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GEOCHEMISTRY OF GROUND WATER IN THE PRECAMBRIAN CRYSTALLINE BEDROCK OF FINLAND IN RELATION TO THE CHEMICAL COMPOSITION OF THE RESERVOIR ROCKS

Esa Rönkä[1], Raimo Uusinoka[2] & Antti Vuorinen[2]

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Comparisons between the chemical composition of certain Precambrian plutonites and schists and the chemistry of the ground water these rocks contain indicate some correlation in the amounts of Ca, the element most easily dissolved from weathering rock, a fact also affecting the prediction of the total hardness of ground water from bedrock of a known composition. The amounts of other important elements in ground water are affected by the mode of weathering of their source minerals rather than their mere abundance in the rocks. The regional variations in the ground water composition mainly depending on the composition of their reservoir rocks are mostly restricted to the values of pH and total hardness, and to Ca, Na and Si contents.

Index words: Plutonites, acid rocks, basic rocks, bedrock fissures, reservoir rock, fracture zone, rock weathering, bedrock chemistry, ground water chemistry, heavy metals, radioactive elements.

1. INTRODUCTION

The chemistry of ground water in the crystalline bedrock of Fennoscandia is treated in numerous studies (Laakso 1966, Lahermo 1970, 1971, Lahermo et al. 1979, Jacks 1972, 1973, Hyyppä 1973). In these studies the quality and quantity of different cations are analysed from waters from wells drilled in different rocks. Thus, data mainly indicating the gross differences in chemical composition of ground waters from acid (silicic) and basic (subsilicic) bedrock have been collected. These show higher contents of nearly all the most important cations in the waters from subsilicic rocks compared with those from silicic rocks.

In the present study, the chemical composition of the rocks yielding the waters analysed are also studied. This study also aims at finding out the possible relationships existing between the chemical composition of the rock and the water pumped from it, mainly as regards the water in the rocks composed of the common rock-forming silicate minerals.

The most important factors affecting the chemical composition of a deposit of ground water in a natural state in the joints and fissures of crystalline bedrock might be listed as follows:

- mineralogical and petrographical composition of the bedrock
- tectonic setting of the bedrock, i.e. the location of the joints, fracture zones, etc. affecting the

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[1] National Board of Waters, Helsinki, Finland
[2] Department of Geology, University of Helsinki, Finland

porosity of the rock material in regard to the bodies of different rocks
- weatherability of the minerals and rocks and the relative mobility sequence of their elements
- solution power of the ground water entering the area
- drainage conditions in the aquifer.

A chemical equilibrium in the ionic state depending on the mineralogical composition of the bedrock has generally been achieved by the ground water occurring in crystalline bedrock. This is due to the relatively slow flow conditions. If this state of equilibrium is radically disturbed, it will be achieved again during about 10 years (Eriksson and Khunakasem 1968).

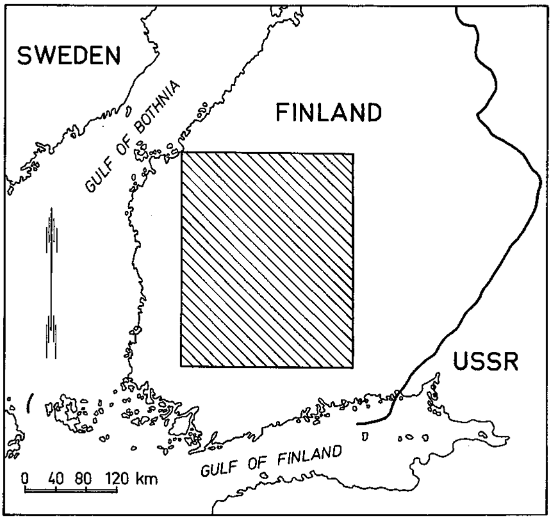


Fig. 1. Location of the study area.

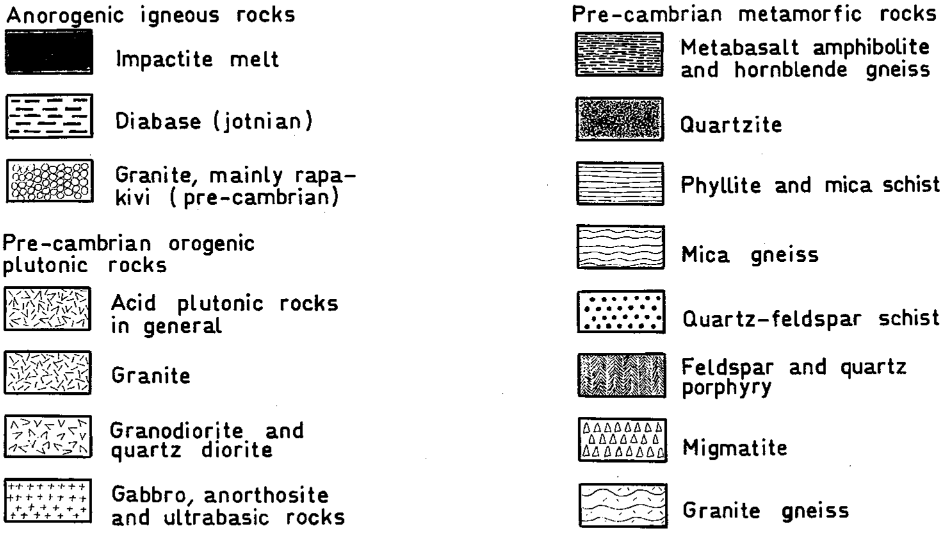
2. STUDY AREA

The study area lies in southern and central Finland roughly within the quadrangle bordered by 61, 63° N and 23, 27° E (Fig. 1).

