and NGU had no influence on the geographical distribution of sampling points. However, the inhomogeneous pattern (see Fig. 1) appears to reflect the occurrence of bedrock wells in Norway. Higher densities are found in the

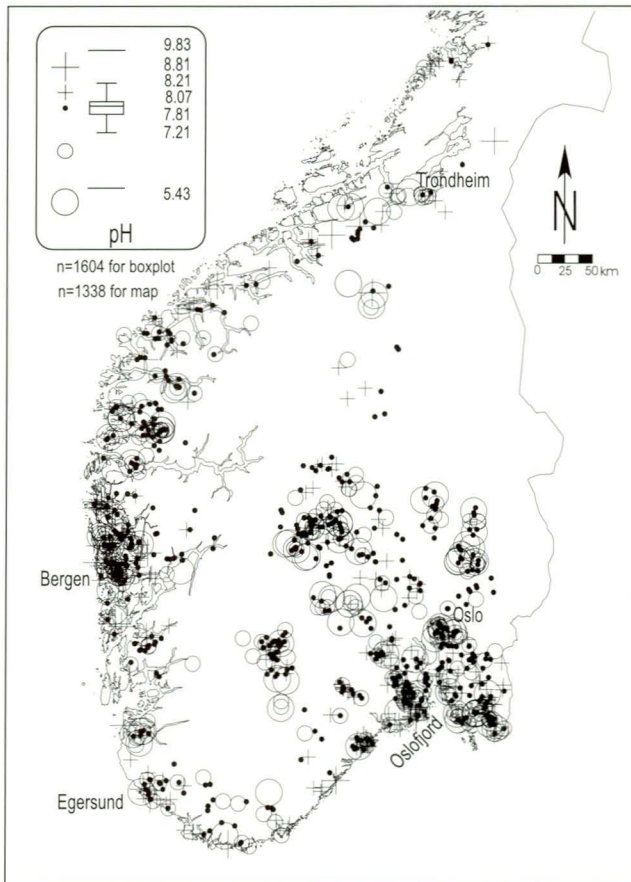


Fig. 1. Map of southern Norway (only 22 samples were obtained from the northern counties) showing the location of 1328 boreholes with coordinates in this area in the Rock\_corr (n=1604) dataset and the distribution of pH in bedrock groundwater. For an explanation of the boxplot in the legend, see Appendix 1. Modified from Banks et al (1998a).

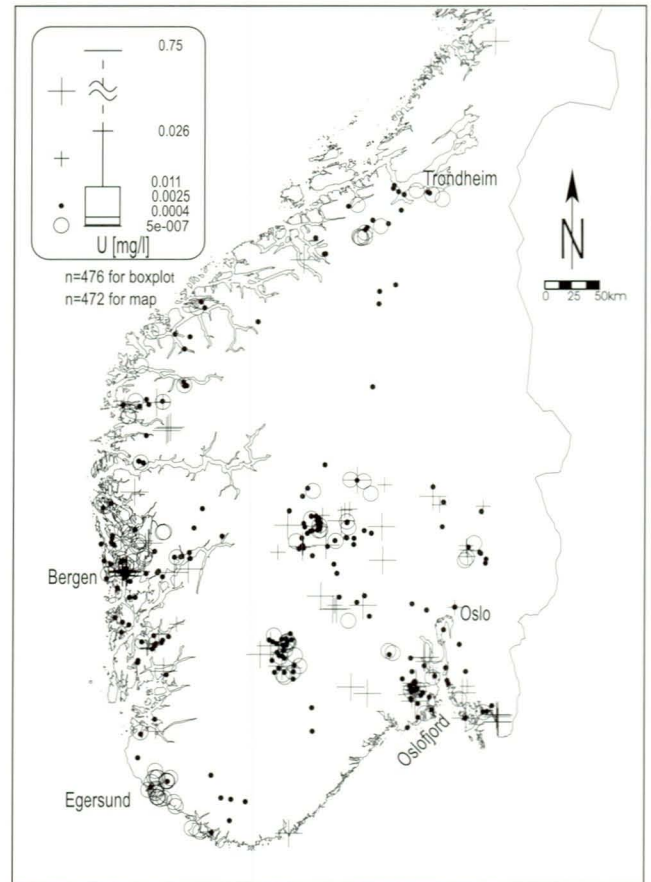


Fig. 2. Map of southern Norway showing the location of the 476 selected boreholes in the Rock\_rep dataset (subset of Rock\_corr) and the distribution of U in the groundwater. For an explanation of the boxplot in the legend, see Appendix 1.

main valleys and along the coast, particularly around Oslofjord and in the Bergen area. Very few samples were obtained from northern Norway, again reflecting the distribution of boreholes, and the three northernmost counties are thus omitted from the maps.

Several local health authorities extended the objective of the project and also submitted groundwater samples from Quaternary aquifers (Banks et al. 1998b). The 72 analysed samples from these aquifers made up an interesting dataset for comparison ('Quat\_corr').

A subset of 476 lithologically and geographically representative samples of bedrock groundwaters ('Rock\_rep', see Fig. 2) was sent to the Bundesanstalt für Geowissenschaften und Rohstoffe in Hannover for analysis of trace elements at extremely low detection limits by ICP-MS techniques (Frenstad et al. 2000).

Sampling protocols and analytical techniques are described in more detail by Banks et al. (1998a) and Frenstad et al. (2000). The data have been presented and interpreted by use of graphical, non-parametric statistical techniques with the software package DAS (Dutter et al. 1992).

### Comparison with drinking water norms

Based on the entire dataset (Rock\_corr), 13.9 % of the bedrock groundwaters displayed higher radon values than the recommended action level of 500 Bq/l. Elevated median values were mainly found in granites and acidic gneisses. Precambrian granites (Sigmond's [1992] lithological group 92) had the highest median value, about 700 Bq/l, and also the highest registered radon content of 19,900 Bq/l (Midtgård et al. 1998). Concentrations above the recommended action level were found in almost all lithological groups, the main exceptions being lithological groups 86 (Caledonian anorthosites and charnockites) and 93 (Precambrian anorthosites and charnockites), where even the medians were below the analytical detection limit of 10 Bq/l. Almost no rock types can thus be considered as entirely acceptable, regarding their groundwater's radon content. Elevated concentration of radon in drinking water may increase the risk of childhood leukaemia, lung cancer and conceivably gastric cancer (Mose et al. 1990).

