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**THE OCCURRENCE AND GEOCHEMISTRY OF FLUORIDES WITH SPECIAL
REFERENCE TO NATURAL WATERS IN FINLAND**

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Geological Survey of Finland (GTK) has collected groundwater samples for chemical analyses in different parts of the country from the 1960s in order to elucidate the geochemical and anthropogenic controls on groundwater quality. One of the most interesting features in the geochemistry of groundwater is the outstandingly high fluoride concentrations in areas composed of a special type of postorogenic granites, i.e. rapakivi granites. The largest rapakivi batholiths are named according to the local names: Wiborg in southeastern Finland, and Laitila, Vehmaa and Ahvenanmaa in southwestern Finland. Coarse-grained K-rich rapakivi granites have higher concentration of fluorine (0.20-0.42%) than other plutonic or metamorphic rocks. The primary fluoride sources for waters are fluorite and fluorapatite, although the common OH⁻-bearing minerals such as micas and amphiboles, containing elevated amounts of fluorine (0.2-1.1%), contribute likewise to fluorides in water.

High fluorine concentrations in rocks are omnipresently reflected as regional fluoride anomalies in soils, groundwater and surface waters. The average F⁻ concentrations in streams and shallow groundwater draining areas composed of rapakivi granites are more than one order of magnitude higher (1-1.5 mg/L) than elsewhere (generally around 0.1 mg/L). The F⁻ distribution in waters from springs, dug wells and drilled bedrock wells shows by and large analogous and consistent anomalous patterns or provinces with each other. In the Laitila and Vehmaa batholiths the southern boundary is, however, transitional due to the glacial transport of abraded fluorine-rich rock material from the northwest to the southeast. In spring and well waters there are similar orders of magnitude of fluorides, while the concentrations are higher in water from drilled wells cutting other types of rocks such as various granitoids and migmatites. The aquifers confined partly or wholly by covering clay and silt deposits show notably higher F⁻ concentrations than water in open aquifers. This is explained by the sorption/desorption properties of clay material in relation to F⁻ ions. The fluoride ion behaves independently of the type and amounts of other dissolved components in water.

According to administered EU directives the upper officially permissible F⁻ concentration in drinking water in Finland is 1.5 mg/L, a level which is frequently exceeded in private household wells and the public groundwater utilities underlying rapakivi granites. This constitutes currently a tedious practical water supply problem in estimated 3 to 4% of the country as fluorides are not easily removed by any feasible cost-effective methods.

Key words (GeoRef Thesaurus, AGI): fluorides, fluorine, granites, rapakivi, soils, geochemistry, surface waters, medical geology, Finland

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INTRODUCTION

Fluorides have been widely in the focus of public and scientific interest because of their important physiological role in the health of man. Their beneficial effect in decreasing the incidence of dental caries is well known while the toxic effects of fluorides, when occurring in abundances in drinking water, cause increased worries (see e.g. Bell et al. 1970, Ericsson 1970, Anon 1977, Fleischer & Robinson 1963, Fleischer et al. 1974, Nanyaro et al. 1984, Susheela 1985, Smith 1988). Fluoride is mainly ingested by humans through the water media. This is a different pathway from most other elements (except for As and U) important to the physiology of man and higher animals.

The interest in fluorides in Finland has been evoked by the fact that there are some certain rock types, i.e. rapakivi granites, which are the most fluorine-rich ordinary rock types (Sahama 1945a, Simonen & Vormaa 1969, Vormaa 1976, Simonen 1987, Haapala & Ehlers 1989, Rämö 1991, 1993, Rämö & Haapala 1995, Laitakari et al. 1996). Since fluoride is a fairly mobile element and it may be associated, among others, with U, Mo, Sn or W mineralizations in granitoidic environment, it has occasionally been used as a pathfinder

element in ore exploration.

The name “rapakivi” is derived from disintegrated, rotten or crumbly rock, a typical feature of the rapakivi granite (see Eskola 1930, Rämö 1993). The profound weathering is characteristic for rapakivi outcrops and large erratic boulders. Sometimes the surface part of rapakivi are more solid than deeper layers. Equally common outer appearance of rapakivi outcrops are glacially polished, smooth plain rock surfaces. The weathered gravel or shingle, called “moro” in Finnish, was for ages used to construct roads.

Fluoride has long been a vital part in the analytic programs for waters in the Geological Survey of Finland (GTK). In the early days an antiquated colorimetric method was used. From 1974 ion-specific electrodes were applied, which allowed the detection limit of 0.05 mg/L. An ionic chromatographic method (Dionex 2000I) was used from 1989 until 1998 (SFS-EN ISO 10304-1). The detection limit was 0.1 mg/L. A new version of the apparatus (Dionex DX-120) is currently facilitated enabling the lowering of the detection limit back to the level of 0.05 mg/L.

GENERAL GEOCHEMISTRY OF FLUORINE

Fluorine (F) is the most electronegative and reactive of elements, and reacts with practically all organic and inorganic substances. In nature it forms compounds as singly charged (-1) fluoride anion. In natural waters fluorine occurs as univalent anion (F⁻).

As a lithophile element fluorine is ubiquitously present in small amounts in silicate minerals and rocks of the lithosphere (Table 1). The average fluorine concentrations in the crust is estimated at 0.05-0.1% or 500-1000 mg/kg and ranks 13th among the elements (Turekian & Wedepohl 1961, Taylor 1964, Bowen 1979, Krauskopf 1979, Adriano 1986, Anon 1995). It is enriched during differentiation in the late stages of crystallizing magmas as well as in the residual solutions and vapour. Consequently, it is concentrated in highly siliceous granitic and alkaline

rocks, and in hydrothermal mineral deposits. Primary fluoriferous haloes are therefore associated with many types of mineral and ore deposits (Hopkins 1977).

Fluorine-rich gases liberated by crystallizing granite masses percolate through rocks and alter them in the vicinity of the granite intrusion and sometimes in the granite itself, giving rise to greisens (Correns 1956). Largely due to fluorite and topaz minerals the F⁻ concentrations of greisens may be up to 2-4%. Fluorine may occur also in limestones associated with tremolite-, actinolite-pyroxene- or with mica-chlorite-skarn formations, where F⁻ concentrations may reach the level of 0.4-1.2%. Part of fluorine may be present in clay material admixed with weathered limestones. It can also be combined with phosphate minerals.

In the late stages of crystallization F⁻ ions can

enter into the structural positions of OH⁻ -ions in minerals such as micas, amphiboles, chlorites and tourmaline (Rankama & Sahama 1950). This is because the ionic radii of both ions, 1.23-1.36Å¹ for F⁻ and 1.37-1.40Å for OH⁻ -ions (and 1.32Å for O²⁻ -ion), respectively, are very similar to each other (see e.g. Correns 1956, Fleischer & Robinson 1963, Koritnig 1972, Allmann 1974, Evans 1995, Brownlow 1996). The main rock-forming minerals without incorpo-

rated anionic hydroxyls (quartz, K-feldspar, plagioclases) do generally accept appreciable amounts of fluorine into their lattices. In some granites fluorine is distinctly concentrated in biotite and hornblende in the later stage of crystallization (Kanisawa 1979). In molten magma the volatile fluorine component is fractionated into apatite and hornblende in an early stage of differentiation and into hornblende and biotite in the later stage. Barth (1947) found that in

Table 1. Fluorine concentrations (mg/kg) in various rock types (Turekian & Wedepohl 1961, Vinogradov 1962, Fleischer & Robinson 1963, Taylor 1964, Fleischer et al. 1974, Koritnig 1972, Bowen 1979, Krauskopf 1979, Kabata-Pendias 1992, Koljonen 1992). Rapakivi granites are not included.

Magmatic (supracrustal) extrusive rocks	Magmatic igneous rocks	Metamorphic rocks (mainly in Finland)	Sedimentary rocks
Phonolite 930 mg/kg	Alkaline rocks, syenite 1000-1200	Granite gneiss 520-850	Sandstone, graywacke 50-180-200-270
Rhyolite, trachyte, dacite 300-480-700	Granite, granodiorite (520 ²)-750-800-850-1300-(1400)	Mica schist 700-1600	Limestone, dolomite 50-220-260-300-330-350
Andesite 210-500	Diorite 500-(1200)	Black schist 160-580	Shale 500-600-700-740-800
Basalt 360-370-400-470-500-510	Gabbro, diabase 300-370-420-500		Oceanic sediments 540 ³ -730-1300 ⁴
	Peridotite, dunite 15-20-50-100		Phosphate rock (phosphorite) 30 000-42 000

Table 2. The element composition (in percent) of the Wiborg and Laitila-Vehmaa rapakivi granites and rapakivi granites according to 1) Simonen and Vormaa (1969), 2) Simonen (1987), 3) Vormaa (1976), Sederholm (1925) and 4) Sahama (1945a), compared with the ordinary granites 6) according to Taylor (1964) and Vinogradov (1962), Turekian and Wedepohl (1961), and Schroll (1968).

Chemical component	1) Wiborg rapakivi	2) rapakivi ⁵	3) Laitila rapakivi	4) All granites rapakivi	5) Rapakivi in GTK files ⁶	6) Ordinary granites
SiO ₂	67.1-76.7%	71.3	72.6	71.8	71.5	67.2-74.3
Al ₂ O ₃	10.7-15.4	12.9	13.3	13	13.1	13.6-15.5
Fe ₂ O ₃ +FeO	1.8- 4.7	3.9	2.9	3.8	3.0	1.9-4.0
MnO	0.02-0.06	0.05	0.04	0.05	0.04	0.03-0.07
MgO	0.02-0.47	0.37	0.25	0.28	0.28	0.28
CaO	0.8- 3.2	1.89	1.18	1.59	1.25	0.7-3.0
Na ₂ O	2.3- 2.9	2.67	2.66	2.83	2.69	3.5-3.8
K ₂ O	4.9- 5.8	5.36	5.60	5.48	5.50	3.04-5.04
F ⁻	0.20-0.42	0.25	0.38	0.23	0.25	0.05-0.09
Count	-	7	-	24-37	88-177	-

¹⁾ The ionic radius is variable depending on the coordination number of the concerned ion and on the composition and structure of the compound in which the ion is involved.

²⁾ High calcium granites

³⁾ Carbonates

⁴⁾ Clays

⁵⁾ Mean of wiborgite (2), dark-coloured wiborgite (2), pyterlite (2), and porphyritic rapakivi granite (1)

⁶⁾ Median values

basalts and gabbros all the fluorine is contained in apatite. In other igneous rocks (e.g. in granites) and in metamorphic rocks fluorine is predominantly present in micas, hornblende and fluorspar.

Granitoids and pegmatite veins intermingled in metamorphic rocks contain the largest fluorine abundances, while mafic and ultramafic rocks show lower concentrations of the concerned element. Ordinary granites contain 0.05-0.14 % fluorine while the concentrations in other igneous and metamorphic rocks are 0.01-0.05 % (Table 1, 2). Metamorphic rocks have generally lost part of their F contents during metamorphic processes since volatile fluorine or ionic fluorides have migrated from the magmatic bodies into the country rock. According to Kanisawa (1979) the fluorine content is highest in alkaline-rich rocks and decreases with advancing differentiation while contents are still high in shallow intrusive granites.

The most important fluorine minerals are fluorite or fluorspar (CaF_2), fluor-apatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$, and ordinary apatite $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH},\text{Cl})$. They are characteristic accessory minerals in many types of rocks including the rapakivi granites. Since fluorite may contain nearly half of fluorine by weight, it contributes substantially to F concentrations in rock and water even though the mineral is present in small quantities (Correns 1956). Pure fluor-apatite could contain up to 3,8% fluorine. Minerals containing appreciable amounts of fluorine, such as topaz $\text{Al}_2(\text{F},\text{OH})_2\text{SiO}_4$, may be met in rapakivi granites (Haapala 1977, Lahti 1997). According to Rämö (1993) most fluorine in rapakivi granites is in fluorite and topaz minerals. Because topaz is very resistant against weathering, it does not significantly contribute to soluble F- concentrations. Furthermore, a mineral called zinnwaldite, containing variable amounts of fluorine, was

found in rapakivi granite (S. Lahti's pers. com.). Fluorine is also associated with Mg in a very rare carbonate mineral called sellaite (Sahama 1945b).

The volcanic and fumarolic gases emitted into air and dissolved in deep groundwaters contribute to the geochemical fluorine circle of the earth (Correns 1956). In fact, fluorine was considered as an essential constituent to render phosphate insoluble enough to form large, economically feasible phosphate deposits (Mansfield 1940). Volcanic gases are rich in fluorine, mainly in the form of HF or H_2F_2 and F_2 , but also as SiF_4 and H_2SiF_6 (Fleischer et al. 1974). Measurement of fluorides in precipitation from coastal areas of India suggest that anthropogenic sources are the major contributors of fluorides in precipitation. Aerosols derived from the sea are reported to be notable fluoride sources in coastal areas of India (Mahadevan et al. 1986).

There are many local man-made sources of fluorine. The largest part of the airborne fluorides are derived from industrial emissions, particularly from Al metallurgy. Fluorine emissions and waste waters can also be released from fertilization industries (e.g. in North Carolina and Florida) and from phosphate and kryolite (Na_3AlF_6) mining operations. Substantial amounts of fluorides are transferred to agricultural soils by phosphate fertilizers. Phosphorites may contain 0.5-4% of fluorine depending on its origin, contents of fluorapatite, and on the process of manufacturing. Part of the fluoride is retained in superphosphate fertilizers (Fleischer et al. 1974). Fertilizers may include even 3% of fluorine (Larsen & Widdowson 1971). Hence, the increasing use of phosphate fertilizers enhances the fluorine input into the environment, particularly in surface runoff. The use of fluorocarbons, insecticides and weed killers may also contribute to local F- concentrations in soils.

COMPOSITION OF FLUORINE-RICH RAPAKIVI AND RELATED GRANITES IN FINLAND

Petrographical composition

Most of the granites are more fluorine-rich than less silicic igneous rocks. Among the granites, the rapakivi-type granites exhibit by far the highest fluorine concentrations (Fig. 1, Table 2). Rapakivi is a Finnish word meaning disintegrated, rotten or crumbly rock, a typical feature for many rapakivi granite outcrops. The name rapakivi was introduced by J.J. Sederholm in 1891 in his publication and has since been used in international geological literature. He was also the first to describe the

occurrence, petrography and chemical composition of the Finnish rapakivi granites including, among others, the large "classical" Wiborg batholith (Viipuri, Vyborg, Viborg).

Rapakivi granites represent the most voluminous continental silicic interplate magmatism on Earth (Rämö & Haapala 1995). The emplacement of the Subjotnian anorogenic rapakivi plutons into the stable platform took place from about 1540 to 1650 million years ago (Suominen 1991, Vaasjoki et al.

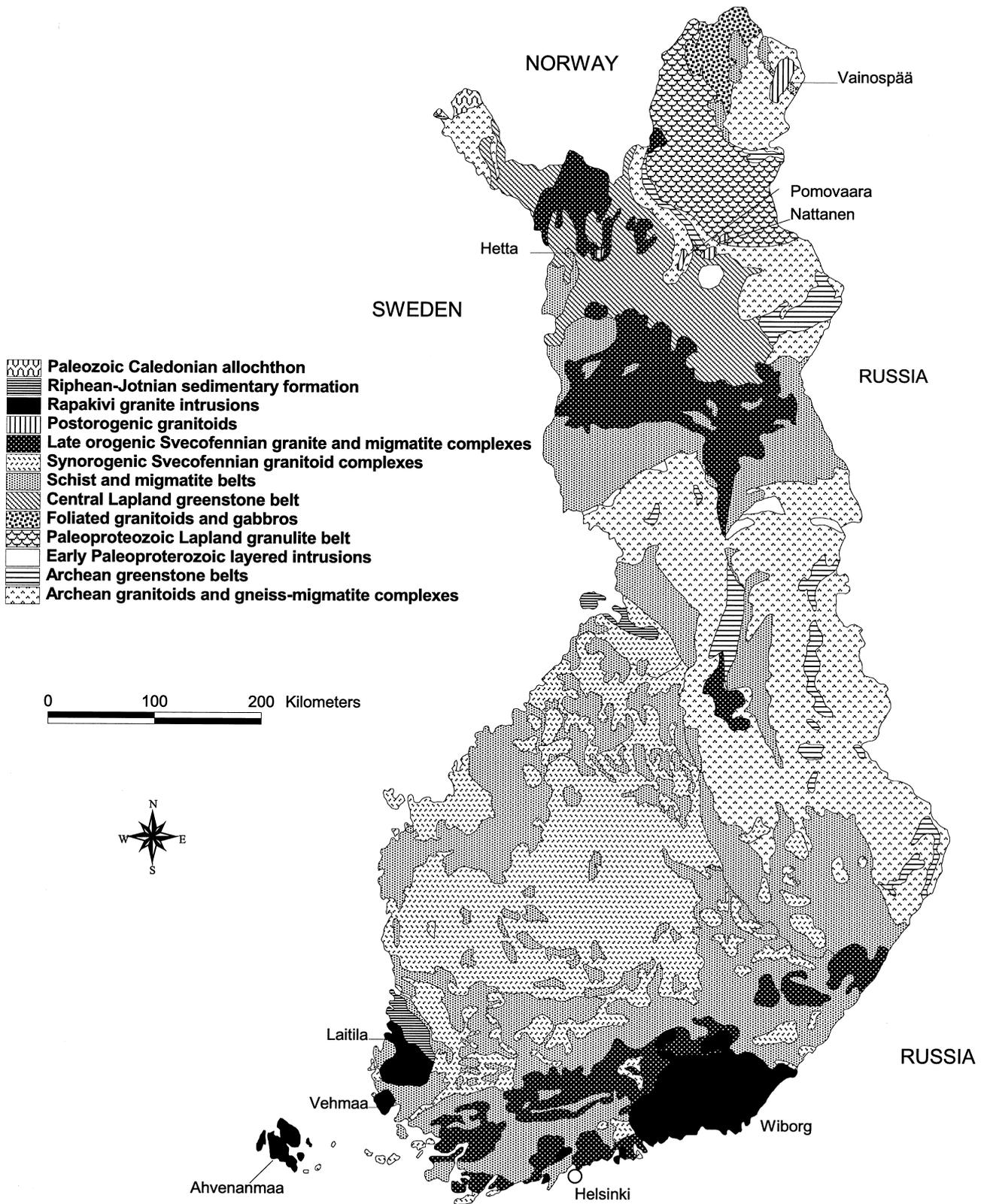


Fig. 1. The Precambrian bedrock of Finland. The main rapakivi batholiths and stocks are marked in black. Some postorogenic granitoids in Lapland (Nattanen, Pomovaara, Vainospää) are also marked. Map modified from Korsman et al. (1997).