The mean annual temperature is about +4 °C in the southern and western part and +3 °C in the northern and eastern part of the area. Annual precipitation is 600–700 mm. The area is snow-covered for about 4 months a year in the west and 4.5 months in the east, and the mean maximum thickness of the snow cover is about 30 to 50 cm, respectively.

The mean absolute elevation of the area is about 100 m above sea level. The topography is characterised by a relatively flat surface with relative height differences of less than 20 m in the west and by a hilly landscape with height differences of 50 to 100 m in the central and eastern part. The height differences of the bedrock surface are less than 50 m in the west. In the east, particularly around Lake Päijänne, the differences are up to 250 m or even more. The differences are, however, strongly levelled by the Quaternary deposits filling the slopes and valleys. There are thousands of lakes in the area, particularly in the central and eastern parts, and the largest basins are those of Päijänne, Näsijärvi and Keitele.

The bedrock (Fig. 2) has been formed during the Svecocarelidic orogeny, whose age is about 1 800 Ma. The rocks (Simonen 1961) belong to



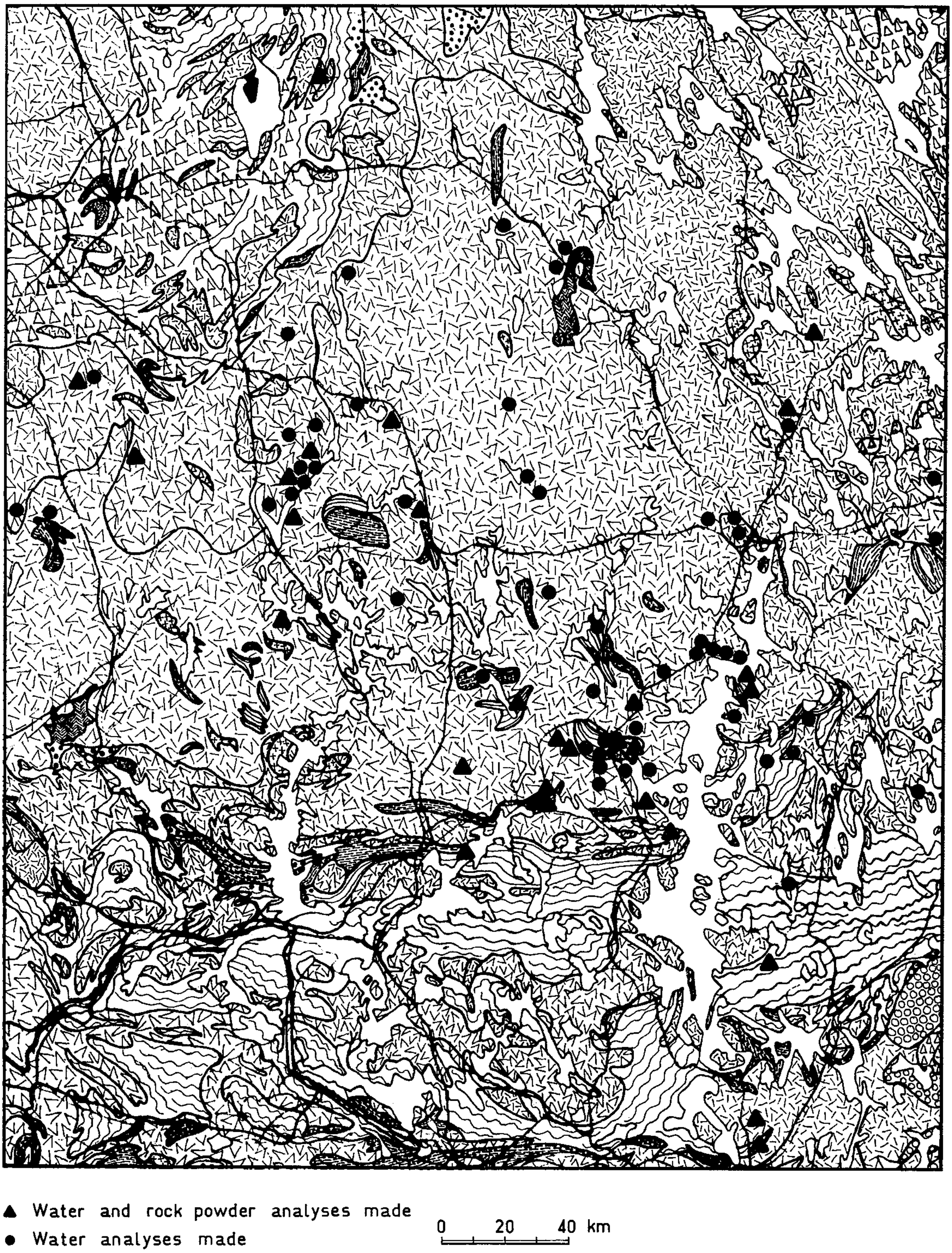


Fig. 2. Prequaternary rocks of the study area (after Simonen 1960) and the sites of the wells investigated.

the Svecofennidic schist belt, trending in an E–W direction in the south and NE–SW in the northwest. The schists consist mainly of mica gneisses and mica schists with some layers of amphibolite and hornblende gneisses. Synorogenic quartz diorites and granodiorites are also frequently met with. Strong migmatization is common. Between the schist belts there is a large area of late-orogenic granites extending from the western part to the northeastern corner. The bedrock has been polished during the Quaternary glaciations so that no larger weathered deposits exist, except some scattered remains on valley floors and in some fracture zones extending deeper in the bedrock. The density of bedrock outcrops is about 2–5 %, being greater in the east than in the west. The Quaternary surficial deposits covering the Precambrian bedrock consist mainly of basal till, often less than 5 m thick. End moraines and glaciofluvial formations consisting of more or less sorted sands and gravels are also common. They are the most important surficial aquifers. Silts and clays are met with in some valleys. Large deposits of peat occur mainly in the west.