Table 1 gives an overview of the drinking water quality regarding major and minor elements for the three datasets

Parameter	Norm	Foot-note	Bedrock aquifer violations (n = 476)	Bedrock aquifer violations (n = 1604)	Quaternary aquifer violations (n = 72)
pH	< 8.5	a	28/476 (5.9%)	97/1604 (6.0%)	1/72 (1%)
	> 6.5	a	7/476 (1.5%)	18/1604 (1.1%)	6/72 (8%)
Radon	< 500 Bq/l	c	79/476 (16.6%)	222/1601 (13.9%)	0/72 (0%)
Fluoride	< 1.5 mg/l	a	76/476 (16.0%)	258/1604 (16.1%)	0/72 (0%)
Sodium	< 20 mg/l	b	149/476 (31.3%)	579/1604 (36.1%)	1/72 (1%)
	< 150 mg/l	a	7/476 (1.5%)	46/1604 (2.9%)	0/72 (0%)
Calcium	< 25 mg/l	b	265/476 (55.7%)	887/1604 (55.3%)	22/72 (31%)
	> 15 mg/l	b	121/476 (25.4%)	422/1604 (26.3%)	40/72 (56%)
Potassium	< 12 mg/l	a	5/476 (1.1%)	16/1604 (1.0%)	0/72 (0%)
Magnesium	< 20 mg/l	a	2/476 (0.4%)	18/1604 (1.1%)	0/72 (0%)
Iron	< 200 mg/l	a	67/476 (14.1%)	274/1604 (17.1%)	12/72 (17%)
Manganese	< 50 mg/l	a	125/476 (26.3%)	445/1604 (27.7%)	10/72 (14%)
Aluminium	< 200 mg/l	a	18/476 (3.8%)	70/1604 (4.4%)	8/72 (11%)
Barium	< 100 µg/l	b	40/476 (8.4%)	122/1604 (7.6%)	6/72 (8%)
Nitrate	< 44 mg/l	a	3/476 (0.6%)	13/1604 (0.8%)	3/72 (4%)

Table 1. Summary of proportion of bedrock and Quaternary aquifer groundwater sources exceeding Norwegian drinking water norms for parameters of health-related or aesthetic significance (after Banks et al. 1998a). Na, Ca, K, Mg, Fe, Mn, Al, Ba by ICP-AES techniques. F<sup>-</sup> and NO<sub>3</sub><sup>-</sup> by ion chromatography (IC).

a = Highest (or lowest) permitted concentration (Sosial- og helsedepartementet 1995)

b = Guideline values (Sosial- og helsedepartementet 1995)

c = Recommended action level (Statens strålevern 1996)

Element	Norm (µg/l)	Bedrock aquifer violations (n = 476)	Element	Norm (µg/l)	Bedrock aquifer violations (n = 476)
Ag – Silver	10 <sup>a</sup>	0/476	Pb – Lead	20 <sup>a</sup>	1/476
Al – Aluminium	200 <sup>a</sup>	38/476 (8 %)	Sb – Antimony	10 <sup>a</sup>	0/476
As – Arsenic	10 <sup>a</sup>	7/476 (1.5 %)	Se – Selenium	10 <sup>a</sup>	1/476
B – Boron	300 <sup>b</sup>	3/476 (0.6 %)	Te – Tellurium	10 <sup>d</sup>	0/476
Be – Beryllium (US norm)	4 <sup>c</sup>	1/476	Tl – Thallium (US norm)	2 <sup>c</sup>	0/476
Be – Beryllium (Russian norm)	0.2 <sup>d</sup>	31/476 (7 %)	Tl – Thallium (Russian norm)	0.1 <sup>d</sup>	2/476
Bi – Bismuth	100 <sup>d</sup>	0/476	U – Uranium (US norm)	30 <sup>c</sup>	58/476 (12%)
Br – Bromine	200 <sup>d</sup>	20/476 (4 %)	U – Uranium (Canadian norm)	100 <sup>e</sup>	13/476 (3%)
Cd – Cadmium	5 <sup>a</sup>	1/476	U – Uranium (Russian norm)	1700 <sup>d</sup>	0/476
Co – Cobalt	100 <sup>d</sup>	0/476	V – Vanadium	100 <sup>d</sup>	0/476
Cr – Chromium	50 <sup>a</sup>	0/476			
Cu – Copper	300 <sup>a</sup>	6/476 (1.3%)			
Hg – Mercury	0.5 <sup>a</sup>	0/476			
Li – Lithium	30 <sup>d</sup>	7/476 (1.5 %)			
Nb – Niobium	10 <sup>d</sup>	0/476	W – Tungsten	50 <sup>d</sup>	1/476
Ni – Nickel	50 <sup>a</sup>	6/476 (1.3 %)	Zn – Zinc	300 <sup>a</sup>	14/476 (3%)

Table 2. Summary of proportion of bedrock groundwater sources exceeding Norwegian (when given), American, Canadian or Russian drinking water norms for minor and trace elements of health-related significance, analysed by ICP-MS techniques (largely after Frengstad et al. 2000).

a = Highest permitted concentration (Sosial- og helsedepartementet 1995)

b = Guideline values (Sosial- og helsedepartementet 1995)

c = American maximum allowable concentration (USEPA 2001).

d = Russian maximum allowable concentration (Kirjuhin et al. 1993)

e = Canadian maximum allowable concentration (Health Canada 1996)

Rock\_rep, Rock\_corr and Quat\_corr. Table 2 summarises the state of drinking water from bedrock wells (Rock\_rep) with respect to minor and trace elements of possible significance for human health. American, Canadian and/or Russian norms are used when no Norwegian limits are set.

16.1% (258 of 1604) of the sampled bedrock groundwaters in Norway had fluoride contents above the maximum admissible concentration (MAC) of 1.5 mg/l. Groundwater from Precambrian granites (Sigmond's [1992] lithological group 92) had the highest median value at 1.69 mg/l fluoride, while the highest individual value of 8.3 mg/l fluoride was found in lithological group 71 (Caledonian granites to tonalites). Due to an inaccuracy in the digital map, many of the sampled boreholes in Caledonian granites in the Bergen area were assigned lithological code 72 (gabbro, diorite and ultramafics [Sigmond 1992]). Thus, Banks et al. (1998a, 2000) and Frengstad et al. (2000) erroneously stated that the highest median and highest single value for fluoride were found in lithological group 72. In fact, fluoride concentrations are

rather low in this group (median value 0.09 mg/l). Granites and gneisses in southern and western Norway yield water with high fluoride values and the distribution of fluoride has much in common with radon. Occurrence of dental fluorosis in children drinking bedrock groundwater has been documented in southern and western Norway (Bjorvatn et al. 1992, Bårdsen et al. 1999). Groundwater derived from Quaternary aquifers has low contents of both radon and fluoride.

Many other elements studied occur in bedrock groundwaters at concentrations above the drinking water quality standards (Tables 1 and 2). If all the analysed parameters (i.e. Ag, Al, As, Cd, Cr, Cu, F, Fe, Hg, K, Mg, Mn, Na, Ni, NO<sub>3</sub><sup>-</sup>, Pb, pH, PO<sub>4</sub><sup>3-</sup>, Rn, Sb, Se, SO<sub>4</sub><sup>2-</sup>, Zn), with a MAC set by Norwegian health authorities are considered together, about 60 % (283 of 476) of the groundwater samples in the dataset Rock\_rep contain concentrations of one or more inorganic parameter above the standards (Ca is not included, as the distinctively Norwegian narrow limits for Ca (15-25 mg/l) are breached

by 82 % of the samples). If fulfilment of the less stringent Norwegian 'guidance levels' (Sosial- og helsedepartementet 1995) is included, about 70 % (336 of 476) of the bedrock wells yield drinking water which does not meet the guidelines. It should be noted that some of the Norwegian norms regarding, e.g., Ca, Fe and Mn, are rather based on aesthetic/practical than toxicological criteria. On the other hand, drinking water standards do not exist in Norway for some trace elements deemed to be of health concern (e.g. Be, Tl, U, V). If the new American limit of 0.03 mg/l (30 µg/l) for uranium is applied, about 12 % of the sampled Norwegian bedrock groundwaters fall outside the norm. The less conservative Canadian limit of 0.1 mg/l (100 µg/l) uranium is breached by 3 % of the groundwaters.