1991). The rapakivi intrusions cut sharply the Paleoproterozoic Svecofennian crust. It is composed of high- and medium-grade metamorphic supracrustal rocks and orogenic plutonic rocks which formed 1870 to 1900 million years ago (Haapala & Ehlers 1989). The rapakivis are composed of many petrographic varieties of coarse-grained K-rich granitic rocks. The main rock-forming minerals are alkali feldspar, plagioclase and quartz. Hornblende and biotite are the most common mafic components while some pyroxene and olivine may also be present.

Based on isotopic studies it is known that the granitic melt of the Finnish rapakivi plutons originated from partial melting of Proterozoic lower crust 1540 to 1650 Ma ago (Haapala & Ehlers 1989, Rämö 1991, 1993, Rämö & Haapala 1995, Laitakari et al. 1996). The magmatic association is bimodal comprising, besides granite, anorthosite, gabbro, diabase and monzonite. Hence, rapakivi granite batholiths are associated with mafic rocks derived from partial melting of subcontinental mantle.

Rapakivi granites are postorogenic and anorogenic rocks distinguished from other granitoidic rocks by their texture and chemistry. Rapakivi granites are predominantly coarse-grained porphyritic granites characterized by large ovoids of alkali feldspar megacrysts, most of which are surrounded by plagioclase (oligoclase-andesine) mantles (Vorma 1975, 1976, Simonen 1980, Haapala & Ehlers 1989, Rämö 1993, Rämö & Haapala 1995, Laitakari et al. 1996). Sometimes the mantle shells are missing. Also quartz and some amphibolite and mica is present.

In Finland, there are four main rapakivi granite provinces: the Wiborg batholith in southeastern Finland (half of the batholith is presently beyond the Finnish-Russian border), two separated batholiths of Laitila and Vehmaa, and the Ahvenanmaa (Åland) batholith in southwestern Finland, which again encompasses most of the Ahvenanmaa archipelago and is largely submerged by the sea (see e.g. Sahama 1945a, Vorma 1976, 1980 1986, Simonen 1987, Haapala & Ehlers 1989, Vorma 1989, Rämö 1991, 1993, Rämö & Haapala 1995, Laitakari et al. 1996, Fig. 1 and 2). In the northern side of the Wiborg batholith there are two satellitic intrusions of Suomeniemi and Ahvenisto (or Mäntyharju). These are composed of coarse-grained biotite- and hornblende-bearing granites without the typical plagioclase-mantled alkali feldspar ovoids (Vorma 1976).

The overwhelming majority of rapakivi granite on the Finnish side of the Wiborg batholith (Fig. 2) is a coarse-grained porphyritic rock with alkali feldspar ovoids surrounded by plagioclase mantles (Vorma 1975, 1976). This type of biotite-hornblende granite is called wiborgite, which covers

76% of the concerned rapakivi area. The dark-coloured wiborgite (5% of the area) contains more mafic silicates (amphibole, olivine) than wiborgite in general. Pyterlite, named after the village of Pyterlahti, is another variety of rapakivi granite (6% of the area). It is likewise a coarse-grained porphyritic granite without mantles of plagioclase around the alkali feldspar ovoids. The even-grained rapakivi granite is a common variety as well (8% of the area). In the rapakivi domain there are also the varieties of equigranular hornblende rapakivi, gray (topaz-bearing) rapakivi, porphyry aplite and quartz porphyry (Simonen 1987, Rämö & Haapala 1995). Recently rapakivi granites have been redefined as A-type granites showing rapakivi texture at least in the larger batholiths (Haapala & Rämö 1992, Rämö & Haapala 1995).

There are three small and isolated rapakivi-type (in geochemical terms) granite intrusions to west of the Wiborg rapakivi batholith along the southern coast of Finland: the Onas, Bodom and Obbnäs granites (Fig. 2). The outer appearance of the Onas, Bodom and Obbnäs rapakivi-type granites is not quite similar to the real rapakivi granites although mineral and chemical composition, the mode of origin, as well as the age are closely related with them. They are mainly composed of medium or coarse-grained hornblende-bearing, often porphyritic biotite granites. The granite stocks of Bodom and Obbnäs are the westernmost known rapakivi intrusions coeval with the Wiborg batholith (Kosunen 1996).

The Laitila batholith is the third largest rapakivi occurrence in Finland (Fig. 2). It is mainly composed of pyterlite-type biotite and hornblende-biotite rapakivi. An ovoidal texture is well developed. There exist also wiborgite type rocks characterized by thin plagioclase mantles around the alkali feldspar ovoids (Vorma 1976, 1989). The Vehmaa batholith, half the size of the Laitila batholith, is composed of a similar type of rapakivis as in the Laitila batholith. An even-grained rapakivi variety is quarried on a large scale for building stone ("Balmoral Red"). To the southeast of Laitila at Mynämäki there are small porphyry aplite occurrences, which are often encountered in rapakivi plutons.

In addition to the extensive Laitila and Vehmaa batholiths there are several small rapakivi granite stocks in southwestern Finland: The Peipohja porphyritic rapakivi stock in Kokemäki is located to the northeast of the Laitila batholith continuing beneath the Satakunta sandstones of Jotnian age. It is a satellitic extension of the Laitila batholith, similar to the small Eurajoki stock, located northwest of the main pluton (see Haapala 1977, 1989). There are two tiny rapakivi plutons along the western coast. One of these is partly submerged by the

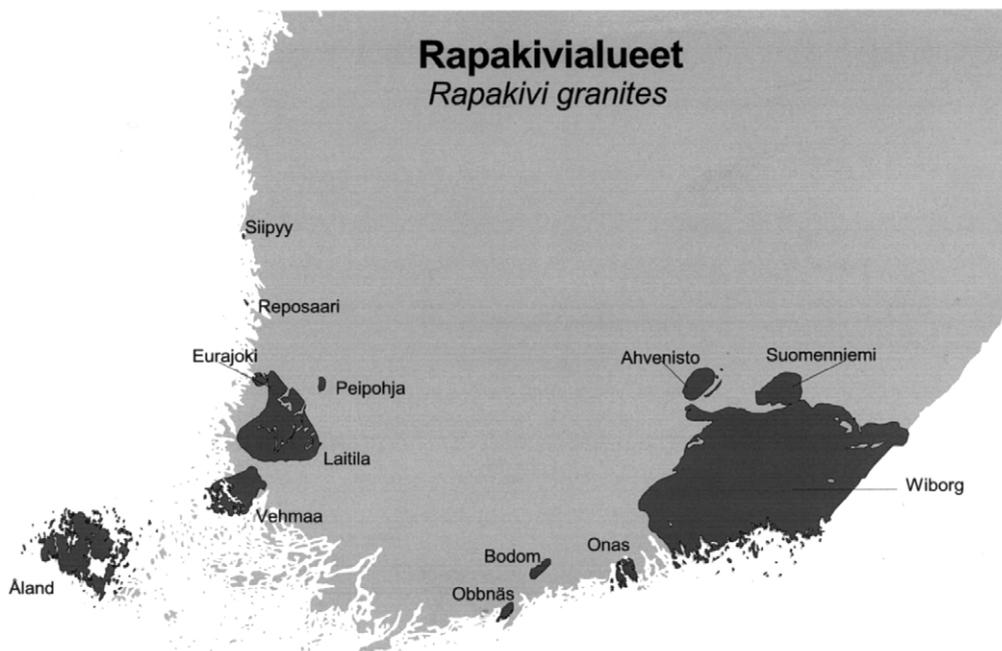


Fig. 2. Subjotnian rapakivi granites and related granites in southern Finland (see Haapala, 1977, Rämö 1993, Rämö & Haapala 1995, Kosunen 1996, Laitakari et al. 1986, 1996). Rapakivi batholiths and stocks: 1. Wiborg, Jaala, Iitti and Suomenniemi, 2. Laitila, 3. Vehmaa, 4. Ahvenanmaa (Åland), 5. Onas, 6. Obbnäs, 7. Bodom, 8. Siipyy, 9. Reposaari, 10. Peipohja, 11. Eurajoki, 12. Mynämäki, 13. Fjälskär.

sea at the promontory of Mäntyluoto, and the other, the Siipyy stock, is located c. 60 kilometres north of the town of Pori. Siipyy is the northernmost known rapakivi outcrop in Finland. Based on erratic blocks, there is a probable rapakivi area under the Bothnian Sea near Vaasa (Laitakari et al. 1996). Furthermore, on the opposite side of the Gulf of Bothnia, in Sweden, there are the Nordingrå and Ragunda rapakivi granite areas (see Vormaa 1976).

The largest part of the Åland rapakivi batholith is submerged by the sea. The Åland rapakivi is composed of several textural types closely following the rapakivi varieties (wiborgite, pyterlite, equigranular rapakivi) encountered in the Wiborg rapakivi batholith (Haapala & Ehlers 1989, Laitakari et al. 1996). The Ahvenanmaa rapakivi batholith is characterized by quite small wiborgitic ovoids and also aplitic granite varieties are met. Furthermore, the coarse-grained K-rich Nattanen, Pomovaara and Vainospää granitoids in central and northern Lapland show similarities with rapakivi granites in terms of

their chemical composition and elevated fluorine concentrations (see Fig. 1, Nurmi & Haapala 1986).

Some occurrences of granophyres and quartz porphyries, regarded as rapakivi granite-type rocks in origin and composition, are inferred to occur in the basin of the Gulf of Bothnia (see Eskola 1928, 1934). This is indicated by the numerous erratic blocks near Vaasa (Laitakari et al. 1996). Furthermore, on the opposite side of the Gulf of Bothnia, in Sweden, there are the Nordingrå and Ragunda rapakivi granite areas (see Vormaa 1976). The Pleistocene continental ice sheets have moved from the north and northwest to the south and southwest along the basin of the Gulf of Bothnia and coastal plain. Hence, abundant porphyry erratics are found in gravel pits along the western coast, south of the town of Vaasa down to Laitila and Vehmaa. On the other hand, material originating from the Laitila and Vehmaa plutons is found in the glacial drift in areas of Turku and Parainen down to Hanko at the southern coast (Fig. 2).

Chemical composition

By comparing the main element compositions of the rapakivi granites with ordinary granites, conspicuously higher Si and K concentrations and K/Na and Fe/(Fe+Mg) ratios and slightly lower Al, Ca, Mg, Na, P and Sr concentrations are recognized (Table 2, Rämö & Haapala 1995). Furthermore, the

rapakivi granites are characteristically rich in F, Li, Rb, Th, U, Y and REE (except Eu). The element composition of till overlying the rapakivi granite shows similarly elevated concentration levels of Y, REE and La (see Koljonen 1992, Salminen 1995).

A particularly characteristic feature in rapakivi

granites is a 3 to 4 times higher concentration of fluorine compared to other granitoids. The difference is still larger when compared with other rock types. The F concentrations in rapakivi granites range typically from 0.20% to 0.42%, whereas the corresponding concentrations in ordinary granites range from 0.05% to 0.14% (Sahama 1945a, Simonen & Vormaa 1969, Vormaa 1976). The F concentrations in granites and charnockites (0.085%), syenites and nepheline syenites (0.095-0.1%), granodiorites (0.02-0.1%), quartzdiorites (0.04%), gabbros (0.002-0.05%) and peridotites (0.002%) decrease in this order (see Koritnig 1951, 1972).

Important fluorine sources in rapakivi granites are micas (mainly muscovite) and amphiboles (mainly hornblende or ferrohastingsite and grünerite). F⁻ ions occupy the OH⁻ positions of the lattices. When occurring in rapakivi granites, these minerals are characteristically enriched in fluorides. In rapakivi biotites F concentrations range from 0.2% to 1.0% and in amphiboles from 0.3% to 1.1% (Simonen & Vormaa 1969). In the common metamorphic rocks of magmatic or sedimentary origin F concentrations in micas, amphiboles and chlorites range generally from 0.01 to 0.06% (Correns 1956). Saether et al. (1981) found that the major portion of the fluorine in oil shales of the Mahogany Zone, Colorado, appears to be associated with the ubiquitous micaceous clay minerals, especially illite.

The somewhat elevated abundances of U and Th (and Sc, Y and La) are typical for the chemical composition of rapakivi granite, as compared with most ordinary granites. According to Wilson and Åkerblom (1982), fluorite is a common accessory mineral in U-rich granites and the F content can be

as high as 0.5%. Lahermo and Juntunen (1991) show, however, that groundwater pumped from drilled wells cutting F-rich rapakivi granites is not particularly rich in U and Rn, which are notably enriched in the granites surrounding the Wiborg rapakivi batholith.

Fluorite is generally the main fluorine source also in ordinary granitic rocks. Englund and Myhrstad (1980) have observed fluorite on fractures in Permian basaltic rocks in southeast Norway. The contributions from biotites, phlogopites, lepidolites (Li-micas) and amphiboles may, however, be important. In intermediate rocks apatite may play a noticeable role. Pegmatites occasionally contain F-rich minerals such as fluorite, apatite, tourmaline and topaz.

A detailed study around a large limestone quarry in Parainen, in the southwestern Finnish archipelago, shows that scattered high F⁻ concentrations in well waters are encountered in areas composed of diversified rock types, such as mica schists and mica gneisses and basic volcanics and amphibolites and amphibolitic gneisses. Also the intercalated limestone and scarn occurrences contain F-rich minerals. Laitakari (1921) analyzed phlogopite, apatite, pargasite and chondrodite from the Parainen limestone, reporting the following fluorine concentrations: 4.2-4.6% (2 samples), 2.7% (1 sample), 1.4-2.9% (6 samples) and 8.6-9.7% (3 samples), respectively. According to Metzger (1945) some marble samples from the same mine contained 13.1 % fluorides. Another source of fluorides in the groundwaters of the Parainen region is plausibly the rapakivi granite material in overburden transported by the continental ice sheet from the Laitila and Vehmaa rapakivi granite batholiths.

FLUORINE IN SOIL

Fluorine is a common constituent in many soils. Its contents are primarily controlled by the occurrence of F-rich minerals but also secondary enrichment or fluorides sorbed onto mineral or organic matter play in many cases a significant role. The amounts of fluorides in soils vary normally from 100 to 300 mg/kg (Groth III 1975). In Norway the F⁻ contents in soil vary from 3 to 730 mg/kg while the average is 300 mg/kg (Larsen & Widdowson 1971). The total fluoride concentrations in soils of the United States ranges from the level of below 100 mg/kg to the concentrations over 1000 mg/kg (McClenahan 1976). In Finland, no comprehensive information is available about the fluorides in soils but some scattered data suggest that the common fluoride amounts in soils are less than one hundred mg/kg.

Glacial till, the most common soil type in Finland, is predominantly of local provenance and, hence, reflects the average lithology of the underlying bedrock. This is neatly demonstrated by the areal distribution of fluorides in the Lapinjärvi map sheet (1 : 100 000) area, situated along the northwestern border of the Wiborg rapakivi batholith, southeastern Finland (Fig. 3, see also Lahermo et al. 1991). Fluoride was analyzed from aqua regia leach of the fine fraction (<0,06 mm) of till. Within the rapakivi area, the fluorine contents range from 50-500 mg/kg (highest F⁻ concentration is 5000 mg/kg). The F⁻ concentrations in the neighbouring areas composed of other types of plutonic and metamorphic rocks are at least one order of magnitude lower (below 60 mg/kg) than in the rapakivi granite areas.

Also in the rapakivi area, Vuorinen et al. (1997) recorded 100-200 mg/kg total fluorine concentrations in the upper part of a sequence composed of glaciofluvial sand (<0.2 mm fraction). The concentrations up to 4500 mg/kg were analyzed in the lower sand layers of the 28.5 m deep drill hole.