3. MATERIAL AND METHODS OF STUDY

The wells chosen for this study have been drilled into bedrock which either crops out or is covered only by a thin sheet of basal till. Glaciofluvial deposits were practically absent. For chemical analyses from both rock and water samples, 28 wells representing different geological conditions were chosen for the present study out of about 100 wells. The rock samples have been taken from the rock powder lifted to the surface by the water used to wash the holes during the boring. Generally, the powder sample has been taken from the bottom of the hole, i.e. from the site where the pump has been sunk. The water samples have been taken only once and about one year after the well has been taken into use. Thus no state of equilibrium has prevailed in the ground water during sampling, and the quality of the water actually used can also be compared for wells in different geological surroundings.

For chemical analyses of the rock powder, the samples were digested in a Teflon-lined acid digestion bomb (Parr 4745). The methods used were a modification of methods by Bernas (1967) and by Ayranci (1977). 200 mg of fine ground sample of rock, dried at 110 °C, was weighed to the Teflon-vessel of the bomb and 1 ml of H_2SO_4 (96 % w/v) was added. Thereafter the vessel was filled with nitrogen and 3 ml of HF (40 % w/v) was added. The bomb was closed, digested 3 h at 140 °C, cooled and 20 ml of saturated aqueous boric-acid solution was added mixing. After reactions were ceased the containings were washed and diluted to a measuring flask of 200 ml with freshly boiled distilled and deionised water and the solution was removed to a bottle of polyethylene. The solutions were protected from atmospheric oxygen by nitrogen. Ferrous iron was determined immediately complexing with 2,2-bibyridyl solution buffered by sodium acetate (Ayranci 1977). The red colored complex was determined by AAS (Perkin Elmer 403) using flow-trough cell at 522 nm. Total iron was determined by the same way reducing first ferric iron by hydroxylamin hydrochloride and also by usual AAS-methods. Titan was determined by "Tiron" (Maxwell 1968) using AAS and trough-flow cell at 380 nm. The concentrations of other elements were determined by normal AAS-methods using a mixed standard solution prepared from Merck Titrisol standard solutions for AAS. Concentrations of the elements in solution were calculated to correspond the composition of a granodioritic rock on the concentrations in stock solution were (mg/l):

Si	200	Fe	20	Ca	10	K	5		
Al	300	Mg	5	Na	5	Mn	10	Ti	4

The analytical error by AAS-determinations was less than ± 5 %. A separate portion of some samples was taken for digestion of sulfides by HCl, HNO_3, and $HClO_4$ and determination of S gravimetrically and Cu, Pb, Zn, and Cd by AAS.

The water analyses have been made according to the methods generally used in the laboratories of the National Board of Waters (Erkomaa and Mäkinen 1975). The determinations and the results are presented in Tables 1–4. Qualitative and semi-quantitative X-ray analyses were made from samples of rock powder to determine the composition and relative quantities of the principal minerals.

Table 1. Chemical analyses of rocks as determined from powder samples from rock wells.

Number of powder sample	Species of rock	Oxides (% wt.)									
		Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	SiO_2 (appr.)
177 002	Granite	18.0	2.61	0.27	1.01	0.55	3.11	6.76	0.41	0.04	70
182 048	Granite	16.1	2.32	0.13	1.45	0.51	2.89	6.87	0.36	0.02	69
443 015	Granite	13.5	1.59	0.23	2.75	0.62	4.76	3.19	0.24	0.04	73
589 003	Granite	17.0	1.88	0.50	5.50	2.59	3.52	2.08	0.76	0.03	66
781 017	Granite	14.8	1.00	0.04	0.45	0.22	2.55	6.54	0.09	0.01	74
936 020	Granite	15.2	4.86	0.05	2.86	0.89	2.79	1.75	0.41	0.08	71
182 040	Granodiorite	18.8	2.05	0.16	1.61	0.52	2.91	7.17	0.55	0.02	66
183 022	Granodiorite	17.6	5.07	3.01	3.38	0.77	3.32	6.04	0.99	0.12	60
249 015	Granodiorite	19.3	2.91	0.07	3.60	1.18	3.35	4.25	0.42	0.06	65
410 002	Granodiorite	18.9	0.99	4.29	7.48	1.83	3.24	4.16	0.65	0.10	59
770 001	Granodiorite	18.0	4.07	0.95	2.08	0.78	2.93	5.82	0.52	0.06	65
989 018	Granodiorite	14.8	2.61	4.42	5.07	2.45	2.86	4.40	0.73	0.12	62
936 015	Granodiorite	17.1	4.90	1.00	5.28	0.54	3.33	3.29	0.40	0.10	64
164 009	Quartz diorite	19.0	4.39	2.42	6.06	2.85	3.88	2.30	0.82	0.10	60
936 025	Quartz diorite	19.6	3.13	3.14	6.86	2.77	3.43	3.17	0.74	0.12	57
182 054	Mica gneiss	15.1	2.96	2.77	4.76	1.78	3.22	3.81	0.55	0.10	65
182 060	Mica gneiss	19.9	2.69	0.18	4.76	0.41	3.39	5.94	0.57	0.06	62
277 023	Mica gneiss	21.0	1.21	0.26	1.94	0.25	5.61	6.05	0.30	0.02	63
291 013	Mica gneiss	13.6	7.67	3.43	1.87	3.85	0.72	1.32	0.52	0.06	67
398 001	Mica gneiss	16.0	4.02	2.53	1.48	2.54	2.05	2.47	0.67	0.03	68
934 001	Mica gneiss	11.8	1.83	0.66	1.13	1.12	2.17	2.08	0.40	0.03	68
936 019	Mica gneiss	18.8	3.25	2.05	5.64	1.14	3.17	3.84	0.40	0.08	61
299 010	Mica schist	18.9	2.78	4.40	1.86	3.51	3.20	5.73	0.80	0.11	59
562 006	Mica schist	16.8	2.08	4.93	3.10	1.80	3.20	3.35	0.70	0.09	64
098 003	Amphibolite	19.1	2.76	5.72	13.17	3.45	3.89	0.82	1.00	0.15	50
277 025	Amphibolite	14.1	6.30	3.89	8.70	4.01	2.90	2.56	1.10	0.20	56
443 012	Amphibolite	19.4	4.43	5.65	11.75	7.89	2.61	1.07	0.58	0.19	46
182 049	Hornblende gneiss	15.1	5.84	4.64	7.04	7.03	2.46	3.20	1.01	0.20	53

Table 2. Average chemical composition of the different rocks as determined from the powder samples from rock wells. M = arithmetic mean, D = standard deviation.