### Lithological control on groundwater chemistry

The lithological subsets Precambrian granites (rock group 92 after Sigmond 1992) and Precambrian anorthosites (rock

group 93) transpired to be the two extreme lithological endpoints for many elements. Many of the Precambrian granites are derived from remelting of metasediments enriched in late-stage incompatible elements like U, F and rare earth elements (REE), while the anorthosites are rather pure andesine rocks. The hydrochemical data from these two lithologies were thus plotted with individual symbols together with the total dataset in cumulative frequency diagrams in order to reveal apparent relative enrichments or depletions (Frenstad et al. 2000). Examples are given in Fig. 3 and the results are summarised in Table 3.

There is a (more or less pronounced) tendency towards elevated concentrations in granitic groundwaters and lower concentrations in anorthositic groundwaters (compared with the entire dataset) for a range of elements, i.e., Be, (Bi), Cd, Ce, F, Hf, (Hg), (In), La, (Li), (Mo), Nb, Pb, Rn, Ta, Th, (Ti), Tl, U, Y, Zr and REE.

Anorthositic groundwater appears to be enriched in Br and I, but these elements are more likely to be marine-

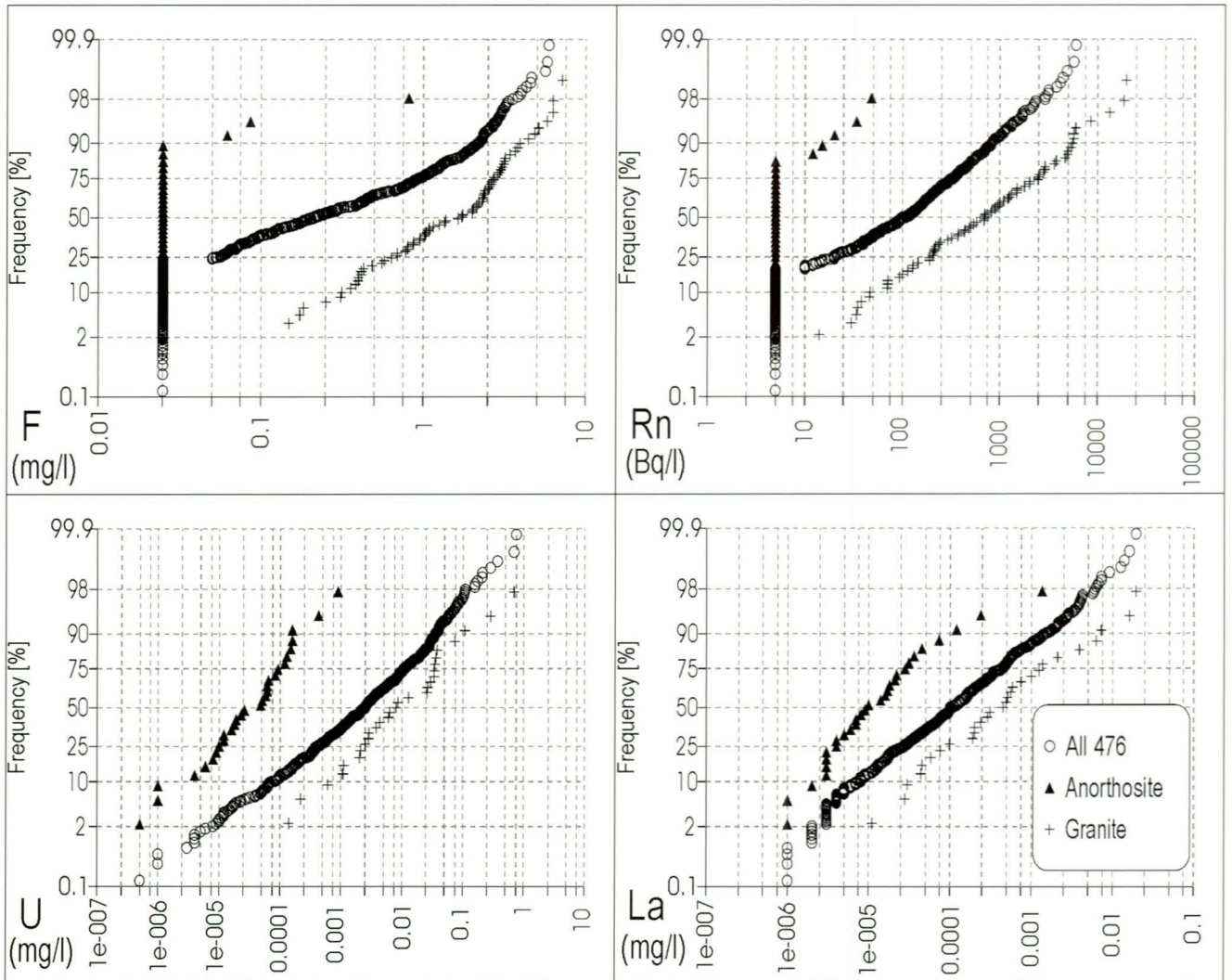


Fig. 3. Cumulative frequency distribution diagrams for selected elements (F, Rn, U and La) showing the distributions for the 476 water samples and the lithological groups 'Precambrian anorthosite' and 'Precambrian granite'. Concentrations less than detection limit are plotted at a value of 1/2 x detection limit.

		Granitic groundwater enriched or depleted relative to 'Rock_rep'		
		Depleted	Neither enriched nor depleted	Enriched
<b>Anorthositic groundwater enriched or depleted relative to 'Rock_rep'</b>	<b>Depleted</b>	As, (Sb)	Ba, Cs, (Li), (Mo), Rb, W	Be, (Bi), Cd, Ce, Hf, (Hg), (In), La, (Li), (Mo), Nb, Pb, Ta, Th, (Ti), Tl, U, Y, Zr, REE. Also Rn, F.
	<b>Neither enriched nor depleted</b>	B, Co, (Cr), Cu,	Ag, Al, Ga Ge, Ni, (Sb), V, Zn	
	<b>Enriched</b>	Se, Te	Br, I, Sn	(Cr)

Table 3. The apparent lithological dependence of element concentrations in crystalline bedrock groundwater assessed on the basis of whether waters from Precambrian granites (lithological code 92) and anorthosites (code 93) exhibit a relative enrichment or depletion compared with the entire (n=476) dataset (after Frengstad et al. 2000).

derived as the Egersund area (where the anorthosites outcrop) is exposed to the North Sea. Generally, these elements (and Cl) exhibit elevated concentrations in groundwater along the coast due to a component of marine aerosols in recharge water, leaching of marine salts from overlying Quaternary deposits, the possible presence of fossil saline water within the bedrock or direct intrusion of seawater. A similar coastal enrichment can be seen for Na, but this is less pronounced, as lithological sources for Na are more important than for Cl.