There are only a few studies available that throw light on the weathering mechanisms of fluoruous

minerals and the fluoride mobilization in soils. Regardless of the low solubility product of fluorite, it is suggested as being one of the main sources of fluorides mobilized into soil solutes. Koritnig (1951) refers to apatite as a stable mineral against chemical dissolution which does not play any meaningful role as a fluoride source. Tourmaline and topaz, sometimes containing small amounts of flu-

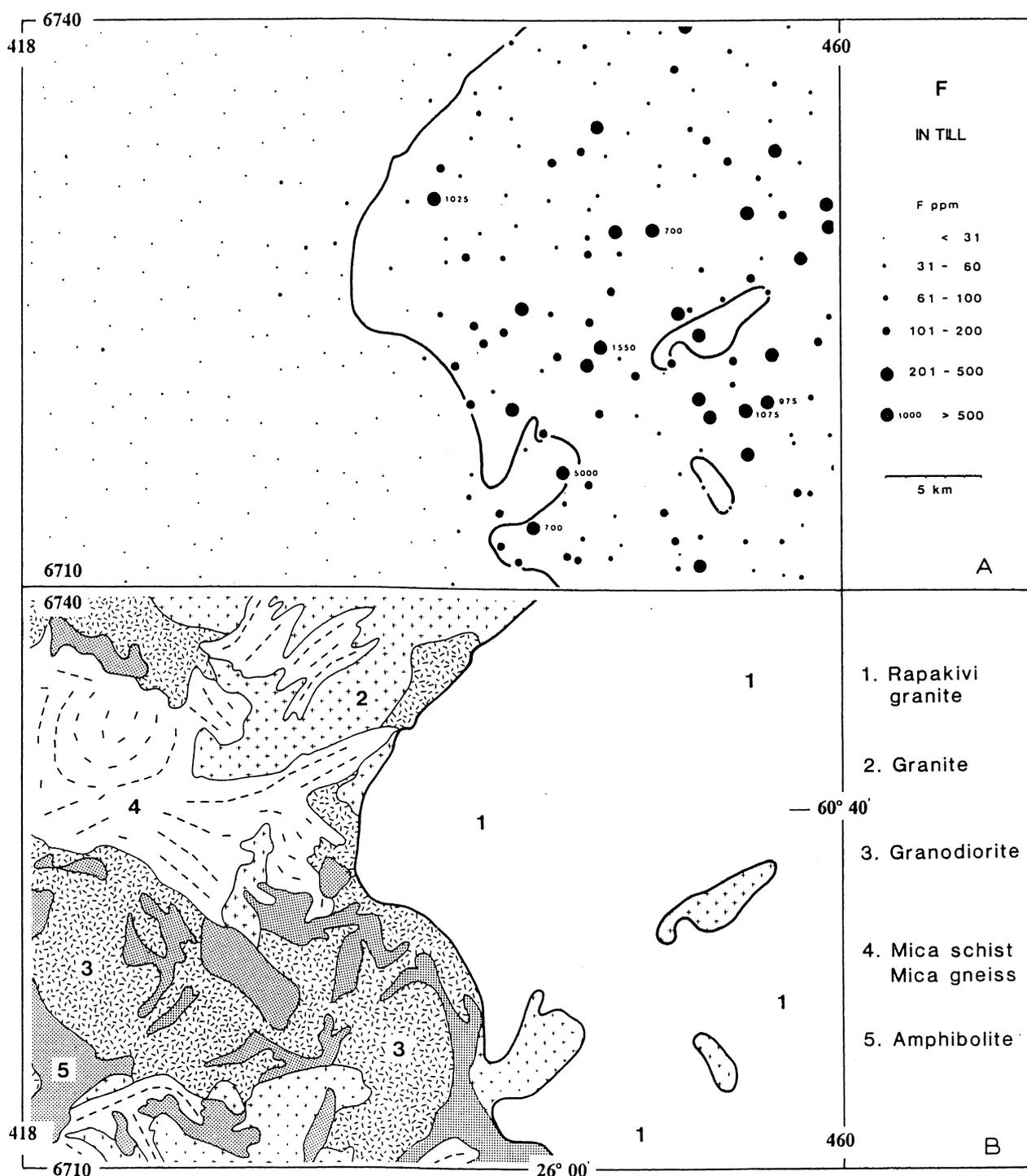


Fig. 3. The distribution of fluorine in the fine fraction (below 64 μ m) of glacial till (chart A) analyzed from aqua regia leach from the Lapinjärvi map sheet area (1:100 000), the northwestern margin of the Wiborg rapakivi batholith, southeastern Finland. The Precambrian bedrock of the area (chart B) simplified according to Laitakari and Simonen (1962). Drawing from Lahermo et al. (1991).

orine, are resistant to weathering.

The role of micas and amphiboles in the occurrence and mobility of fluorides in soils is enhanced by their relative readiness to disintegrate in weathering processes. Fluorides in micas are likely to be released soon after the onset of weathering. Englund and Myhrstad (1980) present in Norway that the main source of fluorides are the minerals containing hydroxyls, such as illites, sericites, chlorites and amphiboles where F^- ions partly replace OH^- groups. According to Koritnig (1972) in clay fractions 80% to 90% of fluorides are contained in muscovite, illite and related minerals of the mica group. The OH^- ions in the crystal-lattice of clay minerals are replaced by F^- ions with the simultaneous release of Al and Fe (Flühler et al. 1982, Polomski et al. 1982a). More than 90% of natural F^- in soils was suggested as being bound to clay particles. Also Hübner (1969) found that fluorides have a tendency to get adsorbed or reciprocally released from clay minerals. These phenomena depend on both the abundance of the clay fraction and the pH level and chemical composition of the soil solution (see also Farrah et al. 1985). Tiljander (1997), Vuorinen (1994, 1996) and Vuorinen et al. (1997) found that F^- leached from the coarse fraction of sand layers was mainly derived from F^- -bearing minerals while the majority of fluorides solubilized from the fine fraction of sand originated from scavenged and sorbed F^- forms in interaction with silica. Most of the fluorides are leached from fluor spar, biotite, hornblende and chlorite. On the other hand, Vuorinen (1998) shows that the organic rich A horizon of soil to a depth of 3 cm and the accumulation zone or B horizon to a depth of 40 cm effectively scavenge fluoride from lake water in the sprinkler infiltration area.

Gilbin and Johnson (1980) and Flühler et al. (1982) consider fluorides comparatively immobile in soil. According to Omuetti and Jones (1980), however, fluorides get effectively mobilized in acid soils (like in Finnish podzols) under a humid climate. The exchange process of hydroxyls by F^- ions in micas, chlorites and amphiboles is more effective in an acid environment, hence the F^- dissolution increases with decreasing pH (Jacks 1973, Englund and Myhrstad 1980, Tiljander 1997). The F^- solubility in soils is lowest in the pH range of 5.0-6.5 (Larsen & Widdowson 1971, Gilpin & Johnson 1980, Adriano 1986) and increases sharply below and above the referred pH-values. The solubility of fluorite in soils may be controlled more by the complex formation of fluorides with Al^{3+} than by the solubility of fluorite mineral. The association of fluoride with phosphates is of particular significance as it may restrict fluoride mobi-

lization. Consequently, fluoride contributes to the insolubility of phosphates important in plant nutrition (Mitchell & Edman 1945). Pickering (1985) demonstrates that the mobility of fluoride tends to be a function of soil type, pH and F^- concentrations in soil solution. The retention is favoured in acidic soils by abundances of clay minerals and poorly crystallized hydrous Al oxides. Jinadasa et al. (1993) found that the uptake of F^- ion by iron oxide minerals (goethite) was most effective at lower pH values. Sahu and Karim (1989) suggested that leaching of fluoride from the topsoil is caused by a number of factors such as topographical features and drainage conditions, pH, alkalinity and the amount of dissolved CO_2 in the soil solution.

Several authors have noticed that extractable F^- concentrations in soils increase from the topsoil down to deeper soil layers, demonstrating the effectiveness and vertical progress of weathering processes. The concentrations depend on the pH distribution, the intensity of the topsoil weathering processes and the amount of clay and humus in the soil material (Larsen & Widdowson 1971, Omuetti & Jones 1980, Adriano 1986, Kabata-Pendias 1992). Omuetti and Jones (1980) recognized that F^- concentrations increase from the topsoil to deeper layers of loess in Illinois. The concentrations of retained F^- ions in soil profiles largely depend on the pH and the amount of micas and clay minerals. The vertical distribution of humus plays a less significant role in F^- distribution.

There are various sink mechanisms which remove fluorides from soil solutions and accumulate them in soils. The colloidal complex of soils and sediments adsorb fluorides much more effectively than chlorides. The involved geochemical processes are anion exchange, precipitation and formation of complexes (Flühler et al. 1982). The OH^- groups in micas, clay minerals and Al-hydroxides in soil can be replaced by F^- ions (Correns 1956). The retention of fluorides or their mobilization may also be determined by the fixation of F^- ions with phosphate. The last-named mechanism is particularly prominent in the biological element cycle.

Humus-rich acid soils adsorb fluorides most effectively below pH 6.5, while increasing amounts of Al and fluorocomplexes were detected in acid solution. Furthermore, F^- retention tends to be most effective in the illuvial (B) horizon while the leached mineral horizon (A) contains less fluorides (Murray 1983). Fluoride retention in sandy calcareous loam is strongest at about pH 5.5. It decreases at both lower and higher pH values (Barrow & Ellis 1986). The multiple functional groups associated with humic acids bind substantial quantities of cations (including Ca, Fe and Al) which provide

adsorption sites for F⁻ ions. Humic acids tend to co-exist with colloidal particles of inorganic nature which are capable of interacting with fluorides. Bower and Hatcher (1967) made experiments which showed that significant amounts of fluorides were adsorbed from dilute solutions (2-16 mg/L F⁻) by clay minerals (kaolinite, halloysite), and precipitated Al(OH)₃ in particular. Simultaneously OH⁻ ions were released. Goethite, montmorillonite and vermiculite adsorbed only traces of fluorides.

According to Wenzel and Blum (1992) in soils that are exposed to prolonged fluorine pollution from an aluminium smelter, the F⁻ solubility shows a minimum at pH 6.0-6.5 and increases at lower and higher pH values. The high concentrations of fluoride under acid conditions is explained by the

occurrence of soluble cationic [AlF]²⁺- and [AlF₂]⁺- complexes. Haidouti (1995) states that the primary cause of Al mobilization is the presence of fluorides, which remove previously stable Al-hydroxides and organometallic compounds.

No significant F⁻ uptake in dilute solutions (1-12 mg/L) was detected using substrates such as calcite, hydrous manganese (+4) oxide, silica or sili-cagel over the range of pH 3-8. When Ca²⁺ - and F⁻ ion concentrations exceed the solubility product of CaF₂, the precipitation causes the loss of fluorides in aqueous solution. The formation of a thin layer of CaF₂ onto mineral grains is a slow reaction. It depends on the degree of saturation of solution in relation to fluorides and calcium, coatings on minerals surfaces and on the pH level (Flühler et al. 1982).

FLUORINE IN ORGANIC MATERIAL

The fluoride content of plants is generally low, except for tea, which may reach F⁻ concentrations up to several thousands of mg/kg (see e.g. Lockwood 1937, Bowen 1966). High F⁻ concentrations can be accumulated in tooth and bones of higher animals and man. The OH⁻ ions in bone apatite can be replaced by fluorides. Although fluoride is an

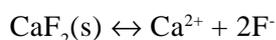
essential component at moderate concentrations excessive amounts may cause dental mottling, or in most serious cases, skeletal fluorosis.

Coal may contain appreciable amount of fluorine, reaching concentrations up to 295 mg/kg (Bell et al. 1970). Hence, coal used in energy generation is one of the major fluoride sources of industrial emissions.

GENERAL GEOCHEMISTRY OF AQUEOUS FLUORIDES

Elemental fluorine, most reactive of the common elements, combines practically with all of the inorganic and organic compounds (Allmann 1974, Koritnig 1972). In minerals and water fluorine occurs as fluoride ions (F⁻), which are released into aqueous solutions during weathering processes. The average weight ratio of F/Cl⁻ in rocks range from 4:1 to 8:1 depending on the rock types. In water discharged from hot springs the F/Cl⁻ ratio is extremely low (0.0006), because fluorides are deposited while Cl⁻ remains in solution.

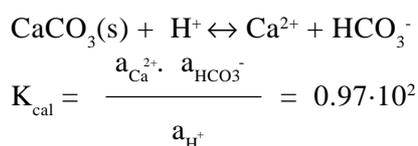
Although fluorides are among the most conservative common elements, they may be precipitated as a sparingly soluble fluorite mineral (CaF₂). The solubility product for fluorite (K_{fluor}) can be determined according to the following dissociation formula (Helgeson 1969):



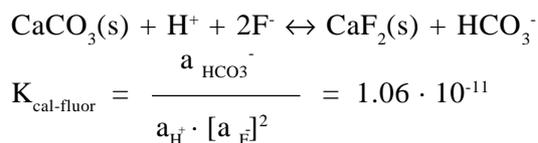
$$K_{\text{fluor}} = [\text{a}_{\text{Ca}^{2+}}][\text{a}_{\text{F}^-}]^2 = 10^{-9.04}$$

where [a_{Ca²⁺}] and [a_{F⁻}] are the activities of the concerned ions. Both Smyshlyaev and Edeleva (1962) and Handa (1975) have reported for K_{fluor} the values of 10^{-10.57}.

Due to the relatively low solubility of fluorite, the occurrence of aqueous F⁻ is predominantly controlled by the availability of free Ca²⁺ ions in water (see Jacks 1973). The dissolution constant of calcium carbonate (CaCO₃) is by far larger than that of fluorite:



Hence, there is ample calcium available in solution. It is also derived from weathering of Ca-containing silicate minerals. When computing the thermodynamic equilibrium in the groundwater system in contact with both calcite and fluorite, a combined equation is derived (Handa 1975):



The above values are taken from Helgeson (1969). The corresponding value by Smyshlyaev and Edeleva (1962) is $3.6 \cdot 10^{-12}$.

From the last equation can be concluded that the aqueous F^- concentrations are proportional to HCO_3^- concentrations and pH values (or inversely proportional to H^+ concentrations). Consequently, highly fluoruous waters are usually HCO_3^- -dominating waters characterized by comparatively high pH. Due to the low solubility product of fluorite Ca concentrations of fluoridic waters are invariably low, and *vice versa*. A good example of this is found in North Tanzania (Nanyaro et al. 1984, Lahermo et al. 1991) and in Rajasthan, India (Handa 1975), where the highly-mineralized Na- HCO_3^- -dominating waters contain very little Ca but are exceptionally high in fluorides. A further indication of this relationship is the positive correlation of fluorides with HCO_3^- concentrations and negative with those of Ca concentrations.

During evaporation and evapotranspiration the concentrations of aqueous solutions in soils and surface water bodies increase. Part of the dissolved CO_2 is lost causing a rise in pH-level, which in turn enhances the precipitation of calcite and fluorite. If the Ca concentrations are low, the F^- abundance may increase. Closed basins exposed to intense evaporation, such as the Great Salt Lake, accumulate fluorides up to 14 mg/L. The high F^- contents in some ponds and lakes in the East African Rift valley region in North Tanzania, Kenya and Ethiopia are explained by, notwithstanding the abundant fluorine in geological environment, also by pro-

longed evaporation in the internal basins (see e.g. Kilham & Hecky 1973, Nanyaro et al. 1984, Gizav 1996). Some lakes and ponds fed by runoff and shallow groundwater leaching fluoruous alkalic rocks may contain fluorides, even as much as 1000-1600 mg/L (see e.g. Gaciri & Davies 1993).

Fluoride-ions can also form soluble complexes with many kinds of inorganic and organic ligands. Aluminium is one of the most common anions to form complexes with fluoride: AlF^{2+} , AlF_2^+ , AlF_3 , $[\text{AlF}_6]^{3-}$, $\text{Al}(\text{OH})\text{F}^+$, $\text{Al}(\text{OH})\text{F}_2$ and $\text{Al}(\text{OH})\text{F}_3^-$. The type of species is controlled by the proportional concentrations of Al and F^- and by the pH level (David & Driscoll 1984, Henriksen et al. 1984, uti & Stumm 1984, Plankey et al. 1986, Cozzarelli et al. 1987, Hem 1989, Neal 1995). Seip and others (1989) demonstrate that the main species in stream water during an acid rainfall episode at Birkenes, in southern Norway, are Al^{3+} and AlF^{2+} , and to a lesser extent $\text{Al}(\text{OH})^{2+}$.

The Al- F^- complexation is suggested as contributing to the high Al concentrations in surface waters and groundwaters draining the rapakivi granite areas (Korkka-Niemi et al. 1993, Lahermo et al. 1996). The rate of Al- F^- -complexation is considerably slower in the pH range 3.3-4.0 typical in acid forest soils, than above pH 4.5, the pH range prevailing in most streams in glaciated basement areas of Finland. The low temperature and pH level favour slow reaction times between dissolved Al and F^- . This is particularly important in the case of acid snow melt when Al concentrations and their potential toxicity are supposed to be highest.