Species of rock	Number of determinations	Oxides (% wt.)									
		Al_2O_3		Fe_2O_3		FeO		CaO		MgO	
		M	D	M	D	M	D	M	D	M	D
Granodiorite	7	17.79	1.53	3.23	1.52	1.99	1.89	4.07	2.03	1.15	0.73
Quartz diorite	2	19.30	0.42	3.76	0.89	2.78	0.51	6.46	0.57	2.81	0.06
Granite	6	15.77	1.61	2.38	1.34	0.20	0.17	2.34	1.82	0.90	0.86
Mica gneiss	7	16.60	3.41	3.38	2.11	1.70	1.32	3.08	1.89	1.58	1.27
Mica schist	2	17.85	1.49	2.43	0.50	4.67	0.38	2.48	0.88	2.66	1.21
Amphibolite	4	16.93	2.72	4.83	1.59	4.98	0.88	10.17	2.80	5.60	2.19

Species of rock	Number of determinations	Oxides (% wt.)									
		Na_2O		K_2O		TiO_2		MnO		SiO_2	
		M	D	M	D	M	D	M	D	M	D
Granodiorite	7	3.13	0.22	5.02	1.36	0.61	0.21	0.08	0.04	63.14	2.67
Quartz diorite	2	3.66	0.32	2.74	0.62	0.78	0.06	0.11	0.01	58.50	2.12
Granite	6	3.27	0.80	4.53	2.45	0.38	0.22	0.04	0.02	70.50	2.88
Mica gneiss	7	2.90	1.52	3.64	1.84	0.49	0.13	0.05	0.03	65.00	2.71
Mica schist	2	3.20	0.00	4.54	1.68	0.75	0.07	0.10	0.01	61.50	3.54
Amphibolite	4	2.97	0.64	1.91	1.15	0.92	0.23	0.19	0.02	51.25	4.27

Table 3. Average chemical composition of the ground water samples from the rock wells of the study area. Group 0 = granodiorites; group 1 = quartz diorites; group 2 = granites; group 3 = mica gneisses; group 4 = mica schists; group 5 = amphibolites, hornblende gneisses; N = number of determinations; M = arithmetic mean; D = standard deviation.

		0		1		2		3		4		5	
		(N=7)		(N=2)		(N=6)		(N=7)		(N=2)		(N=4)	
		M	D	M	D	M	D	M	D	M	D	M	D
Colour	mg Pt/l	25.0	30.8	30.0	28.2	167.5	359.1	13.3	7.5	10.0	0.0	15.0	13.2
pH		6.33	0.59	7.45	1.06	6.82	0.76	6.49	0.81	6.30	0.85	7.30	0.50
Specific conductance	mS/m	18.51	10.58	54.5	41.72	24.87	9.35	14.90	7.33	15.25	9.55	32.00	9.76
Total hardness	dH^o	2.70	2.33	5.34	1.79	3.22	1.66	2.49	1.51	2.36	1.26	6.42	2.21
COD	O_2 mg/l	3.64	3.59	9.75	13.08	1.85	1.24	1.40	0.97	2.50	1.41	0.95	0.65
NH_4	μg/l	25.57	50.67	30.50	23.34	93.50	117.12	6.71	6.55	9.00	1.41	23.25	20.32
NO_3	μg/l	1 154	1 975	1 200	1 697	970	1 582	364	431	1 100	141	695	1 010
NO_2	μg/l	3.57	3.55	1.00	1.41	8.80	7.82	0.57	0.54	3.00	4.24	3.25	2.22
Cl	mg/l	11.00	13.46	25.00	0.00	12.55	12.92	5.77	5.65	2.00	0.00	14.80	18.87
F	mg/l	0.86	0.60	0.31	0.00	0.58	0.57	0.40	0.45	0.16	0.04	0.37	0.43
SO_4	mg/l	12.73	4.51	7.05	7.57	13.28	11.16	18.31	12.65	10.00	6.79	12.65	9.67
PO_4	μg/l	6.00	3.87	10.50	10.61	104.80	193.97	9.71	10.40	6.00	0.00	13.50	14.06
SiO_2	mg/l	16.49	5.90	19.50	3.54	18.97	8.17	17.81	9.30	16.20	1.70	17.28	2.12
Ca	mg/l	12.49	9.43	24.00	14.14	13.83	6.08	11.33	6.56	10.70	4.67	33.50	13.28
Mg	mg/l	4.14	4.49	8.60	0.85	5.57	4.01	3.93	2.68	3.75	2.62	7.50	4.68
Na	mg/l	10.49	10.74	10.90	4.38	19.03	17.17	12.74	14.43	11.75	11.67	15.83	8.66
K	mg/l	5.70	7.45	3.30	0.71	2.72	1.25	2.54	2.05	1.65	0.92	2.88	1.94
Fe	mg/l	0.86	0.94	0.48	0.14	2.71	4.18	1.67	1.95	0.08	0.06	0.11	0.04
Mn	mg/l	0.28	0.42	0.22	0.09	0.56	0.63	0.10	0.11	0.05	0.04	0.12	0.13
Zn	μg/l	180	108	-	-	1 428	2 402	432	465	70	42	677	882
Cu	μg/l	8.67	8.62	-	-	3.75	3.59	28.40	41.32	51.50	54.45	37.50	28.99
Ni	μg/l	5.00	0.00	-	-	7.75	9.14	5.40	6.95	5.00	0.00	2.50	3.54
Pb	μg/l	1.00	0.00	-	-	1.25	1.89	1.20	1.30	2.50	0.71	0.50	0.71
Cd	μg/l	1.00	0.00	-	-	1.00	1.41	0.40	0.55	1.00	0.00	0.50	0.71
^{222}Rn	p Ci/l	8 843	7 546	1 300	424	21 167	34 015	6 100	5 734	3 000	2 828	3 750	1 529
^{226}Ra	p Ci/l	0.71	0.52	0.95	1.20	1.27	1.92	0.40	0.41	0.30	0.14	0.45	0.42
Gross alpha activity	p Ci/l	31.01	65.80	10.25	10.96	87.65	202.03	6.89	5.11	5.90	1.56	42.50	34.10