For some elements, the subsets of Precambrian anorthositic and Precambrian granitic groundwaters show little deviation from the entire dataset (although this does not necessarily mean that the elements are wholly independent of lithological control. For example, Co, Cr, Ge, Ni and V are relatively enriched in Precambrian gneisses and amphi-

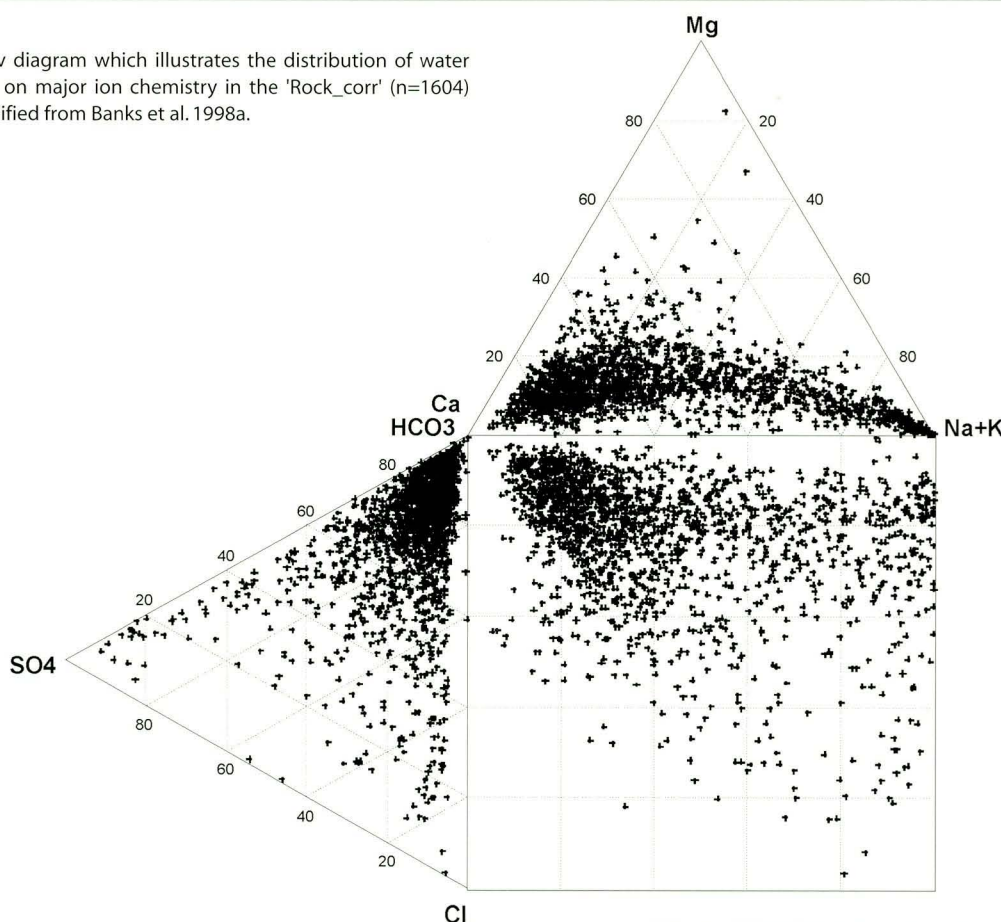
bolites (Code 88 after Sigmond 1992), while Zn exhibits higher concentrations in Permian intrusive rocks (Code 54).

It should also be noted that pH values are generally higher among the Precambrian anorthosites than among the Precambrian granites, though the difference between their median values of 8.05 and 7.82 (in the Rock\_rep, n=476 dataset), respectively, is not statistically significant. The solubility of many elements in groundwater is sensitive to pH variations (Frengstad et al. 2001), which may count for some of the apparent lithological differences.

### The pH-dependence of element concentrations

Major ion chemistry of the 1604 water samples in the Rock\_corr dataset is presented as a Durov plot in Fig. 4. A

Fig. 4. Durov diagram which illustrates the distribution of water types based on major ion chemistry in the 'Rock\_corr' (n=1604) dataset. Modified from Banks et al. 1998a.



thorough description of the different water-types is given in Banks et al. 1998c.

Almost half of the pH values (48%) for crystalline bedrock groundwaters fall between 8.0 and 8.3, regardless of lithology. This pH zone corresponds to a buffered region of the groundwater evolution curve due to calcite precipitation. Negative deviations from this pH zone (i.e. lower pH) are likely to be due to kinetic factors (e.g., short residence time and hydrogeochemical 'immaturity'), while positive deviations indicate complete consumption of calcite precipitation buffering capacity (Banks et al 1998a). pH in groundwater is thus only to a limited extent dependent on the aquifer lithology, but rather on groundwater 'maturity' and the state of equilibrium relative to the calcium carbonate system. The solubility of many minor and trace elements is, in turn, dependent on the pH (and also the redox potential, Eh) of the water. This implies that the distribution of elements in the aquifer matrix of a given lithology will not necessarily be reflected in the composition of a groundwater sample from a borehole in the lithology. Fracture mineralisation, fracture aperture, weathering history (Banks et al.

1998d), residence time and soil cover (Olofsson 1999) are probably more important factors than bulk lithology in determining the groundwater geochemistry of many elements.

There is a slight tendency towards elevated pH values in bedrock groundwaters in coastal areas (Fig. 1). This may be explained by a number of hypotheses:

- the fact that the coast probably represents a discharge area for long regional flow pathways, i.e. emergence of more mature groundwaters.
- a lower extent of isostatic rebound at the coast compared to inland areas; and thus less reactivation and lower permeability of fracture systems may also imply prolonged residence times (Rohr-Torp 1994, Morland 1997).
- leaching of high-pH pore waters from marine clays raised above the postglacial shoreline by isostatic rebound (Hilmo 1989).
- alternatively, high pH may be explained by ion exchange of calcium against marine-derived sodium below the postglacial marine limit (Appelo & Postma 1994). When