Also silicic acid may form F^- -complexes such as $[\text{SiF}_6]^{2-}$. According to Carpenter (1969) most of the fluorine mobilized during weathering is bound to solid detrital fractions, mainly clay minerals, and transported in rivers in suspension.

FLUORIDES IN PRECIPITATION AND IN SURFACE WATERS

There is scant information about the fluoride concentrations in rainwater in Finland. One measurement made in 1992 on the Åland archipelago, southwestern Finland, gave a result of 0.03 mg/L. The typical F^- concentrations in precipitation recorded elsewhere in the world are generally at the range of 0.05-0.20 mg/l. For example, F^- concentrations of 0.09-0.10 mg/L were found in rainwater in Norway (Englund & Myhrstad 1980).

It has been proposed by Carpenter (1969) and Jacks (1973) that most of fluorine in rain and snow, and consequently in rivers, is derived from cyclic salts originating from sea. The background F^- concentrations in precipitation of the coastal areas of India, derived both

from anthropogenic sources and from the sea, range between 0,001-0,012 $\mu\text{g/L}$ (Mahadevan et al. 1986). Airborne soil dust and volcanic exhalations are also important global major F^- sources.

In winter and during dry spells in summer, when runoff and interflow are practically impeded, streams and rivers draining small catchments are composed primarily of base flow, i.e. shallow groundwater discharged into water courses (see Rodhe 1981, Lepistö & Seuna 1990, Bengtsson et al. 1991). Consequently, also the chemistry of F^- concentrations in surface waters is largely controlled by the geochemical processes going on in the soil and in fracture systems of the bedrock. Due to mixing with rainfall and surface

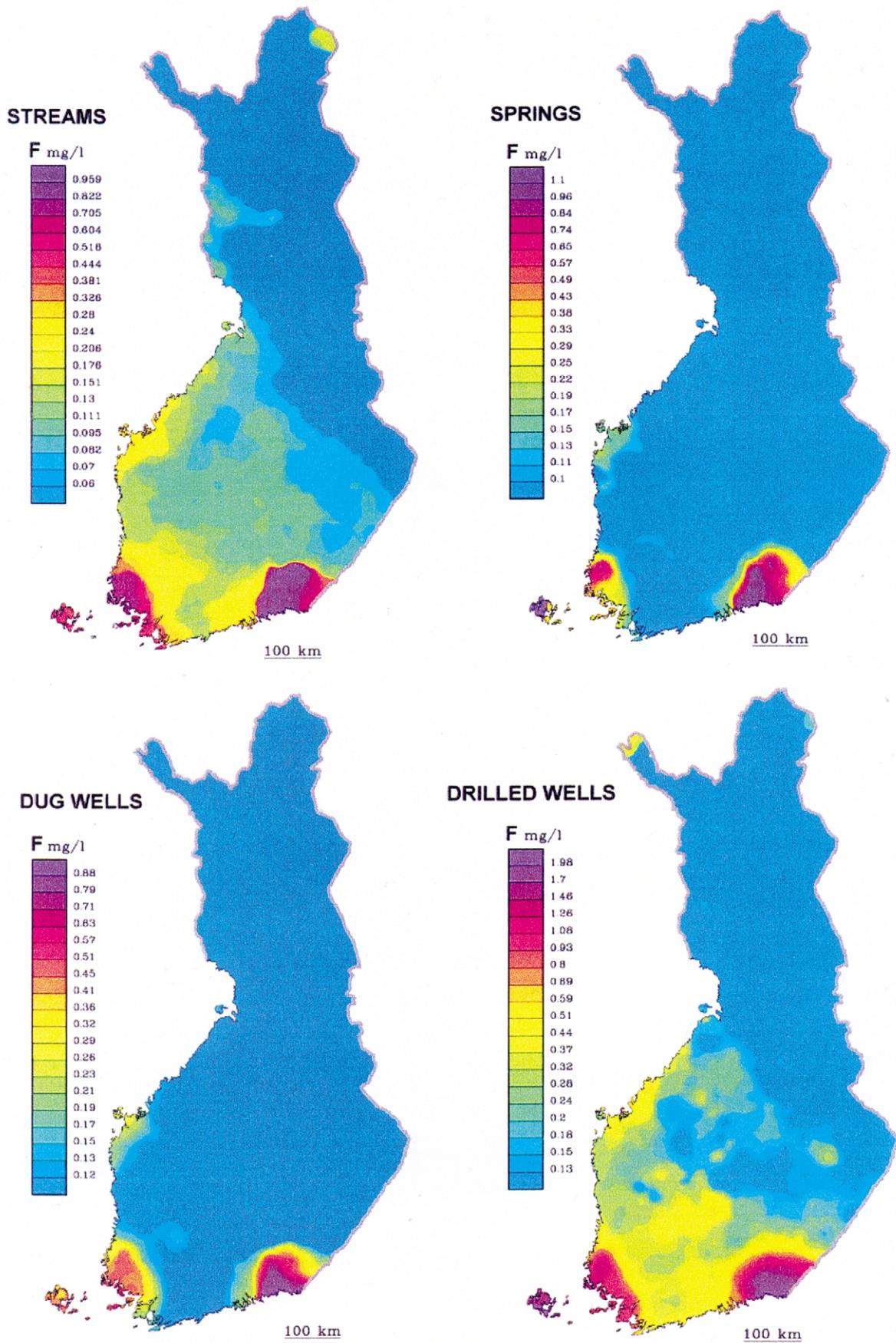


Fig. 4. The fluoride concentrations in water from headwater streams (A), springs and captured springs (B), dug wells (C) and drilled bedrock wells (D). Numbers of sampling sites are 1162, 3505, 5818 and 3500, respectively.

runoff, the average F⁻ concentrations are, however, lower in stream and lake waters than in groundwaters.

In the nationwide hydrogeochemical mapping of headwater streams carried out by the Geological Survey of Finland in August-September 1990 the F⁻ concentrations usually ranged from 0.025 to 0.5 mg/L (between 5% and 95% percentiles of 1165 samples) while the median and mean values were 0.08 mg/L and 0.13 mg/L, respectively (Lahermo & Väänänen 1995, Lahermo et al. 1995, Lahermo et al. 1996). The rapakivi granite batholiths of Wiborg, Laitila, Vehmaa and Ahvenanmaa (Åland) form most extensive fluoride provinces in stream waters (Fig. 4). The highest F⁻ concentrations (1.0-1.5 mg/L) are met in the Wiborg and Vehmaa rapakivi granite areas while in Ahvenanmaa the stream waters contain less fluorides (0.5 mg/L) than in other large rapakivi batholith areas. The baseline F⁻ concentrations are conspicuously higher in the southern half of the country, up to the southern border of Archean granite gneisses (0.025-0.1 mg/L), than in the eastern and northern part of the country (<0.025 mg/L). Streams draining other rapakivi-type coarse-grained granites, e.g. Bodom and Onas granites in southern Finland and the Pomovaara, Nattanen and Vainospää granites in central and northern Lapland (Fig. 1), also show elevated F⁻ concentrations.

Glacial till containing rapakivi or other fluorine-bearing rock material explains the elevated F⁻ concentrations in streams draining large areas in southwest Finland and areas between Vaasa and Pori (see Eskola 1928, 1934). Also local granites can contribute to F⁻ concentrations in stream waters. In the Heikkilänjoki river, which drains porphyritic granites in the Lauhanvuori area, the F⁻ concentration is higher (0.71 mg/L) than in the surrounding rivers (0.27-0.48), which likewise are somewhat higher than in the whole of the country in general (Harju

& Bergman 1978). Furthermore, there are scattered high F⁻ concentrations in stream waters also in the granodiorite areas in Central Finland and in granite areas in Central Lapland as well as along the coastal belt of the Gulf of Bothnia up to the Peräpohja schist belt.

Ryghaug & Bølviken (1987) noticed slightly elevated F⁻ concentrations in stream waters draining coarse-grained granite areas in Norway. Furthermore, the two aluminium plants in the region enhanced F⁻ contents (0.22 mg/L) in only a few nearby streams. For comparison, the average F⁻ concentration in Norwegian drinking water, composed of surface water and shallow groundwater, is 0.06 mg/L (Flaten 1991). The atmospheric transport of industrial emissions from Central Europe and Great Britain is considered as one source of fluorides. Higher concentrations (max 1.2 mg/L) are met, however, in the areas composed of the Permian Drammen granite pluton, reminiscent of rapakivi granites (op.cit.). The average dissolved F⁻ concentrations in major rivers of the world are 0.1-0.2 mg/L (Livingstone 1963).

There is 1.2-1.4 mg/L fluorides in seawater, while in the Baltic Sea the concentrations are appreciably lower. Calculations have shown that the concentrations listed from seawater represent only 0.35% of the evaluated total amount of fluorides eroded from the land. So, 99.65% of fluorine has precipitated in marine sediments (Fleischer et al. 1974). The reason is the great mutual affinity of calcium, phosphate and fluoride, which form in seawater sparingly soluble calciumphosphate or apatite, fluorspar and silicofluorides (Barth 1947, Shacklette et al. 1974). According to Carpenter (1969) calcium carbonate precipitation is the dominating process in the removal of dissolved fluoride from seawater with incorporation into calcium phosphates.

FLUORIDES IN SHALLOW GROUNDWATER

Earlier studies

The first idea of the comprehensive anomalous F⁻ provinces in groundwater was presented by Väre (1959, 1960) in his studies on the quality of drinking water in Finnish rural areas. The 2764 water samples, of which 95 % were untreated groundwater from private wells, were collected from all over the country. The highest average F⁻ concentrations were found in the rapakivi granite areas. The water quality data compiled by Natukka (1963) from groundwater test pumping operations in sand and gravel aquifers, carried out by the consulting com-

pany Maa ja Vesi Oy, showed the analogous areal distribution of fluorides. Also the chemical water analyses sorted out by Laakso (1966) from the wells drilled into bedrock by Vesto Oy exhibited elevated F⁻ concentrations in the rapakivi granite areas.

In another study covering the whole country (170 samples) the mean F⁻ concentrations in groundwater was 0.12 mg/L (Haapala 1974). Concentrations exceeding 0.4 mg/L were met only in the rapakivi granite areas in southeastern and southwestern Finland. Also Mäkinen (1974) published a brief paper

describing F^- concentrations in Finnish groundwaters while his account was based on papers published earlier. In a study carried out in the Kuopio region the mean F^- concentrations in surface waters and dug well waters were 0.06 mg/L and in water from drilled bedrock wells 0.12 mg/L (Korhonen et al. 1975).

The first detailed study on the hydrogeochemis-

try of groundwater in parts of the Wiborg rapakivi granite area in southeastern Finland was published by Lahermo (1971) and Lahermo & Rainio (1972). Later studies compiled an account of fluorides in Finnish groundwaters with comparison to the abnormally fluoruous waters in northern Tanzania (Lahermo et al. 1991).

Later nationwide mapping projects

In 1978-1982 about 5900 water samples were systematically collected all over the country from natural and captured springs, dug wells and drilled bedrock wells by the Geological Survey of Finland (Lahermo et al. 1990). The nationwide hydrogeochemical mapping gives a good picture of the chemical characteristics, among others fluorides, in shallow groundwater occurring in the overburden and in fractures in the underlying bedrock. So far, this survey is the most detailed account on the hydrogeochemistry of fluorides in Finnish shallow groundwaters. A renewed nationwide groundwater mapping project comprising 1000 sampling sites is underway in 1999. In connection to Quaternary geological mapping and special studies particularly in parts of southern Finland the GTK data files have presently grown to contain more than 20 000 groundwater samples

The residence time or “relative age” of ground-

water and the related degree of mineralization increases in the following order of the sampling environments: springs, captured springs, dug wells and drilled bedrock wells. The median and arithmetic mean values of fluorides in the data embracing the whole country are <0.10 mg/L and 0.17 mg/L for natural and captured springs, <0.10 mg/L and 0.21 mg/L for dug wells and 0.31 mg/L and 0.63 mg/L for drilled bedrock wells (Fig. 5a, 5b, Table 3a, 3b). Statistically the F^- concentrations increase with increasing depth of drilled well without dependence on rock type (Table 4).

In another nationwide water quality survey carried out by the Ministry of Social Affairs and National Board of Waters and the Environment (currently the Finnish Environment Institute) 1421 springs and wells were sampled in autumn 1990 (Korkka-Niemi et al. 1993). The median and average F^- concentrations were 0.10 mg/L and 0.39 mg/L,

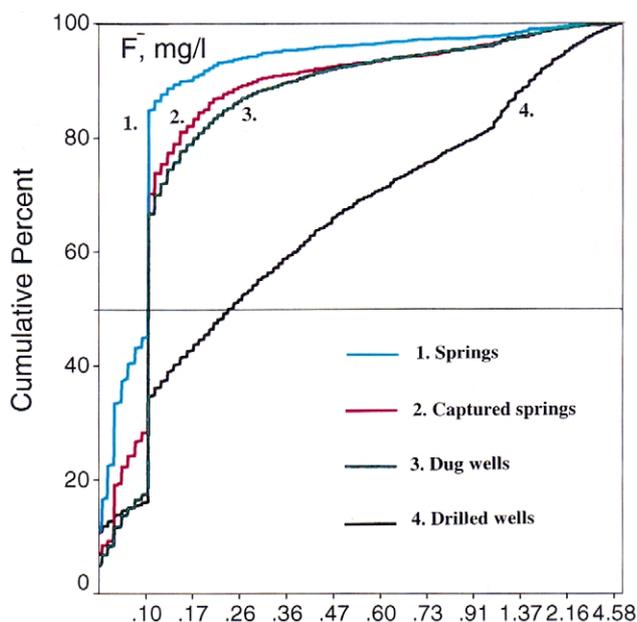


Fig. 5a. The distribution of fluoride concentrations in water from natural springs (1) and captured springs (2), wells dug in overburden (3) and wells drilled in bedrock (4). Bedrock is composed of all kinds of rocks, including rapakivi granite (see Fig. 1). The numbers of sampling sites are 5931 (1), 1700 (2), 3404 (3), and 4183 (4), respectively.

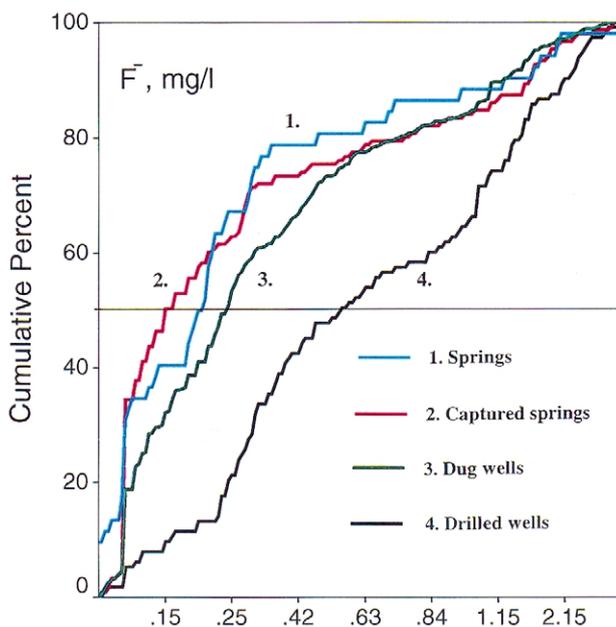


Fig. 5b. The distribution of fluoride concentrations in groundwater derived from aquifers partly or wholly covered by clay and silt deposits. Springs (1), captured springs (2), wells dug in overburden (3) and wells drilled in bedrock (4). Bedrock is composed of all kinds of rocks, including rapakivi granite (see Fig. 1). The numbers of sampling sites are 584 (1), 47 (2), 302 (3), and 113 (4), respectively.

Table 3a. Chemical composition of groundwater in natural and captured springs in whole country (GTK groundwater database 03/1998).

Variable	Min.	Median	Mean	Max.	Count
F ⁻ mg/l	<0.1	<0.1	0.17	4.5	3099
pH, field	3.2	6.2	6.2	9.2	3204
Sp. cond. mS/m +25 °C, field	0.5	6.7	10.0	105	3187
HCO ₃ ⁻ mg/L	0.61	19.5	28.4	366	3108
SO ₄ ²⁻ mg/L	<0.1	6.0	9.3	363	3118
Cl ⁻ mg/L	<0.2	2.4	6.2	151	3118
SiO ₂ mg/L	<1.2	10.6	11.2	40.7	3115
NO ₃ ⁻ mg/L	<0.2	1.0	4.1	98.6	3102
Ca mg/L	0.12	5.0	8.1	115	3123
Mg mg/L	<0.1	1.4	2.5	39.0	3123
Na mg/L	<0.4	2.8	4.5	147	3121
K mg/L	0.09	1.1	2.2	84.0	3121
KMnO ₄ -number mg/L	0.3	4.3	7.5	208	3119
Al µg/L	<1.0	14.0	62.2	2110	1134
Fe mg/L	<0.03	0.05	0.22	29.0	3121
Mo µg/L	<0.03	0.12	0.35	10.1	659

Table 3b. Chemical composition of groundwater in dug wells in whole country (GTK groundwater database 03/1998).