Table 4. Abundance of certain elements in water samples from rock wells and in the corresponding powder samples. Group 0 = granites, granodiorites, quartz diorites; group 1 = mica gneisses, mica schists; group 2 = amphibolites, hornblende gneisses; group 3 = average values of groups 0–2; group 4 = average values from a more abundant material (82 observations); N = number of determinations; M = arithmetic mean; D = standard deviation.

		0 (N=15)		1 (N=9)		2 (N=4)		3 (N=28)		4 (N=82)	
		M	D	M	D	M	D	M	D	M	D
Water sample	Na mg/l	24.36	42.40	12.52	13.17	15.83	8.66	19.34	31.99	16.92	20.99
Powder sample	Na_2O %	3.26	0.54	2.97	1.32	2.97	0.64	3.12	0.86		
Water sample	Fe mg/l	1.55	2.76	1.31	1.82	0.11	0.04	1.27	2.27	0.92	1.81
Powder sample	Fe_2O_3 %	2.96	1.40	3.17	1.88	4.83	1.59	3.29	1.66		
Powder sample	FeO %	1.38	1.62	2.36	1.74	4.98	0.88	2.21	1.96		
Water sample	Mn mg/l	0.380	0.493	0.087	0.099	0.116	0.126	0.248	0.389	0.243	0.347
Powder sample	MnO %	0.068	0.040	0.064	0.033	0.185	0.024	0.084	0.055		
Water sample	Mg mg/l	5.31	4.08	3.89	2.50	7.50	4.68	5.64	3.78	6.40	4.52
Powder sample	MgO %	1.27	0.95	1.82	1.27	5.60	2.19	2.07	1.92		
Water sample	K mg/l	4.19	5.15	2.34	1.85	2.88	1.94	3.41	3.99	4.64	6.82
Powder sample	K_2O %	4.52	1.88	3.84	1.75	1.91	1.15	3.93	1.92		
Water sample	Ca mg/l	14.56	8.98	11.19	5.92	33.50	13.28	16.18	11.23	18.28	11.76
Powder sample	CaO %	3.70	2.22	2.95	1.68	10.17	2.80	4.38	3.19		
Water sample	SiO_2 mg/l	17.88	6.44	17.46	8.11	17.26	2.12	17.66	6.45	18.42	6.40
Powder sample	SiO_2 %	65.47	5.18	64.22	3.07	51.25	4.27	63.04	6.56		

4. RESULTS OF THE INVESTIGATIONS

4.1 Bedrock of the well sites

The rock types were determined from the rock powder by visual inspection and X-ray diffraction analysis. The rock type thus determined in each well site generally agrees with that on the map of Prequaternary rocks (1:100 000). Local differences naturally exist. These are partly due to the fact that the samples have been drilled from the bottom of the wells, whose average depth is more than 60 m.

The bedrock of the well sites consists of the following rocks: granite (6 wells), granodiorite (7 wells), quartz diorite (2 wells), mica gneiss (7 wells), mica schist (2 wells), and amphibolite or hornblende gneiss (4 wells). Granites, granodiorites and quartz diorites are here classified as acid (or silicic) plutonic rocks, mica gneisses and mica schists as acid schists and amphibolites and hornblende gneisses as basic (or subsilicic) rocks.

The X-ray analyses indicate that the minerals of the rocks were quite unaltered. No secondary calcites, zeolites and clay minerals were present, except some chlorite and sericite discovered in some samples. X-ray determinations agreed rather well with the visual inspection of the powders.

The chemical compositions of the rocks agree with the analyses earlier made from these types of Finnish Precambrian rocks (cf. e.g. Lokka 1950). It must however be noted that the amount of SiO_2 has been evaluated according to the sum of the other oxides and by assuming the amount of water, on the basis of the relatively small amounts of mica and other water-bearing minerals, to be 1–2 %.

As to the fracturing of the bedrock, about 30 % of the wells are drilled in a fracture zone clearly seen on a topographic map (1:20 000), and about 15 % of the wells are drilled in a clearly unfractured bedrock. The sites of the wells have not been chosen for geological reasons, but drilled as near the consumers as possible.