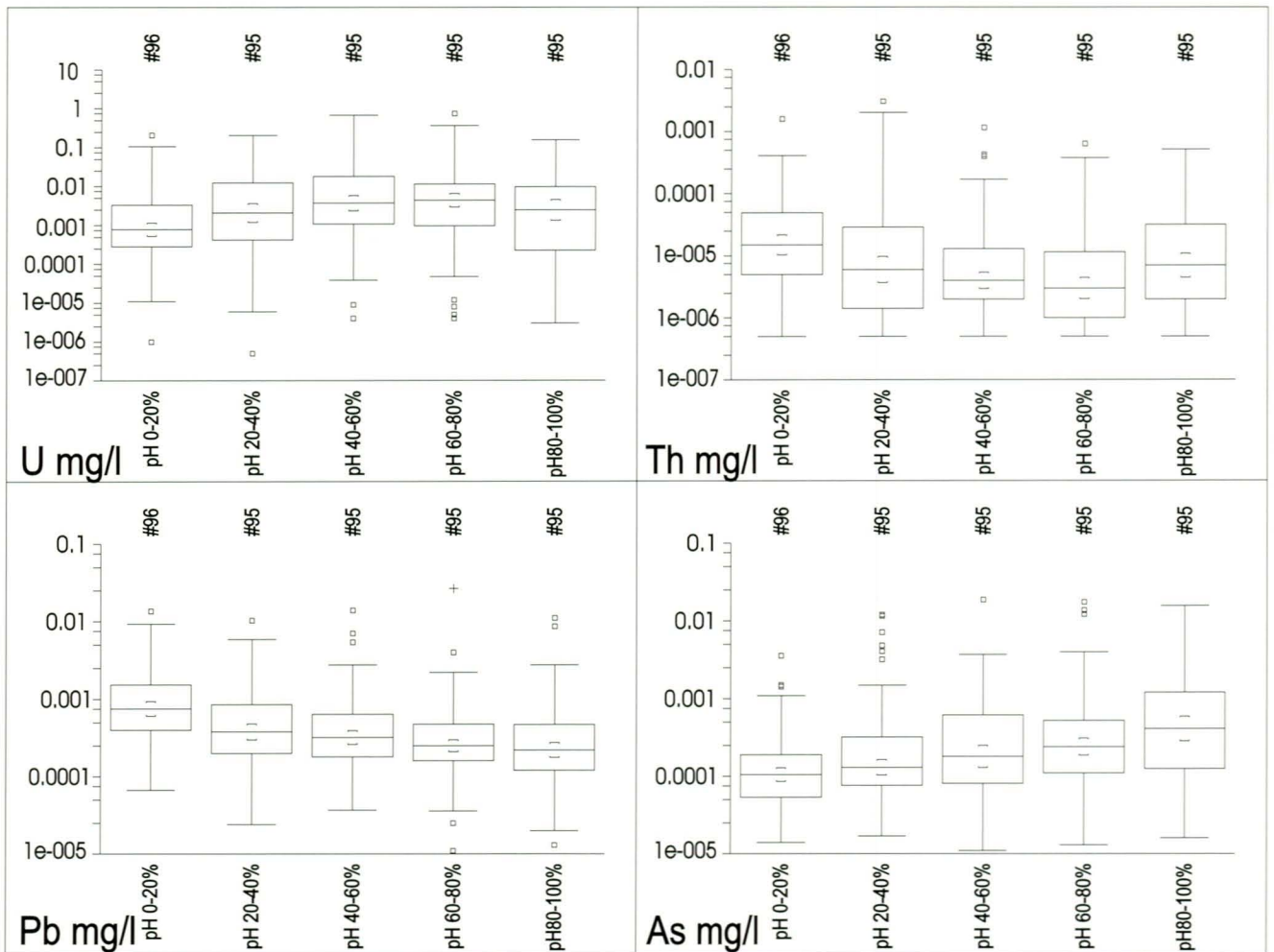


Fig. 5. Boxplots showing the distribution of U,Th,Pb and As in groundwaters dependent on the pH of the samples. The dataset Rock\_rep is divided into five percentile groups according to pH: 0-20% (pH 6.17-7.73); 20-40% (pH 7.74-8.01); 40-60% (pH 8.01-8.13); 60-80% (pH 8.14-8.22); and 80-100% (pH 8.22-9.58). From Frengstad et al. (2000).

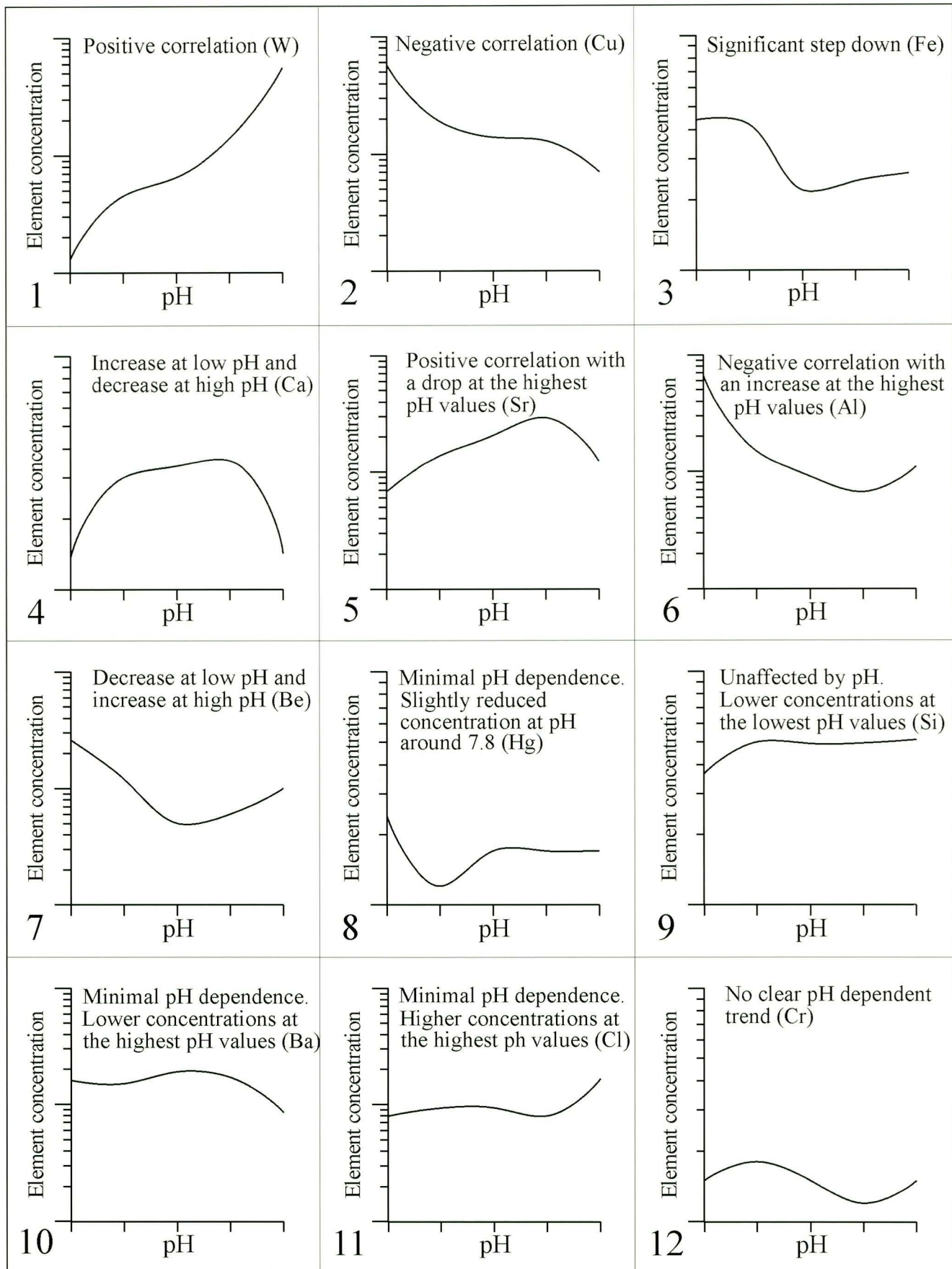
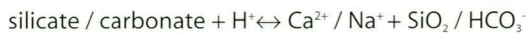


Fig. 6. Twelve examples of characteristic curves of element concentrations in crystalline bedrock groundwaters according to increasing pH illustrated by a line drawn through the median of the five 20 percentile pH groups. Note the number of log cycles. From Frengstad et al. (2001).