Variable	Min.	Median	Mean	Max.	Count
F ⁻ mg/l	<0.1	<0.1	0.21	6.0	7229
pH, field	3.6	6.3	6.3	9.0	7422
Sp. cond. mS/m +25 °C, field	1.4	15.7	20.6	314	7416
HCO ₃ ⁻ mg/L	0.61	38.4	56.4	742	7199
SO ₄ ²⁻ mg/L	0.8	12.5	17.6	650	7224
Cl ⁻ mg/L	<0.2	6.8	14.2	2090	7231
SiO ₂ mg/L	<1.2	11.8	12.4	74.9	7223
NO ₃ ⁻ mg/L	<0.2	3.8	11.6	510	7218
Ca mg/L	0.3	13.6	18.6	3360	7237
Mg mg/L	<0.1	3.0	4.6	210	7237
Na mg/L	0.6	5.6	9.4	480	7235
K mg/L	<0.01	3.1	7.0	520	7234
KMnO ₄ -number mg/L	0.3	7.0	12.1	205	7229
Al µg/L	<1.0	38.1	123	5190	1849
Fe mg/L	<0.03	0.05	0.31	80.0	7232
Mo µg/L	<0.03	0.13	0.27	7.1	1251

Table 4. Chemical composition (medians) of water pumped from wells drilled into bedrock grouped according to depth in whole country (GTK groundwater database 03/1998).

Variable	< 50 m	50-100 m	100-200 m	> 200 m
F ⁻ mg/L	0.14	0.37	0.56	0.69
pH, field	6.7	7.1	7.2	7.1
Sp. cond. mS/m +25 °C, field	25.9	29.5	28.6	24.6
HCO ₃ ⁻ mg/L	77.5	101	104	78.3
SO ₄ ²⁻ mg/L	15.3	17.0	16.0	10.3
Cl ⁻ mg/L	12.0	13.0	11.8	6.8
NO ₃ ⁻ mg/L	2.2	<1.0	<1.0	<1.0
Ca mg/L	20.0	21.0	21.0	17.1
Mg mg/L	6.0	5.6	5.5	4.7
Na mg/L	10.0	16.0	18.5	17.4
K mg/L	3.4	3.1	2.4	2.1
KMnO ₄ -number mg/L	5.4	5.0	4.0	5.1
Al µg/L	5.3	4.5	4.4	4.6
Fe mg/L	0.09	0.05	0.05	0.05
Mo µg/L	0.93	1.1	1.3	1.9
Count	1270	1107	302	24

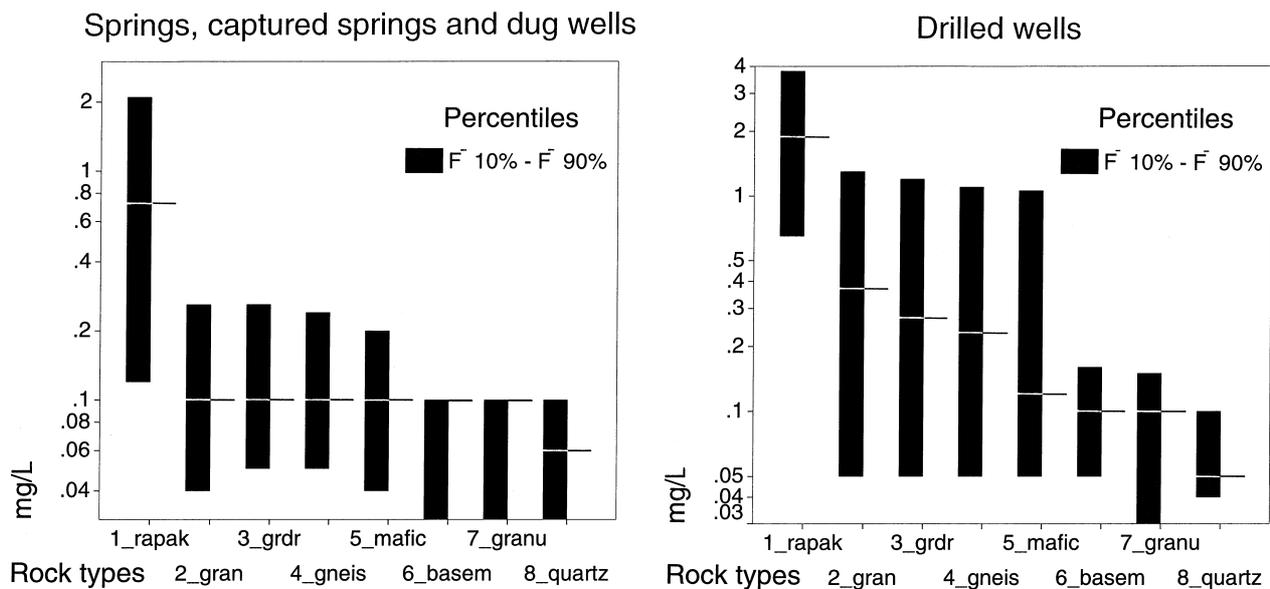


Fig. 6a. The distribution of fluoride concentrations (between 10 and 90 percentiles) and median values (horizontal lines) in springs, captured springs and dug wells draining different rock types presented in order of decreasing F⁻ concentrations. 1. **rapak**, rapakivi granite; 2. **gran**, granite; 3. **grdr**, granodiorite; 4. **gneis**, mica gneiss and mica schist; 5. **mafic**, gabbro, amphibolite, metabasalt, greenstone; 6. **basem**, basement gneiss, mainly granite gneiss; 7. **granu**, granulite; 8. **quartz**, quartzite.

Fig. 6b. The distribution of fluoride concentrations (between 10 and 90 percentiles) and median values (horizontal lines) in bedrock wells drilled into different rock types presented in order of decreasing F⁻ concentrations. For rock types see the previous figure.

Table 5a. Chemical composition of groundwater in ordinary granite areas in whole country (GTK groundwater database 03/1998).

Variable	Min.	Median	Mean	Max.	Count
Springs and captured springs					
F ⁻ mg/L	<0.1	<0.1	0.13	1.7	543
Sp.cond. mS/m +25 °C, field	0.5	6.1	9.6	88.8	547
pH, field	4.3	6.2	6.2	9.2	573
Dug wells					
F ⁻ mg/L	<0.1	<0.1	0.17	2.7	806
Sp.cond. mS/m +25 °C, field	2.2	18.0	21.7	139	831
pH, field	4.1	6.3	6.4	11.1	839
Wells drilled into bedrock					
F ⁻ mg/L	<0.1	0.38	0.6	9.3	571
Sp.cond. mS/m +25°C, field	1.8	25.2	35.7	1100	679
pH, field	4.3	6.9	6.9	10.8	692

Table 5b. Chemical composition of groundwater from wells drilled into ordinary granites in Lapland (northern Finland) and in southwestern Finland (map sheet no. 20) (GTK groundwater database 03/1998).

Variable	Min.	Median	Mean	Max.	Count
Northern Finland (Lapland)					
F ⁻ mg/L	<0.1	<0.1	<0.1	0.76	52
Sp.cond. mS/m +25 °C, field	1.8	11.0	18.9	158	52
pH, field	5.6	6.7	6.6	8.1	48
Southwestern Finland (map sheet no. 20)					
F ⁻ mg/L	<0.1	0.5	0.76	9.3	181
Sp.cond. mS/m +25 °C field	7.5	31.0	46.9	1100	239
pH, field	5.2	7.1	7.1	8.7	250

respectively. Part of the sites were sampled twice in the following spring and summer (421 and 425 sampling sites, respectively). The median and mean values were 0.10-0.11 mg/L and 0.57-0.67 mg/L, respectively. Many of the wells were drilled into bedrock (295 sites) and their median F⁻ concentration was 0.4 mg/L.

The lowest F⁻ concentrations, often below the detection limit (0.1 mg/L), are encountered in areas characterized by granitic basement gneisses, felsic mica gneisses and schists, granulites, quartzites, greenstones and mafic rocks such as amphibolites and gabbros (Fig. 5a, 5b). The median F⁻ concentrations in groundwater from soil aquifers underlain by ordinary granites and granodiorites are distinctly higher and practically always above the detection limit (Table 5a, 5b). In the areas composed of rapakivi granites fluoride concentrations are an order of magnitude higher (generally 0.5-2.0 mg/L) than in the rest of the country (Table 6a, 6b, Laher-

mo 1971, Lahermo & Rainio 1972, Lahermo et al. 1990, Lahermo et al. 1991, Lahermo & Paukola 1993). The figures indicate that there is no meaningful concentration differences between the Wiborg rapakivi area and the Laitila-Vehmaa-Ahvenanmaa rapakivi area.

Although the amount of dissolved electrolytes in the rapakivi areas is 1.5-3.0 times higher in water from dug wells than in spring water, the F⁻ concentrations are slightly higher in more diluted spring waters (Table 6a, 6b). This is presumed to be due to the proportionally higher Ca contents compared with Na concentrations in dug well waters than in springs, which causes the exceedence of the solubility product of fluorite mineral (see Jacks 1973). In water from drilled wells there is substantially more fluorides than in groundwater from overburden and, in harmony with the above mentioned, still lower Ca/Na ratio.

The F⁻ concentrations in spring water from aqui-

Table 6a. Chemical composition of groundwater from rapakivi granite areas in southeastern Finland (Wiborg batholith and Suomenniemi and Ahvenisto satellite plutons/stocks) (GTK groundwater database 03/1998).

Variable	Min.	Median	Mean	Max.	Count
Springs and captured springs					
F ⁻ mg/L	<0.1	0.93	1.1	4.2	130
Sp.cond. mS/m +25 °C, field	3.0	10.1	13.1	85.7	132
pH, field	4.7	6.0	6.0	7.7	
Dug wells					
F ⁻ mg/L	<0.1	0.68	0.93	4.2	323
Sp.cond. mS/m +25 °C, field	4.0	18.9	21.4	80.2	323
pH, field	4.7	6.2	6.2	8.0	319
Wells drilled into bedrock					
F ⁻ mg/L	0.2	1.9	2.1	5.8	148
Sp.cond. mS/m +25 °C, field	5.4	21.6	31.9	253	159
pH, field	5.2	7.1	7.0	9.5	158

Table 6b. Chemical composition of groundwater from rapakivi granite areas in southwestern Finland (Laitila, Vehmaa and Ahvenanmaa batholiths and other minor rapakivi plutons/stocks.) (GTK groundwater database 03/1998).

Variable	Min.	Median	Mean	Max.	Count
Springs and captured springs					
F ⁻ mg/L	<0.1	1.1	1.2	4.1	37
Sp.cond. mS/m +25 °C, field	3.5	6.9	11.0	50.5	3
pH, field	4.8	5.6	5.7	7.4	37
Dug wells					
F ⁻ mg/L	<0.1	0.59	0.85	4.2	114
Sp.cond. mS/m +25 °C, field	3.9	20.2	27.4	139	109
pH, field	5.1	6.4	6.4	7.6	114
Wells drilled into bedrock					
F ⁻ mg/L	<0.1	1.7	1.9	5.0	120
Sp.cond. mS/m +25 °C, field	7.5	52.0	73.0	827	113
pH, field	4.9	7.1	7.0	9.2	120

Table 7a. Chemical composition of groundwater discharged from springs and captured springs in aquifers composed of sand and gravel deposits (mainly eskers and ice-marginal formations, sometimes wave-washed littoral deposits) in rapakivi areas (GTK groundwater database 03/1998).

Variable	Min.	Median	Mean	Max.	Count
F ⁻ mg/L	<0.1	0.93	0.93	2.8	71
pH, field	4.7	6.1	6.2	7.7	72
Sp. cond. mS/m +25C°, field	3.0	10.6	13.0	85.7	72
HCO ₃ ⁻ mg/L	7.3	20.7	29.9	226	72
SO ₄ ²⁻ mg/L	1.2	8.9	10.7	42.0	72
Cl ⁻ mg/L	0.9	5.3	10.1	113	72
SiO ₂ mg/L	6.2	12.2	12.5	22.1	72
NO ₃ ⁻ mg/L	<0.2	1.3	5.8	52.7	72
Ca mg/L	2.4	8.2	11.0	41.9	72
Mg mg/L	<0.1	1.6	2.3	8.9	72
Na mg/L0.8	3.4	6.1	79.0	72	
K mg/L	0.3	1.2	2.4	15.5	72
KMnO ₄ -number mg/L	0.6	4.5	6.2	35.1	72
Al µg/L	1.8	48.7	206	950	35
Fe mg/L	<0.03	0.05	0.2	5.5	72
Mo µg/L	<0.03	0.16	0.23	0.86	28

Table 7b. Chemical composition of groundwater discharged from springs and captured springs in aquifers composed of till deposits (mainly lodgement till, sometimes moraine hummocks and wave-washed surficial till) in rapakivi areas (GTK groundwater database 03/1998).

Variable	Min.	Median	Mean	Max.	Count
F ⁻ mg/L	<0.1	0.88	1.1	4.2	138
pH, field	4.9	5.8	5.9	7.4	137
Sp.cond. mS/m +25C°, field	3.2	8.8	11.8	50.5	137
HCO ₃ ⁻ mg/L	6.1	18.3	26.5	177	139
SO ₄ ²⁻ mg/L	1.0	11.0	12.2	42.0	139
Cl ⁻ mg/L	0.9	3.0	7.8	60.0	138
SiO ₂ mg/L	5.7	12.2	12.5	24.4	138
NO ₃ ⁻ mg/L	<0.2	1.0	5.3	83.4	138
Ca mg/L	1.7	6.3	9.9	37.9	139
Mg mg/L	0.4	1.3	2.2	14.3	139
Na mg/L	1.1	3.2	5.7	61.7	139
K mg/L	0.1	1.4	2.2	15.7	139
KMnO ₄ -number mg/L	0.6	4.4	6.7	52.9	138
Al µg/L	1.9	211	355	2110	64
Fe mg/L	<0.03	0.05	0.13	1.8	139
Mo µg/L	<0.03	0.1	0.24	4.2	60

Table 7c. Chemical composition of groundwater discharged from springs and captured springs in aquifers composed of sand and till and sand deposits overlain by impervious clay and silt layers (mainly valley and hill foot deposits, sometimes flanks of eskers confined by impervious sediments) in rapakivi areas (GTK groundwater database 03/1998).

Variable	Min.	Median	Mean	Max.	Count
F ⁻ mg/L	<0.1	1.5	1.4	4.1	39
pH, field	4.7	6.1	6.1	7.4	37
Sp.cond. mS/m +25 °C, field	5.4	14.7	16.9	50.5	39
HCO ₃ ⁻ mg/L	12.2	30.5	44.4	177	39
SO ₄ ²⁻ mg/L	1.9	12.0	14.5	42.0	39
Cl ⁻ mg/L	1.8	6.4	11.3	60.0	39
SiO ₂ mg/L	8.2	14.0	14.8	24.4	39
NO ₃ ⁻ mg/L	<0.2	1.2	5.6	27.9	39
Ca mg/L	2.6	10.9	13.3	36.9	39
Mg mg/L	<0.1	2.8	3.4	7.9	39
Na mg/L	0.8	6.0	9.4	61.7	39
K mg/L	0.6	2.0	2.5	8.2	39
KMnO ₄ -number mg/L	1.3	4.4	6.1	17.4	39
Al µg/L	2.3	147	387	2110	12
Fe mg/L	<0.03	0.05	0.2	1.8	39
Mo µg/L	0.08	0.22	0.79	4.2	11

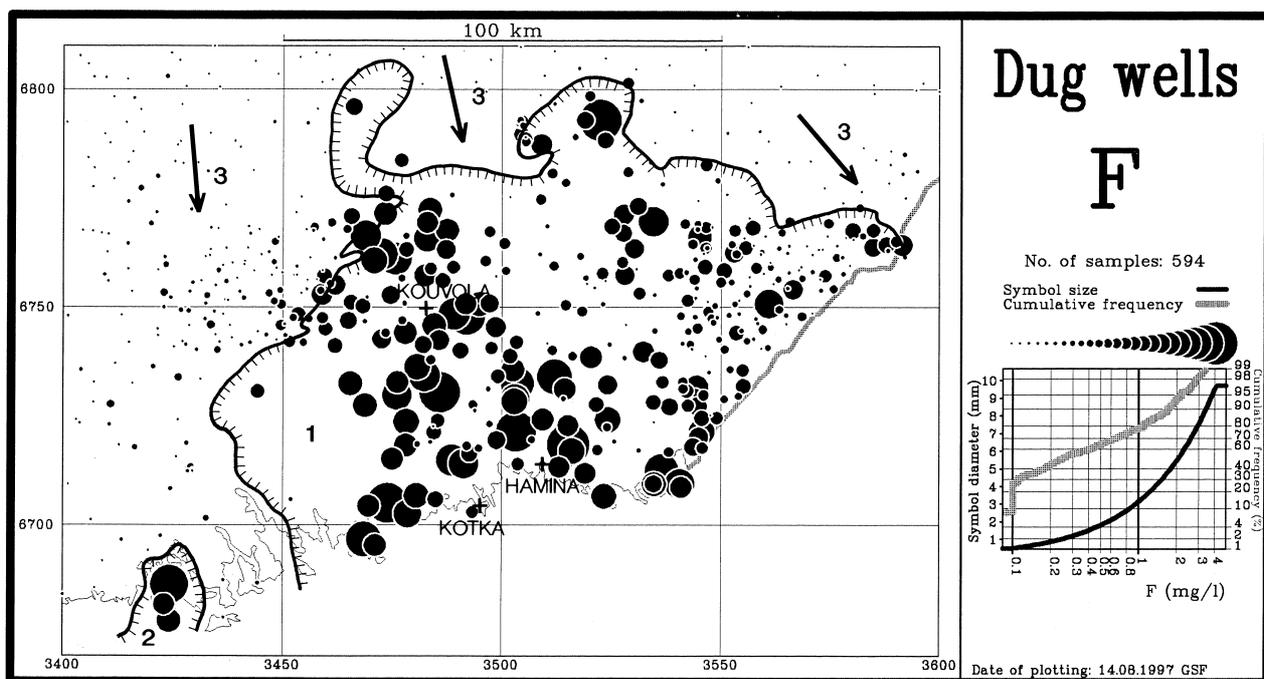


Fig. 7. The fluoride concentrations in water from wells dug in overburden in the Wiborg rapakivi granite and neighbouring bedrock areas, southeastern Finland. The border of the Wiborg (1) and Onas (2) rapakivi granite areas are indicated. The predominant flow directions of the continental ice sheet (3) are also marked (see Hirvas & Nenonen 1990).