4.2 Chemical composition of ground water and contributing factors

4.21 pH and specific conductance

Arithmetic mean of the pH values in the waters from acid plutonic rocks was 6.7, from acid schists 6.4, and from basic rocks 7.3. These values roughly correspond to those obtained by Lahermo (1970

App. 1) from ground waters in similar rocks in northern Finland, but compared with determinations from acid rocks (mean pH = 7.2) in the rapakivi area of SE Finland (Lahermo 1971, p. 25) and in a mica gneiss area (mean pH = 7.3) in S-Ostrobothnia, the latter within the present study area (Uusinoka 1975, p. 45), the pH values here obtained for the acid rocks are notably lower. The pH values show positive correlation with the specific conductance values (R = 0.754). Correlation between specific conductance and total hardness is R = 0.708, between specific conductance and Na R = 0.859, Ca R = 0.697, and Mg R = 0.561. The mean specific conductance of the ground waters from the acid plutonic rocks was 31 mS/m, from the acid schists 15 mS/m, and from the basic rocks 32 mS/m. The specific conductance tends to be higher in the ground waters from basic rocks than in those from acid rocks. This is due to the fact that the basic rocks contain minerals more susceptible to weathering than do the acid rocks. Besides the mineralogical composition of the bedrock, the so-called time factor (e.g. Lahermo 1970, p. 43) is also important. Balance in the ion exchange between ground water and minerals of the rocks is possible in stagnant conditions (Lahermo 1970, Jacks 1972). Disturbance of the balance by pumping the water will lower the specific conductance value. It has been observed that the specific conductance value increases with increasing depth of the rock well (R = 0.501). The deep wells are generally situated in the least fractured bedrock (Carlsson and Olsson 1977, Carlsson 1979), where the ground water flow has been in its minimum which means that stagnant conditions have prevailed there more likely than nearer the surface.

4.22 Total hardness, calcium and magnesium

The arithmetic means (M) of the total hardness value (in °dH = German degree) in the different groups are as follows (D = standard deviation):

acid plutonites	M = 3.26°dH	D = 2.08
acid schists	M = 2.46°dH	D = 1.38
basic rocks	M = 6.42°dH	D = 2.21

These values are much lower than those obtained by Lahermo (1971, p. 25) from the rapakivi area of SE Finland as compared even with the values in the ground waters of the basic rocks in the present study. Values of total hardness similar to those in the present study have been obtained from ground waters of basic rocks from northern Finland, while these values from waters contained in acid rocks of the same area are generally lower (Lahermo 1970, App.1). Values lower than these have also been obtained by Le Grand (1958) in areas of granitic rocks. A weak correlation was found between the total hardness of the ground water and the CaO and MgO contents of the corresponding rock powder samples (°dH–CaO: R = 0.388; °dH–MgO: R = 0.370). The higher alkaline-earth content of basic rocks compared with acid rocks is clearly seen in differences in concentrations of Ca and Mg in ground waters from acid rocks (mean Ca = 14.6 mg/l, mean Mg = 5.3 mg/l) and from basic rocks (33.5 and 7.5 mg/l, respectively). The Ca content of ground waters is also in a good correlation with the CaO content of the corresponding rock powder sample (Fig. 3). This is partly due to the fact that calcium is found to be the element most rapidly removed from weathering rocks (Lahermo 1970, p. 95, Uusinoka 1975, pp. 31–32). This is also shown by the Ca/Mg ratio (Table 5). The same ratio approximately prevails both in the rocks and ground waters in the areas of acid plutonites. In schists and particularly in basic rocks the ratio is notably higher in ground waters indicating a greater tendency of calcium than of magnesium to be dissolved during weathering (cf. also Lahermo 1970).

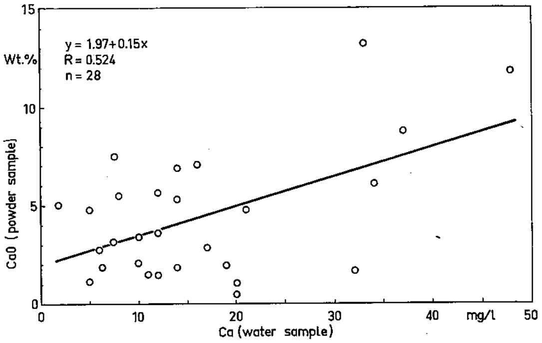


Fig. 3. Relation between Ca content in water samples and CaO content in the corresponding rock powder samples.

Table 5. CaO/MgO and Na_2O/K_2O ratios in samples of rock powder and Ca^{2+}/Mg^{2+} and Na^{+}/K^{+} ratios in samples of ground water contained in these rocks.

	CaO/ MgO	$Ca^{2+}/$ Mg^{2+}	$Na_2O/$ K_2O	$Na^{+}/$ K^{+}
Granite	2.6	2.5	0.7	7.0
Granodiorite	3.5	3.0	0.6	1.8
Quartz diorite	2.3	2.8	1.3	3.3
Mica gneiss	1.9	2.9	0.8	5.0
Mica schist	0.9	2.9	0.7	7.1
Amphibolite	1.8	4.5	1.6	5.5

4.23 Sodium and potassium

As to the distribution of the alkalis in ground water samples from different rocks, it seems that the sodium content tends to be higher in ground water contained in basic rocks while no differences could be observed in potassium content. No correlation exists between the alkali contents of rocks and corresponding ground water. The equal or even greater alkali content in ground water stored in alkali-poor basic rocks must be explained by the greater weatherability of the basic rocks. The differences in geochemical behavior among sodium and potassium is clearly seen in the Na/K ratios in both rock and ground water samples (Table 5). The alkali ratio in ground water is several times greater than in its reservoir rock indicating the immobility of potassium, which has a tendency to be enriched in weathering products while sodium, with a smaller ionic radius and a higher ionic potential than potassium, tends to be leached away (Rankama and Sahama 1950, pp. 431–2).

4.24 Silica

The silica content is of the same magnitude in ground waters contained both in acid and basic rocks. These results show values somewhat higher than those obtained by Lahermo (1970, App. 1, 1971, p. 25). No distinct correlation exists between silica contents of rocks and ground water or between silica and pH.