Ca is removed from the water, the calcite-precipitation buffering mechanism (see above) is exhausted, and pH may increase due to proton-consuming reactions such as:



The empirical relationship between pH and element concentrations in crystalline bedrock groundwaters has been studied. The samples in the Rock\_corr (n=1604) dataset, analysed for major and minor elements, were ranked and divided into five subsets according to increasing pH. The same subdivision was performed on the Rock\_rep (n=476) dataset, analysed for trace elements. The subsets were presented as boxplots for 60 elements or ions (see examples in Fig. 5 and Appendix 1 for explanation of the boxplot). The median values of each subset were used for interpretation of the apparent correlation of increasing pH with the element concentration. An imaginary line could be drawn through the median values of the subsets and 12 characteristic behaviours were identified (Fig. 6).

Element concentrations showed a positive correlation with pH (curve type 1) for elements like F, As and W (prob-

bly reflecting anion exchange for OH<sup>-</sup>, or soluble oxy-anionic phases). As pH is also an indicator of groundwater maturity, the concentrations of elements without any solubility ceiling, like Na and Li, correlated positively with pH. A negative correlation with pH (curve type 2) was observed for NO<sub>3</sub><sup>-</sup> (due to the predominance of nitrate in young, oxidising, hydrochemically immature waters). A negative correlation with pH was also noted for heavy metals such as Cd, Cu, Pb and Zn, due to a typically decreasing aqueous solubility and an increasing tendency to sorption with increasing pH. Elements such as Rn are largely unaffected by pH, but even Rn exhibited decreased concentrations for the immature low-pH groundwaters (curve type 9). For elements including Al, Th, REE and Be, curves (type 6 and 7) with a concentration minimum in the mid pH range were found. In the case of Al, this may reflect the element's amphoteric nature. The opposite trend, with a concentration maximum in the mid pH range was characteristic for Ca, U and Sr (curves type 4 and 5). In the case of Ca, this may reflect the initial accumulation of Ca in evolving groundwaters, followed by its removal via calcite precipitation. Typical marine-derived elements, such

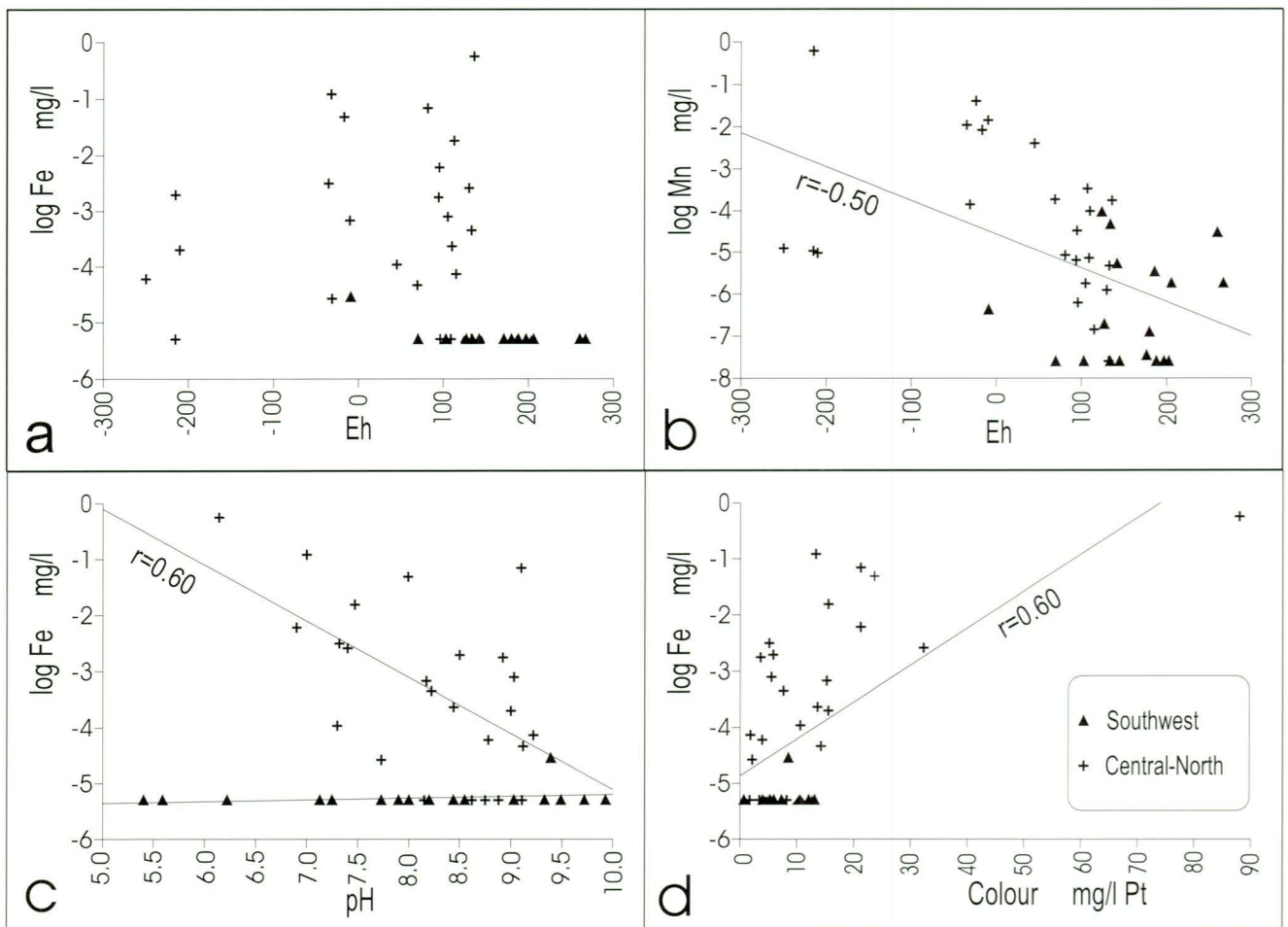


Fig. 7. xy-plots showing a) log Fe concentrations vs. Eh, b) log Mn concentrations vs. Eh, c) log Fe concentrations vs. pH, and d) log Fe concentrations vs. colour for nineteen groundwater samples from boreholes in Precambrian anorthosites, granites and granitic gneisses in Southwest Norway ('Southwest' subset - see Frengstad 2002) and for twenty-five groundwater samples from boreholes in granites and various gneisses of Precambrian age in the counties of Nordland and Nord-Trøndelag ('Central-North' subset - see Brekke 1999). Best fit linear regression lines are based on all samples in diagrams b and d, and for each subset in diagram c.



as Cl and Br, exhibited elevated concentration for the highest pH-percentile (curve type 11), probably because there is a tendency to higher pH values in the coastal areas, as discussed above. A few elements such as Cr, V and Zr showed no clear pH-dependent trend (curve type 12).