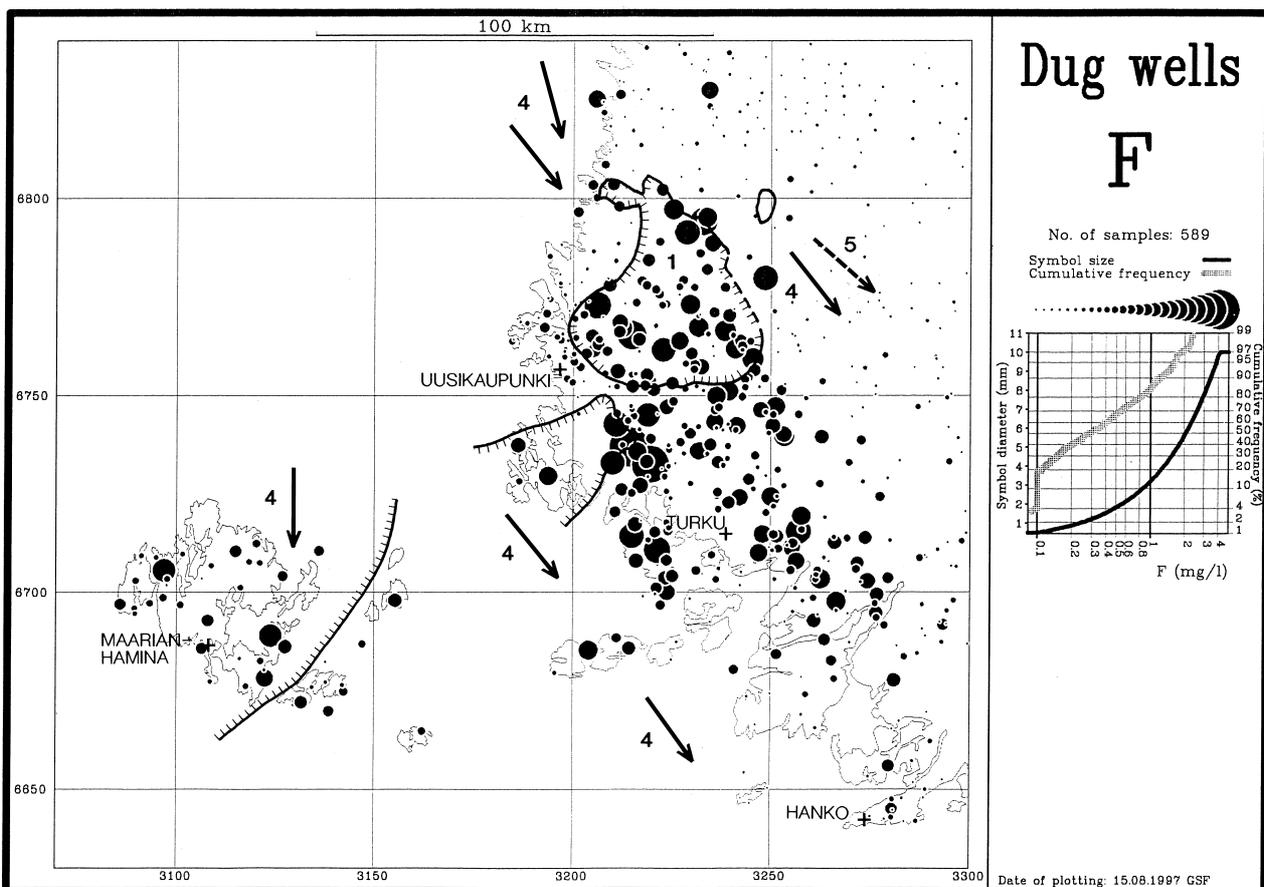


Fig. 8. The fluoride concentrations in water from wells dug in overburden in the Laitila (1), Vehmaa (2) and Ahvenanmaa (3) rapakivi granite batholiths and in neighbouring bedrock areas, southwestern Finland. The predominant flow directions of the continental ice sheet (4) and the boulder trains (5) are also marked (see Hirvas & Nenonen 1990).

Table 8a. Chemical composition of well water from aquifers composed of sand and gravel deposits (mainly eskers and ice-marginal formations, sometimes wave-washed littoral deposits) in rapakivi areas (GTK groundwater database 03/1998).

Variable	Min.	Median	Mean	Max.	Count
F ⁻ mg/L	<0.1	0.62	0.85	4.2	123
pH, field	4.7	6.2	6.3	7.4	124
Sp.cond. mS/m +25 °C, field	4.0	16.4	20.5	139	124
HCO ₃ ⁻ mg/L	6.1	31.1	49.9	420	125
SO ₄ ²⁻ mg/L	1.2	14.9	17.3	110	123
Cl ⁻ mg/L	0.8	8.2	13.7	253	123
SiO ₂ mg/L	3.5	12.6	13.4	27.6	125
NO ₃ ⁻ mg/L	<0.2	2.7	10.7	75.8	123
Ca mg/L	3.3	13.7	17.4	62.7	125
Mg mg/L	0.5	2.5	3.5	23.0	125
Na mg/L	1.4	5.4	9.6	190	125
K mg/L	0.7	3.1	4.6	31.0	125
KMnO ₄ -number mg/L	0.8	5.7	9.0	76.1	123
Al µg/L	0.86	60.4	170	2660	46
Fe mg/L	<0.03	0.05	0.23	6.9	125
Mo µg/L	<0.03	0.08	0.13	0.6	40

Table 8b. Chemical composition of well water from aquifers composed of till deposits (mainly lodgement till, sometimes moraine hummocks and wave-washed surficial till) in rapakivi areas (GTK groundwater database 03/1998).

Variable	Min.	Median	Mean	Max.	Count
F ⁻ mg/L	<0.1	0.62	0.87	4.2	250
pH, field	5.1	6.2	6.2	8.0	245
Sp.cond. mS/m +25 °C, field	3.9	18.5	22.5	106	243
HCO ₃ ⁻ mg/L	6.7	37.2	55.6	500	249
SO ₄ ²⁻ mg/L	2.2	16.5	19.2	70.0	249
Cl ⁻ mg/L	0.7	8.4	13.7	146	250
SiO ₂ mg/L	1.6	12.4	12.8	26.4	250
NO ₃ ⁻ mg/L	<0.2	7.0	13.9	117	250
Ca mg/L	3.1	17.1	22.1	130	250
Mg mg/L	0.5	2.8	4.0	26.0	250
Na mg/L	0.6	6.1	7.7	55.0	250
K mg/L	0.4	3.6	6.6	55.2	250
KMnO ₄ -number mg/L	0.6	7.3	12.9	100	249
Al µg/L	3.7	118	265	1950	110
Fe mg/L	<0.03	0.05	0.11	1.5	250
Mo µg/L	<0.03	0.1	0.27	5.3	105

Table 8c. Chemical composition of well water from aquifers composed of till and sand deposits overlain by impervious clay and silt layers (mainly valley and hill foot deposits, sometimes flanks of eskers confined by impervious sediments) in rapakivi areas. (GTK groundwater database 03/1998).

Variable	Min.	Median	Mean	Max	Count
F ⁻ mg/L	0.19	0.94	1.1	3.4	96
pH, field	4.7	6.4	6.4	7.6	95
Sp.cond. mS/m +25 °C, field	5.0	26.6	30.4	139	96
HCO ₃ ⁻ mg/L	14.6	71.4	106	420	97
SO ₄ ²⁻ mg/L	2.5	17.1	21.2	68.0	96
Cl ⁻ mg/L	1.2	9.5	18.0	253	96
SiO ₂ mg/L	3.0	15.5	15.7	28.5	97
NO ₃ ⁻ mg/L	<0.1	2.9	10.7	63.3	96
Ca mg/L	3.9	24.0	29.3	120	97
Mg mg/L	1.0	5.9	7.4	43.0	97
Na mg/L	0.8	8.8	15.0	190	97
K mg/L	0.9	3.7	5.6	45.0	97
KMnO ₄ -number mg/L	0.6	7.0	14.0	79.6	95
Al µg/L	1.4	187	272	1500	40
Fe mg/L	<0.03	0.07	0.32	6.9	97
Mo µg/L	0.05	0.25	0.43	2.2	38

fers composed either of sand or till deposits do not exhibit much differences (Table 7a, 7b). The same applies to water from dug wells (Table 8a, 8b). Distinctly higher median values are recorded, however, in groundwater from aquifers which are partly or wholly confined by clay and silt deposits (Table 7c, 8c). This is attributed to the ability of fluorides to be adsorbed or released from the clay fraction under changing pH- and Eh-conditions (see Koritnig 1972).

The F⁻ distributions in waters from springs, dug

wells and drilled bedrock wells show by and large analogous and consistent anomalous patterns or provinces with each other. In the northern limit of the Wiborg batholith the boundary between low and high F⁻ concentrations is sharp (Fig. 7). In the Laitila and Vehmaa plutons the southern boundary is transitional and can not be delineated solely by the elevated F⁻ concentrations in groundwater (Fig. 8). This is due to the glacial transport of abraded fluoride-rich rock material from northwest to southeast. The influence of rapakivi-type Onas and Bo-

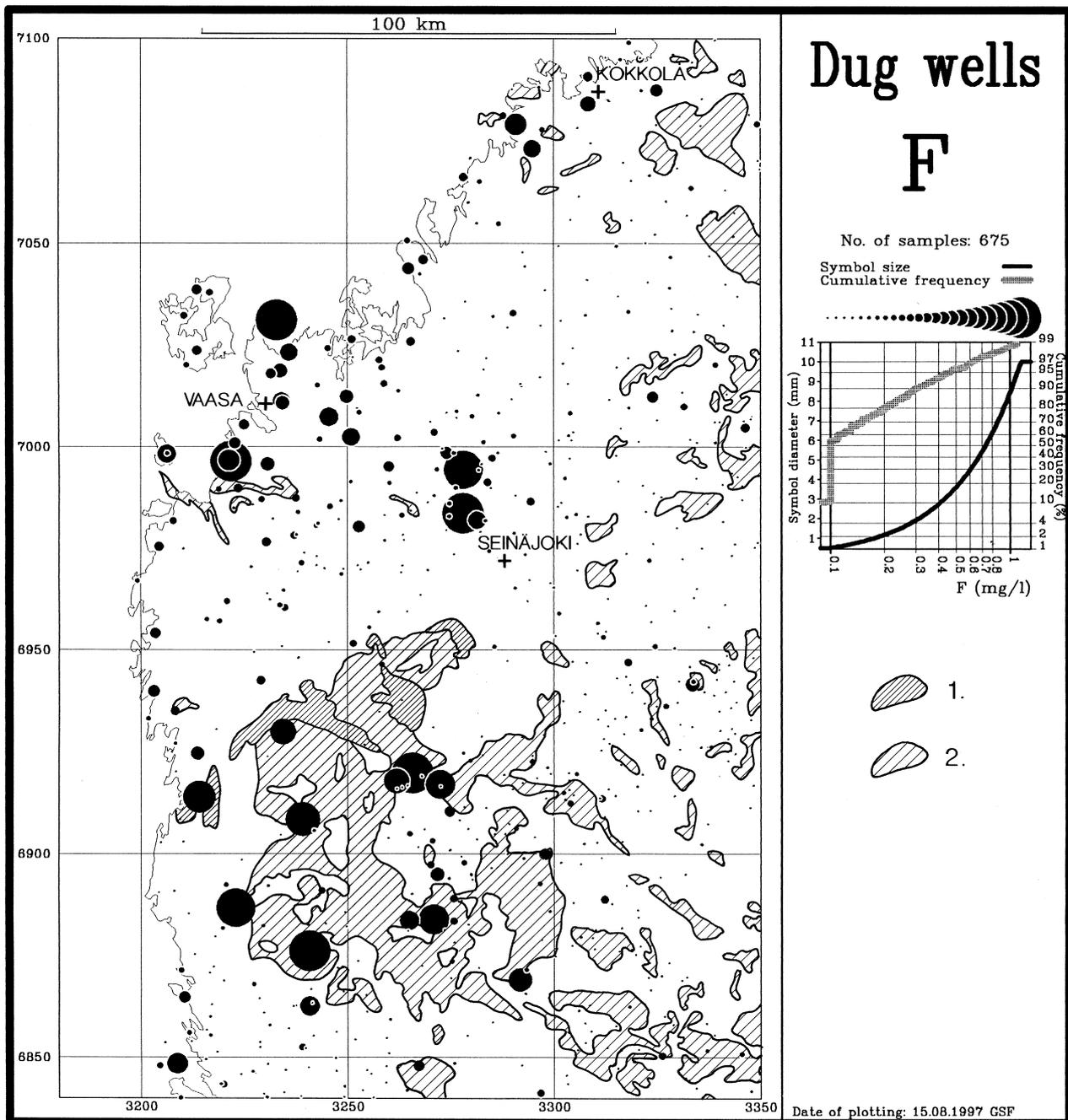


Fig. 9. The fluoride concentrations in water from wells dug into overburden in the Kokkola-Vaasa-Pori area. The areas of pyroxene granitoids (1) and granite (2) are marked (see Korsman et al. 1997).

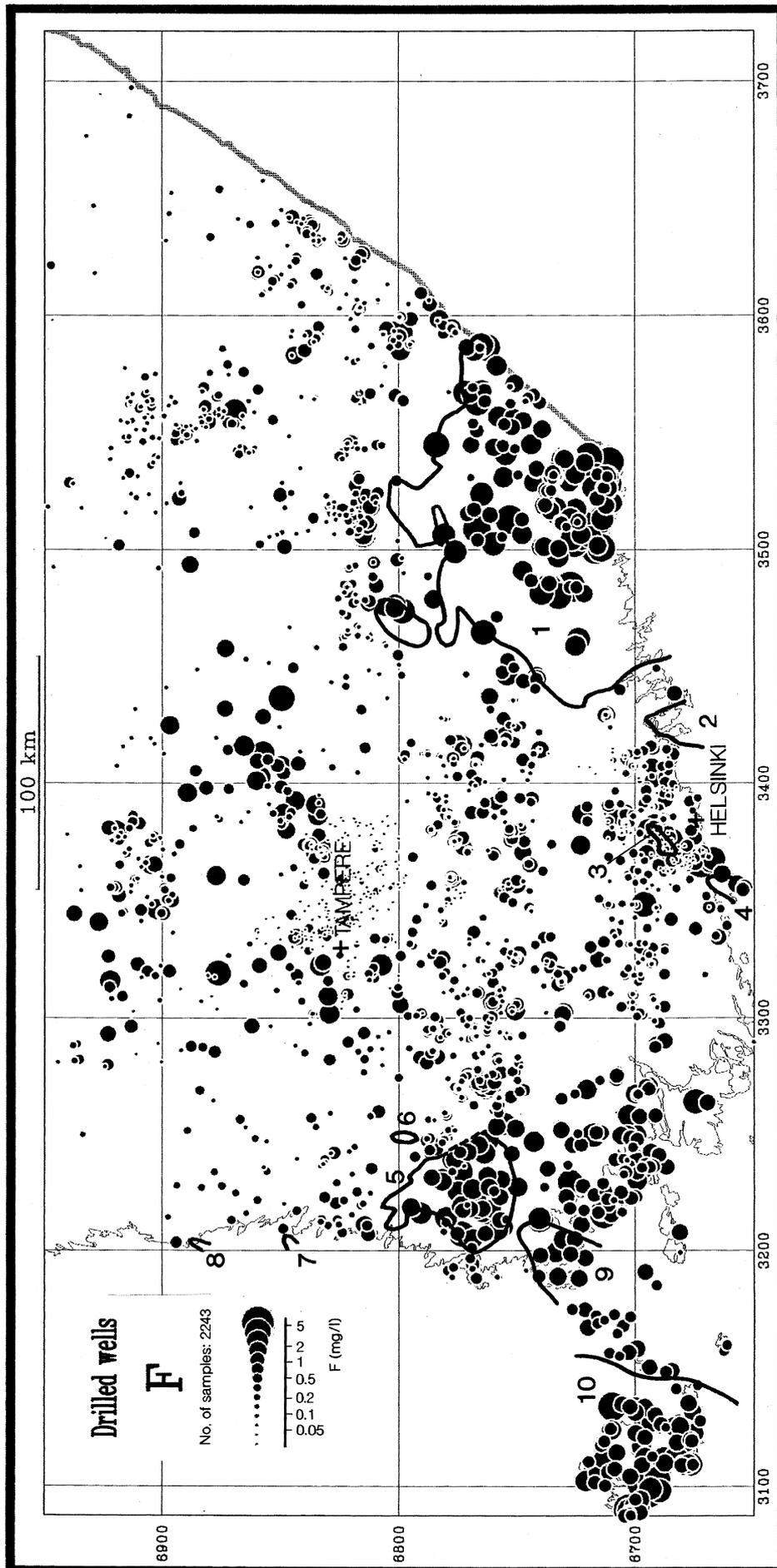


Fig. 10. The fluoride concentrations in water from wells drilled into bedrock in southern Finland. The rapakivi granite areas of Wiborg (1), Onas (2), Bodom (3), Obbnäs (4), Laitila (5), Peipohja (6), Reposaari (7), Siipyy (8), Vehmaa (9) and Ahvenanmaa (10) are marked (see Fig. 2).

dom granites is seen as elevated F^- concentrations in spring and well waters (Punakivi et al. 1977). Also the occurrences of Nattanen, Pomovaara and Vainospää postorogenic granitoids in central and northern Lapland (Fig. 1) could clearly be detected by the elevated F^- concentrations both in spring and stream waters.