4.25 Iron and manganese

According to the arithmetic mean of all the water samples, the iron content (M = 1.27 mg/l) is relatively high, but this value is, however, caused by a few high values only. Most of the observations (77 %) show values less than 1 mg/l. In 52 % of the observations they are below 0.2 mg/l. Values of the order of 1–3 mg/l have been found by Uusinoka (1975, p. 45) in areas of mica gneiss within the present study area. Iron contents ranging from less than 0.005 to 7.69 mg/l in areas of silicic rocks and from less than 0.005 to 22.00 mg/l in areas of subsilicic rocks have been found by Lahermo (1970, App. 1) in his study area in northern Finland. In the rapakivi granite area of SE Finland he has found an average iron content of 3.31 mg/l in ground waters stored in these granites (Lahermo 1971, p. 25). The behavior of iron in ground water is strongly regulated by the redox potential which tends to rise as the oxygen content rises and diminish as the pH value rises (Hem 1970, Lahermo 1972, p. 62). In oxygen-rich ground water in normal pH conditions iron usually occurs as insoluble ferric hydroxide while in reducing conditions it tends to be present as soluble ferrous hydroxide or, in CO_2-rich water, as ferrous bicarbonate. The solubility of ferrous iron is reduced by an abundant bicarbonate content and rise in the pH value (cf. Lahermo 1970, p. 62). The relatively high iron content in ground water stored in bedrock compared with the iron content of the water in surficial deposits can be explained by the oxygen-poor conditions in bedrock fissures (Lahermo 1970, p. 63), and particularly in bedrock overlain by thick surface deposits (Rönkä and Turtiainen 1980) and by clayey beds (Natukka 1960). The iron content also increases with the well depth, which is shown by the correlation coefficient R = 0.505. Manganese seems to have been enriched in the ground water of acid plutonites. A relatively small manganese content in ground waters of subsilicic rocks is reported by Lahermo (1970, App. 1). The present results are not in agreement with those obtained by Le Grand (1958) and Larsson et al. (1972) in which contents of iron and manganese have been found to be greater in ground water stored in gneisses than in that of granites. Some correlation exists between the amounts of iron and manganese in ground water. Manganese is not as susceptible as ferrous iron to oxidation (Eriksson and Khunakasem 1968, Lahermo 1970, p. 63). Both these elements enter the ground water principally due to weathering of dark minerals. The greater susceptibility of iron to oxidize in ground water is indicated by the substantially higher value of the Fe/Mn ratio in ground water than that in rock powder (Tables 2–4).

4.26 Sulphate

No systematic differences could be observed in the sulphate content of ground water samples from different rocks. The values obtained are of the same order as those reported by Lahermo (1970, App. 1) even though those reported by him show higher sulphate contents in areas of subsilicic rocks. Correlation between sulphate content and specific conductance as suggested by Lahermo (1971, p. 33) is, however, not shown by the present results. The chief sources of sulphate are the sulphide minerals. Important sources of sulphate are also the clays rich in organic matter deposited during the Litorina stage of the Baltic Sea. But as to the study area, these Litorina clays are met with only in the northwest. Furthermore, as stated by Lahermo (1971, p. 35) the occurrence of marine chloride is frequently associated with a sulphate content exceeding the usual. The concentrations of sulphate and chloride in ground waters from the rapakivi area of SE Finland (Lahermo 1971, p. 25), whose southern part was widely submerged in the ancient Litorina Sea, are generally much higher than in the present study area. In the study of Lahermo (1971, p. 35) the chloride content has a slight correlation to the sulphate content. No correlation exists between these electrolytes in the present study. The sulphide minerals, though evidently not present in greater quantities in the catchment areas of the wells studied, must be practically the only sources of the sulphates present in these ground waters.

4.27 Phosphate

Phosphate contents show a rather great variation between different water samples. Phosphate seems to have been enriched in ground waters of certain acid plutonites. Anyway the amounts of phosphate dissolved into ground water are as a whole rather slight (Lahermo 1970). Apatite is the sole phosphoric mineral of significance in the rocks of the study area. Its resistance to weathering is rather high (Pettijohn 1975).

4.28 Chlorine and fluorine

Chlorine is present in varying amounts in all the water samples. Its presence is not affected by the composition of the bedrock. The highest contents of chlorine as well as sodium might sometimes be attributed to the fossil salt water entrapped in the fissures of the bedrock in the northwestern part of the study area, which was submerged in the ancient Litorina Sea (Salmi 1963, Hyyppä 1973). Correlation between chlorine and specific conductance is rather good (R = 0.600). The amounts of fluorine in ground water are generally a little higher here than e.g. in the study area of Lahermo (1970) in northern Finland, but notably lower than in the rapakivi area, which is famous for the high fluorine content in ground waters, mean value 1.84 mg/l (Lahermo 1971, p.25). The high fluorine content in the rapakivi area is due to the mineral fluorite commonly occurring in rapakivi granite as an accessory mineral. However, as compared with a larger material of observations (Le Grand 1958), the fluorine content in the ground water of the present study area is generally a little higher. It is interesting to note that in the samples of ground water fluorine is best correlated with phosphate (R = 0.420) thus clearly indicating its origin from apatite.

4.29 Ammonia, nitrite, nitrate and color

The amount of nitrogen compounds in the bedrock itself is practically nil. Thus, their origin in ground water is from the decomposition of organic matter in the surficial deposits. A small amount might also be of atmospheric origin (Lahermo 1970, p. 68). Nitrogen compounds are indicators of pollution also in waters pumped from rock wells. It has been observed that the amount of total nitrogen decreases with increasing depth of the rock wells (Jacks 1973). The color value is strongest among the acid plutonites. The mean value of color in all the water samples (M = 53 mg/l Pt) is best correlated with the iron content (R = 0.842) and with the content of NH_4 (R = 0.738).