Some redox-sensitive elements, such as Fe, Mn (and coprecipitating elements) and S, may be partially governed by redox conditions as well as by pH. Many redox reactions also involve transfer of protons, and will thus often influence or be influenced by the pH of the solution. Practical considerations precluded Eh measurements in all boreholes in the 'Rock\_corr' dataset. However, measurements have been performed with an Eh-electrode on tap water samples from nineteen boreholes in Precambrian anorthosites, granites and gneisses of southern and southwest Norway (Frengstad 2002), and from twenty-five boreholes in Precambrian gneiss and granite in the counties of Nord-Trøndelag and Nordland (data from Brekke 1999). Fig. 7 shows that measured Eh values from southwest Norway ('Southwest' subset) mainly fall between +70 mV and +270 mV with one sample at -9 mV, while measured Eh values from Nord-Trøndelag and Nordland ('Central-North' subset) range from -250 mV to +140 mV. No smell of H<sub>2</sub>S was registered in the samples of the 'Southwest' subset, while a third of the boreholes in the 'Central-North' subset yielded water with some smell of H<sub>2</sub>S.

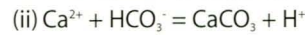
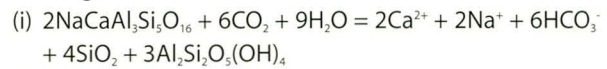
Fe concentrations were below the ICP-AES equipment's analytical detection limit of 0.05 mg/l for almost all samples in the 'Southwest' subset. Log Fe concentrations had practically no correlation with Eh ( $r=-0.19$ , Fig. 7a), but displayed some negative correlation with pH ( $r=-0.60$ ; 'Central-North' subset only, Fig. 7c) and positive correlation with colour ( $r=0.60$ , Fig. 7d), suggesting Fe-mobilisation by humic acids rather than by reduction processes. Elevated iron concentration would typically be expected in reducing environments, due to the solubility of ferrous iron species. However, Fe concentrations may be limited by the insolubility of iron sulphide phases in waters that are rich in hydrogen sulphide (Berner 1981). Fig. 7b shows that log Mn concentrations correlate to some extent with Eh ( $r=-0.50$ ) indicating redox-controlled solubility for this element. In fact, some 28 % of the samples in the 'Rock\_corr' ( $n=1604$ ) dataset exceeded the Norwegian MAC of 0.05 mg/l for Mn (Table 1).

### High-pH, Na-HCO<sub>3</sub><sup>-</sup> groundwaters: silicate weathering or cation exchange?

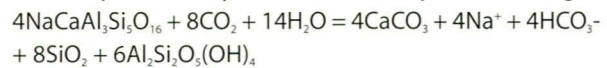
6 % of the bedrock groundwater samples in the dataset have pH values above 8.5 and are characterised by relatively high Na and low Ca concentrations. Two possible explanations for these high pH waters have been investigated through hydrochemical modelling (Frengstad & Banks 2000):

*Hypothesis 1:* Silicate weathering by carbon dioxide consumes protons and produces base cations and alkalinity (i). When the ion concentrations and pH are sufficiently high,

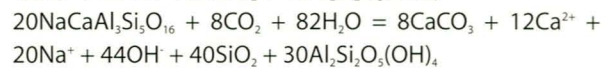
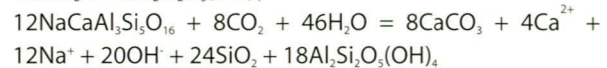
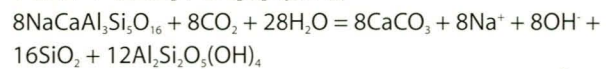
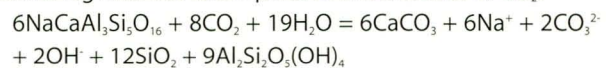
calcite is precipitated (ii), removing Ca from the water and releasing protons, buffering further pH rise. When most of the Ca is consumed, the carbonate buffering system is exhausted and pH may continue to rise. Na continues to accumulate in the water by, for example, continued feldspar weathering.



These equations may be summarised by the following:



If CO<sub>2</sub> is completely consumed (in a system 'closed' with respect to CO<sub>2</sub>), the reaction may progress as described by the net reactions in the equations below. The ratios of Ca<sup>2+</sup> to Na<sup>+</sup> in the final solution will depend on the amount of weathering that has taken place in the absence of CO<sub>2</sub>:



Note that the above equations have been normalised to a fixed amount of available CO<sub>2</sub> (8 moles). The system progresses from:

- (i) a circum-neutral, sodium bicarbonate water in an open CO<sub>2</sub> system (or a closed system prior to CO<sub>2</sub> consumption) to
- (ii) an alkaline sodium bicarbonate water in a closed system.
- (iii) theoretically, the closed system could then further develop to highly alkaline calcium-dominated waters.

*Hypothesis 2:* Under the postglacial marine limit, cation exchange sites on fracture mineralisations and gouge materials were loaded with marine cations (Na<sup>+</sup>) at the end of the ice age. During the ongoing isostatic uplift, fresh Ca-HCO<sub>3</sub><sup>-</sup> groundwater replaces the former Na-Cl<sup>-</sup> groundwater. Ca<sup>2+</sup> expels Na<sup>+</sup> from the exchange sites and the resulting water becomes of Na-HCO<sub>3</sub><sup>-</sup> type. Because Ca<sup>2+</sup> is effectively removed from the water, the calcium carbonate buffer is suppressed and pH may continue to rise.

The geochemical modelling code PHREEQC (Parkhurst 1995) was employed to simulate weathering of a monomineralic silicate system, namely an anorthosite comprising only plagioclase feldspar. The input file specified that a given amount of plagioclase was dissolved in CO<sub>2</sub>-charged pure water in 30 equal steps and precipitation of calcite, chalcidony, kaolinite and gibbsite were permitted if these phases became saturated. The procedure was run for a closed system ( $p\text{CO}_2 = 10^{-1.5}$  atm) using five idealised plagioclase compositions (albite, oligoclase, labradorite, bytownite

and anorthite). The results of the labradorite modelling are shown graphically in Fig. 8. Weathering of labradorite was also simulated under open and closed systems with varying  $\text{CO}_2$  pressure.

In closed systems, three phases of hydrogeochemical evolution were predicted to occur:

- accumulation of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  in solution and rapid increase of pH
- removal of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  due to calcite precipitation (buffering effect on pH at pH 8.0-8.5).  $\text{Na}^+$  continues to accumulate
- continued increase in  $\text{Na}^+$ , alkalinity and pH and eventual re-accumulation of  $\text{Ca}^{2+}$  in system (not shown in the figure).