Along the western coast from Vaasa to Pori there are numerous elevated F^- concentrations in groundwater (Fig. 9). Many of the high F^- concentrations are derived from granite plutons in the Lauhanvuori area and other small granite occurrences, granodiorites and migmatitic gneisses with granite veins. Furthermore, it is plausible that fluorine-rich rock material has been transported by the continental ice sheet from the occurrences of rapakivi and other F^- -rich rock types such as granoporphyrates and quartz porphyries in the Bothnian Bay basin and on the Swedish coast (see Eskola 1928, 1934, Eckermand 1937, Winterhalter et al. 1981, Laitakari et al. 1996). Likewise, glacial transport may be responsible for many of the elevated F^- concentrations in Turku and Parainen areas situated on the lee-side of the Laitila-Vehmaa rapakivi granite plutons (see Taka 1987).

In the category of bedrock groundwater there is a greater number of widely distributed high F^- concentrations outside the rapakivi provinces than in waters from springs and shallow wells (Fig. 10).

Particularly bedrock groundwater in the areas composed of granites, granodiorites and migmatitic gneisses with granite veins in central and western Finland shows numerous elevated F^- concentrations. The wide concentration amplitude is explained by the fact that the local lithology has a direct and stronger effect on water chemistry in individual drilled holes than on the well waters draining the overburden mixed with a variety of rock material. The chemistry of groundwater occurring in sand or till deposits reflects the bedrock composition only indirectly and in a smoother fashion.

In the GTK groundwater database (about 20 000 water samples) there are 12 samples from drilled wells exceeding the 5.0 mg/L F^- concentration. Except one, all the sampling sites are more than 100 meters deep. The highest concentration, 9.3 mg/L, was recorded in a 116 meters deep well cutting migmatized granodiorite located near the Obbnäs rapakivi-type granite massive in Kirkkonummi. At the distance of one kilometer there is another drilled well showing F^- concentration of 8.3 mg/L.

The high TDS values and dominance of sodium (and lithium) over calcium (and strontium) is a common feature for drilled wells characterized by abnormally high F^- concentrations. Also the concentrations of Al, B, Mo and Rn are notably higher than those in groundwater from bedrock in general.

Temporal fluctuation of fluorides in shallow groundwater

Fluoride is one of the components included in the monitoring project of shallow groundwater carried out by the Geological Survey of Finland (Backman et al. 1999). As a typical geogenic element in water its temporal fluctuations are controlled by groundwater recharge and flow regime. Consequently, high F^- concentrations suggest long residence time and water-rock interaction of groundwater while low concentrations are explained by shallow occurrence of groundwater and/or its mixing with contemporary diluted rain water.

In many of the monitoring sites the F^- concentrations are near or even below the detection limit (0.1 mg/L). Hence, the causes for temporal fluctuations can not always be properly interpreted. On the other hand, the monitoring sites located in the rapakivi granite areas exhibit high baseline F^- concentrations. This is manifested by the monitored 120 m deep drilled well in the town of Lappeenranta, southeastern Finland (Fig. 11). Although the F^- concentrations show a remarkable lowering trend,

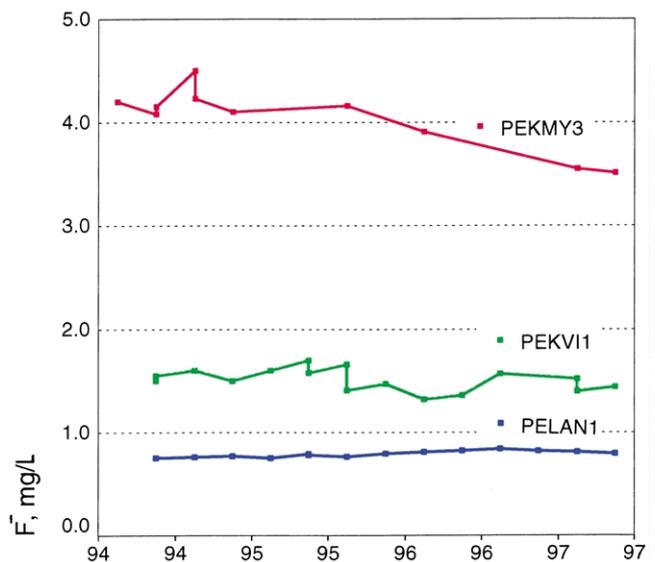


Fig. 11. Temporal fluctuations of fluoride concentrations in three monitoring sites (Backman et al. 1999). 1. Kiila spring, Kemiö, southwestern Finland; 2. Vilkkilä, spring, Virolahti, southeastern Finland; 3. Drilled well (120 m deep), Lappeenranta town, southeastern Finland.

the short time span of monitoring does not justify any fundamental conclusions to be made. The Vilkkilä monitoring spring in Virolahti, southeastern Finland, is also located in the rapakivi area which explains the comparatively abundant fluoride content in water. The spring is located at the lower end of a glaciofluvial esker at the rim of the confining clay deposits. The F⁻ concentrations fluctuate moderately suggesting some effect of recharge on groundwater occurring at shallow depth. The third monitoring site presented here is the Kiila spring in Kemiö, southwestern Finland. Although F⁻ concentrations are lower compared with the two previous cases, contents are somewhat higher than the median values in the whole country due to local

bedrock, which is composed of porphyritic microcline granite. Also glacially transported drift originating from the Laitila and Vehmaa rapakivi batholiths may have an effect on fluorides in the water. The concentration level of fluorides is notably stable, suggesting fairly stationary groundwater conditions in the glaciofluvial aquifer partly confined by clay deposits.

In a survey including drilled private wells in southern Norway F⁻ concentrations fluctuated as a function of precipitation in such a way that profuse rainfall meant low fluoride amounts. The converse was also true (Bjorvatn et al. 1994). Most notable seasonal variations were recorded in wells exhibiting high F⁻ contents (up to 10.5 mg/L).

Fluorides in the public groundwater utilities

The public groundwater utilities are monitored by the Finnish Environment Institute, the Regional Environment Centres and the Ministry of Social Affairs and Health. The number of groundwater supply plants where the upper permissible F⁻ concentration for household water (1.5 mg/L), according to the ordinances issued by the Ministry of Social Affairs and Health (Anon 1994a, 1994b), increased during 1975-1996 from less than 2% to 4% (see Kujala-Räty et al. 1996). The reason for the increasing portion is suggested as being the increasing number of groundwater utilities from which the quality of raw water was analyzed during the concerned period. Practically all the cases of high F⁻ concentrations were localized in the rapakivi granite areas including some cases in the Vaasa area. The areal percentage of rapakivi granites in Finland is

3.8% (see Korsman et al. 1997) corresponding well the number of fluorine groundwater utilities.

The Kaarninko water works, the first one in Finland built in 1903 on the outskirts of the town of Turku, offers an example of a municipal groundwater utility located in a glaciofluvial esker formation in the midst of an urban area (Niemelä 1987). The F⁻ concentrations in pumped water occasionally exceeded 2.0-3.0 mg/L. A large part of the sand and gravel deposits have been excavated while most of the large pits have later been filled in with waste soil and leveled. Heavy traffic and urban population have a strong effect on water quality. In spite of the strong anthropogenic impact on the aquifer, the source of fluoride is presumably the glacially-transported rapakivi material from the Vehmaa and Laitila plutons, 34-40 km to the northwest.

Hydrogeochemical fluoride investigations in Scandinavia

In Sweden and Norway there are not as large rapakivi-type granite areas as in Finland. Hence, also the extensive F⁻-provinces are missing. Occasionally high F⁻ concentrations, particularly in drilled bedrock wells are, however, common. Aastrup and others (1995) have published a report on groundwater chemistry in Sweden and showed that in 2.1% of 1233 dug wells and 25.6% of 9225 drilled bedrock wells the F⁻ concentrations exceeded 1.6 mg/L. In general, groundwater with high fluoride concentrations is found in areas of young granites and pegmatites.

In a survey including 248 drilled private wells in southern Norway the upper 50% of fluoride con-

centrations varied from 0.25 to 10.5 mg/L (Bjorvatn et al. 1994). In groundwater pumped from wells drilled into igneous and metamorphic rocks contain on the average five-times higher F⁻ concentrations (median 0.28 mg/L) than water from shallow wells dug into surficial deposits (Sæther et al. 1995). About in 15% of the samples from drilled wells the F⁻ abundances exceeded the upper recommended limit of 1.5 mg/L. Banks et al. (1995) reported the fluoride values of 0.8 to 4.4 mg/L in the bedrock wells drilled into the Iddlefjord granite in southeast Norway. The concentrations were notably lower in areas composed of gneisses and mica schists.

FLUORIDES IN DEEP GROUNDWATER

In the investigations concerning the deep-seated groundwater occurring in fissures and fractures of Precambrian igneous and metamorphic bedrock several tens of small-diameter exploration drill holes were sampled in different parts of the country (see e.g. Nurmi et al. 1988, Blomqvist et al. 1986, 1989, Lamminen 1995). The upper part of the water column is generally dominated by Ca-Na-HCO₃⁻ type fresh water. An exploration drill hole cutting alkalic granite, biotite gneisses and aplitic granites at Vuolijoki contained 2.5-3.2 mg/L fluorides in water. The lowest concentrations in the same bore hole were in mafic and ultramafic rock environments. The mineral fluorite is the most probable source of dissolved F⁻ in water. Somewhat elevated concentrations up to 1.0 mg/L were detected in groundwaters from monzonite with some intercalated granite and pegmatite veins in Kolari. Near Pori a 613 meter deep experimental drill hole is located in the Jotnian sandstone of Precambrian age. The highest F⁻ concentration recorded in deep groundwater is 1.3 mg/L (Blomqvist et al. 1986).

The southern part of this sandstone basin is bordered by the Laitila rapakivi granite, which may be the main source of fluorides in the groundwater. The deeper groundwater in the same hole is Ca-Na-Cl⁻ rich brine which contains only small amounts of fluorides. This is due to the abundance of calcium, which is a strongly limiting factor of the F⁻ concentrations.

Below the depth of 400 to 1000 metres brackish and saline groundwaters are frequently encountered in fracture systems of the crystalline bedrock. The salinity of Na-Ca-Cl⁻ or Ca-Na-Cl⁻ dominating waters may reach the level of several tens of grammes per litre. The most concentrated deep brine so far analyzed in Finland contained 170 g/L of dissolved solids. It is located at Miihkali, where a 1150 m deep drill hole cuts mica schists, black schists and serpentinites in the sulphide mineral potential area of Outokumpu (Lahermo et al. 1989). In very highly mineralized water at Miihkali the F⁻ concentrations never exceeded 1 mg/L.

THE INTERDEPENDENCE OF FLUORIDE WITH OTHER DISSOLVED COMPONENTS IN WATER

Fluoride concentrations are independent of most of the properties and dissolved components in dilute groundwater (see Lahermo et al. 1990, Lahermo et al. 1996). However, a weak correlations exists between F⁻ and SiO₂ in springs ($r=0.33$, $n=3089$) and dug wells ($r=0.34$, $n=7207$) and between F⁻ and Al in springs ($r=0.26$, $n=1111$) and in dug wells ($r=0.30$, $n=1836$). This suggests that fluoride occurs at least partly as complexes with the concerned correlating components. This complies well with the statement of Koritnig (1972) saying that the aqueous behaviour of F⁻ and SiO₂ is in agreement with their positive correlation in granites and granitic gneisses. There are also discernible correlations of fluorides with bicarbonates in springs ($r=0.31$, $n=3081$) and in wells ($r=0.23$, $n=7183$) and with boron in springs ($r=0.34$, $n=461$).

In slightly more mineralized water occurring in bedrock many of the correlations of fluorides with other dissolved components are more significant than in spring and well waters. Noteworthy correlations exist between F⁻ and pH values and HCO₃⁻ ($r=0.50$, $n=3070$ and $r=0.47$, $n=3319$). This is true also of boron, radon and uranium ($r=0.54$, $n=1247$, $r=0.32$, $n=1526$ and $r=0.20$, $n=3596$), two of them (Rn, U) characteristically occurring together with

fluoride in granitoidic environments. There is significant negative correlation between F⁻ and NO₃⁻ ($r=-0.41$, $n=3614$) suggesting that anthropogenic pollution is not generally a source of fluorides. Slight negative correlations are encountered between F⁻ and O₂, CO₂, Al, K and KMnO₄ consumption ($r=-0.34$, $n=2500$, $r=-0.31$, $n=2534$, $r=-0.16$, $n=1599$, $r=-0.11$, $n=3727$ and $r=-0.11$, $n=3334$) demonstrate that surface waters do not by and large contaminate drilled wells.

Fluorine-rich rapakivi granites are characterized by elevated concentrations of yttrium, scandium and lanthanum. Yttrium is enriched in the rocks from early Proterozoic Svecokarelian rocks and, especially, in rapakivi granites, while concentrations are mostly low in the Archean basement gneisses and early Proterozoic mafic greenstones in eastern and northern Finland (Koljonen 1992). The partial (leached by aqua regia) and total Y concentrations in till underlain by rapakivi granites range from 10-22 mg/kg and 20-40 mg/kg, respectively. The probable Y carrier is the mineral yttrifluorite, a variety of fluorite with some yttrium contents. This explains the close correlation of fluorides in groundwaters and stream waters with partial or total Y concentrations in the fine fraction

(<0.06 m) of till (Lahermo et al. 1996). No information is available about the Y, Sc and La concentrations in natural waters in Finland.

Fluorides coexist with uranium because both of the elements are enriched in late differentiation products of magma, mainly in granites. Fluorine-rich rapakivi granites do not, however, show nota-

bly elevated U concentrations. Anomalously high U concentrations in the fine fraction of till and in bedrock groundwater are consistently encountered in areas composed of ordinary granites and migmatites rich in granite veins in southern Finland (Lahermo & Juntunen 1991).

GEOCHEMICAL APPLICATIONS OF FLUORIDES

Fluorides in ore exploration

The successful use of fluoride in exploration-oriented groundwater surveys is based on the chemical solubility and mobility of fluoride in water. Although the concentrations are largely a function of the proximity of fluorine-bearing mineralizations, other factors could also enhance or suppress the F⁻ concentrations in natural waters (Graham et al. 1975). The presence of ionic Al³⁺, Fe³⁺ and Si⁴⁺ form soluble complexes with F⁻ and increase the amount of dissolved fluorides in saturated solutions in equilibrium with fluorite. However, the complexed F⁻ does not generally amount to more than a fraction of the total dissolved fluoride. As a fairly mobile element, fluoride is among the most suitable hydrogeochemical pathfinders in mineral exploration.

Fluoride is useful in prospecting of Mo-, W- and Sn- ores and beryllium-fluorite deposits associated with granitoids. It can also be used as an indicator for chalcopyrite type deposits (Miller 1979). According to Lalonde (1976) fluorides indicate fluorite-barite veins and many types of massive sulphide deposits (Zn, Cu, Pb and Au) which are associated with both pyrite in mafic volcanic rocks and with diorite or quartz-feldspar porphyrites. The F⁻ concentrations rose to the level of 0.20-0.30 mg/L in the mineralized zones while the background concentrations in groundwater and surface water were 0.05 to 0.15 mg/L.