4.210 Heavy metals (Cu, Zn, Cd, Pb, Ni)

Contents of these metals in ground water for drinking purpose are, as must be expected, extremely low. As to most of these metals, no correlation with the type of the reservoir rock can be observed. But copper has a clear tendency to become enriched in waters stored in schists and basic rocks. This is in agreement with the concentration of copper in different rocks. In his study area in easternmost Finland Salminen (1980) has obtained the following Cu contents in certain rocks (analysed by optical emission quantometer):

	average content (ppm)	standard deviation (ppm)
granite	6.3	6.6
mica schist	42.4	43.0
amphibolite	30.8	38.7

In the present study the average Cu contents in ground waters stored in these types of rocks are roughly a thousand times smaller than those in the rocks listed above.

4.211 Radioactivity

The amounts of ^{222}Rn and ^{226}Ra as well as gross alpha activity are low, but, as should be expected (Asikainen and Kahlos 1979), waters contained in granites show the greatest concentrations of radioactive elements.

5. CONCLUSIONS

The results are generally in agreement with the previous work dealing with chemical geology of ground water in crystalline bedrock (Lahermo 1970, 1971, Jacks 1972, 1973). According to these results the quality of ground water cannot be predicted mainly on the basis of the composition of the bedrock the water is stored in. Correlation between the chemical composition of the bedrock and the ground water it contains exists only in the amounts of calcium, the element most readily dissolved from weathering rock. This fact might be of some help in predicting the total hardness of the ground water. However, owing to the possible variation in the homogeneity of the bedrock in each well site and to the variations among the well capacities of the different sites, even this correlation is not very good. As to the behavior of the other important elements, i.e. Na, K, Mg, Fe, and Si, weatherability as well as the mode of weathering of the particular minerals in which they belong as constituents play a much greater role than the abundance of the elements in the rocks. As to certain elements, other factors, like redox potential for the behavior of iron, is of crucial importance.

Those regional variations in the ground water composition which are found to depend mainly on the composition of the bedrock are mostly restricted to the values of pH and total hardness as well as to the Ca content and to a lesser degree, also to the contents of Na, Si and, in certain cases, like in the rapakivi areas, to F, and, of the trace elements, to Cu.

SUMMARY

For this study 28 rock wells drilled into the Precambrian crystalline bedrock of southern and central Finland were studied by making chemical analyses from both the rock powder obtained during the drilling and from ground water pumped from the wells. The rocks are some of the typical Finnish Precambrian plutonites and schists, i.e. granites, granodiorites and quartz diorites (forming the group here called acid plutonites), mica gneisses and mica schists (the group of acid schists), and amphibolites (the group of basic rocks).

The mean specific conductance of the ground water samples is about 26 mS/m. It tends to be higher in waters contained in the basic rocks than in those in the acid rocks thus indicating greater electrolyte contents in the former group.

Comparisons between the chemical and mineralogical composition of the rocks and the chemistry of the ground water they contain indicate a mentionable correlation in the amounts of calcium, the element most easily dissolved from weathering rock. This correlation also affects the prediction of the total hardness of ground water from bedrock of a known composition. The amounts of other important elements, such as Na, K, Mg, Fe and Si, in ground water are affected by the weatherability and the mode of weathering of their source minerals, and, in the case of Fe, the redox potential of the water rather than the mere abundance of the element in the rocks. Those regional variations in the ground water composition which are found to depend mainly on the composition of their reservoir rocks are mostly restricted to the pH values, the values of total hardness, Ca content, and slightly to the contents of Na and Si.

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Esa Rönkä, Raimo Uusinoka,
Antti Vuorinen

LOPPUTIIVISTELMÄ

Tutkimusta varten valittiin 28 Etelä- ja Keski-Suomessa sijaitsevaa, kiteiseen peruskallioon porattua kaivoa (kuva 2). Näistä tutkittiin kemiallisin analyysein sekä porausjauhe että kalliovesi. Lisäksi määritettiin röntgenanalyysein soijanäytteiden päämineraalit. Kivet, joihin kaivot on porattu, edustavat prekambrisen peruskallioalueemme tyypillisiä syväkiviä ja liuskeita eli graniitteja, granodioriitteja ja kvartsidioriitteja (jotka tässä muodostavat happamien syväkivien ryhmän), kiillegneissejä ja kiilleliuskeita (happamien liuskeiden ryhmä) ja amfiboliitteja (emäksisten liuskeiden ryhmä).

Pohjavesinäytteiden keskimääräinen ominaissähkönjohtokyky on n. 26 mS/m. Se pyrkii olemaan suurempi emäksisten kivilajien kuin happamien kivilajien alueilla osoittaen täten edellisten alueiden kalliovesien suurempaa elektrolyyttipitoisuutta.

Verrattaessa kivien kemialllista ja mineralogista koostumusta niiden sisältämien pohjavesien kemialliseen koostumukseen huomataan kalsiumin määrien korreloivan suhteellisen hyvin. Kalsium on alkuaine, joka useimmiten herkimmin poistuu rapautuvasta kivestä. Tämä korrelaatio auttanee myös arvioitaessa tietyn koostumuksen omaavan kivilajialueen kalliovesien kokonaiskovuutta. Muiden tärkeimpien alkuaineiden, kuten natriumin, kaliumin, magnesiumin raudan ja piin esiintymiseen kalliopohjavesissä vaikuttaa pikemminkin niiden lähdemineraalien rapautumisherkkyys ja rapautumisen luonne kuin niiden suhteellinen runsaus koko kivilajissa. Raudan suhteen on merkittävänä tekijänä veden redox-potentiaali. Ne alueelliset vaihtelut pohjaveden kemiallisessa koostumuksessa, joiden on huomattu pääasiassa riippuvan näitä pohjavesiä ympäröivän kallioperän kemiallisesta koostumuksesta, rajoittuvat etupäässä veden pH-arvoon, kokonaiskovuuden arvoon sekä kalsiumpitoisuuteen ja jossakin määrin myös natriumin ja piin määriin.

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