The modelling does not rule out pure silicate weathering as a mechanism for generation of high-pH,  $\text{Na-HCO}_3^-$  waters

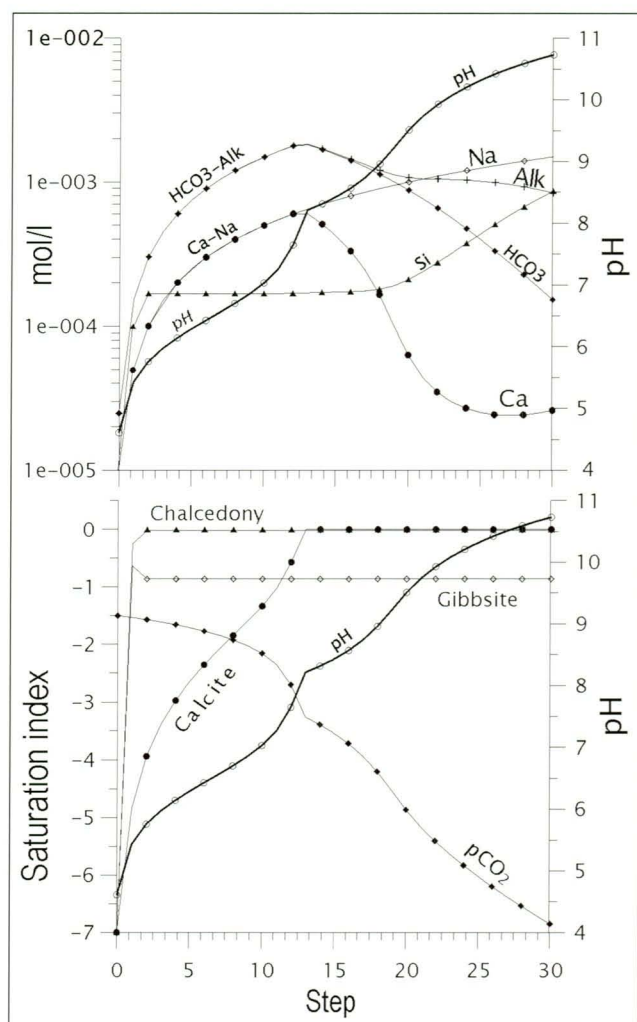


Fig. 8. Modelled evolution of groundwater chemistry, using PHREEQC, by dissolving  $1.5 \cdot 10^{-3}$  moles labradorite (defined as  $\text{NaCaAl}_3\text{Si}_3\text{O}_{16}$ ) in water at  $7^\circ\text{C}$  and initial  $\text{pCO}_2 = 10^{-15}$  atm. (closed  $\text{CO}_2$  system). Precipitation of calcite, kaolinite, gibbsite and chalcidony are permitted if oversaturated. Upper diagram shows the evolution of total element concentrations, and lower diagram shows saturation indices. Note that alkalinity (Alk) is defined as the milliequivalent sum of  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{OH}^-$ . From Frengstad & Banks (2000).

in anorthosites under closed systems, but indicates that a high initial soil gas  $\text{pCO}_2$  of  $10^{-15}$  atm. (100 times higher than atmospheric pressure) is required to obtain the observed concentrations of dissolved ions. Later measurements *in situ* in the Egersund area have confirmed that the  $\text{CO}_2$  pressure in soil gas is adequate to meet the required geochemical conditions (Frengstad 2002). In open systems, soft  $\text{Na-HCO}_3^-$  rich waters may evolve purely by silicate weathering, but in order to achieve the highest pH values observed in actual groundwaters, it appears necessary to invoke either (i) cation exchange to remove Ca and thereby negate the calcite precipitation buffer, or (ii) subsequent system closure with respect to  $\text{CO}_2$ .

## Conclusions

Analyses of groundwater samples from 1604 crystalline bedrock aquifers in Norway reveal great variation in pH, major, minor and trace elements. The majority of samples do not meet Norwegian or international standards for good drinking water quality for inorganic parameters of health concern (e.g. Rn, F, Na, Ba, U) or of practical/aesthetical interest (e.g., Fe, Mn, Ca). Groundwaters from Quaternary drift deposits are less hydrogeochemically 'mature', i.e. lower pH and ionic strength, and have relatively low concentrations of Rn and F.

Many groundwaters from Norwegian bedrock aquifers may thus require some treatment before use. Nevertheless, in Norway, it may be less expensive to treat and develop local groundwater sources than to distribute water from larger regional waterworks among scattered houses and farms in difficult terrain. All drinking water from boreholes should be comprehensively analysed, and small-scale water treatment systems are available for most of the potentially problematic parameters (Banks et al. 2000).

Many parameters (e.g., Be, Cd, F, Pb, Rn, Th, Tl, U and REE) show relative enrichment in granitic groundwaters and depletions in anorthositic groundwaters, as compared to the dataset as a whole. However, the element concentration range within a single lithology is usually much broader than the variation of median values between different lithologies. Thus, it would be misleading to believe that groundwater of problematic inorganic quality is associated only with specific lithologies, and the effect of lithology on groundwater hydrochemistry should not be overemphasised relative to other factors, such as hydrodynamics, kinetics and residence time.

The bias, in the dataset, towards pH values in the range 8.0-8.2, regardless of aquifer lithology, indicates that the calcium carbonate system is one of the main factors governing the hydrogeochemistry.

A significant fraction of the hardrock groundwaters are of  $\text{Na-HCO}_3^-$  type, with pH values  $>8.5$ . This water type may be explained by silicate weathering and subsequent calcite precipitation in a closed system (with respect to atmospheric  $\text{CO}_2$  pressure) as an alternative or supplement to the

more common explanation of ion exchange of  $\text{Ca}^{2+}$  for  $\text{Na}^+$ . The silicate weathering - calcite precipitation model requires a high initial  $\text{CO}_2$  pressure of about  $10^{-1.5}$  atm in the recharge water. *In situ* measurements in soil gas in the Egersund area have suggested that this may not be unrealistic for southern Norway.

pH, together with Eh, is a primary control on the solubility and mobility of many other elements and species in groundwater.

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### Appendix 1

The boxplot provides a graphical data summary where median, quartiles, spread and data outliers are displayed. The box contains the middle 50 % of all data, where the median value is marked with a line that divides the box. The brackets

above and below this line denote a robust 95 % confidence interval on the median. The upper and lower ends of the box (called 'hinges') represent the 75 % quartile and the 25 % quartile, respectively. Lines (called 'whiskers') are drawn from the ends of the box towards the maximum and minimum values, respectively, each containing about 25 % of all data. The whiskers extend up to a maximum of 1.5 times the length of the box and outlying data points are plotted as crosses (near outliers) and squares (far outliers). The boxplot is a useful presentation technique for comparison of different datasets and for revealing skewness of distribution and outlying data points. For the purposes of statistical analysis and graphical presentation, results below the analytical detection limit have been set to a value of half the detection limit.