In the Surprise Lake area, northern Canadian Cordillera, there are metallogenetically specialized intrusive granitoids characterized by the elemental associations of F⁻, Mo, W, Zn, and Sn (S.B. Ballantyne and D.J. Ellwood, an unpublished paper in 1983). This tin-fluorite intrusion is an example of a highly-evolved silicic magma enriched in fluorophile elements such as U, Th, Sn, Rb, Nb, Y, Cs, REE, and Be. By contrast, it is depleted in Sr, Ba, Zr compared with average Ca-poor granites. Burt and Sheridan (1981) located several deposits of uranium and other lithophile elements within small rhyolitic domes by using fluorides as pathfinders.

Fluoride has also a potential for delineating the occurrences of carbonatite massifs. In Labrador F⁻ (and Y) was found to be a useful element in stream waters showing the location of a mineralized peralkaline granite complex, where fluorine constitute a significant portion (up to 3%) of rock (McConnell & Batterson 1987).

Fluorides in soils and stream sediments have occasionally been used as a pathfinder element in ore exploration. The F⁻ dispersion patterns derived from fluorite veins have been detected in soils by using different leaching methods such as TISAB-, HCl- and FeCl₃- solutions. Fluorides were analyzed by the GTK from stream water, organic stream sediments and till in a local geochemical exploration project for tungsten at Pomovaara, central Lapland. The target area is composed of coarse-grained K -rich granites with fairly high F⁻ concentrations which gave rise to elevated F⁻ concentrations in streams and springs.

Schwartz and Friedrich (1973) analyzed the F⁻ concentrations in spring and stream waters and in stream sediments near Osor, Spain. The determination of fluoride in waters and in stream sediments proved to be a useful guide in locating the occurrences of fluorite mineralization in granitoid and metamorphic environment. On the basis of two anomalies in spring waters a number of fluorite veinlets in the granite area were detected. The background (baseline), threshold and anomalous F⁻ concentrations were <0.28 mg/L, 0.28-1.0 mg/L, and >1.0 mg/L, respectively. The mines and flotation plants caused local fluoride anomalies. In Labrador the F⁻ and Y concentrations in stream water and sediments indicate well the distribution of peralkalic granites (McConnell & Batterson 1987). In this respect the stream sediments proved to be more indicative of geochemical characteristics of till than stream waters. Volcanogenic massive sulphide deposits (Cu, Pb, Zn) in Anglesey, North Wales, gave rise to high F⁻ concentrations in stream waters (Simpson et al. 1993). Also buried

granites and aerosols from an aluminium smelter may in places contribute to fluorides in water.

The mineralized zones were reported to be reflected in the distribution patterns of fluorides in snow pack at concentrations ranging from 1 to 10

µg/L. It is suggested that fluorides are evaporated from the overburden as hydrofluoric vapour, which is produced by the reaction of sulphuric acid with fluorite, or as dispersive upward movement from the topsoil enriched in fluorides.

Fluorides as pollutants

In Finland not much attention has been paid so far to the issue of fluoride contamination, except for acute drinking water problems in some “naturally contaminated” fluoride provinces in the rapakivi granite areas. Excessive amounts of fluorides are, however, regarded as pollutants with considerable potential for producing ecological damage in the environment (Groth III 1975). The sources and the ecological impacts of low-level fluoride pollution are summarized below.

Most water bodies in densely populated areas are contaminated to some extent as far as F⁻ concentrations are concerned. This is particularly true in countries with intense agricultural and industrial activities. The natural F⁻ contents of 0.01-0.2 mg/L may rise to the level of 2-3 mg/L in natural waters. The F⁻ concentrations in undiluted leachates from a group of sanitary landfills in Finland ranged from 0.5 to 8.4 mg/L (Kalliokoski et al. 1987). Downstream of an American phosphate factory concentrations of 20 mg/L and even higher were reported (Groth III 1975).

Water pollution from both industrial emissions and wastes and from municipal sewage may raise the F⁻ concentrations in surface waters downstream of the pollution source to 0.5-3.0 mg/L. The non-ferrous metal foundries and steel, glass, tile and ceramics industry and welding operations use fluorine in their processes giving rise to fluorine-rich emissions. Some Al-industrial plants (e.g. in Sege da in the Karelian Republic, Russia) may increase local F⁻ concentrations in vegetation, soil and waters, and in extreme cases, cause severe fluoride toxication among the populace. An alumina reduction plant in the Ohio valley, U.S.A., has increased the soil fluorine contents in the environment. The reversed vertical distribution of fluorides is seen in the soil profiles (down to 30 cm), i.e. the concentrations decrease rather than increase with depth. Due to weathering most soils under natural conditions show lower F⁻ concentrations near the surface than in deeper soil layers at depths of some metres.

The heavy fertilization over a 20-40 years' period has been shown to increase significantly the F⁻ level of surface soils (Robison & Edgington 1946). Also the combustion of coal and F-bearing teflon-type plastics contribute to fluorine in the environment.

Fluorous air pollution significantly enhances the accumulation of fluorides in terrestrial and aqueous vegetation. The bacterially-induced or plant-synthesized conversion of inorganic fluoride into organic fluoride compounds is possible. Fluoride may also behave synergistically with other contaminants, e.g. with Cu, expanding the potential of the ecological damage primarily caused by fluorides.

Air pollution containing high fluorine concentrations is suggested to have been responsible for the damage of pine forests surrounding the Kemira fertilization factory in Oulu in 1970s (Havas 1972). Similar effects were detected around some American aluminium and phosphate plants, where vegetation showed substantially elevated F⁻ concentrations at distances of more than 30 km from the source (Groth III 1975).

Aluminium smelters are known to emit HF, NaF, KF, NaAlF₄ and Na₃AlF₆ as aerosols and tiny particles. In Norway the increase of fluorine in soils can be traced for more than 30 km from smelter while the impact in surface water can be seen only at the distance of 3-5 kilometres (Arnesen et al. 1995). The movement and accumulation of highly reactive F⁻ ions depends on the complex interaction between the liquid and solid phases in soil, like adsorption, ionic exchange, precipitation and complexation (Flühler et al. 1982). In heavily polluted soil F⁻ concentrations decrease downwards in the soil profile while in unpolluted soils the F⁻ concentrations usually increases within the soil depth. In Greece Haidouti (1995) recognized that an alumina production plant has increased the F⁻ contents in soil. More than 90% of the natural fluorine in soils is tightly bound to soil particles.

BIOLOGICAL IMPLICATIONS OF FLUORIDES

Health

Like many other elements fluoride has a dual effect on living nature. It is an essential element in small concentrations but toxic if present in abundance. One of the first records on the harmful effect caused by an excess of fluorides is from Iceland where many sheep died while grazing on grass made toxic by the ash deposition from the eruption of Mount Hekla volcano (Thorarinsson, cited by Shacklette et al. 1974, see also Robinson & Edington 1946). The tephra appeared to be unusually rich in fluorine (up to at least 1500 mg/kg). The new grass growing through ash layers proved also to be toxic.

In 1930s it was demonstrated that fluorides have a beneficial effect on the dental system in small doses by inhibiting dental caries (Eriksson 1970). Furthermore, it was found that the higher fluoride doses disturbed the enamel formation in teeth. It is now unanimously accepted that fluoride is an important micro-nutrient used by man and higher animals as a vital constituent (in apatite) in teeth and bones. Fluoride is among the few elements which are ingested mainly through drinking water. The beneficial F^- concentrations in potable water is quite low 0.8-1.2 mg/L and should not exceed 1.5 mg/L (Anon 1994a). Particularly in the U.S.A there are discussions to lower the upper permissible limit for fluorides. Health authorities have established the "optimal" fluoride intake to prevent dental caries as between 0.05 and 0.07 mg/kg of body weight per day (see Smith 1988).

Throughout most of Finland the F^- concentrations in drinking water are below the level of their beneficial physiological effect (Anon 1995). However, in the areas underlain by the rapakivi granites the average F^- concentrations in consumed groundwater, as well as in surface waters are well within the recommended range of 1.0 to 1.5 mg/L. In these areas the fluoride intake of the population through water may be several milligrammes per day, whereas the estimated intake through Finnish food is only about 0.5 mg/L (Varo & Koivistoinen 1980). Elevated F^- concentrations have been found to reduce the incidence of dental caries in Finland (Pärkö 1975, Parviainen et al. 1977). Significant toxic effects caused by fluorides have not been recorded so far in Finland.

In the hydrogeological mapping carried out by the Geological Survey of Finland 75 % of samples from springs, 69% samples from dug wells and 35% of samples from drilled bedrock wells exhibited F^- concentrations of <0.1 mg/L (together 8593

samples). The public water utilities based on draft of groundwater show equally low concentrations. Regardless of this unfavourable situation the town of Kuopio in central Finland was the only one to fluoridate the public water supply since 1959 in the whole of Scandinavia. The F^- concentrations in tap water were regulated to 0.95-0.99 mg/L. There was, however, persistent public criticism about the fluoridification and discussions about its the benefits and disadvantages. For these reasons the fluoridification was ceased at the end of 1992. The reason for the unpopularity of fluoridation was the fact that the beneficial range of F^- concentrations is quite small and must be carefully monitored. Furthermore, only an insignificant fraction of the supplied water was used for drinking purposes, which made an expensive procedure of fluoridification doubtful. There was also a sort of psychological barriers to add a "poisonous" component into drinking water. Furthermore, because of the usage of fluorour (fluoridic) tooth pastes and a widespread application of the fluoride flushing of teeth to the pupils by the educational administration, the effect of the communal fluoridation of drinking Kuopio water on health was not fully justified.

By the 1960s the fluoridation of the public water supplies in the U.S.A. reached nearly half of the population (Gullström 1967, Fleischer et al. 1974). This has greatly affected the fluorine intake in man. On the other hand, many of the public water supply utilities in U.S.A distribute groundwater containing appreciably high natural F^- concentrations which renders defluoridation of water important.

The mobile fluorides have a tendency to enrich their concentrations in water under tropical conditions due to strong evaporation. Furthermore, the large amounts of drinking water consumed particularly by outdoor labourers working in hot climate aggravates the health problems arising from excess fluoride intake. Tens of millions of people, particularly in East Africa (Tanzania, Kenya and Ethiopia) and in large parts of India and China, are affected by high F^- concentrations in drinking water. For example, in India about 25 million people in 8700 villages are consuming water having fluoride content above 1 mg/L (cited by Agrawal and Vaish 1998). Dental fluorosis, which at the first stage causes merely aesthetic problems by staining the teeth, is quite common in fluoride afflicted areas. The most serious health problem is the decay and destruction of teeth, and in later phase of bones

(skeletal fluorosis), which is encountered particularly in the Arumeru area, northern Tanzania (e.g. Bugaisa 1969, Nanyaro et al. 1984, Lahermo 1987, Lahermo et al. 1991), in India (e.g. Teotia et al. 1981) and in China (e.g. Minggao et al. 1986, Fuhong Reng & Shuqin Jiao 1988, Sahu & Karim 1989, Zheng & Huang 1989, Yong & Hua 1991).

Toxicity and mobility of aqueous aluminium seems to be strongly dependent on the presence of complexing F⁻-ligands (Plankey et al. 1986). A 1000-fold enhancement of aluminium leaching from cooking utensils when 1 mg/L fluoride is present in water has been reported (Savory et al. 1987). This observation is of considerable concern as in many countries drinking water is fluoridated,

and because of the question of neurotoxicity of ingested aluminium. However, only a negligible increase of Al concentrations in fluoridated waters has been found.

There is no definite knowledge about how much herbivorous wild and domestic animals tolerate fluoride without any adverse effects to their health. In domestic cattle the skeletal fluorine concentrations ranging from 1450 to 8000 mg/kg (0.145-0.8%) have been associated with fluorosis (Groth III 1975). On the other hand, animals may be adversely affected by eating forage plants that contain 50 mg/kg (d.w.) or even less of fluoride (see Shacklette et al. 1974).

Plants

Fluoride is not considered as an essential element for plants, nor are soil fluorides recognized as potentially toxic elements to plants by virtue of their apparently low availability (McClenahan 1976). The knowledge of total fluorine concentrations in soil is not meaningful because only the water-soluble F⁻ is a source of the concerned element to plants (Larsen & Widdowson 1971). Available fluoride, different from phosphate, is to a large extent adsorbed by soils particles. Its uptake by plants is controlled by many factors such as soil type, pH and the contents of clay fractions (Adriano 1986).

Most of the plants are poor accumulators of soil fluoride; they rather take it from the air. Some plants such as spinach, lettuce, tea, elderberry and camellia can, however, accumulate substantial amounts (620-3600 mg/kg d.w.) of fluorides (Robinson & Edginton 1946, Hodge & Smith 1972, Fleischer et al. 1974). Phosphatic fertilizers, especially the superphosphates, may contribute to the F⁻ concentrations of agricultural lands. Polomski et al. (1982b) states that long-term F⁻ accumulation in soil may interact with the biological processes in roots and micro-organisms.

TECHNIQUES OF FLUORIDE REMOVAL FROM WATER (DEFLUORIDATION)

Because fluoride is a relatively mobile anion its removal from water is complicated. There is a large variety of methods applied in partial defluoridation of water distributed in public water utilities. They can be divided accordingly: Ionic exchange processes and adsorption (activated alumina or Al(OH)₃, bauxite, active carbon, bone char, zeolite, serpentine, fired clay chips, superphosphate, tricalcium-phosphate and anion-exchangers), precipitation (lime-, alum- and CaCl₂-precipitation), reversal osmosis, electrical methods (electrolysis, electro-dialysis) and VYR-method or artificial recharge (Kantanen 1993, Moges et al., 1996, Liponkoski 1999). The main problems are a deficient removal degree of fluorides and high costs in relation to the achieved results. In an experiment performed at the GTK fluorides were not removed by using activated carbon, alumina or ion exchangers (Kahelin et al. 1998).

Although there are too high F⁻ concentrations in

some groundwater utilities concerning the limit values no major defluoridation plants have been constructed so far. The town of Laitila in a southwestern rapakivi area is building a pilot defluoridation plant which is based on adsorption and ion exchange (Kempac mass) (Liponkoski 1999). Furthermore, Kymenlaakson Vesi Oy has made enquiries about the possibilities to construct a defluoridation plant based on aluminiumhydroxide (alumina) adsorption at Utti, in the southeastern rapakivi area (Lonka et al. 1996). The problem is the high cost of the project in comparison to the slight exceedence of the fluoride limit (1.6-1.7 mg/L) in water produced by artificial recharge.

In Finland, defluoridation, if the referred plants will be built, will target only at partial removal of fluorides in water. This water will then be used to dilute the remaining F⁻ rich water to lower the F⁻ concentrations of distributed water to meet the quality standards.

SUMMARY

Fluorine, which occurs in solution as a mobile fluoride ion (F^-), is an environmentally important element. Overwhelmingly of geological origin it is a minor component of all rocks, soils and natural waters.

The fluorine concentration is exceptionally high in certain postorogenic granite i.e. rapakivi granites (coarse-grained K-rich granites). The largest rapakivi massifs in Finland are the Wiborg batholith in the southeast Finland and the Laitila, Vehmaa and Ahvenanmaa batholiths in the southwest. Small granite occurrences of a similar type are encountered in southern Finland (Onas, Bodom, Obbnäs) and Lapland (Nattanen, Pomovaara, Vainospää).

The most important fluoride mineral in rapakivi granite is fluorite (fluorspar). Fluoride derives largely also from amphiboles and micas, in which the F^- ion can diadochically replace OH^- ions. The ionic radii of both are nearly equal in size.

The areas characterized by high fluorine concentrations in rocks show ubiquitously high F^- concentrations in soil, surface water and groundwater.

In the whole country, the median/mean concentrations of the fluoride in water from springs and captured springs are $<0.10/0.17$ mg/L and in water from dug wells $<0.10/0.21$ mg/L. In water pumped from drilled (bedrock) wells the F^- concentration is

conspicuously higher: median/mean $0.31/0.63$ mg/L. The concentrations increase with depth of the well: median 0.14 mg/L at <50 m depth; 0.37 mg/L at $50-100$ m depth; 0.56 mg/L at $100-200$ m depth, and 0.69 mg/L at > 200 m depth (GTK groundwater database 03/1998).

The F^- concentrations in groundwater from springs and wells underlain by rapakivi granite are roughly one order of magnitude higher than in areas composed of other rocks types. The median/mean values in water from springs and captured springs in the southeastern rapakivi area are $0.93/1.1$ mg/L and in the southwestern rapakivi areas $1.1/1.2$ mg/L. In dug wells in the southeast, the values are $0.68/0.93$ mg/L and in the southwest $0.59/0.85$ mg/L. In water pumped from drilled wells the values in southeast are $1.9/2.1$ mg/L and in the southwest $1.7/1.9$ mg/L (GTK groundwater database 03/1998).

The upper officially permissible F^- concentration in drinking water in Finland is 1.5 mg/L. This value is often exceeded in dug and drilled wells in the rapakivi granite areas. In drilled wells the upper permissible concentration is frequently exceeded also in areas composed of other rock types, such as ordinary granites, granodiorites and migmatites, while high F^- concentrations in water from springs and dug wells are rare.

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